

# Base Pair Dynamic Assisted Charge Transport in DNA<sup>1</sup>

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Submitted November 23, 2001

A one-dimensional model with time-dependent random hopping is proposed to describe charge transport in DNA. It permits the investigation of both diffusion of electrons and their tunneling between different sites in DNA. The tunneling appears to be strongly temperature-dependent. Observations of a strong (exponential) as well as a weak distance dependence of the charge transfer in DNA can be explained in the framework of our model. © 2002 MAIK "Nauka/Interperiodica".

PACS numbers: 87.14.Gg; 34.70.+e

Electronic transport is the basis for a wide range of important biological processes in DNA. Besides, the phenomenon has a fundamental physical interest, since the transport properties of biomolecules are expected to differ considerably from those of macroscopic conductors. Lastly, very recently, material scientists have also turned their attention to charge migration in DNA for the development of DNA-based molecular technologies.

Although the first attempts to measure DNA conductivity [1] and to present a theory of the phenomenon [2] were made almost 40 years ago, the question concerning charge transport through DNA remains unsettled, and there is an impressive quantity of unexplained or partially explained data. Different publications frequently report contradictory results. Two kinds of techniques for acquiring information on charge transport in DNA are used. First, direct or indirect electrical conductivity measurements on micrometer-long DNA ropes are performed [3–7]. Experimental results obtained in this technique are ambiguous. DNA conductivity  $\sigma$  was reported as almost metallic, of the order  $10^4 \Omega^{-1} \text{cm}^{-1}$  [3] (in a recent publication [4], the authors claim they observed even proximity-induced superconductivity in DNA) or semiconducting with  $\sigma \approx 0.1 \Omega^{-1} \text{cm}^{-1}$  [6]. Very recently, experimental techniques have progressed to the point where the conductivity of individual 10-nm-long double-stranded molecules was measured [7], and the result implies that DNA is a good insulator. Clearly this frustrating situation with conductivity measurements means that there are many relevant factors which can influence the charge transport in DNA in different ways and which are hardly controlled in real experiments. The second technique, related to fluorescence quenching measurements on DNA strands doped with donor and acceptor molecules [8–23], seems more reliable, and it is our

main concern here. In this technique, photoexcitation of a donor associated with the stack of base pairs in some fashion allows transfer of an electron to the stack. The migrating electron is trapped finally at the acceptor site, and charge transfer is monitored by the yield of a chemical reaction accompanying the trapping process. The transfer rate is usually assumed to be characterized by a simple exponential law  $\exp(-\beta x)$ , where  $x$  is the donor-acceptor separation. Fitting to this law gives values of  $\beta$  ranging from  $0.1 \text{ \AA}^{-1}$  to  $1.4 \text{ \AA}^{-1}$ .

It is common knowledge that DNA can be treated as a one-dimensional linear chain of stacked base pairs. We believe that in the ground state every base pair contains bound electrons only. Then the charge is carried through DNA by excited electrons (or holes), which can jump between the base pairs. Below, we propose a simple model which, for our purposes, reflects basic features of the electron transport in DNA. The picture includes the following ingredients.

(i) The excited electron states at the base pairs are separated by an energy spacing larger than the temperature and therefore are hardly excited thermally.

(ii) Thermal motions of the DNA base pairs are elastic vibrations with a characteristic frequency  $\omega_b$ .

(iii) Efficient charge transfer between neighboring base pairs takes place for rare events.

(iv) The Coulomb interactions between the electrons and holes can be neglected for describing the hopping transport.

Let us explain point (iii) in more detail. For the static equilibrium DNA helix charge, hopping is expected to be negligibly small, since there is no significant electronic overlapping between adjacent base pairs. Nevertheless, sometimes, due to thermal fluctuations, exclusively favorable configurations for hopping of the base pairs occur, when efficient hopping is possible. If the separation between the pairs is larger than the ampli-

<sup>1</sup> This article was submitted by the authors in English.

tude of their thermal vibrations, then the probability of such events (which can be called “contacts”) is small. Duration of the contact can be estimated as the characteristic oscillation time  $\omega_b^{-1}$ .

Now we discuss the correspondence of the assumptions listed above and experimental data. As a guideline, we use not only data known from the DNA literature but also the data obtained for a wide range of organic linear chain polymers of stacked planar molecules (for a review see [24]). The contacts are related to mutual displacements and orientations of adjacent base pairs. Probably, hopping matrix elements are mostly sensitive to the relative rotations (twist fluctuations) of the base pairs (see, e.g., [25]). The characteristic frequency of these fluctuations,  $\omega_b$ , is usually estimated as being in the region  $10^{11}$ – $10^{12}$  s<sup>-1</sup>. A small probability of the contacts is confirmed by experiment showing that the characteristic electronic hopping time  $\tau$  is larger than  $\omega_b^{-1}$ ; in the experiments [8, 10, 17, 18]  $\omega_b\tau = 10^2$ – $10^3$ . Our first assumption (i) requires  $\Delta E > T$ , where  $\Delta E$  is the spacing, in the spectrum of electron excitations for a base pair. The magnitude of  $\Delta E$  can be measured directly; for the experiments [8–23]  $\Delta E > 500$  K. Therefore, the inequality is satisfied. Rough macroscopical estimations at the Coulomb interaction  $U_c$ , as well as ab initio molecular orbital calculations of  $U_c$ , give few meV [26], and thus the Coulomb energy appears to be smaller (though of the same order) than  $\hbar\omega_b$ . We believe that it is enough to justify neglecting the Coulomb interaction.

The above reasoning leads to a one-dimensional hopping Hamiltonian for the electrons:

$$\mathcal{H} = \hbar \sum_i (\xi_i a_i^+ a_{i+1} + \xi_i^* a_{i+1}^+ a_i). \quad (1)$$

Here  $a_i$  and  $a_i^+$  are electronic annihilation and creation operators at the site (i.e., the base pair) with the number  $i$ , and  $\xi_i$  are the hopping amplitudes, which are time-dependent quantities. The equations for the Heisenberg operators  $a_i$  are

$$\partial_t a_i = -i\xi_i a_{i+1} - i\xi_{i-1}^* a_{i-1}. \quad (2)$$

We assume that different  $\xi_i$  possess independent statistics, since  $\xi_i$  are related to independent thermal pair base fluctuations. The hopping matrix element  $\xi_i$  can decompose into a constant part  $\langle \xi_i \rangle$ , which describes the coherent charge carrier motion in a completely rigid lattice, and a fluctuating part. Since the probability to jump is appreciable during rare events, the coherent part of  $\xi$  can be neglected in comparison with its fluctuating part.

Note that theoretical models based on hopping Hamiltonians similar to Eq. (1) are widely used to describe charge transport in solid-state physics (see, e.g., [27, 28]). For most problems, in this case the

description corresponds to electron migration in a steady energy landscape, including thermally activated jumps over barriers and quantum tunneling through the barriers. This is quite different from our case.

We assume that DNA molecules can be treated as homogeneous ones. Though the molecules are constructed from four different nitrous bases, experimental data [8–22], as well as numerical first principle calculations [26, 29, 30], show that the sequence of base pairs is not a decisive factor determining electron transport in DNA. Quantitatively, this condition can be formulated as  $\delta E < \hbar\omega_b$ , where  $\delta E$  is an energy spacing between the (lowest excited) electron energy levels at different base pairs. The values of  $\delta E$ , known mainly from numerical electronic structure calculations [26, 29, 30], are of the order of meV. Thus,  $\delta E$  is smaller than  $\hbar\omega_b$  for  $\omega_b$  given above, which justifies the picture. In addition, some experiments (see, e.g., [23]) are performed for artificial homogeneous DNA, where  $\delta E = 0$ . One expects that, due to the hopping, electron diffusion occurs on large time scales. For  $\xi$ , treated as white noise, it was demonstrated in the papers [31, 32]. Though our case is essentially different, there is good reason to believe that the same behavior should be observed on time scales larger than the hopping time  $\tau$ .

Below, we examine the particular case related to the fluorescence measurements reported in the papers [8–23]. The donors are photoexcited, and effects related to the excited electron motion to the acceptors are monitored. The energetic gaps  $\delta E_d$  and  $\delta E_a$  between the donor and the acceptor and the base pairs between them are crucial for the hopping rate. The values of  $\delta E_d$  and  $\delta E_a$  (known mainly from ab initio numerical calculations [15, 26, 29, 30]) can be estimated as  $10^2$  meV. We see that the inequalities  $\delta E_d, \delta E_a \gg \hbar\omega_b$  are satisfied. The electron is always bound to the acceptor site more strongly than to a standard base pair, which is  $\delta E_a > 0$ . As for the donors, the sign of  $\delta E_d$  can be either positive or negative. If  $\delta E_d$  is negative, then the scheme of the electronic charge transfer from the donor to the acceptor is quite simple. Initially, the electron leaves the donor, jumping to the neighbor site, and then jumps between the standard base pairs, finally being trapped at the acceptor. The case  $\delta E_d > 0$  is more complicated. In order to have a driving force for the donor–acceptor charge transfer process, the final state with the charge bound to the acceptor should be energetically favorable; that is, the inequality  $\delta E_a > \delta E_d$  has to be satisfied. However, there are some base pairs in-between which play the role of the potential barrier for the electron. Therefore, there are two possibilities for the electron to reach the acceptor. The first possibility is for it to jump initially from the donor to the neighboring site and then to move to the acceptor by multistep hopping over the standard base pairs. The second possibility is by unistep (direct) quantum tunneling from the donor to the acceptor through the barrier.

Since  $\delta E_d \gg \hbar\omega_b$ , the probability for the electron to jump from the donor to the neighboring base pair due to the dynamics of  $\xi$  is negligible. At  $\delta E_d > 0$ , such a jump is possible if the electron absorbs a high-frequency phonon with the frequency  $\omega_{ph} \sim \omega_d (= \delta E_d / \hbar)$ . Correspondingly, at  $\delta E_d < 0$ , the electron jump from the donor is accompanied by emitting high frequency phonons. Such dynamical vibrations with periods as short as tens of femtoseconds (i.e., phonons with  $\omega_{ph} \sim 10^{14} \text{ s}^{-1}$ ) were reported in the literature [33–35]. Since  $\hbar\omega_{ph} > T$ , occupation numbers of such phonons are small. Thus, for  $\delta E_d > 0$ , the probability for the electron to jump from the donor to the neighboring site contains two small factors: the probability of the contact and the probability of absorbing the high frequency phonon. This corresponds to the experimental situation where only a small fraction of the electrons are transported from the donor to the acceptor.

When the electron leaves the donor, it starts to jump between the donor and the acceptor. It can return to the donor or arrive at the acceptor. If  $\delta E_d < 0$ , then the probability to return to the donor is negligible. We assume that even at  $\delta E_d > 0$  the probability of the electron to jump to the donor or to the acceptor is smaller than the probability to jump to the standard base pair. There are two reasons for this assumption. First, the donors and the acceptors have chemical structures different from the standard base pairs, which hinders the contacts. Second, the jump has to be accompanied by phonon emission, which diminishes its probability. The same is valid for the acceptor. Thus, before being finally trapped at the acceptor site, the electron jumps many times back and forth over the base pairs between the donor and the acceptor, “smeared out” homogeneously over all the intermediate base pairs. Then the relative probability for the electron to arrive at the acceptor is determined by the ratio of the probabilities for the electron to jump to the donor and to the acceptor from adjacent base pairs. This relative probability appears to be independent of the separation  $x$  between the donor and the acceptor. That explains why the rate of charge transfer sometimes is almost insensitive to the relative loading of donors and acceptors (see, e.g., [36, 37]). The above picture implies that the total donor–acceptor charge transfer time should be larger than the electronic hopping time  $\tau$ , and this conforms to experimental data (see, e.g., [8]).

Now we consider the quantum tunneling for an electron strongly attached to the donor, which is the case for  $\delta E_d > 0$ . Though the potential barrier depends on time, at the condition  $\delta E_d \gg \hbar\omega_b$ , the probability of the electron tunneling from the donor to the acceptor can be calculated using the adiabatic approximation. To examine the tunneling process, one should consider the quasi-stationary electron state bound at the donor. In the context of our picture, we assume  $\xi \ll \omega_d$ . Then the

energy of the bound state is close to  $-\delta E_d$ . Substituting  $\partial_t$  by  $i\omega_d$  in Eq. (2), one obtains for the state

$$\begin{aligned} a_i &= -\frac{\xi_{i-1}^*}{\omega_d} a_{i-1}, \quad i > 0; \\ a_i &= -\frac{\xi_i}{\omega_d} a_{i+1}, \quad i < 0, \end{aligned} \quad (3)$$

where we used the condition  $\xi \ll \omega_d$ . Then, the probability for the electron to be at the site  $n$  is determined by the average

$$\langle a_n^+ a_n \rangle = \omega_d^{-2n} \left\langle \left| \prod_{i=1}^n \xi_{i-1} \right|^2 \right\rangle. \quad (4)$$

Quantum averaging and averaging over the statistics are performed upon deriving Eq. (4). In addition, at the derivation we substituted  $\langle a_0^+ a_0 \rangle \approx 1$ , which is justified

by  $\langle a_n^+ a_n \rangle \ll 1$ . Note that probability (4) is determined by the simultaneous statistics of  $\xi$ . Remember that different  $\xi_j$  are assumed to be statistically independent. Therefore, the average on the right-hand side of Eq. (4) is a product of  $\langle |\xi_j|^2 \rangle$ . For standard pairs, the quantities can be regarded as site-independent ones. Therefore, the probability of the electron being at the nearest site to the acceptor is proportional to  $\langle |\xi|^2 \rangle^n / \omega_d^{2n}$ , where  $n$  is the number of the standard pairs between the donor and the acceptor.

The jump of the electron from the bound state to the acceptor is accompanied by phonon emission. However, the only  $x$ -dependent factor in the probability of the process is related to the average charge occupation number of a site  $n$  near the acceptor, which was established above. Thus, for the probability we obtain the exponential law  $\exp(-\beta x)$  with

$$\beta = a^{-1} \ln(\omega_d^2 / \langle |\xi|^2 \rangle). \quad (5)$$

Here,  $\xi$  is the hopping probability for the standard base pairs and  $a = 3.4 \text{ \AA}$  is the distance between the base pairs in DNA. Note that  $\omega_d$  depends on the donor type, whereas the average  $\langle |\xi|^2 \rangle$  is mainly related to base pair vibrations. It follows from the above consideration that the exponential law implies the condition  $\beta > a^{-1}$ . This conclusion is in agreement with most published experimental data. As reported in [21], the value  $\beta = 0.1 \text{ \AA}^{-1}$  (thus smaller than  $a^{-1}$ ) is probably related to an attempt to fit a complex behavior (including two processes: diffusion and tunneling) by a simple exponential law.

Let us stress that the quantum tunneling analyzed above is not the standard (static) tunneling described in textbooks. We have to deal with dynamic tunneling, which will be effective only when, due to fluctuations of  $\xi$ , there occurs some kind of bridge from the donor to the acceptor. We found that the exponential law is in fact explained by the small probability of having such a

bridge, which is realized when many contacts between base pairs occur simultaneously. In addition, the probability of this kind of tunneling is strongly dependent on the temperature via  $\langle |\xi|^2 \rangle$ . It is natural to assume that it exponentially depends on the relative displacement  $u$  of the neighboring base pairs. Then (in the harmonic approximation),  $\ln\langle |\xi|^2 \rangle$  contains a term, proportional to  $\langle u^2 \rangle$ , which is proportional to the temperature  $T$ . Thus, we arrive at the expression

$$\beta a = c_1 - c_2 T, \quad (6)$$

where  $c_1$  and  $c_2$  are temperature-independent factors. They can be extracted from the paper [20]:  $c_1 \approx 4$ ,  $c_2 \approx 0.01 \text{ K}^{-1}$ . The values are in agreement with rough estimates  $c_1 \sim a/b$ ,  $c_2 \sim k_B/M\omega_b^2 b^2$ , where  $k_B$  is the Boltzmann constant,  $M$  is the base pair mass, and  $b$  is the electronic penetration length. It can be estimated as  $b \sim \hbar/\sqrt{mE} \sim 1 \text{ \AA}$ , where  $m$  is the effective electron mass and  $E$  is its binding energy at the base pair.

To conclude, for the electron which is strongly bound to the donor, we established two different charge transfer mechanisms: diffusion and tunneling. Diffusion leads to a charge transfer probability independent of the donor–acceptor distance  $x$ . However, the probability contains the small factor related to the electron jump from the donor to a neighboring site. The tunneling leads to the exponential dependence of the probability on  $x$  (with the temperature-dependent length  $\beta^{-1}$ ). Therefore, it is not efficient for large distances. Thus, the exponential law has to be observed for small distances  $x$ , whereas for large distances the charge transfer rate has to be independent of the donor–acceptor distance. Just this kind of behavior was reported very recently [23]. For the case of an electron weakly bound to the donor, the hopping should always dominate over quantum tunneling. This explains why the rate of charge transfer sometimes does not behave exponentially even for small  $x$  [36, 37].

Note that in some cases the interaction of light, ionizing radiation, or chemically active reagents with DNA can result in the loss of an electron at a specific site with the formation of a hole. In this case, the charge transport through DNA can be provided by holes (see, e.g., [14]). The key issues for positive charge carrier transport are the same as for the electrons. As far as the physical picture of charge transport is concerned it is essentially the same for both kinds of carriers, and it can be described in the framework of the same approach.

The research presented in this publication was made possible in part by the Russian Foundation for Basic Research, project no. 00-02-17785. Fruitful discussions with A. Iosselevitch, Yu. Evdokimov, V. Golo, D. Bicout, and T. Costi are gratefully acknowledged.

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