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Soliton-like Solutions and Electron Transfer in DNA

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Abstract. We consider various mechanisms of long-range electron transfer in DNA which enable us to explain recent controversial experiments. We show that continuous super-exchange theory can explain the values of electron rate constants in short fragments of DNA. The soliton-type electron transfer in long segments of DNA is also dealt with.

Key words: Bridging states, nonexponential decay, solitons, self-organized electron states

1. Introduction

Both experimental and theoretial efforts have been focused recently on the problem of long-range electron transfer (ET) through a DNA helix [1–12]. The experimental results on long-range electron transfer in duplex DNA remain controversial.

A well-defined linear helix and repetitive structure is established in the DNA double strand which consists of stack of pyrimidine purine base pairs which are stabilized in space by a ribosyl phosphodiester double strand.

The question of whether DNA with stacked array of aromatic heterocyclic base pairs has structurally inherent potential for transport of over greater distances has been discussed for a long time. It was suggested many years ago that the overlapping π orbitals of the nucleotic bases form a common delocalized electron system of the whole DNA macromolecule and so a Bloch type description of the electron states becomes possible [13–15].

Since the energy bands associated with π stacks are narrow the expected mobilities of charge carriers in DNA should be low. The drift mobility of electrons and holes was calculated for various periodic DNA models using LCAO orbitals [16]. It was shown that for homonucleotides and poly (A–T), poly (G–C) systems the mean free path of charge carriers at room temperatures is about $20 \div 50$ Å, while for the more complicated poly (A–T, G–C) systems the mean free path is less than 5 Å.

This analogy with the previously described mechanism was used to explain the recent Meggers et al. experiments [7] on motion of electron holes in the DNA structure [8]. According to Ratner [8] depending on the energy of excitation, one would expect different mechanistic behaviour: if the ‘bridging states’ (in DNA, these are the intervening base pairs) are very high in energy compared to the initial and final states we should observe superexchange transport, i.e. a rapid exponential decay of the transfer rate. If the intermediate bridging states are comparable in energy, or lower in energy, than the initial state, then one would expect hopping behaviour that decays slowly with distance.

The investigations of electron transfer in a series of structurally well-defined donor-bridge-acceptor (DBA) molecules that incorporate tetracene as the donor and pyromellitimide as acceptor, linked by p-phenylenevinylene oligomers of various lengths provide support for hopping mechanism [9]. Photo-induced electron transfer in this series exhibits very weak distance dependence for donor-acceptor separations as large as 40 Å, with rate constants of the order of 10^{11} s^{-1}. These findings also demonstrate the importance of energy matching between the donor and bridge components for achieving molecular-wire behaviour.

The importance of the efficient charge injection into the bridge with nearly matched energy of the highest occupied electronic state of the donor to the lowest unoccupied state of the bridge has long been recognized [10–12]. However any experimental demonstration of this effect has been lacking as yet. As the energy between the highest occupied state of the donor and an empty eigenstate of the bridge decreases, the rate of charge conduction through the bridge increases rapidly. The fast rate of electron transfer in [9] was achieved by lengthing the bridge which caused the lowest unoccupied molecular orbital energy of the bridge to approach that of donor to within 0,1 eV.

Experiments of several research teams performed in recent years have indicated the efficient charge migration within DNA duplex over a large distances up to $20 \div 40$ Å [1–4].

Mead and Kayyem reported the results of ET experiments in 8-base-pair duplex with ruthenium metal complexes coordinately bound to the $2'$ – ribose positions at each strand’s $5'$ – end [2, 3]. The metal-to-metal distance between the two ruthenium states in the 8-mer duplex was 20,5 Å. The relevant edge-to-edge distance between complexes for the ET process was of the order of 12,5 Å. Mead and Kayyem measured the ET rate between the donor Ru (II) $(NH_3)_4$ (Pyridine) $(\text{amine})^{2+}$ and the acceptor Ru $(\text{bpy})_2$ (imidazole) $(\text{amine})^{3+}$ to be $1,6(\pm 0,4) \cdot 10^6$ s^{-1}.

Brun and Harriman studied distance dependence of rate constants for photo-induced ET between two sets of intercalated donors and acceptors in CT–DNA [4]. The closest D/A edge-to-edge separation distances in this experiment correspond to 3, 4 and 5 intervening DNA base pairs or 10,2, 13,6 and 17,0 (Å). It was demonstrated that ET rate exponentially decays with distance with the decay coefficient $\beta = 0,9$ Å^{-1} close to that obtained for ET in proteins [17].

Beratan et al. reported the results of quantum-chemical calculations for the above DNA mediated ET experiments [5, 6]. They obtained $\beta = 1,2$ Å for Mead and Kayyem experiment and $\beta = 1,6$ Å^{-1} for Brun and Harriman system. The latter is not in good agreement with experimentally determined value of 0,9 Å^{-1}.

The detailed quantum-chemical calculations [5, 6] cannot even qualitatively explain the results of Barton et al. measurements of Ru- to -Rh ET for a tethered and intercalated D/A pair. The closest edge-to-edge separation between the intercalated ligands for the two metal complexes, dppz and phi, was 37,4 Å, corresponding to 11-intervening base pairs. The edge-to-edge separation of the D/A complexes in this duplex is 26 Å. For ET rate the value $K_{ET} \geq 10^9$ s^{-1} was reported.

In other words for the distance almost twice longer than in Mead and Kayyem experiments Barton et al. obtained the rate of ET more than 10^3 times higher. These results demonstrate more complexity than exponential behaviour of ET in DNA.

In this paper we will consider a simple model illustrating the superexchange mechanism via self-organized electron state (SES) in DNA. The possibility of soliton-like excitation to form in the bridge and to transfer charge in DNA will also be discussed.

The paper is arranged as follows. In Section 2 we introduce a mathematical model based on the description of DNA as a deformed thread and derive dynamical equations of an excess electron interacting with finite thread.

In Section 3 we discuss a special case of infinite thread. In this limiting case the soliton type solution of the above equations exists.

In Section 4 we deal with a discrete model of nondeformed and deformed DNA model. We show that the discrete model turns into the continuous model considered in Section 3 in the case of extended electron states.

In Section 5 we consider a discrete number of solutions to the nonlinear equations of continuous model which correspond to the finite DNA thread.

In Section 6 we use the obtained solutions to calculate the superexchange electron transfer in DNA. It is shown that the value of the calculated matrix element of the electron transfer T_{DA} is in good agreement with Barton et al. experiment.

In Section 7 we compare the soliton mechanism of electron transfer in DNA considered in Section 3 with the superexchange mechanism through the self-organized electron states considered in Section 5.

2. Mathematical model

A self-consistent excess electron + DNA deformation state is considered as a SES suitable to explain ET. The central point of the subsequent discussion is the extended nature of SES and the existence of a critical size of a DNA molecule in which such states can arise. To introduce such states let us consider DNA as an elastic thread with length equal to 2R. An electron, inserted in this thread produces displacement $u(x)$ at each point x. The density of elasticity energy U_e of the thread will be equal to:

$$U_e = \frac{k}{2} u'^2(x), \ |x| \leq R. \tag{1}$$

Where k is the elasticity constant. If the electron energy is reckoned from the non-deformed state, the energy of the electron interaction with deformation takes the form:

$$U_{int} = -Gu'(x)\ |\psi(x)|^2. \tag{2}$$

Where G is the deformation potential constant, $\psi(x)$ is the electron wave function. The total Lagrangian: $L = L_{kin} + L_{int} + L_{pot}$, where L_{kin} represents the kinetic electron energy, L_{int}-interaction and L_{pot}-potential energy, takes the form:

$$L = \frac{i\hbar}{2}(\psi^*\dot{\psi} - \dot{\psi}^*\psi) - \frac{\hbar^2}{2m}(\Psi'^*\Psi') + G\Psi^*u'\Psi +$$

$$+\rho\frac{\dot{u}^2}{2} - \frac{k}{2}u'^2, \quad |x| \leq R \tag{3}$$

$$L = \frac{i\hbar}{2}(\Psi^*\dot{\Psi} - \dot{\Psi}^*\Psi) - \frac{\hbar^2}{2m}(\Psi'^*\Psi'), \quad |x| \geq R. \tag{4}$$

where m is the electron effective mass, ρ is the density of the considered thread, $\hbar$ is the Planck constant divided by 2π. The dynamical Euler equations corresponding to Lagrangian (3), (4) are:

$$\frac{\partial}{\partial t}\frac{\partial L}{\partial\dot{\Psi}^*} - \frac{\delta L}{\delta\Psi^*} = 0, \quad \frac{\partial}{\partial t}\frac{\partial L}{\partial\dot{u}} - \frac{\delta L}{\delta u} = 0. \tag{5}$$

Variation of L with respect to $\Psi(x)$ and $u(x)$ leads to the following equations for the wave function Ψ and u:

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} + \frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + G\Psi(x,t)\frac{\partial}{\partial x}u(x,t) = 0, \quad |x| \leq R \tag{6}$$

$$\rho\frac{\partial^2}{\partial t^2}u(x,t) - k\frac{\partial^2}{\partial x^2}u(x,t) + G\frac{\partial}{\partial x}|\Psi(x,t)|^2 -$$

$$-G[|\Psi(x,t)|^2\delta(x-R) - |\Psi(x,t)|^2\delta(x+R)] = 0, \quad |x| \leq R \tag{7}$$

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = 0, \quad |x| > R \tag{8}$$

where $\delta(x)$ is Dirac delta-function. The boundary conditions for Equations (6)–(8) correspond to those of the rod with free boundaries. These conditions correspond to a free DNA molecule in solution and take the form:

$$\left.\frac{\partial}{\partial x}u(x,t)\right|_{|x|=R} = 0. \tag{9}$$

In addition to these boundary conditions the condition of normalization for each solution of Equations (6)–(9) should be fulfilled:

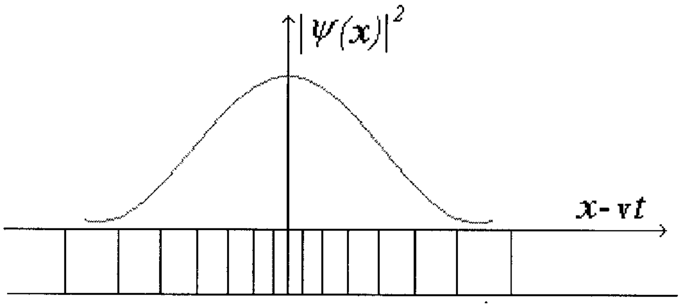

Figure 1. Soliton-like solution in DNA.

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 1. \tag{10}$$

Below we will consider particular important cases of general Equations (6)–(9).

3. Infinite DNA thread

This case corresponds to the limit $R \to \infty$. The system of Equations (6)–(9) reduces to the form:

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + G\Psi(x,t)\frac{\partial}{\partial x}u(x,t) = 0, \tag{11}$$

$$\rho \frac{\partial^2}{\partial t^2}u(x,t) - k\frac{\partial^2}{\partial x^2}u(x,t) + G\frac{\partial}{\partial x}|\Psi(x,t)|^2 = 0. \tag{12}$$

Equations (11), (12) are analogous to those considered by Davydov [18]. Equation (11), (12) have a soliton-type solution;

$$\Psi(x,t) = \exp\left[\frac{it}{\hbar}\left(\frac{mv^2}{2} - w\right)\right]\exp\left[i\frac{mv}{\hbar}(x - vt)\right]\Psi(x - vt) \tag{13}$$

$$u(x,t) = u(x - vt) \tag{14}$$

where w – electron energy, v – is soliton velocity. Substitution of (13), (14) into (11), (12) yields:

$$\Psi(x - vt) = \pm\left(\sqrt{2r}ch\frac{x - vt - x_0}{r}\right)^{-1} \tag{15}$$

$$u(x - vt) = \frac{G}{2k}\frac{1}{(1 - v^2/c^2)}th\frac{x - vt - x_0}{r} \tag{16}$$

$$w = -\frac{\hbar^2}{2mr^2} \tag{17}$$

where x_0 is the arbitrary reference point, c is the sound velocity: $c = \sqrt{k/\rho}$, and r is the characteristic size of soliton:

$$r = \frac{2\hbar^2}{m}\frac{k}{G^2}\left(l - \frac{v^2}{c^2}\right). \tag{18}$$

One soliton solution (15) for electron in deformed DNA is shown in Figure 1. The total energy of soliton E can be found by integrating the density energy $H(x)$ over the whole space:

$$E = \int_{-\infty}^{\infty} H(x)\,dx \tag{19}$$

$$H(x) = \frac{\hbar^2}{2m}(\Psi'^*\Psi') - G\Psi^* u'\Psi + \frac{1}{2}\rho\dot{u}^2 + \frac{1}{2}ku'^2. \tag{20}$$

It follows from (19), (20) that:

$$E = \frac{m}{24\hbar^2}\frac{G^4}{k^2}\frac{5v^2/c^2 - 1}{(1 - v^2/c^2)^3}. \tag{21}$$

Expanding (21) in series of v^2/c^2 for small velocities $v \ll c$ we can obtain from (21) the effective mass soliton M:

$$M = m\left[1 + \frac{G^4}{6k^2c^2}\right]. \tag{22}$$

Thus the obtained solution describes the electron in DNA as a particle with total energy E and effective mass M. We will discuss the applicability of these results for the explanation of long-range electron transfer in DNA in Section 6 and 7.

4. Discrete models

A. THE CASE OF NON-DEFORMED CHAIN

The basic Hamiltonian in superexchange theories of electron transfer through the chain of molecules has the form [19]:

$$H = \sum_i \alpha_i a_i^+ a_i + \sum_{i,j>i} v_{ij}(a_i^+ a_j + a_j^+ a_i) \tag{23}$$

where a_i^+, a_i are the creation and annihilation electron operators on molecule with number i, α_i represents the energy of electron localized on i-th molecule, v_{ij} are the exchange integrals.

The general form of Hamiltonian (23) includes the case considered in electron transfer theory when one value of i corresponds to donor: $i = D$ and another i' to acceptor: $i' = A$.

If we take the wave function of electron in the form

$$|\Psi>=\sum_i b_i(t)a_i^+|0> \tag{24}$$

the equation for amplitudes b_i is given by:

$$i\hbar\frac{\partial b_i}{\partial t}=v_{i-1,i}b_{i-1}+\alpha_i b_i+v_{i,i+1}b_{i+1} \tag{25}$$

Equation (25) represents the case when the exchange integrals v_{ij} differ from zero only for nearest neighbours of the molecule.

To solve the problem of electron transfer we need to calculate the probability for an electron initially residing at site i to pass on to the site j during the time t. The amplitude of this probability can be defined as b_{ij}.

Let the solution of Equation (25) be expressed as $B(t)=[b_{ij}(t)]$ with the initial conditions $b_{ij}(0)=\delta_{ij}$. Accordingly Equation (25) takes the form:

$$i\hbar\frac{\partial B}{\partial t}=BA \tag{26}$$

where the transition matrix A is defined by:

$$A=\begin{pmatrix} \alpha_0 & v_0 & 0 & 0 & \cdot\ \cdot\ \cdot \\ v_1 & \alpha_1 & v_1 & 0 & \cdot\ \cdot\ \cdot \\ 0 & v_2 & \alpha_2 & v_2 & \cdot\ \cdot\ \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot\ \cdot\ \cdot \end{pmatrix}. \tag{27}$$

To find solutions to matrix equations (26) we should determine of eigenvalues and eigenfunctions of the matrix A (27).

It can be shown [20, 21] that if all α_i and v_i are less than a finite constant M, the spectrum of eigenvalues of A extends over a finite interval of the negative real axis and becomes continuous over this interval in the limit of infinite chain. The general solution to Equation (26) takes the form:

$$B(t)=\exp(-i\hbar tA). \tag{28}$$

In particular case, when $v_i=v$ and $\alpha_i=\alpha=-2v$, the analytical solution for $b_{ij}(t)$-amplitudes can be obtained:

$$b_{ij}(t)=i^{(j-i)}e^{2ivt/\hbar}[J_{i-j}(2vt/\hbar)-(-1)^i J_{i+j}(2vt/\hbar)] \tag{29}$$

where $J_v(z)$ is the Bessel function. It follows from (29) that in the case of periodic chain the amplitudes $b_{ij}(t)$ are the oscillation functions of time t. The probabilities of finding an electron at each site of the considered chain exhibit the same oscillations.

B. THE CASE OF THE DEFORMED CHAIN

In this case electron energy on i-th molecule α_i depends on the value of molecules displacements:

$$\alpha_i = \alpha_i(r_1, \ldots, r_N). \tag{30}$$

The total Hamiltonian H takes the form:

$$\tilde{H} = H + T + V \tag{31}$$

where H is determined by (23). T and V are the kinetic and potential energies of the chain:

$$T = \sum_i \frac{M_i}{2}\dot{r}_i^2, \quad V = \sum_i \frac{k_i}{2}(r_i - r_{i+1})^2 \tag{32}$$

where M_i is the mass of i-th molecule, k_i is the elasticity constant characterizing the deformation between i-th and $(i+1)$-th sites.

The equation for amplitudes b_n of wave function (24) takes the form:

$$i\hbar\frac{\partial b_n}{\partial t} = \alpha_n b_n + \sum_{\substack{j \\ (j>n)}} v_{nj} b_j + \sum_{\substack{i \\ (i<n)}} v_{in} b_i. \tag{33}$$

To describe the motions of molecules we can use the Newton equations. In this case the Newton equations of motion determined by Hamiltonian $\tilde{H}$ take the form:

$$M_n \ddot{r}_n = k_n r_{n+1} + k_{n-1} r_{n-1} - (k_n + k_{n-1}) r_n - \sum_{i=1}^{N} \frac{\partial \alpha_i(r_1, \ldots, r_N)}{\partial r_n} b_i^* b_i. \tag{34}$$

Nonlinear dynamical system (33), (34) determines the electron transfer in the deformed chain. Let us consider the linear dependence of values α_i on deformation:

$$\alpha_i(r_1, \ldots, r_N) = \alpha_i^0 + \alpha_i'(r_{i+1} - r_{i-1}). \tag{35}$$

Is the case of uniform chain: $\alpha_i^0 = \alpha$, $\alpha_i' = \alpha'$, $v_i = v$ we can consider the continuous limit, which is valid when the characteristic electron size is larger than the intermolecular distance Δ.

Let us define $r_n(t) = r(n, t)$ and $b_n(t) = b(n, t)$. Introducing the continuous dimensionless variable $\zeta = x/\Delta$ instead of discrete variable n we can write:

$$r(\zeta \pm 1, t) = r(\zeta, t) \pm \frac{\partial r(\zeta, t)}{\partial \zeta} + \frac{1}{2}\frac{\partial^2 r(\zeta, t)}{\partial \zeta^2} \tag{36}$$

$$b(\zeta \pm 1, t) = b(\zeta, t) \pm \frac{\partial b(\zeta, t)}{\partial \zeta}. \tag{37}$$

Using (35), (36) and (37) we get instead of (33), (34) the equations:

$$i\hbar\frac{\partial b}{\partial t} = \left[\alpha + 2\alpha'\frac{\partial r}{\partial \zeta}\right] b + v\left(2b + \frac{\partial^2 b}{\partial \zeta^2}\right) \tag{38}$$

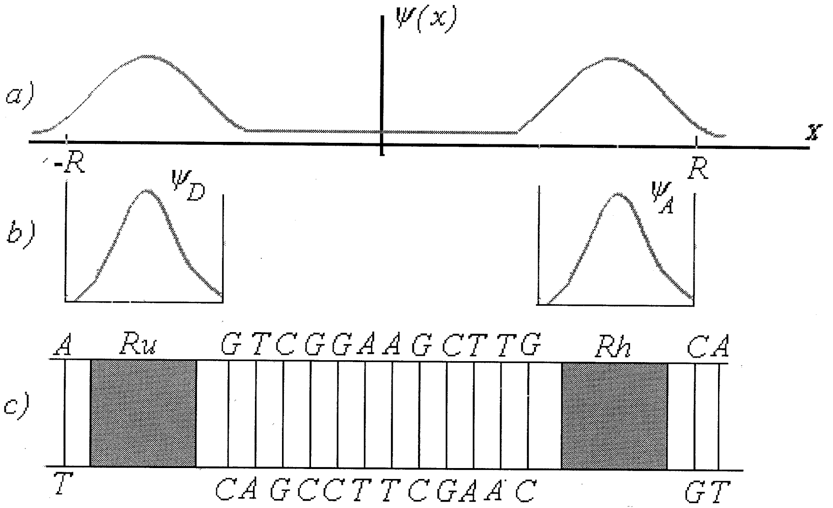

Figure 2. a) $\Psi(x)$ is the wave function of self consistent state; b) Ψ_D, Ψ_A are the wave functions of donor and acceptor; c) The sequence of base pairs and donor-acceptor positions for Barton et al. experiment.

$$M\ddot{r} = k\frac{\partial^2 r}{\partial \zeta^2} + 2\alpha' \frac{\partial}{\partial \zeta} b^* b. \tag{39}$$

With the replacement:

$$b \to \Psi \exp\left[-\frac{i}{\hbar}(\alpha + 2v)\right], \ r \to u, \ 2\alpha'\Delta \to -G, \tag{40}$$

$$v\Delta^2 \to \hbar^2/2m, \ \ k\Delta^2 \to k, \ M \to \rho$$

Equations (38), (39) take the form of Equations (11), (12) for infinite elastic thread, considered in Section 3.

5. The short thread of DNA

In Section 3 we considered the case of infinitely long DNA thread. As pointed out above the DNA duplexes, exploited in electron transfer experiments are relatively short (of length 1,5–2 helical turns, Section 1). These duplexes can be considered quite rigid across the duplex. For such short thread of DNA the soliton solution obtained in Section 3 is not valid.

Below we will consider the stationary solutions of Equations (6)–(9) for a short thread. In this case Equation (7) with the boundary conditions (9) leads to the following expression for equilibrium deformation of the molecule in the presence of the electron:

$$u'(x) = \frac{G}{k}\Psi^2(x) - \frac{G}{k}\Psi^2(R), \ \ |x| \le R, \tag{41}$$

$$u'(x) = 0, \quad |x| \geq R. \tag{42}$$

Using (41), (42) Schroedinger Equation (6) in stationary case takes the form:

$$\frac{\hbar^2}{2m}\Psi''(x) + \frac{G^2}{K}\theta(R - |x|)[\Psi^2(x) - \Psi^2(R)]\Psi(x) - |w|\Psi(x) = 0. \tag{43}$$

Equation (43) was earlier considered in [22, 23]. It has a discrete number of soliton-type solutions: if R is larger than the critical value $R_1 = 5,71\ k\hbar^2/2mG^2$ a one-soliton solution exists. It has a sharp maximum at the origin of the coordinates and tends to zero as the distance from the origin increases. If $R > R_2 > R_1$ where $R_2 = 33,2\ k\hbar^2/2mG^2$ then in addition to the one-soliton a two-soliton solution appears and so on. Figure 2 shows the solution of Equation (43) which has two sharp maxima, occurring at the distance equal to $\pm 2R/3$ from the origin of x axis.

6. Superexchange electron transfer through DNA

As seen from Figure 2 donor and acceptor occur in the region of maxima of the wave function $\Psi(x)$. We will model electron states of donor and acceptor by a deep and narrow rectangular potential wells whose centers coincide with maxima $\Psi(x)$ (Figure 2). Thus we can consider the wave functions of donor Ψ_D and acceptor Ψ_A to be totally localized in the potential wells. Under these assumptions the overlap matrix element of Ψ_D, Ψ_A and Ψ is equal to I:

$$I = \int_{-\infty}^{\infty} \Psi_D(x)\Psi(x)\,dx \approx \Psi(x_D)\int_{-\infty}^{\infty} \Psi_D(x)\,dx. \tag{44}$$

The value of $\Psi(x_D)$ represents the maximum of two-soliton solution. For sufficiently large molecular size R this maximum is equal to:

$$\Psi(x_D) = \frac{1}{4}\frac{G}{\hbar}\sqrt{\frac{m}{k}}. \tag{45}$$

If we put the depth of the rectangular potential well sufficiently deep the donor (acceptor) wave function can be written as:

$$\Psi_D(x) = \sqrt{\frac{2}{d}}\sin\frac{\pi}{d}x, \quad \frac{2}{3}R - d \leq |x| \leq \frac{2}{3}R. \tag{46}$$

It follows from (45), (46) that the value of the overlap integral is:

$$I = \frac{l}{\sqrt{2\pi}}\frac{G}{\hbar}\sqrt{\frac{md}{k}}. \tag{47}$$

According to superexchange theory the rate of transfer to acceptor through intermediate state is proportional to the square of matrix element between donor and acceptor T_{DA}:

$$T_{DA} = \frac{I^2 w^2}{|\Delta E|}, \tag{48}$$

where ΔE is the energy difference between the donor electron state and two-soliton state. The energy of two-soliton state determined by Equation (43) is equal to [22, 23] (see appendix):

$$|w| = \frac{1}{32}\frac{G^4}{k^2}\frac{m}{\hbar^2}. \tag{49}$$

The obtained formulas (47)–(49) determine the superexchange expression for matrix element which will be estimated below.

7. Numerical estimations and discussion

The elasticity constant k in (47)–(49) can be estimated from the following consideration. Characteristic frequencies of longitudinal oscillations of a DNA molecule w are of the order of picoseconds. The molecular groups involved in the molecular structure displace by about 0,1 of the distance between the nearest groups. If we put the distance $\tilde{a}$ between the groups equal to 1 Å and the characteristic frequency $\hbar$ w equal to 10^{-3} eV then from the equality $k(u'(a))^2/2 = \hbar$ w, $u'(a) = 0,1$ we find the elasticity constant to be $k = 3,2 \cdot 10^{-5}$ dyne. The typical values of deformation potential in solids is about several electron-Volts. Assuming that G has the same values in DNA we take G equal to 1 eV. If we put the effective electron mass equal to 10^{-27} g then from (49) we get $|w| = 0,13$ eV. The value of ΔE in DNA is equal to $|\Delta E| \simeq 2$ eV [5, 6]. If we put $d = 1$ Å then from (47), (48) we get the value of the matrix element $T_{DA} = 3 \cdot 10^{-4}$ eV. In [5, 6] the value of the matrix element (reorganization energy 0,4 eV, donor-acceptor free energy difference $\Delta J = -0,75$ eV and the reaction rate $k_{et} = 3 \cdot 10^9$ s^{-1}) was calculated to be $T_{DA} = 1,9 \cdot 10^{-4}$ eV. Our value $T_{DA} = 3 \cdot 10^{-4}$ eV leads to the transfer rate twice greater than that obtained in [1]. In this connection it is worth to emphasize that in experiments [1] a vary fast emission quenching was observed so that the rate of transfer is higher than $3 \cdot 10^9$ s^{-1}. Thus our results are not contradictory to the experiment [1]. It follows from (48) that the matrix element does not decay exponentially as the transfer distance increases. Moreover (48) suggests that it does not depend on distance at all. If it was the case then an electron would be able to transfer through arbitrary distance for a very short time $\sim 10^{-9}$ s. In fact the model developed is not valid for very large transfer distances. We can estimate the limiting distance from the inequality: $\hbar/mR_{\max}^2 \geq \hbar$ w. For the above parameters it gives the value $R_{\max} \sim 100$ Å. For distances $R > R_{\max} ET$ exhibits the usual exponential behaviour. According to [22, 23] the minimal distance for which the considered SES is possible is equal to $R_{\min} = 33,2\ k\hbar^2/2mG^2 = 21$ Å, i.e. the minimal duplex length $l_{\min} = 2R_{\min} = 42$ Å.

It is important that control experiments on photochemical DNA cleavage at the intercalation site proved that the positions of intercalation (donor and acceptor) are usually two base pairs away from the ends (Figure 2). For Barton et al. experiment with ultrafast electron transfer [1] the length of 15-mer DNA duplex was larger than $l_{\min}$. Thus only on the interval 40 ÷ 200 (Å) the nonexponential electron rate dependence is possible. For Mead and Kayyem [2, 3] and Brun and Harriman [4] experiments the DNA length was less than 40 Å and usual exponential dependence was observed.

Finally we can discuss the possibly of one-soliton electron transfer in DNA (Section 3). The criterion for the formation of soliton of this type in short DNA thread is less rigorous than that for two-soliton solution and requires the DNA length to be longer than $2R_1 = 11,42\ k\hbar^2/2mG^2$. For the above parameters this yields $l > 7,3$ Å. According to formula (21) the total energy of this soliton is equal to $E = -0,17$ eV. This energy is much less than the gap between the occupied orbitals and the bottom of the conductivity band in DNA. Thus the soliton mechanism of charge transfer is unprobable in experimental conditions [1–4]. However it can be realized if the conditions of experiment are changed. With this soliton mechanism of long-range electron transfer the transfer rate depends only slightly on the transfer distance if at all.

The possibility of soliton to arise and to mediate electron transfer has been reported in recent experiments [24]. The direct measurements of electrical current as a function of the potential applied across a few DNA molecules associated into a single rope of length at least 600 nm suggests efficient conduction through the rope. This distance-independent transfer also occurs in the experiments with repairing and oxidation reactions in DNA [25–27].

In our opinion further measurements of electron transfer rate with regard to different transfer distances and DNA sequences are required to clarify the mechanism of long-range electron transfer in DNA.

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Appendix

Let’s pass on its Equation (43) to the dimensionless variables using the formulas:

$$\Psi(x) = \sqrt{\frac{k|w|}{2G^2\hbar^2}}\,Y(\tilde{x}) \tag{A1}$$

$$x = \sqrt{\frac{\hbar^2}{2m|w|}}\,\tilde{x}. \tag{A2}$$

Than (43) is rewritten in the form:

$$Y''(\tilde{x}) + [Y^2(\tilde{x}) - Y^2(a)]Y(\tilde{x}) - Y(\tilde{x}) = 0, \quad |\tilde{x}| \le a \tag{A3}$$

$$Y''(\tilde{x}) - Y(\tilde{x}) = 0, \quad |\tilde{x}| > a \tag{A4}$$

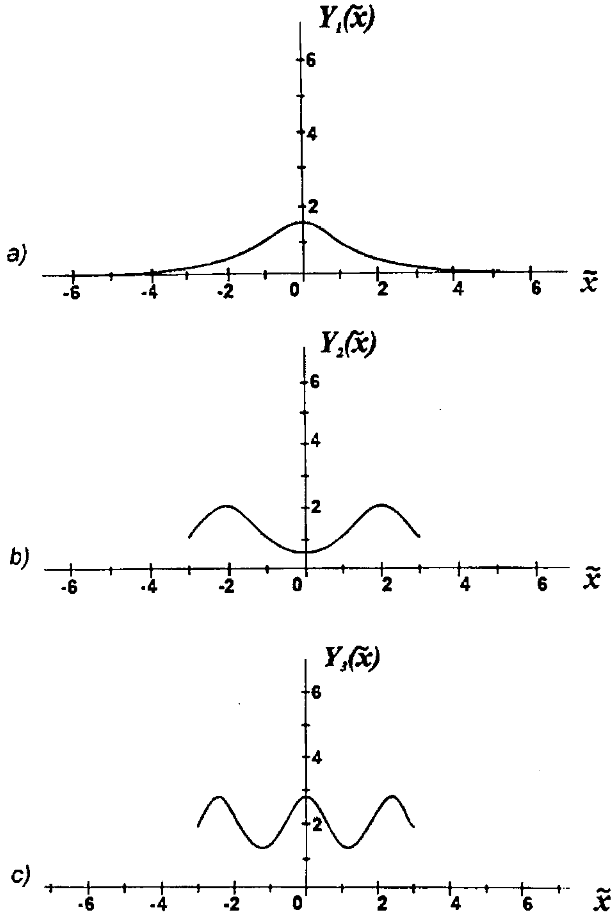

Figure 3. Solutions of Equation (A3), (A4) for different values of a: a) $a = 5.0$, $\zeta = 20.0$; b) $a = 3.0$, $\zeta = 35{,}6$; c) $a = 3.0$, $\zeta = 81{,}7$ where $\zeta = 2G^2\ Rm/k\hbar^2$

where:

$$a = R\sqrt{2m|w|/\hbar^2}.$$

Analytical analysis of Equations (A3), (A4) leads to the following conclusions [22, 23]:

1) For each positive a the problem (A3), (A4) has an infinite number of solutions. The solutions with number n has n-maxima (Figure 3) and looks like a segment of periodic function with the period T:

$$T = \frac{4a}{2n-1}. \tag{A5}$$

2) The relative positions of maxima and minima of solutions on the segment $[-a, a]$ are independent of a. For example, for $n = 2$ there exists one minimum at $\tilde{x} = 0$ and two maxima at

$$\tilde{x} = \pm\frac{2}{3}a. \qquad \text{(Figure 2b)}$$

3) Oscillation amplitude of solution is independent of a and n: $M_n(a) - m_n(a) = \sqrt{2}$.

4) The maximum $M(a)$ is unbound for $a \to 0$:

$$M_n(a) \approx \frac{C_n}{a}, \quad C_n = \frac{\pi(2n-1)}{2\sqrt{2}}. \tag{A6}$$

5) The solution with $n = 1$ tends to 'soliton' solution as $a \to \infty$:

$$Y(\tilde{x}) = \frac{2}{\cosh \tilde{x}} \tag{A7}$$

(10), (A1), (A2) yield the expression for the electron energy w:

$$w = -\frac{2}{\Gamma^2}\frac{G^4 m}{k^2\hbar^2} \tag{A8}$$

where Γ is a function of parameter $a : \Gamma = \Gamma(a)$. As $a \to \infty$ the value Γ for two maximum solution with two maxima tends to 8. For $a > 6$ the deviation of $\Gamma(a)$ from its asymptotical value is less than 6%.

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