Sequence Dependent Hole Evolution in DNA

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Abstract. The paper examines the dynamical behavior of a radical cation (G^{+*}) generated in a double stranded DNA for different oligonucleotide sequences. The resonance hole tunneling through an oligonucleotide sequence is studied by the method of numerical integration of self-consistent quantum-mechanical equations. The hole motion is considered quantum mechanically and nucleotide base oscillations are treated classically. The results obtained demonstrate a strong dependence of charge transfer on the type of nucleotide sequence. The rates of the hole transfer are calculated for different nucleotide sequences and compared with experimental data on the transfer from (G^{+*}) to a GGG unit.

Key words: Hopping, nucleotide pair, superexchange, tunneling

1. Introduction

In recent years the problem of charge transfer along a double DNA helix has been the focus of attention [1–10]. Presently it is well known that a DNA molecule in equilibrium state does not have any free charge carriers. Free electrons (anion-radicals) or holes (cation-radicals) can arise there either as a result of chemical reactions or upon photoexcitation.

The damage produced in a DNA molecule by ionizing radiation plays a great role in the processes of the cell death (as a result of the loss of a fission capacity), and appearance of mutations which lead to mutagenesis, carcinogenesis and, in a more general sense, aging of an organism [11–17]. The capacity of irradiation-induced charge carriers for travelling large distances owes to the fact that the damaged DNA sites are not necessarily the ones, which were the initial targets of irradiation.

It has been commonly believed for a long time that the migration of charges arising in an irradiated DNA is the domain of radiobiology which deals with the chemical nature of radicals and their localization on the sites determining a sequence of chemical, biochemical and biological processes which can lead to the cell damage. Close relationship between radiobiology and molecular biochemistry has become most noticeable in recent years as it has been realized that the reactions of charge transfer between proteins and DNA play an important role in such biochemical processes as replication, transcription and reparation of a DNA [17].

An understanding of the fact that the processes of charge transfer along a DNA are of great utility for designing DNA-based molecular devices and using DNA as wires in molecular electronic circuits has lead researchers to realize that the study of these processes is the realm of many sciences including nanotechnology and molecular electronics [4].

The hypothesis that a DNA may have conducting properties was first put forward in [18] shortly after the DNA helical structure had been discovered by Watson and Crick. As was noted in [18], a well-determined linear structure of a DNA consisting of stacks of pyrimidine-purine bases resembles stacking in unidimensional aromatic crystals. Numerous discussions have been devoted to the problem of whether a DNA with its aromatic compounds in the shape of stacks of heterocyclic base pairs forms a profile of a potential energy along which a charged particle can be transferred over a large distance.

Recent experiments on charge transfer in DNA have demonstrated a strong dependence of this transfer on the type of oligonucleotide sequence [1, 10] and still remain discrepant. Under these conditions of special importance for understanding and interpretation of the processes in question are experiments on oxidation and reduction of DNA fragments with specially chosen nucleotide sequences. Experiments where holes (cation-radicals) played the role of charge carriers revealed some regularities in the hole motion determined by the DNA structure [1].

The main aim of this work is to model the migration dynamics of cation-radicals in a nucleotide chain and to compare the results obtained with the experiment. In most recent experiments donors and acceptors of charge carriers were sewed by covalent bonds on a nucleotide chain with well-determined sequence of base pairs. In particular, P.T. Henderson et al. [1] obtained relative values for the constants of the reactions of charge transfer from the excited cation-radical G^{+*} to the guanine triplet GGG separated by one, two, three and four AT base pairs. Their method of measurements based on a competition between the charge transfer along a DNA and its trapping in the surrounding water could not give detailed information on the hole transfer dynamics.

To investigate the transfer dynamics in depth we introduce in §2 a simple mathematical model where Watson-Crick pairs are represented as independent oscillators described by classical motion equations and the hole transfer along a chain of bases is depicted by quantum-mechanical equations. The selfconsistent quantum-mechanical equations based on this approach determine joint dynamics of a hole and a sequence of bases.

The main difficulty in modeling the transfer dynamics is concerned with a great number of the model parameters whose physical meaning is determined in §3 reasoning from currently available experimental and theoretical data on DNA. In §4 we present the results of numerical calculations of self-consistent dynamical equations describing cooperative dynamics of a hole and bases for various types of base pair sequences used in the experiments [1]. In §5 we discuss the results obtained and compare them with other theoretical approaches.

Figure 1. Pairs of Watson-Crick oscillators: a) nucleotide pair, b) equivalent oscillator, c) schematic sketch of a hole transfer from a donor to an acceptor along a sequence of sites. IHC-incoherent (hopping) channel, QC-quantum channel.

2. Quantum-Mechanical Model

In this model a DNA is considered as a chain composed of sites. Each site presents a nucleotide pair (Figure 1a) which is treated as a harmonic oscillator (Figure 1b).

In describing migration of a charge in protein macromolecules and DNA either of two different mechanisms of charge transfer is dealt with. One of them implies incoherent hopping charge transfer.

In this case the charge hops from one site to another residing at each for some time and thus travels over a bridge of sites from a donor to an acceptor (incoherent channel, (IHC)-in Figure 1c). So, in the case of hopping mechanism, each site to which the charge hops serves as an actual chemical intermediate.

The other mechanism implies superexchange. It corresponds to tunneling of a charge from a donor to an acceptor in one hop (quantum channel, (QC)-in Figure 1c). In this case the charge cannot be found at any site of the bridge between the donor and the acceptor, its presence at the bridge sites is just virtual.

Modeling of the hole transfer along a chain of sites is based on the Hamiltonian:

$$H_h = \sum_i^N \alpha_i |i\rangle\langle i| + \sum_{i,j}^N v_{ij} |i\rangle\langle j| + \sum_i^N \alpha'_i q_i |i\rangle\langle i| \quad (1)$$

where α_i is the hole energy at the i -th site; v_{ij} -are the matrix elements of the hole transition from the i -th to the j -th site; α'_i is the coupling constant for the hole interaction with displacement q_i at the i -th site.

Expression (1) presents a tight binding Hamiltonian for a hole corresponding to the case when the hole localized at the i -th site is in the state $|i\rangle$.

In the absence of dynamical fluctuations, when $\alpha'_i = 0$, Hamiltonian (1) describes a coherent motion of a hole. In the general case motions within a site cannot be neglected. We take these motions into account by introducing a linear dependence between the hole energy at i -th site and the site displacement q_i .

Hamiltonian H_{osc} describing oscillations of a DNA presents the sum of contributions of each nucleotide pair considered as an independent harmonic oscillator with the effective mass M_i and the frequency ω_i (Figure 1a, b):

$$H_{osc} = \sum_i^N \frac{p_i^2}{2M_i} + \sum_i^N k_i \frac{q_i^2}{2} \quad (2)$$

Here $p_i(t)$ and $q_i(t)$ are the impulse and the displacement of the relative motion of the i -th nucleotide pair at the moment t respectively, k_i is the elastic constant.

In our simplified model of a DNA we believe that the planes of nucleotide base pairs are parallel to each other at each instant of time and the distances between neighboring planes are unchanged (Figure 2). The transfer of a hole in a DNA is determined by overlapping of its wave functions at neighboring sites. If a hole travels along one DNA chain (Figure 2), then, in view of the model geometry, the overlapping integrals are virtually independent of the displacements within the sites irrespective of their value. Thus in Hamiltonian (1) we take into account the displacement dependencies for only the diagonal matrix elements.

In view of the fact that the mass of a nucleotide is several orders of magnitude larger than the mass of a hole, the motion of nucleotides can be described by classical equations and that of a hole- by quantum mechanical ones.

Figure 2. Hole transfer along a DNA chain. Large amplitude of oscillations at the GGG sites illustrates the appearance of the so-called 'open states' of a DNA.

The motion equations for the Hamiltonian $H = H_h + H_{osc}$ in the neighboring approximation lead to the following system of differential equations (see Appendix):

$$i \frac{db_i}{d\tilde{t}} = \eta_i b_i + \eta_{i,i+1} b_{i+1} + \eta_{i,i-1} b_{i-1} + \kappa_i \omega_i^2 u_i b_i \quad (3)$$

$$\frac{d^2 u_i}{d\tilde{t}^2} = -\omega_i' \frac{du_i}{d\tilde{t}} - \omega_i^2 u_i - |b_i|^2 \quad (4)$$

Equations (3) present a Schrödinger equation for the probability amplitudes b_i describing an evolution of an excitation in a deformed chain, while equations (4) are classical motion equations for the site dynamics. The system under investigation is akin in form with model equations exploited by Davydov and his coworkers for understanding the excitations transfer in proteins [19, 20] (for review see [21] and references therein).

The quantities involved in (3), (4) are related to the parameters of the Hamiltonian H as:

$$\eta_i = \tau \alpha_i / \hbar, \eta_{ij} = \tau v_{ij} / \hbar, \omega_i^2 = \tau k_i / M_i, q_i = \beta u_i$$

$$\kappa_i \omega_i^2 = \tau^3 (\alpha_i')^2 / M_i \hbar, \beta_i = \tau^2 \alpha_i' / M_i, t = \tau \tilde{t} \quad (5)$$

where $\hbar$ is the Planck's constant, τ is an arbitrary time scale relating time t and dimensionless variable $\tilde{t}$ with respect to which differentiation in (4) is performed; ω_i' is the frequency determining the damping of a site oscillations; κ_i plays the role of dimensionless coupling constant.

Table I. Oxidation potentials of some nucleotides (solvent is acetonitrile [22])

base	Oxidation potential (eV)
thymine (T)	1,9
cytosine (C)	1,9
adenine (A)	1,69
inosine (I)	1,4
guanine (G)	1,24
7-desaguanine (Z)	0,95

The above-presented model is the simplest one to describe the hole dynamics in a DNA. However, for the purposes of actual modeling even with the use of supercomputers, further simplifying assumptions are required which will be considered in the next section.

3. Model Parameters

We will model the hole dynamics in various sequences composed of guanines G, adenines A and thymine T used in the experiments [1] with the help of equations (3), (4).

However even in the case of short chains consisting of few sites, the system (3), (4) contains too many parameters which makes impracticable its analysis (without exact specifying of the parameters).

Table I lists the values of oxidation potentials α_i for some nucleotide bases, which were found by electrochemical measurements of individual nucleotides [22].

Presently there are no direct measurements for oxidation potentials of π – stacked bases. They are usually taken to be equal to the oxidation potentials of individual nucleotides in a relevant polar solvent.

Recently, hole matrix elements v_{ij} have been calculated by quantum-chemical method for various nucleotide pairs [23] to fall in the range (0,03–0,16 eV) (see Table II).

The values of matrix elements for nucleotides occurring on different DNA strands are less by an order of magnitude (see Table III).

High-frequency intramolecular oscillations in a DNA corresponding to oscillations of bases within a site can be characterized by the mean value $\omega = 2,236 \cdot 10^{11} \text{ sec}^{-1}$ [24] So, in our model of independent oscillators we put $\omega_i = \omega = 2,236 \cdot 10^{11} \text{ sec}^{-1}$ for all nucleotide pairs and $\omega'_i = \omega' \cong 10^9 \text{ sec}^{-1}$ for the oscillator damping.

Figure 3 a)-f). Sequences considered in calculations. Black circles indicate the hole path.

Table II. Matrix elements of the hole transfer between neighbouring nucleotides v_{ij} residing on the same DNA strand (for standard geometry: 3,38Å is the distance between neighbouring nucleotides pairs; 36° is the rotation angle for neighbouring pairs)

Nucleotide pair	v_{ij} (eV)	Nucleotide pair	v_{ij} (eV)
GG	0,084	TG	0,085
GA	0,089	TA	0,086
GT	0,137	TT	0,158
GC	0,110	TC	0,076
AG	0,049	CG	0,042
AA	0,030	CA	0,029
AT	0,105	CT	0,1
AC	0,061	CC	0,041

Table III. Matrix elements of the hole transfer between neighbouring nucleotides occurring on different DNA strands [23]

Nucleotide pair	v_{ij} (eV)	Nucleotide pair	v_{ij} (eV)
GG	0,0193	GA	0,0211
AA	0,0347	AG	0,0213
TT	0,0032	AT	0,0163
CC	0,0007	TA	0,0163

4. Calculation of the Transfer Rate

According to [1], the hole initially arises at the site G_1 (Figure 3), the DNA chain being nondeformed, i.e. $q_i(0) = \dot{q}_i(0) = 0$. Accordingly, in equations (3)-(4) we will take $u_i(0) = \dot{u}_i(0) = 0$. The values of matrix elements η_{ij} involved in (3) are determined by Tables II, III, and relations (5); the values of oxidation potentials are listed in table I; the value of τ in (5) is chosen to be 10^{-14} sec. The only undefined parameters are the quantities κ_i . In numerical calculations their values were chosen from the condition of the best agreement with the experiment. Having performed a great number of numerical experiments we put κ_i equal to: $\kappa = 2, 518$.

With regard to the above assumptions, integration of (3), (4) was performed by Runge-Kutta method. We presumed the hole to be initially localized at the site G_1 : $|b_{G_1}(0)|^2 = 1$, and used the normalizing condition:

$$\sum_i |b_i|^2 = 1 \quad (6)$$

Figure 4. Time – dependencies of $|b_i|^2$ the probabilities of the occurrence of a hole on site i for the cases a)-f) shown on Figure 3. At $t = 0$ the hole is localized at G_1 site.

to check the accuracy of calculations.

Since guanine has the lowermost oxidation potential, the hole travels along guanine bases. The paths of the hole motion for sequences from [1] are shown in Figure 3.

The results of calculation of the probability distribution $|b_i(t)|^2$ for the cases (a)-(f) in the neighbourhood of parameters under consideration (Figure 3) are shown in Figure 4 (a)-(f). Under conditions of the experiment [1] the transfer rate was determined by the number of damaged DNA molecules which appeared in the sequences of Figure 3 (a)-(f) upon trapping of a hole by a guanine triplet. The time during which a hole passed from G_1 to the guanine triplet GGG was found to be: $\tilde{t}_a = 5$, $\tilde{t}_b = 350$, $\tilde{t}_c = 3500$, $\tilde{t}_d = 44500$, $\tilde{t}_e = 290$, $\tilde{t}_f = 426$.

This corresponds to the absolute transfer rates: $K_a = 2 \cdot 10^{13} \text{ sec}^{-1}$; $K_b = 2,86 \cdot 10^{11} \text{ sec}^{-1}$; $K_c = 2,86 \cdot 10^{10} \text{ sec}^{-1}$; $K_d = 2,25 \cdot 10^9 \text{ sec}^{-1}$; $K_e = 3,45 \cdot 10^{11} \text{ sec}^{-1}$; $K_f = 1,25 \cdot 10^{11} \text{ sec}^{-1}$ where we use the usual definition for the rate

Figure 4. Continued.

Table IV. Comparison of theoretical relative values of the transfer rates with the experimental ones

	a	b	c	d	e	f
K_{rel}	224	3,2	0,32	0,025	3,9	2,63
K_{exp}	30	3,2	0,44	0,03	3,0	3,4

constant: $K = 1/\tau$, τ -is the time of transfer. Let us determine the relative reaction rates by the relation: $K_{rel}^i = \frac{K_i}{K_0}$, where $K_0 = 8,9 \cdot 10^{10} \text{ sec}^{-1}$. Table IV compares experimental K_{exp}^i and theoretical K_{rel}^i values of the relative reaction rates.

Figure 4. Continued.

5. Discussion of the Results

Except for the case (a), the calculated values of the reaction rates appear to be rather close to the experimental ones. The case (a) corresponds to the fastest transfer reaction. As remarked above, the relative reaction rates were found from the number of DNA molecules damaged upon a hole transfer. In determining the reaction rate we implicitly believed that the fastest process is the DNA damage. In the case (a) this assumption probably fails and the reaction rate is determined by the time required for breaking the DNA strand rather than by the time of the hole transfer to a guanine triplet. Agreement with the experiment is achieved if the time of the DNA damage is: $t_{damage} = 3,7 \cdot 10^{-13}$ sec.

The results obtained only partially support the idea of the hopping mechanism of the cation-radical transfer in DNA. As is seen from Table IV, in the cases (b), (e) and (f) the transfer rate is of the same order of magnitude notwithstanding the fact that in the cases (e) and (f) the hole path is two nucleotide pairs longer than that in the case (b). At the same time, the transfer time in the case (c) is an order

Figure 4. Continued.

of magnitude larger than in (b) and in the case (d) it is two order of magnitude larger than in (b). A qualitative distinction between the cases (e), (f) and (c), (d) is in the fact that in the latter cases the hole passes from G_1 to GGG in one hop: the probability of the hole occurrence at the intermediate sites remains close to zero during the whole process of transition. Accordingly if the length of the bridge between a donor and an acceptor increases by one nucleotide pair, the transfer rate decreases by an order of magnitude.

In the cases (e) and (f) the hole does not hop directly to the triplet GGG, it first travels to G_3 and then from G_3 to GGG. This way of transfer is illustrated by the arising of nonzero probability $|b_{G_3}|^2$ (Figure 4(e), (f)).

At the same time it should be emphasized that the picture of the transfer suggested by the calculations is more complicated than the view of a hole as hopping from one guanine site to another.

In the cases (e) and (f) the hole, having hopped to the site G_3 , resides there for some time, thus demonstrating typical quantum-mechanical behavior. To describe these F.C. Grozema et al. [25, 26] developed a consistent quantum-mechanical theory similar to the one presented in this work. In modeling the experimental results of [1] they concluded (so as we did) that the migration of holes in the considered sequences occurs mainly the tunneling mechanism. The fundamental difference between our approach and the one used in [25, 26] lies in the fact that

Figure 4. Continued.

in describing irreversible charge transfer the authors of [25, 26] introduce damping directly in the equation (3) as an imaginary addition to the hole energy. As a result, the normalizing condition (6) does not conserved there. Another difference is that the sites in [25, 26] are modeled as rigid and held together by springs. Thus, the distance between the bases changes as the sites oscillate, which fact is assumed not to reflect on the exchange matrix elements. However this assumption is only valid for weak oscillations and fails to describe such phenomena as formation of open states and denaturation of a DNA [27].

In conclusion it may be said that presently there is no theory, which could predict exactly the transfer rate for a given nucleotide sequence. The approach developed in this work presents only the first steps in working out such a theory. Nevertheless, our model though having numerous simplifying assumptions can predict the results of experiments on charge transfer for short irregular nucleotide sequence.

Figure 4. Continued.

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Appendix

We will show that the Hamiltonian $H = H_h + H_{osc}$ of eqns. (1), (2) leads to the system of differential eqns. (3) and (4). Let us seek the solution of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H |\Psi\rangle \quad (A1)$$

in the form $|\Psi\rangle = \sum_n b_n(t) |n\rangle$, where $b_n(t)$ is the probability amplitude describing the excitation evolution on the site n . Substituting $|\Psi\rangle$ in (A1) and taking into account that $v_{i,j} = v_{j,i}^*$ we will get for $b_n(t)$

$$i/\hbar \frac{db_n}{dt} = \alpha_n b_n + \alpha'_n q_n b_n + \sum_{n'} v_{nn'} b_{n'} \quad (\text{A2})$$

With the use of transformation eqns. (5), eqn. (A2) in the neighbourhood approximation takes the form of eqn. (3).

The displacements q_n can be described by the classical equation of motion, because the site masses M_n are much larger than electron one. To derive this let us average the total Hamiltonian H over the state $|\Psi\rangle$:

$$\langle \Psi | H | \Psi \rangle = H_{osc} + \langle \Psi | H_h | \Psi \rangle \quad (\text{A3})$$

The equations of motion for Hamiltonian (A3) take the form:

$$M_i \frac{d^2 q_i}{dt^2} = -\gamma_i \frac{dq_i}{dt} - k_i q_i - \alpha'_i |b_i|^2 \quad (\text{A4})$$

where γ_i are friction coefficients. With the use of transformation eqns. (5), eqns. (A4) take the form of eqn.(4).

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