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Combined hopping–superexchange model of a hole transfer in DNA

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Abstract

Relative hole transfer rates in DNA have been investigated in a number of nucleotide sequences experimentally. Calculation of the transfer rates in DNA is performed relying on the assumption that the transfer is realized as hopping of a hole on guanine sites, each hop being calculated on the basis of superexchange theory. It is shown that the medium reorganization energy and free energy changes play an important role in determining the transfer rate and the type of a nucleotide sequence. The results of the calculations are compared with experimental data covering a range of available sequences.

1. Introduction

Reactions of charge transfer provide an example of one of the simplest types of process underlying the functioning of biological systems. Charge migration in DNA is a rapidly developing area that has attracted both theoretical and experimental attention [1–7]. Unique stacking and overlapping of π-electrons in DNA may provide a preferred path for charge transfer [2,3]. This opens up the potential to consider DNA as a wire in nanoelectronics and various molecular devices [1]. Among the useful applications of the assembly properties of DNA are the so-called biochips [8]. Currently, the chips are usually read out optically, but further miniaturization might require new detection schemes, which could rely on the conducting properties of DNA. So far, these properties have not been completely understood as evidenced by discrepancies in the literature.

The sequence dependence of charge transfer in DNA has been a topic of significant interest in recent years. Numerous experimental studies of charge migration through DNA have been centered on hole transfer, resulting in reports on its widely varying distance dependence [4–7,9,10]. It has recently been suggested that, depending on the particular sequence, charge transfer in DNA may occur by different mechanisms, such as hopping, superexchange, thermally activated transfer, or molecular-wire transport. In various experimental conditions, the rate of charge transfer in oligonucleotides may differ by several orders of magnitude [9]. All this suggests a demand for a simple but flexible theoretical description which would provide a correct order of magnitude for the transfer rate in various nucleotide sequences. This could enable potential identification of a nucleotide sequence by the mere measurement of the charge transfer rate.

To calculate the transfer rate in various nucleotide sequences, here we consider a combined mechanism of charge transfer in DNA which includes hopping and superexchange transfer. We first present the theoretical framework and model followed by example calculations with experimental comparisons. We conclude with a discussion of the implications for using this analysis in a wider experimental context.

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2. A combined model of charge transfer

From the large phenomenological literature on charge transfer in DNA, we start with the experiments on hole transfer [4–7] in which some regularities have been noted. In these experiments, a hole arises at a certain site of a nucleotide sequence as a result of photoexcitation. In the experiments considered [4–7], the site was guanine, G, which has the lowest oxidation potential compared to the other nucleotides. In this picture, the hole travels along the nucleotide chain hopping on the sites containing other guanines. As this takes place, the sites containing A–T pairs play the role of bridges between guanine sites. The bridges present potential barriers for the hopping of the hole and are overcome largely via quantum-mechanical tunneling.

To describe a hole transfer over bridge sites, we will rely upon the Marcus formula [11]. Accordingly, the rate constant K_{DA} of a nonadiabatic charge transfer from a donor D to an acceptor A is determined by the effective electronic coupling H_{DA} and a thermally weighted Frank–Condon factor F:

$$K_{DA} = \frac{2\pi}{\hbar}|H_{DA}|^2 F, \tag{1}$$

$$F = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\Delta J + \lambda)^2}{4\lambda k_B T}\right], \tag{2}$$

where λ is reorganization energy; ΔJ is the change in free energy as a charge passes from a donor to an acceptor; T is absolute temperature; $\hbar$ is Plank's constant divided by 2π; and k_B is Boltzmann's constant. The parameters that affect the rate of charge transfer, such as ΔJ, λ and H_{DA} have a DNA sequence dependence of their own.

The charge coupling H_{DA} can be calculated with an effective tight-binding Hamiltonian $\hat{H}$ with diagonal elements determined by oxidation energies of the bases and off-diagonal elements equal to the corresponding charge coupling of neighboring bases:

$$\hat{H} = \sum_{i,j} \alpha_{ij} \mid i\rangle\langle j \mid, \tag{3}$$

where indices $i(j)$, $0 \leqslant i(j) \leqslant N+1$ number sites involved in charge transfer; $\alpha_{i,j}$ (the so-called exchange integrals) are parameters of the Hamiltonian (3). For our system the state of a hole on the ith site is described by a wave function $|i\rangle$.

In the most detailed description of the system under study, each site corresponds to a single atom with which an electron can be associated in the course of transfer. The problem is simplified computationally if we consider a site to be a group of atoms or even molecules. In the currently considered case of charge transfer in DNA, most of the quantum-mechanical calculations including calculation of the states in individual nucleotides have already been performed and so each nucleotide can be treated as one site [2].

According to the results of previous theoretical analysis [12], the rate of hole transfer from the guanine site G_n over a bridge to the G_{n+1}th site is determined by the matrix element $H_{G_n,G_{n+1}}$:

$$H_{G_n,G_{n+1}} = \alpha_{G_n,1} H_{1M}(E_0) \alpha_{M,G_{n+1}}, \tag{4}$$

$$H_{1,M}(E_0) = \left\langle \delta_1 \mid (E_0 - \hat{H}')^{-1} \mid \delta_M \right\rangle,$$

where the site G_n is chosen as a donor and the site G_{n+1} – as an acceptor; $H_{1,M}(E_0)$ is the Green function for the bridge Hamiltonian $\hat{H}'$, i.e., Hamiltonian (3) missing the donor and the acceptor, that is, the terms $i = G_n$ and $i = G_{n+1}$ ($\langle\delta_1|$ and $\langle\delta_M|$ – are the hole wave functions at first and last sites of the bridge).

Accordingly, we will use the following computational scheme. In an arbitrary nucleotide sequence along which a charge travels, we will note the sites containing guanines. Each site containing only guanines (along which a hole travels without overcoming any barriers) will be considered as one effective guanine site. To each effective guanine site we will assign the same effective energy E_0. In addition, we will assign zero change in the free energy to each hop between intermediate effective guanines, i.e., we will take $\Delta J = 0$ in formula (2) in this case. In this view, a hole hops on the effective guanine sites G_n^{eff}, over the bridging ones. The total time of transfer is a sum of time intervals required for a hole to overcome all the bridge sites. Our model results from the analysis of a set of experimental data on charge transfer in nucleotide sequences and suggests a scenario in which *Gs* are oxidized as the hole migrates from the donor G^+ to the acceptor *GGG* (or *GG*), so that *Gs* act as 'relay stations' for the positive charge [4,13,14]. According to this picture, the charge tunnels reversibly between the *Gs* until it is trapped by H_2O or the *GGG* (or *GG*) sequence or an acceptor in general case. In this model of transfer, free energy changes and heat releases only at the final stage of the hole trapping on the acceptor.

A combined mechanism of hole transport in a DNA duplex $G_i(T-A)_nG_{i+1}$ containing guanine bases G_i, G_{i+1} separated by $(T-A)_n$ bridges was proposed earlier [3,5,15] using model values of the transfer matrix elements α_{ij}. The mechanism was analyzed in detail [3,15] utilizing the intrastrand and interstrand hole transfer matrix elements [2]. Those authors [3,15], however, did not take into account the dependence of the Frank–Condon factor (FC) on the type of nucleotide sequence constituting the bridges. In this Letter, we include this effect explicitly in the calculations of the transfer rates.

If the rate of transfer over an individual bridge is determined by formula (1) then, given the above assumptions, the total transfer rate K will be inversely proportional to the sum:

$$K^{-1} \sim \sum |H_{G_n,G_{n+1}}|^{-2} \sqrt{\lambda_{G_n,G_{n+1}}} \times \exp \frac{\left(\lambda_{G_n,G_{n+1}} + \Delta J_{G_n,G_{n+1}}\right)^2}{4K_B T \lambda_{G_n,G_{n+1}}}, \quad (5)$$

where the summation is performed over all the effective guanine sites. The quantities $\lambda_{G_n,G_{n+1}}$ and $\Delta J_{G_n,G_{n+1}}$ represent the energies of the medium reorganization and free energy changes which occurs as a hole passes between neighboring effective guanine sites.

If a DNA resides in a solution, the main contribution into the medium reorganization energy is made by the polarization of the solvent and the DNA molecule itself. In a continuum approximation, we can consider this system as a heterogeneous dielectric medium and assign different dielectric permittivities to its different regions. In this approximation, the reorganization energy $\lambda_{G_n,G_{n+1}}$ is given by the expression [16]:

$$\lambda_{G_n,G_{n+1}} = \sum_q \frac{e^2 \alpha_q}{8\pi} \int_{v_q} \left(\vec{E}_{G_n} - \vec{E}_{G_{n-1}}\right)^2 \mathrm{d}v, \quad (6)$$

where q represents different dielectric regions, e is the charge of an electron, $\alpha_q = \varepsilon_{\mathrm{op},q}^{-1} - \varepsilon_{\mathrm{st},q}^{-1}$, $\varepsilon_{\mathrm{op},q}$, $\varepsilon_{\mathrm{st},q}$, are optical and static dielectric constants of each region q, and $\vec{E}_{G_n,G_{n+1}}$ are the vectors of the electric fields determined by the charge distribution on the G_n/G_{n+1} in vacuum.

In a homogeneous case Equation (6) gives a simple and widely used expression for the solvent reorganization energy: $\lambda_{G_n,G_{n+1}} = e^2\alpha_q(1/2a_D + 1/2a_A)$. This expression models the donor (G_n) and the acceptor (G_{n+1}) as two conducting spheres embedded in a dielectric continuum, where a_D and a_A are the radii of the donor and the acceptor spherical cavities. This model has been successful in describing a range of mean field solvent effects for nucleic acid oligomers in saline solution [8].

3. Calculation of transfer rates

To calculate the matrix elements $H_{G_n,G_{n+1}}$ involved in the expression for K (Eq. (5)) we need the quantities α_{ij}. Nondiagonal components α_{ij} have been calculated recently by quantum-mechanical methods in model systems containing two nucleobases. All possible pairs of intrastrand combinations as well as several interstrand pairs were calculated [2] (Table 1). The authors of [17–19] extended that study on hole transfer matrix elements in DNA to systems which consist of three Watson–Crick pairs. Table 1 also shows experimentally measured values of diagonal components α_{ii} which may be interpreted as the nucleotide oxidation potentials. The values of oxidation potentials were determined by electrochemical measurements performed on individual nucleotides [20]. For π-stacked bases, direct measurements of oxidation potentials are unavailable. They are usually taken to be equal to oxidation potentials of individual nucleotides in an appropriate polar solvent.

To calculate the transfer rate from relations (3)–(5) we must know the values of $H_{G_n,G_{n+1}}$ for the bridge sites. Below we will deal with short nucleotide sequences where the bridges contain one, two and three nucleotide pairs. In all the cases considered the value of E_0 was taken to be the same and was chosen to give the best agreement with experiment. For the parameter values shown in Table 1 the best agreement occurs at $|E_0| = 0.47$ eV.

It should be noticed that many experiments measure not absolute, but relative transfer rates determined by the number of DNA molecules damaged in the course of transfer [4–7]. In comparing the results of various experiments between themselves and with our theory it is of crucial importance to use ones performed under similar conditions, since changes in pH, temperature,

Table 1
Matrix elements of an electron transition (in eV) between neighboring nucleotides in DNA – duplexes [2,3]

Transitions inside the chain

	5′ → 3′					3′ → 5′			
	A	C	T	G		A	C	T	G
A	0.030	0.061	0.105	0.049	A	0.030	0.029	0.086	0.089
C	0.029	0.041	0.1	0.042	C	0.061	0.041	0.076	0.110
T	0.086	0.076	0.158	0.085	T	0.105	0.1	0.158	0.137
G	0.089	0.110	0.137	0.084	G	0.049	0.042	0.085	0.084

Transitions between the chains

	5′ → 5′					3′ → 3′			
	A	C	T	G		A	C	T	G
A	0.035	0	0.016	0.021	A	0.062	0	0.016	0.021
C	0	0.0007	0	0	C	0	0	0	0
T	0.016	0	0.002	0	T	0.007	0	0.002	0
G	0.021	0	0.009	0.019	G	0.021	0	0	0.043

Oxidation potentials [20] (in acetonitril solution)

A	C	T	G
1.69	1.9	1.9	1.24

and sample preparation conditions can affect the results considerably.

Fig. 1 shows the sequences in which we studied a hole transfer. We have circled guanines which play the role of donors and acceptors as defined in previous studies [4,6,7]. Generally speaking, there are many paths along which a hole can travel from a donor to an acceptor (guanine sites located at the sequence end

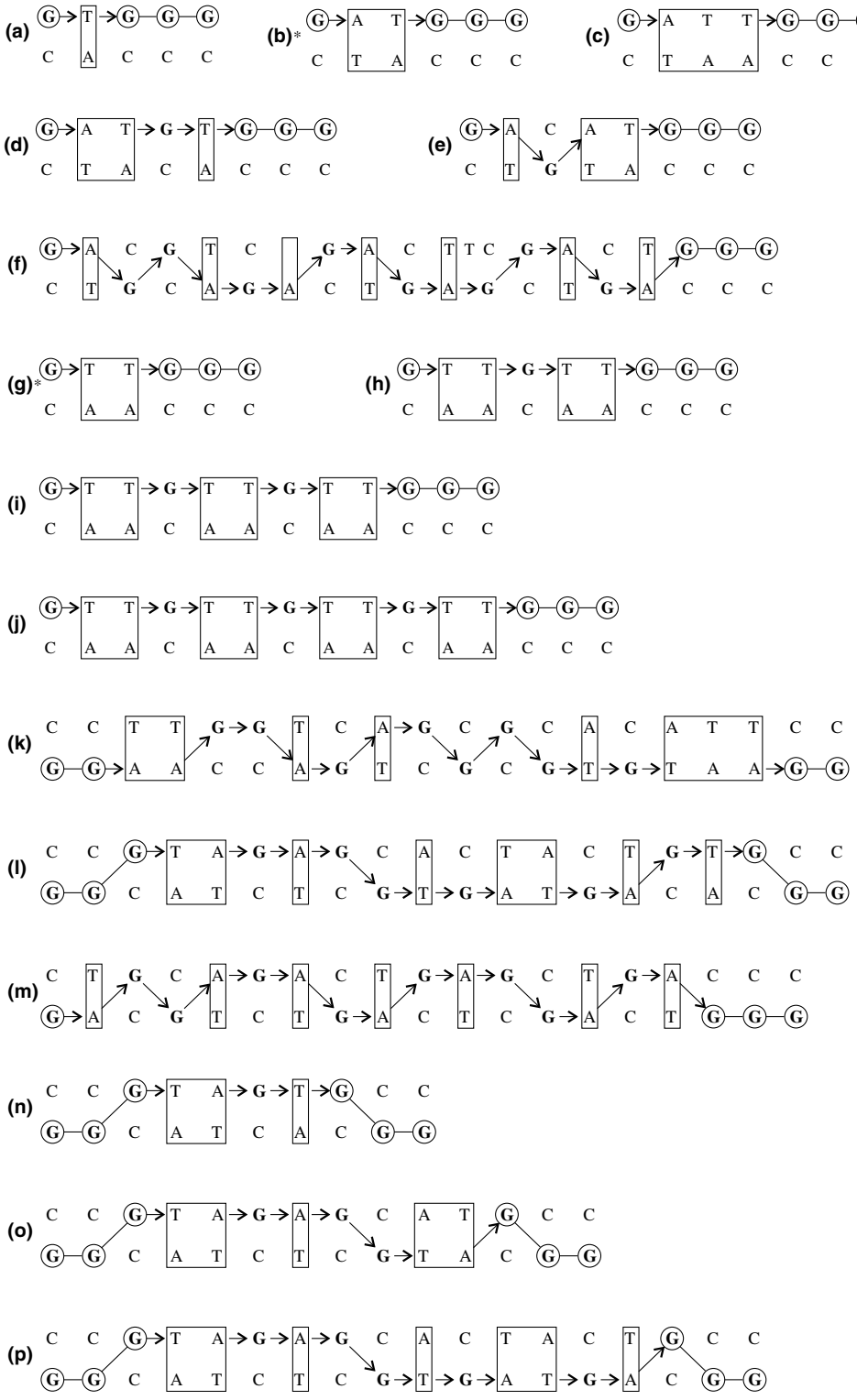

Fig. 1. Sequences used in [4,6,7]. Arrows indicate optimum paths of a hole migration. Circles mark guanines that play the role of donors (acceptors). All sequences have directions $5' \rightarrow 3'$ except f and m (the latter have opposite directions).

opposite to the acceptor sites). The choice of the optimal path depends (apart from $H_{G_n,G_{n+1}}$) on the values of reorganization energy $\lambda_{G_n,G_{n+1}}$ and free energy changes $\Delta J_{G_n,G_{n+1}}$. In the case of a DNA oligomer in a solution, the values of reorganization energy determined by solvation effects and the polarization contribution of the DNA molecule itself can be rather high and may dominate in the choice of the optimal path of a hole transfer in a nucleotide sequence. Previous authors [16] calculated the energy of the medium reorganization as a result of a charge transfer in the DNA calculated from relation (6) where the summation was performed over four regions with different values of dielectric constants. Although the authors [16] used some special parameter values in their calculations, in all the cases they concluded that at rather long distances of transfer ($\geqslant$10 Å) the reorganization energy (6) depends on the distance only slightly. The same results were obtained in other more recent studies [21]. Relying on this observation, we will assume that the medium reorganization energy does not change significantly for bridges consisting of three and more nucleotide pairs.

Table 2 compares experimental and calculated values of relative transfer rates $K_{\text{theor}} = 3.2\ K_i/K_{oi}$, where K_i is the value of the transfer rate for the ith sequence out of those shown in Fig. 1a–f [4], calculated by formula (5); K_{oi} is the value of the transfer rate for the reference sequence (sequence b in Fig. 1a–f), $K_{theor} = 8.8K_i/K_{oi}$ for the sequences of Fig. 1g–j [7] with the reference sequence g and $K_{theor} = 0.9K_i/K_{oi}$ for the sequences of Fig. 1k–p [22] with the reference sequences l, o. Column K_{calc} lists relative reaction rates for sequences a–p in Fig 1 with equal λ and $\Delta J = 0$ for all bridges. Column K'_{calc} lists relative reaction rates which were calculated after we introduced the model the parameters λ_1, λ_2, λ_3, and ΔJ (where λ_1, λ_2, λ_3 – correspond to the values of reorganization energy for one, two and three AT base pairs in the bridge, respectively), whose values (together with E_0) were considered to be similar for all the sequences and were chosen to obtain the best agreement with the experiment. To this end we optimized a target function of the form $F(E_0, \lambda_1, \lambda_2, \lambda_3, \Delta J) = \Sigma(K_{\text{exp}} - K'_{\text{calc}})^2$, which covered the whole body of experimental data. At $E_0 = -0.47$ eV, $\lambda_1 = 0.3$ eV, $\lambda_2 = 0.4$ eV, $\lambda_3 = 0.62$ eV, $J = -0.7$ eV, we found a minimum of the function. Asterisks mark the sequences which were considered as references for a relevant group of experiments.

Table 2 demonstrates that in all the cases considered, experimental and theoretical values have approximately the same order of magnitude. In view of the fact that the scatter in the transfer rates may be six orders of magnitude [9], depending on the experimental conditions and the type of a sequence, the results for our method are quite encouraging.

Table 2
Comparison of experimental values of relative reaction rates K_{exp} [4,6,7,22] with theoretical ones K_{calc}, K'_{calc}

Sequence	K_{exp}	K_{calc}	K'_{calc}
(a)	30	608.3	30
(b)*	3.2	3.2	3.2
(c)	0.44	0.06	0.45
(d)	3.0	3.18	0.55
(e)	3.4	0.18	0.18
(f)	3.4	2.17	0.29
(g)*	8.8	8.8	8.8
(h)	2.8	4.4	1.3
(i)	1.4 (0.88)	2.9	0.7
(j)	0.9	2.2	0.5
(k)	0.5	0.0027	0.0076
(l)*	0.9	0.9	0.9
(m)	2.5	2.6	1.88
(n)	1.2	9.4	2.35
(o)*	0.9	0.9	0.9
(p)	0.9	4.17	0.84

Column K'_{calc} lists relative reaction rates which were calculated after we had introduced in the model the parameters λ_1, λ_2, λ_3, ΔJ, whose values (together with E_0) were found to be similar for all the sequences and were chosen from the condition of the best agreement with the experiment. To this end we constructed an optimizing function of the form $F(E_0, \lambda_1, \lambda_2, \lambda_3, \Delta J) = \Sigma(K_{\text{exp}} - K'_{\text{calc}})^2$, which covered the whole body of experimental data. At $E_0 = -0.47$ eV, $\lambda_1 = 0.3$ eV, $\lambda_2 = 0.4$ eV, $\lambda_3 = 0.62$ eV, $\Delta J = -0.7$ eV, we found the local minimum of the function. Asterisks mark the sequences which were considered as references for a relevant group of experiments.

4. Discussion

At present, a great body of data has been accumulated on charge transfer in nucleotide sequences and new information continues to be produced. We have excluded from consideration the experiments where there are bridges containing more than three A–T pairs. The reason is that at the bridges where the number of A–T pairs $n > 3$, a crossover in the type of transfer takes place [3,23–25]. In this case, the mechanism of superexchange through a bridge gives way to a mechanism in which a hole appears on bridge sites as a result of thermal fluctuations which leads to their complete oxidation. A hole formed on bridge sites in this way may be thought to travel over the bridges and relation (4) becomes invalid.

As is shown above, an experimentally measured hole transfer rate in a DNA molecule strongly depends on the type of a nucleotide sequence. However, current theoretical estimations of electron tunneling probabilities in specific double helices of oligonucleotides made with the use of matrix elements of an overlap integral of electronic orbital of neighboring nucleotides in DNA are based only on a significantly idealized (nearly to planar) model of base pairing. They do not take into account either the significant heterogeneity of nucleotide geometry parameters in a DNA molecule observed in X-ray or

NMR experiments or the existence of large 'propeller' and 'buckle' deformation fluctuations of the planar structure of H-bonding bases occurring at finite temperature in solution. These deformations, as is known, can reach 50° [26–29]. In addition, DNA thermal fluctuations break the global helix symmetry and may localize the wave function (HOMO and LUMO) to different areas on a time scale much less than nanoseconds. According to [2], an increase of the rise value by 0.3 Å, which corresponds to the standard deviation for this base-step parameter (due to thermal motion of DNA), will increase this matrix element by a numerical factor of 1.6 and its contribution to the intrastrand hopping rate by a factor of 2.6. Thermal fluctuations in DNA on the order of an Å or two are easily observed on the subnanosecond time scale in solvated molecular dynamics simulations at room temperature [30].

Inaccuracy in the calculations of the medium reorganization energy λ and free energy changes ΔJ leads to still greater errors in determining of the transfer rate in view of the exponential dependence of K on λ and ΔJ (2) [16,21]. It is common practice to point out two contributions into the reorganization energy: the internal reorganization λ_i and solvent contribution λ_s. According to [16], in a DNA, λ_i is determined by a low-polar region occupied by the DNA molecule itself, while λ_s is determined by the surrounding solvent. In a more general case, λ_i is also associated with geometry changes of donor and acceptor. According to [16], in a DNA, the internal contribution into λ_i (λ_i<0.4–0.06 eV) is much less than the external one determined by the solvent: $\lambda_i < \lambda_s$. On the other hand, estimations of the value of λ_s in the range from 0.5 to 3 eV made in [16] do not take into account delocalization of the hole which leads to considerable overestimation of λ_s.

Presently, there exist various estimations of the value of λ. In experiments [31] λ was found to be: $\lambda = 0.35$ eV. The value $\lambda = 0.35$ eV was also used to calculate the transfer rate of a hole in DNA sequences of various types [32]. In [33] the reorganization energy was calculated as $\lambda = 0.23$ and 0.27 eV with 0 and 2 intervening pairs (~7 Å distance change). According to recent works [34,35] experimentally measured values of reorganization energy λ fall in the range (0.43–1.7 eV). Our value $\lambda = 0.62$ eV seems quite reasonable in the context of the lack of full clearness as to the exact value of this quantity. As a result, a discrepancy between theoretical and experimental transfer rates can be an order of magnitude or more.

It is well known that a pure aqueous medium represented as a dielectric continuum is just the first approximation to taking into account the macromolecule's surroundings. Essentially all biological reactions, especially those concerning DNA, proceed in a salt solution of finite concentration. Solution environments are known to affect conformational, dynamical and thermodynamic behavior especially in terms of the dielectric constants. When nucleotides in the form of a DNA oligomer are bound to a surface, their physical chemistry is also drastically altered in part due to the change in dielectric [8].

In order to introduce the effects of solution environment and instantaneous thermal fluctuations further computer simulation will be used to investigate a more quantitative model of the hopping rates. The methods used here which give qualitative predictions of the transfer rates in various types of nucleotides, can be used in conjunction with the thermal statistical averaging from simulations and may improve the accuracy further in comparison with experiment.

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