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Hopping and Superexchange Mechanisms of Charge Transfer in DNA

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To the 50th anniversary of the discovery of the DNA double helix

Abstract—A theory of hole transfer in nucleotide sequences was constructed, which assumes that a hole moves by hopping between guanines. Each hop across an adenine–thymine bridge connecting neighboring guanines occurs by a superexchange mechanism. Experimental and theoretical data were compared for different types of nucleotide sequences.

Key words: DNA, electron, hole, nucleotide

By the present time, numerous experiments have established that, in DNA, the effective charge transfer over quite a long distance is possible [1–8]. This fact holds extraordinary promises for microelectronics and nanotechnology, in which DNA molecules can be used as molecular conductors and new types of molecular devices [9]. At the same time, there are as yet no reliable approaches to calculating and predicting the results of experiments on charge transfer in DNA.

In this work, to calculate the effective charge transfer in DNA, we consider an approach based on the concepts of the hopping and superexchange mechanisms of charge transfer in molecular systems [10–12].

From a great body of contradictory experimental data on charge transfer in DNA, we analyze the results of hole transfer experiments [6–8], in which certain regularities were revealed. In these experiments, a hole was created in a certain region of a nucleotide sequence by photoexcitation. Specifically, a hole was produced in a region containing guanine (or guanine doublet), whose oxidation potential is the lowest among nucleotides. The hole thus created moves along the nucleotide chain by hopping between guanine-containing regions. Regions containing adenine, thymine, or cytosine serve as bridges connecting guanine sites. Such bridges are potential barriers to the motion of the hole, which are negotiated by quantum-mechanical tunneling.

We describe the tunneling through bridging sites in terms of the Hamiltonian

$$\hat{H} = \sum_{i,j} \alpha_{ij} |i\rangle\langle j|, \tag{1}$$

where the subscripts i and j ($0 \le i, j \le N + 1$) number the sites involved in charge transfer and α_{ij} are the exchange integrals (parameters of Hamiltonian (1)). It is assumed that the state of the hole at the ith site is described by the wave function $|i\rangle$.

According to the theory of chemical reactions [13–15], the rate of hole transfer from guanine site G_n across a bridge to site G_{n+1} is determined by the matrix element $H_{G_n,G_{n+1}}$:

$$\begin{aligned} H_{G_n,G_{n+1}} &= \alpha_{G_n,1} H_{1,M}(E_0) \alpha_{M,G_{n+1}}, \\ H_{1,M}(E_0) &= \langle \delta_1 | (E_0 - \hat{H}')^{-1} | \delta_M \rangle. \end{aligned} \tag{2}$$

Here, the sites G_n and G_{n+1} are taken to be a donor and acceptor, respectively; and $H_{1,M}(E_0)$ is Green's function for the bridge Hamiltonian $\hat{H}'$, which is obtained from Hamiltonian (1) by ignoring the donor and acceptor, i.e., by eliminating the states $\langle \delta_1 |$ and $|\delta_M \rangle$ of the hole at the first and last sites of the bridge.

Thus, we will use the following calculation procedure. In an arbitrary nucleotide sequence, along

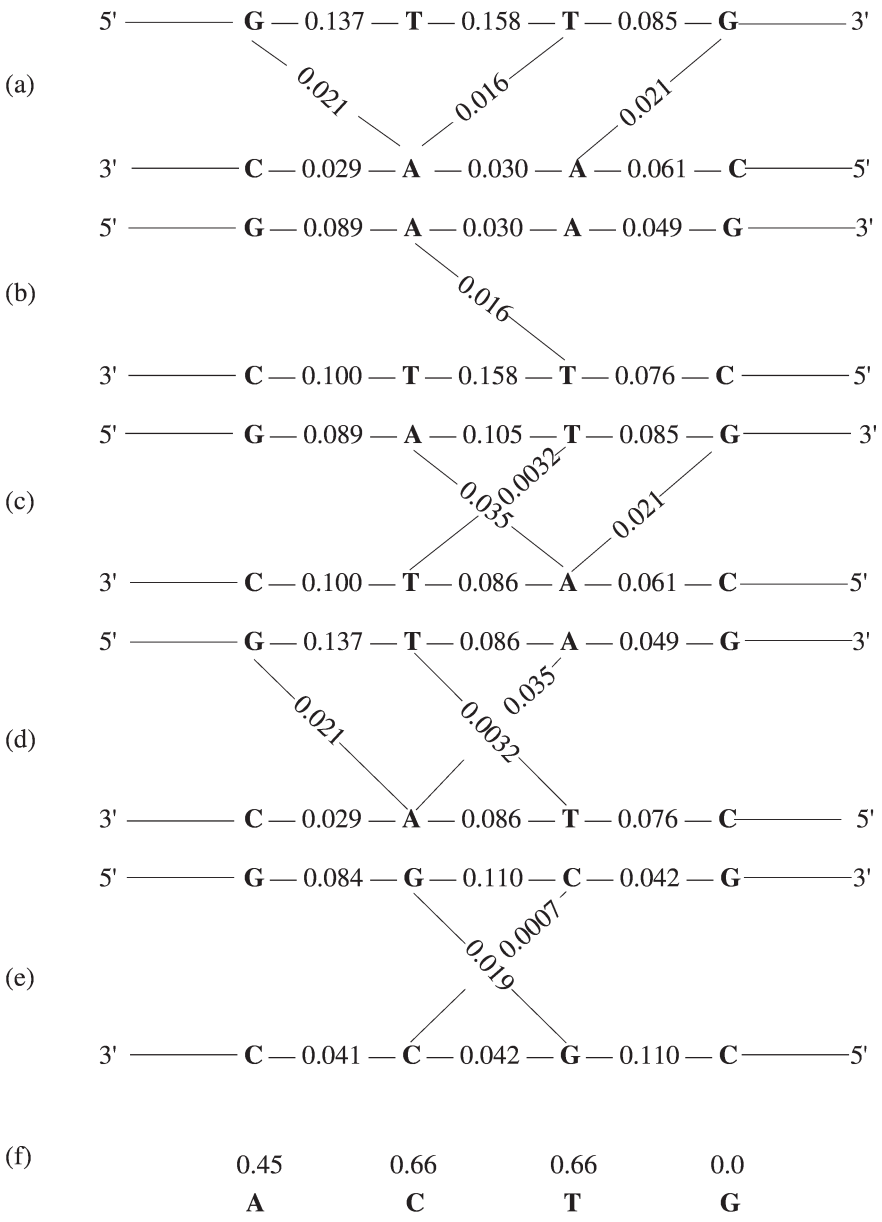

Fig. 1. Matrix elements (eV) of electron transitions between the nearest neighboring nucleotides in DNA duplexes. Transitions both within a chain and between chains are presented. The numbers in the panel (f) are the ionization potentials.

which there is transfer, we mark all the guanine-containing regions, thus marking bridging regions as well. Let us regard each region containing only guanines, through which the hole moves without a barrier, as a single effective guanine site. Let each effective guanine site be assigned the same effective energy E_0.

The entire pattern of transfer looks like the motion of the hole between effective guanine sites G_n^{eff} by hopping across bridging sites.

The total transfer time is the sum of the times it takes for the hole to move across all the bridging sites.

Under the assumption that the rate of transfer across a single bridge is mainly determined by bridge matrix element (2), the total transfer rate K is found from the expression

$$K^{-1} \approx \sum_n \left| H_{G_n, G_{n+1}} \right|^{-2}, \qquad (3)$$

where the summation is taken over all the effective guanine sites.

To calculate the matrix elements $H_{G_n, G_{n+1}}$ in expression (3) for K, it is necessary to know α_{ij}. The off-diagonal matrix elements α_{ij} have recently been

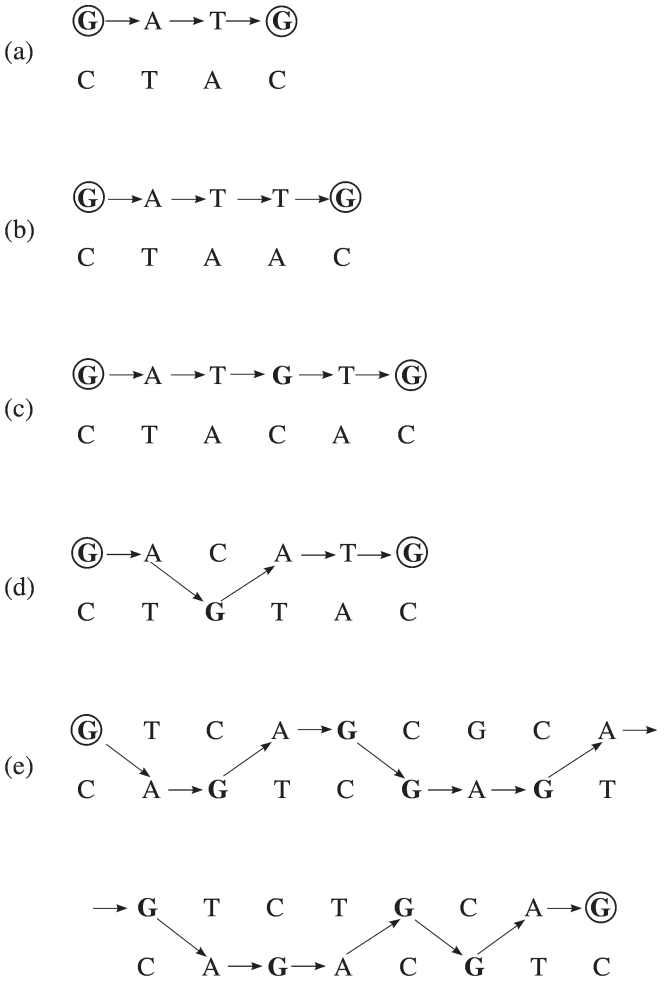

Fig. 2. Sequences used by Meggers *et al.* [6]. The arrows indicate the optimal hole transfer pathways. The circled letters denote guanines acting as donors or acceptors.

calculated by quantum-chemical methods [16] (see Fig. 1, which shows transitions both within a chain and between chains).

The interactions within a chain are strong, whereas the guanine–thymine, thymine–thymine, and adenine–thymine interactions between chains are much weaker. Noticeable exceptions are the adenine–adenine interactions of both types, which are equally strong. Figure 1 also presents the experimentally measured values of the diagonal matrix elements α_{ij}, which have the meaning of the nucleotide ionization potentials. The oxidation potentials presented in Fig. 1 were determined by electrochemical measurements for isolated nucleotides [17]. Directly measured values of the oxidation potentials for π base stacks are as yet unavailable. They are usually taken to be equal to the oxidation potentials of isolated nucleotides in the corresponding polar solvent.

To calculate the hole transfer rate from expressions (1)–(3), it is necessary to know $H_{1,M}(E_0)$ for bridging regions. Below, we consider the hole transfer in short nucleotide sequences with bridges containing one, two, or three nucleotide pairs. In all the cases, when calculating $H_{1,M}(E_0)$, the energy E_0 was taken to be the same and was chosen so that it provided the best fit to experimental data. For the parameter values given in Fig. 1, the fit to experimental data was the best at $E_0 = -0.5$ eV.

It is significant that most of experiments measure not the absolute, but the relative, transfer rate, which is determined by the number of DNA molecules broken down in the charge transfer.

In comparing the results of different experiments, of primary importance is the requirement that the experiments whose results are being compared should be carried out under identical conditions, since

Comparison of the experimental relative transfer rates K_{exp} [6] with the theoretical relative transfer rates K_{theor}

Sequence	K_{exp}	K_{theor}
a	3.2	3.2
b	0.44	0.06
c	3.0	3.18
d	3.4	0.18
e	3.4	1.34

changing the pH, temperature, sample preparation conditions, etc., may strongly change the results obtained. This requirement is met by the experiments performed by Meggers *et al.* [6].

Figure 2 presents the sequences in which the hole transfer was considered. The circled letters denote guanines acting as donors or acceptors in the experiments carried out by Meggers *et al.* [6]. The bold letters designate guanines that separate bridging sites. Generally speaking, there are lots of pathways through which the hole can move from a donor to an acceptor (one of the guanine sites located at the sequence end that is opposite to the end at which there are donor sites). The arrows indicate the optimal hole transfer pathways determined from the matrix element α_{ij} values presented in Fig. 1.

The table lists the results of comparing the experimental and calculated values of the relative transfer rates $K_{rel} = 3.2K_i/K_{0i}$, where K_i is the value of transfer rate (3) for the ith sequence and K_{0i} is the transfer rate value for a reference sequence (the reference sequence in Fig. 2 is the sequence a).

The table shows that the experimental and calculated values in all the cases considered agree in order of magnitude. Since the scatter of the rate transfer, depending on the experimental conditions and the type of sequence, is six orders of magnitude [18], the result obtained can be considered satisfactory.

By now, an ample body of nonsystematized data on charge transfer in nucleotide sequences has been accumulated and continues to rapidly grow. We excluded from consideration the experiments where donor guanines (represented by the circled letters at the left end of a chain) are separated from acceptor guanines (represented by the circled letters at the right end of the chain) by a single AT pair. We suppose [19] that the tunneling across such a bridge is too fast, and the transfer rate in this case is determined not by the processes described by expressions (1)–(3) but by slower processes competing with the tunneling through the AT pair. We also eliminated from consideration the experiments where there are bridges containing more than three AT pairs.

This is because of the fact that, across bridges containing more than three AT pairs, there is crossover [20]. In this case, the mechanism of superexchange across a bridge is replaced by a mechanism in which a hole because of a thermal fluctuation arrives at bridging sites, causing their actual oxidation. The hole thus created at bridging sites actually moves between bridging sites, and expression (2) becomes invalid.

In conclusion, we note that the method proposed allows one not only to explain a considerable part of the results of experiments on hole transfer in DNA but also to make qualitative predictions of the hole transfer rates in various types of oligonucleotides.

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