A Possible Mechanism of the Nonexponential Electron Transfer in DNA

V. D. Lakhno

Reactions of electron transfer in DNA play an important role in biosynthesis, radiation-induced degradation, and post radiation repair of the molecule. However, it was not until recent years that experimental studies of electron transfer in DNA were started [1-4]. The results of the studies were found to be so controversial that none of presently available theoretical models is able to comprehensively describe all of them. The electron transfer between two metal atoms (R_u) intercalated into DNA and separated from one another by eight pairs of nucleotide bases was measured in [1, 2]. The electron transfer distance between the centers of the metal atoms was 20.5 Å. The distance between the edges of the R_u-containing intercalated complexes was substantially shorter (12.5 Å). The rate constant of the electron transfer reaction measured experimentally was k_{et} = 1.6 ($\pm$ 0.4) $\times 10^6$ s^{-1}. The electron transfer rate in the donor-acceptor pairs composed of different reactants with different distances between them was measured in [3]. The distances between the reagents were 10.2, 13.1, and 17.0 Å. The rate constant of the electron transfer reaction was shown to be an exponential function of the donor-acceptor distance r_{DA}:

$$k_{et} \sim \exp[-b\, r_{DA}] \tag{1}$$

where b = 0.9 Å^{-1}.

Beratan *et al.* considered the quantum chemical model of this reaction based on the superexchange theory and found that b = 1.6 Å^{-1} [5, 6]. Similar calculations based on experiments conducted by Mead and Kayyem gave b = 1.2 Å^{-1} [5, 6]. However, the theoretical approach developed in [5, 6] fails to provide even a qualitative explanation of the results obtained by Barton, Tarro, and others. According to these data, the electron transfer distance is 37.4 or 26 Å (distances between centers or edges of R_u- and R_h-containing molecular complexes, respectively) [4]. The rate constant of the electron transfer reaction was calculated to be $k_{et} \geq 10^9$ s^{-1} [4]. In other words, for the electron transfer distances almost twice longer than in experiments described in [1-3], the electron transfer rate measured by Barton, Tarro, and others was almost three orders of magnitude higher. Thus, the electron transfer rate dependence on the donor-acceptor distance in DNA molecule is nonexponential.

Numerous experimental data about the intramolecular electron transfer in proteins are also consistent with the suggestion of the nonexponential dependence on the donor-acceptor distance [7].

The goal of this work was to consider a simple model of the electron transfer reaction in DNA based on the collective excited state (CES) superexchange mechanism. This model should be qualitatively consistent with experimental data on electron transfer in DNA.

The self-consistent electron state and electron-induced molecular deformations were considered as a DNA CES. The crucial point of the approach considered below is that CES is delocalized over the DNA molecule. In other words, there is the minimum possible size of the excited states of this type. If the donor-acceptor distance is less than this critical size, these states are unable to mediate the electron transfer reaction.

To provide the required characteristics of CES, consider DNA as an elastic strand bearing an electron. Let the displacement in the DNA molecule elements induced by the electron transfer to the molecule at point x be $u(\mathbf{x})$. Then, the elastic energy of the strand at the segment of length 2R is

$$F_{el} = \frac{k}{2} \int_{-R}^{R} u'^2(x)\, dx, \tag{2}$$

where k is the elasticity constant.

If the electron energy in an undeformed molecule is taken as a zero energy level, the electron interaction with deformation may be described as

$$F_{\text{int}} = -G \int_{-R}^{R} u'(x)|\Psi|^2 dx, \qquad (3)$$

where G is the potential of molecule deformation; $\Psi(x)$ is the electron wave function.

The total energy functional can be written as

$$F = F_{kin} + F_{el} + F_{int},$$

where F_{kin} is the electron kinetic energy.

The variation parameters of the total energy functional F are the electron wave function $\Psi(x)$ and the displacement amplitude $u(x)$. Assuming that the entire molecule deformation is concentrated within a $2R$ segment (i.e., $u'(\pm R) = 0$), the F variation over $u(x)$ would give the following equations for the electron-induced equilibrium deformation of the molecule:

$$u'(x) = \frac{G}{k}\Psi^2(x) - \frac{G}{k}\Psi^2(R), \quad |x| \le R, \qquad (4)$$

$$u'(x) = 0, \quad |x| \ge R. \qquad (5)$$

In this case, the F variation over the wave function $\Psi(x)$ gives Shroedinger's equation. In combination with equations (4) and (5), it can be written as
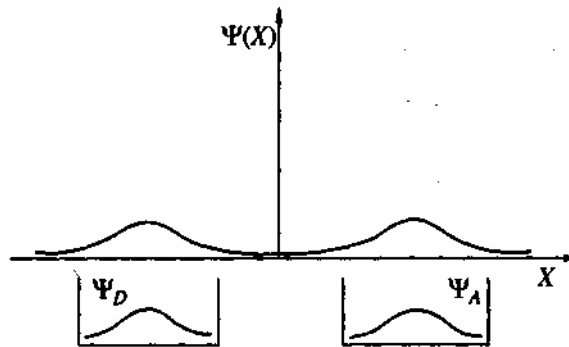
$$\frac{\hbar^2}{2m}\Psi''(x) + \frac{G^2}{k} q(R - |x|) \times [\Psi^2(x) - \Psi^2(R)]\Psi(x) - |W|\Psi(x) = 0, \qquad (6)$$

where m is the effective mass of the electron; W is the electron energy; $q(x)$ is the Heaviside function.

The nonlinear equation (6) was considered in detail in the preceding works [8, 9], According to [8, 9], the nonlinear Shroedinger's equation (6) has a discrete set of soliton-like solutions. At $R > R_1$ (R_1 is a certain critical value), there is a one-soliton solution with a sharp maximum at the origin of the coordinates. The one-soliton solution approaches zero as the distance from the origin of the coordinates increases. At $R > R_2 > R_1$, in addition to the one-soliton solution, there is a two-soliton solution, etc. A solution of equation (6) with two sufficiently sharp maximums located at $\pm 2/3R$ from the origin of coordinates is shown in the figure. Let the electron donor and acceptor be located near the maximums as shown in the figure. The electron state in the donor and acceptor is simulated by narrow, deep, rectangular potential wells. Thus, the electron can be considered to be completely localized within the wells.

Let Ψ_D be the wave function of the electron donor. Then, the matrix element I of the overlap between the donor wave function and state $\Psi(x)$ is

$$I = \int_{-\infty}^{\infty} \Psi_D(x)\Psi(x)dx = \Psi(x_D) \int_{-\infty}^{\infty} \Psi_D(x)dx. \qquad (7)$$

Wave functions of electron donor and acceptor (Ψ_D and Ψ_A, respectively). $\Psi(x)$ is the wave function of the self-consistent electron state.

The value of $\Psi(x_D)$ is the maximum amplitude of the two-soliton solution. According to [8, 9], at sufficiently large R, the value of $\Psi(x_D)$ is

$$\Psi(x_D) = \frac{1}{4}\frac{G}{\hbar}\sqrt{\frac{m}{k}}.$$ (8)

If the width of the rectangular potential well is d and the well itself is deep enough, the wave function Ψ_D of the electron donor in the ground state is

$$\Psi_D(x) = \sqrt{\frac{2}{d}}\sin\frac{p}{d}x, \qquad \frac{2}{3}R - d \le |x| \le \frac{2}{3}R.$$ (9)

The overlap integral can be calculated from equation (8) and (9) as

$$I = \frac{1}{\sqrt{2p}}\frac{G}{\hbar}\sqrt{\frac{md}{k}}$$ (10)

According to the superexchange theory, the reaction rate of the electron transfer to an acceptor through an intermediate state is proportional to the second power of the matrix element T_{DA} between the acceptor and donor:

$$T_{DA} = \frac{I^2 W^2}{|\Delta E|},$$ (11)

where $\Delta \AA$ is the energy difference between the electron ground state in the donor and the two-soliton state.

According to [8, 9], the two-soliton state energy can be calculated from equation (6) as

$$|W| = \frac{1}{32}\frac{G^4}{k^2}\frac{m}{\hbar^2}$$ (12)

The elastic constant k included in these equations can be determined as follows. Characteristic times of the longitudinal oscillations of a DNA molecule (w) fall within the picosecond range. The amplitudes of displacement of the molecular groups of DNA are about 10% of the distance between the neighboring groups. Let the distance between the molecular groups (a) be 1 Å and characteristic frequency $\hbar\omega$ be 10^{-3} eV. Then, the elastic constant value can be calculated from the following equation: $k(u'(a))^2 a/2 = \hbar\omega$, $u'(a) = 0.1$ as $k = 3.2 \times 10^{-5}$ dyn. Characteristic values of deformation potential G in solid bodies are from 1 to 10 eV. Let the G value in DNA be 1 eV. Because the effective electron mass m is 10^{-27} r, the value of $|W|$ calculated from equation (12) is $|W| = 0.13$ eV. The value of ΔE for DNA molecule is $|\Delta E| \approx 2$ eV [5, 6]. Assuming that $d = 1$ Å, it follows from equations (10) and (11) that the matrix element T_{DA} is 3×10^{-4} eV. The matrix element T_{DA} was calculated in [5] for the experimental conditions studied by Barton, Tarro, and coworkers. [4] (reorganization energy, 0.4 eV; free-energy difference between the donor and acceptor, $\Delta J = -0.75$ eV; and reaction-rate constant, $k_{et} = 3 \times 10^9$ s^{-1}). The value of the matrix element was found to be $T_{DA} = 1.9 \times 10^{-4}$ eV [5]. According to our calculations, the value of T_{DA} is 3×10^{-4} eV, which gives an electron transfer rate twice higher than that value calculated in [4]. However, note that it was also observed in [4] that the luminescence quenching of the photoexcited donor is very fast. Therefore, the rate of electron transfer from the photo-excited donor should be faster than 3×10^9 s^{-1}. Thus, the results of our calculations are in agreement with the experimental data obtained in [4]. It follows from equation (11) that, in contrast to the majority of cases described by the superexchange theory, the matrix element of the electron transfer process described by the mechanism considered above is not an exponentially decreasing function of the electron transfer distance. Moreover, it follows from equation (11) that, within the framework of the model considered in this work, the matrix element T_{DA} does not

depend on the electron transfer distance at all. If this were the case, the electron transfer at infinitely large distances would be possible within very short time intervals (about 10^{-9} s). However, the model considered in this work is valid only at distances shorter than a certain threshold value R_{max}.

The threshold value R_{max} can be estimated from the following inequality: $\hbar^2/mR_{max}^2 \geq \hbar\omega$. For the parameters listed above, $R_{max} \sim 100$ Å. At $R > R_{max}$, the matrix element is a common exponential function of distance. According to [8, 9], there is also the minimal distance $R_{min} = 33.2 k\hbar^2/2mG^2 = 21$ Å, at which the state of the type considered above can still be formed. Thus, the nonexponential dependence of the rate of electron transfer can be observed within the distance range from 21 to 100 Å, which is in agreement with experimental findings.

ACKNOWLEDGMENTS

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