Charge transfer along DNA dimers, trimers and polymers

Constantinos Simserides¹

¹National and Kapodistrian University of Athens, Faculty of Physics, Panepistimiopolis, 15784 Zografos, Athens, Greece

(Dated: December 30, 2013)

The transfer of electrons and holes along DNA dimers, trimers and polymers is described at the base-pair level, using the relevant on-site energies of the base-pairs and the hopping parameters between successive base-pairs. The temporal and spatial evolution of carriers along a N base-pair DNA segment is determined, solving a system of N coupled differential equations. Useful physical quantities are calculated including the pure mean carrier transfer rate k, the inverse decay length β used for exponential fit \( (k = k_0 \exp(-βd)) \) of the transfer rate as a function of the charge transfer distance \( d = N \times 3.4 \, Å \) and the exponent η used for a power law fit \( (k = k_0 N^{-η}) \) of the transfer rate as function of the number of monomers N. Among others, the electron and hole transfer along the polymers poly(dG)-poly(dC), poly(dA)-poly(dT), GCCGCG..., ATATAT... is studied. β (η) falls in the range \( ≈ 0.2 - 2 \, Å^{-1} \) (1.7 - 17), \( k_0 \) (\( k_0' \)) is usually \( ≈ 10^{-2} - 10^{-1} \) (10^{-2} - 10^{-1}) PHz although, generally, it falls in the wider range \( ≈ 10^{-4} - 10^{-3} \) (10^{-4} - 10^{-3}) PHz. The results are compared with past predictions and experiments. Our approach illustrates to which extent a specific DNA segment can serve as an efficient medium for charge transfer.

PACS numbers: 87.14.gk, 82.39.Jn, 73.63.-b

Charge transfer along DNA is crucial for molecular biology, genetics, and nanotechnology. Here we present a convenient way to quantify electron or hole transfer along DNA segments using a tight-binding approach which can be easily implemented by interested colleagues. To date all the tight-binding parameters relevant to charge transport along DNA either for electrons (traveling through LUMOs) or for holes (traveling through HOMOs) are available in the literature. Here we use them to study the temporal and spatial evolution of a carrier along DNA. The transport of electrons or holes can be described at either (I) the base-pair level or (II) the single base level. We need the relevant on-site energies of either (I) the base-pairs or (II) the single base level. In addition, we need the hopping parameters between either (I) successive base-pairs or (II) neighboring bases taking all possible combinations into account ([Ia] successive bases in the same strand, [IIb] complementary bases within a base-pair, and [Iic] diagonally located bases of successive base-pairs in opposite strands). To calculate the temporal and spatial evolution of carriers along a N base-pair segment of DNA one has to solve a system of either (I) N or (II) 2N coupled differential equations. Here we use the simplest approach (I) to examine charge transfer in B-DNA dimers, trimers and polymers. Taking the relevant literature into account, we use the on-site energies and the hopping parameters shown in Tables. We denote adenine (A), thymine (T), guanine (G), cytosine (C), and the relevant base-pairs A-T and G-C. YX signifies two successive base-pairs: the bases Y and X of two successive base-pairs (Y-Ycomplex and X-Xcomplex separated and twisted by 3.4 Å and 36°) are located at the same strand in the direction 5’ – 3’.

For a description at the base-pair level, the time-dependent single carrier (hole/electron) wave function of the DNA segment of interest, \( \Psi_{H/L}^{DNA}(r, t) \), is considered as a linear combination of base-pair wave functions with time-dependent coefficients, \( \Psi_{H/L}^{DNA}(r, t) = \sum_{i=1}^{N} A_{µ}(t) \Psi_{H/L}^{(bp)}(r) \). \( \Psi_{H/L}^{(bp)}(r) \) is the \( µ \)th base-pair’s HOMO or LUMO wave function \( (H/L) \). The sum is extended over all base-pairs of the DNA segment under consideration. \( |A_{µ}(t)|^2 \) gives the probability of finding the carrier at base-pair \( µ \), at time \( t \). Starting from the time-dependent Schrödinger equation, \( i\hbar \frac{\partial \Psi_{H/L}^{DNA}(r, t)}{\partial t} = H_{H/L} \Psi_{H/L}^{DNA}(r, t) \), following the procedure described in Ref. 4, we obtain that the time evolution of \( A_{µ}(t) \) obeys the tight-binding system of differential equations

\[
\frac{dA_{µ}}{dt} = E_{H/L}^{bp}(µ) A_{µ} + t_{H/L}^{bp(µ;µ−1)} A_{µ−1} + t_{H/L}^{bp(µ;µ+1)} A_{µ+1}.
\]

(1)

\( E_{H/L}^{bp}(µ) \) is the on-site energy of base-pair \( µ \), and \( t_{H/L}^{bp(µ;µ′)} \) is the hopping parameter between base-pair \( µ \) and base-pair \( µ′ \). We can solve numerically the system of equations and obtain, through \( A_{µ}(t) \), the time evolution of a carrier propagating along the DNA segment of interest.

Regarding the tight-binding description of hole transport, the corresponding tight-binding parameters should be taken with the opposite sign of the calculated on-site energies and transfer hopping integrals. This means that for describing hole transport at the base-pair level, the on-site energies \( E_{H}^{bp} \) presented in the second row of Table and the hopping transfer integrals \( t_{H/L}^{bp} \) presented in the second column of Table should be used with opposite signs to provide the tight-binding parameters of Eq. The on-site energies \( E_{H/L}^{bp} \) for the two possible base-pairs A-T and G-C, calculated by various authors, are listed in Table. \( E_{H/L}^{bp} \) used are the values actually used for the solution of Eq. in this article. The
hopping parameters $t_{H/L}^{bp}$ for all possible combinations of successive base-pairs, calculated by various authors, are given in Table III. $t_{H/L}^{bp \text{ used}}$ are the values actually used for the solution of Eq. (1) in this article. Due to the symmetry between base-pair dimers XY and X_compl Y_compl, the number of different hopping parameters is reduced from sixteen to ten. In Table III base-pair dimers exhibiting the same transfer parameters are listed together in the first column. We include in Table III the values listed: in Table 3 of Ref. [4], in Table II or Ref. [14], in Table 5 (“Best Estimates”) of Ref. [12], in Table 4 of Ref. [16] (two estimations given), in Table 2 of Ref. [17], and the values extracted approximately from Fig. 4 of Ref. [3]. In Refs. [12, 17] all values given are positive, in Ref. [14] the authors explicitly state that they quote absolute values, while in Refs. [3, 4] the sign is included. In Ref. [4] all $t_{H}^{bp}$ and $t_{L}^{bp}$ have been calculated, while in Ref. [3] only the values of $t_{H}^{bp}$ for a few cases are approximately given. According to Ref. [19] the approximation used in Ref. [14] in general overestimates the transfer integrals. Summarizing, taking all the above into account, we use the values $E_{H/L}^{bp \text{ used}}$ and $t_{H/L}^{bp \text{ used}}$.

TABLE I: The on-site energies $E_{H/L}^{bp}$ for the two possible base-pairs A-T and G-C, calculated by various authors. $E_{H/L}^{bp \text{ used}}$ are the values actually used for the solution of Eq. (1) in this article. The first $\pi-\pi^*$ transition energies $E_{\pi-\pi^*}$ for the two B-DNA base-pairs are also shown. Except for Ref. [4] these are ab initio calculations which tend to overestimate the first $\pi-\pi^*$ transition energy. All energies are given in eV.

| B-DNA base-pair | A-T | G-C | reference |
|-----------------|-----|-----|-----------|
| $E_{H}^{bp}$    | –8.3| –8.0| [4]       |
| $E_{L}^{bp}$    | –4.9| –4.5| [4]       |
| $E_{\pi-\pi^*}$ | 3.4 | 3.5 | [4]       |
| $E_{H/L}^{fp}$  | –(7.8–8.2) | –(6.3–7.7) | [7–12] |
| $E_{H/L}^{fp \text{ first pr.}}$ | 6.4 | 4.3–6.3 | [12, 13] |
| $E_{H/L}^{fp \text{ used}}$ | 8.3 | 8.0 | [4] |
| $E_{L}^{fp \text{ used}}$ | –4.9 | –4.5 | [4] |

TABLE II: The hopping parameters between successive base-pairs for all possible combinations. $t_{H/L}^{bp}$ ($t_{H/L}^{fp}$) refers to hole (electron) hopping through HOMOs (LUMOs). The notation is given in the text. The values listed in Table III of Ref. [4], in Table II or Ref. [14], in Table 5 (“Best Estimates”) of Ref. [13], in Table 4 of Ref. [16] (two estimations given), in Table 2 of Ref. [17], and the values extracted approximately from Fig. 4 of Ref. [3] are shown. These quantities represent the parameters $t_{H/L}^{bp(\mu,\mu \pm 1)}$ which appear in Eq. (1). Finally, $t_{H/L}^{bp \text{ used}}$ are the parameters actually used in this work for the solution of Eq. (1). All hopping integrals $t_{H/L}^{bp}$ are given in meV.

| Base-pair sequence | $t_{H}^{bp}$ | $t_{L}^{bp}$ | $t_{H}^{bp}$ | $t_{L}^{bp}$ | $t_{H}^{bp}$ | $t_{L}^{bp}$ | $t_{H/L}^{bp \text{ used}}$ | $t_{L/L}^{bp \text{ used}}$ |
|-------------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------------------|---------------------------|
| AA, TT            | –8           | 26           | –25          | 8–17         | 19(19)       | 22           | 20                        | 29                        |
| AT                | 20           | 55           | –5           | 25           | –50          | 35(51)       | 43                        | 30                        |
| AG, CT            | 2            | 26           | –2           | 25           | –50          | 35(51)       | 43                        | 30                        |
| AC, GT            | 47           | 50           | –4           | 27           | –50          | 35(51)       | 43                        | 30                        |
| TA                | 47           | 50           | –4           | 27           | –50          | 35(51)       | 43                        | 30                        |
| TG, CA            | 79           | 122          | –7           | 50           | –160         | 71(108)      | 60                        | –135                      |
| GC                | 79           | 122          | –7           | 50           | –160         | 71(108)      | 60                        | –135                      |
| CG                | –44          | 78           | –44          | 78           | –8           | 51(84)       | 74                        | 50                        |

We define the column vector matrix $\vec{x}(t)$ made from $A_j(t)$, $j = 1, \ldots, N$. Hence, $\dot{\vec{x}}(t) = \vec{A}\vec{x}(t)$, $\vec{A} = -\hbar \Delta \Lambda$. A
is a symmetric tridiagonal matrix. To proceed, we use the eigenvalue method, i.e., we look for solutions of the form \( \tilde{\xi}(t) = e^{\imath \lambda t} \). If \( \tilde{\xi}(t) = \lambda \tilde{\xi} \), \( A \tilde{v} = \lambda \tilde{v} \), or \( \Lambda \tilde{v} = \lambda \tilde{v} \), with \( \lambda = -\frac{i}{\hbar} \). Having checked that the normalized eigenvectors \( \tilde{v} \) corresponding to the eigenvalues \( \lambda_k \) are linearly independent, the solution is \( \tilde{\xi}(t) = \sum_{k=1}^{N} c_k e^{\imath \lambda_k t} \). From the initial conditions we determine \( c_i(t) \).

For dimers, supposing that \( \lambda_2 \geq \lambda_1 \), we obtain the period of \( |A_{\mu}(t)|^2, \mu = 1, 2, T = \frac{2\pi}{\lambda_2 - \lambda_1} \). For a dimer consisting of two identical monomers with purine on purine (GG \( \equiv \) CC, AA \( \equiv \) TT), \( \lambda_{1,2} = \frac{E_{bp}}{2} \mp t_{bp} \). Then, if we initialize the carrier in monomer 1, \( |A_1(t)|^2 = \frac{1}{2} + \frac{1}{2} \cos(\lambda_{2,1} t) \), \( |A_2(t)|^2 = \frac{1}{2} - \frac{1}{2} \cos(\lambda_{2,1} t) \). For a dimer consisting of two identical monomers with purine on pyrimidine (GC, CG, AT, TA), the problem is identical. For a dimer made up of different monomers (AG \( \equiv \) CT, AC \( \equiv \) GT, TG \( \equiv \) CA, TC \( \equiv \) GA), \( \lambda_{1,2} = \frac{E_{bp} + E_{bp}'}{2} + \frac{\sqrt{(E_{bp} - E_{bp}')^2 + t_{bp}^2}}{2} \). Hence, for identical monomers \( T = \frac{2\pi}{\lambda_{1,2}} \), for different monomers, \( T = \frac{2\pi h}{2(E_{bp} - E_{bp}') + (\Delta \beta_{1,2})^2} \). The maximum transfer percentage of the carrier from base-pair 1 to base-pair 2, \( p = \frac{1}{2}c_1c_1c_2c_2 \). This refers to the maximum of \( |A_2(t)|^2 \). For identical (different) monomers, \( p = 1 \). For identical monomers, \( \frac{p}{T} = \frac{2(E_{bp})}{h} \). For holes, when purines are crosswise to pyrimidines (GT \( \equiv \) AC, CA \( \equiv \) TG) \( p \) is negligible, hence, we expect that insertion of these dimers in a sequence of DNA base-pairs will disrupt hole transfer. Also AG \( \equiv \) CT has very small \( p \). Generally, electrons have smaller \( p \) than holes. In contrast to the cases of holes, when purines are NOT crosswise to pyrimidines (GA \( \equiv \) TC, CT \( \equiv \) AG) \( p \) is negligible, hence, we expect that insertion of these dimers in a sequence of DNA base-pairs will disrupt electron transfer. Generally, in cases of different monomers \( T \) is smaller than in cases of identical monomers due to the extra term containing \( \Delta \beta_{1,2} = E_{bp} - E_{bp}' \). Overall, carrier transfer is more difficult for different monomers compared to identical monomers. If \( |A_2(0)|^2 = 0 \), a pure mean transfer rate can be defined as \( k = \frac{\langle A_2(0)^2 \rangle}{t_{mean}} \), where \( t_{mean} \) is the first time \( |A_2(t)|^2 \) becomes equal to \( \langle A_2(0)^2 \rangle \) i.e. “the mean transfer time”. Figure 1 shows \( T, p, p/T \) and \( k = \langle |A_2(t)|^2 \rangle/t_{mean} \).

For trimers, supposing that \( \lambda_1 \leq \lambda_2 \leq \lambda_3 \), we conclude that \( |A_{\mu}(t)|^2, \mu = 1, 2, 3 \) are sums of terms containing constants and periodic functions with periods \( T_{31} = \frac{h}{\lambda_3 - \lambda_2} \), \( T_{32} = \frac{h}{\lambda_3 - \lambda_2} \). There are 8 trimers consisting of identical monomers. In the cases of 0 times crosswise purines \( \lambda_2 = E_{bp}, \lambda_{1,3} = E_{bp} \mp t_{bp} \sqrt{2} \). Hence, two periods are involved in \( |A_{\mu}(t)|^2, \mu = 1, 2, 3 \): \( T_M = \frac{\sqrt{h^2 - 4h^4(\Delta \beta_{1,2})^2}}{2h} \Rightarrow T_M = \frac{2\pi h}{2(E_{bp} - E_{bp}' + \sqrt{2})} \). Hence, two periods are involved in \( |A_{\mu}(t)|^2, \mu = 1, 2, 3 \): \( T_M = \frac{\sqrt{h^2 - 4h^4(\Delta \beta_{1,2})^2}}{2h} \). Since \( T_M = \frac{2\pi h}{2(E_{bp} - E_{bp}' + \sqrt{2})} \), it follows that \( |A_{\mu}(t)|^2, \mu = 1, 2, 3 \) are periodic. Conclusively, in all cases of a trimer consisting of identical monomers, \( |A_{\mu}(t)|^2, \mu = 1, 2, 3 \) are periodic with period \( T_M \). Suppose that we have a trimer consisting of different monomers. There are 24 different such trimers. For example, suppose that we refer to HOMO charge transfer in GAC \( \equiv \) GTC, then with \( E_{bp}'' > E_{bp} \), \( \lambda_2 = E_{bp}, \lambda_{1,3} = E_{bp} + \sqrt{2} t_{bp} \). Three periods are involved in \( |A_{\mu}(t)|^2, \mu = 1, 2, 3 \). With \( \Delta \beta_{1,2} = E_{bp} - E_{bp}'' \), \( T_{M(31)} = \frac{2\pi h}{2(E_{bp} - E_{bp}' + \sqrt{2})} \) and \( T_{M(32)} = \frac{2\pi h}{2(E_{bp} - E_{bp}' + \sqrt{2})} \). The HOMO pure mean transfer rate \( k \) for all possible trimers is shown in Fig. 2. For trimers consisting of identical monomers, then \( k \approx 1.3109 \frac{h}{T} \). As expected, \( k \) is very small when trimers include dimers with very small \( k \), primarily purines crosswise to pyrimidines (GT \( \equiv \) AC, CA \( \equiv \) TG), secondarily AG \( \equiv \) CT, thirdly GC.

For polymers, supposing that \( |A_0(0)|^2 = 0 \), for a polymer consisting of \( N \) monomers, a pure mean transfer rate can be defined as \( k = \langle |A_N(t)|^2 \rangle/t_{N_{mean}} \), where \( t_{N_{mean}} \) is the first time \( |A_N(t)|^2 \) becomes equal to \( \langle |A_N(t)|^2 \rangle \) i.e. “the mean transfer time”. Increasing the number of base-pairs or monomers \( N \), we study various characteristic polymers: poly(dG)-poly(dC), poly(dA)-poly(dT), GCGGCG..., CGCGCG..., ATATAT..., TATATA... as well as DNA segments that have been experimentally studied in the past. If we fit \( k(d) \) – i.e. the pure mean transfer rate \( k \) as a function of the charge transfer distance \( d = N \times 3.4 \) Å– exponentially, as \( k = k_0 \exp(-\beta d) \), we obtain an estimation of \( k_0 \) and of the distance dependence parameter or inverse decay length \( \beta \) [24]. These quantities are displayed in Table III. If, instead, we fit \( k(N) \) – i.e. the pure mean transfer rate \( k \) as a function of the number of monomers \( N \) – in a power law, as \( k = k_0 N^{-\eta} \), we obtain an estimation of \( k_0 \) and \( \eta \). These quantities are displayed in Table IV. Values of \( \beta \), in the range \( 0.3-1.5 \) Å\(^{-1}\), for various compounds, have been.
displayed in the literature at least 30 years now, see e.g Table IV of Ref. [20]. In Table III the values of $\beta$ are in the range $\approx 0.2-2$ Å$^{-1}$, with smaller values for periodic polymers like ATATAT... poly(dG)-poly(dC), poly(dA)-poly(dT). However, for efficient charge transfer, a small value of $\beta$ is not enough; one should also take into account the magnitude of $k_0$. The values of $k_0$ assumed in Ref. [20] are $10^{-2}$-10$^{-1}$ PHz which coincides with most of the $k_0$ values shown in Table III although generally, the values of $k_0$ fall in the wider range $\approx 10^{-4}$-10 PHz. For the power law fit, $\eta \approx 1.7 - 17$; most of the $k_0'$ values shown in Table IV are in the range $\approx 10^{-2}$-10$^{-1}$ PHz, although generally, the values of $k_0'$ fall in the wider range $\approx 10^{-4}$-10$^3$ PHz. The $\beta$-value for charge transfer from an initial site (donor) to a final site (acceptor) depends on the mediating molecules, the so-called bridge. From Table III we conclude that there are no universal values of $\beta$ and $k_0$ for DNA, instead, each specific DNA segment is unique and one should use an efficient and easy way to predict $\beta$ and $k_0$ of each DNA segment under investigation. It is hoped that the present work will contribute in this direction. $\beta$ values for different systems include
approximately 1.0 - 1.4 Å⁻¹ for protein-bridged systems [21, 22], ≈ 1.55 - 1.65 Å⁻¹ for aqueous glass bridges [21], ≈ 0.2 - 1.4 Å⁻¹ for DNA segments [22, 28], ≈ 0.8 - 1.0 Å⁻¹ for saturated hydrocarbon bridges [26, 30], ≈ 0.2 - 0.6 Å⁻¹ for unsaturated phenylene [31, 32], polyyne [33, 34] and polyyne [35, 36] bridges, and much smaller values (< 0.05 Å⁻¹), suggesting a molecular-wire-like behavior, for a p-phenylenevinylene bridge [37]. Hence, it seems that charge transfer in ATATAT..., poly(dG)-poly(dC) and poly(dA)-poly(dT) is almost molecular-wire-like. Since a carrier can migrate along DNA over 200 Å [22, 27, 38], in the present calculations for polymers d is extending up to 204 Å (N up to 60 base-pairs).

![FIG. 2: HOMO pure mean transfer rate k for all trimers.](image)

| DNA segment | k₀ (Phz) | β (Å⁻¹) | C.C. | H/L |
|-------------|---------|---------|-----|-----|
| poly(dG)-poly(dC) | 0.176 ± 0.007 | 0.189 ± 0.008 | 0.988 | H |
| poly(dG)-poly(dC) | 0.035 ± 0.001 | 0.189 ± 0.007 | 0.989 | L |
| poly(dA)-poly(dT) | 0.035 ± 0.001 | 0.189 ± 0.008 | 0.988 | H |
| poly(dA)-poly(dT) | 0.051 ± 0.002 | 0.189 ± 0.008 | 0.989 | L |
| GCGGCCG... | 0.032 ± 0.003 | 0.358 ± 0.023 | 0.988 | H |
| ATATAT... | 0.057 ± 0.002 | 0.168 ± 0.008 | 0.985 | H |
| CGGCCG... | 0.932 ± 0.233 | 0.871 ± 0.074 | 0.994 | H |
| TATATA... | 0.110 ± 0.005 | 0.251 ± 0.012 | 0.985 | H |
| AGTGCAGCTTTCGA | 0.059 ± 0.002 | 0.685 ± 0.008 | 1.000 | H |
| AGTGCAGCTTTCGA | 0.8 ± 2.6 × 10⁻³ | 0.197 ± 0.059 | 0.808 | L |
| TAGATGGTATTAGA | 4.306 ± 5.001 | 1.321 ± 0.342 | 0.998 | H |
| TAGATGGTATTAGA | 2.877 ± 0.833 | 2.154 ± 0.085 | 1.000 | L |

In Ref. [39] the authors calculated the complex band structure of poly(dA)-poly(dT) and poly(dG)-poly(dC) using an ab initio tight-binding method based on density-functional theory and obtained the energy dependence $\beta(E)$. Since the states with large $\beta$ values don’t play a significant role in conduction they noticed that only the smallest $\beta(E)$ states, described by a semielliptical-like curve in the band-gap region are important. This branch reaches a maximum $\beta$ value near midgap, called the branch point, $\beta_{bp}$, ≈ 1.5 Å⁻¹ both for poly(dA)-poly(dT) and poly(dG)-poly(dC). Since in molecular electronics metallic contacts are made at the two ends of the molecule and electronic current is carried by electrons tunneling from the metal with energies in the band-gap region, the branch point plays an important role in the conductance. Although the above hold when metal contacts are attached to the molecule, in photoinduced charge transfer experiments, we are interested in states close to the top of the valence band i.e. the HOMO or close to the bottom of the conduction band i.e. the LUMO. For the top of the valence band of poly(dA)-poly(dT) [Fig.1a of Ref. [39]] $\beta$ ≈ 0.4 Å⁻¹ and for poly(dG)-poly(dC) [Fig.1b of Ref. [39]] $\beta$ ≈ 0.2 Å⁻¹, close to the values predicted in the present work (≈ 0.2 Å⁻¹ both for poly(dA)-poly(dT) and poly(dG)-poly(dC) cf. Table III).

In Ref. [40] Giese et al. studied experimentally the hole transfer in the DNA segment [G] (T)n [GGG] TATATATTACGC. (T)n denotes the bridge made up from n T-A monomers between the hole donor [G] and the hole acceptor [GGG] denoted by square brackets, before the TATATATTACGC tail. In Fig. 3 the computed $k(d)$ i.e. the pure mean transfer rate as a function of the distance from the hole donor to the middle of the hole acceptor is shown. In accordance with the experiment [40] we find two regions with different distance dependence. For $n = 1, 2, 3$ the distance dependence is strong becoming much weaker for $n ≥ 4$. For the strong distance dependence range, we find $\beta$ ≈ 0.8 Å⁻¹. In the experiment [Fig. 3 of Ref. [40]] the authors find qualitatively the same behavior, estimating $\beta$ ≈ 0.6 Å⁻¹ for $n = 1, 2, 3$. For $n = 4, . . . , 16$ we compute a much weaker distance dependence with $\beta$ ≈ 0.07 Å⁻¹.

In Ref. [41] the authors demonstrated rapid photoinduced electron transfer over a distance of greater than 40 Å between metallointercalators tethered to the 5’ termini.

TABLE IV: $k'_0$ and $\eta$ of the power fit $k = k'_0 N^{-\eta}$ for various DNA polymers. C.C. is the correlation coefficient.

| DNA segment | $k'_0$ (Phz) | $\eta$ | C.C. | H/L |
|-------------|-------------|-------|-----|-----|
| poly(dG)-poly(dC) | 0.359 ± 0.004 | 1.893 ± 0.002 | 1.000 | H |
| poly(dG)-poly(dC) | 0.072 ± 0.000 | 1.895 ± 0.002 | 1.000 | L |
| poly(dA)-poly(dT) | 0.072 ± 0.000 | 1.892 ± 0.002 | 1.000 | H |
| poly(dA)-poly(dT) | 0.105 ± 0.000 | 1.893 ± 0.000 | 1.000 | L |
| GCGGCCG... | 0.087 ± 0.008 | 3.176 ± 0.127 | 0.993 | H |
| ATATAT... | 0.117 ± 0.004 | 1.776 ± 0.035 | 0.994 | H |
| CGGCC... | 5.082 ± 1.619 | 6.715 ± 0.458 | 0.994 | H |
| TATATA... | 0.236 ± 0.007 | 2.295 ± 0.035 | 0.997 | H |
| AGTGCAGCTTTCGA | 1.383 ± 0.826 | 4.487 ± 0.487 | 0.997 | H |
| AGTGCAGCTTTCGA | (2.2 ± 1.0) × 10⁻³ | 2.176 ± 0.543 | 0.761 | L |
| TAGATGGTATTAGA | 46.300 ± 53.288 | 9.902 ± 1.660 | 0.998 | H |
| TAGATGGTATTAGA | 203.457 ± 99.552 | 16.708 ± 0.706 | 1.000 | L |

TABLE III: $k_0$ and $\beta$ of the exponential fit $k = k_0 \exp(-\beta d)$ for various DNA polymers. C.C. is the correlation coefficient.
of AGTGCCAAGCTTGCA. The authors [41] mentioned that “the photoinduced electron transfer between intercalators occurs very rapidly over > 40 Å through the DNA helix over a pathway consisting of π-stacked base-pairs.” Then, from Marcus theory [20] they estimated β to be ≤ 0.2 Å⁻¹. We observe (Table III) that for electron transfer (through LUMOs) we also find β ≤ 0.2 Å⁻¹, while for hole transfer (through HOMOs) we find β ≈ 0.7 Å⁻¹. Similar weak distance dependence with β ≤ 0.2 Å⁻¹ was found in Ref. [42].

In Ref. [43] the authors study hole transfer in the DNA sequence ACGCACGTCGATAATTACG [bridge] GGGTATTATATTACGC. The [bridge] is made up of TT dimers separated by G monomers. In the experiment [43], [bridge] is either TT (one TT step) or TTGTTTGTGGTTTTT (four TT steps). The values of these parameters are not universal, depend on the specific DNA segment and are different for electrons and holes.

that there are two distinct regions (i) one step (S1) to two steps (S2), and (ii) more than two steps (up to eight steps are included in the graphs).

A handy method to examine the charge transfer properties of DNA segments was displayed. Useful physical quantities were obtained including the pure mean carrier transfer rate k, the inverse decay length β used for an exponential fit (k = k₀exp(−βd)) of the transfer rate as a function of the charge transfer distance d = N × 3.4 Å and the exponent η used for a power law fit (k = k₀N⁻η) of the transfer rate as function of the number of monomers N. The values of these parameters are not universal, depend on the specific DNA segment and are different for electrons and holes.

* Electronic address: csimseri@phys.uoa.gr
URL: [http://users.uoa.gr/~csimseri/](http://users.uoa.gr/~csimseri/)
[1] J.C. Genereux and J.K. Barton, Chem. Rev. 110, 1642 (2010).
[2] B. Giese, Annu. Rev. Biochem. 71, 51 (2002).
[3] R.G. Endres, D.L. Cox, and R.R.P. Singh, Rev. Mod. Phys. 76, 195 (2004).
[4] L.G.D. Hawke, G. Kalosakas, and C. Simserides, Eur.
Phys. J. E 32, 291 (2010); ibid. 34, 118, (2011).

[5] K. Senthilkumar, F.C. Grozema, C.F. Guerra, et al., J. Am. Chem. Soc. 127, 14894 (2005).

[6] Y. J. Yan and H. Zhang, J. Theor. Comput. Chem. 1, 225 (2002).

[7] H. Sugiyama and I. Saito, J. Am. Chem. Soc. 118, 7063 (1996).

[8] M. Hutter and T. Clark, J. Am. Chem. Soc. 118, 7574 (1996).

[9] H. Zhang, X.Q. Li, P. Ham, X.Y. Yu, and Y.J. Yan, J. Chem. Phys. 117, 4578 (2002).

[10] X. Li, Z. Cai, and M.D. Sevilla, J. Phys. Chem. B 105, 10115 (2001).

[11] X. Li, Z. Cai, and M.D. Sevilla, J. Phys. Chem. A 106, 9345 (2002).

[12] M. K. Shukla and J. Leszczynski, J. Phys. Chem. A 106, 4709 (2002).

[13] D. Varsano, R. Di Felice, M. A. L. Marques, and A. Rubio, J. Phys. Chem. B 110, 7129 (2006).

[14] A. A. Voityuk, J. Jortner, M. Bixon, and N. Rösch, J. Chem. Phys. 114, 5614 (2001).

[15] A. Migliore, S. Corni, D. Varsano, M.L. Klein, and R. Di Felice, J. Phys. Chem. B 113, 9402 (2009).

[16] T. Kubár, P. B. Woiczikowski, G. Cuniberti, and M. Elstner, J. Phys. Chem. B 112, 7937 (2008).

[17] A. Ivanova, P. Shushkov, and N. Rösch, J. Phys. Chem. A 112, 7106 (2008).

[18] L. G. D. Hawke, G. Kalosakas, and C. Simserides, Mol. Phys. 107, 1755 (2009).

[19] L. Blancafort and A. A. Voityuk, J. Phys. Chem. A 110, 6426 (2006).

[20] R.A. Marcus and N. Sutin, Biochim. Biophys. Acta 811, 265 (1985) and references therein.

[21] H.B. Gray and J.R. Winkler, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 3534.

[22] C.C. Moser, J.M. Keske, K. Warncke, R.S. Farid, P.L. Dutton, Nature 355, 796 (1992).

[23] K. Kawai and T. Majima, Acc. Chem. Res., Publication Date (Web): June 27, 2013, DOI: 10.1021/ar400079s

[24] F.D. Lewis, T. Wu, Y. Zhang, R.L. Letsinger, S.R. Greenfield, M.R. Wasielewski, Science 277, 673 (1997).

[25] C.Z. Wan, T. Fiebig, O. Schiemann, J.K. Barton, A.H. Zewail, Proc. Natl. Acad. Sci. U.S.A. 97, 14052 (2000).

[26] R.E. Holmlin, P.J. Dandliker, J.K. Barton, Angew. Chem. Int. Edn. Engl. 36, 2715 (1998).

[27] P.T. Henderson, D. Jones, G. Hampikian, et al., Proc. Natl. Acad. Sci. USA 96, 8353 (1999).

[28] G. Kalosakas and E. Spanou, Phys. Chem. Chem. Phys. 15, 15339 (2013).

[29] M.D. Johnson, J.R. Miller, N.S. Green, G.L. Closs, J. Phys. Chem. 93, 1173 (1989).

[30] H. Oevering, M.N. Paddon-Row, M. Heppener, et al., J. Am. Chem. Soc. 109, 3258 (1987).

[31] A. Helms, D. Heller, G. McLendon, J. Am. Chem. Soc. 114, 6227 (1992).

[32] A.-C. Ribou, J.-P. Launay, K. Takahashi, T. Nihira, S. Tarutani, C.W. Spangler, Inorg. Chem. 33, 1325 (1994).

[33] F. Effenberger and H.C. Wolf, New J. Chem. 15, 117 (1991).

[34] L.M. Tolbert, Acc. Chem. Res. 25, 561 (1992).

[35] V. Grosshenny, A. Harriman, R. Ziessel, Angew. Chem. Int. Edn. Engl. 34, 2705 (1996).

[36] S.B. Sachs, S.P. Dudek, R.P. Hsung, et al., J. Am. Chem. Soc. 119, 10563 (1997).

[37] W.B. Davis, W.A. Svec, M.A. Ratner, M.R. Wasielewski, Nature 396, 60 (1998).

[38] E. Meggers, M.E. Michel-Beyerle, B. Giese, J. Am. Chem. Soc. 120, 12950 (1998).

[39] Hao Wang, J.P. Lewis, and O.F. Sankey, Phys. Rev. Lett. 93, (2004) 016401.

[40] B. Giese, J. Amaudrut, A.-K. Kohler, M. Spormann and S. Wessely, Nature 412, 318 (2001).

[41] C.J. Murphy, M.R. Arkin, Y. Jenkins, N.D. Ghatlia, S.H. Bosmann, N.J. Turro, J.K. Barton, Science 262, 1025 (1993).

[42] M.R. Arkin, E.D.A. Stemp, R.E. Holmlin, J.K. Barton, A. Hormann, E.J.C. Olson, P.F. Barbara, Science 273, 475 (1996).

[43] B. Giese, S. Wessely, M. Spormann, U. Lindemann, E. Meggers, and M.E. Michel-Beyerle, Angew. Chem. Int. Ed. 38, 996 (1999).