Distance dependence of hole transfer rates from G radical cations to GGG traps in DNA

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Relative reaction rates for hole transfer between G radical cations and GGG triplets in DNA, through different bridges of varying lengths, are numerically calculated and the obtained results are compared with corresponding experimental observations [Giese et al., 2001, Nature, 412, 318; Angew. Chem. Int. Ed., 1999, 38, 996]. Hole donors and acceptors are separated either by (T–A) bridges or by N repeated barriers consisting of (T–A,T–A) double base-pairs which are connected through single G–C base-pairs. In the former case, hole transfer rates show a strong exponential decrease with the length of the bridge for short bridges, while a switching to weak distance dependence has been observed for longer bridges. In the latter case, a power law seems to better describe the distance dependence of charge transfer rates. All these experimental observations are qualitatively reproduced by our simulations without any adjustable parameter, considering only tunneling as the charge transfer mechanism. Physical insights into the mechanism providing the switching behavior in the case of (T–A), bridges are presented through an analysis of the eigenfunctions of the system.

I. Introduction

Charge transport in DNA has been studied intensively in the last two decades due to its potential applications in both nanotechnology and biology.1–3 The interested reader can be referred, for example, to the reviews4,5 and references therein. Despite the intensive research, open questions still remain and novel suggestions for charge transfer mechanisms in DNA continually appear.6,7 Different mechanisms, ranging from single-step tunneling to thermal activation and charge hopping (or combinations of these and intermediate mechanisms), have been proposed to account for various experimental measurements regarding charge transfer in DNA.

Early experimental studies have generated holes within a DNA double strand and monitored the efficiency of charge transfer in hole traps formed by guanine (G) doublets or triplets.8–11 Here we focus on the experiments conducted by Giese and collaborators, investigating hole transfer between guanine radical cations (donors) and GGG traps (acceptors) within appropriately synthesized DNA segments. In these works donors and acceptors are separated either by (T–A)n bridges consisting of a varying number n of A–T base-pairs,11 or by N repeated barriers formed by (T–A)2 base-pair doublets interrupted by single G–C base-pairs (see Fig. 6a below) with N varying from 1 to 4.10 In the former experiments, the charge transfer rates exhibit a strong exponential dependence on the length of the bridge for n = 1–3, but the behavior is switched to weak distance dependence for longer bridges with n > 3.11 In the latter experiments, the charge transfer rates seem to follow a power law (polynomial) dependence on the donor-acceptor distance.10

The crossover from exponential to weak distance dependence observed in the case of (T–A)n bridges is generally attributed to a switching of the mechanism of charge transfer from single-step tunneling of the hole to its thermal activation on the higher-energy states of the bridge and propagation through these states until reaching the acceptor.11–15 An alternative scenario reproducing this behavior, without requiring thermal activation or a change in the mechanism of charge transfer, has been discussed in ref. 16. The crossover behavior is explained within a unified theoretical model in ref. 14 and 16, while more phenomenological models are used in other works. On the other hand, models of hopping transport of the hole lead to power law dependencies of charge transfer rates17 and are able to account for the experimental results referring to the case of multiple (T–A)2 barriers.18

In the present work, using a simple model with no adjustable parameters, we show that a single mechanism qualitatively reproduces this wealth of experimental observations. We emphasize that although there are many theoretical studies successfully reproducing the results of either the one or the other experiment10,11 mentioned above, we are not aware of any model explaining both experiments at the same time, using the same set of parameters. Apart from reproducing these experiments in a single framework, we stress that there is not any free parameter in our calculations which has been adjusted to...
improve the results. The electronic parameters used here have been independently calculated elsewhere.19

II. Model

Hole transfer rates are calculated in our simulations through the solution of the Schrödinger equation in terms of the energy eigenvalues and eigenstates. To this end the Hamiltonian of the system in the tight-binding approximation is considered. We use the tight-binding description at the single-base level,19 where the HOMO wavefunctions of the individual bases (local states) of the simulated DNA sequence provide the basis set of the hole Hilbert space. The hole can move between neighboring bases, occupying the corresponding local HOMO state. Thus, for a DNA sequence consisting of L base-pairs, the dimension of the Hilbert space is 2L. The non-zero matrix elements of the 2L × 2L Hamiltonian matrix are the diagonal on-site energies and the non-diagonal hopping transfer integrals between neighboring bases (five non-diagonal elements at each row, except for the rows corresponding to bases at the two ends of the examined DNA sequence where there are three non-diagonal elements).

The values of these electronic parameters are obtained from ref. 19, resulting from a recently introduced description of π molecular orbitals in planar organic molecules.20 In particular, the diagonal Hamiltonian matrix elements are given by the base HOMO energies $E_n^\text{h}$ from Table 1 of ref. 19 (taken with opposite signs because they refer to holes), while the non-diagonal interbase hopping transfer integrals $t_{ij}$ are obtained from the first columns of Tables 4–7 of ref. 19 (taken with opposite signs too) depending on whether they refer to intra-base-pair hoppings (Table 4), or intrastrand hoppings between adjacent bases (Table 5), or interstrand hoppings between bases of adjacent base-pairs (Tables 6 and 7). Diagonalizing the Hamiltonian matrix, the corresponding energy eigenvalues $E_n$ and eigenstates $|h_n\rangle$ are obtained (2L totally).

In the experiments under discussion,10,11 the hole is photochemically injected into the donor site, forming a guanine radical cation G*. Therefore, the initial condition for the hole wavefunction is $|\Psi(t = 0)\rangle = |\phi_1\rangle$, where $|\phi_1\rangle$ corresponds to the local HOMO state of the guanine donor (denoted as G22 in ref. 10 and 11). Schrödinger equation yields for the time-dependent hole wavefunction

$$|\Psi(t)\rangle = \sum_n \langle h_n | \phi_1 \rangle \exp \left(-\frac{iE_n t}{\hbar}\right) |h_n\rangle,$$

where the sum is over all the energy eigenstates $|h_n\rangle$. If $|\phi_{m-2}\rangle$, $|\phi_{m-1}\rangle$, and $|\phi_{m}\rangle$ represent the local states of the three consecutive guanines of the GGG acceptor, then the probability to find the hole at the acceptor is

$$P_{\text{acc.}}(t) = \sum_{l=m-2}^{m} |\langle \phi_l | \Psi(t) \rangle|^2$$

$$= \sum_{l=m-2}^{m} \left| \sum_n \langle h_n | \phi_l \rangle \langle \phi_l | h_n \rangle \exp \left(-\frac{iE_n t}{\hbar}\right) \right|^2.$$

The probability $P_{\text{acc.}}(t)$ can be readily obtained numerically from the calculated energy eigenstates and eigenvalues. Our approach is similar, but simpler, to that of ref. 16, where a more complicated model has been used that includes decay of charge states and energy spectra with complex values, thus introducing arbitrary free parameters for the imaginary parts of the on-site energies.

Since we are interested in relative hole transfer rates for a series of DNA sequences (both experiments10,11 provide relative rates), these can be directly obtained from the time-averaged probabilities, $P_{\text{acc.}}$, to find the hole at the acceptor. In addition to this method, a Monte Carlo scheme for calculating relative transfer rates has been also employed: the system is probed at every time $t_{\text{probe}}$. Then a random number $x$ is drawn from a uniform distribution in the region [0,1]. If $x < P_{\text{acc}}(t)$ then we consider that the hole has been transferred to GGG and the transfer time is measured, otherwise the process is continued as time passes. This procedure is repeated for a large number of realizations (of the order of thousands) and the mean transfer time is calculated. The charge transfer rate is the inverse of mean transfer time. By varying $t_{\text{probe}}$ from nsec to fsec, it has been tested that the arbitrary value of $t_{\text{probe}}$ does affect the magnitudes of the calculated transfer rates, as expected, but not their ratios, thus playing no role in computing relative transfer rates. Either using this Monte Carlo scheme, or the time-averaged probabilities $P_{\text{acc.}}$ from eqn (2), the obtained relative transfer rates are the same.

The donor local state $|\phi_1\rangle$ is considered as the initial condition $|\Psi(t = 0)\rangle$ in our simulations, to describe the initial photochemical injection of the hole at the guanine donor. This choice is in accordance with other theoretical studies, investigating transfer rates of photoinduced holes in DNA, through the solution of the time-dependent Schrödinger equation (examining either the same DNA system with the (T–A)$_n$ bridge as in the current work, or experimentally studied DNA hairpins). An alternative potential choice of initial condition would be the corresponding energy eigenstate of the system that is mainly localized at the guanine donor, $|h_D\rangle$ (which, however, has a small, but nonzero, component at the bases of the bridge located near the donor). Such a state could arise through the relaxation of the photoinjected hole, if this relaxation is faster than the hole transfer to the acceptor. Considering $|h_D\rangle$ as the initial condition, this state is stationary exhibiting no evolution, apart from a phase $\exp(-iE_D t/\hbar)$. Therefore, the relative transfer rates in this case are simply provided, within our approach, through the projections of the donor eigenstate $|h_D\rangle$ at the three GGG acceptor sites. As we see below, the choice of $|\phi_1\rangle$ as the initial condition successfully reproduces all the variety of experimental observations presented in ref. 10 and 11, while the corresponding choice of $|h_D\rangle$ fails to describe these experiments, resulting always in exponentially decaying transfer rates independently of the length and the composition of the bridge.

III. Results and discussion

A. Hole transfer over (T–A)$_n$ bridges

We first present results for the DNA sequences examined in ref. 11, where the G* donor and the GGG acceptor are
separated by (T–A)$_n$ bridges consisting of $n$ A–T base-pairs, with $n$ varying from 1 to 16. At the top of Fig. 1 the simulated DNA sequences are depicted. The base-pairs shown to the right of the GGG acceptor have been used in order to simulate similar DNA segments as those investigated experimentally.$^{11}$ On the contrary, we do not include in our system the sequence to the left of the G$^{++}$ donor because we are interested in the hole migration from the donor towards the acceptor. Since we consider relative transfer rates, ignoring the segment at the left of the donor, which is common in all examined sequences, it does not affect our results.

The plot in Fig. 1 shows the dependence of the calculated relative hole transfer rates on the length of the bridge (expressed in terms of the number $n$ of A–T base-pairs). The experimentally observed distinct change in the distance dependence of the relative transfer rates is reproduced in our simulations. The switching from a strong to weak distance dependence is demonstrated through a change in the slope of the two distinct regions of the plot by almost two orders of magnitude (from $-1.1$ Å$^{-1}$ for the first 4 data points, to $-0.03$ Å$^{-1}$ for the rest of the data with $n > 4$). A numerical discrepancy between the experimental and the calculated results is that the switching of the behavior that is obtained for $n > 4$ in Fig. 1 is observed for $n > 3$ in ref. 11. A similar behavior is observed in simulations using the tight-binding description at the base-pair level$^{19}$ (where the corresponding base-pair HOMO wavefunctions are considered as the local states providing the basis set), instead of the single-base level. Again a switching to weak distance dependence occurs for $n > 4$ in this case.

Fig. 2 focuses on the first part (exhibiting the strong distance dependence) of the plot $\ln(k_{\text{rel}}) = f(\Delta r)$, where $\Delta r$ is the charge transfer distance from the donor to the acceptor. For linear dependencies, as those shown in Fig. 2, the slope of the corresponding linear fits provides the inverse decay length $b$, describing transfer rates that decay exponentially with the donor–acceptor distance

$$k \sim \exp(-b\Delta r).$$

For quantitative comparisons, the corresponding values of $b$ are obtained from the slopes of the linear fits shown in Fig. 2 for the experimental data (diamonds) and numerical simulations using two different sets of tight-binding parameters: the ones from ref. 19 used in this work (circles) and those from ref. 21 calculated from first principles methods (squares). For the experimental data the linear fit gives a correlation coefficient 1.000 and $b = 0.6$ Å$^{-1}$, while for the numerical results with the electronic parameters from ref. 19 (from ref. 21) it gives a correlation coefficient 0.999 (0.982) and $b = 1.1$ Å$^{-1}$ ($b = 1.3$ Å$^{-1}$). We see that the numerical results within our model overestimate the experimental value of $b$ by a factor of 2. Estimates of $b$ arising from various analytical approximations (see for example eqn (16.117) of ref. 23 or eqn (6) of ref. 12)
result in $\beta = 2-2.5$ Å⁻¹ or $\beta = 2.3-4$ Å⁻¹ using the parameters from ref. 19 or 21, respectively.

There is a discussion on whether for short (T−A)$_n$ bridges (for $n < 4$, corresponding to the first part of Fig. 1 with the strong distance dependence, where the single-step tunneling is considered as the transfer mechanism) the hole resides at all on the bridge or not. Fig. 3 (top) presents the numerically obtained average occupation probabilities of the donor, bridge, and acceptor, as a function of the number $n$ of A−T base-pairs in the bridge. It can be seen that for any value of $n$ the average bridge occupation probability is of the order of $10^{-2}$. Further, for $n > 2$ there is a higher probability for the hole to be found at the bridge than at the GGG acceptor, while for $n = 2$ these probabilities are about the same. The lower panel of Fig. 3 shows that the bridge probability is mainly distributed at the first A−T base-pair closer to the donor. Though the bridge occupancy percentage of this base-pair drops as the length of the bridge increases, it still remains more than 50% for all the examined sequences up to $n = 16$. The percentage of the second next to the donor A−T base-pair becomes smaller than 10% for $n > 4$.

In order to investigate the physical mechanism which determines the observed crossover in the bridge length dependence of the transfer rates, or equivalently of the acceptor occupation probability, within the simple model used, we examine the distance dependent behavior of the energy spectrum and eigenfunction properties of the system. To reduce the number of eigenstates and make the analysis more clear, we use the tight-binding description at the base-pair level for the DNA sequence $G^+\text{(T−A)}_n\text{GGG}$, since, as it is mentioned above, a similar behavior is obtained either with the base-pair or the single-base description. Thus for a bridge containing $n$ A−T base-pairs, the considered system has $n + 4$ eigenstates. The tight-binding parameters are taken form ref. 19: the $E_{\text{bp}}^H$ from Table 2 for the on-site energies and the $t_{\text{bp}}^H$ from Table 3 for the hopping integrals (all of them with opposite sign).

**Fig. 3** Top: bridge, donor, and acceptor average occupation probabilities obtained from the simulations of the experiments containing the (T−A)$_n$ bridges. Circles represent the average probability for finding the hole on the bridge, stars show the donor average occupation probability, and open triangles correspond to the GGG acceptor average occupation probability. Bottom: percentage of the total bridge occupation probability distributed on the next to the donor A−T base-pair (squares) and the second next to the donor A−T base-pair (diamonds). Lines are guides to the eye.

**Fig. 4** Energy eigenvalues of the donor−bridge−acceptor $G^+\text{(T−A)}_n\text{GGG}$ system, obtained with the tight-binding description at the base-pair level, for various lengths of the bridge. Open blue circles at the top show the eigenvalues of the $n$ bridge states, for bridges containing from $n = 1$ to $n = 10$ A−T base-pairs. The filled diamond at the left corresponds to the energy of the eigenstate which is mainly localized at the donor, while the open squares at the right correspond to the energies of the three delocalized states of the GGG acceptor. Red stars show the analytically obtained energies of the bridge and the acceptor states within the LCAO approximation (see text).
Fig. 4 shows the energy eigenvalues of the system for bridge lengths varying from 1 to 10 A–T base-pairs. Because the difference in the G–C and A–T base-pair HOMO energies is large compared to the corresponding hopping transfer integrals, the energy spectrum is well separated into two regions; the higher energy part occupied by the delocalized states at the bridge and the lower energy part occupied by the donor state and the delocalized states at the acceptor. Moreover, since there is no substantial mixing of the bridge and the donor–acceptor states, the n delocalized states at the bridge can be accurately described through the simple LCAO (linear combination of atomic orbitals), or Hückel result: 
\[
E(k) = E_{\text{H}} + 2t_{\text{H}} \cos \frac{k \pi}{n+1},
\]
with \(k = 1, \ldots, n\) (see for example eqn (20.21) of the classical textbook\(^2\)), where \(E_{\text{H}} = E_{\text{GGG}}^{\text{AT}} = 8.3\ \text{eV}\) and \(t_{\text{H}} = E_{\text{GGG}}^{\text{TT}} = 8\ \text{meV}\)\(^1\),\(^9\) while, similarly, the three delocalized states at the GGG acceptor can be described by the same formula with \(n = 3\) and \(E_{\text{H}} = E_{\text{GGG}}^{\text{AT}} = 8.0\ \text{eV}\) and \(t_{\text{H}} = E_{\text{GGG}}^{\text{TT}} = 62\ \text{meV}\) [ref. 19] (the analytical LCAO results for the bridge and acceptor delocalized states are shown by red stars in Fig. 4). Of course the energy of the donor state equals to \(E_{\text{H}}^{\text{GGG}} = 8.0\ \text{eV}\). We see that there is not any drastic change in the energy spectrum of the system as \(n\) is varied. As expected, with increasing \(n\) the bridge states fill more densely the band region \(E_{\text{GGG}}^{\text{AT}} \pm 2E_{\text{GGG}}^{\text{TT}}\), without spreading further towards the donor–acceptor energies. The donor–acceptor energies are insensitive to the length of the bridge, even for \(n = 1\).

Since the energy spectrum of the system cannot provide any hint for the underlying mechanism of the switching observed in the simulations for \(n = 4\), we examine proper features of the corresponding energy eigenfunctions. It can be seen from eqn (2) that the probability \(P_{\text{acc}}\) of the hole to be found at the acceptor is given through products of the form \(\langle h_i | \phi_d | h_n \rangle\), \(i.e., \) products of the overlaps of each eigenstate with the donor local state \(|\phi_d\rangle\) and the acceptor local states \(|\phi_i\rangle\), with \(l = m - 2, m - 1, m\) corresponding to the three G sites of the acceptor (denoted as \(|\phi_A\rangle\)). Since the eigenstates of the system can be grouped into three categories (donor, bridge, and acceptor eigenstates), we can examine the distance dependent contribution of each group at the probability \(P_{\text{acc}}\).

(a) The donor eigenstate \(|h_d\rangle\). The overlap of this eigenfunction with the local \(|\phi_d\rangle\) state is of the order of 1 (for \(n = 1\) is around 0.8, but for larger \(n\) is almost 1). Thus the product \(\langle h_d | \phi_d | h_n \rangle\) is almost equal to its overlap with an acceptor local state \(|\phi_A\rangle\). The latter overlap is of the order of \(\sim 0.1\) for \(n = 1\), but it drops exponentially as \(n\) increases, giving the exponential decrease of the product \(\langle h_d | \phi_d | h_n \rangle\) with the length of the bridge, shown by stars in Fig. 5.

(b) An acceptor eigenstate \(|h_A\rangle\). The overlap of this eigenfunction with a local \(|\phi_A\rangle\) state is close to \(1/\sqrt{2}\), because of its delocalization at the GGG triplet (for \(n = 1\) is around 0.6, but for larger \(n\) is almost 0.707). However, similarly to the previous case, its overlap \(\langle h_A | \phi_d \rangle\) with the donor local state decreases exponentially with the bridge length, resulting in the distance dependent product \(\langle h_A | \phi_d | h_n \rangle\) depicted by open squares in Fig. 5.

(c) A bridge eigenstate \(|h_B\rangle\). Because these eigenstates are delocalized along the bridge, their overlaps with the neighboring to the bridge local states \(|\phi_d\rangle\) and \(|\phi_A\rangle\) do not exhibit a dramatic change with the bridge length (see open triangles and diamonds in Fig. 5), but they rather show a weak dependence of the order of \(1/\sqrt{n}\) (the corresponding slope in a log-log plot is around \(-0.4\)). Thus the products \(\langle h_B | \phi_d | h_n \rangle\) have also a weak bridge length dependence, as it can be seen from the filled circles in Fig. 5.

Therefore this analysis of the eigenfunction overlaps with the local donor and acceptor states demonstrates that the contribution of the donor and acceptor eigenstates to the hole transfer drops exponentially with the size of the bridge, while the bridge eigenstates have a contribution characterized by a much weaker distance dependence. Fig. 5 shows that for \(n < 4\) the overlap products of the donor and acceptor eigenstates (stars and open squares) are significantly larger than the corresponding ones of the bridge eigenstates (filled circles), but because of their exponential decrease they become much smaller than the latter ones for \(n > 4\). For \(n = 4\) all these overlap products are of the same order of magnitude and thus there is a similar contribution from all eigenstates. This means that the acceptor occupation probability and the hole transfer rate within the used model, are determined by the donor and acceptor eigenstates for \(n < 4\), exhibiting thus the strong exponential dependence on the bridge length, but the bridge states dominate for longer bridges revealing their much weaker distance dependence. We mention that the role of the bridge delocalized eigenstates for providing a crossover to a weak distance dependence of charge transfer rates has been also pointed out in ref. 16.

In a different model, taking thermal activation into account, it has been found that variable-range hopping between partially
delocalized states of the bridge provides an explanation for the weak distance dependence of transfer rates.\textsuperscript{14} Other more phenomenological models also interpret this weak dependence through thermally assisted hopping on the bridge. In all these models the switching of the behavior of charge transfer rates is due to a change of the transfer mechanism from tunneling to thermally activated hopping. Despite the apparent similarity between bridge occupation (and the role of bridge states) in the model used here and the thermally assisted hopping through the bridge states in these models, our model does not show any change in the mechanism as the only existing transport mechanism is tunneling. Bridge occupation is not inconsistent with zero temperature tunneling. The switching in our case is provided through the change of the nature (and the properties) of the eigenfunctions dominating tunneling.

Hole transfer along (A–T)\textsubscript{n} bridges has been spectroscopically studied over different time scales by Lewis and collaborators.\textsuperscript{25,26} In these works DNA hairpins of different lengths, containing a different number \( n = 1, \ldots, 7 \) of A–T base-pairs, were conjugated with stilbene chromophores (stilbenediether, Sd, as a hairpin linker and stilbenedicarboxamide, Sa, as a capping group) and a detailed investigation of charge transfer kinetics was presented. Following selective photoexcitation of Sa, the radical anion Sa\textsuperscript{+} was formed, injecting a hole which was transferred through the (A–T)\textsubscript{n} tract on the hole acceptor Sd, resulting in the radical cation Sd\textsuperscript{+}. Transient spectroscopy was used to extract rate constants for the injection of the hole in the bridge and the hole arrival at the acceptor Sd. In these works there is a difference with respect to Giese’s experiments\textsuperscript{11} simulated here, due to the presence of the electrostatic potential of the negatively charged Sa\textsuperscript{+} (after the charge separation) which should affect hole migration to the acceptor. Despite this slightly different physical situation, these experiments\textsuperscript{25,26} showed a rather similar behavior like the one considered here; hole arrival times at the acceptor were strongly distance dependent up to \( n = 4 \), while they were relatively insensitive to distance for \( n = 5–7 \) (see Fig. 3 of ref. 26). However, this change of the behavior was not so abrupt like the one considered here.\textsuperscript{11} One important observation of these experiments was the population of the bridge before the hole arrives at the acceptor in the cases \( n > 2 \) and that the rate constant of hole injection at the bridge was independent of the donor–acceptor distance (see Fig. 6 of ref. 25). Note the similarity of these observations to the results presented in Fig. 3 (top), where the probability of finding the hole at the bridge is much larger than that at the acceptor for \( n > 2 \) (\( n = 2 \) is an intermediate case, like in ref. 25) and the bridge occupation probability is independent of the donor–acceptor distance. However, these similarities should be taken with caution because of the above mentioned different physical situation.

### B. Hole transfer over bridges containing (T–A)\textsubscript{2} barriers

Results for the DNA sequences investigated in ref. 10 are shown in Fig. 6. Now the bridges consist of a number \( N \) (varied from 1 to 4) of (T–A)\textsubscript{2} barriers separated by single G–C units, as shown
at the top of Fig. 6. It seems that in this case the hole transfer rates follow a power law (polynomial) decay of the form

$$k \sim N^{-\eta},$$

(4) rather than the exponential decay of eqn (3) (see Fig. 1 of ref. 10). To perform the same comparison for the numerical results obtained in our simulations, we plot in Fig. 6 the variation of \(\ln(k_{rel})\) with the charge transfer distance \(\Delta r\) (Fig. 6 middle) and also with \(\ln N\) (Fig. 6 bottom). Linear dependency in the former (latter) case implies exponential (power law) decay and the slope of the corresponding line provides the inverse decay length \(\beta\) (the exponent \(\eta\)). Numerical results are presented using electronic parameters from both ref. 19 and 21. Linear fits of the plots \(\ln(k_{rel}) = f(\Delta r)\) (Fig. 6 middle) give the following correlation coefficients and \(\beta\) values: 0.982 and \(\beta = 0.07 \text{ Å}^{-1}\) for the experimental data, 0.943 and \(\beta = 0.15 \text{ Å}^{-1}\) for the numerical simulations with the electronic parameters from ref. 19, and 0.936 and \(\beta = 0.05 \text{ Å}^{-1}\) for the numerical simulations with parameters from ref. 21. Corresponding linear fits of the plots \(\ln(k_{rel}) = f(\ln N)\) (Fig. 6 bottom) give correlation coefficient 1.000 and exponent \(\eta = 1.7\) for the experimental results, and 0.990 (0.987) and \(\eta = 3.4\) (\(\eta = 1.2\)) for the numerical calculations using tight-binding parameters from ref. 19 (from ref. 21). The numerical results, as happens with the experimental data too, exhibit better fits with the power law decay, eqn (4), than with the exponential decay, eqn (3). Regarding quantitative comparisons of the corresponding exponents \(\eta\), the simulations with the parameters from ref. 19 overestimate the experimental value by a factor of 2, while those with parameters from ref. 21 underestimate this value by a factor of 0.7.

A similar analysis has been performed in this case, like that in the previous subsection, concerning the bridge-length dependence of the overlaps of the energy eigenfunctions with the donor and acceptor local states and their corresponding products that determine the acceptor occupation probability and thus the relative transfer rate. As in the previous case, the overlaps of the donor eigenstate with an acceptor local state, and of an acceptor eigenstate with the donor local state, drop exponentially with the length of the bridge. These strong exponential decays determine the behavior of the products \(\langle h_D | \phi_A \rangle\) and \(\langle h_A | \phi_D \rangle\) and thus the corresponding contribution of the donor and acceptor eigenstates to the hole transfer rate. Regarding the bridge energy eigenfunctions, these can be separated to eigenstates distributed at the guanines of the bridge (G-bridge eigenstates) and eigenstates extended over the A-T base-pairs of the bridge (AT-bridge eigenstates). The G-bridge eigenstates are generally extended over all guanines of the bridge for \(N > 2\). For \(N = 2\) the unique G-bridge eigenstate is dominantly located at the single guanine of the bridge, while for \(N = 1\) there are obviously no such bridge eigenstates. The AT-bridge eigenstates are generally extended along all the \(N\) (T-A)$_2$ barriers of the bridge. The overlaps and the corresponding products of both G-bridge and AT-bridge eigenstates with the donor and acceptor local states exhibit a weak decrease with the length of the bridge and, as a result, these eigenstates are responsible for the obtained distance dependence of hole transfer rates.

As is discussed at the end of Section II, if the initial hole wavefunction \(\langle \Psi(t = 0) \rangle\) is given by the donor eigenstate \(| h_D \rangle\), then the relative transfer rates are provided through the overlaps of this eigenstate with the acceptor local states. We have mentioned that these overlaps exhibit an exponential decrease with the length of the bridge, for both cases: either for bridges containing multiple (T-A)$_2$ barriers (see the discussion in the previous paragraph), or for (T-A)$_n$ bridges (see the data shown by stars in Fig. 5 and the related discussion in the previous subsection). Therefore, assuming \(\langle \Psi(t = 0) \rangle = | h_D \rangle\) always results in exponentially decreasing charge transfer rates, within our approach, and fails to reproduce the experimental observations,10,11 in sharp contrast to the case \(\langle \Psi(t = 0) \rangle = | \phi_1 \rangle\) considered here.

IV. Conclusions

We have shown that a simple model considering only the tunneling mechanism accounts for all the characteristics of the rich behavior observed experimentally10,11 concerning relative hole transfer rates from G$^+$ radical cations to GGG triplets: the switching from strong to weak distance dependence for (T-A)$_n$ bridges as well as the power law decay for bridges consisting of repeated (T-A)$_2$ barriers.

Comparison at a quantitative level shows that the numerical simulations result in exponential decays and power law exponents deviating by about a factor of 2 from the experimental values, while the crossover from strong to weak distance dependence occurs for \(n > 4\) instead of \(n > 3\). Note however that our calculations do not contain any adjustable parameters and, further, correspond to zero temperature, thus ignoring thermal fluctuations of the DNA average structure. Fluctuations affect the electronic parameters governing charge transfer and the resulting properties4,21,22,27–31 and may be responsible for the obtained quantitative deviations from the experimental results. Neglecting fluctuations is a drastic simplification of the model discussed here. However, the dependence of the used electronic parameters on DNA conformational changes can be calculated, with the methodology presented in ref. 19. These results can then be used for describing the effect of the fluctuations within the model, and to show whether the competition between dynamically induced localization of the bridge states and instantaneous well-coupled conformations of the bases can affect the obtained distance dependence of charge transfer rates.

A detailed analysis of the energy spectrum and eigenfunction properties has been presented for the case of (T-A)$_n$ bridges, in order to explain the crossover of transfer rates from an exponential to a weak dependence on the length of the bridge. We have shown that charge transfer is dominated by the eigenstates localized at the donor and at the acceptor for short bridges, and the strong exponential decrease with the length of the bridge reflects the exponential drop of their corresponding overlaps with the local states at the acceptor and the donor.
sites, respectively. The switching of the charge transfer to a weaker dependence for longer bridges, is due to the contribution of the delocalized bridge eigenstates, which dominate for larger bridge lengths because their corresponding overlaps with the local states at the acceptor and the donor sites exhibit a much weaker variation with the length of the bridge.

The presented results show that tunneling alone accounts for several experimental observations, explained through different charge transfer mechanisms in the literature until now. This does not exclude of course the possibility that indeed different mechanisms can come into play in various circumstances. However the current explanation of such different behaviors in a single framework, without any adjustable parameter, provides an attracting alternative, possibly suggesting a reconsideration of the physical mechanisms applied in DNA charge transfer.

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References