

Polarons in DNA Oligomers

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There has been much study of the transport of a hole created by photoinduced electron transfer to a hole donor, **D**, in a sequence **D**(A/T)_{*n*}**A**, where **A** is a hole acceptor, A is adenine, paired with thymine, T, and *n* is the number of A/Ts in the sequence. The majority of the studies have been carried out for the case where the negative charge remains on the hole donor, creating a Coulomb well for the hole, thus a Coulomb barrier it must tunnel through or surmount. Recent experiments have shown that introduction into the A/T series of a G/C base pair, where G is guanine, C cytosine, can considerably enhance hole transport, as measured by the number of charge pairs (**D**[−]**G**⁺ or **D**[−]**A**⁺, depending on the experiment) created. Zeidan et al., using perylenediimide, **P**, as the hole donor, found that the yield of **P**[−]**G**⁺ pairs decreased from 100% to 19% as the point of insertion of the G/C into the A/Ts moved from next to **P** to the fourth site (*n* = 3) from the **P**. When the G/C was inserted at the fifth site from the donor or beyond, the yield dropped to <5% within the accuracy of the experiments. Zeidan et al. attributed these findings to formation of a polaron with the hole delocalized over the first three or four A/T sites after the donor. Earlier calculations by Conwell et al. had predicted the existence of a hole polaron delocalized over ~four A/T sites for an all A/T sequence. However, the situation of the Zeidan et al. experiments differs in there being a G present and a negative potential for the initial As on the chain. We have calculated the hole wave functions for the sequences specified by Zeidan et al. for different values of the potential difference *V*₀ between the donor and the first A, allowing the potential to decrease as 1/*r* as the distance from the hole donor increases, and taking into account the important effect of water in forming a polaron. We find there is a competition for the hole between the Coulomb well and the G, which, relative to the As, represents a potential well of ~0.4 eV. When G dominates and there are As beyond G in the sequence, we find, in agreement with Zeidan et al., that the wave function includes a polaron over the first three or four sites. However, the polaron has the sequence AGA, G being at its peak. We consider the significance of the finding of Zeidan et al. that a radical pair is not formed, within the 5% accuracy of their measurements, for G five sites or more from the donor.

Introduction

In some of the earliest experimental studies of transport on the base stack of B-DNA in solution, Giese et al. injected a hole onto a G (paired with a cytosine, C) heading a series of A/Ts.¹ The holes were found to move along the As, their number decreasing rapidly as they traversed the first three As (by a factor ~8 at each A). The survivors, however, were found to go through many more As with little further decrease.^{2,3} Giese's explanation of these results was that the holes tunnel through the first three As, because the energy of G is ~0.4 eV less than that of A, and are then thermally excited onto the bridge of As. On the bridge, Giese proposed, the hole wave function is localized on an A, and the holes progress by hopping between As.

Giese's picture was first seriously questioned by Bixon and Jortner, who found that with this picture it was not possible to explain both the steep decrease in the number of holes as they traverse the initial three As and the very slow decrease as they traverse further As.⁴ Similar decreases of hole concentration in traversing a few As, followed by a slow decrease in going through further As, were found in many later experiments where the initial injecting G (or G/C) was replaced by a suitable hole-donor molecule; this replacement allows a hole to be photoinduced on the first A, leaving behind a negative charge on the

hole-donor. Many people have suggested that the negative charge can result in trapping of the hole on the As close to the donor.⁵

The question of whether the hole is localized on a single base or delocalized over a number of bases has been much discussed. In some of the earliest discussions of the behavior of an excess electron or a hole on a DNA chain, it was assumed that it became a polaron by inducing nonuniform spacing of the bases on which it resided,⁶ as is the case for conducting polymers. When the effect on the excess electron or the hole was further considered, it was realized that the polarization of its surroundings, notably water, made a much larger contribution to the binding energy of the polaron than possible changes in base spacing. Calculations of Basko and Conwell,⁷ and later Conwell and Bloch,⁸ found that, for a sequence of all As (without any negative charge due to the hole donor), |*ψψ**| of the hole polaron is spread over ~four sites. It is implicit in those calculations that the hole wave function would spread over the entire chain, but the electrostatic interaction with the water dipoles limits its spread to a few sites.^{7,9}

There are various kinds of experimental evidence that the wave functions for holes in DNA are delocalized,¹⁰ including experiments of Schuster's^{6,11} and Barton's^{12,13} groups. Some of these references offer evidence that the delocalized region, a polaron, is ~four sites in length in an all-A sequence. Nevertheless, Voityuk, using CASSCF and CAS-PT2, purports to show

that the hole wave function is localized on a single site.¹⁴ On the other hand, QM/MM calculations based on the model of Basko and Conwell found the wave function to be delocalized over a number of sites.¹⁵ In any case, as noted above, calculations using the polaron theory described have accounted for many properties found for holes in DNA. Thus, this polaron theory has served as a coarse-grained model for DNA. We show below that it can account for recent results obtained by Zeidan et al.

Some Recent Experiments. In recent studies of hole transport, Zeidan et al. used as a hole donor a perylenediimide chromophore, P, incorporated, at the head of an A/T series, into a DNA hairpin in aqueous buffer solution.¹⁷ They also incorporated, in the series of A/T pairs, a G/C pair with the G inserted in the line of As, n sites from the P, with $n = 1, 2, 3, 4, 5$, and added a terminal G at site 7. On laser excitation of P in these samples, they found photoinduced electron transfer to P with a quantum yield near unity. To study the motion of the resulting hole on the chain, they used a series of femtosecond pulses, separated in time by picoseconds or tenths of a picosecond, to obtain time-resolved transient absorption spectra.¹⁶

It was expected that, after creation by the laser pulse, those holes that escaped being trapped in the Coulomb well of the negatively charged donor would proceed from the first A after the donor to the proximal G, the energy of the G being ~ 0.4 eV less than that of A. As the G is moved from being next to the donor to three sites away from it, the percentage of holes being trapped there decreases only from 100% to 19%. In Giese's experiments, for three As following the hole donor (G in that case), the percentage of holes that make it through three As to the detector Gs is only 3%.¹ This emphasizes the claim of Zeidan et al. that the transport mode is not tunneling in their case.

As the holes make their way by diffusion and drift from the first A to the proximal G, their distribution over the chain would be determined initially by the part of the oligomer they have already experienced. Once some of them arrive at the G, which is an event well marked in the transient absorption data of Zeidan et al., if one takes into account that they are moving slowly, probably due to fluctuations, and that some are returning to recombine, it is expected that the holes are spread over the chain between the first A and G. For Zeidan et al.'s sample 3G, where the sequence is PAAG, according to their Figure 2 that time is ~ 1.6 ps. From this point in time until the absorption decays, ~ 170 ps, the distribution over the chain should be essentially that of the stationary wave function for a hole on the oligomer.

For the sequence AAAAG ($n = 5$) and larger n , Zeidan et al. found that fewer than 5% of the injected holes arrived at the G, 5% being the limit of accuracy of their experiments.¹⁶ They suggested the following interpretation for their data. For short A tracts, as in 2G–4G, hole injection into the A tract leads to a single delocalized polaron (A_n)⁺. The fact that the holes do not reach the G in AAAAG is taken by them to mean that the limit of delocalization of the (A_n)⁺ polaron is four As. They noted that this is the extent of delocalization of the all-A polaron found by Conwell and collaborators in ref 8 and therefore constitutes evidence for the theory in ref 7 and 8.

Calculations. In what follows we will extend the theory for the polaron to the case where introduction of the hole results in a negative potential on the donor and the As following the donor. We modeled the DNA as two straight chains, for the two sets of bases, placed inside a cylindrical cavity with the diameter of the double helix. The chains were taken to be at distances $\pm R_h$

from the axis of the cylinder, R_h taken as 0.3 nm to approximate B-DNA. It was shown in ref 17 that neglecting the helical structure of the bases in our calculations does not lead to significant error. Water and positive ions (Na^+) were outside the cavity but none inside due to the hydrophobicity of the bases. The hole is assumed to be delocalized over the bases.

The calculations were done using the Hamiltonian described earlier,¹⁷ a generalization of our earlier calculations⁷ to the case of two chains of bases

$$H(\psi_{nj}, \psi_{nj}^*) = H_0(\psi_{nj}, \psi_{nj}^*) + \frac{1}{2} \sum_{n,n'} \sum_{j,j'} g_{n-n'}^{jj'} |\psi_{nj}|^2 |\psi_{n'j'}|^2 \quad (1)$$

where

$$H_0(\psi_{nj}, \psi_{nj}^*) = - \sum_{nj} t_{n,j;n+1,j} \Psi_{nj} \Psi_{n+1,j}^* + \sum_{nj} \Delta_{nj} \Psi_{nj} \Psi_{nj}^* - t_{\perp} \sum_n \Psi_{nj} \Psi_{nj'}^* + \text{c.c.} \quad (2)$$

Here ψ_{nj} is the amplitude of the wave function at the n th site (base) on the j th chain. The summations over n, n' are to be taken over all the sites on a chain, and those over $j, j' = 1, 2$ cover the two chains of the duplex. The first term in H_0 is the usual tight-binding term, with $-t_{n,j;n+1,j}$ the transfer integral. The second term in H_0 allows for different energy of the hole on different bases, with Δ_{nj} the hole energy on the n th base of the j th chain relative to that of the HOMO of adenine, which we have chosen to be our zero of energy. The last term allows interchain transfer, with the quantity $-t_{\perp}$ representing the interchain coupling. c.c. refers to the complex conjugates of the terms in $t_{n,j;n+1,j}$ and t_{\perp} . Finally, the last term on the right of eq 1 represents the effect on the hole energy of the polarization charge it induces in the water.

The values of the coefficients $g_{n-n'}^{jj'}$ determining the interaction with water were determined in ref 17 by solving Laplace's equation subject to the appropriate boundary conditions. These values are plotted vs $n - n'$ in Figure 2 of ref 17. For the energies of the bases we used the values measured for the isolated bases in solution, refs 18 and 19. Relative to the value for adenine, these are thymine 0.7 eV, guanine -0.4 eV, and cytosine 0.5 eV. For the transfer integral $t_{n,j;n+1,j}$, we used the calculated values of Voityuk et al.²⁰ For AA neighbors they, and also Senthilkumar et al.,²¹ obtained a value ~ 0.03 eV for the transfer integral. In a more recent calculation Grozema et al., incorporating the effect of thermal fluctuations, obtained the value of the AA transfer integral as 0.046 eV.⁵ We used both of these values in our calculations and found very little difference in the final results. As discussed earlier, the polaron properties are relatively insensitive to the value of the transfer integral.⁷ The transverse transfer integral t_{\perp} was taken from Dauxois et al.²²

To take into account the negative charge on the hole donor, we took the potential energy at the first base in the sequence of As to be $-V_0$, a parameter in the calculations. As noted earlier, the large injection into the first three As seen by Zeidan et al. indicates a Coulomb barrier in their samples much smaller than assumed in ref 5. The hole donor used by Zeidan et al., perylenediimide, is a large molecule, replacing a base pair in their DNA hairpins, and undoubtedly causing large strain in the B-DNA structure. It is surely not describable as a point

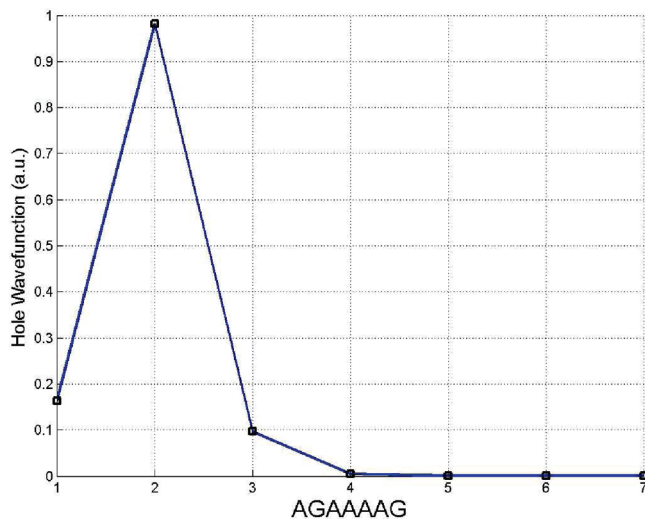


Figure 1. Calculated wave function of polaron for the sequence indicated on one chain of a duplex DNA for $V_0 = -0.3$ eV. The calculated energy was -1.258 eV.

charge $-e$, e being the charge on the electron, at a distance a , the interbase spacing, from the first A. For calculation purposes we assumed that the value of its potential at the first A could be represented as due to a point charge e' such that $[(e')^2/\epsilon a] = V_0$, ϵ being the dielectric constant. The magnitude of the potential on the bases due to the donor ion then decreases with distance as $1/na$.

The polaron wave functions and energies are determined by diagonalizing the matrix obtained from the Hamiltonian 1 and 2 with the additional term $-V_0/n$. Calculation is simplified by taking the term $(1/2)\sum_n \sum_{ij} g_{n-n'}^{ij} |\psi_{n'}|^2$ as part of the diagonal elements of the matrix. In setting up the trial wave functions the hole was always inserted at the first A. We carried out the calculations for the DNA sequences used by Zeidan et al. in ref 16. Some results are shown in the figures below.

Results and Discussion

The wave function for the sequence AGAAAAG, labeled 2G,¹⁶ is shown in Figure 1 for $V_0 = 0.3$ eV. It peaks at the G at site 2. Calculations for V_0 taken as 0.2 or 0.4 eV yielded essentially the same wave functions, differing by the former being slightly smaller at the first A, the latter slightly larger at the first A. The energies were -1.310 eV for 0.4 eV, -1.258 eV for 0.3 eV. In Figures 2 and 3 are the wave functions for the sequences AAGAAAG and AAAGAAG, 3G and 4G, respectively, in the notation of ref 16, for $V_0 = 0.3$ eV. The energies are -1.205 and -1.192 eV, respectively. As noted above, Zeidan et al. suggest that injection of holes into hairpins 2G–4G leads to a single delocalized radical cation $(A_n)^+$, which they suggest is the polaron. The calculated wave functions for 2G–4G, however, as seen in Figures 1–3, show instead a polaron AGA centered on G in each of these cases. The wave function of this polaron is quite similar to that found earlier for a G surrounded on both sides by a series of As.⁸

Concerning hairpin 5G, the fact that the yield of P^-G^+ pairs is less than 5% led Zeidan et al. to conclude that the delocalization length of the polaron, taken by them to be $(A_n)^+$, is no more than 4 As. According to our calculations, there are two possible scenarios for 5G. For a small barrier, $V_0 \leq 0.2$ eV, the wave function would be as in Figure 4 and absorption at G would be observed, presumably corresponding to a yield between 5% and 19%, the latter being the yield for 4G. If the

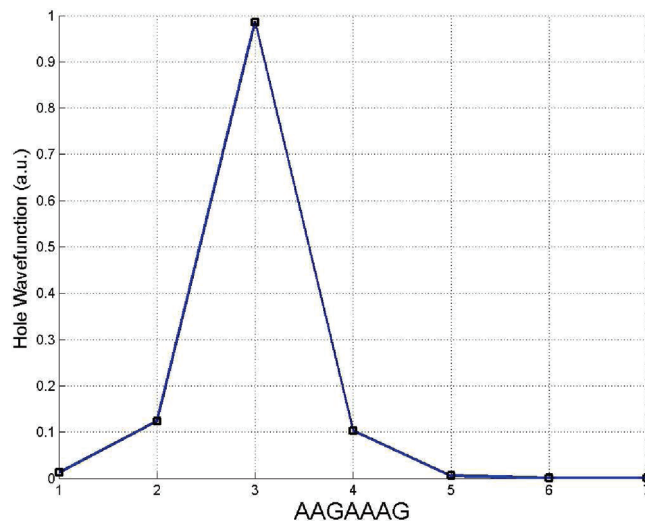


Figure 2. Calculated wave function of polaron for the sequence indicated on one chain of a duplex DNA for $V_0 = -0.3$ eV. The calculated energy was -1.205 eV.

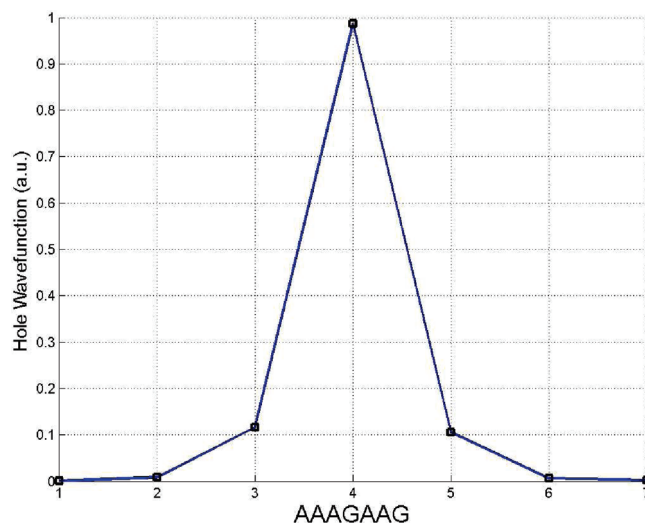


Figure 3. Calculated wave function of polaron for the sequence indicated on one chain of a duplex DNA for $V_0 = -0.3$ eV. The calculated energy was -1.192 eV.

barrier were larger, 0.3 eV in our example, according to Figure 5 the hole would be trapped in the Coulomb barrier and no absorption due to G would be observed. We believe that, although the numbers we use may not apply to the particular hairpins used, we have taken into account the relevant factors, and Figure 5 gives the correct scenario for sequences 5G and 7G. We note that this behavior is not special to the case of a sequence with four As before the G; if we raise the barrier for AAAGAAG from 0.3 to 0.375 eV the peak of the wave function shifts to the first A.

We can understand this behavior as resulting from a competition for the hole between the Coulomb well due to the donor and the well due to the guanine, which relative to an A represents a well of ~ 0.4 eV. The relative importance of the G depends, of course, on how far it is from the donor and on the size of V_0 . In the limit of small V_0 , G will dominate and the experiment can be interpreted as giving rise to a P^-G^+ pair. In the limit of large V_0 the hole will be trapped in the Coulomb barrier. Note also that, when there is a polaron formed in a sequence such as those studied here, it is always of the form AGA because the low energy of G compared to A will result

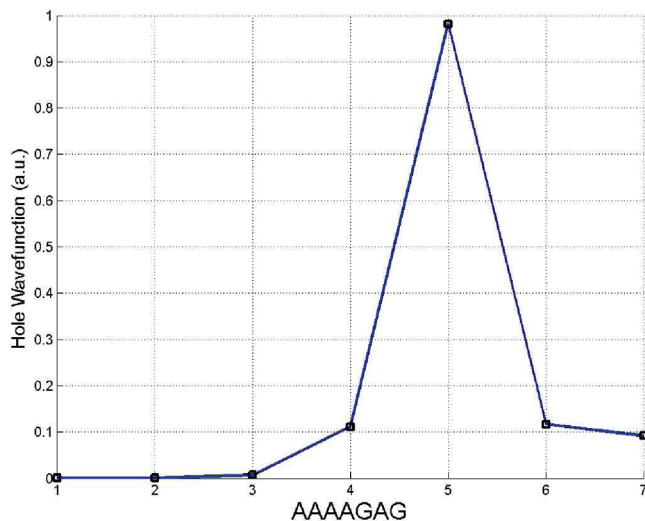


Figure 4. Calculated wave function of polaron for the sequence indicated on one chain of a duplex DNA for $V_0 = -0.2$ eV. The calculated energy was -1.145 eV.

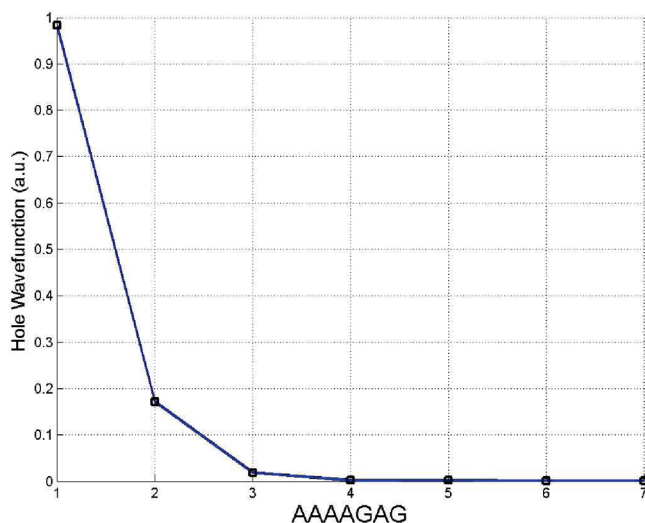


Figure 5. Calculated wave function of polaron for the sequence indicated on one chain of a duplex DNA for $V_0 = -0.3$ eV. The calculated energy was -0.9899 eV.

in the wave function being concentrated there. The formation of a three or four A polaron suggested by Zeidan et al. does not occur because of the boundary condition imposed on the first A or As by the negative charge on the donor.

Concluding Remarks. Qualitatively at least the data of Zeidan et al. for the time-averaged behavior of a hole injected into a sequence $A_nGA_{5-n}G$ are well fitted for $n = 1-3$ by a polaron model for charge transport. However, the polaron that is formed has the sequence AGA rather than consisting of As only. Their not finding formation of a radical ion pair between the hole donor and a G separated from it by four As may not be evidence for the existence of a polaron consisting of four

As as they suggest. Rather, we believe, it is due to the Coulomb well arising from the donor being too deep for the hole to get to the G. More generally, we conclude that boundary conditions affect polaron generation and may in fact prevent it. That, in turn, may affect conduction. It is possible to avoid such effects in photoinduced hole generation, for example, by using a donor that, perhaps due to additional chemical reactions, is not left with a negative charge. An example of such a donor is anthraquinone.³

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