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The Role of Hole Traps in DNA

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Two types of whole trap have been discussed for DNA. One type was introduced by Reynaud et al. (Jour. Am. Chem. Soc. 2013, 135, 3953) to account for the properties of whole conduction in an adenine-thymine (AT) DNA. In their treatment there is associated with each adenine a conducting state A_i and a trap state t_i. These states are assumed to survive unchanged as the hole moves along the chain, leaving partial hole populations on A_i and t_i . We point out that traps such as t_i cannot exist on DNA. A second type of trap, found in simulations for a hole introduced into AT DNA, is due to the polarization of the surrounding water by the hole when it is localized on an adenine, thus a kind of self-trapping. Currently the weight of experimental data strongly favors hopping as the transport mechanism, but the details of the hopping process are not entirely clear. We suggest that the self-trapping, plus some assistance by positive ions to exit the traps, can account for whole conduction [1,2].

The discovery of charge transport in DNA aroused great interest because of possible applications in molecular electronics and in biology, thus acting to spur a great deal of experimental and theoretical work [1]. The most extensive measurements of transport in DNA have been carried out by Lewis and associates at Northwestern University and elsewhere. Evolving over a number of years, a typical experimental setup of the Lewis group included at one end a hole donor, denoted Sa, followed by a chain of adenine-thymines (ATs), (alternatively guanine-cytosines (GCs)), and, at the other end, for detection, a hole acceptor denoted Sd, with energy somewhat smaller than that on Sa to ensure conduction [2]. Injection of a hole was accomplished by exciting Sa with light, giving rise to a low-energy empty level on Sa. Into this an electron from a neighboring adenine moves, creating a hole on the series of As. In the experiments the passage of the hole down the chain of As and into the detector was followed carefully by a variety of measurements, leading to the determination of the time for hole injection, the hole arrival rate, k_a, at the hole acceptor, and the charge separation quantum yield, Φ_{cs} [3].

Many people have suggested that in very short chains, up to perhaps two or three base pairs, holes propagate by super exchange or tunneling [2].Consistent with this mechanism, in very short AT chains the charge transfer has been found to decrease exponentially with the length of the short chain [4]. For longer chains it has been widely speculated that, beyond the tunneling range, propagation is by incoherent hopping, and a strong case has been made for this mechanism. In what follows we consider only fairly short chains, in the range 3 to 7 base pairs.

Recently a different transport mechanism has been proposed for relatively short chains, up to 7 ATs, described as intermediate between superexchange and hopping [5]. The new mechanism is based on a new Hamiltonian, H_s. Although H_s is also a tight-binding Hamiltonian, it has an important innovation in that each adenine is characterized as having two energy levels for holes, one being the usual conducting state, A_i on the i'th adenine, the other a localized state or trap, denoted $t_{i,}$ on the i'th adenine. The t_i energies are smaller than the A_i energies by a quantity called the localization energy, $E_{loc,}$ which is taken as a variable parameter in the simulations employing H_s. To allow for phonon scattering of the holes H_s is augmented by two terms, H_B for a bath of phonons and H_{SB} denoting the interaction between the system and the bath [5].

In no part of H_s is there a term for the interaction of the holes with water. The importance of water in determining the motion of injected holes in DNA has been particularly emphasized by Kubar and Elstner [6,7]. They cited polarization as a dominant factor affecting hole transport, one which "will be a major task for future work".

The Renaud model does not take into account the reorganization of the solvent around the DNA during the hole propagation, and the charge localization effects induced by the polar surroundings. The justification they state for this neglect is that the time required for solvent reorganization is long compared to the transit time of the hole from Sa to Sd. In fact, as will be discussed below, there is significant solvent reorganization on a femtosecond scale, whereas the transit time from Sa to Sd is nanoseconds [3].

In general, "solvent reorganization" due to the addition of a hole may involve many different components of the DNA: the water surrounding the DNA, the ions, such as Na^+, added to the water to make the whole neutral, relative motions of the bases or base pairs, etc. Perhaps the shortest time for reorganization is that involved in the response of the water to introduction of a hole. This time has been deduced by simulations using cp2k for a DNA consisting of a series of ATs in water [8,9]. It was found that immediately upon introduction of the hole its wavefunction is spread over 5 adenines, the length of the QM region in this simulation [8,9]. Within 20 fs, however, the hole is localized on a single one of these adenines [8,10]. It was shown that the contraction of the hole, that we have called self-trapping, is due to the polarization set up by the hole in the surrounding water [10,11]. That this can happen on a fs time scale can be attributed to the librational motion of the water molecules [10]. The water molecule has two librational modes, L_1 and L_2, with resonant frequencies of ~11.5 and 23 THZ [12]. The former, more abundant mode, has a period of ~88 fs, the latter ~50 fs. According to their frequencies these modes are at least partially excited at 300 K. The periods are small enough to allow some rotation of the water dipoles on a fs time scale and in this way account for a rising polarization in the 5 to 20 fs time range. Thus, in contradiction to the requirement for the validity of the Renaud et al. analysis, the time required for the solvent to reorganize is a very small fraction of the hole transit time from Sa to Sb, which, as stated above, is ~ nanoseconds.

Consider a hole injected into the first adenine, A_1, of a series of

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ATs. In the situation examined by Renaud et al. and by Lewis and collaborators, a polarization similar to that just discussed above will be set up around A_1. In the Lewis experiments this polarization must act as a trap that, in addition to the negative charge left on Sa, keeps the hole from moving. In the Renaud et al. formalism, it can be considered that this trap takes the place of t_1, but it cannot act over the entire transit time of the hole as the Renaud trap t_1 is supposed to. If the hole were to move on to A_2, the water polarization would surround A_2 and there would no longer be a trap on t_1. The hole delocalization predicted by Renaud et al. will not occur under these circumstances. Neglect of the self-trapping of the hole contributes also to the prediction with the Renaud model of a hole injection rate two orders of magnitude larger than the rate found experimentally by Lewis and coworkers [5].

The situation studied by Lewis and coworkers is considerably complicated by the negative charge left on Sa as a result of the hole introduction. However, it is possible to study hole transport in DNA without introducing this negative charge. This was done by Schuster and his group ~ 15 years ago [13]. To introduce the hole they covalently linked an anthraquinone to a 5' end of duplex DNA. Exposure to light and subsequent chemistry involving the anthraquinone results in injection into the DNA of a radical cation and regeneration of the anthraquinone [14]. Transport measurements on holes introduced by this procedure in DNAs of various sequences, usually involving guanines, led to a transit time of the hole between adjacent bases of 10^{-7} s, somewhat longer than what the Lewis group found for a series of As.

According to our earlier simulations the hole becomes self-trapped in ~ 20 fs [8]. Our simulations showing the trapped hole were carried out only to 250 fs. Mantz et al carried out simulations to 5 ps, showing that the hole remained trapped at least that long [9]. As will be indicated in the next paragraph, experiments show that the hole remains trapped for a much longer time.

To allow hopping of the hole to an adjacent A two conditions must be satisfied. First, the negative charge surrounding the hole must be broken up sufficiently to allow the hole to move to the next A. Measurements of Lewis and collaborators [15] have shown that the average time for a nearest neighbor hop in a DNA of length ~ 6 ATs is 1.2 ns; it is reasonable to expect that the trapping time is of this order of magnitude. Lewis et al. attribute this low hopping rate to adiabatic charge transfer in a highly polar solvent with reorganization energy λ ~0.83 eV. I suggest that the low hopping rate is more naturally attributed to the difficulty of breaking up the polarization-induced self-trapping. A reasonable assumption is that it is broken up by positive ions in the solution, usually Na^+, coming into the neighborhood. This is expected to be a slow process because there are not many positive ions in the solution, and their surroundings do not encourage them to move rapidly.

The second condition that must be satisfied for hole hopping is that at the time the hole is able to move the energy of the hole on the next A must be lower than (or within ~kT of) the energy of the hole on the A on which it is trapped. It is expected that this condition will be satisfied sooner or later; coupling of the charge transfer parameters to the solvent degrees of freedom results in large fluctuations of the energy of the As, up to ~ 0.4 eV [6,7,16-18]. When both of these conditions to allow hopping can be satisfied, it is expected that the hole hops down the chain by a series of self-trapping and release events. A small electric field, due to the difference in potential between Sd and Sa, ensures that the majority of hops are in the field direction.

Consider now what happens after a hole is created on a chain of ATs in the case studied by Lewis and collaborators, where the introduction of the hole leaves a negative charge on Sa. The Lewis group showed that, due to the existence of reversible hole injection, after the hole is introduced an exciplex is formed, consisting of Sa^- and A_1^+, which persists for picoseconds [19]. Breakup of the exciplex allows the hole to move to A_2. Arrival at A_2 was termed by Lewis et al. hole injection on the view that hole hopping began when the hole arrived at A_2. Blaustein et al. have calculated the kinetics of charge separation on the chain of As according to this model [15]. However, according to our simulation described earlier, the hole is self-trapped on A_2 before it can move to the next A. We suggest that from this point in time the hole follows the same routine of release and retrapping repeatedly to hop between As as was described above for the hole in an AT chain where the hole goes directly into A_1.

In summary, we are suggesting that the hopping rate for a hole traveling along a DNA of length ~ half a dozen ATs is determined by cycles of self-trapping in the surrounding water followed by release due to intervention of some positive ions in the solution. We suggest that this model applies as well to hole conduction in a series of GCs.

References

1. Genereux JC, Barton JK (2010) Mechanisms for DNA charge transport. Chem Rev 110: 1642-1662.
2. Lewis FD, Zhu H, Daublain P, Fiebig T, Raytchev M, et al. (2006) Crossover from superexchange to hopping as the mechanism for photoinduced charge transfer in DNA hairpin conjugates. J Am Chem Soc 128: 791-800.
3. Lewis FD, Zhu H, Daublain P, Cohen B, Wasielewski MR (2006) Hole mobility in DNA a tracts. Angew Chem Int Ed Engl 45: 7982-7985.
4. Berlin YA, Burin AL, Ratner MA (2001) Charge hopping in DNA. J Am Chem Soc 123: 260-268.
5. Renaud N, Berlin YA, Lewis FD, Ratner MA (2013) Between superexchange and hopping: an intermediate charge-transfer mechanism in poly(A)-poly(T) DNA hairpins. J Am Chem Soc 135: 3953-3963.
6. Kubar T, Elstner M (2008) What governs the charge transfer in DNA? The role of DNA conformation and environment. J Phys Chem B 112: 8788-8798.
7. Kubar T, Kleinekathofer U, Elstner M (2009) Solvent fluctuations drive the hole transfer in DNA: a mixed quantum-classical study. J Phys Chem B 113: 13107-13117.
8. Kinz-Thompson CD, Conwell EM (2010) Proton Transfer in Adenine−Thymine Radical Cation Embedded in B-Form DNA. J Phys Chem Lett 1: 1403-1407.
9. Mantz YA, Gervasio FL, Laino T, Parrinello M (2007) Solvent effects on charge spatial extent in DNA and implications for transfer. Phys Rev Lett 99: 058104.
10. Kravec SM, Kinz-Thompson CD, Conwell EM (2011) Localization of a hole on an adenine-thymine radical cation in B-form DNA in water. J Phys Chem B 115: 6166-6171.
11. Voityuk AA (2005) Charge transfer in DNA: hole charge is confined to a single base pair due to solvation effects. J Chem Phys 122: 204904.
12. Zelsmann HR (1995) Temperature-dependence of the optical-constants for liquid H2O and D2O in the far IR region. J Mol Struct 350: 95–114.
13. Conwell EM, Rakhmanova SV (2000) Polarons in DNA. Proc Natl Acad Sci U S A 97: 4556-4560.
14. Schuster GB (2000) Long-range charge transfer in DNA: transient structural distortions control the distance dependence. Acc Chem Res 33: 253-260.
15. Blaustein GS, Lewis FD, Burin AL (2010) Kinetics of charge separation in poly(A)-poly(T) DNA hairpins. J Phys Chem B 114: 6732-6739.
16. Voityuk AA, Siriwong K, Rosch N (2004) Environmental fluctuations facilitate electron-hole transfer from guanine to adenine in DNA pi stacks. Angew Chem Int Ed Engl 43: 624-627.

17. Steinbrecher T, Koslowski T, Case DA (2008) Direct simulation of electron transfer reactions in DNA radical cations. J Phys Chem B 112: 16935-16944.

18. Kubar T, Woiczikowski PB, Cuniberti G, Elstner M (2008) Efficient calculation of charge-transfer matrix elements for hole transfer in DNA. J Phys Chem B 112: 7937-7947.

19. Lewis F, Zhu H, Daublain P, Sigmund K, Fiebig T, et al. (2008) Getting to guanine: mechanism and dynamics of charge separation and charge recombination in DNA revisited. Photochem Photobiol Sci 7: 534-539.