

## Polaron Motion in DNA

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We have shown that, for reasonable values of the parameters, stationary polarons, i.e., radical anions or cations extended over 5–7 base pairs, depending on base sequence, can exist in DNA. Here we report the results of an investigation of the drift motion of the polarons aimed at determining whether their formation can lead to rapid motion of charges introduced on DNA stacks. Starting from the same tight-binding Hamiltonian, we have used two different techniques for giving the polarons the kinetic energy required to make them move. We have applied these to the cases of DNA duplexes made up of (i) a single base pair repeated and (ii) a random sequence of base pairs, although we avoided sequences in which two guanines are next to each other. We find that the time required to deform the stack to produce a polaron after a hole or an extra electron is inserted into a DNA stack with uniformly spaced bases is  $\sim 4$  ps. For a DNA duplex made from the repetition of a single base pair, both theoretical techniques show that the polaron can move continuously, retaining its shape. Under a small electric field,  $5 \times 10^3$  V/cm, the polaron moves slowly, covering a distance of 7 bases in  $\sim 140$  ps. For DNA made up of random bases, the center of the polaron can hop on a picosecond time scale between guanines or between a guanine and an adenine, separated by up to a few bases. The possibility that polaron motion could account for the rapid hole transit found by some researchers is discussed.

### Introduction

There has been a great deal of controversy concerning transport of an excess electron or a hole on the DNA base pair stack. In the case of holes, a number of experiments can be explained by “hopping” between guanines by means of tunneling through base pairs having ionization potentials higher than that of guanine.<sup>1–4</sup> However, there are still experiments that cannot be explained by this mechanism. The experiment of Wan et al. showed a much more rapid hole transport, 1.0–1.7 nm covered in 5 ps, than could be explained by such hopping.<sup>5</sup> Wan et al. found, however, that the number of holes engaging in this rapid transport decreased strongly with increasing distance from the source. Their explanation is that the hole range is limited by stacking disorder, which is dynamic due to molecular motion and static due to defects in the stack.

It was noted that the mobility implied by the rapid transport observed by Wan et al. is  $0.2 \text{ cm}^2/\text{Vs}$ ,<sup>6</sup> on the order of that found for polarons drifting on conjugated polymer chains.<sup>7,8</sup> Polaron hopping, which might be expected to be a much slower process than drifting, had been suggested earlier to explain the transport found on DNA stacks.<sup>9,10</sup> These findings led to a calculation of the properties of a stationary polaron on a DNA stack using a technique that had been used for polarons in conjugated polymers.<sup>6</sup> In the present paper, we extend these calculations to determine the properties of drifting polarons.

A difficult part of the calculation for polaron properties is choosing parameters for DNA, particularly the transfer integral  $t$  between a pair of adjacent bases on the stack. Ab initio calculations of the two energy levels for a pair of overlapped

guanine bases gave the level separation as 0.72 eV at a distance of 3.4 Å.<sup>11</sup> On a simple Huckel model, this corresponds to a transfer integral  $t = 0.36$  eV. Allowing for less than perfect overlap, we chose  $t = 0.3$  eV.<sup>6</sup> This value is less than the theoretical value calculated by Dee and Baur.<sup>12</sup> Another, smaller, value of  $t$  has been derived from the observation that traveling through an A/T base pair reduces the hole transfer rate by a factor 10.<sup>1,2</sup> Applying superexchange theory, Bixon et al. take the reduction factor,  $1/10$ , to equal  $(t/\lambda)^2$ , where  $\lambda$  is the low-frequency reorganization energy for hole transfer.<sup>3</sup> From this they conclude that  $t = 0.18$  eV.<sup>13</sup> For the duplex case,  $t$  would be larger.

In our earlier calculations of the stationary polaron energy, we obtained results for  $t$  values of 0.2 and 0.1 eV in addition to those for 0.3 eV.<sup>6</sup> For a DNA duplex stack consisting of C/G alternating with A/T, the lower  $t$  values led to hole polarons that were wider and closer in energy to the nearest filled level, specifically, 0.03 eV above for  $t = 0.2$  and 0.001 eV above for  $t = 0.1$  eV compared with 0.25 eV for  $t = 0.3$  eV. With these energies, the polarons for the smaller  $t$  values would not be stable at room temperature. It should be remembered, however, that these calculations took into account only the contribution to the energy arising from the displacements of the bases. They do not take into account the polarization of the surroundings of the charge. For the conjugated polymers, while calculations based on the same model give the polaron level 0.2 eV from the appropriate band edge for reasonably long chains,<sup>14,15</sup> measurements by infrared absorption give the distance of the polaron levels from the band edge as 0.5 or 0.6 eV.<sup>15</sup> Another polymer, poly(methylphenylsilane), was found, from comparison of experimental mobility data and theory, to have a polaron formation energy of 0.28 eV.<sup>16</sup> We believe that, with polarization effects included, polarons in DNA should be stable at room temperature and below even if  $t$  is 0.18 eV, provided that thermal

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motions of the DNA or the defect concentration are not so large as to greatly reduce the effective overlap.

In what follows, we will first describe the two techniques we have used to calculate the polaron properties. Solutions will be presented for the time-independent polarons that result. We will then follow the evolution of the polaron in time  $t$  starting from a uniformly spaced stack with one missing electron at  $t = 0$ . Finally, we will study the solutions of the equations of motion corresponding to moving polarons.

### Equations of Motion

Both types of calculation can be derived from the Su–Schrieffer–Heeger (SSH) Hamiltonian,<sup>17</sup> modified to allow the inclusion of an electric field. The modified form, introduced by Ono and Terai,<sup>18</sup> is

$$H = \sum_{n,s} d_n c_{n,s}^+ c_{n,s} - (t_0 - \alpha(u_{n+1} - u_n)) [e^{i\gamma A} c_{n,s}^+ c_{n+1,s} + e^{-i\gamma A} c_{n+1,s}^+ c_{n,s}] + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \dot{u}_n^2 \quad (1)$$

Here  $u_n$  is the displacement of the base pair at site  $n$ ,  $c_{n,s}^+$  is the creation (annihilation) operator for an electron with spin  $s$  at site  $n$ ,  $d_n$ 's are on-site energies and  $A$  the time-dependent vector potential. The subscript  $s$  will be dropped because none of the quantities we will be concerned with is spin dependent.  $\gamma = ea/\hbar c$ , where  $a$  is the distance between base pairs under uniform spacing,  $c$  the light velocity and  $e$  the electronic charge. The transfer integral  $t$  has been split into  $t_0$ , the value for a stack with uniform spacing, and a term representing the change in  $t$  due to a base displacement,  $\alpha$  representing  $\partial t / \partial u$ . The first line of  $H$  represents the electronic Hamiltonian  $H_{el}$ , while the second line represents the base pair motions,  $K$  being the spring constant and  $M$  the mass of a base pair. Classical treatment of the base motion should be justified by the large masses of the base pairs.

In the first technique, to be called the SS method because it is due to Su and Schrieffer,<sup>19</sup> the vector potential  $A$  is set equal to zero for all times. The electronic energies are determined by diagonalizing  $H_{el}$ , the first two terms of eq 1, for fixed values of the displacements  $u_n$ . Thus the electronic energies are the eigenvalues  $\epsilon_v$  of the matrix

$$\mathbf{H}_{n,n'} = \begin{cases} -t_0 + \alpha(u_{n+1} - u_n), & n' = n + 1 \\ -t_0 + \alpha(u_n - u_{n-1}), & n' = n - 1 \\ d_n, & n' = n \end{cases} \quad (2)$$

Then the total electronic energy

$$E = \sum_{\text{over occupied states}} \epsilon_v \quad (3)$$

is a functional of all the displacements  $u_n$ . There are  $N$  energy levels. For neutral DNA, all  $N$  states are doubly occupied.

The time evolution of the displacements is found from

$$M \ddot{u}_n = - \frac{\delta E}{\delta u_n} + K(u_{n+1} - 2u_n + u_{n-1}) \quad (4)$$

To evaluate the functional derivative analytically would require elaborate calculations. Therefore, it is evaluated numerically. Initial values are chosen for the displacements  $u_n(0)$  and the velocities  $w_n(0)$  ( $w_n = du_n/dt$ ). The total energy is then found for the set of  $u_n(0)$ . Following that, the system is integrated as follows:

$$\begin{aligned} w_n(1) &= w_n(0) + \frac{1}{M} [-E(\{u_1(0), \dots, u_n(0) + \Delta, \dots, \\ &\quad u_N(0)\})/\Delta - E(\{u_1(0), \dots, u_n(0), \dots, u_N(0)\})/\Delta] + \\ &\quad K(u_{n+1}(0) - 2u_n(0) + u_{n-1}(0))\Delta\tau \quad (5) \\ u_n(1) &= u_n(0) + w_n(1)\Delta\tau \end{aligned}$$

Here  $\Delta$  is an arbitrarily small displacement, which can be the same for all  $n$ , and  $\Delta\tau$  is a small time interval compared to  $(1/\omega_0) = (4K/M)^{-1/2}$ . When  $w_n(1)$  and  $u_n(1)$  are obtained, the procedure must be repeated for the next time step, etc.

The displacements and their first derivatives are taken to obey the periodic boundary conditions

$$\begin{aligned} u_{N+1}(t) &= u_1(t) \\ w_{N+1}(t) &= w_1(t) \end{aligned} \quad (6)$$

No additional conditions or requirements are applied.

To obtain a static solution in this method, one has to set the first derivatives  $w_n$  equal to zero after each iteration. Thus system 5 acquires one more line

$$w_n(1) = 0 \quad (7)$$

In the second technique, to be called the OT technique because it is due to Ono and Terai,<sup>18</sup> the vector potential is taken to be nonzero when an electric field is applied. If  $A = A_0 t$ , then the field is  $E = -(1/c) dA/dt = -A_0/c$ . The field is measured in units of  $E_0 = \hbar\omega_0/ea = 5.8 \times 10^5$  V/cm for the DNA parameters, where  $\omega_0 = (4K/M)^{1/2}$ . Thus,  $E/E_0 = A_0/E_0c = A_0\gamma/\omega_0$ .

We introduce the relative displacement  $y_n = u_{n+1} - u_n$ . In this method, we do not assume that electrons are in the ground states with the energies defined by the displacements but instead solve the time-dependent Schrodinger equation for  $\psi_v$ , the  $v$ th wave function, using again only the first two terms in the Hamiltonian (eq 1)

$$i\hbar \frac{\partial \psi_v(n,t)}{\partial t} = d_n \psi_v(n,t) - (t_0 - \alpha y_n) e^{-i\gamma A} \psi_v(n+1,t) - (t_0 - \alpha y_{n-1}) e^{i\gamma A} \psi_v(n-1,t) \quad (8)$$

The corresponding classical equation of motion for the relative displacements is

$$\begin{aligned} M \ddot{y}_n(t) &= -K(2y_n - y_{n+1} - y_{n-1}) + \\ &\alpha \sum_{\text{over occupied states}} \{e^{i\gamma A} [\psi_v^*(n+1) \psi_v(n+2) - 2\psi_v^*(n) \psi_v(n+1) + \psi_v^*(n-1) \psi_v(n)] + c.c.\} \quad (9) \end{aligned}$$

For a stationary solution, eq 8 reduces to the usual eigenvalue problem

$$\epsilon_v \psi_v(n) = d_n \psi_v(n) - (t_0 - \alpha y_n) e^{-i\gamma A} \psi_v(n+1) - (t_0 - \alpha y_{n-1}) e^{i\gamma A} \psi_v(n-1) \quad (10)$$

where we must set  $A = 0$ . We also require that the energy be minimized with respect to  $y_n$ . With the energy obtained from eq 8 the latter condition leads to

$$y_n = - \frac{2\alpha}{K} \sum_{\text{over occupied states}} \psi_v(n+1) \psi_v(n) \quad (11)$$

because  $\psi_n$  may be taken real for  $A = 0$ .

Equations 10 and 11 are solved numerically by iteration. Periodic boundary conditions are applied to both  $y_n$  and the wave functions. After guessing a set of relative displacements, we solved eq 10 for these displacements. Corrected displacements are then found by substituting the wave functions found in this way into eq 11, etc. The iterations are found to converge rapidly.

To find a solution of eqs 8 and 9 which depends on time, we have the following numerical scheme. Let us denote the first derivatives of  $y_n$  by  $g_n$ . Suppose that we know the wave functions, the displacements, and their first derivatives at a time  $t_j$ , these values being  $\psi_v(n, t_j)$ ,  $y_n(t_j)$ , and  $g_n(t_j)$ , respectively. Then their values at a time  $t_{j+1}$ , later by  $\Delta t$ , are found as follows:

$$\psi_v(t_{j+1}) = \sum_{\mu} C_{\mu,v} e^{-i\epsilon_{\mu}\Delta t/\hbar} \varphi_{\mu} \quad (12)$$

$$g_n(t_{j+1}) = g_n(t_j) + F(\{y_n(t_j)\}, \{\psi_v(n, t_j)\}, A(t_j))\Delta t \quad (13)$$

$$y_n(t_{j+1}) = y_n(t_j) + g_n(t_j)\Delta t \quad (14)$$

with

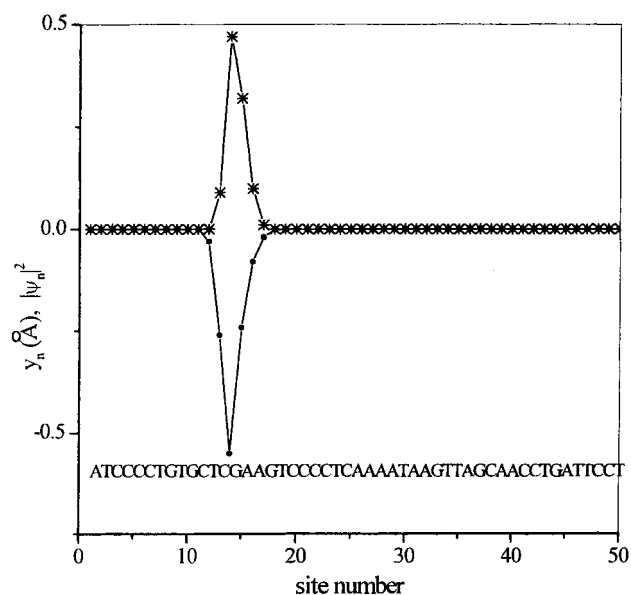
$$C_{\mu,v} = \langle \varphi_{\mu} | \psi_v(t_j) \rangle$$

Here  $\epsilon_{\mu}$  and  $\varphi_{\mu}$  are the eigenvalues and the corresponding eigenfunctions found from eq 10 for the values  $y_n(t_j)$ , and  $F(\{y_n\}, \{\psi_v(n)\}, A)$  is  $1/M$  times the right-hand side of eq 9 evaluated at  $t_j$ . Periodic boundary conditions continue to be enforced for  $y_n$ ,  $g_n$ , and  $\psi_v(n)$ . Usually, this scheme starts with a static solution as an initial condition. That is,  $\psi_v(n, 0)$  and  $y_n(0)$  are taken to be a solution of eqs 10 and 11, and  $g_n(0) = 0$ .

### Static Solutions

For the calculations that follow, we use  $t_0 = 0.3$  eV and  $\alpha = 0.6$  eV/Å, both obtained from the ab initio calculations of ref 11 as discussed above. The elastic constant  $K$ , derived from the measured sound velocity along the stacks, was taken as  $0.85$  eV/Å<sup>2</sup>. The mass  $M$  was chosen as the mass of a duplex pair because the pairs are joined by hydrogen bonds. Calculations were carried out for the case of duplex DNA with the same base pair occupying all sites and for DNA with a random arrangement of the base pairs. As shown earlier, results are not very different if we assume that there is a single base rather than a base pair on each site.<sup>6</sup> Ab initio calculations for the ionization potential of a 5'-G/C-3' pair and of a 5'-A/T-3' pair carried out by Sugiyama and Saito<sup>11</sup> give the former lower by 0.65 eV. Thus, if we take the energy level of the latter pair as the zero of our energy scale, the site energy  $d_n$  of the former would be 0.65 eV. The energies of 5'-C/G-3' and 5'-T/A-3' base pairs are not supplied, but guided by other calculations in ref 11, we chose  $d_n$  for the former to be 0.35 eV and  $d_n$  for the latter to be 0.15 eV. All of the  $d_n$  values are rather arbitrary, but it is easily verified that within wide limits these values are not critical to our conclusions.

The results for a random arrangement of base pairs calculated from eqs 10 and 11 are shown in Figure 1 along with the base arrangement for one of the strands of the duplex. The results obtained from the other technique, eqs 5 and 7, are quite similar. Comparison of these results with those for a different random arrangement of the bases, Figure 4 of ref 6, shows that, as expected, the shape of the polaron and the polaron wave function are somewhat dependent on the detailed arrangement of the bases. Nevertheless, a polaron solution was found regardless of the arrangement of the bases, including an arrangement with a G/C at the center surrounded on each side by a series of four



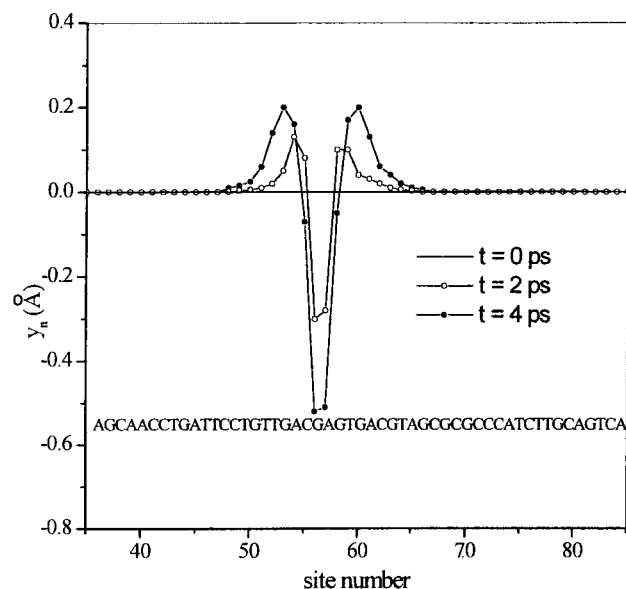
**Figure 1.** (•) Change in the interbase distance ( $y_n$ ) with site number for a polaron with the bases on one side of the duplex arranged as shown. (\*)  $|\psi|^2$  for the hole on the polaron.

A/Ts. In all these cases, the largest relative displacement  $y_n$  is at or next to a guanine site, but it decreases less rapidly with distance from this guanine site in the stationary polaron shown in ref 6 because there is another guanine closer than in the present case. The close proximity of another guanine also explains the fact that the extent of the polaron distortion and of the associated hole wave function is somewhat smaller,  $\sim 5$  sites for the case of ref 6 rather than the  $\sim 6$  sites in the case of Figure 1. For the DNA made up of a single base pair, the polaron width is a little larger still,  $\sim 7$  sites, and the maximum magnitude of  $y_n$  is  $\sim 15\%$  smaller. Correspondingly, the hole polaron energy level is higher for the random base pair case, 0.36 eV above the highest filled level compared with 0.30 eV above for the single base pair case. In summary, for  $t = 0.3$  eV for the many sequences we calculated, the width of the polaron was between 5 and 7 sites, although the shape of the polaron and the wave function varied considerably with sequence. For  $t = 0.2$  eV, where the polaron was generally wider, we did find a considerable narrowing of the polaron for a sequence that included 5 G/Cs, as discussed in ref 6.

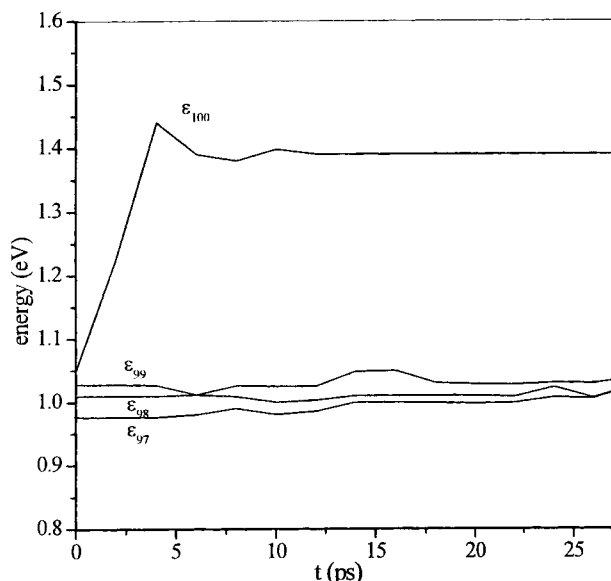
### Polaron Formation

To study the formation of a polaron, one needs first to obtain a static undistorted solution. For the SS technique, the static solution is obtained by solving eqs 2 and 3 for a stack of  $N$  base pairs fully occupied by  $2N$   $\pi$  electrons. At  $t = 0$ ,  $y_n = 0$  and  $w_n = 0$ . For the OT technique, the static solution is obtained by solving eqs 10 and 11 with  $A = 0$ , also for a stack of  $N$  base pairs with  $2N$   $\pi$  electrons. Here, too,  $y_n = 0$  at  $t = 0$ . To observe the formation of a polaron, we take the static undistorted solutions as initial conditions for dynamic eqs 5 and 7 in the SS technique and for eqs 12–14 in the OT technique. For the hole polaron, these dynamic equations are then solved for  $N$  base pairs occupied by  $2N - 1$   $\pi$  electrons.

The resulting polaron formation calculated by the OT technique for the case of random base pairs in zero electric field is shown in Figure 2. The displacements of the 100 pair stack are shown at  $t = 0, 2$ , and 4 ps. It is seen that, starting from the undistorted chain at  $t = 0$ , the polaron is partially formed at 2 ps and fully formed at 4 ps. Note that the polaron differs a little

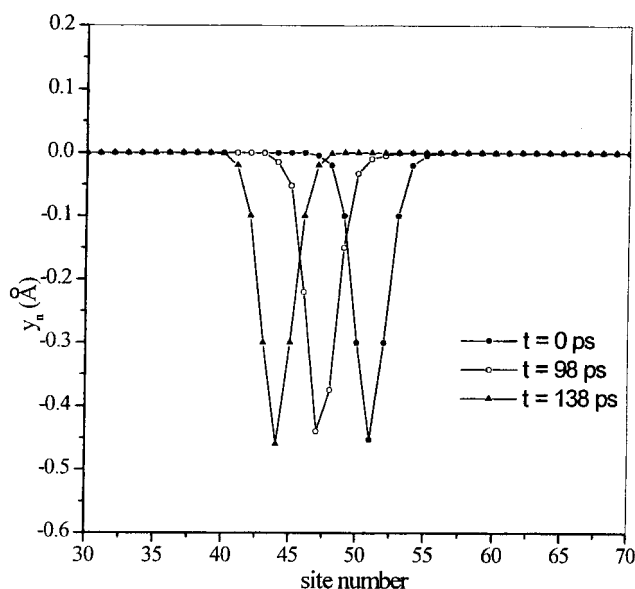


**Figure 2.** Polaron configuration vs time, i.e., polaron formation, calculated by the OT method for zero field.



**Figure 3.** Energy of the four top levels in the valence band vs time elapsed after hole insertion for the case of Figure 2.

from that shown in Figure 1 because the base sequence is not the same in the two cases. The formation of the polaron can also be seen from the behavior of the energy levels. In Figure 3, we show the evolution with time of the top four energy levels. While levels 97 to 99 change little with time, the level occupied by the hole, number 100, is seen to rise strongly, reaching a peak at 5 ps. The peak represents an overshoot; over time, the energy level settles at a value of 0.35–0.36 eV above that of level 99, in good agreement with the value found earlier in the stationary polaron calculations. Formation of the polaron was also studied by the SS technique, giving results almost identical to those of Figures 2 and 3. The time of formation is much longer than was found for polarons in polyacetylene. In their studies of polaron formation in polyacetylene by the first technique, Su and Schrieffer<sup>19</sup> found that the time for polaron formation was only tenths of a picosecond, in agreement with later experiments. The longer formation time is the result of the sites being much more massive and the coupling to acoustic modes smaller.



**Figure 4.** Motion of a polaron in a single base pair case for a field of  $5.8 \times 10^3$  V/cm.

Polaron formation was also investigated for DNA made up of a single base pair repeated. Surprisingly, the formation time was found to be much longer than that for the case of the randomly arranged base pairs. Calculations of  $y_n$  versus  $n$  for different times by the SS technique gave the result that it took close to 58 ps to obtain a fully formed polaron. To understand its evolution in time, it is useful to study the behavior of the energy levels as a function of time. It is seen that the top level only starts to split off from the ones below at  $\sim 45$  ps. Calculations by the OT technique gave an even longer time,  $\sim 90$  ps, before the top level starts to split off. With the SS technique, the hole level reached its peak at  $\sim 52$  ps and then, having overshoot, as seen earlier in the case of Figure 3, decreased somewhat and tended to reach a steady value. Thus, the actual formation time, according to the second technique, was not much different from that found earlier for the random base case. We speculate that the earlier initiation of the actual deformation process in the random base case is the result of the symmetry already being broken so that there is one most favorable site for the hole.

### Dynamics

For polaron motion to occur, there must be kinetic energy in the system. The SS technique achieves this by assigning a velocity to each site as an initial condition. In the OT technique, the energy is supplied by the electric field. In both cases, this kinetic energy is shared with the other bases on the stack, although scattering as such is not included in our calculations.

Figure 4 shows propagation of the polaron in an electric field on a stack made up of a single base pair. To the accuracy of the Hamiltonian (eq 1), where we have assumed the same value of  $t$  for every pair of bases, it does not matter whether the single base pair is G/C or A/T. The polaron starts at  $t = 0$  as a stationary polaron given by eqs 10 and 11 and propagates smoothly, essentially unchanged in shape. For a field of  $5.8 \times 10^3$  V/cm, the polaron moved 7 bases, or 24 Å, in 138 ps. The SS technique with initial velocities assigned according to  $du_n/dt = 0.01(u_{n+1} - u_n)$  also yielded smooth motion of the polaron with its shape essentially unchanged. It must be noted, however, that this distribution of initial velocities was chosen for its simplicity and only causes little change in the shape of the



polaron because the velocities assigned to the bases are quite small, essentially 0.01 times thermal velocity. Ideally, initial velocities should be chosen such that they result in the polaron maintaining its shape and the chain as a whole not moving, but satisfying these conditions presents a difficult mathematical problem.

In the experiments of Porath et al., the transport of charge injected into a single-base-pair duplex DNA molecule was observed.<sup>20</sup> Provided that the thermal motion of the bases is not so vigorous as to effectively cut off the overlap of adjacent bases (which should be the case at low temperatures at least), polaron motion like that shown in Figure 4 could be what is observed in these experiments. Although bands of considerable width may exist (even with  $t_0 = 0.18$  eV, the bandwidth is  $\sim 3/4$  eV), charges injected into a polymer at a contact are expected to go into polaron states because these states have lower energy; this was shown above and in ref 6 for DNA. It is expected that, as in other polymers, the polaron states are prepared by thermal motions of the stack.<sup>21,22</sup> At some of the highest fields used in the experiments of Porath et al., it is possible that the polarons are dissociated and transport is by free holes or electrons.<sup>23</sup>

To obtain polaron motion for the case of random base pairs, it is necessary to give the polarons greater velocity to overcome the energy differences between base pairs. This results in more energy being transferred into random motions of the base pairs, obscuring what is happening to the polaron. We were not able to follow the motion of the polaron with the OT technique but could carry out some simulations yielding results of interest by the SS technique. The initial velocity assigned to the sites was given by  $du_n/dt = 0.06(u_{n+1} - u_n)$ , still small enough that the shape of the polaron did not change much in the time it was observed. For a case with alternating bases CGCGCG... on one stack and the complementary bases on the other stack, the polaron was found to hop rapidly between like pairs, thus skipping every other pair. The center of the polaron moved  $\sim 5$  bases in 10 ps. Another interesting case involved a random arrangement of bases in which one stack contained the sequence CTCGAAGTCCCCTCAAATA in the direction of motion. The polaron, initially centered on the first G/C, moved 2 bases to the right, so that it was centered on an A/T, within 4 ps and then moved no further. These results suggest that the polaron center can hop from one G/C to another G/C or to an A/T within the region over which the polaron wave function extends, i.e., within two or three sites, and continue hopping as the polaron center moves provided a G or an A is available within two or three sites. This hopping process is much more rapid than polaron drift in the single base stack. Although the process is in some respects similar to the "hopping" process that involves superexchange tunneling between guanines,<sup>1-4</sup> it appears to be more rapid. The time scale for that process has been estimated to be nanoseconds.<sup>3</sup> There remains the possibility of polaron hopping over larger distances, involving phonon assistance to match energies at the initial and final sites, as suggested in refs 9 and 10. This is expected to be a much slower process than the others discussed here.

The question remains whether the considerations of this paper can account for the observation in ref 5 of a 5 ps transit time for an injected hole over a distance of 17 Å. If the hole were immediately injected into a polaron level, it might, according to our calculations, cover such a distance in more or less the observed time for an appropriate base sequence. However, in our simulations, the motion was essentially field-driven even in the SS case, whereas in the experiments, the motion was diffusive. Diffusion means that the carrier is as likely to move

backward as forward in the absence of a concentration gradient and that transit times are in general longer. Of course, there is a spread of diffusion times, and over a short distance, it is conceivable that the fastest carriers would consistently have moved forward. Also, it is not clear whether the sequence used in the experiments of ref 5 would support such rapid motion over the required distance. To have a G or an A available every 2 or 3 sites would require taking the view that each site consists of a single base, with frequent hops taking place from one strand of the duplex to the other.

The situation is different if a hole created on a stack by photoinduced charge transfer from an acceptor is not directly injected into a polaron level. In that case, the energy of the system could be lowered if on injection the stack begins to deform to create the polaron. Creation of the polaron takes 4 ps, according to the simulation above. Although we simplified the simulation by assuming the polaron remains stationary during formation, the hole would actually be moving during the formation process. It appears that it would move faster before the polaron is fully formed than after, in effect having a smaller inertia beforehand. It is perhaps conceivable then that even in this case the hole might cover 17 Å in 5 ps, although there is still the fact that the motion in the experiments is diffusive rather than field-driven.

## Summary

With the parameters we have used, the stationary polaron width in the single base case is  $\sim 7$  sites, while in the random base case it is 5 or 6 sites depending on the particular base sequence. As discussed in ref 6, if the transfer integral were smaller the polaron would be wider. The biggest decrease in spacing between adjacent base pairs on the stack is  $\sim 0.4$  to 0.5 Å, found at the center of the polaron. The hole energy level is 0.30 eV above the HOMO for DNA made up of a single base and 0.36 eV above the HOMO in the random base case.

For the single base case, simulations by both theoretical techniques show the polaron moving continuously, albeit slowly, maintaining its shape. In an electric field of  $5 \times 10^3$  V/cm, it moves on the average 1 base/20 ps. For the random base case, the motion is not smooth or continuous, which is not surprising because the shape of the polaron depends on the local base sequence. A new type of hopping motion was found in which the center of the polaron moved in a ps time frame from one G/C to another or to an A/T, provided the next G or A was within 2 or 3 sites. This type of motion might conceivably account for the hopping between Gs reported in refs 1 and 2.

## References and Notes

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