

Pathways of polaron and bipolaron transport in DNA double strands

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We investigate the pathways of polaron and bipolaron transports in DNA double strands with an extended Su–Schrieffer–Heeger model involving the effects of solvent polarization. We find that the long-range transport of polaron/bipolaron under high electric field at low temperature is the field-facilitated sequential tunneling through spatial-disordered potential barriers via multiple intrastrand and interstrand pathways. Although the interstrand pathways may be very active and effective in some DNA sequences, the intrastrand ones always dominate the charge transfer when the excess charge moves close to the final acceptor. © 2008 American Institute of Physics. [DOI: 10.1063/1.2902279]

I. INTRODUCTION

The observation that radical cations in DNA double strands can move on a significant length scale has attracted increasing interests, since it implies a wide application of DNA in nanoelectric devices.^{1–3} Various studies have indicated that excess charges may migrate through DNA by a series of hopping processes.^{4–8} In order to improve the performance of DNA based nanodevices, the detailed information of the pathways of charge transport is highly required. Some works suggested that the intrastrand charge transfer (CT) is the only effective pathway for the long-range transport and the interstrand one plays little role,^{9–11} but some theoretical calculations reached an opposite conclusion basing on the large interstrand couplings between purine bases.^{12–16} Some experiments seemed to support the theoretical argument, for example, Giese *et al.* found the positive charge of the first formed G⁺ can quickly transfer to the adjacent G of the complementary strand before it arrives at the final acceptor GGG;¹⁷ Cichon *et al.* also reported an effective interstrand charge transfer in PDA:DNA hybrids.¹⁸ However, whether the interstrand pathways in those experiments are as efficient as the intrastrand ones is still an open question. In this paper, we will clarify the pathways of the long-range charge transport in DNA with a model calculation in the real time domain, basing on the phonon-assisted polaronlike hopping mechanism.¹⁹

The phonon-assisted polaronlike hopping means that the radical cation can be stabilized by a distortion of DNA and its nearby environment (water molecules and/or counterions) to spread the charge over several bases.^{20–23} Polarons are trapped around base G due to its lowest ionization potential (IP), and move from one G unit (or multiple G units) to another (or other multiple units) by the thermal activation and/or electric field driven. Recently, there have been active discussions about the polaron trapping and hopping in

DNA.^{24–27} In addition to polarons, hole bipolarons have been theoretically proved to be chemical stable when a dication (or two holes) introduced into a DNA molecule, first by us²⁸ then confirmed by Apalkon *et al.*²⁹ The bipolaron can move quite a long distance through DNA from one trapping center to another. The bipolaron can be detected by photoinduced absorption combining with the photoinduced absorption-detected magnetic resonance.

The present work extended much of our previous one in Ref. 28, with two zigzagging interstrand coupling terms added in the model [cf. Eq. (2)]. The motivation of this paper is to clarify the dynamical pathways of polaron and bipolaron transport in DNA double strands, with the purpose of the interpretation of some experiments. Although the direct links to those experiments are not easily made, our calculations reveal some essential physics of the charge transport in DNA and obtained some consistent results with the experimental observations on the qualitative level.

This paper is organized as follows. In next section, we present a tight-binding model for the DNA double strands structure, then describe the methodology for the dynamical evolution. In Sec. III, we elucidate the basic principles of multipathway polaron/bipolaron transport in a simple structure; and then in Sec. IV, we apply our theory to the polaron transport in a specified DNA sequence that was used in Giese's experiments. Finally, a short summary is given in Sec. V.

II. MODEL AND METHOD

The model we adopt is the celebrated Su–Schrieffer–Heeger (SSH) model^{30,31} which has been remarkably successful to describe the electrical properties of π -conjugated systems with strong electron-phonon (e-ph) interactions. In addition to conducting polymers, the SSH model has also been extended to charge-density-wave materials,³² carbon nanotubes,³³ and DNA molecules.^{25,34} Here, we extend it to incorporate the double strand coupling considering structural details of Watson–Crick (WC) base pairs, G/C, C/G, A/T,

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and T/A. Further, the solvent polarization and electric field are concerned by two additional terms H_C and H_E whose meaning will be specified below; i.e., we write

$$H = H_S + H_C + H_E. \quad (1)$$

The first term H_S is the extended double strand SSH Hamiltonian,

$$H_S = \sum_{j,n} \left\{ \epsilon_{j,n} c_{j,n}^+ c_{j,n} - [t_0 - \alpha(u_{j,n+1} - u_{j,n})] \right. \\ \times (c_{j,n}^+ c_{j,n+1} + \text{H.c.}) + \frac{K}{2}(u_{j,n+1} - u_{j,n})^2 + \frac{M}{2} \dot{u}_{j,n}^2 \left. \right\} \\ + \sum_n [t_{\parallel} c_{I,n}^+ c_{II,n} + t_{\backslash} c_{I,n}^+ c_{II,n+1} + t_{//} c_{I,n+1}^+ c_{II,n} + \text{H.c.}], \quad (2)$$

where $j=I,II$ is the strand index. $c_{j,n}^+$ ($c_{j,n}$) denotes the creation (annihilation) operator of an electron at the n th base of strand j with the on-site energy of $\epsilon_{j,n}$, while $u_{j,n}$ stands for the intrastrand displacement of the base from its equilibrium position. The interstrand lattice distortion is neglected in the present work. The on-site energy parameters are chosen from Ref. 35: ϵ_T is taken as the zero of our energy scale, which determines $\epsilon_C=0.21$ eV; $\epsilon_A=0.9$ eV and $\epsilon_G=1.39$ eV. The other intrastrand interaction parameters are chosen following Ref. 34; i.e., the zero-displacement hopping integral $t_0=0.3$ eV, and the e-ph coupling $\alpha=0.6$ eV/Å. The spring constant $K=0.85$ eV/Å², being derived from the measured sound velocity along the stacks. Considering the effects of backbone in DNA structure, we chose the mass of single base equals to that of a base pair in Ref. 34, $M=4.35 \times 10^{-22}$ g.

In our model, three possible couplings between two strands are considered and denoted by t_{\parallel} , t_{\backslash} , and $t_{//}$, where t_{\parallel} describes the base-base coupling within WC pairs; t_{\backslash} and $t_{//}$ account for the zigzagging couplings.³⁶ According to the *ab initio* calculations,^{16,37} the base-base coupling within WC pairs is on the same order of the intrastrand one but the zigzagging coupling is smaller, so we choose $t_{\parallel}=t_0$ and $t_{\backslash}=t_{//}=0.2t_0$.

The second term in Eq. (1) describes the mean-field electron-electron (e-e) interaction, which is screened in the solvent by the polarizable and/or counterion surroundings that are crucial for the stability of DNA molecules.^{3,38,39} So we adopt the screened Coulomb potential (SCP) continuum solvent model,⁴⁰

$$H_C = \frac{1}{4\pi} \sum_{j,n} \left\{ \frac{\Delta w_{j,n}}{R_{j,n}} \left[\frac{1}{D(R_{j,n})} - 1 \right] \right. \\ \left. + \sum_{(j',m) \neq (j,n)} \frac{\Delta w_{j',m}}{r_{j,n;j',m} D(r_{j,n;j',m})} \right\} c_{j,n}^+ c_{j,n}, \quad (3)$$

where $R_{j,n}$ is the effective size of base pair n at strand j . $r_{j,n;j',m}$ is the distance between base (j,n) and (j',m) , and only interaction between the nearest-neighbor base pairs is concerned. $\Delta w_{j,n} \equiv \langle c_{j,n}^+ c_{j,n} \rangle_0 - \langle c_{j,n}^+ c_{j,n} \rangle$ gives the change of the electron mean occupation number on the specified

strand-base site upon the hole injection into the initially charge-neutral DNA molecule. $\langle c_{j,n}^+ c_{j,n} \rangle_0 = 2$ by assuming there are two active, spin-free, degenerate states involved in each (j,n) site. $D(r)$ is the screening function and related to the dielectric function $\epsilon(r)$ by

$$\epsilon(r) = D(r) \left[1 + \frac{r}{D(r)} \frac{d}{dr} D(r) \right]^{-1}. \quad (4)$$

We can recast Eq. (3) to a familiar mean-field e-e interaction form,

$$H_C = \sum_{j,n} \left(U_c \Delta w_{j,n} + \sum_{(j',m) \neq (j,n)} V_c \Delta w_{j',m} \right) c_{j,n}^+ c_{j,n}. \quad (5)$$

In the present work, we only concern the weak-screened on-site e-e interaction ($V_c=0$), in which case $\epsilon(r)=\epsilon_0$ to produce $D(r)=\epsilon_0$, and a reasonable estimation in DNA molecular gives the on-site e-e interaction $U_0 \sim t_0$. A more detailed discussion on the effect of polarizable surrounding with the SCP model can be found in Ref. 28.

The external electric field is taken into account in the Coulomb gauge by a scalar potential. The longitudinal field with its direction along the strands is the main concern of this work. The transverse field may be curial when the helix conformation of the strands becomes important.⁴¹ The longitudinal electric field contribution to the Hamiltonian is $H_E = -(p_e + p_i)E$,⁴² where $p_e = -|e| \sum_{j,n} x_{j,n} c_{j,n}^+ c_{j,n}$ is the electronic, $p_i = |e| \sum_{j,n} x_{j,n} w_{j,n,0}$ is the ionic dipole moment of the chain, $x_{j,n} = (n-1)a + u_{j,n}$ is the monomer position operator, and $a = 3.4$ Å is the distance between two adjacent base pairs. Now the electric field effects on the Hamiltonian reads,

$$H_E = |e|E \sum_{j,n} [(n-1)a + u_{j,n}] (c_{j,n}^+ c_{j,n} - w_{j,n,0}). \quad (6)$$

The field is chosen in units of $E_0 = \hbar \omega_0 / ea = 5.8 \times 10^5$ V/cm for the DNA parameters,²⁵ where $\omega_0 = (4K/M)^{1/2}$.

Let us make some comments on the longitudinal applied field. It is chosen to represent an applied field in some experimental measurement of electrical transport through DNA molecules. For example, in the experiments of Porath *et al.*² individual short double strand poly(G)-poly(C) DNA molecules were deposited between two nanoelectrodes (with a 8 nm gap) by electrostatic trapping. When the bias voltage (about several volts) is applied, a high electric field (about 10–20 E_0) across DNA molecular thus forms. More similar experimental setups are summarized in Porath's review article in Ref. 19. The approximate strength of the applied field in the present work is about 20 E_0 (1 V/nm), which is on the same order of magnitude as that in those experimental measurements. Thus, the applied field in the present work is physically relevant.

The equations of motion for the base displacements are

$$M \ddot{u}_{j,n}(t) = -K[2u_{j,n}(t) - u_{j,n+1}(t) - u_{j,n-1}(t)] \\ + 2\alpha[w_{j,n,n+1}(t) - w_{j,n,n-1}(t)] + eE(t) \\ \times [w_{j,n,n}(t) - w_{j,n,0}], \quad (7)$$

where w is the density matrix. In the mean-field approxima-

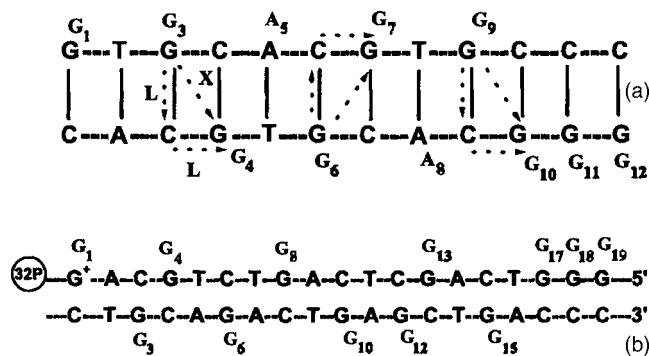


FIG. 1. The structure of DNA double strands in our calculations. (a) A simple structure; (b) the sequence used in Giese's experiment (Ref. 17).

tion, the elements of the density matrix are described by

$$w_{j,n,n'}(t) = \sum_k \Psi_{j,n,k}(t) f_k \Psi_{j,n',k}^*(t), \quad (8)$$

where f_k is the time-independent distribution function determined by initial occupation (being 0, 1, or 2). $\Psi_{j,n,k}$ are the solutions to the time-dependent Schrödinger equation:

$$i\hbar \dot{\Psi}_{j,n,k}(t) = \sum_{n'} h_{j,n,n'}(t) \Psi_{j,n',k}(t), \quad (9)$$

where $h_{j,n,n'}$ accounts for all the electric contributions in Eq. (1) for strand j .

The coupled differential equations [Eqs. (7) and (9)] are solved by a modified midpoint method.⁴³ The starting geometry is obtained by minimizing the total energy of the DNA double strands with excess charge(s) (one hole for polaron and two for bipolaron) in the absence of the electric field, i.e., we have the initial geometry of one strand with a polaron (or bipolaron) but the other charge neutral. We then solve the equations self-consistently under the fixed end boundary condition. The electric field that keeps constant after a smooth turn on is chosen as

$$E(t) = \begin{cases} E \exp[-(t - T_C)^2/T_W^2] & \text{for } t < T_C \\ E & \text{for } t \geq T_C, \end{cases} \quad (10)$$

where $T_C=500$ fs is the center and $T_W=250$ fs is the width of the Gaussian turn-on field.

In what follows, we first deal with a simple structure of the DNA double strands [Fig. 1(a)], and then concentrate on a specific sequence in Giese's experiments [Fig. 1(b)].¹⁷

III. MULTIPATHWAY TRANSPORT OF POLARON AND BIPOLARON IN A SIMPLE STRUCTURE

Two possible interstrand CT pathways are implied in our model, one is the base-to-base CT within one WC pair; and the other is the zigzagging interstrand CT from one trapping center to adjacent one belonging to the complementary strand, being shorten as "I-type" and "X-type" pathway, respectively. The former results from the strong coupling between two bases through hydrogen bonds in a duplex pair that makes a hole inserted into one base easily transfer to the other.^{44,45} Figure 1(a) is the simple structure of DNA double strands aforementioned, where the hole trapping center G

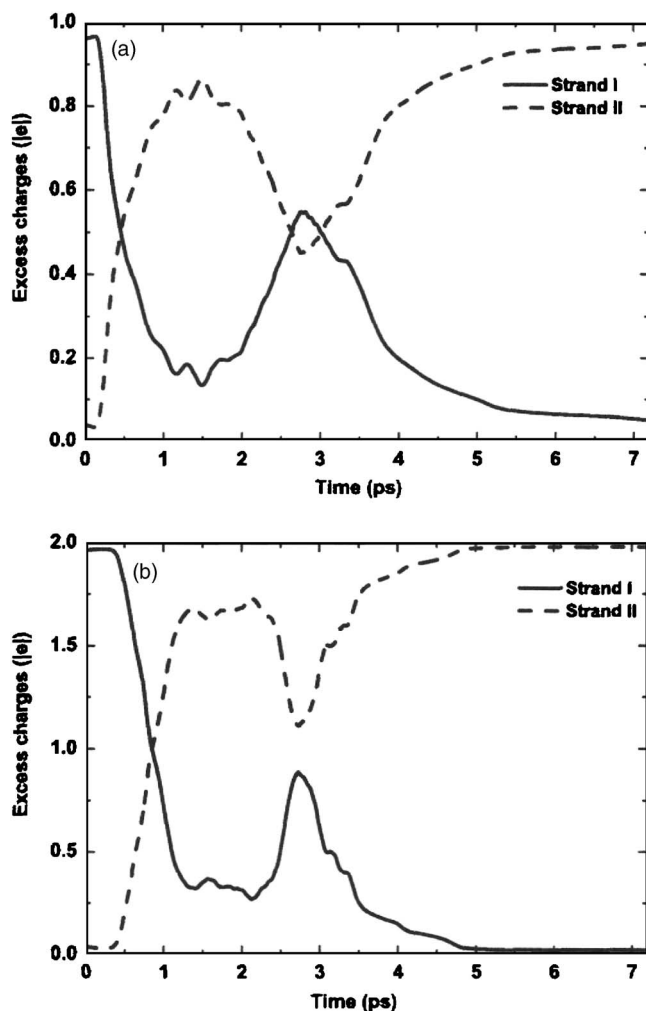


FIG. 2. The time evolution of total excess charges of each strand. (a) For polaron transport; (b) for bipolaron transport.

bases are labeled by the site indices, and interstrand CT pathways between adjacent G bases are indicated by the arrows.

For the deeply localized state of polaron/bipolaron in DNA, a sufficient high electric field is required for the electron/hole to migrate a long distance in the random base pairs sequence at low temperature.^{25,28} Thus, we apply an electric field $E=20E_0$ then follow the motion of polaron/bipolaron in the real time domain. Here, we add some comments on the linear vibronic approximation in the SSH model [cf. Eq. (2)] under such a high electric field. It has been proved to be a good approximation for conducting polymers and DNA in the limit of small-scale lattice distortions and weak high-order electron-lattice couplings.⁴⁶ When an external electric field is applied, unless the field strength is higher than that required for electrical breakdown, the field-dependent lattice distortion is still on a small scale (as in the present paper). In such a case, although the field strength may be high ($10-20E_0$), the linear vibronic SSH model is still acceptable.

Starting with a polaron/bipolaron being localized in the left end of strand I at $t=0$, the time evolutions of the total excess charge(s) for each strand are plotted in Fig. 2. Three interstrand CT (CT_{1-3}) processes take place successively

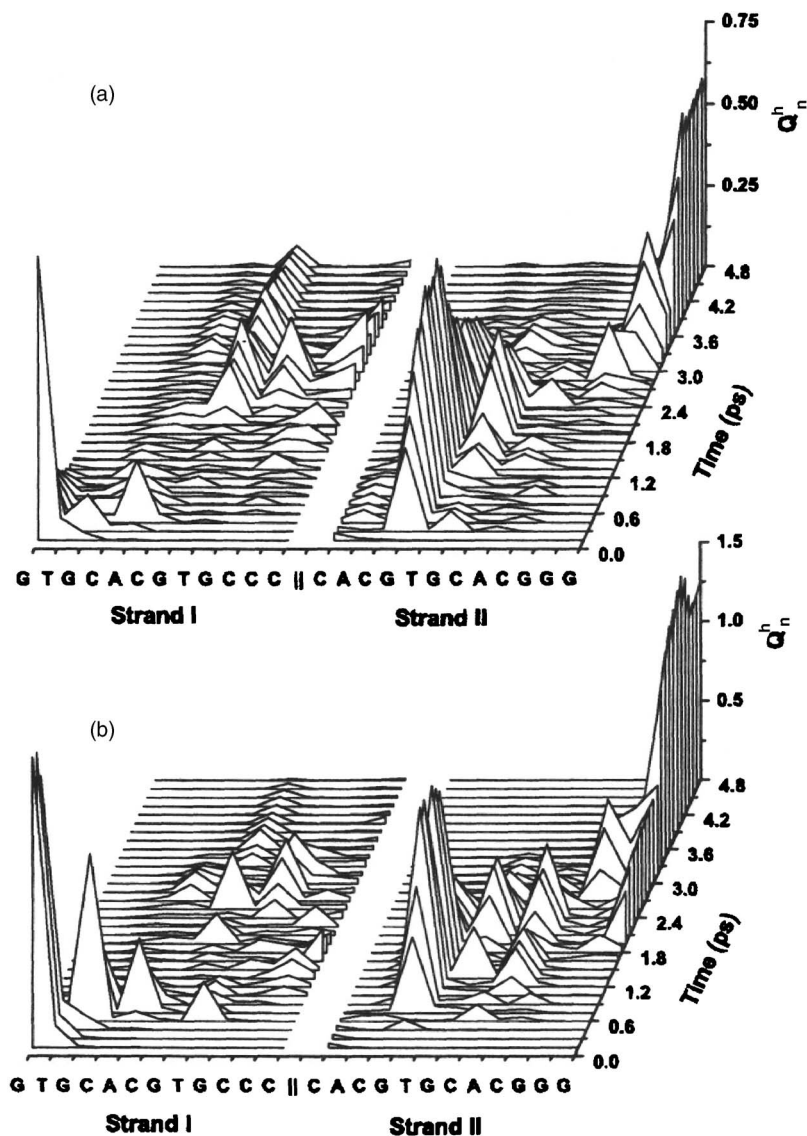


FIG. 3. The excess charge distribution as a function of time and site. (a) For polaron transport; (b) for bipolaron transport.

both for polaron and bipolaron transports [Figs. 2(a) and 2(b)]. The polaron/bipolaron transfers from strand I to II at 0.2–1.5 ps (CT₁); and then transfers back to strand I at 1.5–2.8 ps (CT₂); finally, to the trapping center GGG at 2.8–5.5 ps (CT₃).

Two characters of interstrand CT in Fig. 2 are worth to be noted. First, the transferred charge(s) is fractional and changes continuously at $0 < t < 4$ ps. Detail studies reveal that it is induced by the sequential tunneling of polaron/bipolaron through spatial-disordered potential barriers via multiple pathways (cf. Fig. 3). Second, if the excess charge(s) has transferred onto the strand with the final acceptor GGG (with the lowest oxidation potential) and their distance is no larger than $3a$, it is inclined to transport along this strand and ignoring possible interstrand pathways in the front (see Fig. 2 at $t > 3$ ps).

To elucidate the sequential tunneling of polaron/bipolaron in more details, we define the excess charge(s) distribution function as $Q_{j,n}^h(t) = w_{j,n,0} - \langle c_{j,n}^+ c_{j,n} \rangle(t)$ and present its time evolution at $0 \leq t \leq 4.8$ ps in Fig. 3(a). As shown there, after the polaron migrates from G₁ to G₃ at ~ 0.3 ps by means of the field-assisted intrastrand tunneling,

it has two possible pathways to proceed, (I) G₃→G₇ intrastrand two-step tunneling bridged by A₅; (II) G₃→G₄ interstrand tunneling via $L+X$ pathways. At $t \sim 1.5$ ps, the excess charge has transferred from strand I to strand II and reformed a well-shaped polaron at G₄. The polaron stays at G₄ for quite a long time (~ 2 ps) before it makes further intrastrand CT to G₆. The long-time trapping may result from the high potential barrier T₅ along the transport path. The polaron at G₆ also has two possible pathways to proceed, intrastrand two-step tunneling G₆→G₁₀ bridged by A₈ and interstrand tunneling G₆→G₇ via $L+X$ pathways. However, only about half of the charge transfers from strand II to strand I this time, resulting from the long-range attraction from the final acceptor G₁₀G₁₁G₁₂ on strand II. G₇ is another single trapping center as G₄, on which a small fraction of the charge rests for about 2.5 ps before the polaron migrating to the right end at $t \sim 5$ ps.

In our calculations, the polaron can travel about 37 Å in 5 ps under the electric field $E = 20E_0$. If considering the time required to form a polaron (~ 4 ps) after injecting a hole,²⁵ one can estimate that the average speed of the polaron trans-

port is $\sim 4 \text{ \AA/ps}$, being on the same scale of that in Wan's experiment, where a hole can travel 17 \AA distance in 5 ps .⁴⁷

The sequential tunneling of bipolaron through spatial-disordered potential barriers via multiple pathways is very similar to that of polaron, as shown in Figs. 2(b) and 3(b). The new character is A_8 plays a more important role for bipolaron tunneling from G_6 to G_{10} . It indicates that if the distance between nearest G bases is too long (longer than $3a$), the base A with the second lowest oxidation potential can act as a bridge to assist the long-range transport. This role of base A has been confirmed by Lewis's experimental observation that the radical cation transport through A in the sequence GAG is much faster than that through T in GTG.⁴⁸

From above calculations of polaron/bipolaron transport in a simple structure of the DNA double strands, we can arrive at two conclusions as follows, (1) the long-range transport of polaron/bipolaron under high electric field is the field-facilitated sequential tunneling through spatial-disordered potential barriers via multiple intrastrand and interstrand pathways; (2) if the charge transfer occurring far from the final acceptor GGG, the interstrand pathway is as efficient as the intrastrand one, otherwise, the intrastrand pathway with the final acceptor will dominate.

IV. MULTIPATHWAY TRANSPORT OF POLARON IN AN EXPERIMENTAL STRUCTURE

After elucidating the basic principles of multipathway polaron/bipolaron transport in a simple structure, we further investigate the polaron transport in a specified DNA sequence that was used in Giese's experiments [see Fig. 1(b)].¹⁷ Although the behavior of charge transport in those chemical radical cation doping experiments is of some differences from that in aforementioned conductance measurements (i.e., the thermal hopping versus field-driven motion), the fundamental physics should be the same. In order to reveal the essential physics, we elucidated the dynamical pathways of polaron transport driven by a high electric field at low temperatures. As will be demonstrated, our results accounts for those chemical doping experiments on the qualitative level.

The low temperature in the present work motivates the application of a high electric field. Since the thermal hopping of charges in DNA has proved to be the variable range hopping (VRH),⁴⁹ we can estimate the lowest limit of the electric field (to play the role of thermal activation) with the aid of activationless VRH theory. It means that electric field can counteract the thermal activation energy in VRH when $E \geq 2k_B T / e\gamma$, where k_B is the Boltzmann constant and γ is the localization length of the carrier wave function (about several angstroms in DNA). We found that the estimated electric field to counteract the activation energy at room temperature (as in Giese's experiments) in VRH is on the same order of magnitude as that applied in our calculations ($10\text{--}20E_0$).

We start the calculation with a static polaron being localized at site G_1 (denoted by G_{23}^+ in Giese's experiments), then trace the polaron transport in the real time domain under a high electric field ($E=20E_0$). The time evolution of the total excess charge and its distribution function $Q_{j,n}^h(t)$ are

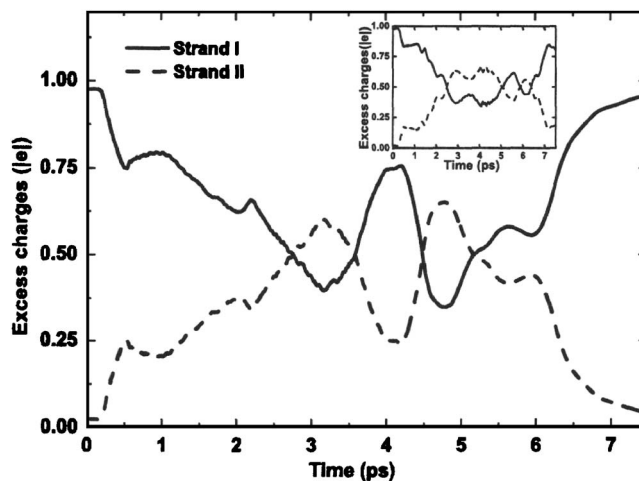


FIG. 4. The time evolution of total excess charges of each strand for polaron transport in the structure of Fig. 1(b) ($t_{\parallel}=t_{\perp}=0.2t_0$). The inset is that at $t_{\parallel}=t_{\perp}=0.25t_0$ for comparison.

plotted in Figs. 4 and 5, respectively. With reference to Fig. 4, we can see that six interstrand CT processes (CT_{1-6}) sequentially occur at $0.2 \rightarrow 0.44 \rightarrow 1.0 \rightarrow 3.2 \rightarrow 4.07 \rightarrow 4.84 \rightarrow 7.7 \text{ ps}$ for the polaron transport. The transferred charge continuously changes between 0 and 1, which is similar to that in the aforementioned simple structure. It indicates that the long-range transport of polaron here is also the field-facilitated sequential tunneling through spatial-disordered potential barriers.

As shown in Fig. 1(b), the adjacent G bases in the specified sequence belong to different strands (except the final acceptor GGG) and being separated by only one A/T base pair. According to the second conclusion of Sec. III, the interstrand CT in this case should be very active and efficient, which is confirmed by Fig. 5(a). By referring to Fig. 5(a), one can see that CT_2 ($G_3 \rightarrow G_4$) and CT_4 ($G_{12} \rightarrow G_{13}$) take $L+X$ -type pathways, while the others can only take L -type ones due to the absence of adjacent G units belonging to different strands.

Another significant character of Fig. 5(a) is base A not only can act as a bridge to assist the long-range transport but also can do as another hole trapping center. To clarify this point in more details, we defined a new parameter $Q_T^h(j,n) = \int_0^{t_T} Q_{j,n}^h(t) dt / t_T$ to give the total (excess) charge distribution probability on each site during the polaron transport process $0 \leq t \leq t_T$ ($t_T=7.7 \text{ ps}$ here). It is implied in above definition that the summation over all sites is equal to one. The calculated Q_T^h is shown in Fig. 5(b), which shows that base A between two G bases (GAG) can bridge the sequential tunneling of polaron as demonstrated before, while that next to single G (GA) can assist the polaron trapping, and the sum of Q_T^h of total GA units (excluding GAG) is as large as 0.40. This new role of base A (in unit GA) has been also observed in experiments.¹⁷

In order to verify our approximation on the strength of the zigzagging coupling in the model, we then calculate the time evolution of the total excess charge at $t_{\parallel}=t_{\perp}=0.25t_0$ and depict the result in the insert of Fig. 4. The behavior of the dynamical transport of polaron in this case is much the same

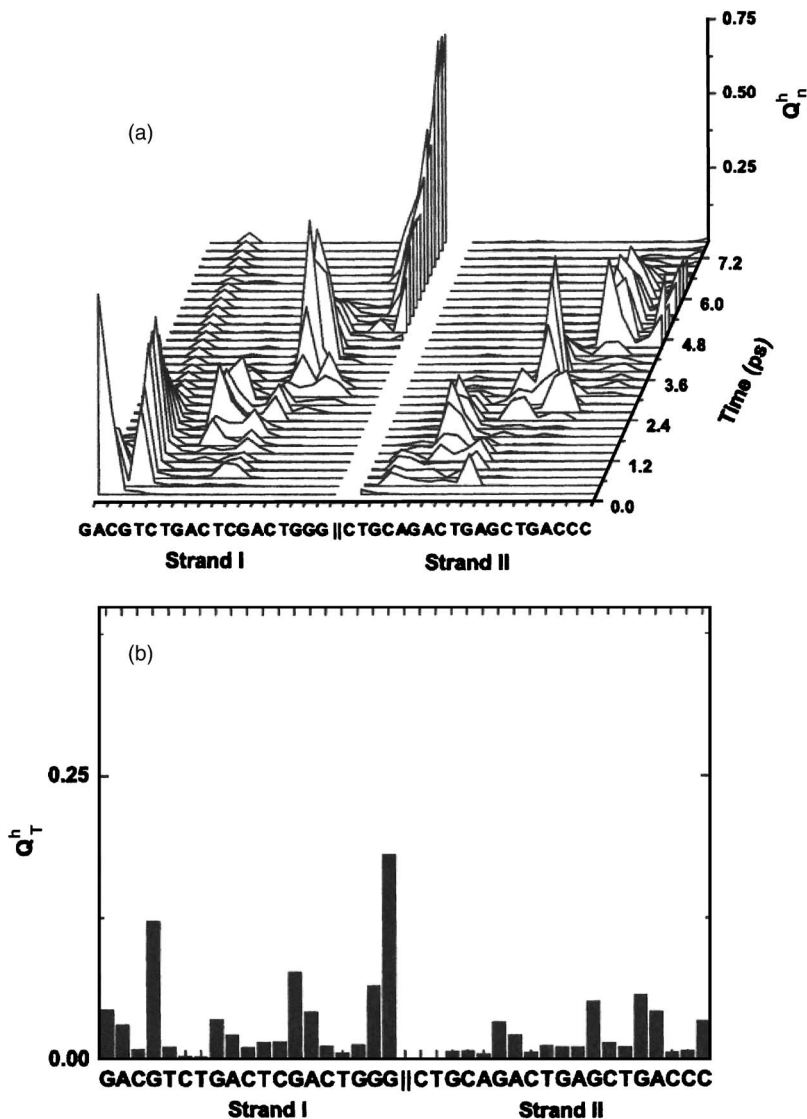


FIG. 5. (a) The excess charge distribution as a function of time and site for polaron transport in the structure of Fig. 1(b); (b) is the total excess charge distribution probability on each site in the process of polaron transport.

as that at $t_{\parallel}=t_{\perp}=0.2t_0$, except the slower average speed of polaron in the former owing to the subsegment localization [at G_{12} – G_{13} , cf. Fig. 1(b)] induced by stronger interstrand couplings. Such kind of subsegment localization has been confirmed by other choices of zigzagging couplings.

The length of the experimental structure in Fig. 1(b) is ~ 54 Å. In our calculations, the polaron takes about 7.7 ps to transport over this distance under the electric field $E=20E_0$, thus its average speed is almost as fast as that along the shorter strands in Fig. 1(a). It is in accord with the experimental observation that the charge transport over 54 Å is nearly as efficient as that over 10 Å.¹⁷

In literatures, Giese's experiment was ever theoretically interpreted by Bixon and co-workers with the energetic control of the hole migration mechanism.^{37,50} They demonstrated that the coupling between the nearest-neighbor $G_j^+ \cdots G_{j\pm 1}$ bridge bases is resonant (“+” indicating the hole position) while G_j^+T intrastrand coupling is off-resonant, as are the interstrand G_j^+C and G_j^+A couplings. For the dynamical pathways of polaron transport, the resonant coupling contributes to the very fast transport $G_3 \rightarrow G_4$ and $G_{12} \rightarrow G_{13}$, as shown in Figs. 4 and 5(a); while the off-resonant couplings (high barriers) obstruct the polaron tunneling at low tempera-

ture, resulting in the long-time rest and large excess charge distribution probability on-site G_4 and G_{13} , as shown in Figs. 5(a) and 5(b). Therefore, our current study has contained the essential points of the energetic control of the hole migration mechanism.

V. SUMMARY AND CONCLUDING REMARKS

In summary, we have investigated the transport pathways of polaron and bipolaron in DNA double strands. The long-range transport of polaron/bipolaron under high electric field is found being the field-facilitated sequential tunneling through spatial-disordered potential barriers via multiple intrastrand and interstrand pathways. If the charge transfer occurring far from the final acceptor GGG, the role of the interstrand pathway is the same important as that of the intrastrand one, otherwise, the intrastrand pathway with the final acceptor will dominate. When applying our theory to a DNA double strands used in the experiment, we have obtained some consistent results with the experimental observations.

Since temperature plays little role in the field-facilitated tunneling, its effect has not been involved in above model

and calculations. The sufficient high electric field ($eEa \gg k_B T_0$, where k_B and T_0 are the Boltzmann constant and room temperature, respectively) makes our results being valid at low temperature within a wide region. Even so, when extending this work to high temperature, two kinds of temperature effects should be discussed. The first is the temperature-dependent occupation number of the polaron/bipolaron energy level through the Fermi–Dirac distribution function. However, this effect seems not so important for charge transport in DNA based nanodevices due to the large gap between the Fermi level (around the chemical potential of metal electrodes) and the polaron/bipolaron level ($>30k_B T_0$).^{3,28} The second is the dissipation effect from the strong coupling between DNA and the heat bath. Dissipation in DNA may change the charge transfer rate dramatically.⁵¹ We will address the dissipation effect for the long-range polaron/bipolaron transport in DNA in our near future work.

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