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Polaron tunneling dynamics of a linear polymer of nucleotides

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Abstract
The formation of polaron and its migration in a DNA chain are studied within a semiclassical Peyrard–Bishop–Holstein polaron model. Comparing the energetics of the polaron system found from the quantum-chemical and semiclassical calculations, we extract the charge–phonon coupling constant for poly-DNA sequences. The coupling constant is found to be larger for G–C than for the A–T pairs. With this coupling constant we study tunneling in DNA. The rates and the nature of tunneling have strong dependence on the DNA sequence. By changing the trap positions in the molecular bridge the tunneling rate can be varied by up to seven orders of magnitude.

The discovery of conductance in DNA has attracted many researchers to investigate the transport properties [1–9] of DNA. For the (G–C)(A–T)$_N$(G–C)$_3$ DNA sequences the mechanism of charge transfer is more or less clear [1–4] and is described by the competition between tunneling and hopping transfer. But for the poly- and mixed DNA sequences the experimental data observed by different groups are often contradictory. In some experiments a high conductivity was obtained [6, 7], while in others the conductivity was rather low [8, 9]. In the works devoted to simulation of charge transfer in DNA within the tight-binding Hamiltonian [10, 11] or the system of kinetic equations [3, 4], no explanation of this phenomena was found. In these models the charge transfer integral between the nearest base pairs and the energy gap between the states were the key parameters. At the same time the models did not take into account consistently the effect of geometry fluctuations or phonons on the charge transfer processes in the DNA molecule. This is despite the fact that already in 1956 Marcus pointed out [12] that geometry fluctuations can activate and strongly affect an electronic transition between two states.

Therefore, the models taking into account the interaction of the migrating charge with the DNA lattice [13–18] should be invoked for an adequate investigation of the charge transfer in DNA. For example for the DNA molecule, an application of the polaron model has shown promising results for description of the charge migration [5, 13–15, 19] and for the explanation of the temperature dependence of the DNA conductance [5, 6, 20]. However, while the polaron formation and polaron size in the poly- and mixed DNA chains have been widely reported in the literature, the problem of polaron migration in time has not received serious attention [18, 21]. Consideration of the charge transfer dynamics can indeed help to interpret the available experimental results and provide a more realistic picture for the DNA conductance.

In this paper, we used the Peyrard–Bishop–Holstein (PBH) model [13, 19] for the time-dependent evolution of polaron migration. We demonstrate the possibility to design an artificial DNA molecule with semiconductor or insulating behaviors simply by placing a trap at the correct points. The study is based on the analysis of charge transfer from the donor to the acceptor through a molecular bridge composed of the potential barriers (A–T pairs) and the charge traps (G–C pairs). We show that in the mixed DNA molecules the transfer rate of the charge strongly depends on the sequences, i.e., on the positions of the traps between the donor and the acceptor. This position determines the relation between the rate of charge trapping and the rate of charge escape from the trap. Depending on this ratio the tunneling between the donor and the acceptor can be described either as a sequential tunneling or coherent tunneling through a trap. This difference strongly affects the final rate of charge transfer. We show that

the time of polaron tunneling can be changed by as much as 10^7 times by changing the position of the trap. The slower transfer occurs when the polaron trapping rate is much slower than the escape rate. On the other hand, the fastest polaron transfer occurs when the trapping and the escape rates are equal. In this case the tunneling has the coherent nature and the polaron only partially occupies the trap.

We focus here on the DNA structures where the guanine and the adenine are stacked in one DNA strand. In this case, there is only one degree of freedom for the charge transfer—the longitudinal one-dimensional charge tunneling through a single strand. The polaron tunneling is described by the system of equations within the PBH model [13, 19], where the charge motion is treated quantum-mechanically while the polaron tunneling classically. The PBH model is based on coupling of the charge's on-site energy with the structural motion at each lattice site of DNA. Specifically, the charge occupation on the ith DNA site leads to transverse stretching of the hydrogen bonds connecting the bases within the base pair and lattice distortion of their geometry. The PBH model consist of three parts: Hamiltonians describing charge hopping between two nearest base pairs, transverse motion of the bases within the pair and the charge–lattice interaction. The Schrödinger equation describing the dynamics of the charge within the DNA chain with n sites is determined by the Hamiltonians which include the tight-binding and the charge–lattice interaction terms, and has the form

$$i\hbar\frac{d\Psi_i}{dt} = -V_{i-1,i}\Psi_{i-1} - V_{i,i+1}\Psi_{i+1} + \chi_i y_i \Psi_i - \epsilon_i \Psi_i, \quad (1)$$

where Ψ_i is the probability amplitude for the charge to be on the ith base pair, $V_{i-1,i}(V_{i,i+1})$ is the transfer integral between the nearest base pairs, χ_i is the charge–vibrational coupling constant for the ith site, ϵ_i is the on-site energy, y_i determines the stretching at the ith site, i.e. the displacement of the atomic structure. The motion of the stretching displacement y_i is described by the Newton equation as [19]

$$m\frac{d^2y_i}{dt^2} = -V'_M(y_i) - W'(y_i, y_{i-1}) - W'(y_{i+1}, y_i) - \chi|\Psi_i|^2 - m\gamma\frac{dy_i}{dt} \quad (2)$$

where m is the base pair mass, γ is the friction parameter ($\gamma = 1\ \mathrm{ps}^{-1}$ [13]), $V_M(y_i)$ is the Morse potential which takes care of the effective interactions between complementary bases and $W(y_i, y_{i-1})$ is the nearest-neighbor potential of interactions of the stacked base pairs [19]. The parameters for the deformation potential and the interaction potential are taken from [19].

The self-consistent solution of the time-dependent Schrödinger and Newton equations has been applied to evaluate in time the propagation of the probability amplitude and the position of the stretching displacement with a time step $\Delta t = 1$ fs. Here the Schrödinger equation (1) is presented as

$$\left[1 + \frac{i}{2\hbar}\mathcal{H}\Delta t\right]\Psi(t + \Delta t) = \left[1 - \frac{i}{2\hbar}\mathcal{H}\Delta t\right]\Psi(t) \quad (3)$$

where the Hamiltonian $\mathcal{H}$ is a function of the stretching displacements $y_i(t)$. The three-point difference scheme for the first-order time derivation of the stretching parameter has been used in equation (2). For the stationary solution of equations (1) and (2), the initial occupation probability is assumed to be close to unity on the donor site. This solution is taken as the initial state ($t = 0$) for studying the polaron dynamics. Our calculations are restricted to low temperatures, and hence the polaron dynamics is governed by the quantum mechanical processes.

At first we analyze the equilibrium stationary polaronic states within a finite region of the DNA chain. Several physical parameters, such as the on-site energy ϵ_i, transfer integral between the nearest base pairs $V_{i-1,i}(V_{i,i+1})$ and the charge-vibrational coupling constant χ, determine the polaron shape and propagation velocity. The on-site energy for the A–T pair has been assigned to be zero, while for the single G–C pair we applied $\epsilon_i = -0.4$ eV, for the $(G–C)_2$ state the $\epsilon_i = -0.87$ eV and for the $(G–C)_3$ state the $\epsilon_i = -1.08$ eV [22]. The velocity of polaron propagation has been found to be strongly dependent on the magnitude of the charge transfer integral [21] plus the trapping energies for hole in $(G–C)_N$ traps also depends on this parameter [14]. According to the theoretical estimations within the quantum-chemical theory, the value of $V_{i-1,i}(V_{i,i+1})$ lies in the range of 0.05–0.3 eV [23–25], while experiments indicate the value of this parameter to be 0.01 eV [26, 27]. Because of the discrepancy between the theoretical estimations and experimental data, throughout this paper the average value $V_{i-1,i} = V_{i,i+1} = 0.1$ eV has been used. The charge–vibration coupling constant χ_i is the main parameter regulating the stretching of the polaron to the nearest sites [19] and the magnitude of y_i. The value of χ_i depends on the geometries of the DNA sites participating in the formation of the polaron. The shift of the state energy due to the polaron occupation $\chi_i y_i$ in the absence of the DNA–solvent interactions can be described by the inner-sphere reorganization energy ($\approx 0.5\lambda_i$ in [23])

$$\frac{1}{2}\lambda_N \approx \sum_{i=1}^{N}\chi_i y_i, \quad (4)$$

where N is the number of sites occupied by the polaron. Recently, the exponential decrease of the inner-sphere reorganization energy with the elongation of the DNA chain was found within the quantum-chemical calculations for the $(G–C)_N$ and the $(A–T)_N$ chains [23]. The geometry relaxation was found to have a maximum at the center of the polaron, which agrees with the results obtained within the PBH model [19].

The reorganization energy λ_N found in [23] are shown in table 1 for the $(G–C)_N$ and the $(A–T)_N$ chains. From these data we can estimate the coupling constants χ_i for different systems. The corresponding results for χ_i are shown in table 1. We have found that the coupling constant is smaller for the A–T base pair than for the G–C pair. We also determine the tendency in the dependence of the coupling constant on the size of the complexes; the coupling constant decreases with increasing sizes of the $(G–C)_N$ and $(A–T)_N$ chains.

With the values of coupling constants derived for different base pairs we now study the properties of the polaronic state

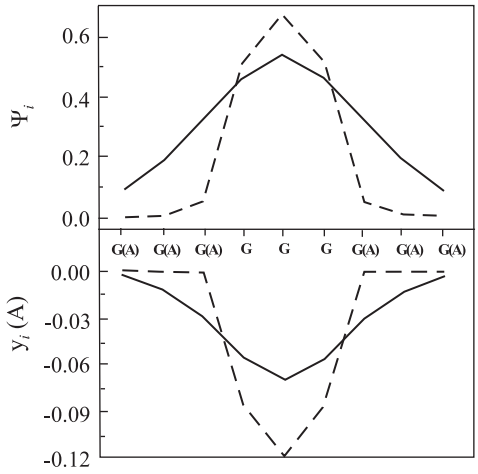

Figure 1. The wavefunction Ψ_i and the lattice displacement y_i for the polarons formed in GGGGGGGGG (solid line) and AAAGGGAAA (dashed line) chains.

Table 1. The values of $\frac{1}{2}\lambda_N$ and χ_i for the $(\text{G–C})_N$ and the $(\text{A–T})_N$ complexes.

	$\frac{1}{2}\lambda_N$ (eV)[a]	χ_i (eV Å^{-1})
$(\text{G–C})_{N=1}$	0.360	1.60
$(\text{G–C})_{N=2}$	0.310	1.15
$(\text{G–C})_{N=3}$	0.265	0.90
$(\text{G–C})_{N=4}$	0.225	0.60
$(\text{A–T})_{N=1}$	0.185	1.05
$(\text{A–T})_{N=2}$	0.165	0.53
$(\text{A–T})_{N=3}$	0.140	0.40
$(\text{A–T})_{N=4}$	0.125	0.30

[a] Simulation results are from [23].

in the poly- and mixed DNA chains. In the poly(dG)-poly(dC) and the poly(dA)-poly(dT) DNA molecules, according to our calculations the polaron occupies mostly 7–9 sites. In the mixed DNA chain, the polaron stretching is limited by the difference between the coupling constants χ_i, and on-site energies ϵ_i, for A–T and G–C pairs (see table 1). The results for GGGGGGGGG and AAAGGGAAA chains are shown in figure 1. The polaron in the AAAGGGAAA structure is mostly localized within the GGG due to high potential barriers between guanines and adenines (1.08 eV) [22].

The value of the coupling constant also determines the polaron stretching, but its effect is strong only in the structure with low potential barriers. An example of such structures is the AAAAGAAAA chain where the energy gap between the A–T and the G–C is only 0.4 eV. The results for the AAAAGAAAA structure are shown in figure 2(a) for two cases: (i) when the value of the coupling constant is the same over the whole chain and is equal to $\chi_i = 0.6$ eV Å^{-1} [22], and (ii) when the coupling constant is different for G–C and A–T base pairs. Clearly, the introduction of different coupling constants χ_i for A–T and G–C pairs provides stronger localization of the polaron within the G–C trap.

The effect of the coupling constant on the polaron localization in the GGGGAGGGG chain is illustrated in figure 2(b). Actually, for this chain the polaron vibration mode

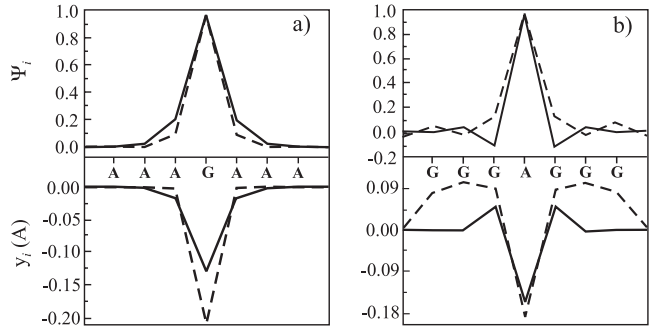

Figure 2. The wavefunction Ψ_i and the lattice displacement y_i for polarons formed on (a) G–C for $\chi_i = 0.6$ eV Å^{-1} (solid line) and $\chi_{\text{G–C}} = 1.6$ eV Å^{-1}, $\chi_{\text{A–T}} = 0.4$ eV Å^{-1} (dashed line) and on (b) A–T $\chi_i = 0.6$ eV Å^{-1} (solid line) and $\chi_{\text{G–C}} = 0.9$ eV Å^{-1}, $\chi_{\text{A–T}} = 1.05$ eV Å^{-1} (dashed line).

is outside of the lattice band of the A–T site [19]. When the coupling constant $\chi_i = 0.6$ eV Å^{-1} is the same over the whole DNA chain, the vibration mode is only marginally delocalized. The energy of this state is -0.81 eV, while the potential barrier between the $(\text{G–C})_N$ and A–T site is -0.87 eV. The polaron in this case is almost localized at the A–T site. When we introduce the dependence of the coupling constant on the site type (figure 2(b) (dashed line)), the energy of the state becomes -0.56 eV and the polaron becomes delocalized over the three nearest G–C sites from each side of the A–T pair.

To study polaron tunneling between the DNA traps, we first compare the energies of the polaronic states in different types of traps. Localization of the polaron in the $(\text{G–C})_N$ traps shifts the energy of state to a lower value. This is the energy of the polaron which is the eigenvalue of the Hamiltonian corresponding to equation (1). The energy of the polaron can also be estimated from the on-site energy ϵ_i and the electronic energy $\chi_i y_i$ [19]

$$E_{\text{tot}} \simeq \sum_{i=1}^{N} \chi_i y_i + \sum_{i=1}^{N} \epsilon_i / N = \frac{1}{2}\lambda_N + \sum_{i=1}^{N} \epsilon_i / N. \qquad (5)$$

For the energy difference between the polaronic states in different traps we have found the values -0.20 eV for G–C and $(\text{G–C})_2$ traps and -0.43 eV for G–C and $(\text{G–C})_3$ traps. Inclusion of inner-sphere reorganization energy into the charge transfer model has brought down these values to $\Delta\epsilon = -0.47$ eV and $\Delta\epsilon = -0.68$ eV, respectively [22]. A direct comparison with the experimental results in the solvent [28] would require evaluation of the solvent reorganization energy [29], which is beyond the scope of this work. However, for the results that follow, in particular for the polaron migration dynamics, the solvent contribution perhaps is not the dominant one.

The low energy gap between the states of the $(\text{G–C})_N$ traps results in the competition between two processes in the mixed DNA [30]: (i) the trapping of the polaron within the trap and (ii) the tunneling of the polaron between the $(\text{G–C})_N$ traps. To study the problem of polaron tunneling between the DNA traps we have performed a numerical simulation of the polaron dynamics in a mixed DNA chain. Here the first G–C

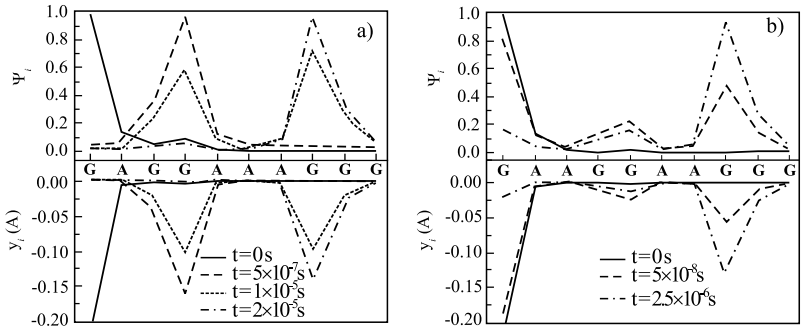

Figure 3. The dynamics of propagation of the wavefunction Ψ_i and the lattice displacement y_i in the chains: (a) $G(A)_1GG(A)_3GGG$ and (b) $G(A)_2GG(A)_2GGG$.

trap is a donor with localized charge on it in the initial state and the $(G–C)_3$ trap is an acceptor. For the system without any additional traps, i.e. a DNA chain with only the donor and the acceptor ($(G)(A)_n(G)_3$), we have found an exponential dependence of the tunneling rate on the tunneling distance. Let t_n be the tunneling time for the structure $(G)(A)_n(G)_3$. We then have for the normalized rate, $t_1/t_n = 0.6 \times 10^{-1}$ for $n = 2$, 1.4×10^{-3} for $n = 3$, and 0.6×10^{-5} for $n = 4$ ($t_n = 0.5$ ns). These data are in a good agreement with the tunneling rates in the experimental results [31].

The new features in the polaron tunneling process are observed for the mixed DNA structure with an additional trap between the donor and the acceptor. Here we study the system with the $(G–C)_2$ trap in the $(A–T)_6$ molecular bridge. The dispersion of the site energies of the G–C base pairs within the $(G–C)_3$ where the guanine at the end has a higher site energy than guanines located close to the sequence center [23], has been taken into account. In the case of the $(G–C)_2$ trap located close to the donor site (G–C) the polaron is stretched over the donor and the trap. As a result the polaron quickly tunnels to the $(G–C)_2$ trap (figure 3(a)). The polaron occupation process takes some time and finally the polaron tunnels to the acceptor. In this case, tunneling from the donor to the acceptor states has the sequential nature and the tunneling processes from the donor to the trap and from the trap to the acceptor are uncorrelated.

When the $(G–C)_2$ trap is placed exactly in the middle of the $(A–T)_6$ bridge, a significant change in the polaron tunneling dynamics is observed (figure 3(b)). In this case, the rate of charge tunneling from the donor to the trap is almost equal to the rate of tunneling from the trap to the acceptor. Therefore, the polaron is only partially localized on the trap and the final polaron tunneling from the donor to the acceptor is a coherent process. The curve for $t = 10^{-6}$ s in figure 3(b) shows the occurrence of the resonance effect due to the coincidence of the trap site energy with the site energy of the last guanine within the $(G–C)_3$ acceptor. The rate of charge tunneling in figure 3 is in good agreement with the experimental results [32], where the transfer from a donor to an acceptor in similar systems was estimated to be 10^{-8}–10^{-6} s.

In figure 4 the dependence of the occupation probability of different traps within the DNA chain is shown for (a) $G(A)_1GG(A)_3GGG$ and (b) $G(A)_2GG(A)_2GGG$ structures. We again see a completely different nature of tunneling for different positions of the trap. When the trap is close to the donor, the charge transfer process is the sequential incoherent tunneling, i.e., when the polaron spends a long time within the trap. But if the trap is moved closer to the center of the tunneling bridge then the tunneling becomes coherent. However, when the position of the $(G–C)_2$ trap is closer to the acceptor as in the $G(A)_3GG(A)_1GGG$ structure, the polaron is not localized on the trap but tunnels directly from the donor to the acceptor. Since the trap does not participate in the charge transfer, the width of the potential barrier for the polaron covers the whole molecular bridge $(A)_3GG(A)_1$ and coherent tunneling from the donor to the acceptor occurs in the range of $t = 200$ s. This is 10^7 times slower than the time for coherent tunneling through the trap (see in figures 3(b) and 4(b)). Therefore, the transfer mechanism for the $G(A)_3GG(A)_1GGG$ sequence is similar to that for the $G(A)_6GGG$ structure.

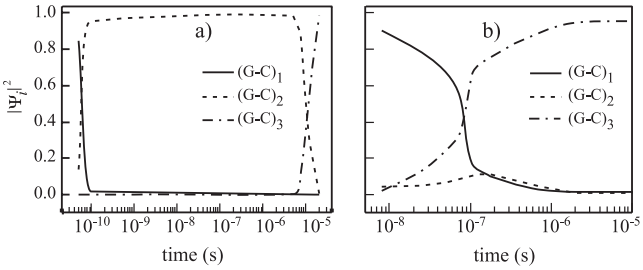

Figure 4. The dependence of the occupation probability $|\Psi_i|^2$ on time for the chains: (a) $G(A)_1GG(A)_3GGG$ and (b) $G(A)_2GG(A)_2GGG$.

In conclusion, from the results of the *ab initio* quantum mechanical calculations, we obtained the charge–vibration coupling constants in the Peyrard–Bishop–Holstein model for polarons formed in the $(G–C)_N$ and the $(A–T)_N$ DNA molecules. We have found that the coupling constants are larger for the $(G–C)_N$ complex than for the $(A–T)_N$. In the poly- DNA molecule, the polaron occupies nine DNA base pairs, while in the mixed DNA the size of the polaron is strongly affected by the potential gap between the A–T and the G–C sites. In addition to the properties of the stationary polaronic state, we have also studied the dynamics of the polaron tunneling from the donor to the acceptor. We have found a very strong dependence of the tunneling rates on the structure of the tunneling bridge. The position of additional traps within the bridge strongly affects the nature of the

tunneling process and the rates. By changing the position we can change the tunneling rate up to seven orders of magnitude. For the fastest tunneling rate we need the coherent tunneling, i.e., tunneling to each of the traps should be almost equal to the escape rate from the trap.

Acknowledgments

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