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Abstract
The velocity of polaron migration in the long poly-DNA chain (∼40 base pairs) in an applied electric field has been studied within a polaron model. A small polaron shows a slow propagation and strong tolerance to the electric field, while a large polaron is much faster and less stable with increasing electric field. Moreover, the conductance of the DNA molecule within the polaron model is found to be sensitive to structural disorders in the DNA geometry.

The application of the biological systems in developing nanoelectronic devices has been recognized as one of the most intriguing and promising techniques in recent years. This is due to the molecular recognition and self-assembly properties that allows them to perform reparation of the damaged structures by the non-invasive technology and self-incorporation of molecular blocks into the well-structured systems. The DNA molecule is one such biological system. The interest in DNA, while originally derived as it is the source of genetic information, has been significantly elevated due to the discovery of DNA conductance [1–10].

Understanding the mechanism of charge migration in a complex molecule such as DNA is a difficult problem. Just as in the field of condensed matter, in simple DNA sequences, if the donor and the acceptor are separated by a single potential barrier, the charge transfer has been adequately explained by the competition of quantum tunneling and incoherent hopping [2, 3] that has also been experimentally confirmed [11, 12]. However, the observed conductance of a long DNA molecule with both poly- and mixed sequences, varies from insulating to a metallic behavior [4–7]. To clarify this issue, the simulations of the charge transfer in the DNA molecule are required. For the description of transport phenomena in polymer chains, a polaron model has been known to be very successful [13, 14]. For DNA, this model has shown recently to provide promising results as well [4, 8–10, 15, 16], especially for explaining the temperature dependence of the DNA conductance [4, 8, 15]. Moreover, additional advantage of the polaron model, in comparison to the popular models such as the tight-binding approach or the system of kinetic equations, is that it includes the interaction of the migrating charge with the DNA lattice.

In this paper, we have used the polaron model for the simulation of the dynamics of hole propagation in the poly-DNA molecules. We have found that the polaron size, additionally to the disorders in the DNA structure, can be reason for variation of the DNA conductance in different experiments [4–7]. The high resistivity of the DNA molecule observed in some experiments [6, 7] can be attributed to the disorder effect and the formation of the small polaron, while formation of the large polaron and disorder-free DNA structure should provide a low resistivity, as in the papers [4, 5]. The polaron localization is found to be controlled by the charge transfer integral and the charge-vibrational coupling constant. Therefore, the DNA sequences, the helical conformations and the solvent environment will be the main factors controlling the intrinsic conductance of the disorder-free DNA. For example, the poly(dG)–poly(dC) and poly(dA)–poly(dT) molecules have shown different conductance in the experiment [4] that is a result of different values of the charge transfer integral and the charge-vibrational coupling constant indicated for the A–T and G–C base pairs [17, 18].

We have simulated the polaron propagation through the poly-DNA using the Peyrard–Bishop–Holstein (PBH) model [9, 10], which combines a quantum-mechanical treatment of charge motion with a classical treatment of the lattice distortion dynamics. In a poly chain, each strand contains only one base type. The purine and pyrimidine bases are characterized by different ionization potential (⩾1.0 eV [17]). Because they belong to the opposite strands in the poly-DNA, the main mechanism of charge migration is longitudinal one-dimensional tunneling along a single strand containing purine bases. The application of the polaron

model for description of the charge transfer in the poly-DNA molecule is limited by the temperature due to the dependence of the structural disorder induced by the polaron on the thermal fluctuations [15]. It has been found, that the formation of the polaron in the DNA chain can occurs below 70 K, otherwise the polaronic character of charge transfer is vanishing [15]. Therefore, the model used in this work, without taking into account the influence of temperature on structural disorder (see [15]), is relevant for the low temperature regime.

An electric field is applied to the system using the method of [14], specifically, the charge transfer integral V is multiplied by a complex exponential phase factor that includes the electromagnetic vector potential A. For a uniform constant electric field E, we take $A(t) = -cEt$, thereby satisfying $E = -dA/c\,dt$. Here, c is the speed of light, and we have taken $A = 0$ at time $t = 0$. The uniform electric field is included via its uniform vector potential, rather than with its non-uniform scalar potential [9], in order that periodic boundary conditions can be utilized.

With the modifications for the electric field, the coupled system of nonlinear equations based on the PBH model is

$$i\hbar \frac{d\Psi_n}{dt} = -V e^{-i(ed/\hbar c)A(t)}\Psi_{n-1} - V e^{i(ed/\hbar c)A(t)}\Psi_{n+1} + \chi y_n \Psi_n + \epsilon_n \Psi_n, \tag{1}$$

and

$$m \frac{d^2 y_n}{dt^2} = -\frac{dV_M(y_n)}{dy_n} - \frac{dW(y_n, y_{n-1})}{dy_n} - \frac{dW(y_{n+1}, y_n)}{dy_n} - \chi |\Psi_n|^2 - m\gamma \frac{dy_n}{dt} \tag{2}$$

where Ψ_n is the probability amplitude for the charge on the nth base pair, V is the nearest-neighbor transfer integral between the base pairs, χ is the charge-vibrational coupling constant, ϵ_n is the on-site energy for base site n, y_n is the amount by which the nth base site is displaced from its equilibrium position, m is the polaron mass on the single site, γ is the friction parameter, $V_M(y_n)$ is the Morse potential, and $W(y_n, y_{n-1})$ is the interaction of neighboring stacked base pairs, e is the electronic charge, and d is the interbase spacing ($d = 3.4$ Å). The expressions and parameters for $V_M(y_n)$ and $W(y_n, y_{i-n})$ are taken from [9]. In poly-DNA, χ and V are constant with respect to the lattice site, and in the absence of disorder, we choose ϵ_n to be at the origin.

In our simulations, a polaron is initially created by numerically solving the system of nonlinear equations (1) and (2) in a stationary situation (i.e., for $d^2 y_n/dt^2 = dy_n/dt = 0$ and $i\hbar\,d\Psi_n/dt =$ constant) with a modified Powell hybrid method. Initial estimates for y_n and Ψ_n are chosen to be non-zero only for ten consecutive base pairs. Due to the uniformity and stability of the system, the solution is largely insensitive to the initial estimates. The resulting initial solution can be seen in figure 1 for $t = 0$ ps. The lattice displacement y_n and the charge density $|\Psi_n|^2$ coincide and have the same overall shape. Together they comprise a polaron that, for the parameters chosen here, is spread over approximately thirteen lattice sites but has a definite peak in the center. In the polaron's vicinity, the displacement y_n, and therefore the distortion energy χy_n, are negative, creating a quantum well
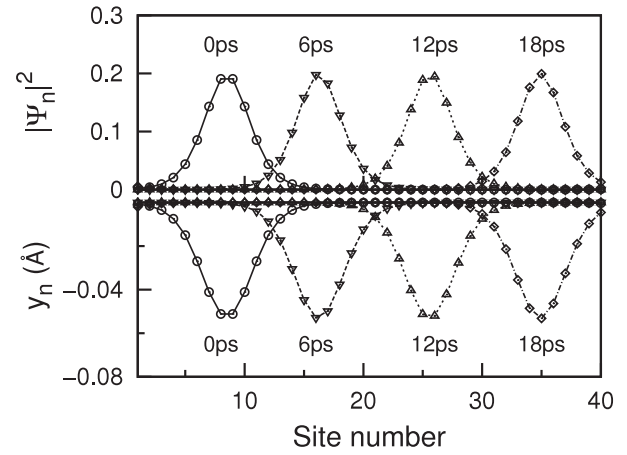

Figure 1. Polaron dynamics: the charge density $|\Psi_n|^2$ and the lattice displacement y_n propagating through poly-DNA for $E = 0.016$ mV Å^{-1} ($\chi = 0.6$ eV Å^{-1}, $V = 0.1$ eV, $m = 300$ amu).

in the otherwise uniform energy profile of the poly-DNA. The wavefunction Ψ_n is consequently localized within this well and the polaron is stable against small perturbations. Moreover, if no electric field is applied ($E = 0$), the polaron remains completely stationary because the initial solution corresponds to a stable equilibrium.

In an electric field the positively charged polaron moves in the direction of the field (figure 1) for a constant electric field of $E = 0.016$ mV Å^{-1}. Clearly, as the polaron migrates both the charge density and lattice displacement move in unison, i.e., the wavefunction and its formed quantum well travel together. Because of the stabilizing effect of the lattice distortion, the polaron retains the same overall shape as it migrates; however, our calculations indicate that in larger electric fields, the polaron becomes slightly more localized over time.

In the following, we study polaron shape and propagation in poly-DNA under the influence of an electric field. We focus specifically on the effect of three physical parameters, χ, V, and m. The value of the charge-vibrational coupling constant χ determines the decrease in on-site energy in the charged-state geometry, and has been estimated theoretically to be in the range of 0.3–1.5 eV [18]. Its value predominantly depends on the nature of the state geometry and its extension, which can be influenced by the structural parameters of DNA and the solvent environment as well. The charge in DNA can be spread in two directions: in parallel to the propagation pathway— longitudinal direction and perpendicular—transverse direction. The spreading of the charge in the longitudinal direction significantly decreases χ [17]. For the transverse case, a charge can occupy a single purine base that suggests a larger value of χ than does a charge that is partially delocalized over a base pair [18]. The degree of charge delocalization also governs the value of the polaron mass m. If the charge is localized on a single base then $m \approx 150$ amu, and this value increases with extension of the geometry of the state in the transverse direction. The value of the charge transfer integral V depends strongly on the configuration of the DNA geometry, and can be influenced by the solvent environment as well [20].
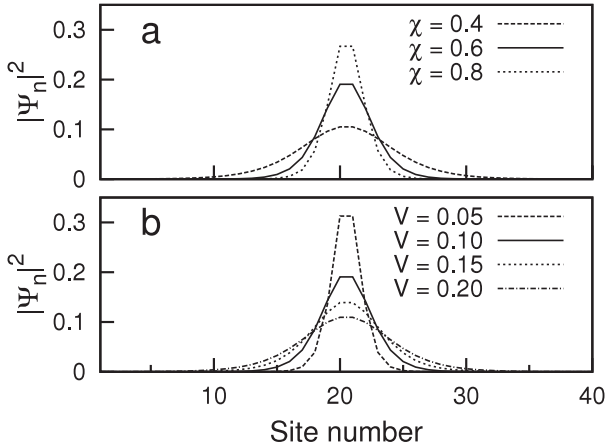
Figure 2. Polaron shape in poly-DNA for varying values of (a) χ and (b) V. In (a), $V = 0.1$ eV, $m = 300$ amu, and χ is given in units of eV Å^{-1}. In (b), $\chi = 0.6$ eV Å^{-1}, $m = 300$ amu, and V is given in units of eV.

Theoretical estimations place the value of V in the range of 0.05–0.3 eV [17, 19], while experiments indicate the value of V to be $\ll$0.01 eV [20, 21]. Throughout this paper, we use the values $\chi = 0.6$ eV Å^{-1}, $V = 0.1$ eV, and $m = 300$ amu as reference points, and consider the effects of deviating from these values as we study polaron shape and polaron response to applied electric fields.

The uniform system used in our simulations is ideal for studying the effect of model parameters on the polaron shape since, as mentioned above, the polaron remains stationary in the absence of an electric field. Figure 2(a) shows the effect of changing the coupling constant χ under these circumstances. As is evident in the figure, increasing χ results in greater polaron localization: the polaron occupies fewer lattice sites, with a correspondingly larger charge density and lattice distortion at the center of the polaron. Conversely, decreasing χ has the opposite effect. Figure 2(b) shows the shape of the polaron at varying values of the charge transfer integral V. The effect is opposite to that observed when adjusting χ: increasing (decreasing) V causes a decrease (increase) in polaron localization. This is expected since the larger the charge transfer integral, the more the polaron will spread out to neighboring sites. In accordance with equation (2), the value of m has no effect on the polaron's shape: in the stationary state the time derivative $m\gamma \, dy_n/dt$ in equation (2) equals zero.

After the polaron is initially created, a constant uniform electric field E is applied and we study the resulting polaron motion in time. The probability amplitude and the position of the stretching displacement in time are evaluated from the self-consistent solution of the time-dependent Schrödinger (equation (1)) and Newton equations (equation (2)) with a time step of 0.1 fs. Simulations show that there exists a maximum electric field E_{max} that the polaron can tolerate; for $E > E_{max}$, the lattice displacement and charge density become unsynchronized and irregular. The value of E_{max} depends on the system's parameters and in all cases studied, the more delocalized the polaron, the smaller the value of E_{max}. As such, increasing χ and γ or decreasing V leads to a polaron capable

of tolerating larger fields, whereas E_{max} is mostly independent of m. A highly localized polaron causes a large localized lattice distortion, which effectively acts as a quantum well. By decreasing the energy in its vicinity, a more localized polaron is therefore more stable, and consequently, it is reasonable that the polaron would be able to remain well-formed in the presence of stronger electric fields.

The application of an electric field effects polaron migration (figure 1). Moreover, provided that $E < E_{max}$, the polaron remains well-formed and the motion is continuous. Further, in the presence of a field the polaron moves at a constant velocity. This result can be explained as follows: (i) our system represents poly-DNA under periodic boundary conditions, so the system parameters do not vary with location; (ii) the applied electric field is uniform and constant; (iii) the polaron maintains a constant shape as it travels; and (iv) the friction term $m\gamma \, dy_n/dt$ prevents the charge from continually accelerating. These factors ensure that after a brief period of acceleration from the initial stationary state, the polaron's velocity does not vary.

The velocity does depend, however, on the system parameters and on the applied electric field strength. The dependence of the velocity of the polaron propagation on γ is linear. Raising γ from 0.1 to 10 ps^{-1} reduces the polaron velocity up to 4 times. For the following calculations we are taking $\gamma = 1$ ps^{-1}. Figures 3(a)–(c) show how the velocity of the polaron varies with E for different values of χ, V, and m respectively. These graphs all display a similar behavior, but the magnitudes and slopes in the plots are very sensitive to the values of χ, V, and m. In particular, an increase in the velocity—and therefore conductance—can be achieved by decreasing the coupling constant χ, by increasing the charge transfer integral V, or by decreasing the polaron mass m. Analysis of both χ and V suggest that an increase in polaron localization produces a decrease in velocity. It should be noted, however, that this correlation need not be a general mathematical rule; for example, by changing m it is possible to change the polaron's velocity without affecting its localization at all. Other model parameters, such as the friction constant γ, also affect the velocity, but do not change the qualitative behavior observed in figure 3.

Structural disorder in the poly-DNA can drastically alter the polaron propagation. An irregularity at a base site k can produce a quantum barrier or well, which we represent with a non-zero value of ϵ_k. Because the energy of the polaron ($\epsilon_n + \chi y_n$) is lower than the on-site energy at the $k + 1$ site, the polaron is able to traverse the barrier ($\epsilon_k > 0$) in the case of a very low barrier ($\epsilon_k \approx 0.01$ eV) in conjunction with a large electric field ($E \gtrsim 0.1$ mV Å^{-1}). Otherwise, the polaron is unable to traverse site k for any $E < E_{max}$, instead coming to a stop just before the irregularity. The situation for quantum wells ($\epsilon_k < 0$) is very different. For very shallow wells ($\epsilon_k \gtrsim -0.05$ eV), the polaron completely enters the well for any E, although a large electric field ($E \gtrsim 0.1$ mV Å^{-1}) can dislodge the polaron if the well is extremely shallow ($\epsilon_k \gtrsim -0.01$ eV). For deeper wells (-0.2 eV $\lesssim \epsilon_k \lesssim -0.05$ eV), the polaron splits into two, with one polaron halting prior to the well and the second entering the well (figure 4). In this
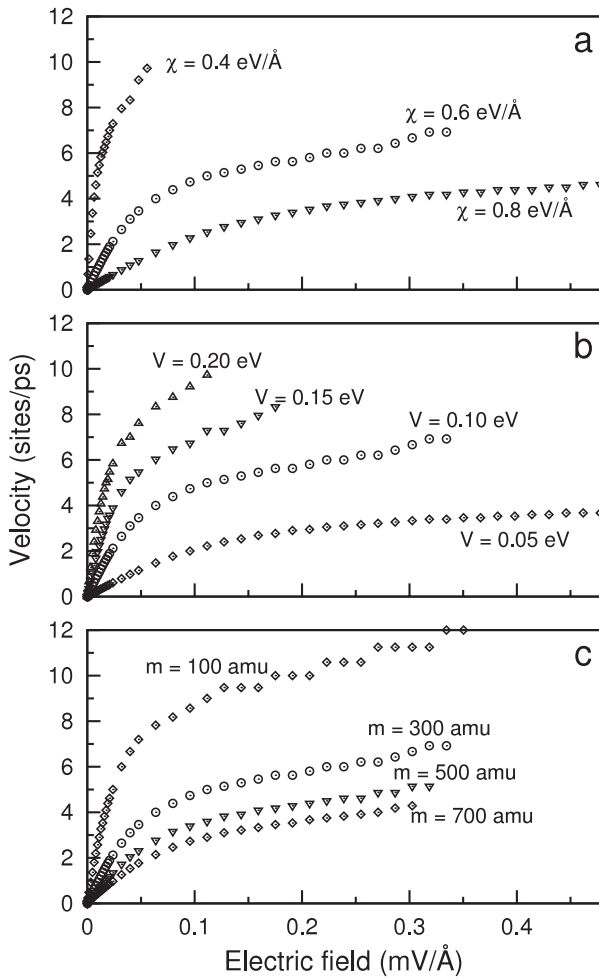
Figure 3. Propagation velocity of a polaron through poly-DNA as a function of applied electric field for varying values of (a) χ, (b) V, and (c) m. Points corresponding to $E > E_{max}$ are absent as they do not represent accurate values. Unless specified otherwise in the figure, $\chi = 0.6$ eV Å^{-1}, $V = 0.1$ eV, and $m = 300$ amu.
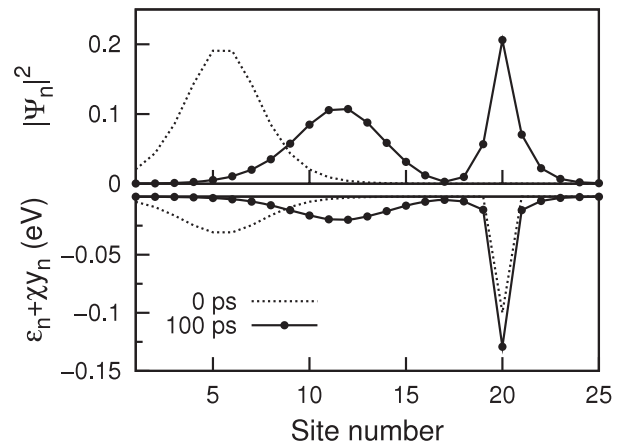

Figure 4. The dynamics of the polaron propagation through poly-DNA with a disorder-induced well at site $n = 20$. For the initial solution $t = 0$ ps (dotted line) the polaron is placed at the beginning of the chain and therefore, the polaron is not presented in the well ($\chi y_{20} = 0$ eV). For the $t = 100$ ps (solid line) the polaron moves closer to this well and splits into two polarons, one of which is localized before the well and the second occupies the well ($\chi y_{20} = 0.029$ eV).

case, the initial polaron stops before the irregularity, but then part of it tunnels from the polaron-induced well (χy_n) into the disorder-induced well (ϵ_k). For $\epsilon_k < -0.2$ eV we had only one polaron, which stops prior to the well. It should be emphasized that the above analysis applies only to poly-DNA. In the mixed DNA molecule characterized by the potential profile with random location of the barriers and the wells, the system is generally unstable and the polaron tunnels through barriers to reach distant wells if the on-site energy of this well (ϵ_k) is lower than the energy of the polaron ($\epsilon_n + \chi y_n$) [18].

In conclusion, the velocity of polaron propagation and hence the DNA conductance is mostly determined by the polaron size in transverse and longitudinal directions. A decrease of χ induced by partial delocalization of the charge from the purine base to the whole base pair [17] provides the extension of the polaron size in the longitudinal direction and significantly increases the DNA conductance. For example, a decrease of χ by 0.2 eV can increase the conductance by $\sim$6–10 times depending on the electric field value. The polaron can be destroyed at high electric fields, which then changes

the mechanism of charge transfer in the DNA molecule and therefore, will cause a discontinuity in the conductance characteristics. A large polaron has higher velocity but is less tolerant to the electric field. The structural disorders, which form a barrier $\lesssim 0.05$ eV (well) on the polaron pathway, depending on energetic conditions and electric field magnitude, can stop (trap) the polaron and cause a fast decrease of the DNA conductance resulting in an insulating behavior.

Acknowledgments

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