Trapping and motion of polarons in weakly disordered DNA molecules

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Abstract

Polaron effects for charge migration in DNA molecules have been previously considered within the Peyrard–Bishop–Holstein model. When a uniform electric field is applied, the polaron moves asymptotically at a constant velocity, provided dissipative effects are taken into account, and then current flows through DNA. Disorder originating from interactions with a random environment of solute molecules and ions surrounding the DNA molecule could prevent charge migration due to the localization of the carrier wavefunction. We studied numerically the Peyrard–Bishop–Holstein model when the disordered DNA molecule is subjected to a uniform electric field. We found the threshold value of the electric field to observe polaron motion when disorder is present. We also calculated the fluctuations of the electric current and found that they provide valuable information about the polaron dynamics.

1. Introduction

In DNA molecules, as in other polymers, an extra electron or hole distorts the lattice to form a charged polaron that extends over several sites of the lattice. In recent years, polarons and charge transport in DNA have attracted considerable attention (see [1] for a review). This interest is in part motivated by experiments on electric transport through dry and wet DNA molecules that revealed a variety of results, ranging from ohmic-like [2–5], semiconducting [6–10] and insulating [11, 12] behaviors. The dynamics of the polaron can be described by an effective one-dimensional approach, referred to as the Peyrard–Bishop–Holstein (PBH) model [13–15], in which the electronic wavefunction obeys the time-dependent Schrödinger equation and the lattice distortion is treated classically by a Newtonian equation of motion beyond the linear approximation.

The PBH polaron subjected to a direct current (dc) electric field performs Bloch oscillations [16] when the Bloch period is shorter than the relaxation time [17]. At a much larger time, the carriers lose their phase coherence through scattering

processes and the polaron moves classically with a uniform velocity [18]. The PBH model assumes that the DNA molecule is uniform with the same value of the site energy at every base. Nevertheless, the environment of solute molecules and ions surrounding the DNA molecule can affect not only the sugar-phosphate backbone but also the base molecules. Disorder originating from interactions with the random environment could prevent charge migration at low temperature due to the occurrence of Anderson localization [21]. Therefore, the polaron could be trapped unless the dc electric field exceeds a threshold value. Since the threshold field will depend on the magnitude of disorder, its magnitude will carry relevant information about the influence of the random environment on the charge transfer in DNA.

In this work we report on a more general description of the polaron dynamics by introducing disorder into the well-established PBH model [13–15]. The paper is organized as follows. In section 2 we describe the effective one-dimensional model corresponding to a homopolymer DNA. We use a non-adiabatic dynamical evolution method, in which carriers obey the Schrödinger equation and the deformable lattice is treated

1

classically. We also introduce the model of disorder due to the interaction with the random environment of the DNA molecule. Physical magnitudes that characterize the dynamics of the polaron are introduced in section 3. Afterwards, in section 4 we turn ourselves to the main topic of the paper, the dynamics of the polaron in weakly disordered DNA. In contrast to the standard PBH model, we find that polarons can be trapped by weak disorder at low values of the applied electric field and current cannot flow through the DNA molecule. The polaron becomes mobile when the electric field is larger than a threshold value that depends on the magnitude of disorder. Our final comments and discussions are contained in section 5.

2. Polarons in the PBH model

We consider a one-dimensional tight-binding model corresponding to a homopolymer DNA. The Schrödinger equation for the carrier subjected to a dc electric field F is

$$i\hbar \frac{d\psi_n}{dt} = \varepsilon_n \psi_n - T(e^{i\omega_B t} \psi_{n+1} + e^{-i\omega_B t} \psi_{n-1}) + \chi y_n \psi_n, \quad (1)$$

where ψ_n is the probability amplitude for the charge carrier located at the nth base. The parameter $\omega_B = eFa/\hbar$ is the Bloch frequency ($a = 3.4$ Å in DNA). Notice that $\hbar\omega_B = eFa$ is the potential drop between nearest-neighbor nucleotides along the stacking direction. The molecular energy levels ε_n are assumed to be uncorrelated random variables due to the interaction with the environment. We consider static disorder and neglect time fluctuations of the site energies. Thus, our model does not take into account the dynamics of water molecules in DNA (wet DNA). The hopping integral is restricted to nearest-neighbor nucleotides and its magnitude is given by T. The coupling of the carrier to the uniform electric field is taken into account by the phase factor in the hopping integral. Therefore, periodic boundary conditions can be easily implemented [18]. The last term in equation (1) describes the carrier–lattice coupling through the constant χ and the stretching displacement y_n of the nth nucleotide from its equilibrium position.

The DNA lattice is described classically by Newton's equations of motion for the displacement y_n

$$m \frac{d^2 y_n}{dt^2} = -V'_M(y_n) - W'(y_n, y_{n-1}) - W'(y_n, y_{n+1})$$
$$- \chi |\psi_n|^2 - m\gamma \frac{dy_n}{dt}, \quad (2)$$

where m is the nucleotide mass and the prime indicates differentiation with respect to y_n. The last term in equation (2) takes into account the energy dissipation of the lattice. In the PBH model, the Morse potential

$$V_M(y_n) = V_0(e^{-\alpha y_n} - 1)^2 \quad (3)$$

arises from the anharmonic interaction with the sugar-phosphate backbone as well as between complementary base pairs. In addition, the anharmonic coupling between nearest-neighbor nucleotides along the staking direction is described by the potential [15]

$$W(y_n, y_{n-1}) = \frac{k}{4}(2 + e^{-\beta(y_n + y_{n-1})})(y_n - y_{n-1})^2. \quad (4)$$
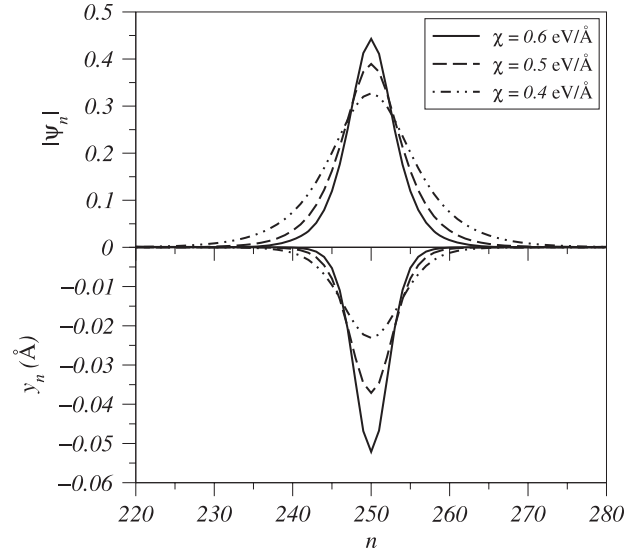

Figure 1. Modulus of the carrier wavefunction (upper panel) and lattice displacement (lower panel) in the homogeneous homopolymer DNA molecule at $t = 0$ for different values of χ.

The dynamics of the PBH model at finite temperature have been addressed by Kawano and Maruyama by subjecting the lattice degrees of freedom to Langevin molecular dynamics [19]. They found a good agreement between numerical results and experiments on the mean velocity of the polaron. Therefore, the classical description of the lattice dynamics provides an accurate framework to deal with polarons in DNA.

According to [15], the model parameters are given by $m = 300$ amu, $V_0 = 0.04$ eV, $\alpha = 4.45$ Å^{-1}, $k = 0.04$ eV Å^{-2}, $\beta = 0.35$ Å^{-1} and $T = 0.1$ eV. The chosen value of the parameter V_0 is compatible with poly(A)-poly(T) synthetic DNA [20]. It should be stressed that the effects of the random environment on the lattice dynamics is neglected hereafter. This assumption is reasonable due to the large mass of the nucleotides as compared to the mass of counterions.

We numerically solved the set of nonlinear equations (1) and (2) using a Runge–Kutta method of 4th order, considering a homopolymer DNA molecule under periodic boundary conditions. The initial polaron state in an unbiased lattice ($F = 0$) is obtained according to the procedure given in [14], including the dissipative term in equation (2) with $\gamma = 50$ THz. Once the stationary solution is found, it is then taken as the initial condition at $t = 0$ to solve equations (1) and (2) with $F \neq 0$.

The initial polaron obtained in our simulations in the unbiased and uniform DNA molecule is shown in figure 1 for different values of electron–lattice coupling constant χ and the lattice size $N = 500$. The polaron is narrower as χ increases, as expected.

3. Polaron motion and electric current density

As mentioned above, in the steady state the polaron moves with constant velocity in the uniform lattice ($\varepsilon_n = 0$). The steady-state velocity increases sublinearly with the applied electric
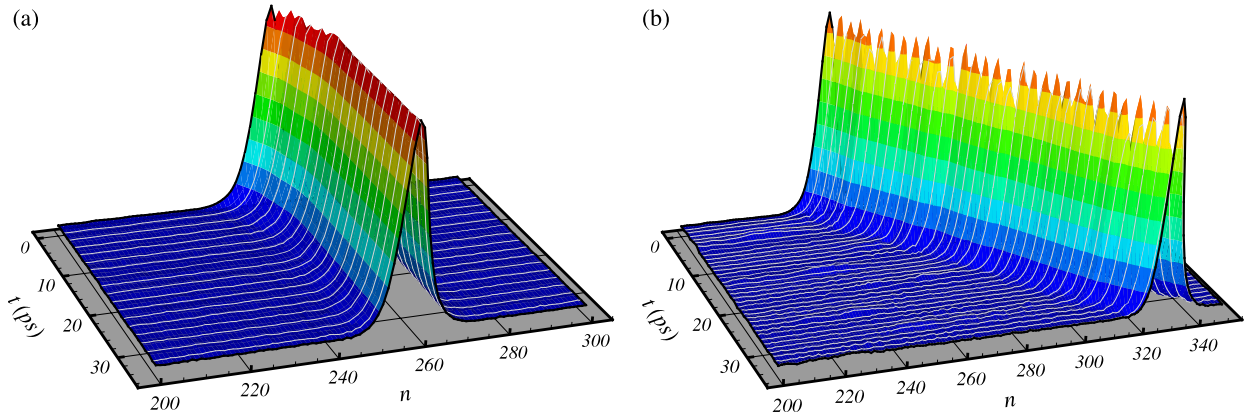
Figure 2. Modulus of the carrier wavefunction $|\psi_n(t)|$ as a function of position and time in a lattice of $N = 500$ sites for $\chi = 0.6$ eV Å^{-1}, $W = 3$ meV and (a) $F = 5$ kV cm^{-1} and (b) $F = 12$ kV cm^{-1}.
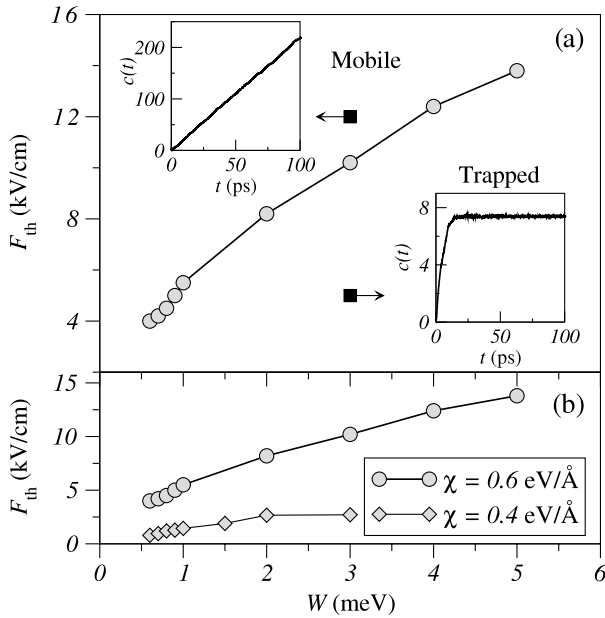(This figure is in colour only in the electronic version)

Figure 3. (a) Threshold electric field, F_{th}, above which the polaron becomes mobile, as a function of the magnitude of disorder for $\chi = 0.6$ eV Å^{-1}. The insets show the centroid as a function of time for the values of electric field and magnitude of disorder marked by solid squares. (b) Comparison of the threshold electric field, F_{th}, for $\chi = 0.4$ and 0.6 eV Å^{-1}.

field [18]. It is important to stress that in this model the polaron moves at constant velocity even for tiny values of the dc electric field, yielding a nonvanishing average current density $J(t)$ through the DNA

$$J(t) = \frac{\hbar e}{m_e N a^2} \sum_{n=1}^{N} \text{Im}[\psi_n^*(e^{i\omega_B t}\psi_{n+1} - e^{-i\omega_B t}\psi_{n-1})], \quad (5)$$

where m_e is the electron mass. We will show below that the polaron can be trapped when disorder is taken into account, and the electric field must exceed a threshold value to observe a mobile polaron. Disorder arising from the interactions with the environment is modeled by assuming that the molecular energy

levels form a random sequence. Thus, we take $\varepsilon_n = \bar{\varepsilon} + \Delta\varepsilon_n$ where the probability distribution for the uncorrelated random variables $\Delta\varepsilon_n$ is set as $\mathcal{P}(\Delta\varepsilon_n) = (1/W)\,\theta(W/2 - |\Delta\varepsilon_n|)$, θ being the Heaviside step function. W will be referred to as magnitude of disorder.

To characterize the trapping or motion of the polaron, we will study the centroid $c(t) = x(t) - x(0)$ of the carrier wavefunction, with $x(t) = \sum_n n|\psi_n(t)|^2$. When the polaron moves at constant velocity and electric current flows through the DNA molecule, namely $c(t) \sim t$, we will consider also the autocorrelation function

$$R(t) = \lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \int_{-\mathcal{T}/2}^{\mathcal{T}/2} J(t')[J(t'+t) - J(t')]\,dt' \quad (6)$$

as well as its Fourier transform, $R(\omega)$, referred to as the power spectral density.

4. Results

The time-domain evolution of the polaron in the weakly disordered DNA molecule depends on the magnitude of the dc electric field. For a given magnitude of disorder W, the polaron cannot move with constant velocity at low fields. Figure 2(a) shows the modulus of the wavefunction in a lattice of $N = 500$ sites as a function of position and time, when $W = 3$ meV for $\chi = 0.6$ eV Å^{-1} and $F = 5$ kV cm^{-1} (we set $\gamma = 5$ THz hereafter). Initially the polaron is centered at site $n = N/2 = 250$ and drifts during ~ 5 ps until it is trapped around site 257. Notice that the centroid of the polaron remains constant and no signatures of oscillations are found, indicating that the trapping mechanism is not dynamical localization [17] but localization by disorder. To observe the detrapping of the polaron, the electric field should be stronger than a threshold field. Figure 2(b) shows the modulus of the wavefunction when $F = 12$ kV cm^{-1} in the same lattice as in figure 2(a). Clearly the centroid increases linearly in time, indicating a constant velocity motion of the polaron.

Figure 3(a) shows the threshold electric field, F_{th}, above which the polaron becomes mobile, when $\chi = 0.6$ eV Å^{-1}.
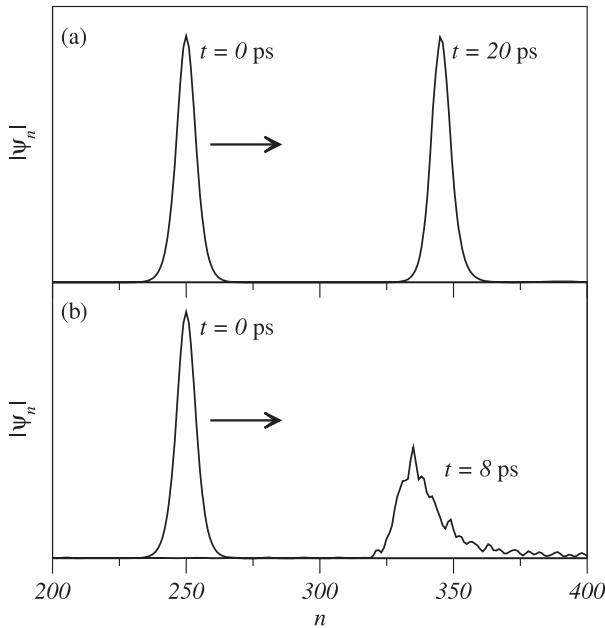
Figure 4. Snapshots of the modulus of the carrier wavefunction at times indicated on each curve when (a) $F = 3$ kV cm^{-1} and (b) $F = 5$ kV cm^{-1}. The remaining parameters are $\chi = 0.4$ eV Å^{-1} and $W = 1$ meV.

Figure 5. Power spectral density for $\chi = 0.6$ eV Å^{-1} and (a) $F = 5$ kV cm^{-1} and (b) $F = 12$ kV cm^{-1}. The magnitude of disorder is indicated on each curve. The upper curve in panel (b) is shifted upwards for clarity. The arrows indicate the value of the Bloch frequency $\omega_B = eFa/\hbar$ at each magnitude of the electric field.

As mentioned above, the threshold electric field depends on the magnitude of disorder, W. The dependence is slightly sublinear in the chosen range of parameters. Figure 3(b) compares the threshold field for $\chi = 0.4$ and 0.6 eV Å^{-1}. We observe a clear decrease of F_{th} as the electron–lattice coupling constant decreases and the lattice becomes stiffer.

It should be mentioned that the polaron is unstable at high electric field. In general we have found that the electric field above which the polaron becomes unstable increases upon increasing the electron–lattice coupling constant, in agreement with previous results [18]. Figure 4(a) shows the modulus of the carrier wavefunction of a stable polaron, in which its shape remains unchanged when $W = 1$ meV, $\chi = 0.4$ eV Å^{-1} and $F = 3$ kV cm^{-1}. The instability is clearly seen in figure 4(b) when the electric field is $F = 5$ kV cm^{-1}. In this case the carrier wavefunction loses its initial shape on increasing time. In general we have found that magnitude of disorder above which the polaron becomes unstable increases upon increasing the electron–lattice coupling constant. In addition, the polaron becomes unstable at a large magnitude of disorder, larger than the values used in the present work.

The frequencies involved in the polaron dynamics under an external bias can be determined accurately by calculating the power spectral density. Figure 5 displays this magnitude for $\chi = 0.6$ eV Å^{-1} and two different values of the electric field. The integration time in (6) was $\mathcal{T} = 300$ ps. Remarkably, in all cases we found that the power spectral density shows a clear maximum at the Bloch frequency $\omega_B = eFa/\hbar$. Disorder broadens the observed peak and satellite peaks appear at higher frequencies. The origin of the peak at the Bloch frequency is related to the breathing motion of the carrier. The width of the wavefunction oscillates harmonically with the
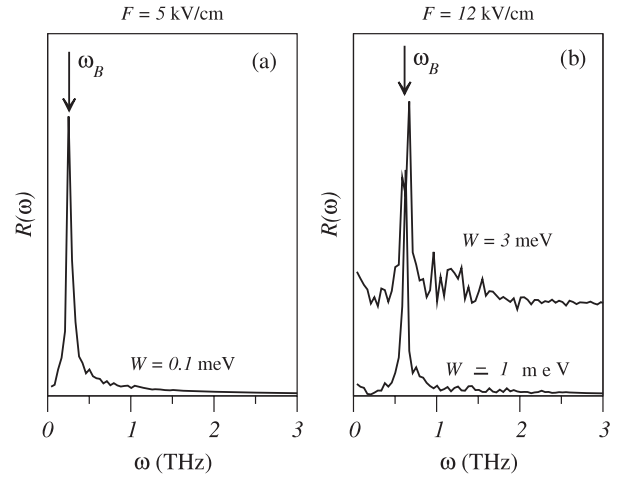
Bloch frequency and this oscillation is reflected in the averaged current density (5). It is worth stressing that in this regime of parameters including dissipation, the polaron does not perform Bloch oscillations. In other words, the centroid $c(t)$ does not oscillate but displays a uniform motion, increasing linearly with time (see left inset in figure 3(a)).

5. Conclusions

It is believed that charge migrates along the coupled π-orbitals of neighboring bases in DNA. Solute molecules and ions surrounding the DNA molecule may have a deep impact on the charge transport and, in particular, on the dynamics of large polarons. The environment affects not only the negatively-charged sugar-phosphate backbone but also the base molecules. As a consequence, the molecular levels can fluctuate around their ideal values due to the interaction with the environment. Therefore, realistic models of polaron transport should take these fluctuations into account. We have generalized the Peyrard–Bishop–Holstein model to include random site energies, neglecting the environment effects on the lattice dynamics. An applied dc electric field along the stacking direction drives the polaron migration.

As a major result we found that the polaron remains trapped in weakly disordered DNA molecules and low electric field. In other words, the electric field must exceed a threshold value to move the polaron. The threshold electric field becomes larger with an increasing magnitude of disorder. The occurrence of a threshold field effectively opens a gap in the current–voltage characteristic curve of the DNA molecule. We also found that the threshold electric field decreases as the lattice becomes stiffer. It should be mentioned that polaron trapping in the presence of an electric field and different site energies was also found in the time-dependent Su–Schrieffer–Heeger model [22].

From our analysis it became apparent that the polaron moves with a constant velocity or it is trapped, for the chosen parameters. In the latter case, when the magnitude of disorder is large enough, the DNA conductance decreases and the molecule becomes insulating at zero temperature. The study of polaron dynamics in disordered DNA at finite temperature is under progress and it will be reported elsewhere. Surprisingly, the power spectral density presents a clear peak at the Bloch frequency $\omega_B = eFa/\hbar$ when a current flows through the DNA. We related this behavior to the breathing motion of the polaron.

Acknowledgments

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