Effect of base-pair inhomogeneities on charge transport along the DNA molecule, mediated by twist and radial polarons

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Abstract. Some recent results for a three-dimensional, semi-classical, tight-binding model for DNA show that there are two types of polarons, namely radial and twist polarons, which can transport charge along the DNA molecule. However, the existence of two types of base pairs in real DNA makes it crucial to find out if charge transport also exists in DNA chains with different base pairs. In this paper, we address this problem in its simple case, a homogeneous chain except for a single different base pair, which we call a base-pair inhomogeneity, and its effect on charge transport. Radial polarons experience either reflection or trapping. However, twist polarons are good candidates for charge transport along real DNA. This transport is also very robust with respect to weak parametric and diagonal disorder.
1. Introduction

Charge transport in biomolecules is of relevance in many biological functions. Moreover, electronic transport plays a well-known and fundamental role in many biological processes, such as nervous conduction, photosynthesis, cellular respiration and redox reactions. Recently, DNA-mediated charge transport has focused much attention on experiments that have been conducted to determine its conductive properties, and theoretical studies have addressed the possibility of charge transport and its efficiency [1]. The importance of charge transport through DNA is significant because some mutations in living systems and radical migrations are critical issues in carcinogenesis studies and may yield insight into damage prevention or repair processes [2]–[4]. Moreover, charge transport has been demonstrated to proceed within HeLa cell nuclei [5] as well as in the nucleosome core particles [6], and can provide a practical method of genetic screening for known gene sequences and an alternative method to hybridization-based arrays [7]. Material scientists have considered the possibility that DNA is an object of fundamental physical interest for the development of DNA-based molecular technologies, as it possesses ideal structural and molecular recognition properties for use in self-assembling nanodevices with a definite molecular architecture [8].

Photochemical electron-transfer experiments have been carried out with femtosecond resolution, and have shown, with the precise control of the DNA sequences, a fast time scale (\(\leq 5\) ps) process, attributed to charge mobility along an unperturbed double strand, and a slower process (\(\leq 75\) ps), which they believe reflects charge hopping between perturbed domains along the DNA strand [9].

Experimental results have shown that DNA acts as a linear chain with overlapping \(\pi\) orbitals located at the stacked base pairs and its conductivity is very sensitive to disruption, caused by base-pair mistakes or interactions with proteins, in the base-pair stack. The transfer can be either slowed down or inhibited completely [10] depending on the base-pair sequences.

Moreover, the robust, malleable one-dimensional structure of DNA can be used to design electronic devices based on biomaterials [11]–[15].

The structure of the bent double-helix \(\lambda\)-DNA can be modelled by a network of oscillators taking into account deformations of the hydrogen bonds within a base pair and twist motions.
between consecutive base pairs. The three-dimensional semi-classical tight-binding model for DNA, which was first proposed in [16, 17], assumes that the electron motion is predominantly influenced by vibrational modes of the double helix. The non-linear interaction between the electron and the vibrational modes is responsible for the formation of polarons or electron–vibron breathers. These are localized excitation patterns that can be static, producing charge localization, or mobile, bringing about charge transport. Some other models with inhomogeneities have also been considered [18].

A variant of this model has been proposed in [19], which eliminates the restriction of the previous one, and the perturbation of the spatial variables were small enough to perform a linear approximation in the dynamical equations. Two types of polarons arise depending on the parameter $\alpha$, which describes the coupling between the transfer integral and the distance between nucleotides and the form of activation: radial polarons and twist polarons. For radial polarons, the deformations associated with the electronic charge affect mainly the radial variables, and for twist polarons, the angular ones. In the latter case, the moving polaron is slower than in the previous one, but it is more robust with respect to the introduction of parametric disorder. See [19] for details and [20] for twist polarons in another model.

In this paper, we consider the movement of polarons along the DNA chains made out of different base pairs. The most simple one consists of homogeneous DNA chains except for a single different base pair, which we call base-pair inhomogeneity.

We have found that when charge transport is mediated by means of a twist polaron, this moving carrier can transport charge along a base-pair inhomogeneity in a very efficient way. Moreover, charge transport persists under the introduction of a high degree of parametric disorder, which represents the inherent disorder in the surrounding medium and the inhomogeneous distribution of counterions along the DNA duplex [21]. On the other hand, radial polarons are either reflected or trapped by the base-pair inhomogeneity, making them poor candidates for charge transport along heterogeneous DNA at least in the framework of the tight-binding models.

2. DNA model

2.1. Description

We consider a variant [19] of the model Hamiltonian for charge transport along DNA, which was first proposed in [16]. We use the full dynamical equations of the system instead of performing linear approximations based on the assumption that the deformations of the molecule were small.

These models were designed to implement the basic characteristics of the DNA double-helix structure needed for a proper description of the charge transport dynamics. The starting point is the twist-opening model [22]–[24], which has taken into account the helicoidal structure of DNA and the torsional deformations induced by the opening of the base pairs. The bases are considered as single non-deformable objects. The helicoidal structure of the DNA is described in a cylindrical reference system and the $n$th base pair has two degrees of freedom, namely $(r_n, \phi_n)$, where $r_n$ represents the radial displacement of the base pair from the equilibrium value $R_0$, and $\phi_n$ represents the angular deviation from equilibrium angles with respect to a fixed external reference frame. As we are interested in base-pair vibrations and not in acoustic motions, the centre-of-mass of each base pair is fixed, i.e. the
two bases in a base pair are constrained to move symmetrically with respect to the axis of the molecule. Moreover, the distance between two neighbouring base-pair planes will be treated as fixed, since the DNA is less deformable in the axial direction than within the base-pair planes [22].

A sketch of the helicoidal structure of the DNA model is shown in figure 1. Transverse displacements of the base pairs are deformations of the H bonds, and the angular twist and the radial vibrational motion evolve independently on two different time scales. Then they can be considered as decoupled degrees of freedom in the harmonic approximation of the normal-mode vibrations [25].

2.2. Hamiltonian

The Hamiltonian for electron transport along a strand of DNA is given by $\hat{H} = \hat{H}_{el} + \hat{H}_{rad} + \hat{H}_{twist}$, where $\hat{H}_{el}$ corresponds to the part related to the particle-charge transport over the base pairs, $\hat{H}_{rad}$ describes the dynamics of the H-bond vibrations and $\hat{H}_{twist}$ is the part corresponding to the dynamics of the relative twist angle between two consecutive base pairs. This electronic part is described by a tight-binding system of the form

$$\hat{H}_{el} = \sum_{n} E_n |n\rangle \langle n| - V_{n-1,n} |n-1\rangle \langle n| - V_{n+1,n} |n+1\rangle \langle n|, \quad (1)$$

where $|n\rangle$ represents a localized state of the charge carrier at the $n$th base pair. The quantities $\{V_{n,n-1}\}$ are the nearest-neighbour transfer integrals along base pairs and $\{E_n\}$ are the energy on-site matrix elements. A general electronic state is given by $|\Psi\rangle = \sum_{n} c_n(t) |n\rangle$, where $c_n(t)$ is the probability amplitude for finding the charged particle in the state $|n\rangle$. The time evolution of $\{c_n(t)\}$ is obtained from the Schrödinger equation $i\hbar (\partial |\Psi\rangle / \partial t) = \hat{H}_{el} |\Psi\rangle$.

The nucleotides are large molecules and they move much more slowly than a charged particle; then the lattice oscillators can be described classically and $\hat{H}_{rad}$ and $\hat{H}_{twist}$ are, de facto, classical Hamiltonians. For homogeneous chains they are given by (omitting the hat
\[ H_{rad} = \sum_n \left[ \frac{1}{2M} (p^r_n)^2 + \frac{M \Omega^2_{r,n}}{2} r^2_n \right], \quad (2) \]

\[ H_{twist} = \sum_n \left[ \frac{1}{2J} (p^\phi_n)^2 + \frac{J \Omega^2_{\phi}}{2} (\phi_n - \phi_{n-1})^2 \right], \quad (3) \]

where \( p^r_n \) and \( p^\phi_n \) are the conjugate momenta of the radial and angular co-ordinates, respectively. In these expressions, \( M \) is the mass of each base pair \( (M = 2m, m \) being an average estimation of the nucleotide mass), \( J = MR^2_0 \) is the moment of inertia of each base pair and \( \Omega_{r,n} \) is the linear radial frequency which is proportional to the strength of the hydrogen bonds. Indeed, for an homogeneous chain all these frequencies are equal, i.e. \( \Omega^2_{r,n} = b_n \Omega^2_0 \) with \( b_n = 1 \) \( \forall n \).

In general, the ionization potential of different nucleotides differs by a value in the range 0.2–1.0 eV [27]. In our model, this implies different values of the on-site energies \( E^0_n \) for each base pair. In this work, we have focused on geometrical effects due to the stretching of the chain over the charge, and we have considered \( E^0_n \) independent of the type of base.

The electronic part of the Hamiltonian, \( \hat{H}_e \), has a dependence on the structural variables \( r_n \) and \( \phi_n \) through the dependence of the matrix elements \( E_n \) and \( V_{n,n-1} \) on them. The energy on-site matrix elements are given by \( E_n = E^0_n + k r_n \) [28], expressing the modulation of the on-site electronic energies \( \{ E^0_n \} \) by the radial deformations of the base pairs. The transfer matrix elements \( V_{n,n-1} \), which are responsible for the transport of the electron along the stacked base pairs, are assumed to depend on the distance between two consecutive bases along a strand \( d_{n,n-1} \) according to \( V_{n,n-1} = V_0 (1 - \alpha d_{n,n-1}) \), where \( \alpha \) is a parameter that describes the influence of the distance between nucleotides, and the latter is determined by

\[ d_{n,n-1} = \sqrt{a^2 + (R_0 + r_n)^2 + (R_0 + r_{n-1})^2 - 2(R_0 + r_n)(R_0 + r_{n-1}) \cos(\theta_0 + \theta_{n,n-1})} - l_0, \quad (4) \]

with \( l_0 = (a^2 + 4R_0^2 \sin^2(\theta_0/2))^{1/2}, \) where \( a \) is the vertical distance between two consecutive base pairs.

In this paper, as in [19], we have not used the expansion of this expression up to first-order around the equilibrium positions, as was performed in [16, 17]. This allows us to consider parameters that allow larger deformations in the angular variables.

Realistic parameters for the DNA are given in [23, 29]. We have considered: \( a = 3.4 \text{ Å}, \) \( m = 300 \text{ amu}, R_0 = 10 \text{ Å}, \) \( \Omega_r = 8 \times 10^{12} \text{ s}^{-1}, \) \( \Omega_\phi = 9 \times 10^{11} \text{ s}^{-1}. \) By \textit{ab initio} calculations, the transfer integral between adjacent nucleotides was found to be of the order of 0.1–0.4 eV.
Although this transfer integral is different for each pair of different nucleotides, we will consider the same value for all neighbouring cases $V_0 = 0.1 \text{ eV}$, a widely used assumption valid to reproduce ab initio results and experiments [33, 34].

We scale the time according to $t \rightarrow \Omega_\tau t$, and we introduce the dimensionless quantities $\tilde{r}_n = r_n(M\Omega_\tau^2/V_0)^{1/2}$, $\tilde{k}_n = k_n/(M\Omega_\tau^2V_0)^{1/2}$, $\tilde{E}_n = E_n/V_0$, $\tilde{\Omega} = \Omega_\phi/\Omega_\tau$, $\tilde{V} = V_0/(J\Omega_\tau^2)$, $\tilde{\alpha} = \alpha(V_0/M\Omega_\tau^2)^{1/2}$ and $\tilde{R}_0 = R_0(M\Omega_\tau^2/V_0)^{1/2}$.

2.3. Dynamical equations

Using the expectation value of the electronic contribution to the Hamiltonian, the new classical Hamiltonian \( \bar{H} = \langle \phi | \hat{H} | \phi \rangle/V_0 \) is given in the scaled variables (omitting the tildes) by

\[
\bar{H} = \sum_n \left\{ \frac{1}{2} (\dot{r}_n^2 + b_n r_n^2) + \frac{1}{2} R_0^2 (\dot{\phi}_n^2 + \Omega^2 (\phi_n - \phi_{n-1})^2) \right\} + (E_n^0 + kr_n) |c_n|^2 - (1 - \alpha d_{n,n-1}) (c_n^* c_{n-1} + c_{n-1}^* c_n) \right\}. \tag{5}
\]

The Schrödinger equation and the Hamiltonian equations lead to the scaled dynamical equations of the system

\[
i \tau \dot{c}_n = (E_n^0 + kr_n) c_n - (1 - \alpha d_{n+1,n}) c_{n+1} - (1 - \alpha d_{n,n-1}) c_{n-1}, \tag{6}
\]

\[
\ddot{r}_n = -b_n r_n - k |c_n|^2 - \alpha \left[ \frac{\partial d_{n,n-1}}{\partial r_n} (c_n^* c_{n-1} + c_{n-1}^* c_n) + \frac{\partial d_{n+1,n}}{\partial r_n} (c_{n+1}^* c_{n+1} + c_{n+1}^* c_n) \right], \tag{7}
\]

\[
\ddot{\phi}_n = -\Omega^2 (2\phi_n - \phi_{n-1} - \phi_{n+1}) - \alpha V \left[ \frac{\partial d_{n,n-1}}{\partial \phi_n} (c_n^* c_{n-1} + c_{n-1}^* c_n) + \frac{\partial d_{n+1,n}}{\partial \phi_n} (c_{n+1}^* c_{n+1} + c_{n+1}^* c_n) \right], \tag{8}
\]

where the quantity $\tau = h\Omega_\tau/V_0$ measures the time-scale separation between the fast electron motion and the slow bond vibrations. In the ordered case, with $E_n = E_0$, $\forall n$, in the limit $\alpha = 0$, the set of coupled equations represents the Holstein system, widely used in studies of polaron dynamics in one-dimensional lattices. Also, for $\alpha = k = 0$, and random $E_0^n$, the Anderson model is obtained.

The scaled parameters take the values $\tau = 0.053$, $\Omega^2 = 0.013$, $V = 2.5 \times 10^{-4}$, $R_0 = 63.1$ and $l_0 = 44.5$. We fix the value $k = 1$ and consider the parameter $\alpha$ as adjustable.

3. Charge transport mediated by mobile polarons

3.1. Mobile polarons

The principal interest of this paper consists of the study of charge transport along the double strand by moving polarons in the presence of a base-pair inhomogeneity. First, we have to obtain localized stationary solutions of equations (6)–(8). In the appendix, we present the

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procedure followed for obtaining these stationary solutions for different cases: homogeneous chains and inhomogeneous chains. The polaron motion can be activated under certain conditions. A systematic method to do this, known as the *pinning mode* method [35], consists of perturbing the (zero) velocities of the ground state with localized, spatially antisymmetric modes obtained in the vicinity of a bifurcation. This method leads to moving entities with very low radiation, but has the inconvenience of being applicable only in the neighbourhood of certain values of the parameters. An alternative is the discrete gradient method [36], perturbing the (zero) velocities of the stationary state \( \{ r_n(0) \}, \{ \phi_n(0) \} \) in a direction parallel to the vectors \( (\nabla r)_n = (r_{n+1} - r_{n-1}) \) and/or \( (\nabla \phi)_n = (\phi_{n+1} - \phi_{n-1}) \). Although this method does not guarantee mobility, it nevertheless proves to be successful in a wide parameter range. We will denote the energy of the perturbation as \( \Delta K = \lambda^2 / 2 \), where \( \lambda \) is the modulus of the vector used to perturb the system (parallel to \( \nabla r_n \) and/or \( \nabla \phi_n \)). This energy gives us the difference in energy between the moving polaron and the static one, and it is usually called the activation energy.

### 3.2. Homogeneous chains

In this section, we recall the basic results obtained in [19] (see details therein). For homogeneous chains in the absence of diagonal disorder, \( E^0_n = E^0 \), \( \forall n \), and if the parameter \( \alpha \) is small enough, it is not possible to move the polarons by perturbing the angular variables. Mobility can be accomplished only by perturbing through the radial variables. However, for larger values of the parameter \( \alpha (\alpha \gtrsim 0.01) \), the polarons can only be moved by perturbing the angular variables, i.e. perturbations of the radial variables cannot activate mobility. Nevertheless, for intermediate values of the parameter \( \alpha (0.005 \lesssim \alpha \lesssim 0.01) \), the polarons can become mobile by perturbing any set of variables, the radial or the angular ones. The movement is rather different: when the polaron propagation is activated by means of only radial perturbations, its characteristics are similar to the radial movability regime, and similarly when it is activated by angular perturbations. A detailed analysis of these different regimes can be found in [19]. In general, radial movability requires less energy and has higher velocity when compared with the angular one. Also, the limits of these regimes are not exact, depending on the kinetic energy of the perturbation.

If a disorder in the on-site energies \( E^0_n \) is introduced, with random values \(| E^0_n | < \Delta E \), we find that moving polarons exist below a critical value \( \Delta E_{\text{crit}} \). Beyond this value, polarons cannot be moved. In general, as shown in figure 2, corresponding to the mixed regime where a polaron can be activated (in the absence of disorder), by means of both angular and radial perturbations, the mobility induced by angular activation is more robust with respect to parametric disorder. If the disorder is high enough, radial perturbations that could move a polaron destroy it. Thus, it can only be activated by means of angular perturbations. In this case, the movement is similar to the ordered case, the polaron has lower velocity, and the activation energy is higher than in the radial movability regime.

As shown in figure 2, it can be appreciated that for a polaron in the mixed regime, and if \( \Delta E \) is high enough, it is impossible to move it with radial perturbations, but only with angular perturbations. In this situation, the movement is very similar to the ordered case.

### 3.3. DNA chains with a base-pair inhomogeneity

The studies of polarons in homogeneous chains are only applicable to synthetic DNA made up of a single type of base pair. In real DNA, the two different base pairs, A-T and G-C,
Figure 2. Velocity of the polaron as a function of the energy $\Delta K$ corresponding to the mixed regime when the polaron is activated by means of angular perturbations ($\alpha = 0.01$). ○, —, disordered case with $\Delta E = 0.05$; Δ, --, ordered case.

combine in different ways constituting the genetic code. Thus, as a first step in this direction, we consider a homogeneous DNA chain except for a single base pair of a different type. Systems of this type are easily synthesized and the numerical and theoretical results could be compared with the experimental ones. The outcome would help to determine the actual DNA parameters and, hence, the type of polarons that can be expected. There are two different systems: (a) a hard-inhomogeneity, i.e. an A-T DNA chain with a C-G inhomogeneity; and (b) a soft inhomogeneity, i.e. a C-G DNA chain, with an A-T inhomogeneity.

We activate the motion of a stationary polaron, using the discrete-gradient method, at a site about a hundred sites away form the location of the inhomogeneity. Different types of moving polarons can be obtained: radial, twist and mixed ones with different energies, and we observe whether the polarons are reflected, refracted or trapped.

- **Soft inhomogeneity.** In this case, radial polarons moving along a chain of C-G base pairs are trapped by the soft A-T base pair as shown in figure 3. Trapping is caused by resonances between the polaron and the stationary state centred at the inhomogeneity.

  However, when the polarons are activated by twist modes, the moving polarons are always transmitted. The inhomogeneity acts as a potential well, as shown in figure 4. Note that the polaron briefly adopts the shape of the ground state while passing through the inhomogeneity.

- **Hard inhomogeneity.** In this case, a radial polaron moving along a chain of A-T base pairs interacts with the C-G inhomogeneity and is always reflected, as shown in figure 5. This phenomenon is due to the impossibility of resonances, because the profiles of the radial components of the polaron and the stationary one, located at the inhomogeneity, are different.
Figure 3. Soft inhomogeneity and radial polarons. Trapping phenomenon due to the interaction between a moving radial polaron in a C-G chain with an A-T base pair.

Figure 4. Soft inhomogeneity and twist polarons. Transmission phenomenon due to the interaction between a moving polaron in a C-G chain with an A-T base pair.

If the moving polaron is of the twist type, it is always transmitted as shown in figure 6. In this case, the behaviour is similar to the movement of a particle through a potential barrier, i.e. its velocity first decreases and then increases until its entry value. Note that again the polaron adopts briefly the shape of the ground state while passing through the inhomogeneity.

In the mixed regime, the phenomena correspond exactly to the type of polaron activated. Finally, we have performed all the previous simulations introducing a small parametric disorder; in all cases the results are qualitatively similar and are summarized in table 1.

The results are clear: the only possible candidate for charge transport mediated by polarons in an inhomogeneous chain are the twist modes. Accurate experiments are needed to find out
good values of the parameters and for determining which kind of regime is possible in DNA and, therefore, if polarons may have a role in charge transport.

Some preliminary numerical tests with a more realistic model where the ionization energy of a C-G base pair is lower than the A-T base pair by a value of the order of 0.5 eV, show a trapping phenomenon, similar to that observed experimentally [37], where charge moves in an A-T chain by means of twist modes and reach a C-G base pair. In all other cases, we have always observed a reflection phenomenon. This problem will be the object of further research.
Table 1. Different types of moving polarons and their behaviour when they interact with a local inhomogeneity in C-G and A-T chains.

|          | Radial moving regime | Twist moving regime | Mixed regime |
|----------|----------------------|---------------------|--------------|
|          |                      |                     | Radial       |
|          |                      |                     | perturbations|
| A-T chain| Reflection           | Transmission        | Reflection   |
| C-G chain| Trapping             | Transmission        | Transmission |

4. Conclusions

We have considered a fully non-linear, three-dimensional, semi-classical, tight-binding model for charge transport in DNA with a single base-pair inhomogeneity. Two types of this inhomogeneity were considered: soft, composed of G-G base pairs with an A-T inhomogeneity and hard, with the complementary composition.

In a previous work [19], it has been described that in this system there exist two types of polarons, twist polarons and radial polarons, for which the electronic variables are coupled essentially with the radial or angular modes. The existence of these polarons depends both on the system parameters and how the movement of the polaron is activated. The properties of the two types of moving polarons are different. In general, the twist polarons are more robust with respect to parametric disorder, the polaron has lower velocity and the activation energy is higher than in the radial movability regime.

In an inhomogeneous chain with a single different base pair as a local inhomogeneity, we have observed that moving polarons activated by angular perturbations are always transmitted by the inhomogeneity. If the polarons are activated by radial perturbations, we have never observed a transmission of the charge across the inhomogeneity.

Some recent experiments on electron transfer in the DNA molecule [37] show that electrons can migrate over long distances between a triplet C-G base pair and a C-G base pair separated by a number \( n \) of A-T base pairs. Moreover, the triplet C-G base pairs act as a sink for holes in the chain. In our model, by decreasing the ionization energy of the C-G base pair slightly, as observed in real DNA, we are able to reproduce the experimental results. Some more detailed numerical simulations are currently underway and will be published in due time. Also, these experimental techniques are probably useful to contrast our results experimentally.

In our model, we have considered a DNA chain in the vacuum. We have focused on the polaronic character of the charge carrier and its interaction with the chain. If the influence of the medium is not too strong, it is expected that the results would be similar to those obtained in the vacuum. In fact, they are in agreement with some experimental observations on DNA in aqueous solutions [37]. The inclusion of thermal effects will be the subject of further studies, although in similar systems it has been shown that the main characteristics of the charge transport do not change very much when the temperature is considered [38].

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Appendix. Stationary polaron-like states

In this section, we describe the procedure followed for obtaining linearly stable, stationary localized states of our model given by equations (6)–(8). These solutions have been used in the previous section to generate mobile polarons. Since the adiabatic parameter $\tau$ is small enough, the fastest variables are $\{c_n\}$, with a characteristic frequency (the linear frequency of the uncoupled system) of order $1/\tau \sim 19$, followed by $\{r_n\}$ with frequency unity and $\{\phi_n\}$ with $\Omega_\phi \sim 0.11$. We can suppose initially that $r_n$ and $\phi_n$ are constant, i.e. we use the Born–Oppenheimer approximation. For this purpose, we use a modification of the numerical method outlined in [28, 39]. We substitute $c_n = \Phi_n \exp(-iEt/\tau)$ in equation (6), with time-independent $\Phi_n$s, and we obtain a non-linear difference system $E\Phi = \hat{A}\Phi/\|\hat{A}\Phi\|$ from which a map $\Phi' = \hat{A}\Phi/\|\hat{A}\Phi\|$ is constructed, $\|\cdot\|$ being the quadratic norm.

Thus, using equations (6)–(8), the stationary solutions must be attractors of the map:

$$r_n' = -\frac{k}{b_n}|c_n|^2,$$

$$\phi_n' = \frac{1}{2}(\phi_{n+1} + \phi_{n-1})$$

$$c_n' = \frac{[(E_n + kr_n)c_n - (1 - \alpha d_n)c_{n+1} - (1 - \alpha d_n)c_{n-1}]}{||[(E_n + kr_n)c_n - (1 - \alpha d_n)c_{n+1} - (1 - \alpha d_n)c_{n-1}]||},$$

where $d' = d(r', \phi')$. The starting point is a completely localized state given by $c_n = \delta_{n,0}$, $r_n = 0$ and $\phi_n = 0$, $\forall n$. Then the map is applied until convergence is achieved. In this way, both stationary solutions and their energy $E$ can be obtained.

First, we have analysed the homogeneous and ordered case, i.e. $E_n^0 = E_0$, which arises in synthetic DNA (the constant $E_0$ can be set to zero by means of a gauge transformation). As shown in figure A.1, in a typical ground state the charge is fairly localized at a few sites, and the amplitudes decay monotonically and exponentially with increasing distance from the central site. The associated patterns of the static radial and relative angular displacements are similar.

We can introduce a certain degree of parametric disorder in the on-site electronic energy $E_n^0$ by means of a random potential $E_n^0 \in [-\Delta E, \Delta E]$, with mean value zero and different interval sizes $\Delta E$. In this case, the localized excitation patterns do not change qualitatively,
Figure A.1. Profiles of the ground state in the homogeneous and ordered chain: (a) wave function amplitudes $|c_n|^2$; (b) static radial displacements $r_n$; and (c) static twist elongations $\theta_{n,n-1}$.

Figure A.2. Profiles of the ground state in the homogeneous and disordered chain: (a) wave function amplitudes $|C_n|^2$; (b) static radial displacements $r_n$; and (c) static twist elongations $\theta_{n,n-1}$.

as shown in figure A.2. However, as the translational invariance is broken by the disorder, the localized excitation pattern is not symmetric with respect to a lattice site, which is different from the ordered case. Also, the localization is enhanced with the disorder, due to Anderson localization [40].
Figure A.3. Profiles of the ground state in a C-G chain centred in an A-T base pair inhomogeneity: (a) wave function amplitudes $|C_n|^2$; (b) static radial displacements $r_n$; and (c) static twist elongations $\theta_{n,n-1}$.

Figure A.4. Profiles of the ground state in an A-T chain centred in a C-G base pair inhomogeneity: (a) wave function amplitudes $|C_n|^2$; (b) static radial displacements $r_n$; and (c) static twist elongations $\theta_{n,n-1}$.

We consider now a chain with a local inhomogeneity due to the existence of a single base pair which is different from the other ones (without disorder). Our results show that the ground state centred in a site far from this local inhomogeneity is qualitatively similar to that obtained in the homogeneous chain case. Nevertheless, differences appear if we consider the
stationary state centred in the inhomogeneity. In a C-G chain, with an A-T base pair as the local inhomogeneity, the shape of the ground state is qualitatively similar to that obtained in the homogeneous case, as shown in figure A.3. In an A-T chain, with a C-G base pair as the local inhomogeneity, the static radial displacements are different, as shown in figure A.4. As we have seen in the previous section, this fact determines the transmission, reflection or trapping of a moving polaron by the inhomogeneity.

References

[1] Gasper S M and Schuster G B 1997 J. Am. Chem. Soc. 119 12762
[2] Boiteux S, Gellon L and Guibourt N 2002 Free Radic. Biol. Med. 32 1244
[3] Burrows C J and Muller J G 1998 Chem. Rev. 98 1109
[4] Friedman K A and Heller A 2001 J. Phys. Chem. B 105 11859
[5] Núñez M E, Holmquist G and Barton J 2001 Biochemistry 40 12465
[6] Núñez M E et al 2000 Biochemistry 39 6190
[7] Boon E M, Ceres D M, Drummond T G, Hill M G and Barton J K 2000 Nat. Biotechnol. 18 1096 (erratum 1318)
[8] Mao C et al 2000 Nature 407 605
[9] Wan C et al 1999 Proc. Natl Acad. Sci. USA 96 6014
[10] Wan C et al 2000 Proc. Natl Acad. Sci. USA 97 14052
[11] Ratner M 1999 Nature 397 480
[12] Fink H W and Schönenberger C 1999 Nature 398 407
[13] Tran P, Alavi B and Gruner G 2000 Phys. Rev. Lett. 85 1564
[14] Braun E, Eichen Y, Sivan U and Ben-Yoseph G 1998 Nature 391 775
[15] Porath D, Bezyradin A, de Vries S and Dekker C 2000 Nature 403 635
[16] Hennig D, Archilla J F R and Agarwal J 2003 Physica D 180 256
[17] Archilla J F R, Hennig D and Agarwal J 2003 Localization and Energy Transfer in Nonlinear Systems ed L Vázquez, M P Zorzano and R S Mackay (Singapore: World Scientific) pp 153–60
[18] Muto V 1992 Nanobiology 1 325
[19] Palermo F, Archilla J F R, Hennig D and Romero F R 2003 J. Phys. A: Math. Gen. submitted
[20] Zhang W, Govorov A O and Ulloa S E 2002 Phys. Rev. B 66 060303
[21] Barnett R N, Cleveland C L, Joy A, Landman U and Schuster G B 2001 Science 294 567
[22] Barbi M 1998 PhD Thesis Università degli Studi di Firenze
[23] Barbi M, Cocco S and Peyrard M 1999 Phys. Lett. A 253 358
[24] Barbi M, Cocco S, Peyrard M and Ruffo S 1999 J. Biol. Phys. 24 97
[25] Cocco S and Monasson R 2000 J. Chem. Phys. 112 10017
[26] Salerno M 1991 Phys. Rev. A 44 5292
[27] Brunaud G et al 2002 Phys. Chem. Chem. Phys. 4 6072
[28] Kalosakas G, Aubry S and Tsironis G P 1998 Phys. Rev. B 58 3094
[29] Stryer L 1995 Biochemistry (New York: Freeman)
[30] Sugiyama H and Saito I 1996 J. Am. Chem. Soc. 118 7063
[31] Voityuk A A et al 2001 J. Chem. Phys. 114 5614
[32] Zhang H et al 2002 J. Chem. Phys. 117 4578
[33] Cuniberti G et al 2002 Phys. Rev. B 65 241314
[34] Berlin Y A, Burin A L and Ratner M A 2000 Superlatt. Microstruct. 28 241
[35] Chen D, Aubry S and Tsironis G P 1996 Phys. Rev. Lett. 112 4776
[36] Ibáñes M, Sancho J M and Tsironis G P 2002 Phys. Rev. E 65 041902
[37] Giese B, Amaudrut J, Köhler K, Spormann M and Wessely S 2001 Nature 412 318
[38] Hennig D, Archilla J F R, Dorignac J and Starikov E 2003 Phys. Rev. B submitted
[39] Voulgarakis N K and Tsironis G P 2001 Phys. Rev. B 63 14302
[40] Anderson P W 1958 Phys. Rev. 109 1492