Radial and twist charge transport in a 3D DNA model. Effect of disorder and impurities

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Transparencies: http://www.us.es/gfnl

Previous results

D. Heenig, J.F.R. Archilla, J. Agarwall,Physica D (To appear, 2003); J.F.R. Archilla, J. Agarwall, D. Heenig, World Scientific, special issue (To appear 2003)

Electronic transport through DNA

- Important role for biological functions. Biosynthesis and DNA repair mechanism after radiation damage.M.D. Purugganan *et al*. Science **247**, 6548 (1988); D.N. Beratan *et al*., *ibid*. **258**, 1740 (1997), C.J. Murphy *et al*., *ibid* **262**, 1025 (1993); M.R. Arkin *et al*., *ibid*. **273**, 475 (1996); P.J. Dandliker *et al*., *ibid*. **257**, 1465 (1997).
- Technological interest. Applications in molecular electronics based in biomaterials. M. Ratner, Nature **397**, 480 (1999); A. Yu. Kasumov *et al*., Science **291**, 280 (2001).

Experimental results are controversial (variety DNA sequences, layouts and conditions)

- DNA behaves as a well conducting one-dimensional molecular wire. D.B. Hall *et al*., Nature **382**, 731 (1996); D.B. Hall *et al*., J. Am. Chem. Soc. **119**, 5045 (1997); M.R. Arkin *et al*., Chem. Biol. **4**, 369 (1997); Y. Okahata *et al*., J. Am. Chem. Soc. **120**, 6165 (1998); F.D. Lewis *et al*., Science **277**, 673 (1997); E. Meggers *et al*., **120**, 12950 (1998); H.W. Fink *et al*., Nature **398**, 407 (1999); P. Tran *et al*., Phys. Rev. Lett. **85**, 1564 (2000); B. Giese *et al*., Nature **397**, 480 (1999).
- DNA is insulating. E. Braun *et al*.,Nature **391**, 775 (1998).
- DNA can be a semiconductor. D. Porath *et al*., Nature **403**, 635 (2000).

At present: Charge carriers can hop along the DNA over distances of at least a few nanometers. Electronic transport through DNA molecules over larger distances is not clear

Theoretical models

The DNA structure is ideal for electron/hole transfer. It has been proposed that charge transference through DNA proceeds along a one-dimensional pathway constituted by the overlap between π-orbitals in neighboring base pairs. D.D. Eley, D.I. Spivey, Trans. Faraday Soc. 58, 411 (1962). DNA can be viewed as a "molecular wire", a one dimensional twisted chain of stacked base pairs with a somewhat flexible structure. Y.B. Berlin *et al*, Super lattices Microstruct., **28**, 241 (2000).

Conduction mechanisms

- Coherent tunneling. D.D. Eley, D.I. Spivey, Trans. Faraday Soc. 58, 411 (1962).
- Incoherent phonon-assisted hopping. D. Ly *et al*., J. Am. Chem. Soc. **118**, 8747 (1996). J. Jortner, Proc. Nat. Acad. Sci. USA, **95**, 12759 (1998)
- Classical diffusion under thermal fluctuations. R. Bruinsma *et al*., Phys. Rev. Lett. **85**, 4393 (2000).
- Variable range hopping between localized states. Z.G. Yu Xueyu Song, Phys. Rev. Lett. **86**, 6018 (2001).
- Charge carriers assisted by solitons. Z. Hermon *et al*., Europhys. Lett. **43**, 482 (1998).
- Charge carrier assisted by polarons. E. Conwell *et al*., Proc. Nat. Acad. Sci. USA, **97**, 4556 (2000); S.V. Rakhmanova *et al*., J. Phys. Chem. B **105**, 2056 (2001); D. Ly *et al*., J. Am. Chem. Soc. **121**, 9400 (1999); S. Komineas *et al*., Phys. Rev. E **65**, 061905 (2002); D.M. Baso, E.M. Conwell, Phys. Rev. E **65**, 061902 (2002).

Polaron charge transport model

- The charge carriers can have a polaron character. Nonlinear approach based on the concepts of polarons and breather solutions.

- Structure of the double helix modeled by a network of oscillators. M. Peyrard, A.R. Bishop, Phys. Rev. Lett. **62**, 2755 (1989); L.V. Yakushevich, Quart. Rev. Biophys. **26**, 201 (1993). We consider a variant of the twist-opening model. M. Barbi, PhD Thesis, Università degli Studi di Firenze (1998); M. Barbi *et al*. Phys. Lett. A **253**, 358 (1999); M. Barbi *et al*. Jou. Biol. Phys. **24,** 97 (1999).

- Electronic motion described by a tight-binding system

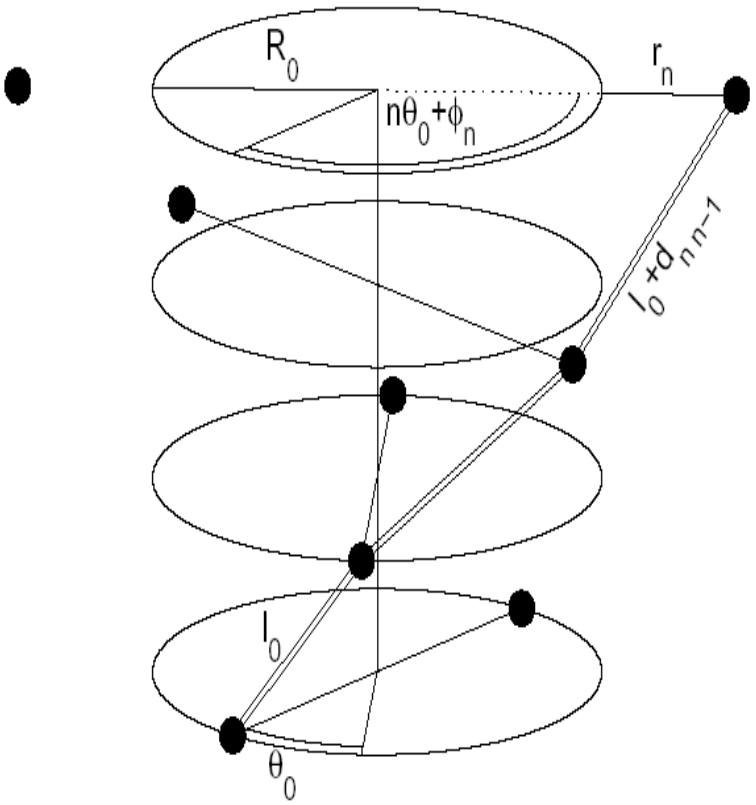
- We consider different cases:

  - An ordered homogeneous chain, as arises in synthetics DNA (ideal conditions)

  - A disordered chain. We introduce random parametric disorder in order to study the stability of this charge transport mechanism under the impact of this effect.

  - An homogeneous chain with a local inhomogeneity, to study the interaction of the polaron with different base pairs. The effect of the base sequence can be crucial for the dynamical behavior of localized movable distortions. M. Salerno. Phys. Rev. A **44**, 5292 (1991).

The model



- Helicoidal structure of DNA described in a cylindrical reference system. We consider deformations of the hydrogen bond within a base pair and twist motions between adjacent base pairs. We treat the distance between two neighboring base pair planes as fixed.
- We consider all molecular potentials in their harmonic limits.
- The harmonic treatment implies that the angular and radial motions evolve on different time scales. We regard them as decoupled variables. S. Cocco, R. Monasson, J. Chem. Phys. **112**, 10017 (2000)
- Three dimensional, semi classical, tight-binding system.

$\{r_n\}$ represent the radial displacements from its equilibrium value R_0.
$\{\phi_n\}$ represent the angular displacements from its equilibrium value $n\theta_0$.
$\{\theta_n\}= \phi_n - \phi_{n-1}$,deviation of the relative angle between two adjacent base pair from its equilibrium value θ_0.
l_0+d_{nn-1}, distance between two consecutive base pairs; l_0 equilibrium distance

Hamiltonian

Hamiltonian of the system $\widehat{H} = \widehat{H}_{el} + \widehat{H}_{rad} + \widehat{H}_{twist}$

Particle charge transport Hamiltonian

$$\widehat{H}_{el} = \sum_n E_n |n\rangle\langle n| - V_{n-1,n}|n-1\rangle\langle n| - V_{n+1,n}|n+1\rangle\langle n|$$

$$E_n = E_n^0 + k r_n \qquad V_{n,n-1} = V_0(1 - \alpha d_{n,n-1})$$

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

$$l_0 = (a^2 + 4R_0^2 \sin^2(\theta_0/2))^{1/2}$$

Lattice oscillations Hamiltonian (classical)

$$H_{rad} = \sum_n \left[\frac{1}{2M}(p_n^r)^2 + \frac{M\Omega_{r_n}^2}{2} r_n^2 \right],$$

$$H_{twist} = \sum_n \left[\frac{1}{2J}(p_n^\phi)^2 + \frac{J\Omega_\phi^2}{2} (\phi_n - \phi_{n-1})^2 \right]$$

Parameter values

Realistic parameter for DNA molecules. M. Barbi *et al.*, Phys. Lett. A **253**, 358 (1999); L. Stryer, *Biochemistry*, Freeman, New York, 1995.

- a=3.4 Å
- m=300 amu
- R_0=10 Å
- Ω_ϕ=9 10^{11} s^{-1}
- V_0=0.1 eV
- M=2m
- $J=MR_0^2$
- θ_0=36 º
- No reliable data for parameters α and k. Adjustable parameters

Ω_r=8 10^{12} s^{-1}.Radial frequency in a homogeneous model.

As Ω_r^2 is proportional to the strength of the hydrogen bond, we consider $\Omega_{rn}^2 = b_n \Omega_r^2$

- Homogeneous case: b_n =1.0
- Inhomogeneous case:b_n =0.8 (A-T), b_n =1.2 (C-G). We introduce the inhomogeneity by distinguishing double and triple hydrogen bonds M. Salerno. Phys. Rev. A **44**, 5292 (1991). We study an homogeneous chain with a local inhomogeneity (all base pairs identical except one)

In the disordered case, we introduce parametric disorder in the on-site electronic energy by means of a random potential $E_n^0 \in [-\Delta E, \Delta E]$.

Dynamical equations (I)

General charge state: $|\Psi\rangle = \sum_n c_n(t)|n\rangle$

New time scale: $t \rightarrow \Omega_r t$ 1 t.u. ~ 0.1 ps

Separation between time scales: $\tau = \hbar\Omega_r/V_0$

Dimensionless quantities:

$$\tilde{r}_n = \sqrt{\frac{M\Omega_r^2}{V_0}}\, r_n\,, \qquad \tilde{k}_n = \frac{k_n}{\sqrt{M\Omega_r^2 V_0}}\,, \qquad \tilde{E}_n^0 = \frac{E_n^0}{V_0}$$

$$\tilde{\Omega} = \frac{\Omega_\theta}{\Omega_r}\,, \quad \tilde{V} = \frac{V_0}{J\,\Omega_r^2}\,, \quad \tilde{\alpha} = \sqrt{\frac{V_0}{M\,\Omega_r^2}}\,\alpha\,, \quad \tilde{R}_0 = \sqrt{\frac{M\,\Omega_r^2}{V_0}}\,R_0$$

Numerical values (omitting tildes):

$\tau = 0.053,\ \Omega^2 = 0.013,\ V = 2.5\times 10^{-4}$

$R_0 = 63.1 \quad l_0 = 44.5$

k=1, α adjustable,

Dynamical equations (II)

$$
\begin{aligned}
\mathrm{i}\,\tau\dot{c}_n &= (E_n + k\,r_n)\,c_n \\
&\quad -(1-\alpha\,d_{n+1,n})\,c_{n+1} - (1-\alpha\,d_{n\,n-1})\,c_{n-1}, \\
\ddot{r}_n &= -b_n r_n - k\,|c_n|^2 \\
&\quad -\alpha\left[\frac{\partial d_n}{\partial r_n}(c_n^* c_{n-1} + c_n c_{n-1}^*) + \frac{\partial d_{n+1}}{\partial r_n}(c_{n+1}^* c_n + c_{n+1} c_n^*)\right], \\
\ddot{\phi}_n &= -\Omega^2\,(2\phi_n - \phi_{n-1} - \phi_{n+1}) \\
&\quad -\alpha\,V\left[\frac{\partial d_n}{\partial \phi_n}(c_n^* c_{n-1} + c_n c_{n-1}^*) + \frac{\partial d_{n+1}}{\partial \phi_n}(c_{n+1}^* c_n + c_{n+1} c_n^*)\right]
\end{aligned}
$$

The case $\alpha=0$ and $E_n^0=E_0$ corresponds to a Holstein system. T.D. Holstein, Ann. Phys. NY **8**, 325 (1959).

The case $\alpha=0$ and $k=0$ and random E_n^0 corresponds to the Anderson model. P.W. Anderson, Phys. Rev. **109**, 1492 (1958).

Localised polaron-like states

Frequencies of the linear system:

- Charge ~ 19
- Radial variables ~ 1
- Angular variables ~ 0.11

→ Born-Oppenheimer approximation

Ground state computed with the numerical map method. G. Kalosakas *et al*., Phys. Rev. B **58**, 3094 (1998); N.K. Voulgaris, G.P. Tsironis, Phys. Rev. B **63**, 14302 (2001). The stationary solution must be an attractor of the map:

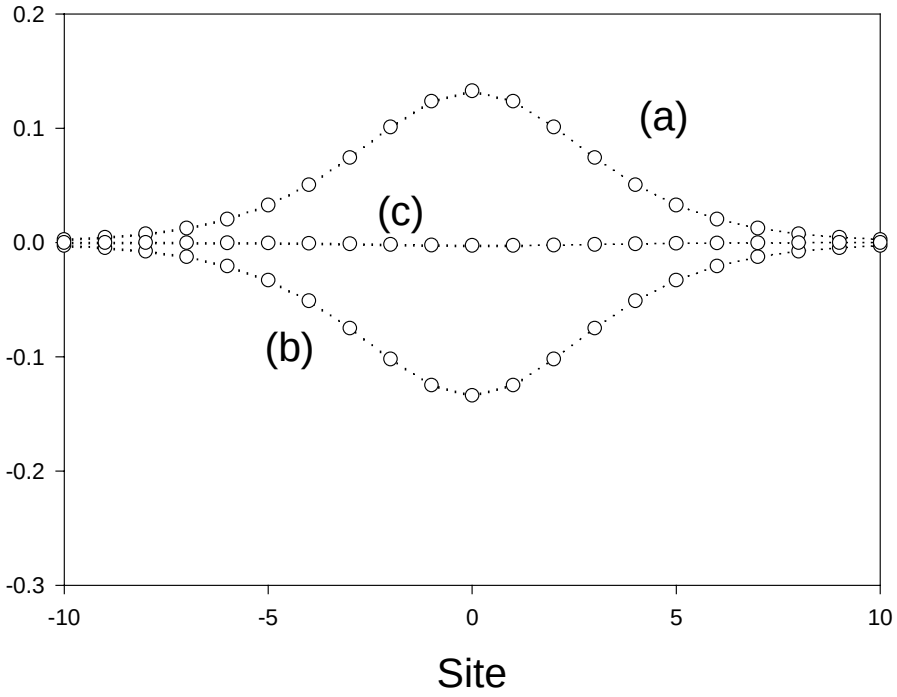
$$r'_n = -\frac{k}{b_n}|c_n|^2 - \frac{\alpha}{b_n}\left[\frac{\partial d_{n,n-1}}{\partial r_n}(c_n^* c_{n-1} + c_n c_{n-1}^*) + \frac{\partial d_{n+1,n}}{\partial r_n}(c_{n+1}^* c_n + c_{n+1} c_n^*)\right],$$

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

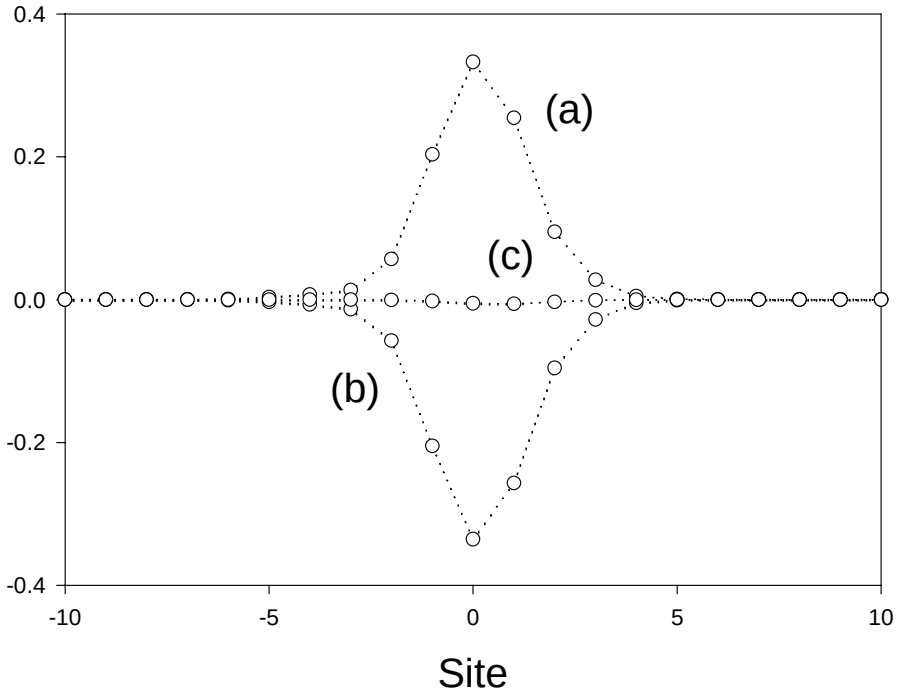
$$c'_n = \frac{[(E_n + k\,r'_n)\,c_n - (1 - \alpha\,d'_{n+1,n})\,c_{n+1} - (1 - \alpha\,d'_{n\,n-1})\,c_{n-1}]}{\|(E_n + k\,r'_n)\,c_n - (1 - \alpha\,d'_{n+1,n})\,c_{n+1} - (1 - \alpha\,d'_{n\,n-1})\,c_{n-1}\|},$$

$$d' = d(r', \phi')$$

Ground states (Homogeneous chain)



Profiles of the stationary polaron state in an ordered chain. (a) Wave function amplitudes $|c_n|$. (b) The static radial displacements r_n. (c) The static twists elongations θ_{nn-1}



Profiles of the stationary polaron state in a disordered chain. (a) Wave function amplitudes $|c_n|$. (b) The static radial displacements r_n. (c) The static twists elongations θ_{nn-1}

Participation number

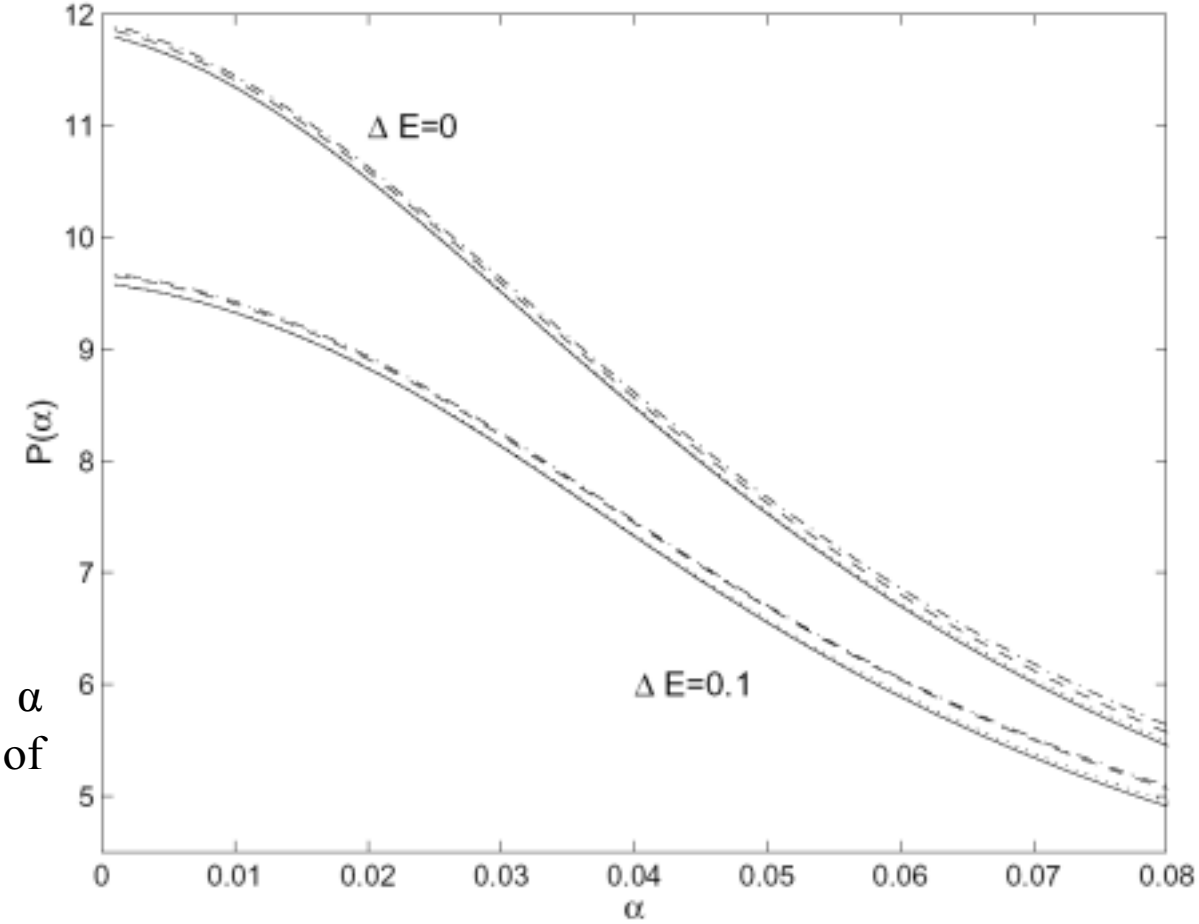
Degree of localization

$$L = \frac{\sum_n |u_n|^2}{(\sum_n |u_n|)^2}$$

Participation number

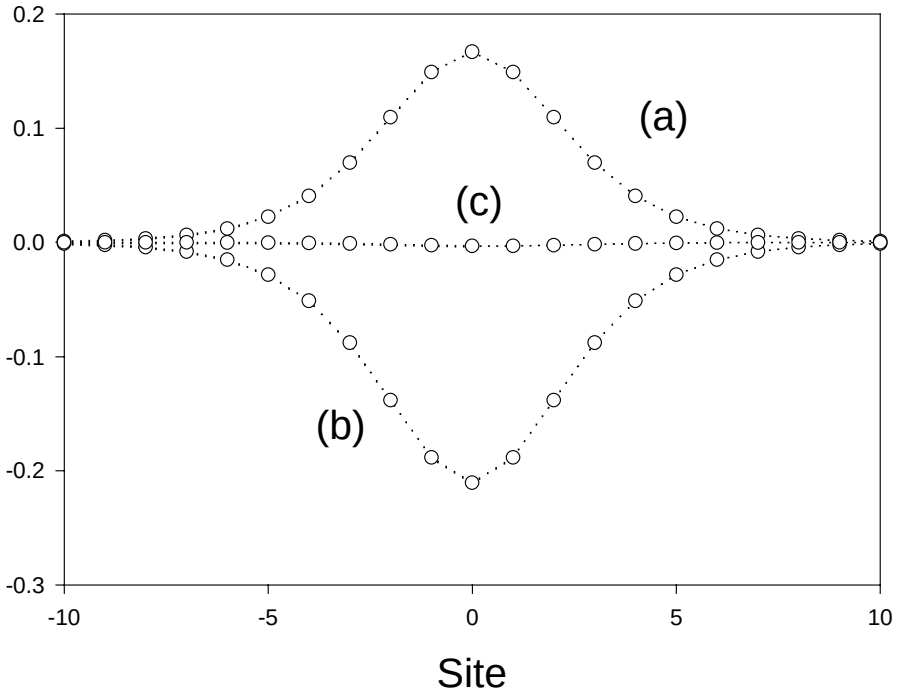
$$P = 1/L$$

- The value of parameter α determines the degree of charge localization

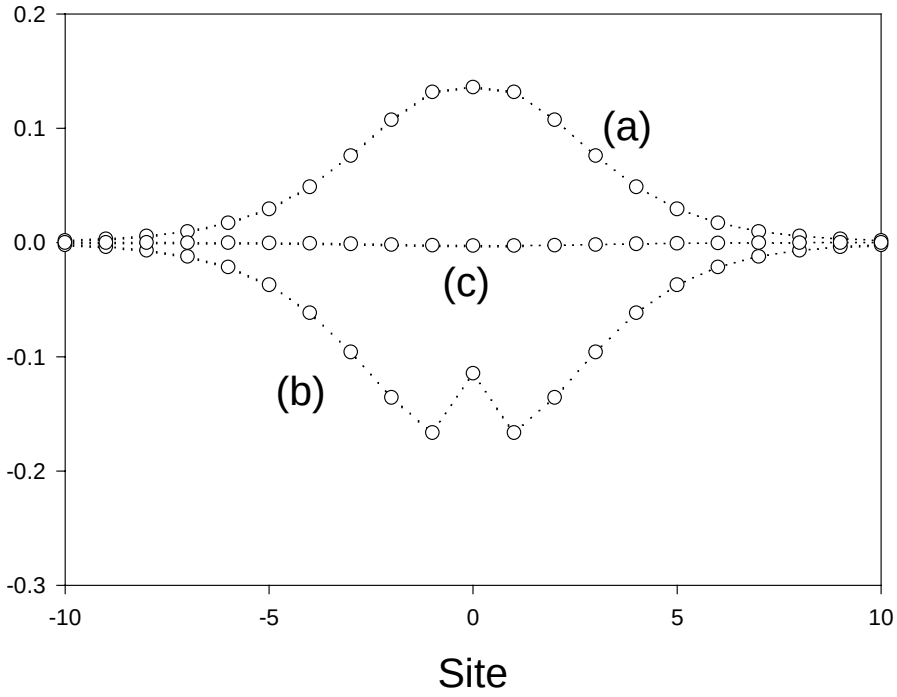


Participation number for electronic probabilities, radial displacements, angular twists and density of energy for the homogeneous and the inhomogeneous case

Ground states (A-T chain)

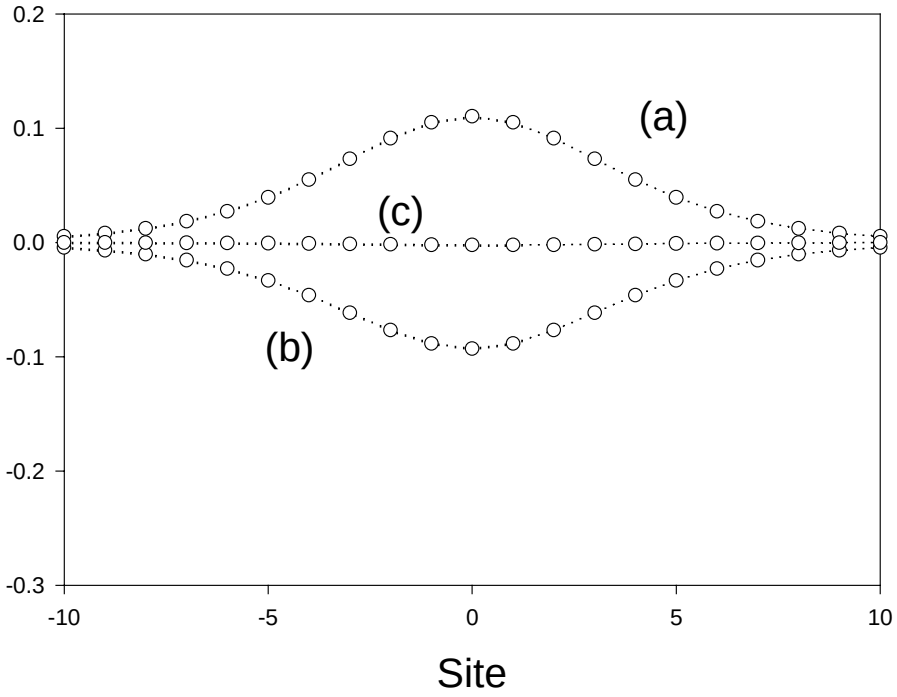


Profiles of the stationary polaron state in a homogeneous chain. (a) Wave function amplitudes $|c_n|$. (b) The static radial displacements r_n. (c) The static twists elongations θ_{nn-1}

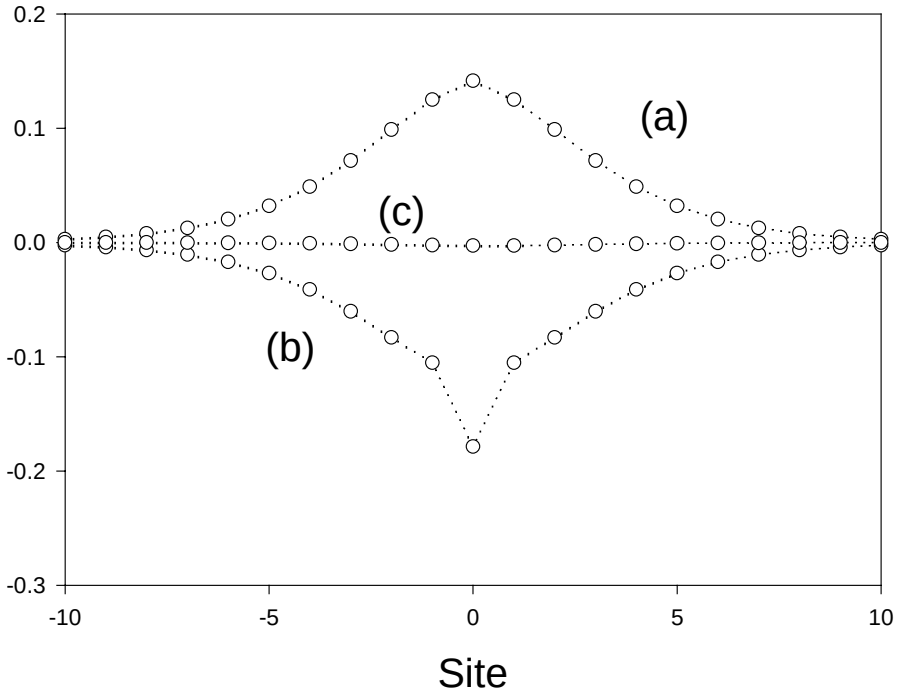


Profiles of the stationary polaron state centered in the inhomogeneity. (a) Wave function amplitudes $|c_n|$. (b) The static radial displacements r_n. (c) The static twists elongations θ_{nn-1}

Ground states (C-G chain)



Profiles of the stationary polaron state in a homogeneous chain. (a) Wave function amplitudes $|c_n|$. (b) The static radial displacements r_n. (c) The static twists elongations θ_{nn-1}



Profiles of the stationary polaron state centered in the inhomogeneity. (a) Wave function amplitudes $|c_n|$. (b) The static radial displacements r_n. (c) The static twists elongations θ_{nn-1}

Charge transport mediated by mobile polarons

Stationary solutions can be activated by perturbing the ground state with a localized, spatially antisymmetric mode obtained in the vicinity of a bifurcation (pinning mode). D. Chen *et al*., Phys. Rev. Lett. **77**, 4776 (1996).

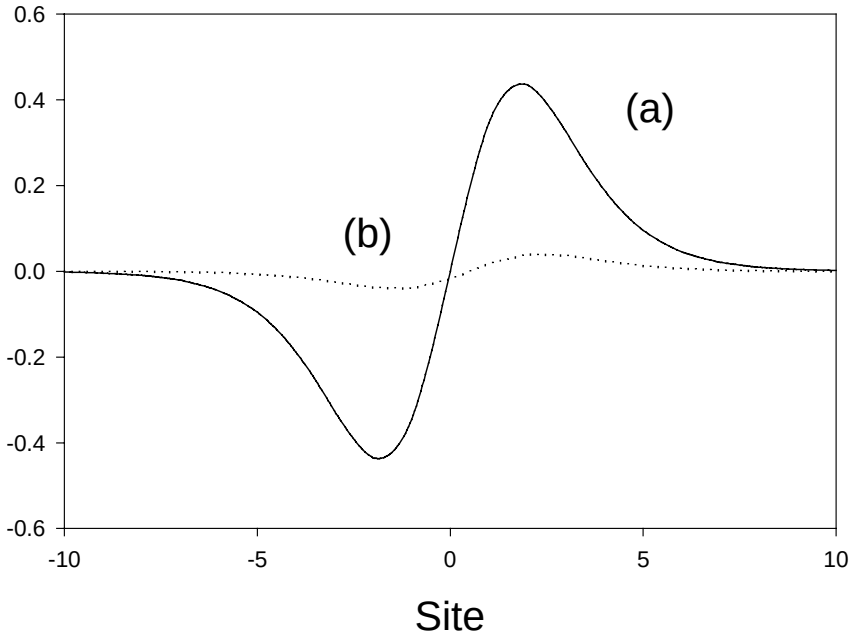
We use the discrete gradient method, perturbing the velocities of the stationary state in a direction parallel to the vector

$$(\nabla r)_n = (r_{n+1} - r_{n-1})$$

and/or

$$(\nabla \phi)_n = (\phi_{n+1} - \phi_{n-1})$$

Although mobility is not guaranteed, it has been probed successfully in a wide range of parameters. M. Ibañes *et al*., Phys. Rev. E **65**, 041902, (2002)



Components of the discrete gradient vector. (a) radial components. (b) angular components.

Previous results

A similar model to study polaron-like charge transport in periodic and randomly disordered DNA has been proposed recently. D. Heenig, J.F.R. Archilla, J. Agarwall,Physica D (To appear, 2003); J.F.R. Archilla, J. Agarwall, D. Heenig, World Scientific, special issue (To appear 2003):

- Parameter α, that represents the coupling between the transfer integral and the distance between nucleotides, fairly small.

- Homogeneous chain

- Charge transport in DNA is mediated by coupling of the charge carrying unit with the hydrogen bond deformations.

- Only perturbations in radial variables can activate polarons.

- This transport survives to a small amount of parametric and structural disorder

Charge transport in an homogeneous chain in absence of disorder

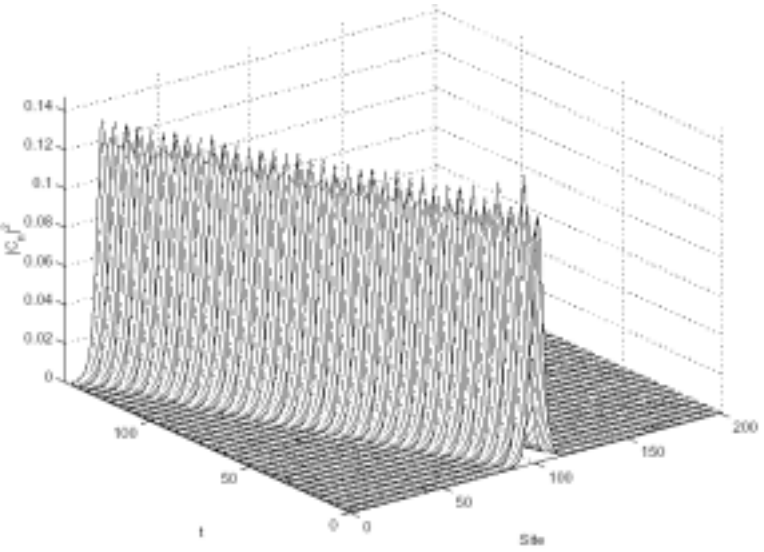
The value of parameter α is of particular importance, determining the mobility properties of the charge. We have studied a range of values of this parameter consistent with the suppositions of the model. We have found three different regimes:

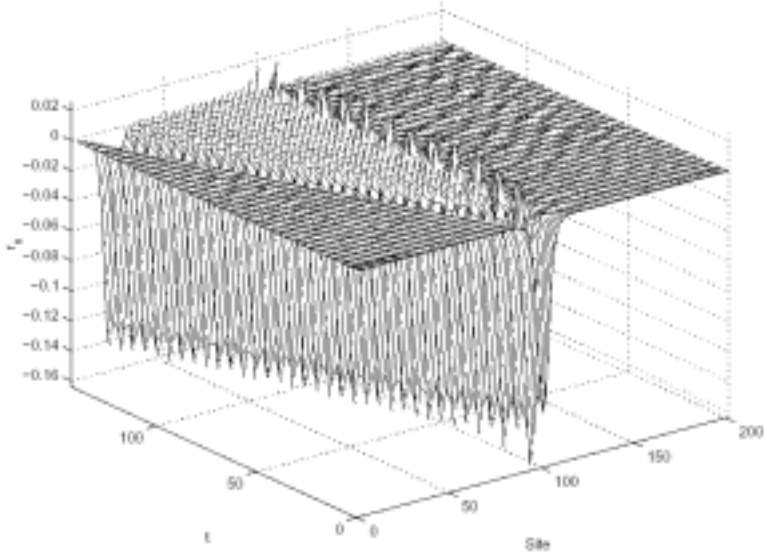
- Radial movability regime
  - α small (α ~0.0005)
  - It is not possible to move polarons by perturbing the angular variables. Only perturbation in radial ones can activate it.

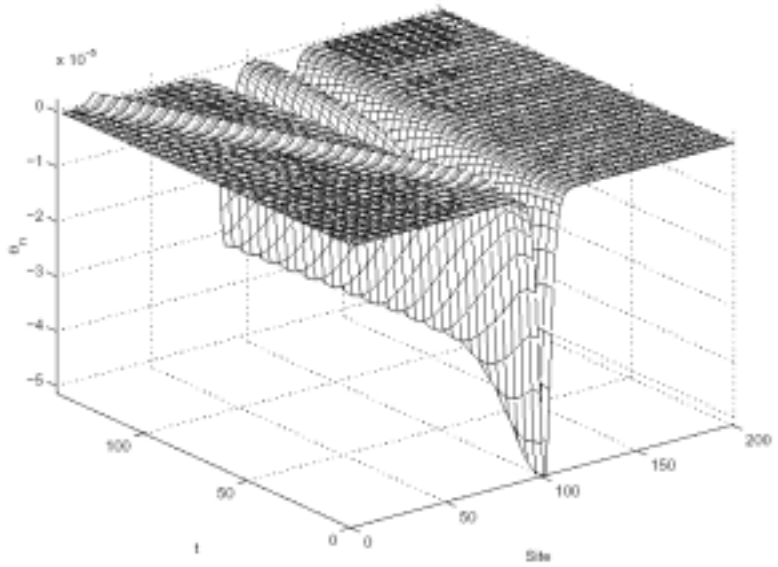
- Mixed regime
  - α not too small (α ~0.01)
  - It is possible to move polarons by perturbing the angular and/or radial variables.

- Twist movability regime
  - Larger values of α (α ~0.05)
  - It is not possible to move polarons by perturbing the radial variables. Only perturbation in angular ones can activate it.

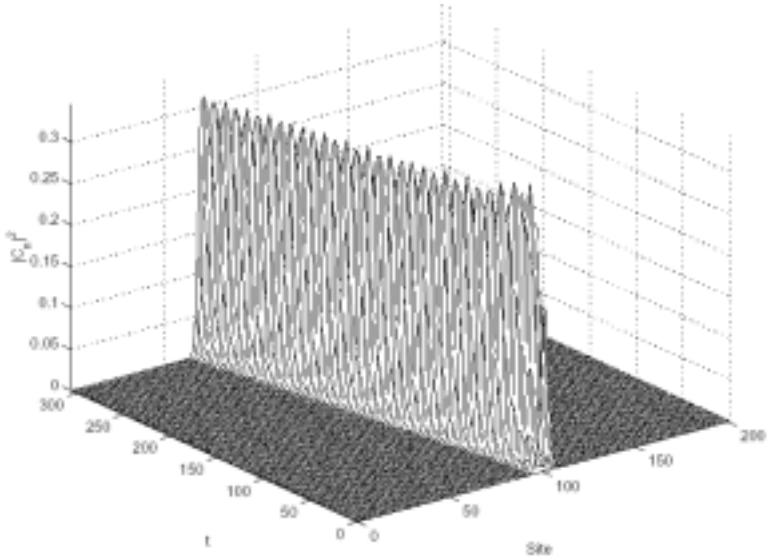
Homogeneous chain. Radial movability regime

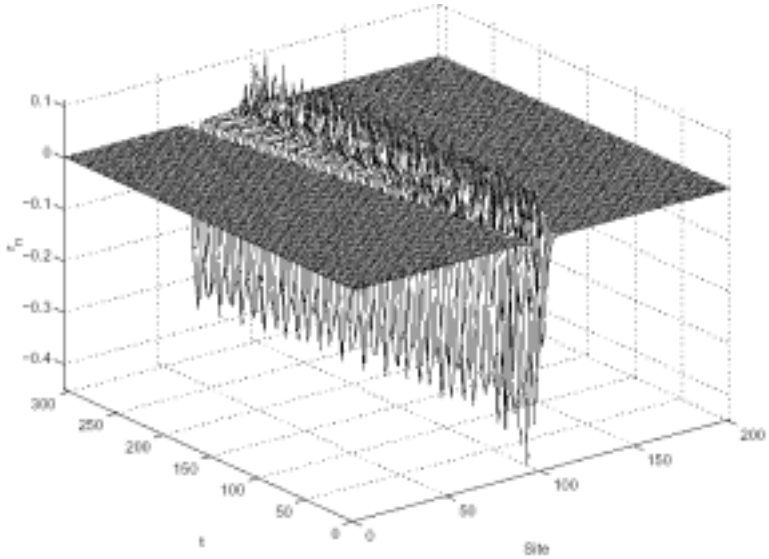


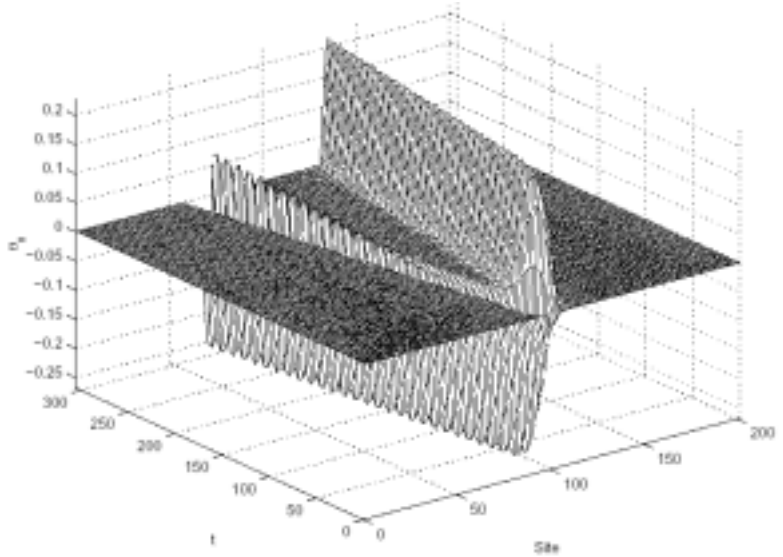




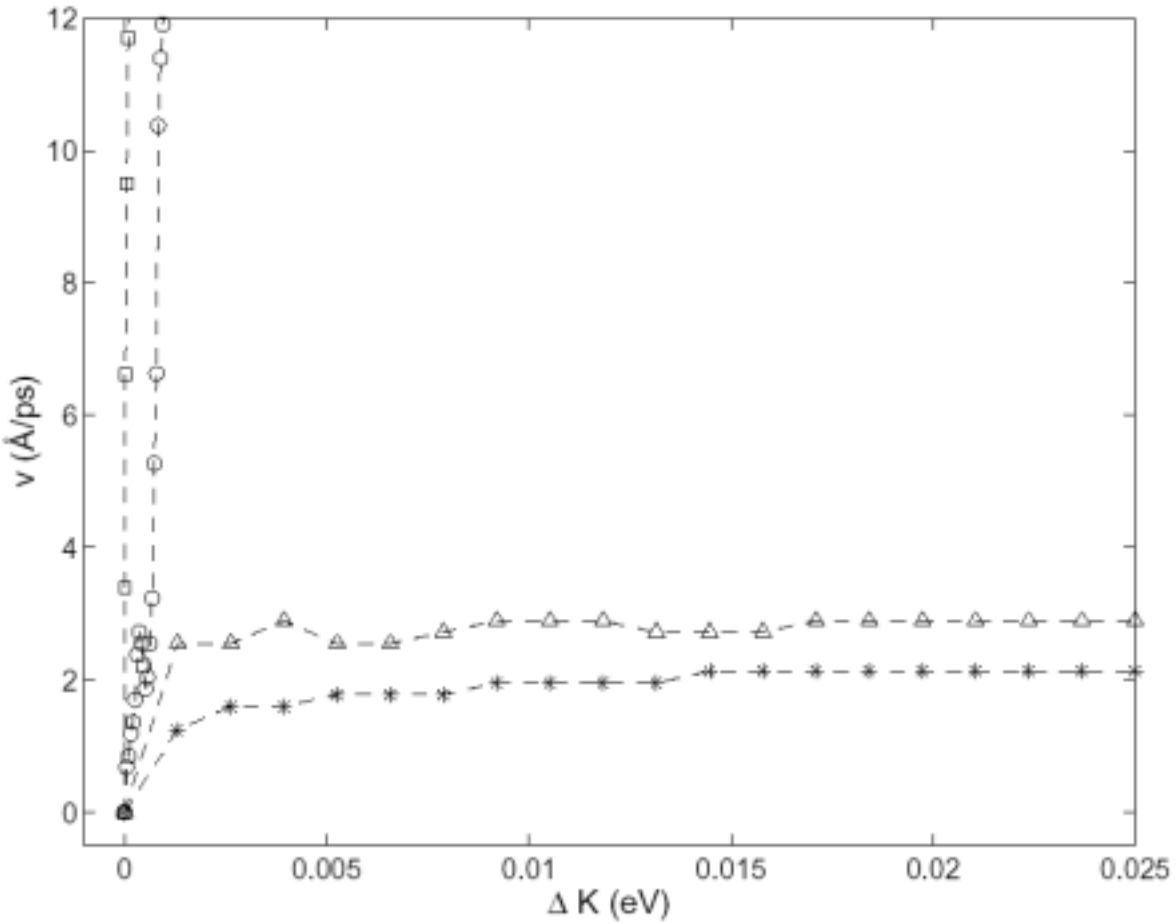
Homogeneous chain. Twist movability regime







Comparison between different regimes



Squares: Radial regime; Circles: Mixed regime, radial activation; Triangles: Mixed regime, angular activation; Starts: Twist regime

Homogeneous chain. Disordered case

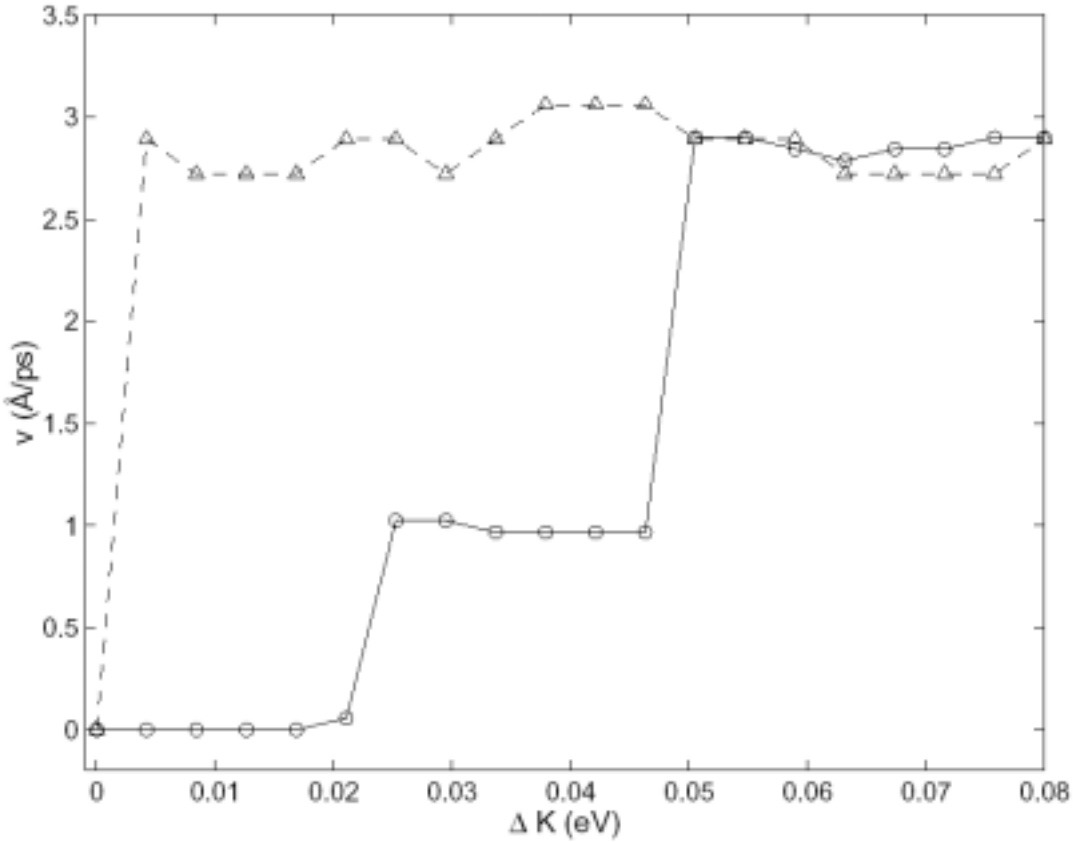
Movable polarons exist below a critical value of the disorder ΔE_{cric}

- Radial movability regime. Mobility is very sensitive to disorder. Only a small degree of disorder allows activation of the polaron ($\Delta E_{cric} \sim 0.05$).

- Twist movability regime. Moving polaron is very robust with respect to disorder ($\Delta E_{cric} \sim 0.5$)

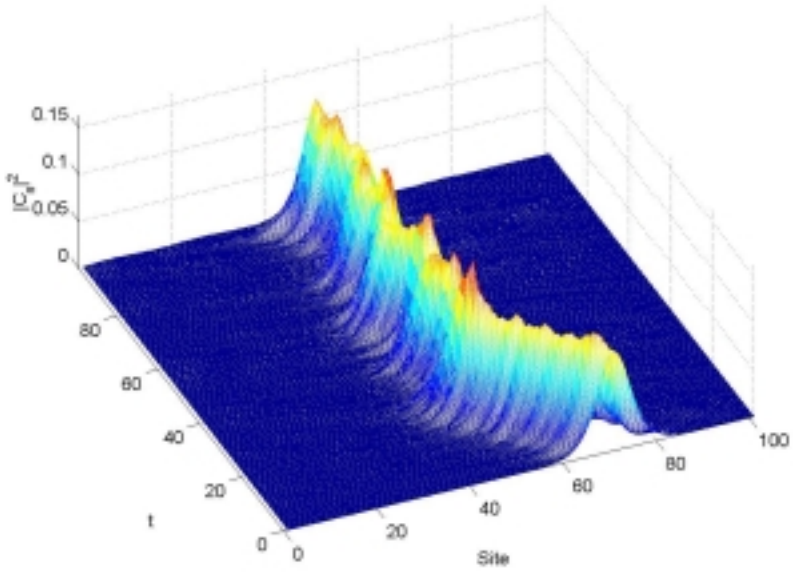
- Mixed regime. Angular activation leads more robust (but slower) polarons than radial activation. If disorder is high enough, only angular activation is possible, with a movement similar to the ordered case.

Homogeneous chain. Disordered case. Mixed regime

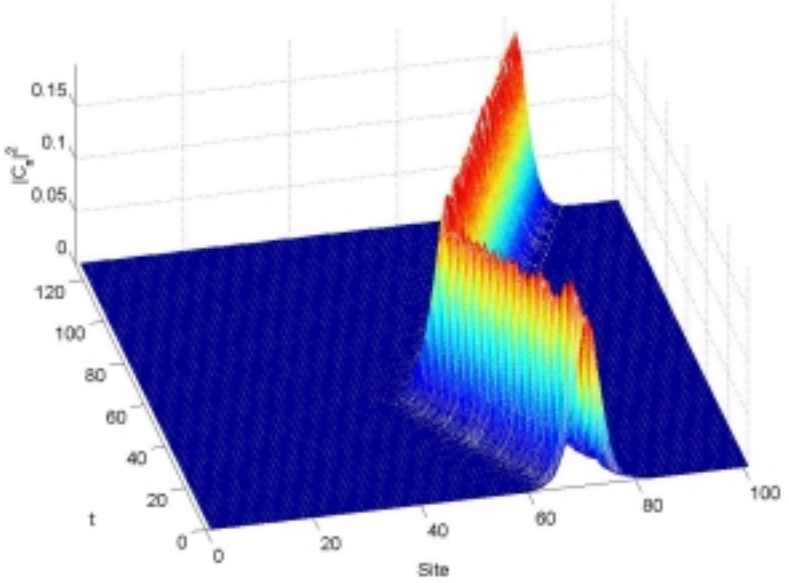


Circles: Disordered case; Triangles: Ordered one

Inhomogeneous chain. Radial movability regime



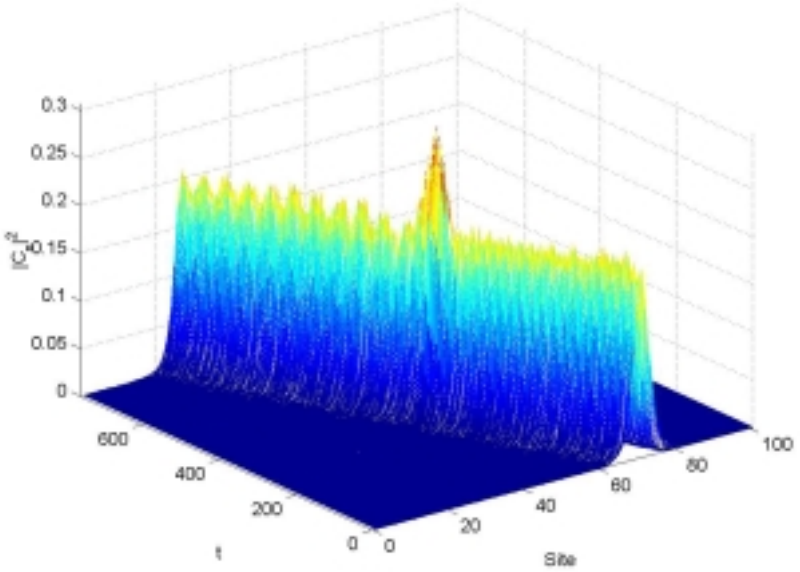
Trapping phenomenon due to the interaction between a moving polaron in a G-C chain with a A-T base pair



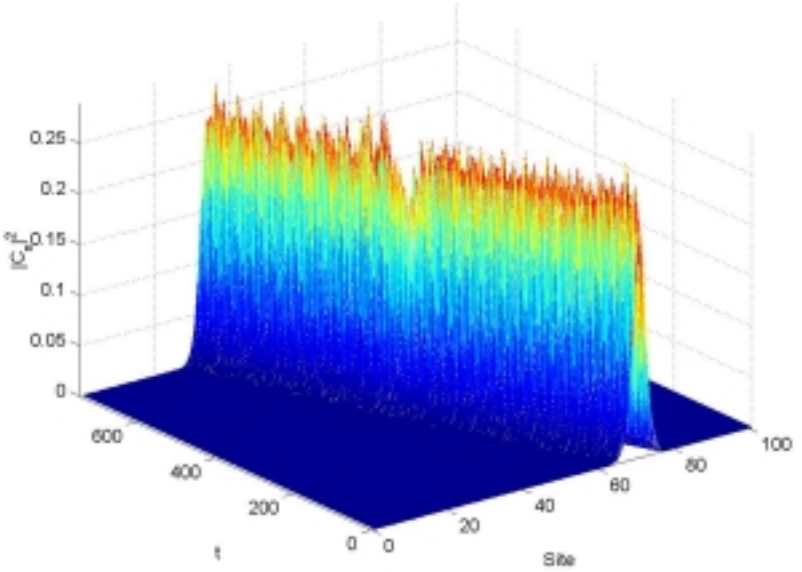
Reflection phenomenon due to the interaction between a moving polaron in a A-T chain with a G-C base pair

Trapping and reflection phenomenon as found in the interaction between a moving breather and an impurity in a Klein Gordon chain. J. Cuevas *et al*. J. Phys. A: Math. Gen. **35,** 10519 (2002)

Inhomogeneous chain. Twist movability regime



Transmission phenomenon due to the interaction between a moving polaron in a G-C chain with a A-T base pair. The inhomogeneity acts as a potential well.



Transmission phenomenon due to the interaction between a moving polaron in a A-T chain with a G-C base pair. The inhomogeneity acts as a potential barrier.

As movement is due to angular modes, there no exist trapping o reflection phenomenon as in radial regime.

Inhomogeneous chain. Movability

	Radial movability regime	**Twist movability regime**	**Mixed regime Radial activation**	**Mixed regime angular (and radial) activation**
A-T chain	Reflection	Transmission	Reflection	Transmission
G-C chain	Trapping	Transmission	Trapping	Transmission

Conclusions

- Analysis of the influence of the radial and angular perturbations on the properties of moving polarons in a three-dimensional, semi-classical, tight-binding model for DNA in both the ordered and disordered case.
- Three regimes in function of the coupling of the transfer integral with the deformations of the hydrogen bonds.
- Properties of the moving polaron different in each regime. Mobility induced by angular activation is more robust with respect to parametric disorder, has lower velocity and the activation energy is higher than in radial movability regime.
- Moving polaron activated by angular perturbations can travel along an inhomogeneous chain with different base pairs. Polarons activated only by radial perturbations not.

References: F. Palmero, JFR Archilla, D. Hennig and F. Romero. *Nonlinear charge transport in DNA mediated by twist modes*. Submitted to Phys. Lett. A.; F. Palmero, JFR Archilla, D. Hennig and F. Romero. *Nonlinear charge transport in inhomogeneous DNA*. In preparation