Nonlinear charge transport mechanism in periodic and disordered DNA

A three dimensional model for polarons in DNA

D Hennig, JFR Archilla and J Agarwal

Physics Department, Theoretical Physics Institute, Freie Universität Berlin

Nonlinear Physics Group (GFNL), University of Sevilla, Spain

http://www.us.es/gfnl

Work supported by the hospitality of the Theoretical Physics Institute, FU-Berlin, and by the European Commission under the RTN project, HPRN-CT-1999-00163 (LOCNET), during 2002.

DNA conductivity

- Biological functions
  - Repair after radiation
  - Biosynthesis
- Applications
  - Electronic biomaterials
  - Molecular wires
- Mechanism:
  - Overlap between π-orbitals

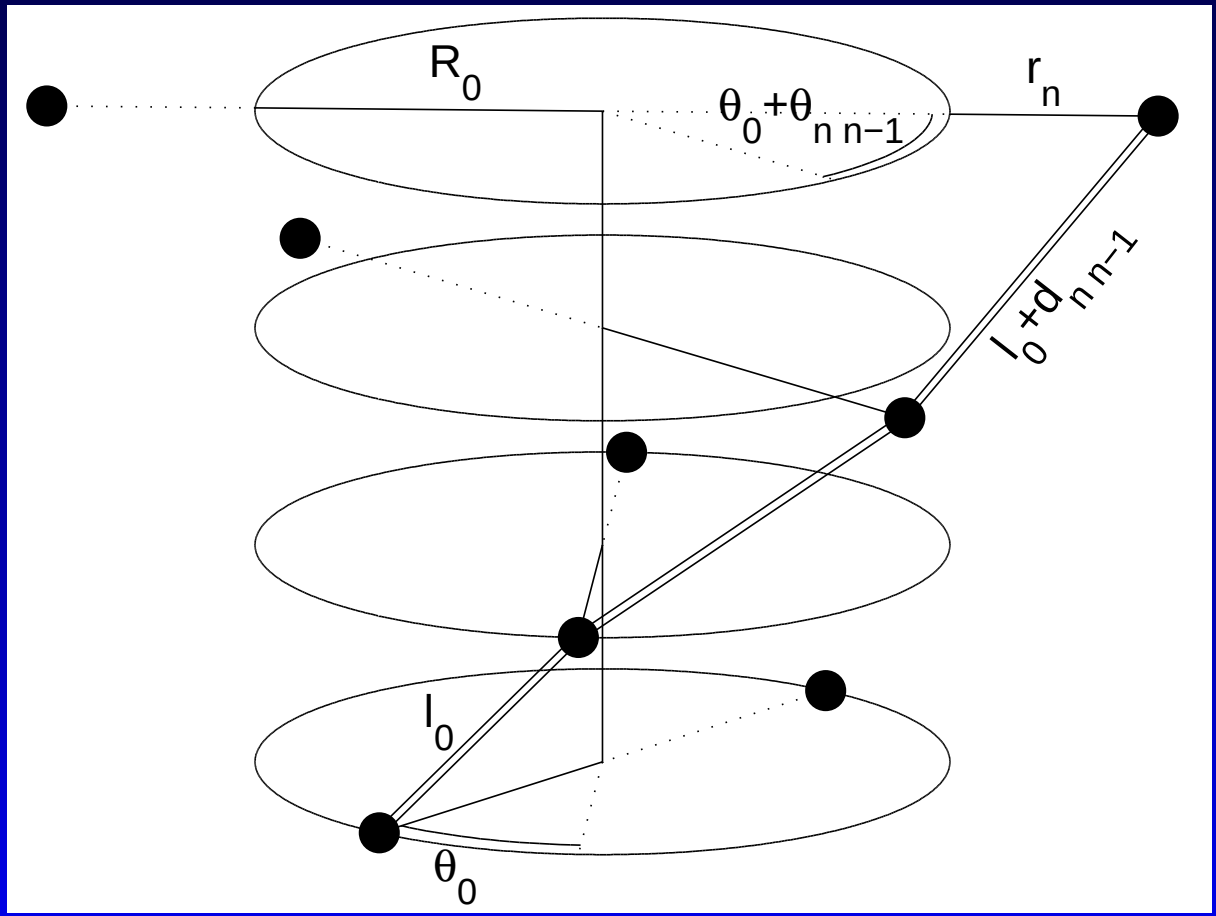
Controversial results

- Experimental:
  - Good conductor:
    Fink et al, Nature, 1999;
    Tran et al,Phys. Rev. Lett. 2000.
  - Insulator: *Braun et al*, Nature, 1998
  - Semiconductor: *Porath et al.*, 2000.
- Theoretical:
  - No D–C conductivity:
    de Pablo et al,Phys. Rev. Lett. 2000
  - Conductor:
    Jortner et al, Proc. Nat. Acad. Sci. 1998.
    Chen et al, Sol. Stat. Comm. 1999.
    Hjort et al., Phys. Rev. Lett. 2001.

Models for charge transport

- - Coherent tunneling
  - Classical Diffusion
  - Incoherent phonon-assisted hopping
  - Hopping between localized states
  - Polarons
  - Solitons
- Our model:
  - Nonlinear approach
  - Three-dimensional network of oscillators
  - Base pair picture
  - Deformation of the hydrogen bonds
  - Twist and radial motion
  - Electron tight-binding system

Sketch of the model



Description of the system

- Total Hamiltonian operator:

$$\hat{H} = \hat{H}_{el} + H_{rad} + H_{twist}$$

- Vibronic Hamiltonian:

$$H_{rad} = \sum_n \frac{(p_n^r)^2}{2\,M_n} + \frac{M_n\,\Omega_r^2}{2}\,r_n^2$$

- Twist Hamiltonian:

$$H_{twist} = \sum_n \frac{\left(p^{\theta}_{n\,n-1}\right)^2}{2\,J_{n\,n-1}} + \frac{J_{n\,n-1}\,\Omega_\theta^2}{2}\,\theta^2_{n\,n-1}$$

Tight–binding system

- Electron Hamiltonian operator:

$$\hat{H}_{el} = \sum_n E_n \, |n><n| \; - \; V_{n-1\,n} \, |n-1><n| \; - \; V_{n+1\,n} \, |n+1><n|$$

- $|n>$ represents the state of the electron localized at one site
- Diagonal matrix elements, or energies at one site:

$$<n| \, \hat{H}_{el} \, |n> = E_n$$

- Off–diagonal elements, or transfer integral:

$$<n| \, \hat{H}_{el} \, |n-1> = \; - V_{n\,n-1}$$

Classical Hamiltonian

- Expected value of the total Hamiltonian:

$$H_{clas} = < \Phi | \hat{H} | \Phi > = H_{el} + H_{rad} + H_{twist}$$

- State of the system:

$$|\Phi > = \sum_n c_n(t) |n > \quad \text{with} \quad < \Phi | \Phi > = 1$$

- Electron Hamiltonian:

$$\begin{aligned} H_{el} &= < \Phi | \hat{H}_{el} | \Phi > \\ &= \sum_n E_n |c_n|^2 - V_{n\,n-1} \left(c_n^* c_{n-1} + c_n c_{n-1}^* \right) \end{aligned}$$

Evolution equations

- Radial variables:

$$\dot{p}^r_n \;=\; M\,\ddot{r}_n \;=\; -\,\frac{\partial\, H_{clas}}{\partial\, r_n}$$

- Twist variables:

$$\dot{p}^\theta_{n\,n-1} \;=\; J\,\ddot{\theta}_{n\,n-1} \;=\; -\,\frac{\partial\, H_{clas}}{\partial\, \theta_{n\,n-1}}$$

- Electron variables:

$$\mathrm{i}\,\hbar\,\frac{d\,|\Phi>}{d\,t} \;=\; \hat{H}_{el}\,|\Phi> \quad \text{or} \quad \dot{c}_n \;=\; -\,\frac{\mathrm{i}}{\hbar}\,\frac{\partial\, H_{clas}}{\partial\, c^*_n}$$

Interactions

Diagonal: Electron–radial vibrations

$$E_n = E_n^0 + k\, r_n$$

Transfer integral:

$$V_{n\,n-1} = V_0\,(1 - \alpha\, d_{n\,n-1})$$

Distance between consecutive bases:

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

Linearized distance:

$$d_{n\,n-1} \simeq \frac{R_0}{l_0}\,[\,(\,1 - \cos\theta_0\,)\,(r_n + r_{n-1}) \;+\; \sin\theta_0\, R_0\, \theta_{n\,n-1}\,]$$

Dimensionless equations

Electronic part:

$$\begin{aligned} i\,\tau\dot{c}_n &= (E_n^0 + k\,r_n)\,c_n \\ &- (1-\alpha\,d_{n+1,n})\,c_{n+1} - (1-\alpha\,d_{n\,n-1})\,c_{n-1} \end{aligned}$$

Radial part:

$$\begin{aligned} \ddot{r}_n &= -r_n - k\,|c_n|^2 - \alpha\,\frac{R_0}{l_0}\,(1-\cos\theta_0) \\ &\times \left\{ [c_{n+1}^* c_n + c_{n+1} c_n^*] + [c_n^* c_{n-1} + c_n c_{n-1}^*] \right\} \end{aligned}$$

Angular part:

$$\ddot{\theta}_{n\,n-1} = -\Omega^2\,\theta_{n\,n-1} - \alpha\,V\,\frac{R_0^2}{l_0}\,\sin\theta_0\,[c_n^*\,c_{n-1} + c_n\,c_{n-1}^*]$$

Time scale: 1.6 ps, $1/\tau \approx 4$, $\Omega \approx 0.08$

Related models

- Holstein model:

  $\alpha = 0$ and homogeneous $E_n^0 = E_0$.

  $$i\,\tau \dot{c}_n = (E_0 + k\,r_n)\,c_n - c_{n+1} - c_{n-1}$$

- Anderson model:

  $\alpha = 0$, $k = 0$ and random E_n^0.

  $$i\,\tau \dot{c}_n = E_n^0\,c_n - c_{n+1} - c_{n-1}$$

- Without electron:

  Barbi–Cocco-Peyrard model

Localized polaron–like states

- Born–Oppenheimer approximation:
  Slow variables r_n and $\theta_{n,n-1}$ supposed constants.
- Method:
  - Substitution of stationary solutions:

$$c_n = \Phi_n \, \exp[-i \, E \, t/\tau]$$

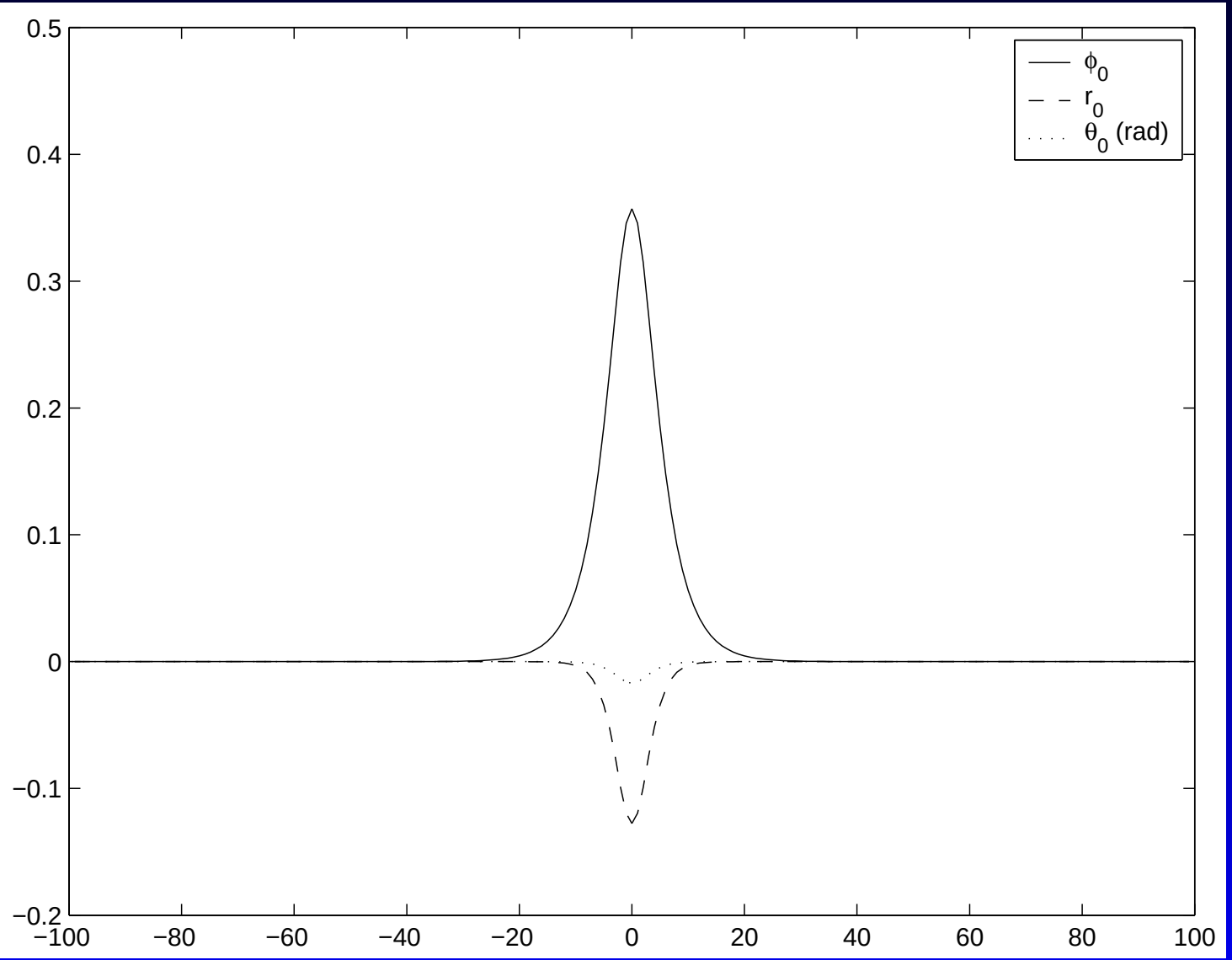
  - Leads to a nonlinear difference system:

$$E\phi = \hat{A} \cdot \phi$$

  - Solution are £xed points of the numerical map:

$$\phi' = \pm \hat{A} \cdot \phi / \| \hat{A} \cdot \phi \|$$

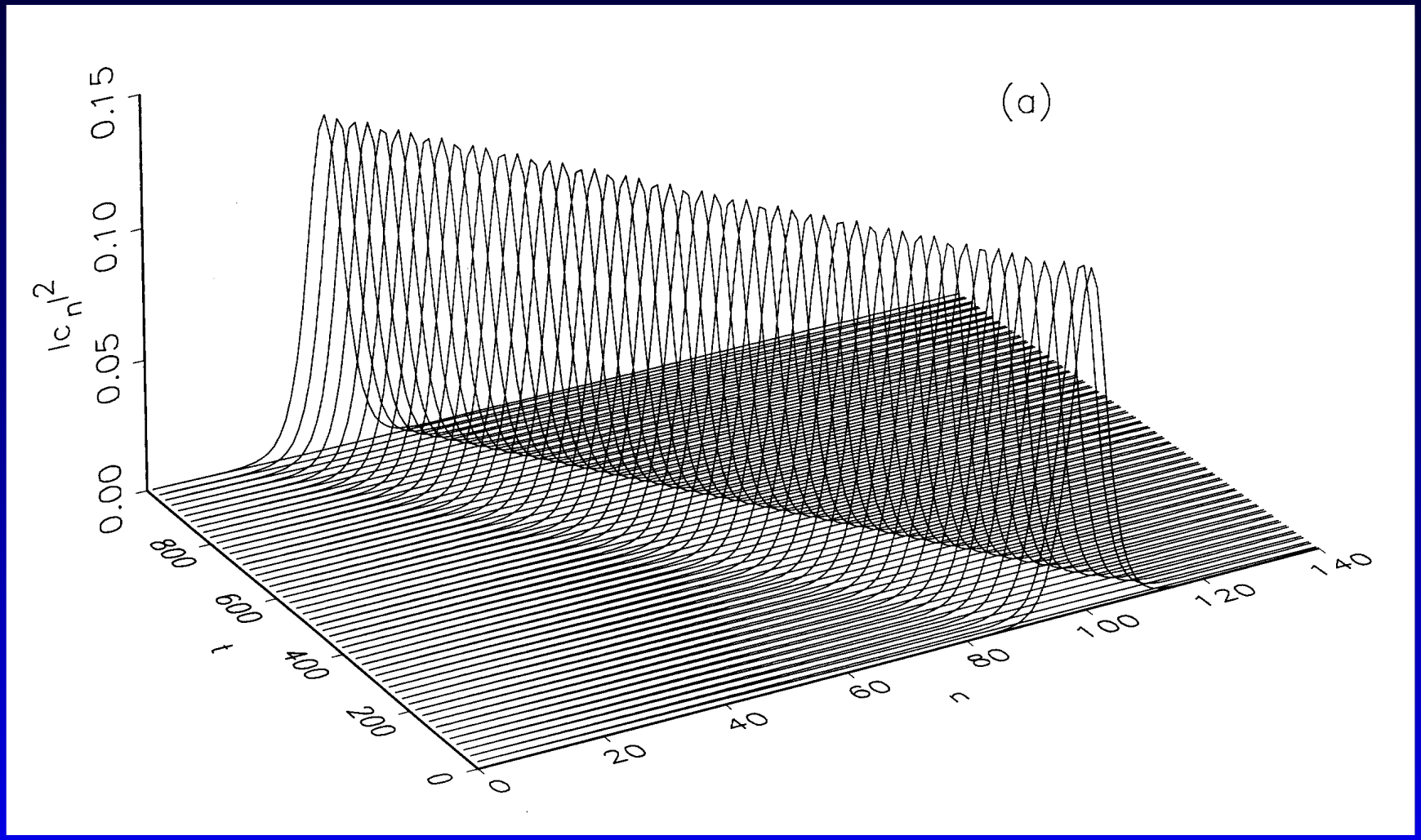
Profiles of the polarons



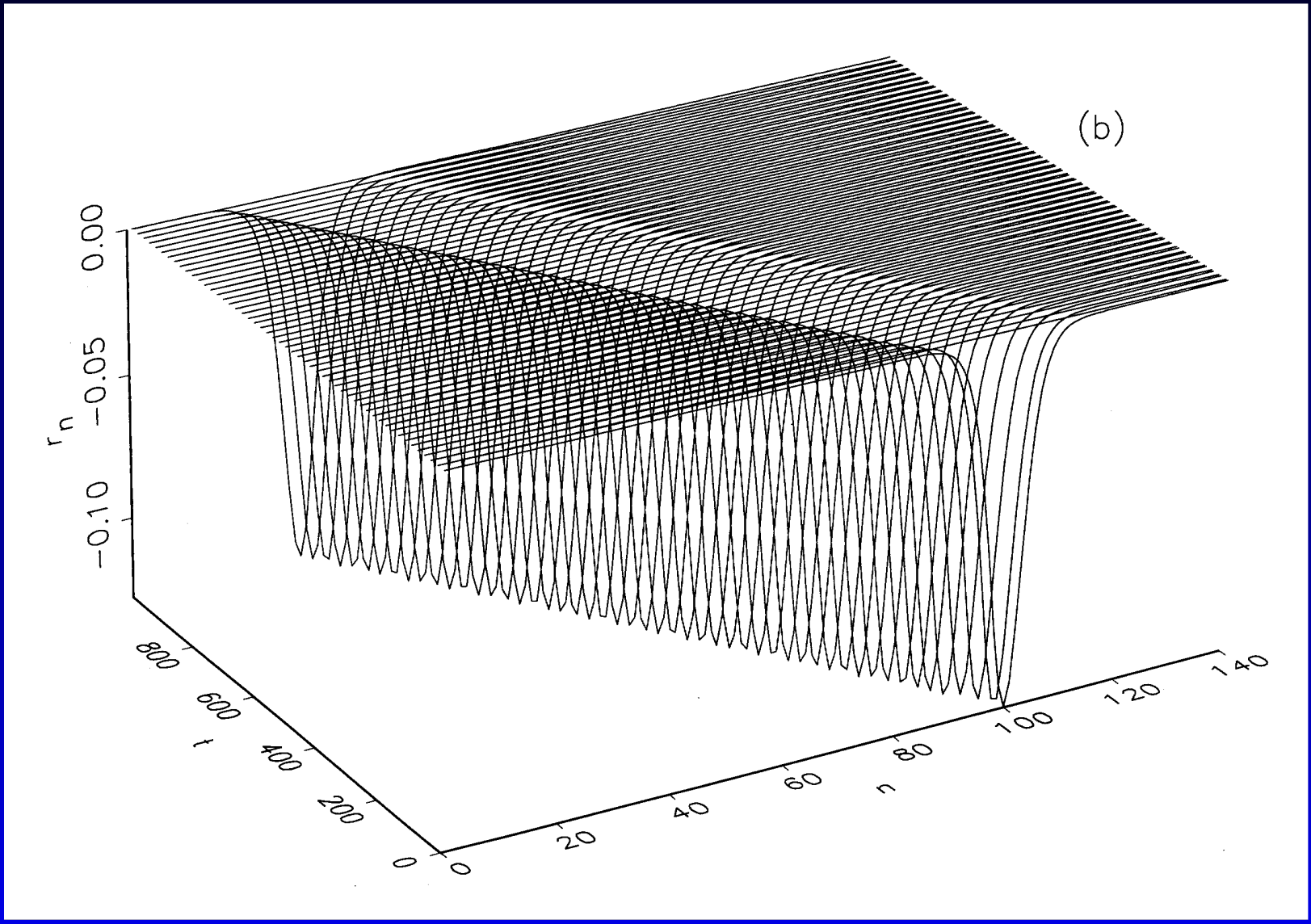
Activation of polaron motion

- Method:
  Pinning mode: perturbation with an antisymmetric localized mode.
- Cases:
  - Homogeneous system
  - Diagonal disorder: $E_n^0 = E_0 + \Delta E$. ΔE random.
  - Random double helix structure:
    $r_n \in [r_0 - \Delta, r_0 + \Delta]$
    $\theta_n \in [\theta_0 - \Delta, \theta_0 + \Delta]$

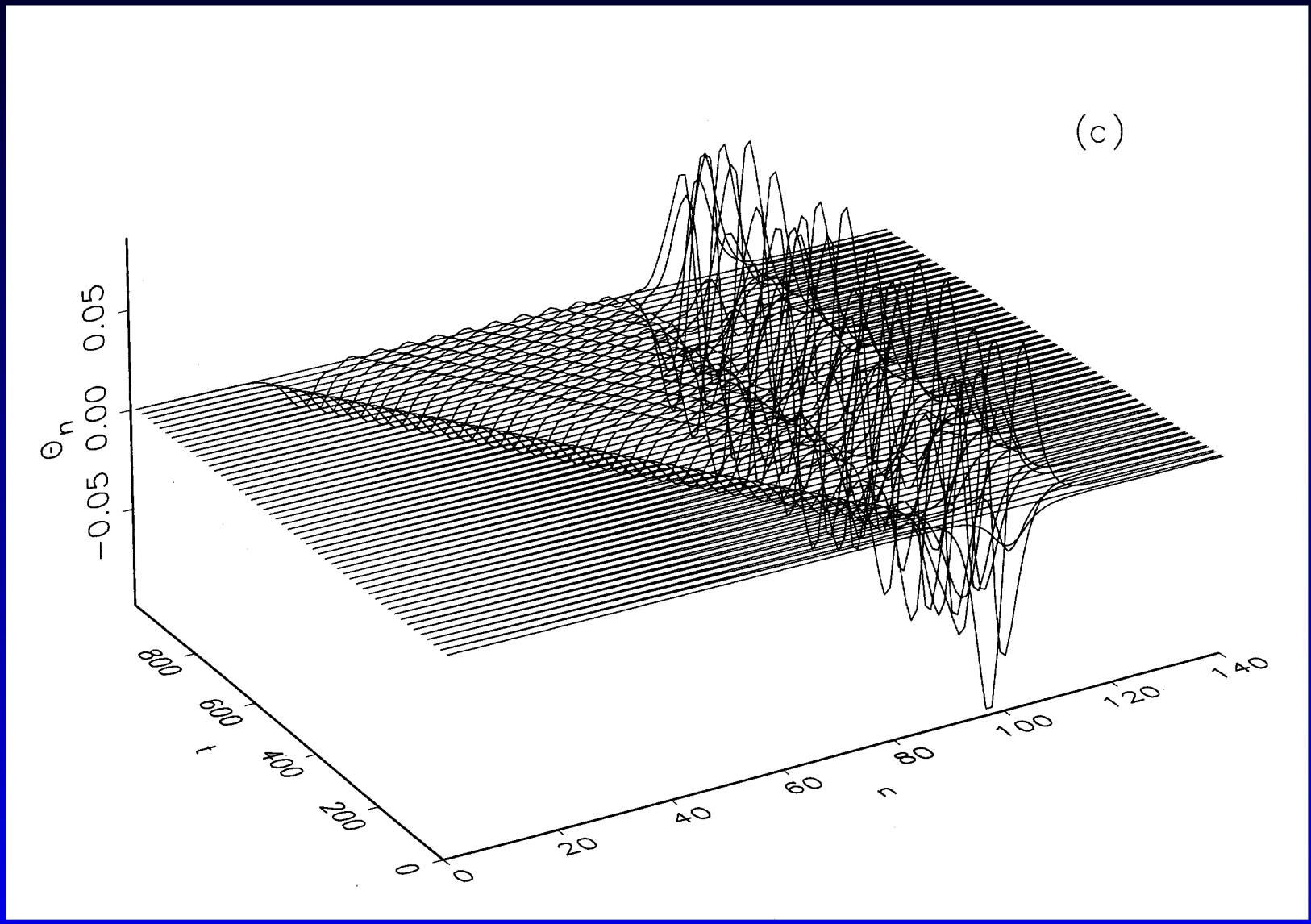
Electron movement



Radial displacement



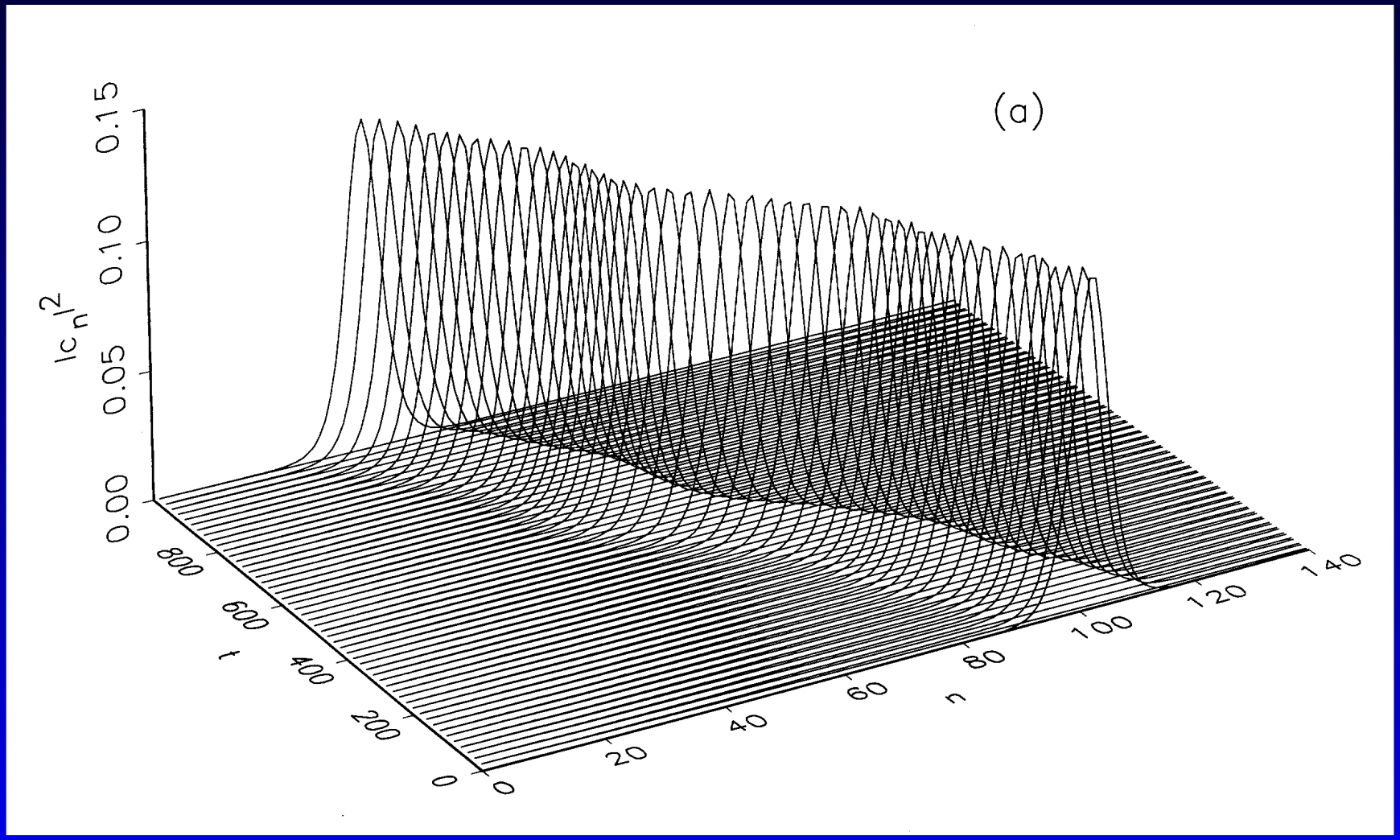
Angular displacement



Diagonal static disorder

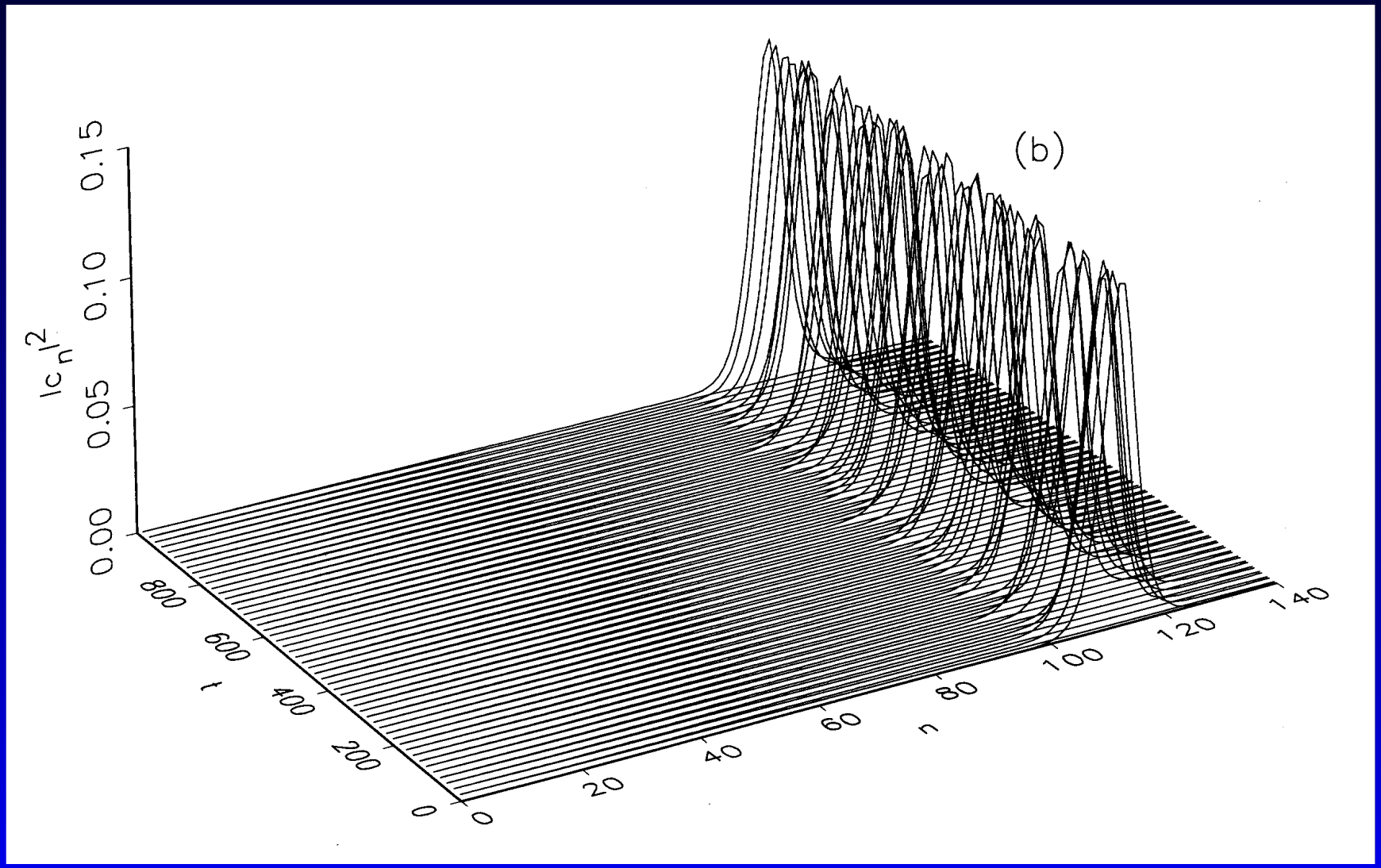
- Caused by different base–pairs
- E_n^0 random numbers with $|E_n^0| < \Delta E$
- Conductivity persists for $|\Delta E| < \Delta_{crit}$
- No conductivity beyond Δ_{crit}
- Experimentally found in *Fink et al*, Nature, 1999.

Weak diagonal disorder



$\Delta E = 0.05$

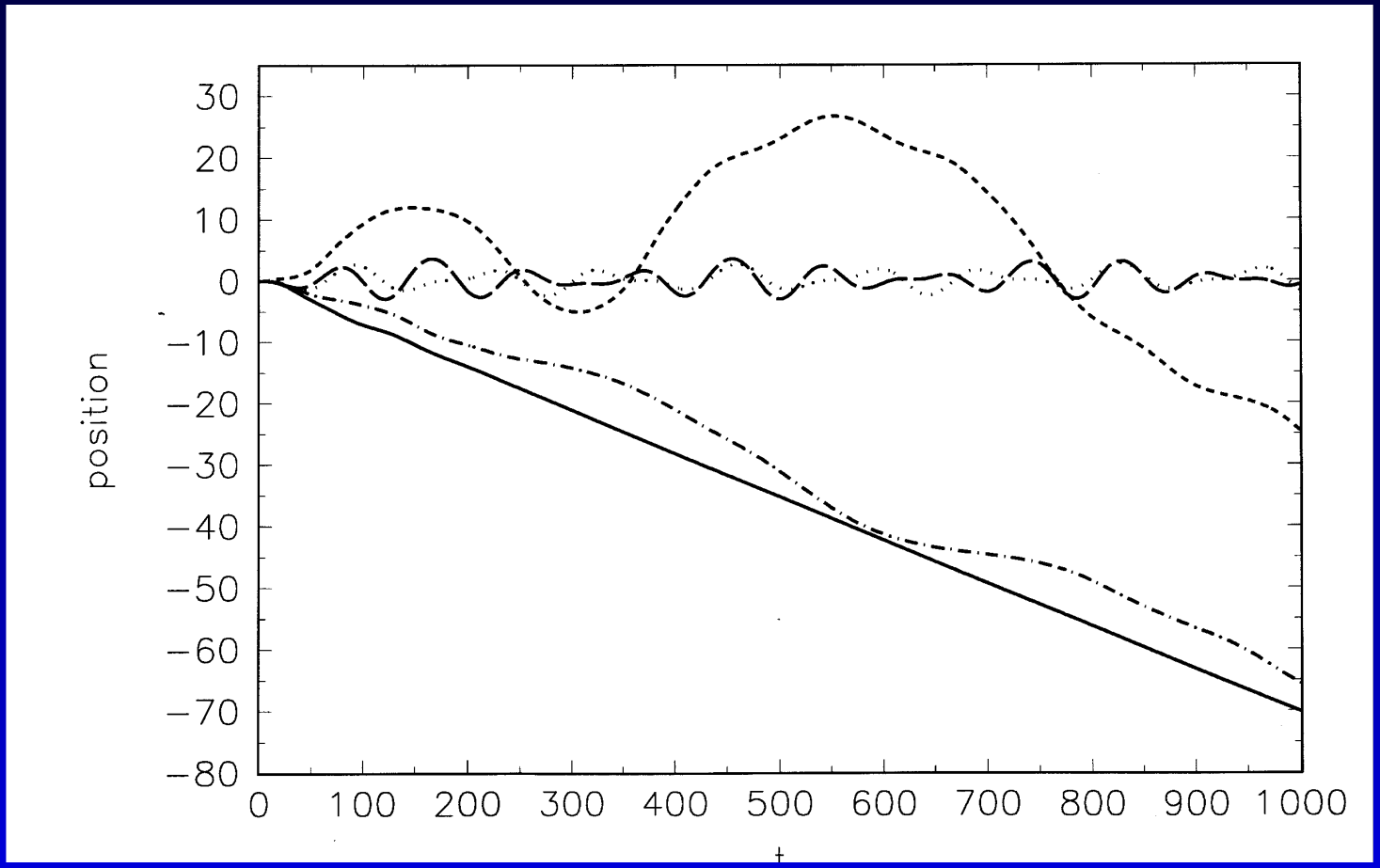
Strong diagonal disorder



$\Delta E = 0.5$

Diagonal disorder

$$\bar{n}(t) = \sum_n n|c_n(t)|^2$$



ΔE : 0.0 (–), 0.025(- -),0.05 (—·), 0.1 (··), 0.5 (– –)

Non–diagonal disorder

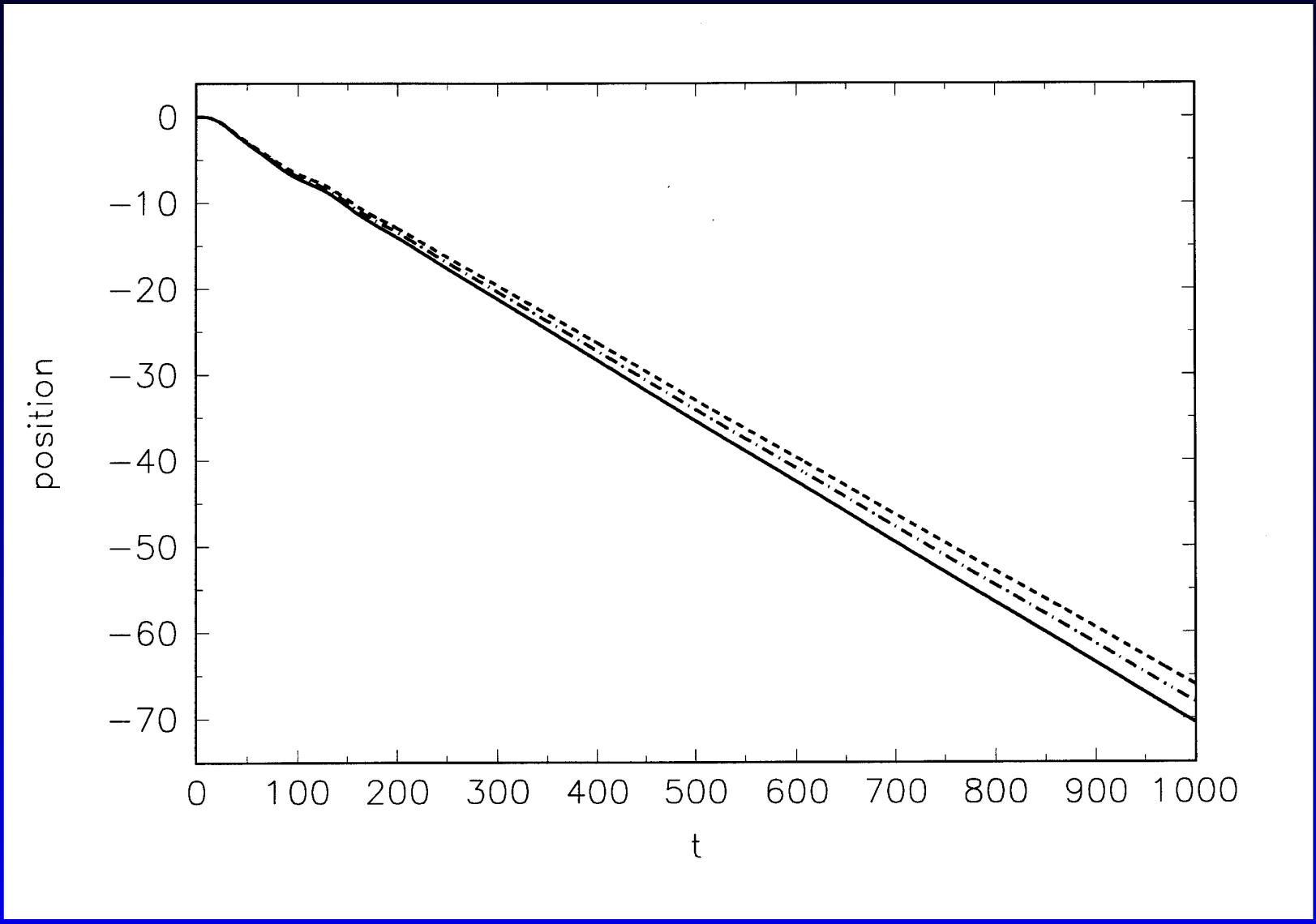
Irregular deviations from the helix structure

- Causes:
  - DNA buffeted by water molecules
  - Interactions with the solvent
- Modeled by random θ_0 and R_0
- Appear in:

$$V_{n\,n-1} = V_0\,(1 - \alpha d_{n\,n-1})$$

- Result: Small diminution of the velocity

Non–diagonal disorder



Standard deviations of r_n and $\theta_{n,n-1}$: 1% (–), 5% ($-\cdot$), 10% (- -)

Linear analysis

- Linear system analysis
  - Linear spectrum
  - Energy and nonlinearity degree
  - Expected Floquet eigenvalues
- Tail analysis
  - Inverse decay length
  - Breadth of the polaron
  - Energy of the moving polaron
- Floquet analysis
  - Stability
  - Coupling of variables
  - Effect of the disorder

Linear system analysis

$$
\begin{aligned}
i\,\tau\,\dot{c}_n &= -c_{n+1} - c_{n-1} \\
\ddot{r}_n &= -r_n \\
\ddot{\theta}_{n\,n-1} &= -\Omega^2\,\theta_{n\,n-1}
\end{aligned}
$$

- Ground state: $c_n(t) = \phi_n \exp(-i\frac{E\,t}{\tau})$
- Discrete Schrödinger equation:

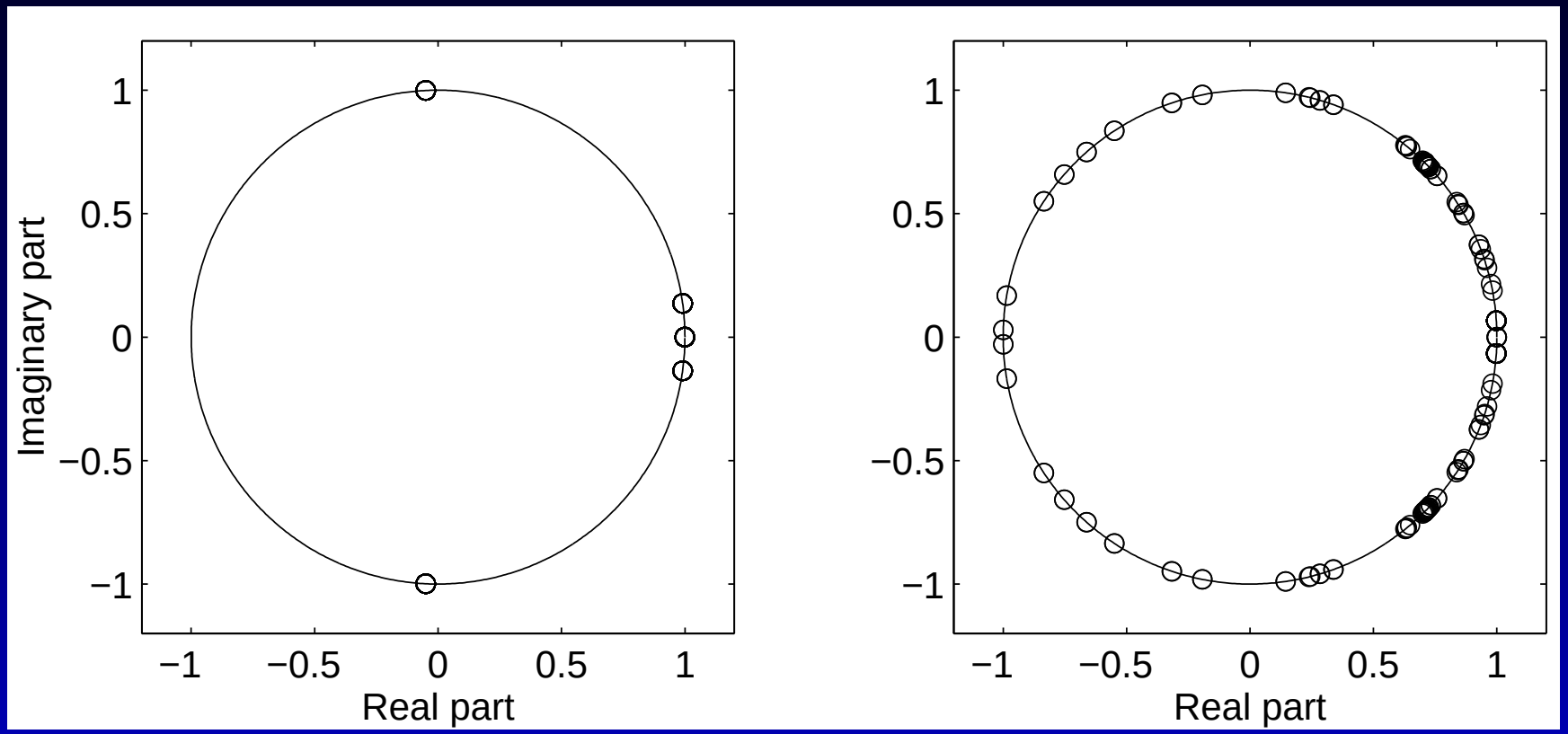
$$E\,\phi_n = -\phi_{n+1} - \phi_{n-1}$$

- Linear modes: $\phi_n = \exp(i\,q\,n)$
- Result: $E = -e^{i\,q} - e^{-i\,q} = -2\,\cos q$
- $E = -2$ for the $q = 0$ mode

Consequences

- Three time scales:
  - Polaron: $|w_p| = |E|/\tau \gtrsim 8$
  - Radial variables: w_r=1
  - Angular variables: $\Omega \simeq 0.08$
- Expected Floquet eigenvalues:
  - $r_n(T) = \exp(i\,2\,\pi\,/w_p)\,r_n(0)$
  - $\theta_{n\,n-1}(T) = \exp(i\,2\,\pi\,\Omega/w_p)\,\theta_{n\,n-1}(0)$
- Expected Floquet arguments:
  - $2\,\pi\,/w_p \lesssim 45^\circ$
  - $2\,\pi\,\Omega/w_p \lesssim 4^\circ$

Expected Floquet multipliers



Linear uncoupled (left) and actual system (right)

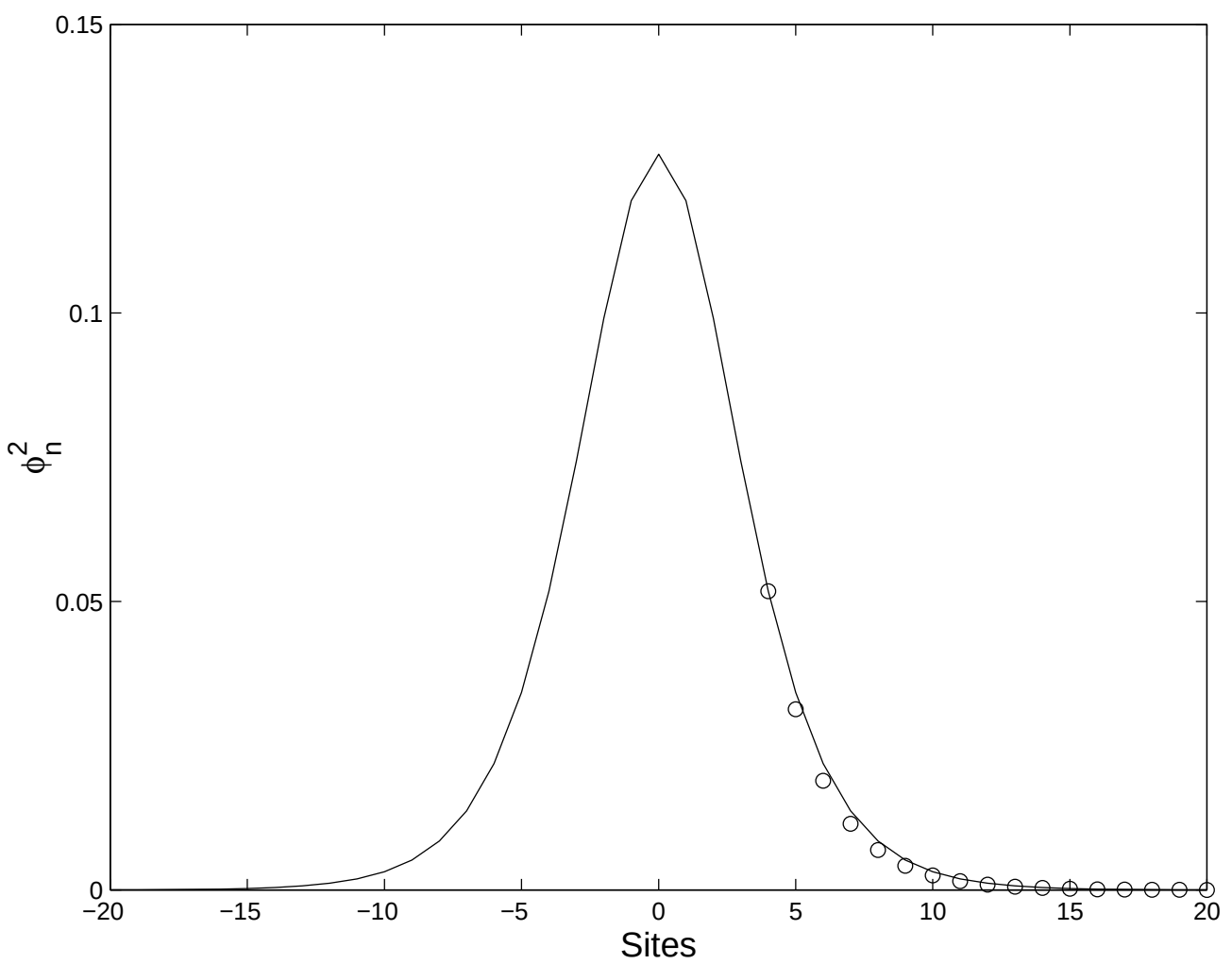
Tail analysis. Static polaron.

- Tail mode: $c_n(t) = \phi_n \exp(-\xi\, n - i\, q\, n)$
- Equations:
  $E = -2\, \cos(q)\, \cosh(\xi)\ ;\ 2\, \sin(q)\, \sinh(\xi) = 0$
- Energy: $E = -2 \cos(\xi) < -2$ for $q = 0$
- Breadth: $n_0 = 4.5/\xi$

ξ	2	1	0.5	0.15	0.075
n_0	2.25	4.5	9	30	60
E	-7	-3	-2.25	-2.02	-2.006

- Example: $E = -2.0635 \longrightarrow n_0 = 18$

Example of breadth



$$E = -2.0635 \longrightarrow n_0 = 18$$

Tail analysis. Moving polaron.

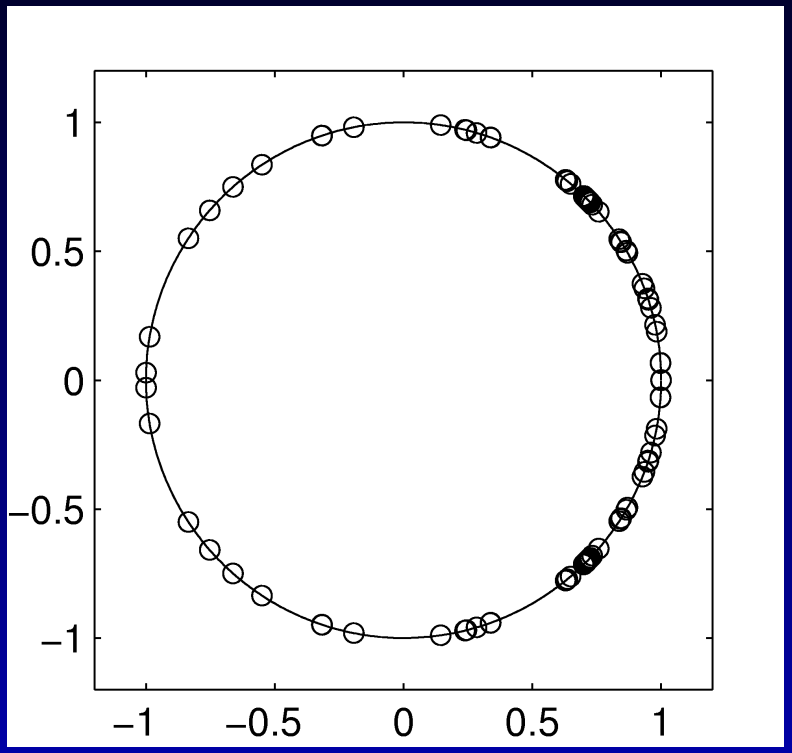
- Moving tail:
  $c_n = e^{-\xi\,(n + v\,t)}\, e^{-i\,q\,n}\, e^{-i\,E\,t/\tau}$
- Equations:

$$E = -2\,\cos(q)\,\cosh(\xi)$$

$$\tau\,\xi\,v = 2\,\sin(q)\,\sinh(\xi)$$

- Unknowns: E, ξ, q, v
- Numeric v and $\xi \longrightarrow E \approx$ static E
- Result: the moving energy is stored mainly in the spatial variables.

Floquet analysis



- Stability
- Coupling of variables and pinning mode
- Disorder effect

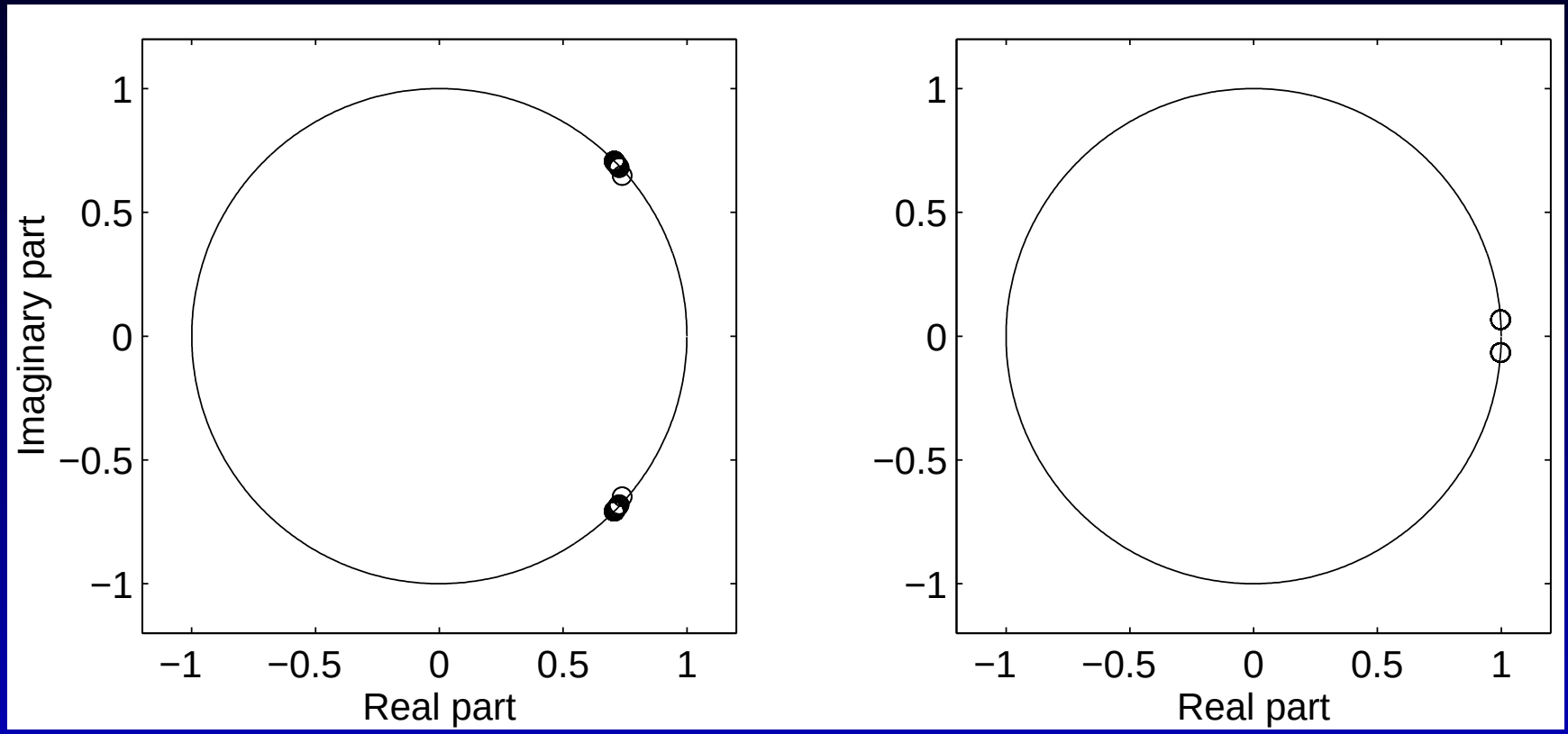
Coupling of variables

Floquet submatrices:

$$F = \begin{pmatrix} F_{cc} & F_{cr} & F_{c\theta} \\ F_{rc} & F_{rr} & F_{r\theta} \\ F_{\theta c} & F_{\theta r} & F_{\theta\theta} \end{pmatrix}$$

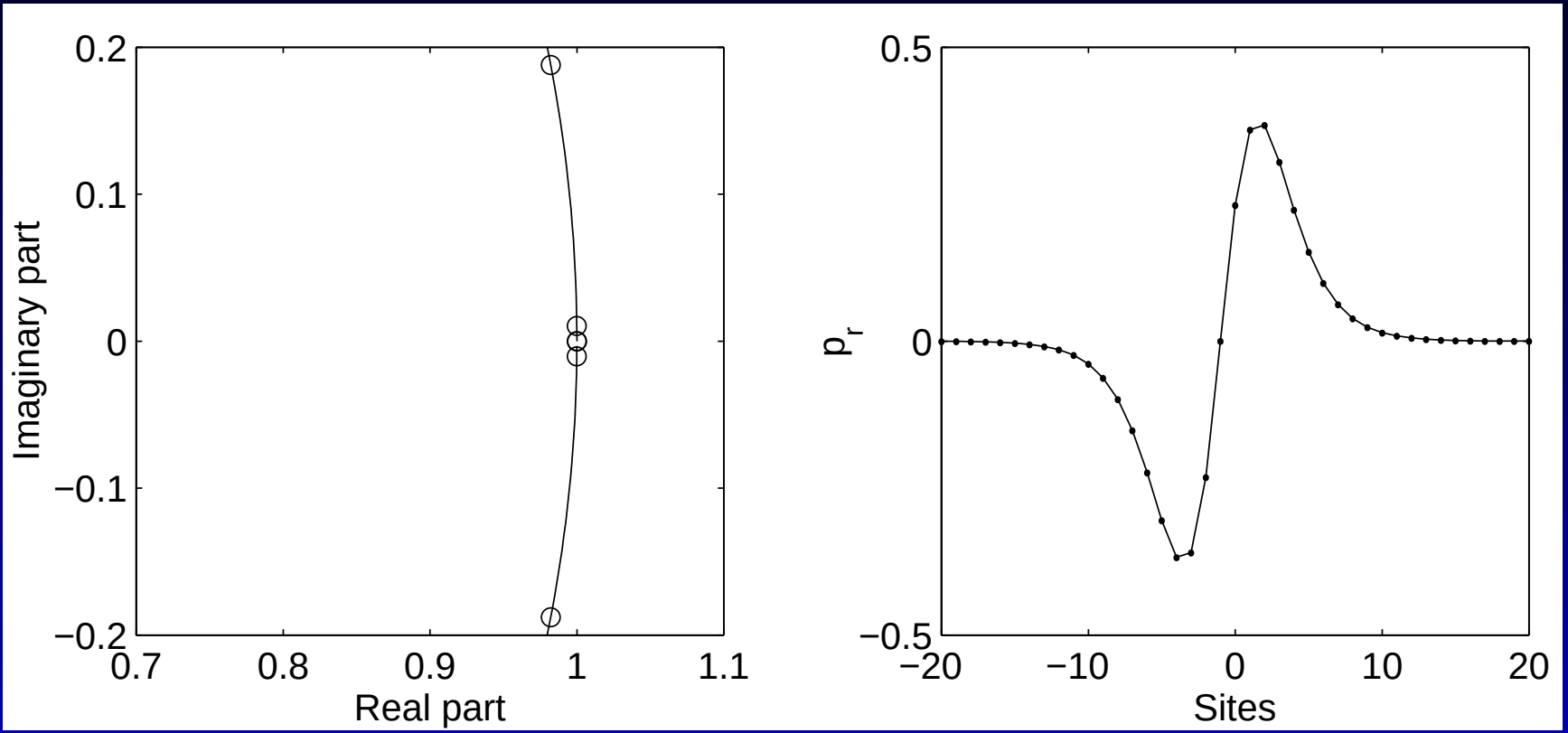
- $F_{cc} \longrightarrow$ Born-Oppenheimer approximation.
- $F_{C\,R} = (F_{cc}\ F_{cr}; F_{rc}\ F_{rr}) \longrightarrow$ Pinning mode
- Result: Mobility is a consequence of r_n–c_n coupling.

Floquet submatrices eigenvalues



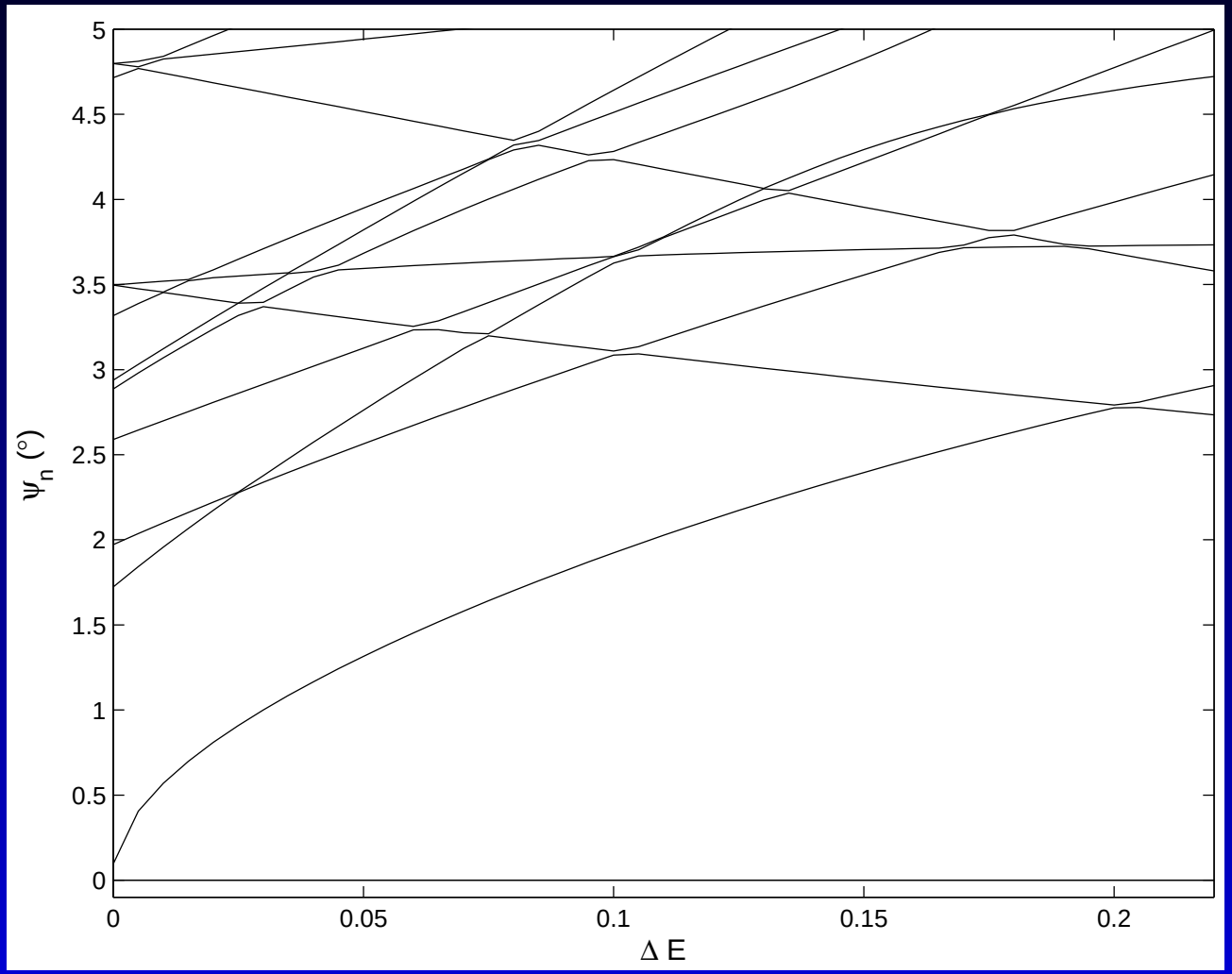
Floquet multipliers for r_n and $\theta_{n,n-1}$

Pinning mode



Floquet multipliers for c_n–r_n and pinning mode profile. Ordered case.

Floquet arguments and disorder



- The pinning mode eigenvalues separate from $(1, 0)$

Conclusions

- Nonlinear, three dimensional model for charge transport in DNA, including the stretching and twisting degrees of freedom
- Localized polarons with a local compression and unwinding of the helix exist as localized, static and moving entities
- Charge transport survives to a signi£cant degree of diagonal and structural disorder
- We relate magnitudes as the polaron energy, inverse decay length, wave number, velocity and breadth of the polarons, and obtain the effect of the different couplings and the disorder on the movability

Planned extensions

- Allow larger values of r_n and $\theta_{n\,n-1}$, outside the linear approximations of $d_{n\,n-1}$
- Electric field
- Temperature
- Multiple electrons

Some information

Nonlinear charge transport mechanism in periodic and disordered DNA.

Authors: D Hennig, JFR Archilla and J Agarwal

Fachbereich Physik, Institut für Theoretische Physik, Freie Universität Berlin
Grupo de Física No Lineal (GFNL), Universidad de Sevilla, Spain

Submitted to Physica D

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