DNA Conductivity: Our Most Recent Results

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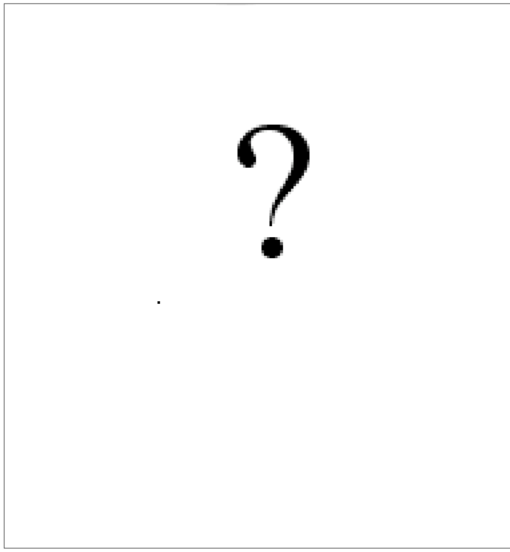
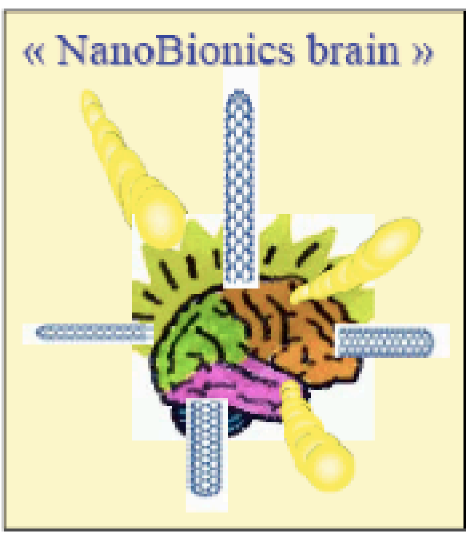
MOTIVATION

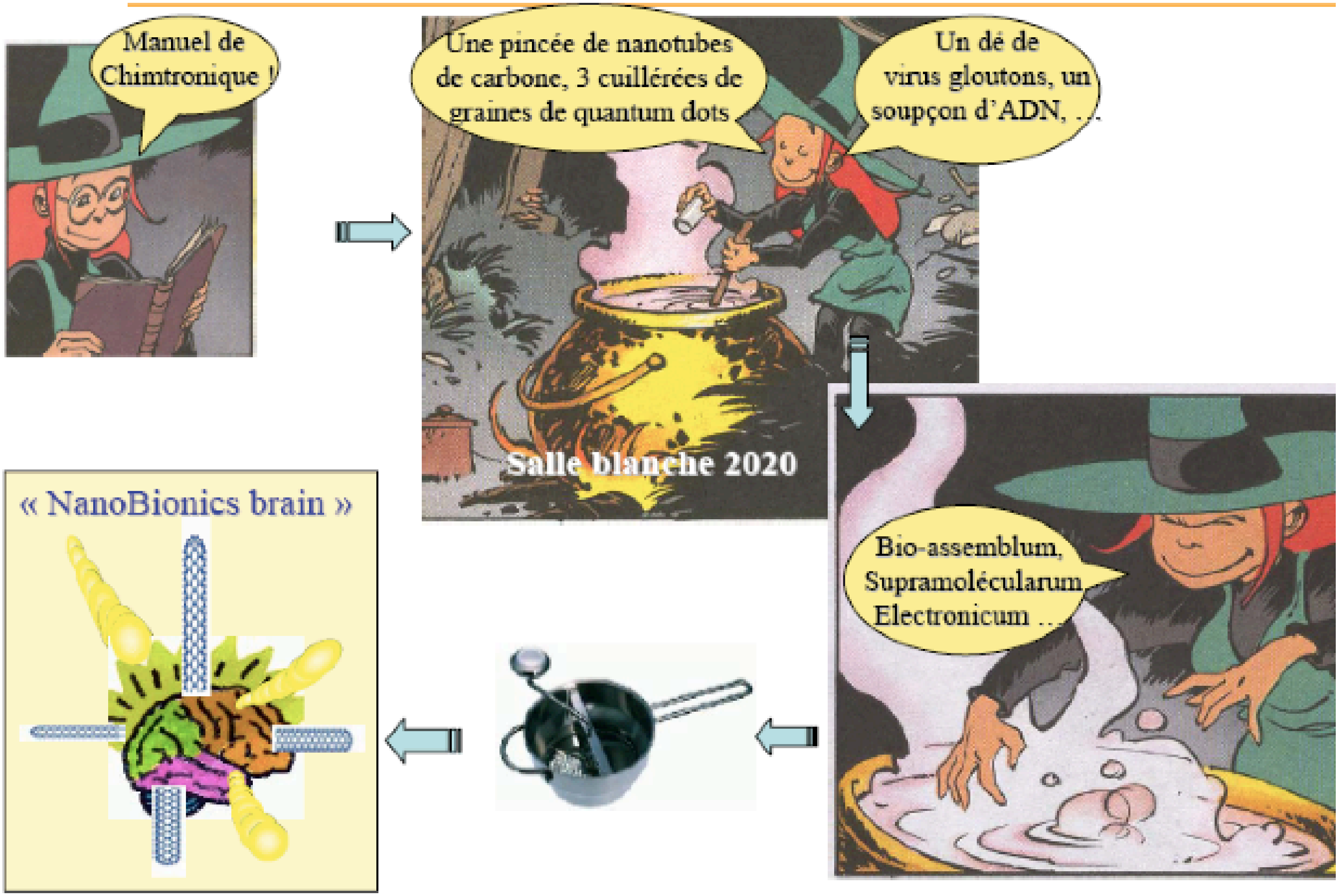

?


Une pincée de nanotubes
de carbone, 3 cuillérées de
graines de quantum dots
Un dé de
virus gloutons, un
soupçon d'ADN, …
Salle blanche 2020


Bio-assemblum,
Supramolécularum
Electronicum …


« NanoBionics brain »

MOTIVATION


Manuel de Chimtronique !
Une pincée de nanotubes de carbone, 3 cuillérées de graines de quantum dots
Un dé de virus gloutons, un soupçon d'ADN, …
Salle blanche 2020
Bio-assemblum, Supramoléculorum Electronicum …
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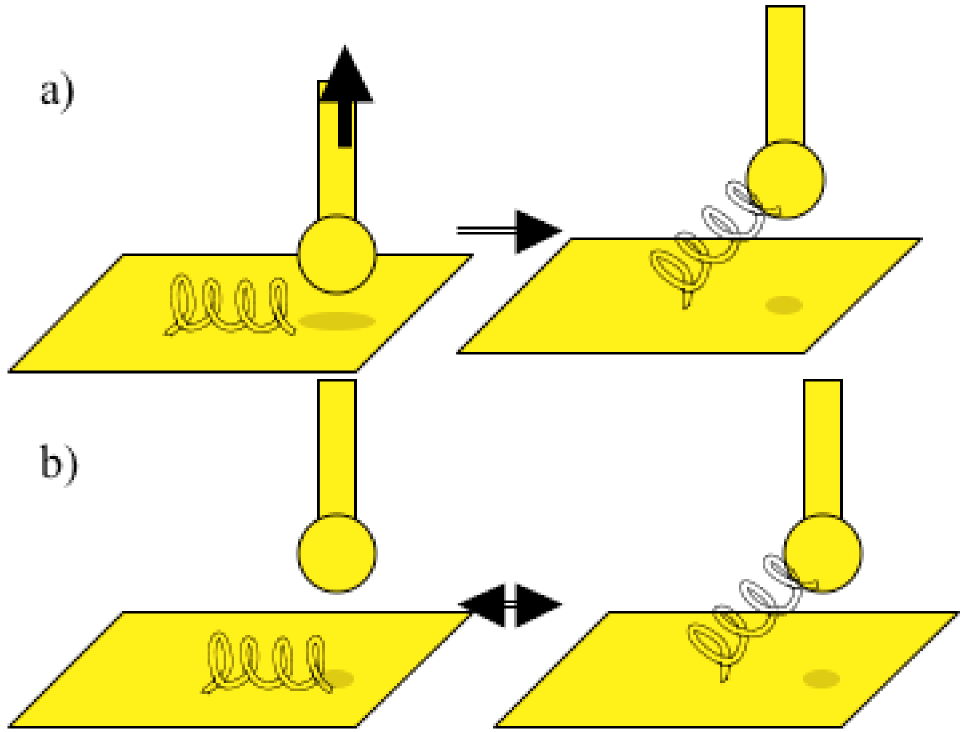
Topics for today:

- DNA conductivity is *temperature independent*

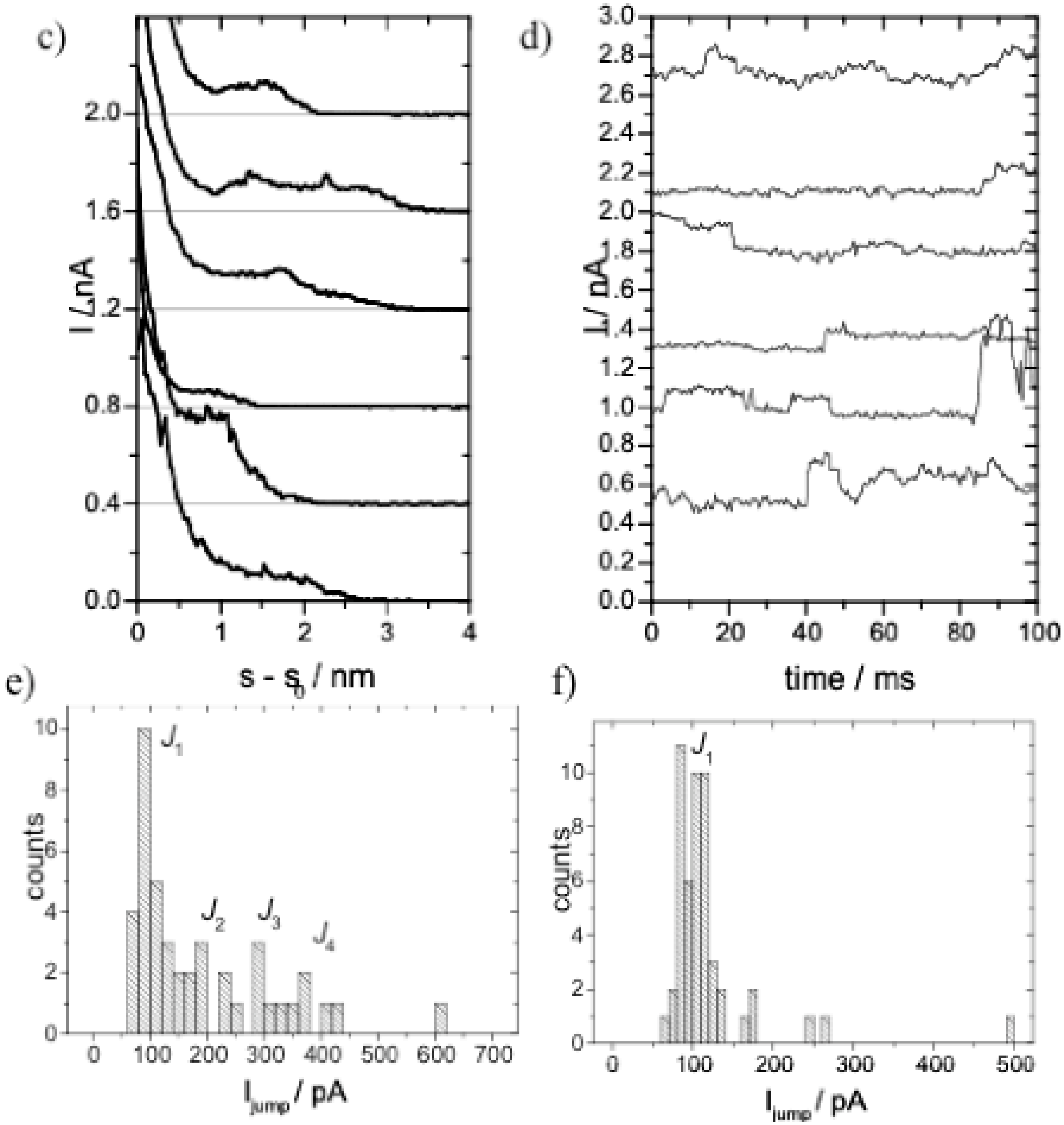
- *Acoustic modes* in DNA duplexes and their role in DNA charge transport

DNA conductivity is ***temperature independent***

Two experimental techniques (Richard Nichols *et al.*)

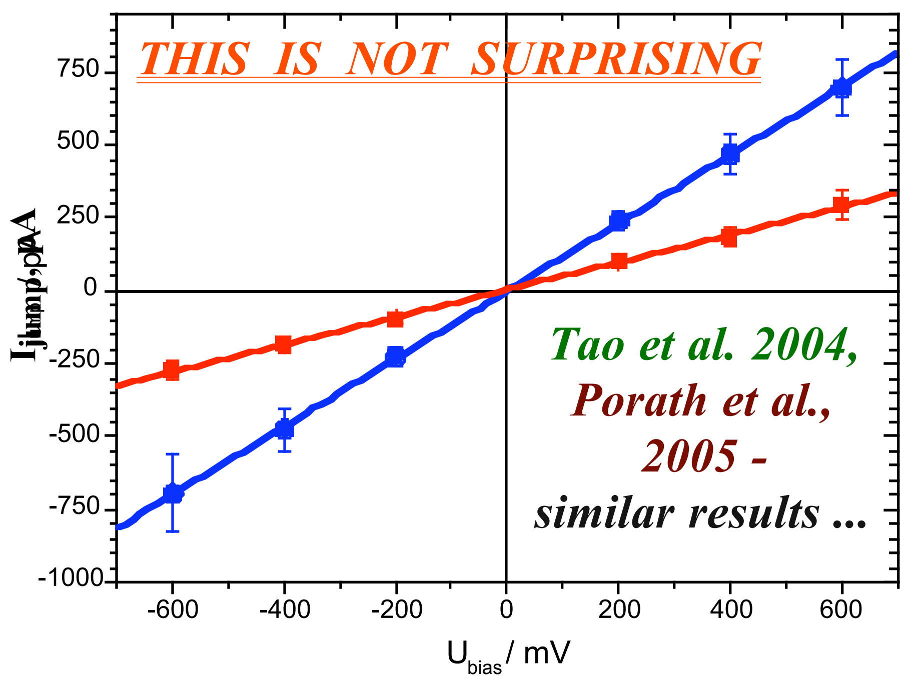


a) shows the ***I*(s)-technique** where the GOLDEN tip is withdrawn from the GOLDEN surface while a DNA molecule bridges the gap.
b) shows the ***I*(*t*)-technique** where the GOLDEN tip - GOLDEN substrate gap is fixed and a DNA molecule spontaneously bridges the gap.

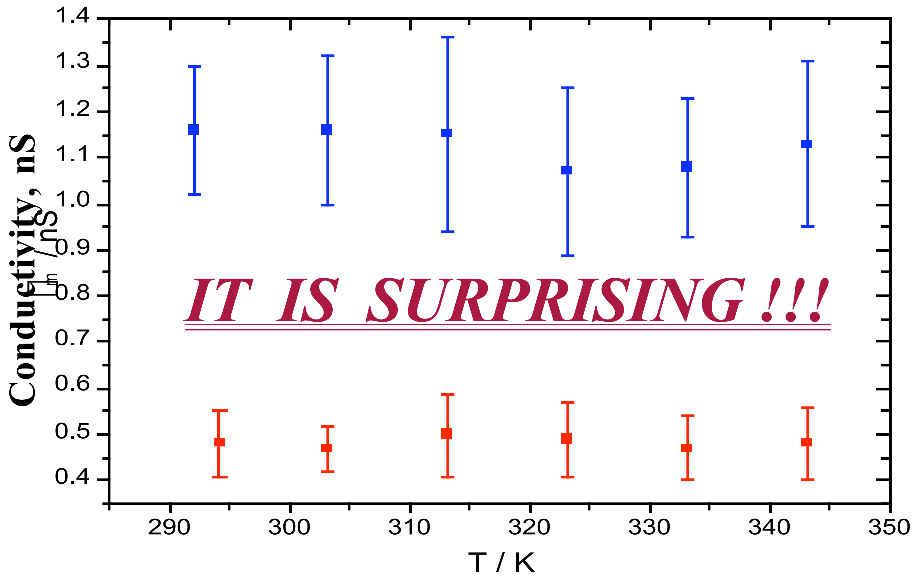


Characteristic results for both $I(s)$ and $I(t)$-technique are shown in c) and d) respectively.

The resulting histograms are shown in e) ($I(s)$) and f) ($I(t)$).

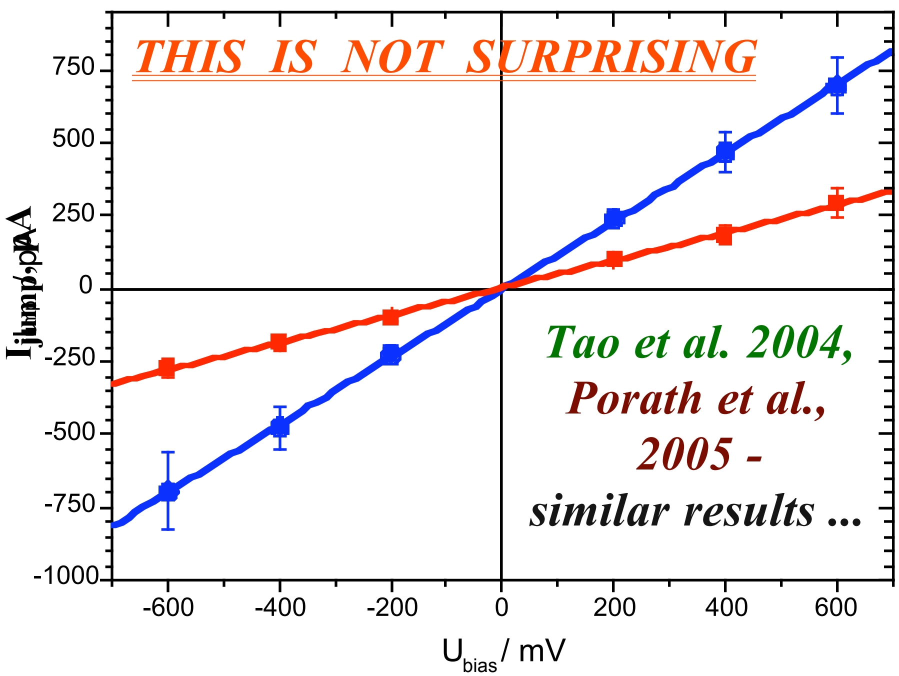


The jump current using the *I*(*t*) method as a function of the tip substrate potential for both $(dA)_{15}$-$(dT)_{15}$ and $(dG)_{15}$-$(dC)_{15}$.



The single molecule conductance as a function of the substrate temperature at zero bias for both $(dA)_{15}$-$(dT)_{15}$ and $(dG)_{15}$-$(dC)_{15}$.

DNA duplex	Conductance / nS
HS-C_3-(dA) (dT)-C_3-SH	0.51 ± 0.08
HS-C_3-(dG) (dC)-C_3-SH	1.2 ± 0.2



The jump current using the *I*(*t*) method as a function of the tip substrate potential for both $(dA)_{15}$-$(dT)_{15}$ and $(dG)_{15}$-$(dC)_{15}$.

Acoustic modes in DNA duplexes

Internal energy for the Debye model of a crystal lattice with 3 acoustic and 3s-3 optical modes

$$\mathcal{E} = \mathcal{E}_0 + Nk_B T\left[3\mathcal{D}\left(\frac{\Theta}{T}\right) + \sum_{j=4}^{3s} \frac{\Theta_j/T}{e^{\Theta_j/T}-1}\right]$$

where the *Debye function* $\mathcal{D}(z)$ is

$$\mathcal{D}(z) = \frac{3}{z^3}\int_0^z \frac{x^3dx}{e^x-1}.$$

Θ stands for the Debye temperature

At high temperatures, $T \gg \Theta_j$ (and, consequently, $T \gg \Theta$)

we get $z \ll 1$ and $\mathcal{D}(0) = 1$

And what is the Debye temperature for a typical DNA ???

It is about 160^{o} K,

if one takes the *velocity of sound* in B-DNA
to be about 1900 m/sec
(M. B. Hakim, S. M. Lindsay, and J. Powell, *Biopolymers*, 1984, vol. **23**, p. 1185)
and the B-DNA *lattice constant* of 3.4 Å.

whereas the DNA measurements were carried out at room temperature !!!

Therefore, one may speak of

free acoustic polarons

as possible charge carriers

responsible for DNA conductivity.

To check this hypothesis, we have to know,

1) what DNA acoustic modes are looking like **and**

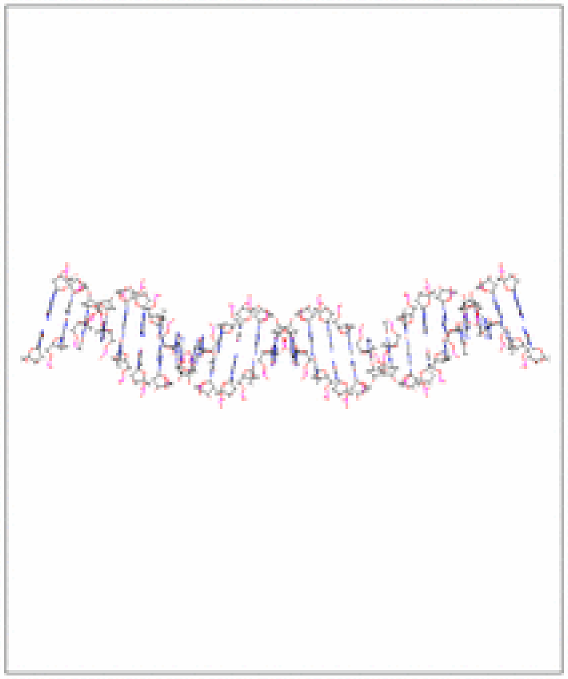
2) whether free acoustic polarons are possible along DNA duplexes

DNA acoustic modes

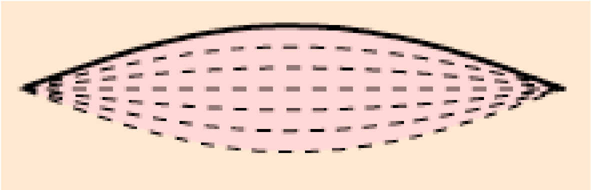
can be estimated using
“elastic network” model

(coarse-graining model of DNA assuming that nucleotides are rigid bodies)

DNA acoustic mode 1

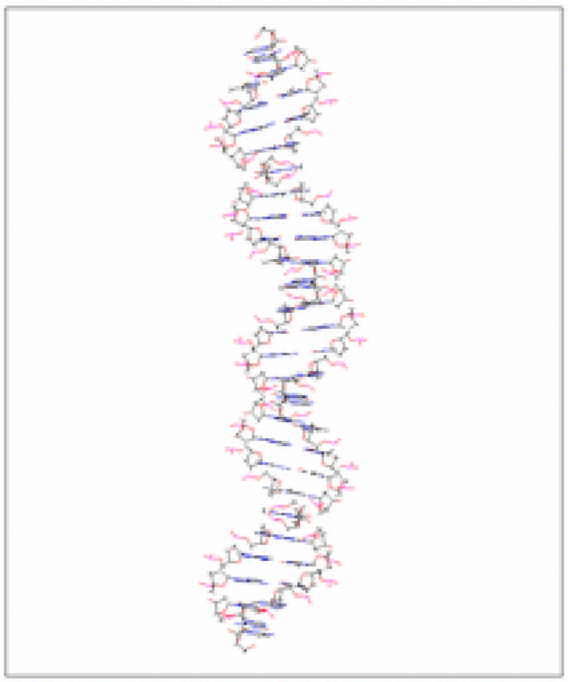


If Z is the double-helical axis and the ends are fixed by electrodes,



it is "guitar string" ***BENDING*** in X-direction.

<u>DNA acoustic mode 2</u>



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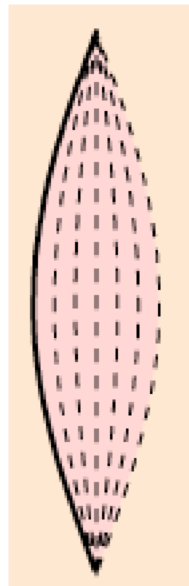
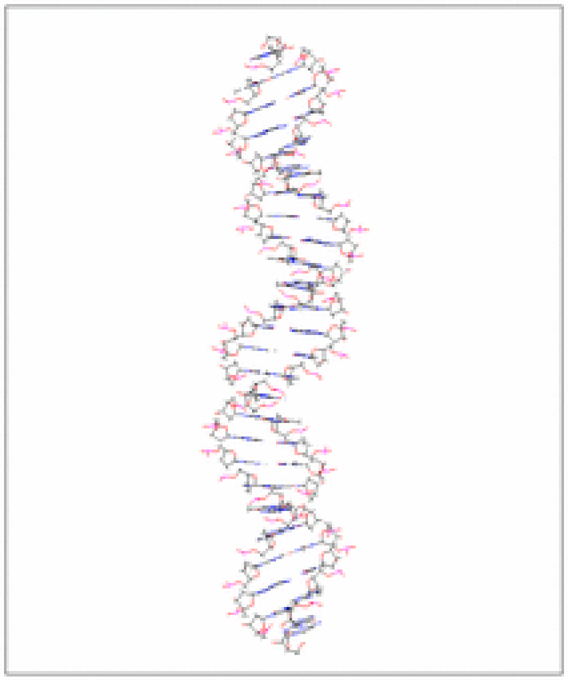
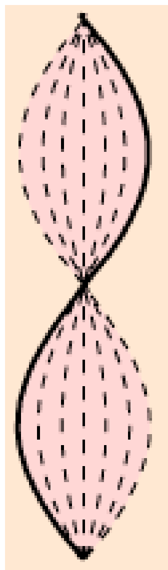


This is "guitar string" ***<u>BENDING</u>*** in Y-direction.

DNA acoustic mode 3





This mode is much more than just the 2nd harmonics of the "guitar string" *BENDING,* since DNA is compressible:

It is *TWISTING* together with changes in the *double-helical PITCH*

To check numerically, whether *free acoustic polarons* are possible in DNA duplexes:

1) to generate deformed DNA conformations according to its acoustic modes

2) to calculate and compare conductance along DNA duplexes in their equilibrium and deformed conformations

DNA static ballistic conductivity

$$G = \lim_{\omega \to 0} \frac{\langle \hat{I} \rangle}{V} = -e^2 \hbar \pi \lim_{\omega \to 0} \sum_{\alpha,\beta} \left| \langle \alpha | \hat{v}_x | \beta \rangle \right|^2 \frac{f_\alpha - f_\beta}{\varepsilon_\alpha - \varepsilon_\beta} \delta\left(\varepsilon_\alpha - \varepsilon_\beta - \hbar\omega\right)$$

Above is the

conventional Kubo formula,

in terms of eigenstates and eigenfunctions

$$G = 2\left(\frac{e^2}{h}\right) \mathrm{Tr}\left[\left(i\hbar\hat{v}_x\right) \mathrm{Im}\hat{\mathcal{G}}(E) \left(i\hbar\hat{v}_x\right) \mathrm{Im}\hat{\mathcal{G}}(E)\right]$$

$$\mathrm{Im}\hat{\mathcal{G}}(E) = \frac{1}{2i}\left[\hat{\mathcal{G}}^R(E) - \hat{\mathcal{G}}^A(E)\right]$$

... recast in the Green function form

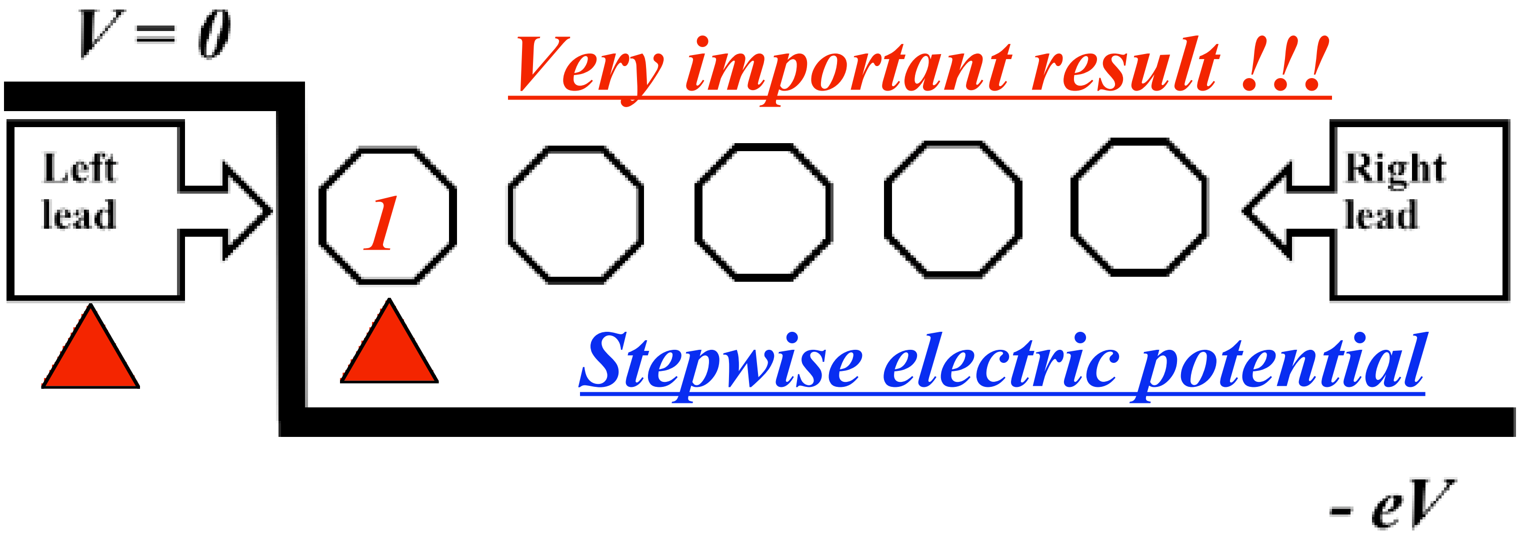
To estimate DNA conductivity we need:

- ***Velocity of the charge flow*** **through DNA**

- ***Green function*** **of DNA**

  (in the standard *Extended Hückel* approximation)

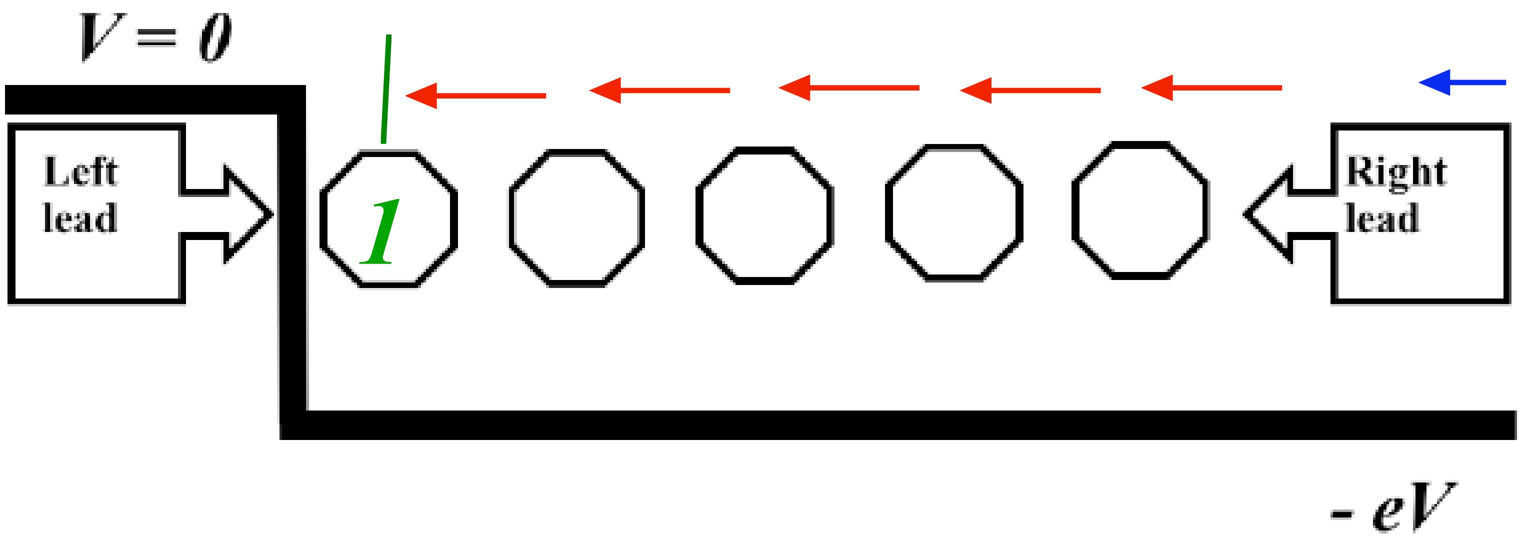
Very important result !!!



$$\hat{v}_x = -\frac{t}{i\hbar}\sum_{j=1}^{m}\left(\hat{c}^{\dagger}_{0,j}\hat{c}_{1,j} - \hat{c}^{\dagger}_{1,j}\hat{c}_{0,j}\right)$$

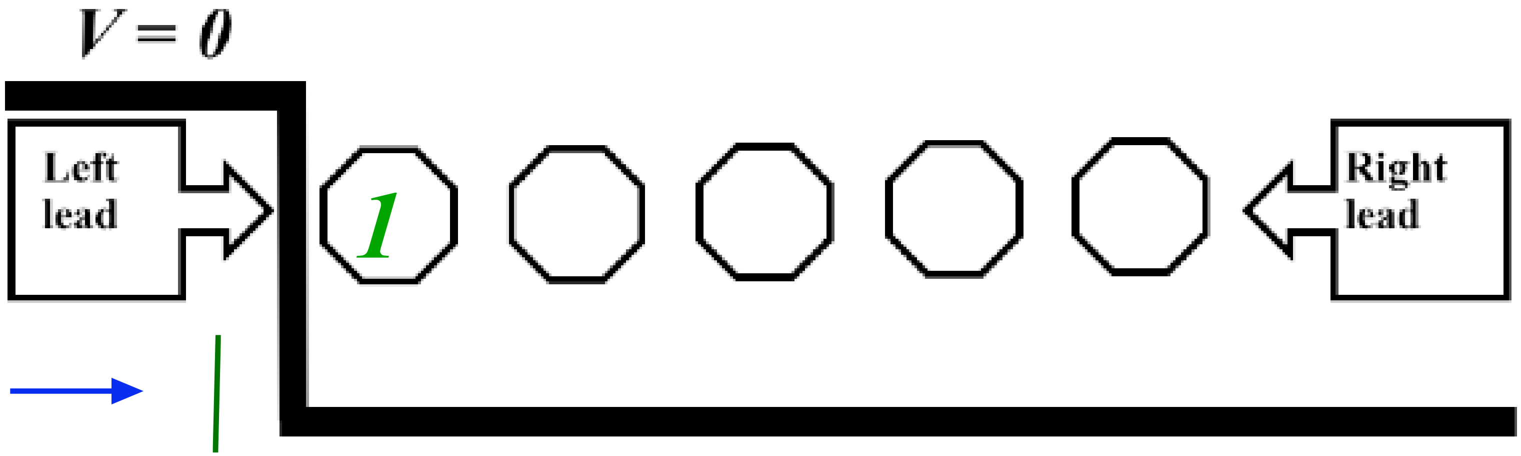
Charge velocity operator for the whole system !!!

To find the DNA Green function we need 2 steps:



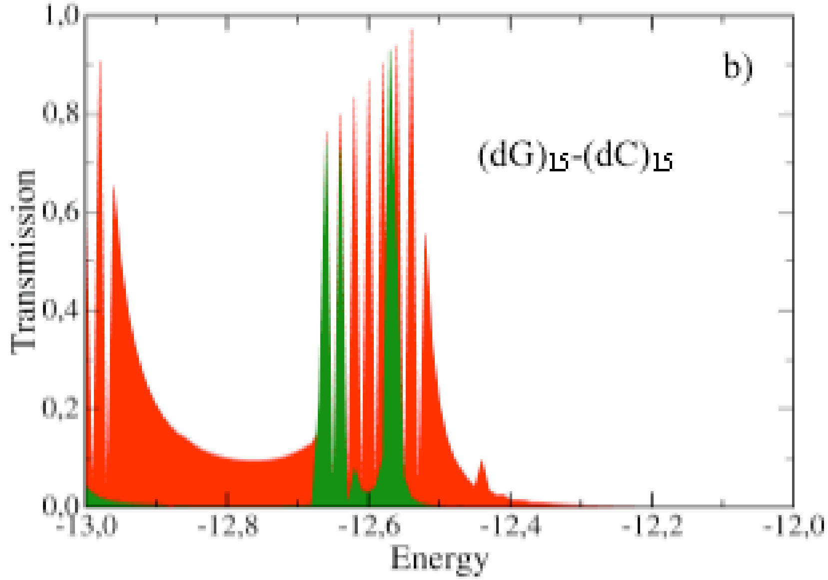
$$\boldsymbol{\Sigma}_{i-1} = \mathbf{V}_{i-1,i}\left(E\mathbf{I} - \mathbf{V}_{i,i} - \boldsymbol{\Sigma}_{i}\right)^{-1}\mathbf{V}_{i,i-1}$$

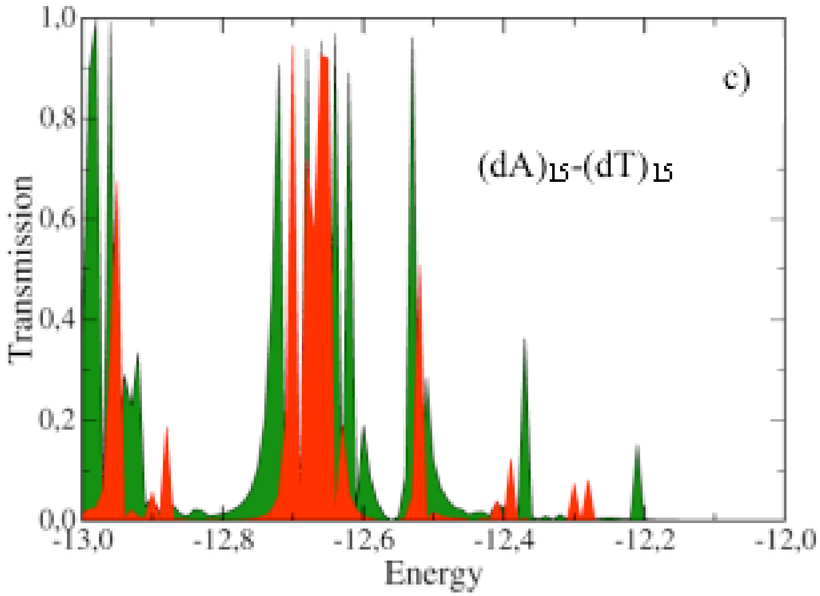
1. Back-iteration of Dyson equation



$$\left[E\mathbf{I}-\mathbf{H}-\boldsymbol{\Sigma}_l(E)-\boldsymbol{\Sigma}_r(E)\right]\hat{\mathcal{G}}(E)=\mathbf{I}$$

2. Full Green function of the contact between the left lead and the 1st layer





The Fermi level (defined here as halfway between the energies of the highest occupied and lowest unoccupied orbitals at 0 K) is around –12.05 eV for all graphs. Red graphs correspond to the transmission spectra of the duplexes in their ideal B-DNA conformation, the green ones depict those in the presence of deformations along DNA acoustic modes

Conclusions

Acoustic polaron formation promotes charge transport in (dA)-(dT) systems

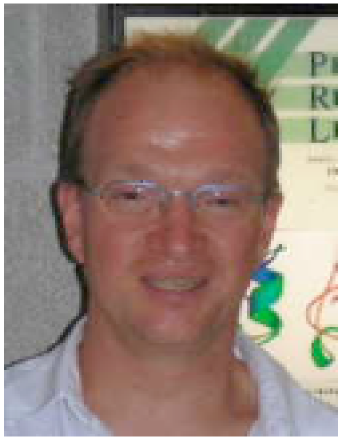
Acoustic polaron formation interfers charge transport in (dG)-(dC)

Outlook

Influence of DNA dynamics on the faster time scales

The exact molecular structure of transmissive pathways (conductive channels) in DNA

Co-authors:



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