What does theory tell us about electron transfer and electron transport in DNA?

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Ordnung mikroskopischer Freiheitsgrade

Elektronische Korrelationen
und Magnetismus
Universität Augsburg

- What is DNA?

  `www.nature.com/nature/dna50`

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- Why do we want to understand the behaviour of electrons in DNA?

⟶ biology

→ radiation damage and repair

→ biochemical sensors

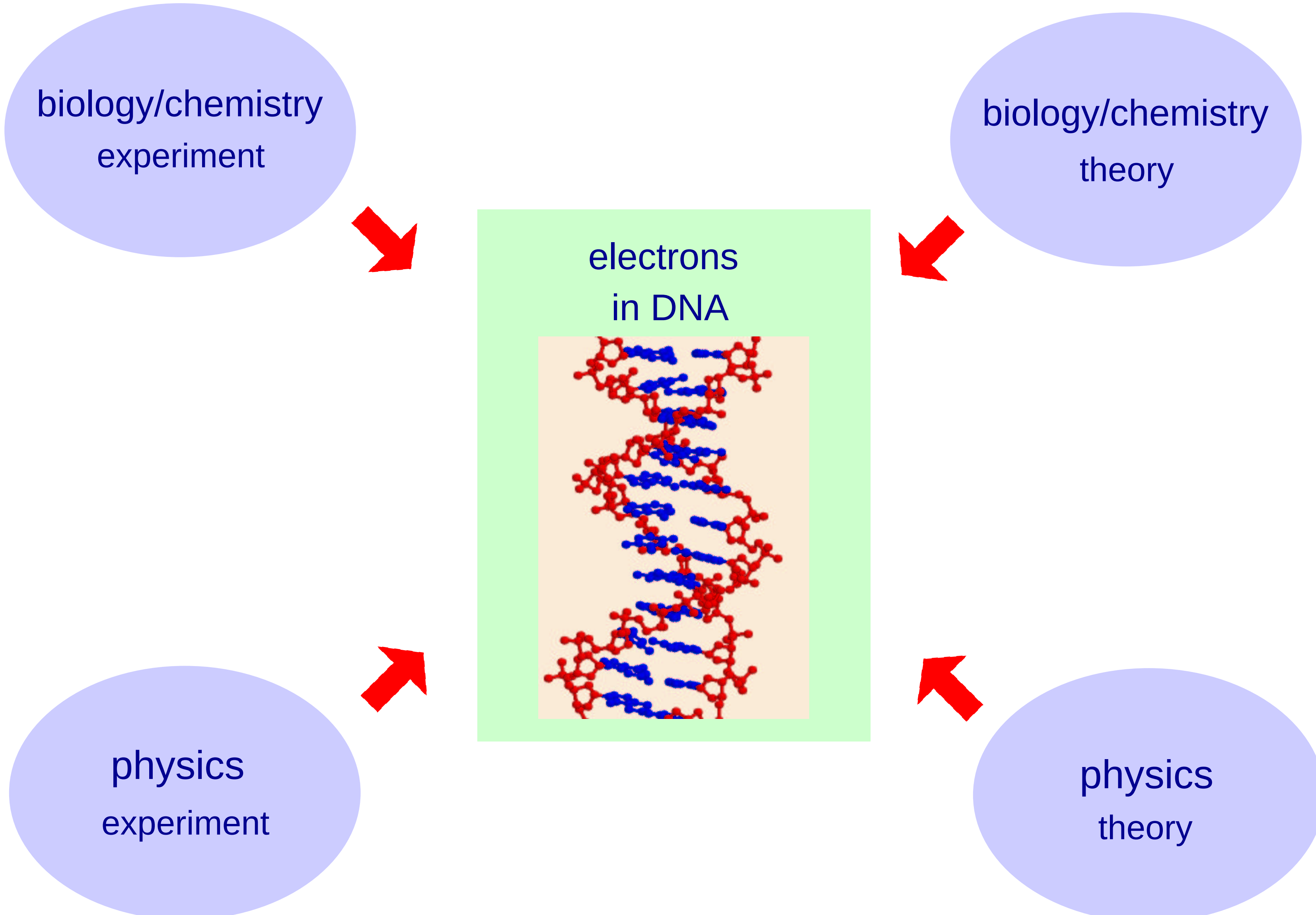
E. M. Boon and J. K. Barton, Curr. Op. in Struct. Biol. **12**, 320 (2002)

⟶ nanotechnology

→ molecular electronics

C. Dekker and M. Ratner, Physics World, August 2001

D. Porath, G. Cuniberti, and R. Di Felice, Topics in Current Chemistry **237**, (in print)


biology/chemistry
experiment
biology/chemistry
theory
electrons
in DNA
physics
experiment
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theory

Experiments on electron transfer (biology)

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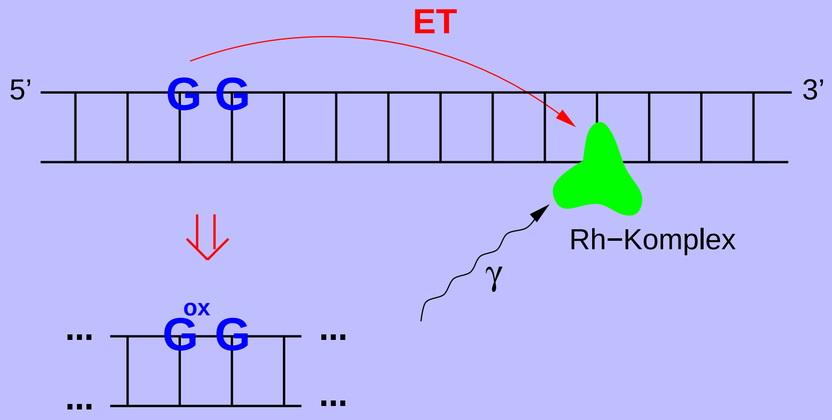
D.B. Hall, R.E. Holmlin, J.K. Barton
Oxidative DNA damage through long-range electron transfer
Nature **382**, 731 (1996)



long range electron transfer, up to 37Å

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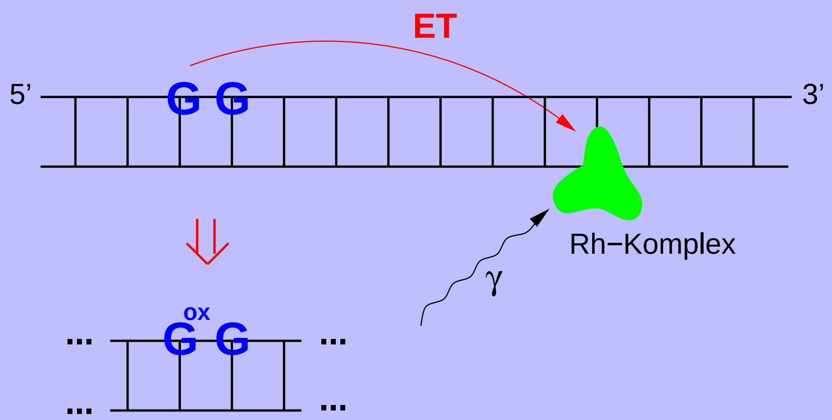
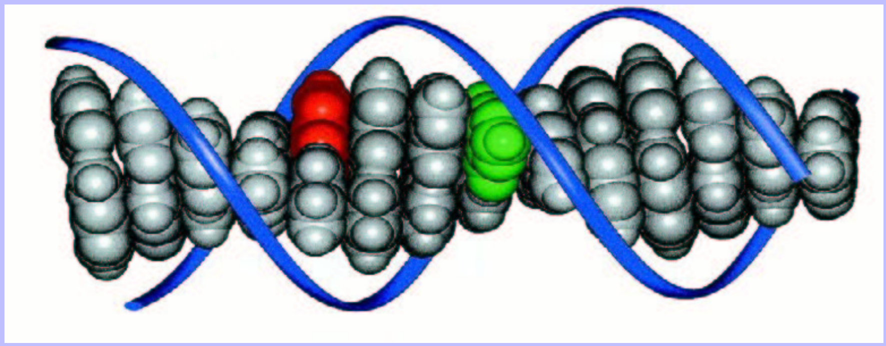


long range electron transfer, up to 37Å

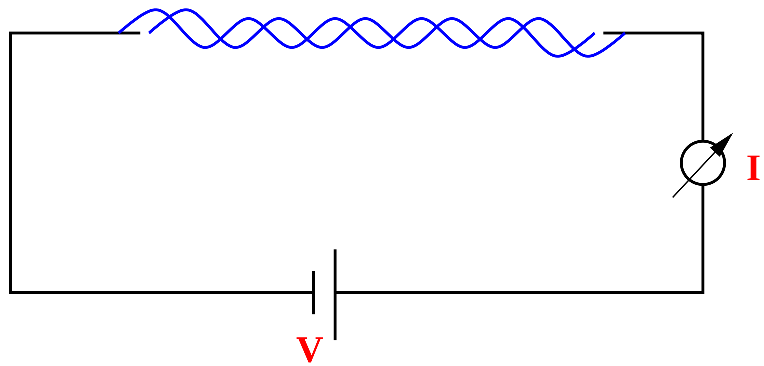
C. Wan et al.
Femtosecond direct observation of charge transfer between bases in DNA
Proc. Natl. Acad. Sci. U.S.A. **97**, 14052 (2000)



exponential decay of electron transfer rate

$\Longrightarrow$ no clear picture

Experiments on electron transport (physics)



Storm et al. Appl. Phys. Lett. **79**, 3881 (2001)	$\rho = \infty$
Porath et al. Nature **403**, 635 (2000)	semiconducting
Fink & Schönenberger Nature **398**, 407 (1999)	metallic
Kasumov et al. Science **291**, 280 (2001)	superconducting

$\Longrightarrow$ no clear picture

What can theory provide for understanding electron transfer and electron transport in DNA?

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general:

- identify a suitable model
- extract information on physical properties
- compare with experimental observations
- propose new experiments
- develop a suitable language

The problem

Ingredients for a successful theoretical description unclear

Questions:

1. How far can we go with ab-initio approaches?
2. What is the role of disorder?
3. Is there a difference between electron transfer and electron transport?
4. Is it possible to describe electron transfer/transport in DNA within a purely quantum mechanical approach?
5. How useful is the picture of electronic bands in DNA?
6. What is the role of phononic degrees of freedom?
7. What about electronic correlations in DNA?
8. Is there a connection between electron transfer in DNA and quantum impurity physics (such as Kondo physics?)
9. Do we expect to see Luttinger liquid behaviour?

Q1 How far can we go with ab-initio approaches?

here: density-functional calculations for a variety of situations:

- dry DNA

  E. Artacho, M. Machado, D. Sanchez-Portal, P. Ordejon, and J.M. Soler

  Electrons in Dry DNA from Density Functional Calculations

  Mol. Phys. **101**, 1587 (2003)

- wet DNA

  F.L. Gervasio, P. Carloni, and M. Parrinello

  Electronic Structure of Wet DNA

  Phys. Rev. Lett. **89**, 108102 (2002)

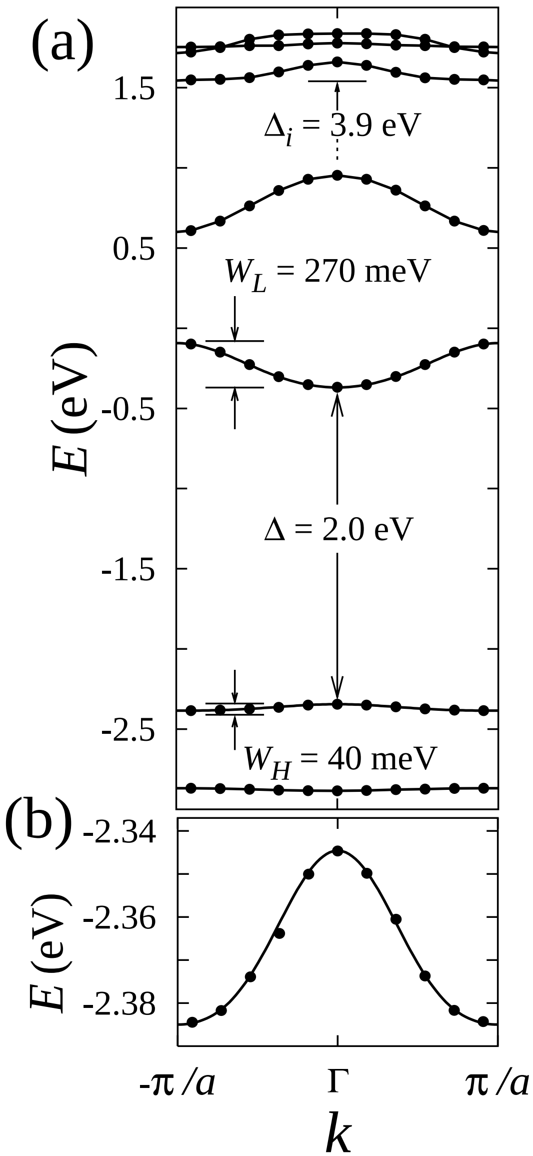
- overstreched DNA

  P. Maragakis, R. L. Barnett, E. Kaxiras, M. Elstner, and T. Frauenheim

  Electronic structure of overstretched DNA

  Phys. Rev. B **66**, 241104 (2002)

$\Longrightarrow$ importance of structure, environment, and genetic sequence results: electronic structure of dry DNA [Artacho et al.]

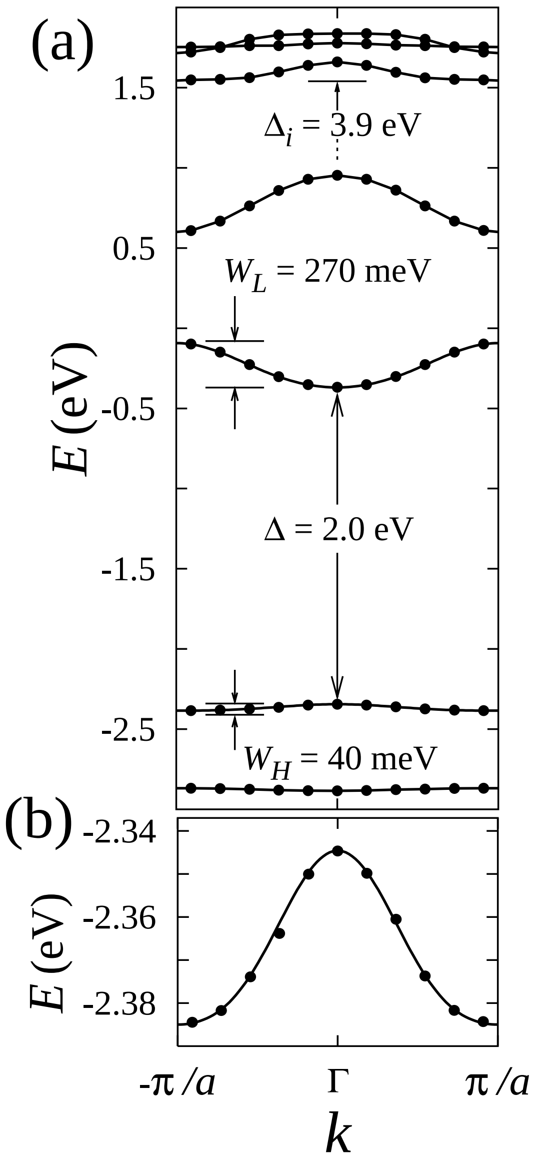


calculations for

G G G G G G G G G G
C C C C C C C C C C

$\Longrightarrow$ 725 atoms per unit cell

results: electronic structure of dry DNA [Artacho et al.]



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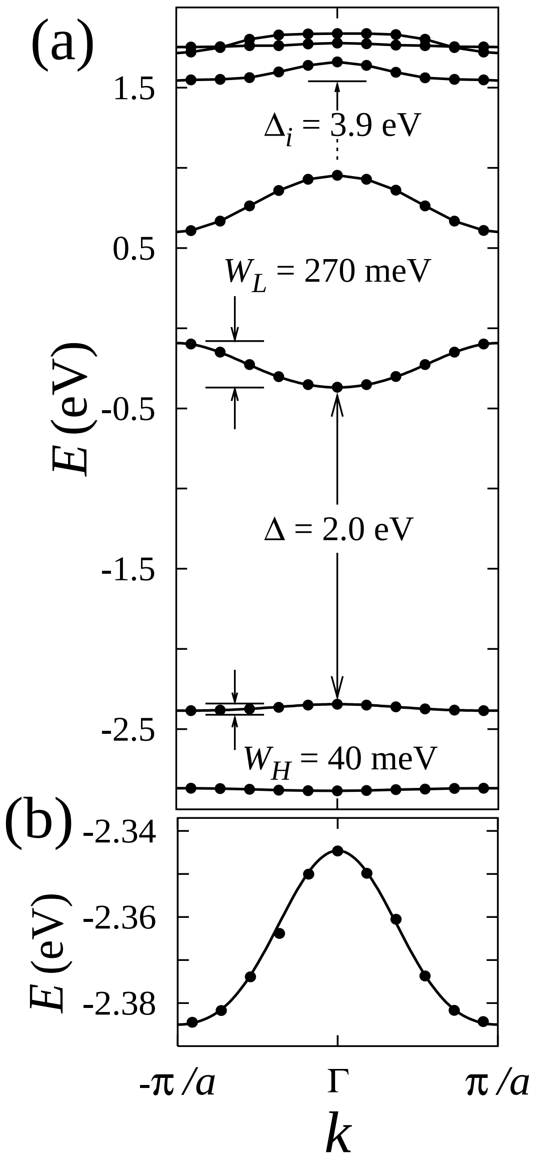

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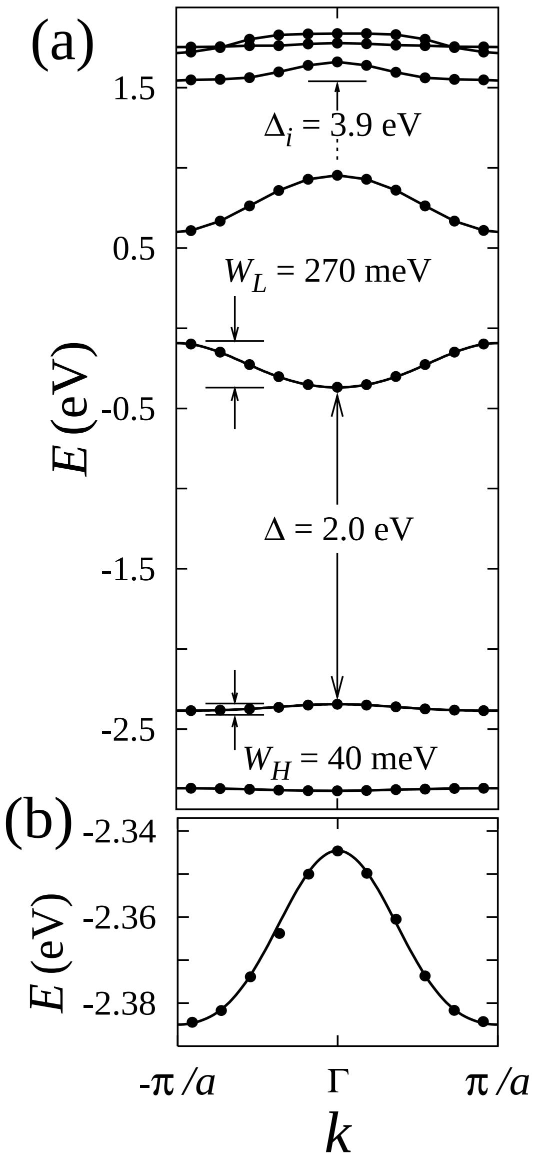

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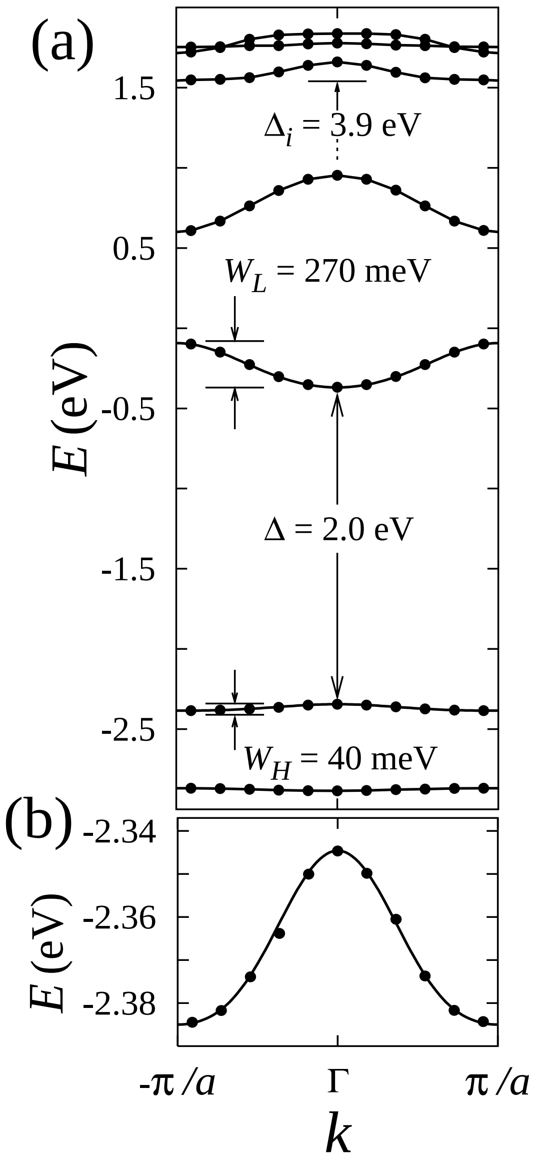

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but:

$$W \ll W_{\text{disorder}} \;, \quad W \ll W_{\text{el-ph}}$$

$\Longrightarrow$ DFT output only as a starting point for further calculations

Q2 What is the role of disorder?

sequence of base pairs:

periodic

G G G G G G G G G G
C C C C C C C C C C

Q2 What is the role of disorder?

sequence of base pairs:

periodic										in nature									
G	**G**	**G**	**G**	**G**	**G**	**G**	**G**	**G**	**G**	**G**	**A**	**C**	**C**	**A**	**T**	**A**	**G**	**G**	**T**
C	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**T**	**G**	**G**	**T**	**A**	**T**	**C**	**C**	**A**

$\Longrightarrow$ strong disorder potential

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sequence of base pairs:

periodic	in nature
G G G G G G G G G G	**G A C C A T A G G T**
C C C C C C C C C C	**C T G G T A T C C A**

$\Longrightarrow$ strong disorder potential

possible model:

one-dimensional Anderson model

$$H = -t \sum_l \left(c_l^\dagger c_{l+1} + c_{l+1}^\dagger c_l \right) + \sum_l \varepsilon_l c_l^\dagger c_l$$

- ε_l: random
  $\Longrightarrow$ all electronic states are localized
- electronic transport via some hopping mechanism

theoretical implementation of this idea:

Z.G. Yu and X. Song

Variable Range Hopping and Electrical Conductivity along the DNA Double Helix

Phys. Rev. Lett. **86**, 6018 (2001)

$+$ disorder induced by structural fluctuations theoretical implementation of this idea:

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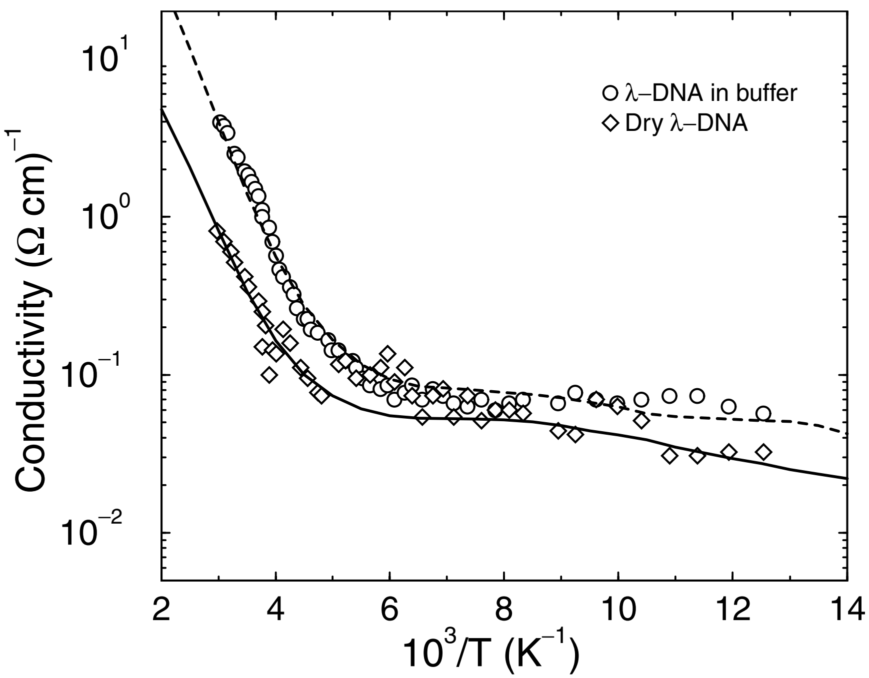

⟹ very good agreement with experiments by:

P. Tran, B. Alavi, and G. Gruner

Phys. Rev. Lett. 85, 1564 (2000)

[AC conductivity]

problems:

1. data not conclusive

variable range hopping predicts:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right]$$

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$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right]$$

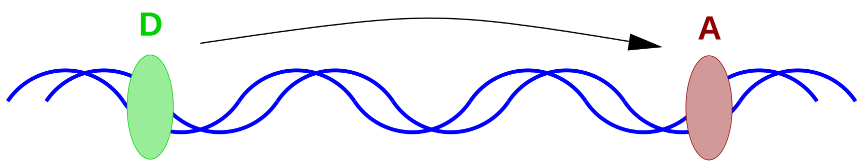
2. mechanism for AC conductivity

N.P. Armitage, M. Briman, G. Gruner
Charge Transfer and Charge Transport on the Double Helix
cond-mat/0309360

"... we have found that the considerable AC conductivity of DNA
can be attributed largely to relaxational losses
of the surrounding water dipoles."

Q3 . . . difference between electron transfer and electron transport?

electron transfer



- decay of excited state $\exp(-kt)$
- electron transfer rate $k \propto \exp(-\beta R)$

β small $\longrightarrow$ long range electron transfer

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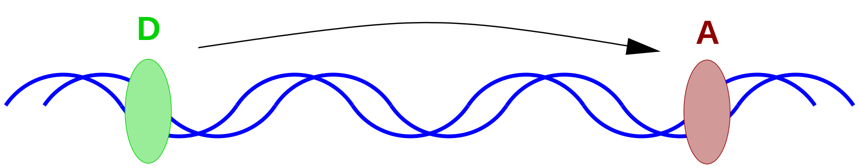

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N.P. Armitage et al., cond-mat/0309360:

"... the information gained from luminescence quenching measurements and the like is not directly related to their conductivity i.e. the ability to behave as a molecular wire. Although the descriptor 'wire-like' has been applied to sequences where a small β has been found, such terminology is misleading."

electron transfer $\not\Longrightarrow$ **electron transport**

the main differences between electron transfer and electron transport:

- electron transfer involves high energies ($\sim$ eV)
- electron transport is of interest for small V

but: the same medium

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solid-state analogy:

high energy electron-hole excitation in semiconductors

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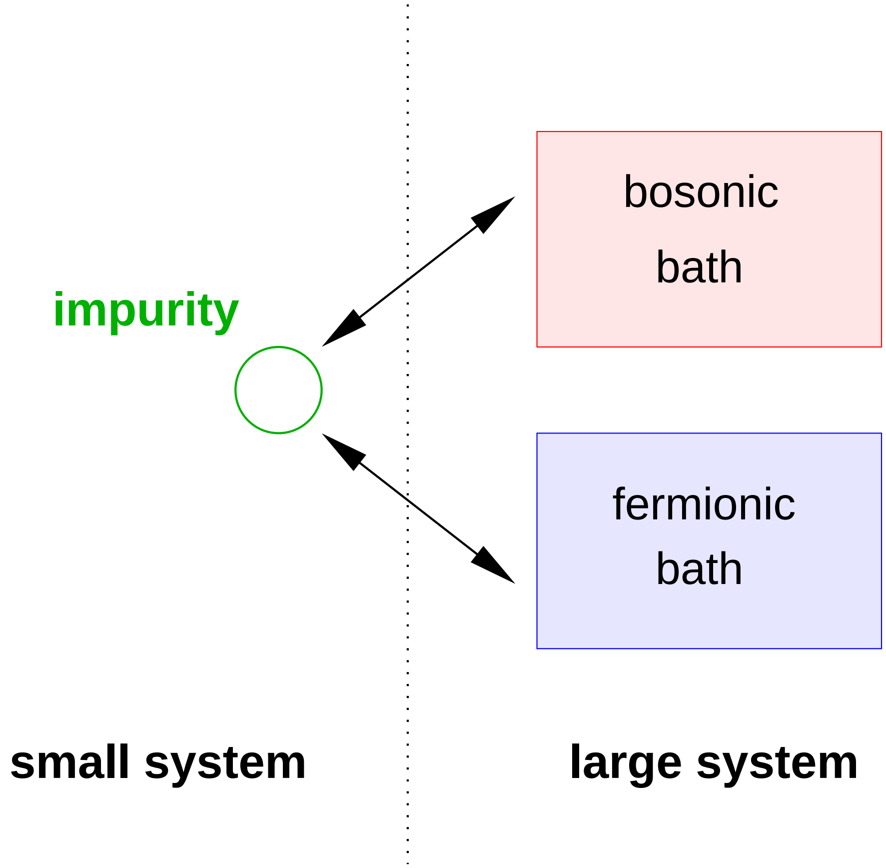
challenge for the theory:

Calculate both electron transfer (rate k) and electron transport (conductivity σ) for the same model (and if possible within the same approach).

Q8 . . . connection to quantum impurity physics?



— might have a complicated structure

— small number of degrees of freedom

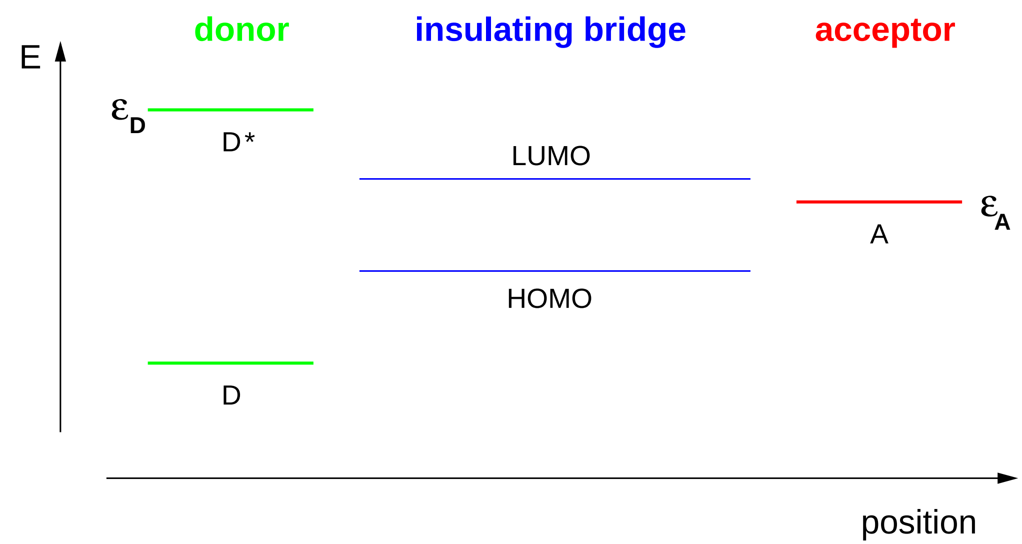
— simple structure

— continuous spectrum of degrees of freedom

R.G. Endres, D.L. Cox, R.R.P. Singh, and S.K. Pati

Mediation of Long Range Charge Transfer by Kondo Bound States

Phys. Rev. Lett. **88**, 166601 (2002)



$\Longrightarrow$ single impurity Anderson model

impurity = donor/acceptor

fermionic bath = bridge states

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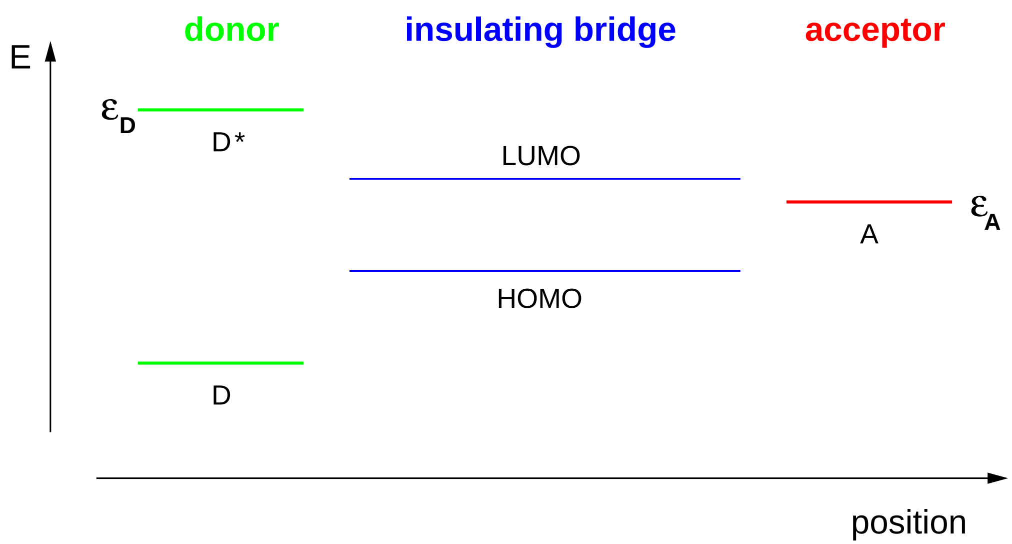


$\Longrightarrow$ single impurity Anderson model

impurity $=$ donor/acceptor

fermionic bath $=$ bridge states

- long range charge transfer between donor and acceptor centers mediated by Kondo bound states
- $\beta \approx 0.1 \text{Å}^{-1}$

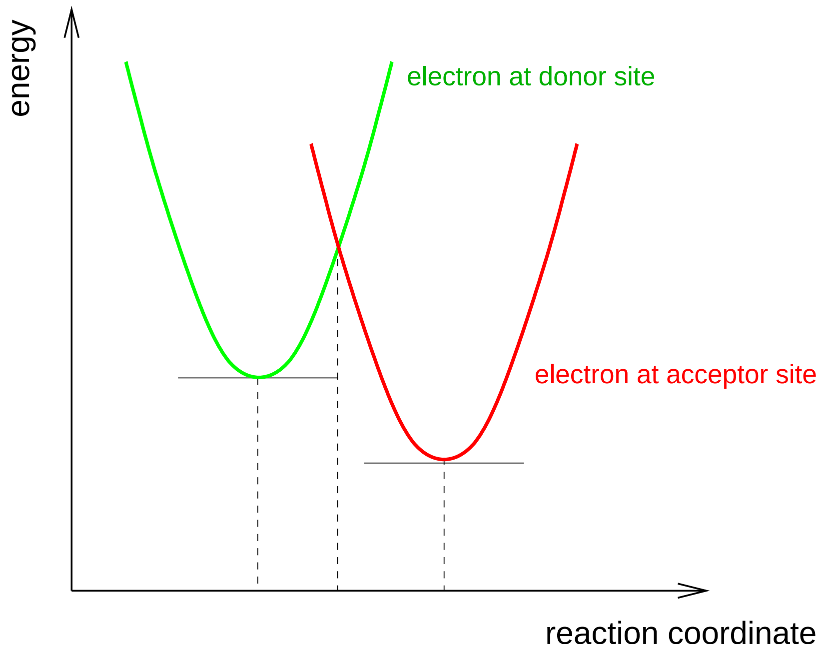
A. Garg, J.N. Onuchic, and V. Ambegaokar

Effect of friction on electron transfer in biomolecules

J. Chem. Phys. **83**, 4491 (1985)

impurity = spin 1/2

- $|\uparrow\rangle$: electron at donor site
- $|\downarrow\rangle$: electron at acceptor site



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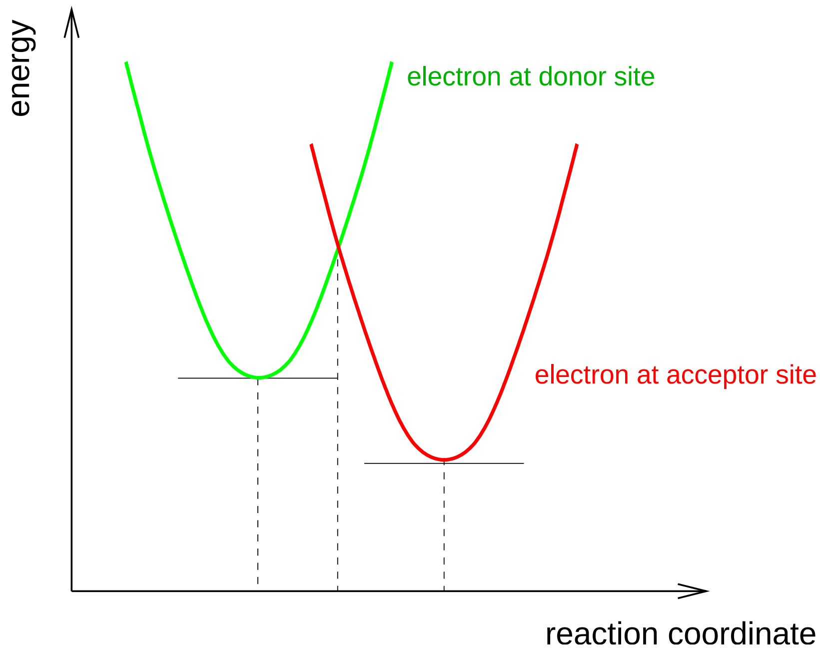

spin-boson model

$$\begin{aligned} H &= -\frac{1}{2}\Delta\sigma_x + \frac{1}{2}\epsilon\sigma_z + \sum_i \omega_i a^\dagger_{i\sigma} a_{i\sigma} \\ &+ \frac{1}{2}\sigma_z \sum_i \lambda_i (a_i + a_i^\dagger) \end{aligned}$$

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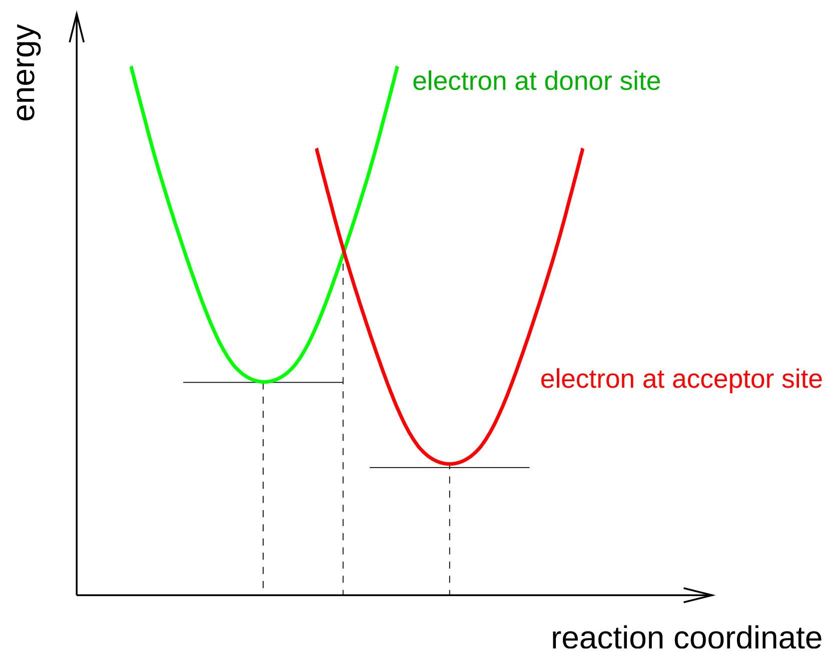

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relation to DNA: M. R. D'Orsogna and R. Bruinsma, Phys. Rev. Lett. **90**, 078301 (2003)

Summary

<u>the initial question:</u>

What does theory tell us about electron transfer and electron transport in DNA?

$\Longrightarrow$ different possible viewpoints

- ab-initio
- disorder
- quantum impurity physics

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- disorder
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open questions:

- What is a proper starting point for a theoretical investigation?
- Is it possible to treat electron transfer and electron transport within the same framework?