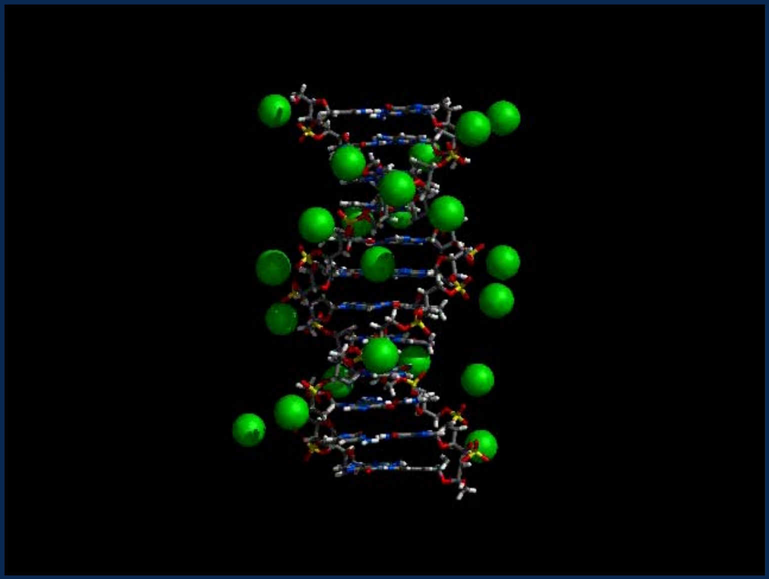
TECHNISCHE UNIVERSITÄT DRESDEN

complex nano materials

Faculty for Mechanical Engineering, Institute for Materials Science and Max Bergmann Center of Biomaterials



Charge transport in DNA molecular wires: combining molecular dynamics with model Hamiltonian approaches

Rafael Gutierrez
Dresden University of Technology
Germany

Outline

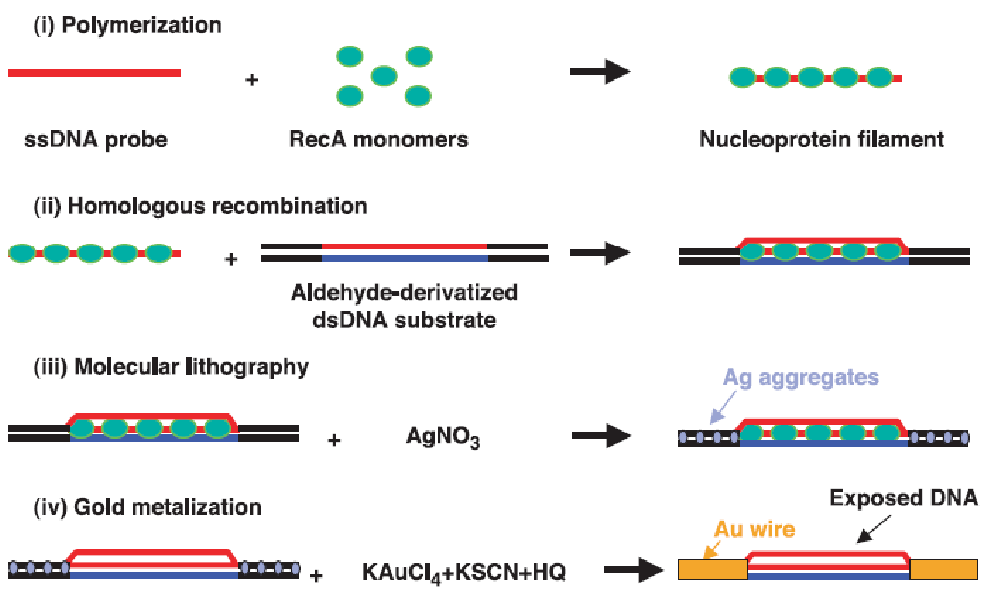
1. perspectives for DNA in nanoelectronics
2. electrical transport in DNA: experimental overview
3. modeling charge transport in DNA molecular wires: MD simulations and model Hamiltonians
4. outlook

TECHNISCHE UNIVERSITÄT DRESDEN

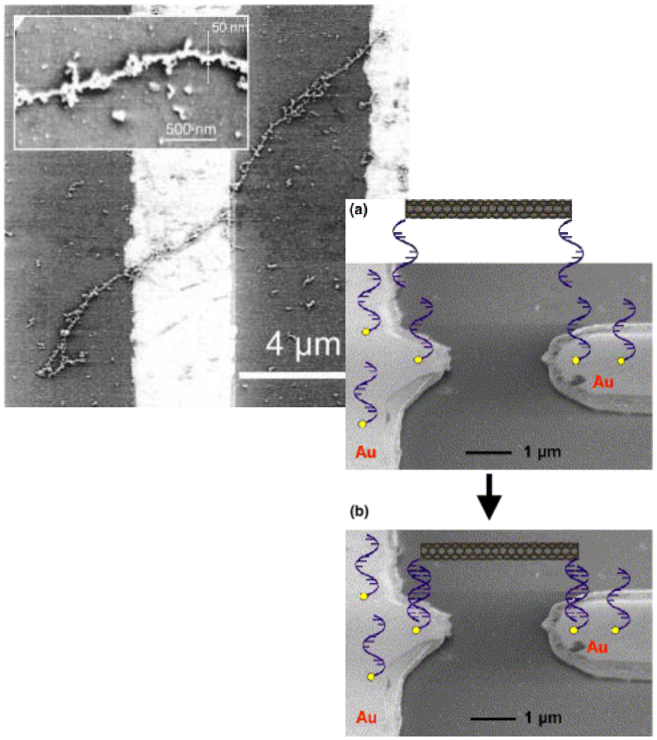
Institute for Materials Science, Chair of Materials Science and Nanotechnology

Exploit assembling via self-recognition

Sequence-Specific Molecular Lithography on Single DNA Molecules
K. Keren *et al.*, Science 297, 72 (2002)



Construction of highly conductive nanowires on a DNA template
J. Richter *et al.*, APL. 78, 536 (2001)



Very dispersed results

Insulator

- *DNA-templated assembly and electrode attachment of a conducting silver wire,* E. Braun *et al.*, Nature 391, 775 (1998)

Semiconductor

- *Direct Measurements of Electrical Transport Through DNA Molecules* D. Porath *et al*., Nature 403, 635 (2000)

Conductor (non-zero current at low bias)

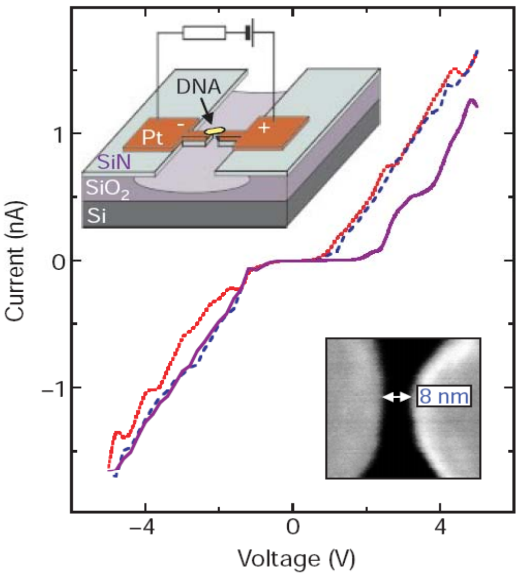
- *Direct Conductance Measurement of Single DNA Molecules in Aqueous Solution,* B. Xu, P. Zhang, X. Li, N. Tao, Nano Lett. 4, 1105 (2004).
- *Direct measurement of electrical transport through single DNA molecules of complex sequence,* H. Cohen *et al.*, PNAS 102,11589 (2005)
- *Direct Electrical Measurements on Single-Molecule Genomic DNA Using Single-Walled Carbon Nanotubes,* S. Roy, *et al.,* Nano Letters 8, 26 (2008)

Problem: No systematic studies available (base-sequence effects, solvent, temperature…)

Single molecule measurements

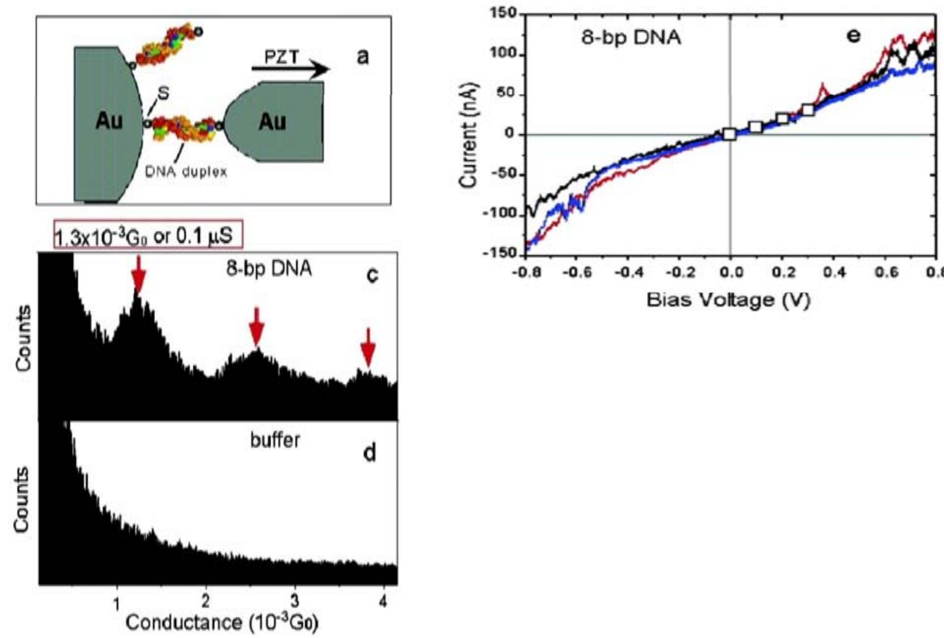
Direct measurement of electrical transport through DNAmolecules
D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, Nature **403**, 635 (2000)

poly(G)$_{30}$-poly(C)$_{30}$

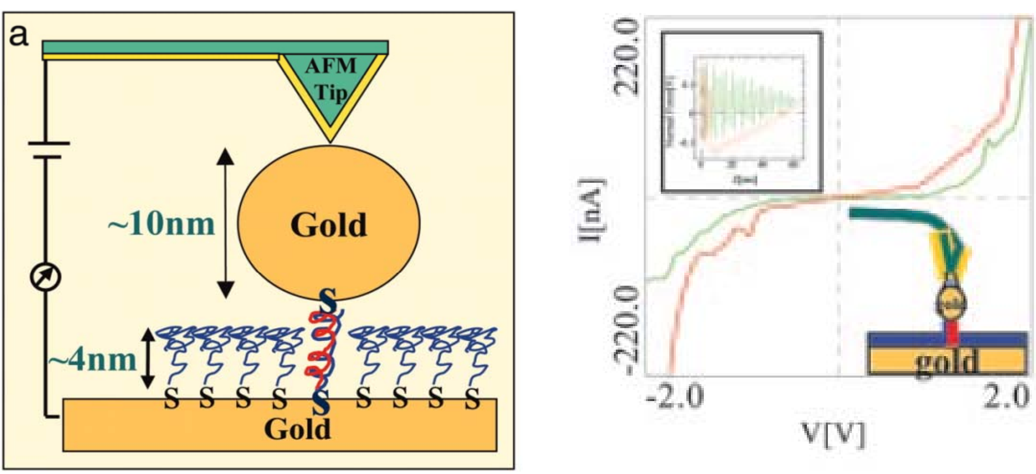


Direct Conductance Measurement of Single DNA Molecules in Aqueous Solution , B. Xu, P. Zhang, X. Li, N. Tao, Nano Lett. **4**, 1105 (2004).

wet-Poly(GC)



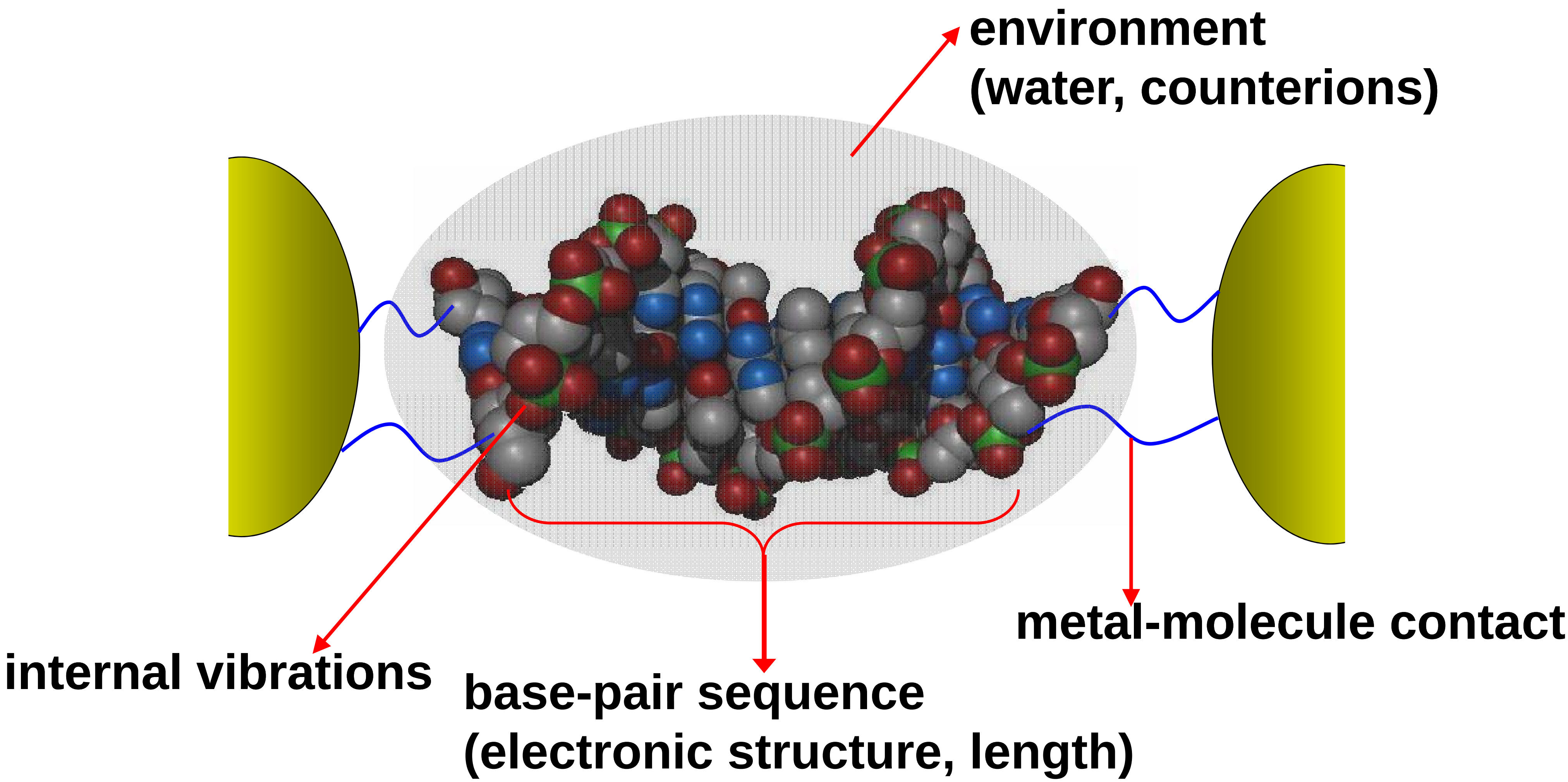
Direct measurement of electrical transport through single DNA molecules of complex sequence, H. Cohen *et al.,* PNAS **102**,11589 (2005)



?

ı-dresden.de/

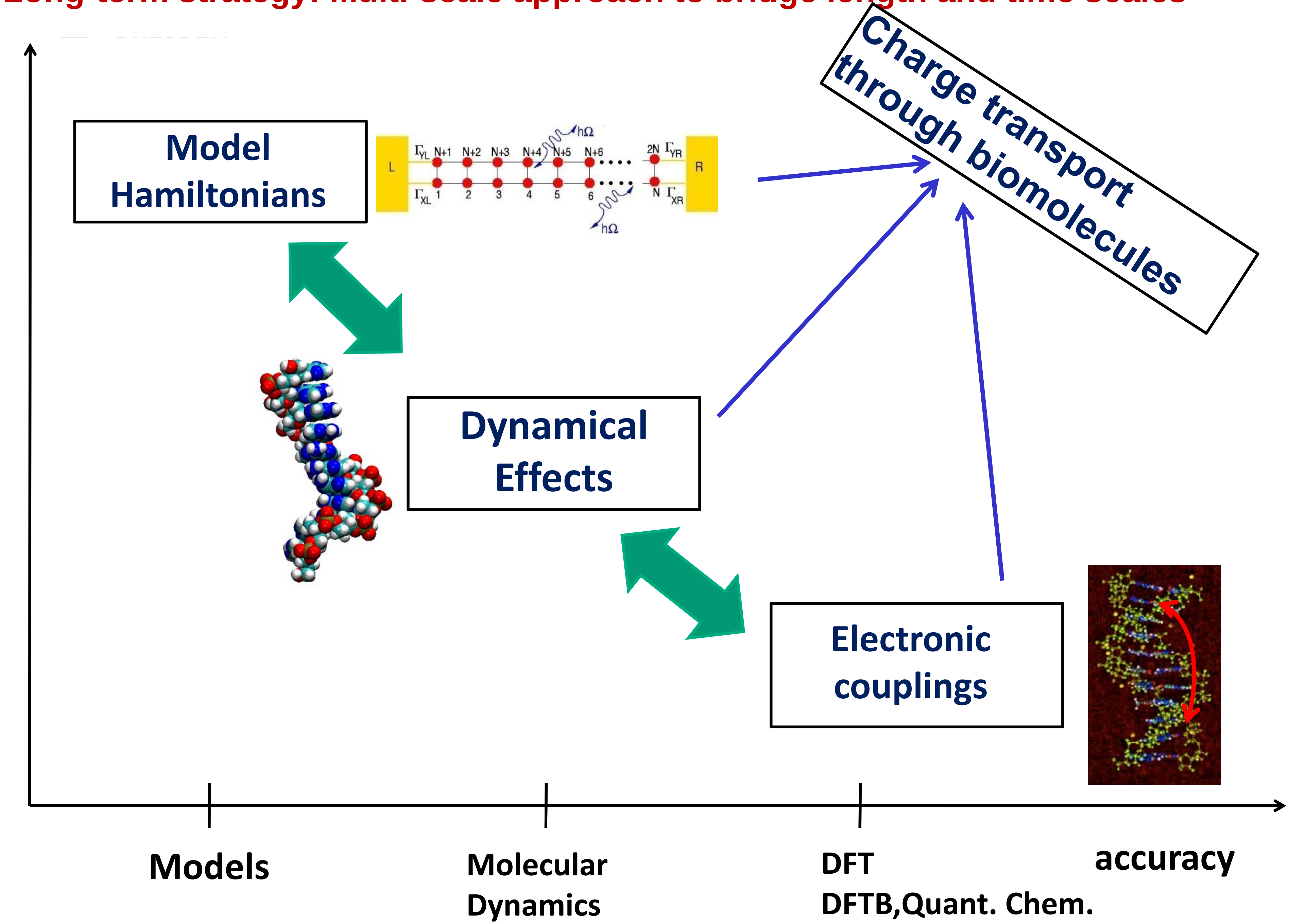
Diversity of experimental results:
DNA is a (very) complex molecular wire



Concurrent transport chanels!?

Modeling charge transport

Long-term strategy: Multi-scale approach to bridge length and time scales

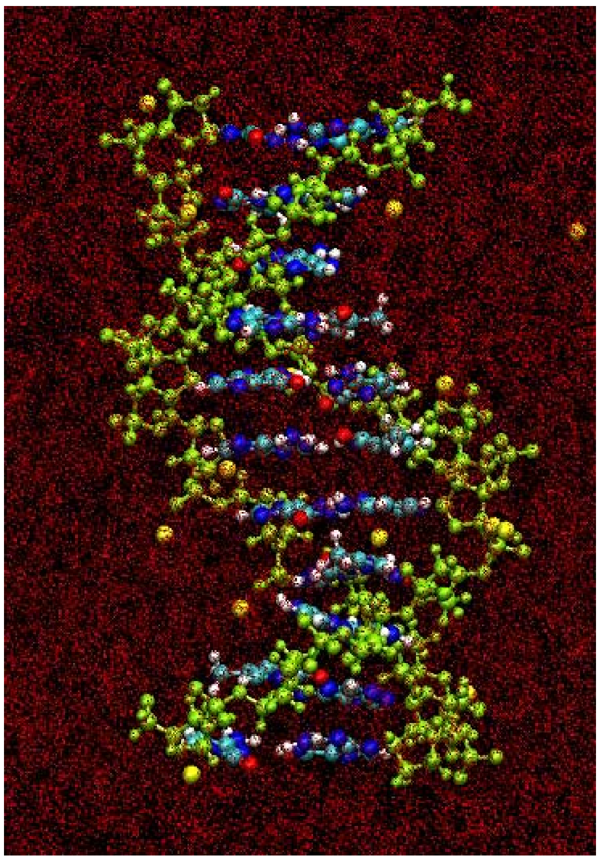


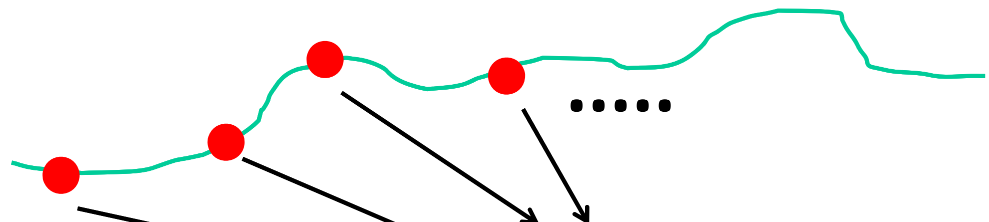
http://nano.tu-dresden.de/

modeling charge transport in DNA molecular wires: Hybrid MD simulations/model Hamiltonian

Institute for Materials Science, Chair of Materials Science and Nanotechnology

Idea: map **DFT(B)**-based electronic structure onto **TB-Hamiltonian along MD trajectory**





$$\varepsilon_j(t), V_{j,j+1}(t)$$

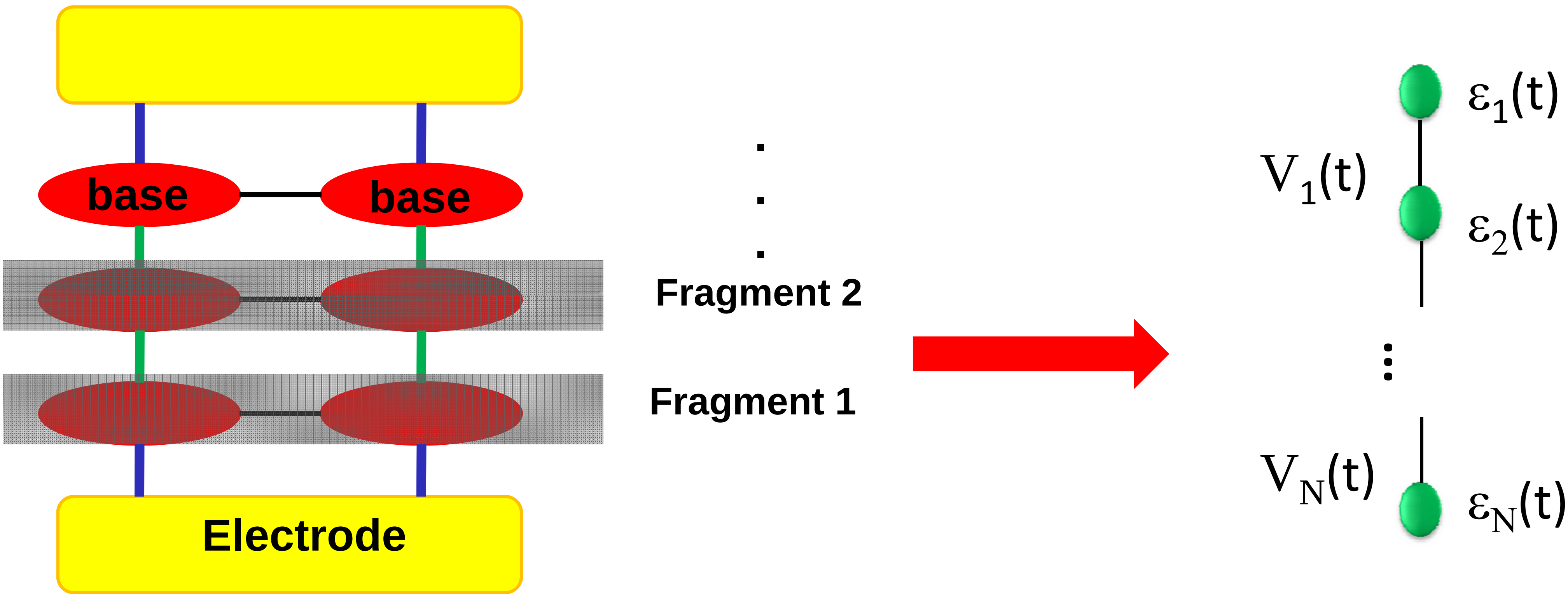
$$P(\{\varepsilon_j\}), P(\{V_{j,j+1}\})$$

Probability distributions

$$\left\langle \varepsilon_j(t)\varepsilon_l(t+\tau)\right\rangle$$

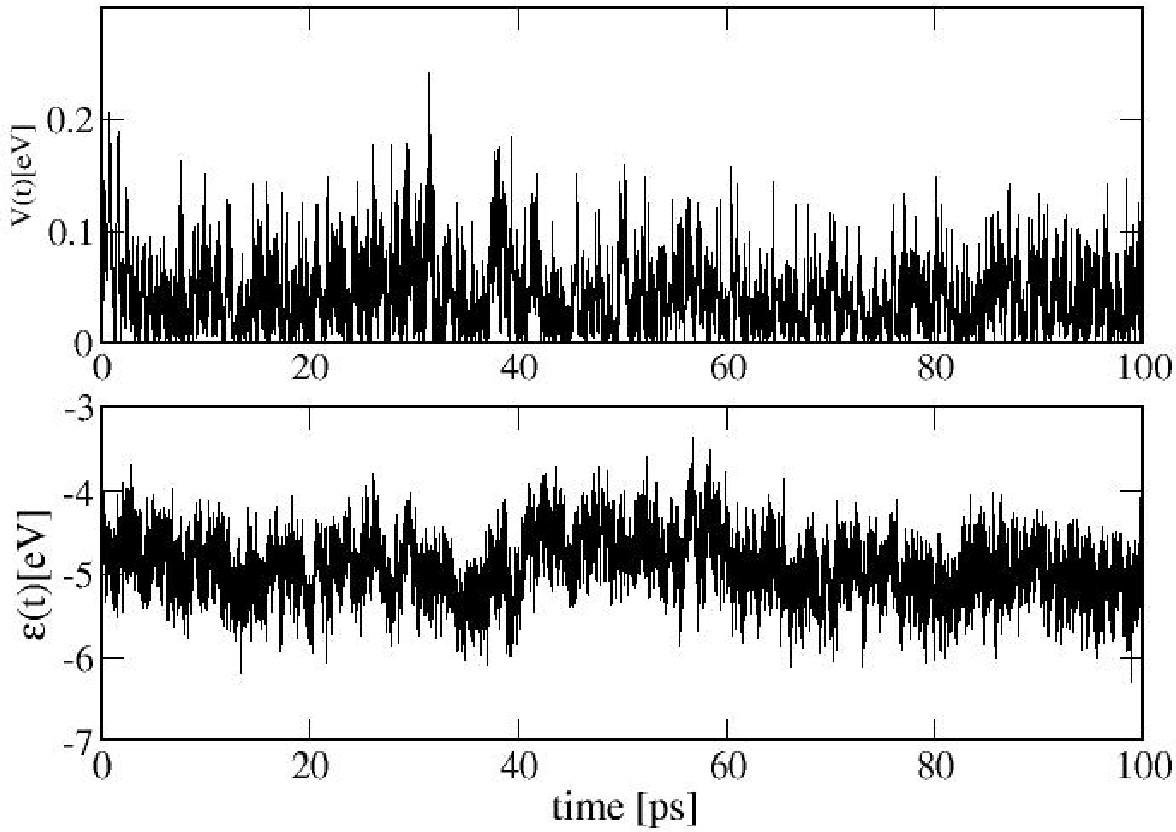
Correlation functions

Coarse-graining of the electronic structure



Efficient calculation of charge-transfer matrix elements for hole transfer in DNA

T:. Kubar, P. B. Woiczikowski, G. Cuniberti, and M. Elstner . J. Phys. Chem. B, **112**, 7937 (2008)



Time series of effective ionization energies and nearest-neighbor thopping integrals
Structural and solvent dynamics encoded in the time series!

Charge transport and dynamics in short DNA wires

TECHNISCHE UNIVERSITÄT DRESDEN

Institute for Materials Science, Chair of Materials Science and Nanotechnology

	static B-DNA	average MD values	static A-DNA
XY	5'-XY-3'	5'-YX-3'	5'-XY-3'
	T_{ij}	$\langle T_{ij} \rangle \pm \sigma$	T_{ij}
intrastrand			
AA	0.013	0.058 ± 0.037	0.070
GG	0.052	0.029 ± 0.023	0.012
GA	0.053	0.034 ± 0.027	0.023
interstrand			
GC	0.017	0.012 ± 0.012	0.006
AT	0.035	0.037 ± 0.029	0.018
GT	0.020	0.016 ± 0.013	0.010

-Average values of electronic parameters **different** from static calculations

- **Fluctuations** are of the **same order** of magnitude as the averages

T_{ij}=<HOMO fragment **i** | H | HOMO fragment **j** >

P. B. Woiczikowski, T. Kubar, R. Gutierrez, R. A. Caetano, G. Cuniberti, and M. Elstner
J. Chem. Phys. **130**, 215104 (2009)

First approach to the problem:

assume charge transfer in rigid bridge provides the **shortest** time scale τ_{TE} compared with typical scales of dynamical fluctuations τ_{dyn}

→ adiabatic limit

→Compute quantum-mechanical transmission **at each time step**

$$T(E,t=t_j)=Tr\left[\Gamma_R(E)G^r(E,t=t_j)\Gamma_L(E)G^a(E,t=t_j)\right]$$

$$\Gamma_{R/L}(E)=i\left[\Sigma^r_{R/L}(E)-\Sigma^a_{R/L}(E)\right]$$

$$\left[G^r(E,t=t_j)\right]^{-1}=E-H(t=t_j)-\Sigma^r_L(E)-\Sigma^r_R(E)$$

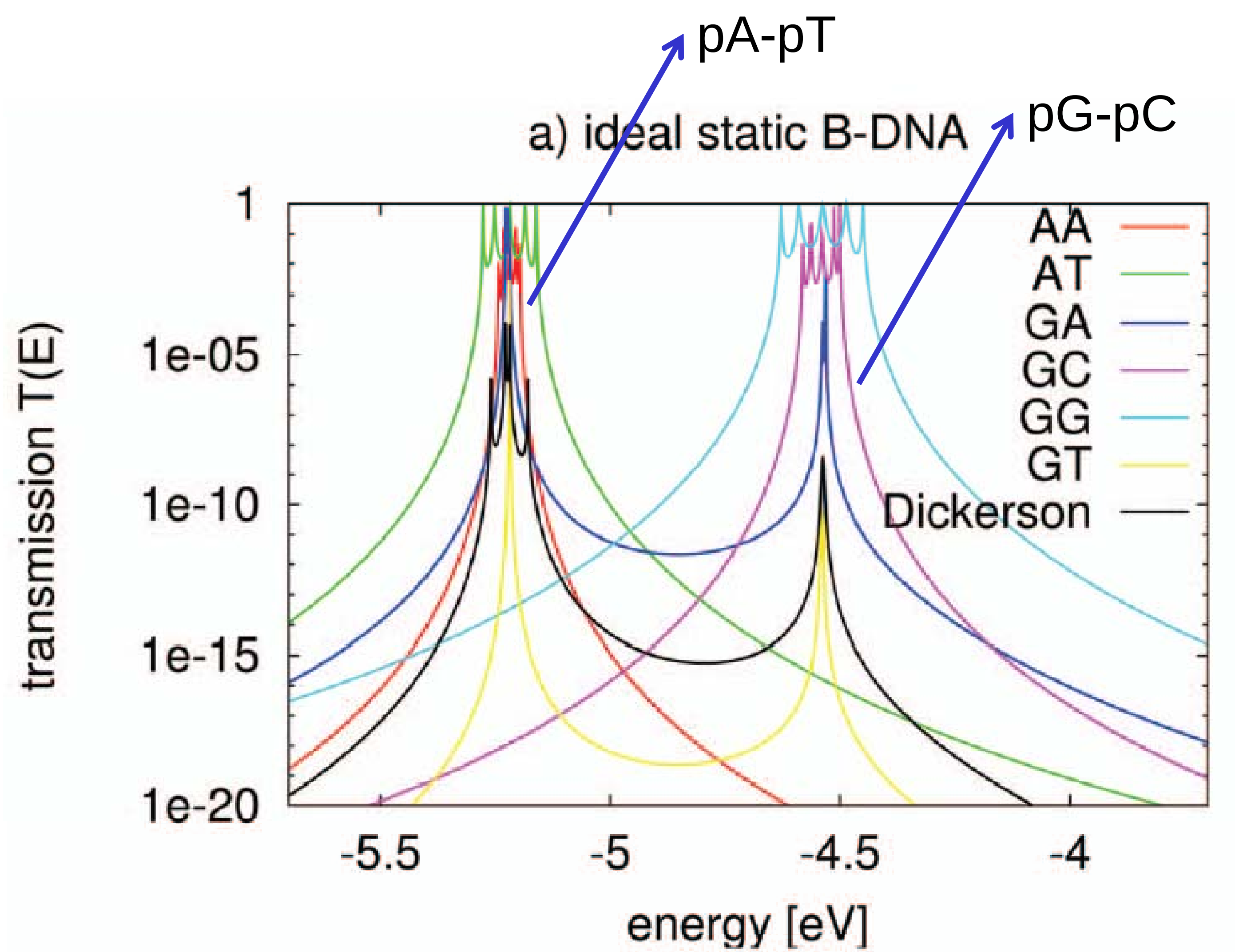
→ Perform time average $T(E)=\frac{1}{t_{MD}}\sum_i T(E,t=t_j)$

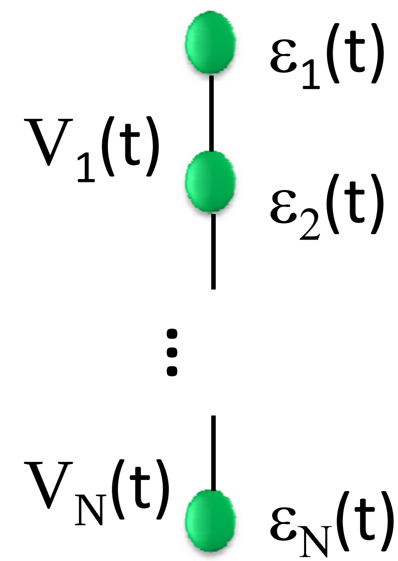
P. B. Woiczikowski, T. Kubar, R. Gutierrez, R. A. Caetano, G. Cuniberti, and M. Elstner
J. Chem. Phys. **130**, 215104 (2009)

TECHNISCHE UNIVERSITÄT DRESDEN

Charge transport and dynamics in short DNA wires

Institute for Materials Science, Chair of Materials Science and Nanotechnology

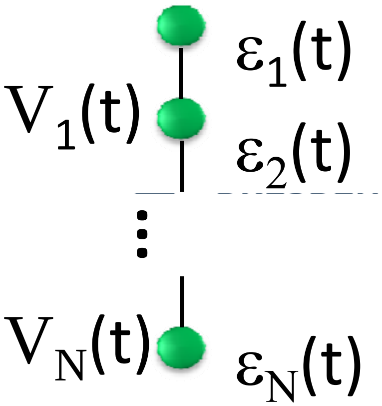


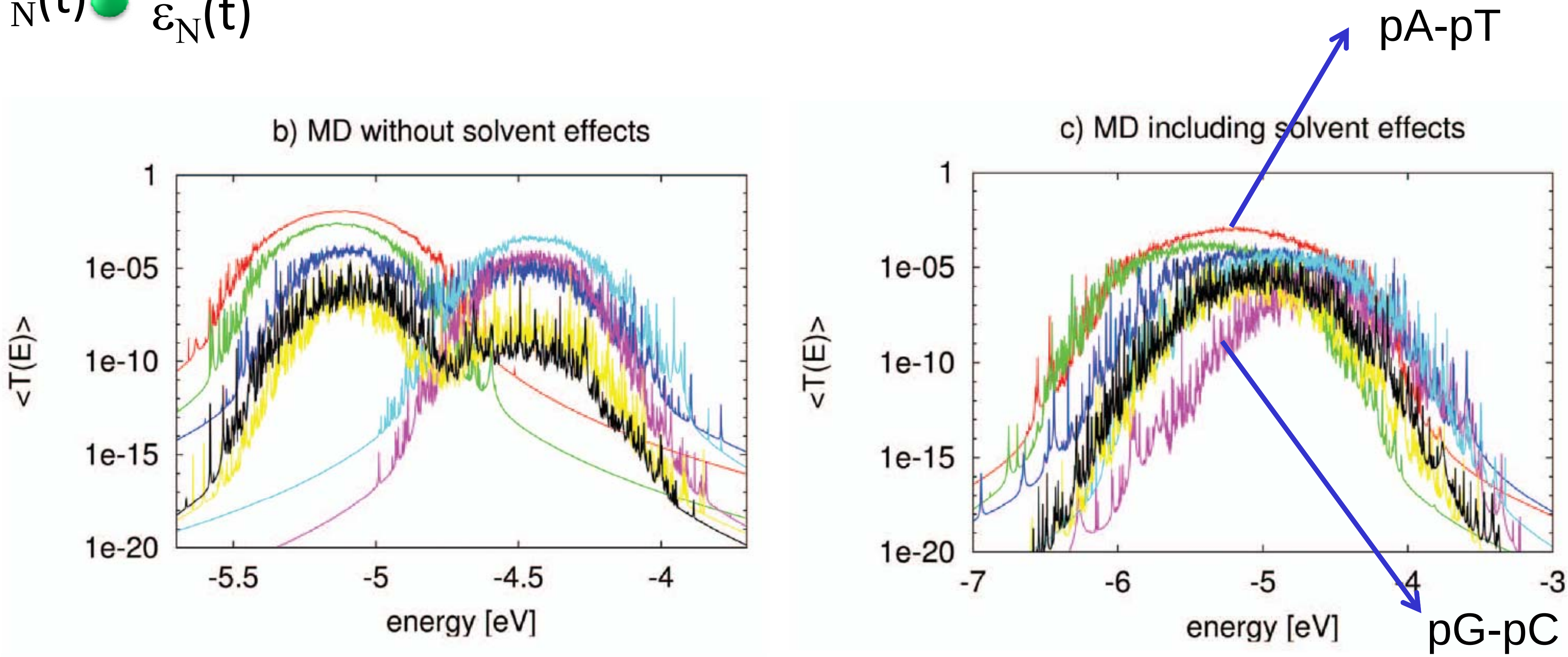


Static structures display resonances at eigenenergies

P. B. Woiczikowski, T. Kubar, R. Gutierrez, R. A. Caetano, G. Cuniberti, and M. Elstner
J. Chem. Phys. **130**, 215104 (2009)

Charge transport and dynamics in short DNA wires



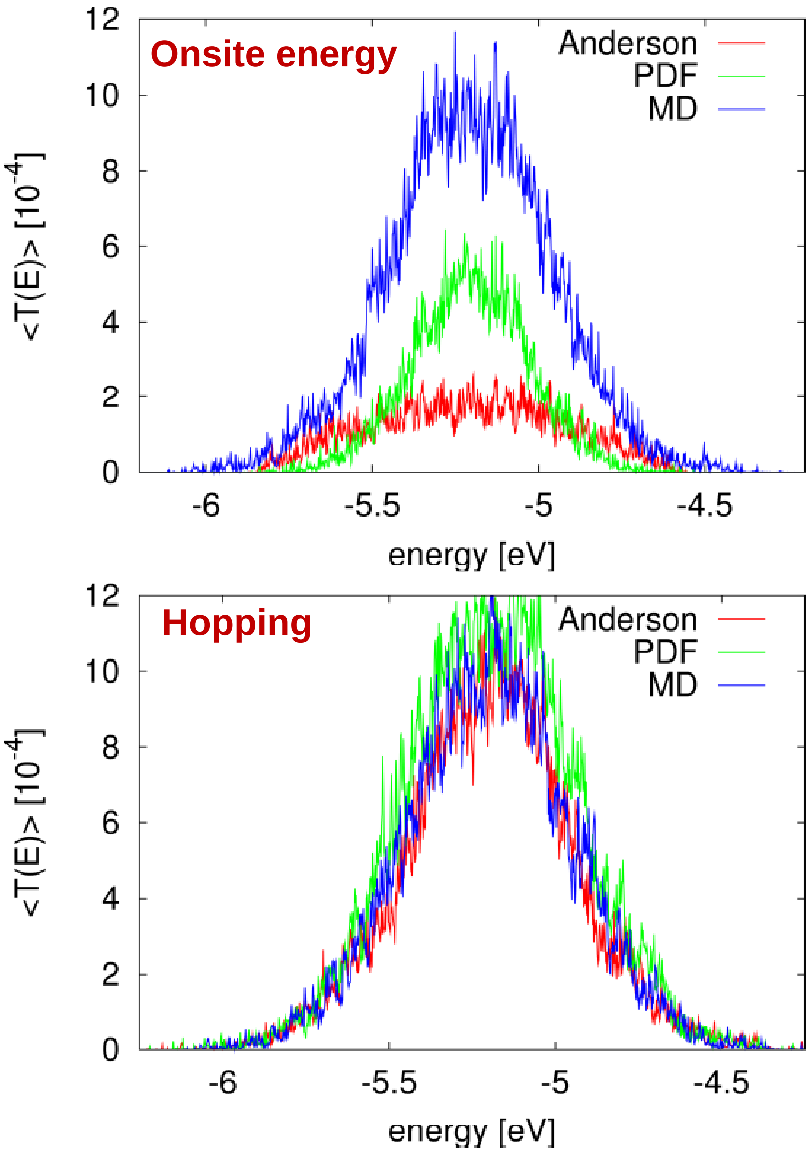


Dynamical disorder-induced broadening of transmission spectra (base dynamics and solvent fluctuations)

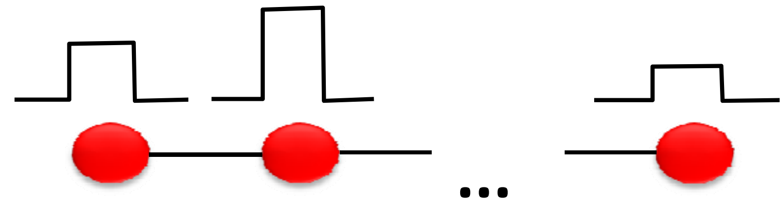
P. B. Woiczikowski, T. Kubar, R. Gutierrez, R. A. Caetano, G. Cuniberti, and M. Elstner
J. Chem. Phys. **130**, 215104 (2009)

Charge transport and dynamics in short DNA wires

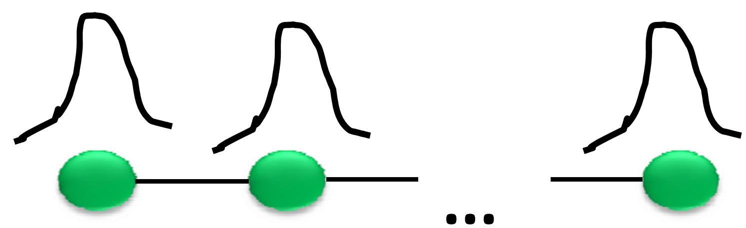
Correlations matter !



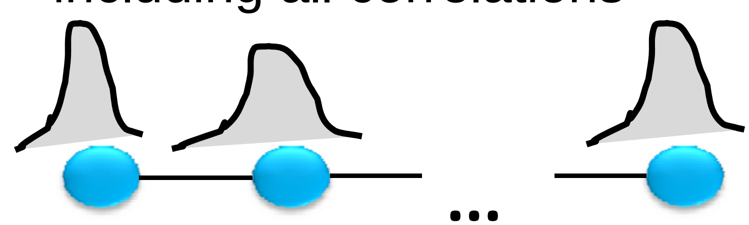
Anderson disorder



Gaussian-like (PDF)
local correlations only



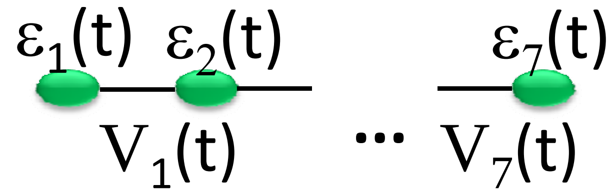
Full time series from MD
including all correlations



Hopping integrals are self-averaging!

P. B. Woiczikowski, T. Kubar, R. Gutierrez, R. A. Caetano, G. Cuniberti, and M. Elstner
J. Chem. Phys. **130**, 215104 (2009)

Beyond coherent transport: Linear chain coupled to a dynamical environment



$$
\begin{aligned}
H &= \sum_j \langle \epsilon_j \rangle d_j^\dagger d_j - \sum_j \langle V_{j,j+1} \rangle \left(d_j^\dagger d_j + \text{h.c.} \right) \\
&+ H_{\text{bath}} + H_{\text{el-bath}} + H_{\text{tunnel}} + H_{\text{leads}} \\
H_{\text{bath}} &= \sum_\alpha \Omega_\alpha B_\alpha^\dagger B_\alpha \\
H_{\text{el-bath}} &= \sum_{\alpha,j} \lambda_\alpha d_j^\dagger d_j (B_\alpha + B_\alpha^\dagger) \\
H_{\text{tunnel}} &= \sum_{\mathbf{k},\alpha,j} \left(t_{\mathbf{k},j} c_{\mathbf{k}}^\dagger d_j + \text{h.c.} \right) \\
H_{\text{leads}} &= \sum_{\mathbf{k},\alpha} \epsilon_{\mathbf{k},\alpha} c_{\mathbf{k},\alpha}^\dagger c_{\mathbf{k},\alpha}
\end{aligned}
$$

$$\langle \varepsilon_j \rangle, \langle V_{j,j+1} \rangle$$

Time average quantities

Only local correlations

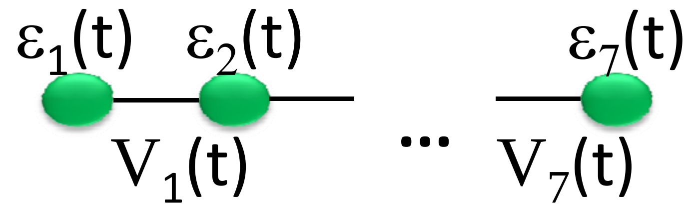
Fully parametrized model Hamiltonians !

R. Gutierrez, R. A. Caetano, B. P. Woiczikowski, T. Kubar, M. Elstner, and G. Cuniberti
Phys. Rev. Lett. **102**, 208102 (2009)

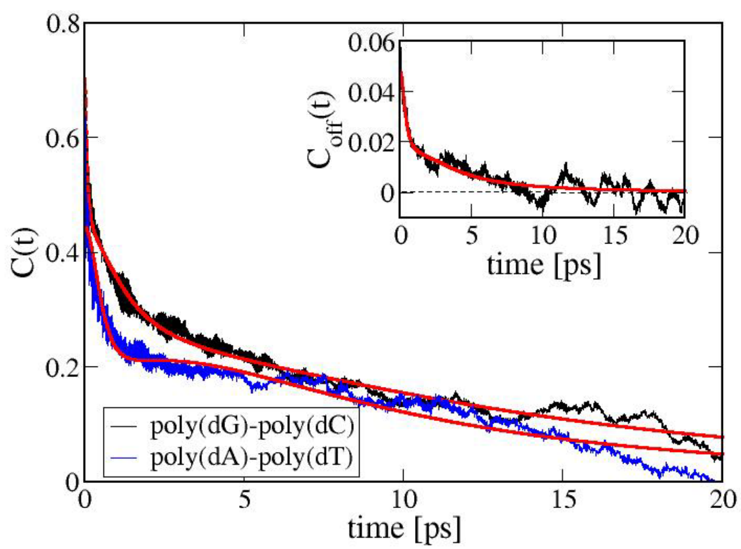
Parametrizing the environment: bosonic bath

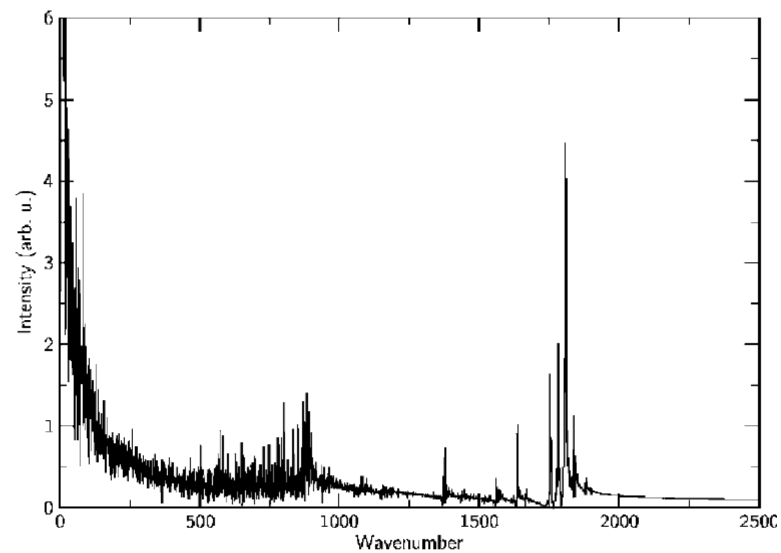
$$C(t) \rightarrow J(\omega)$$

$$J(\omega) = \frac{2}{\pi} \tanh \frac{\omega}{2k_B T} \underbrace{\int_0^\infty dt \; \cos(\omega t)\, C(t)}_{C(\omega)}$$



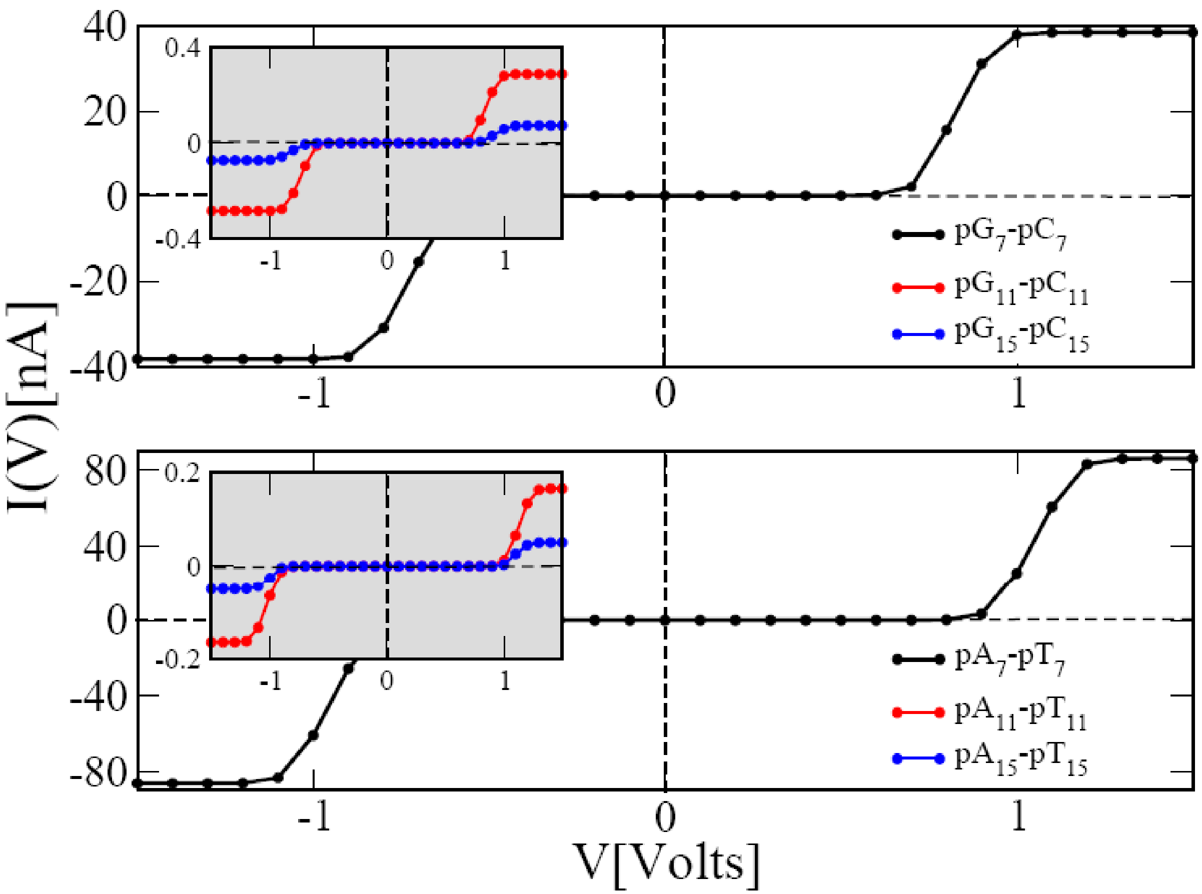
Correlation functions **C(t)** ←→ spectral density **J(ω)**





R. Gutierrez, R. A. Caetano, B. P. Woiczikowski, T. Kubar, M. Elstner, and G. Cuniberti
Phys. Rev. Lett. **102**, 208102 (2009)

Beyond coherent transport: I-V characteristics



Strong length dependence

Poly(A)$_7$-poly(T)$_7$ shows larger I(V)

Less clear for longer sequences

R. Gutierrez, R. A. Caetano, B. P. Woiczikowski, T. Kubar, M. Elstner, and G. Cuniberti
Phys. Rev. Lett. **102**, 208102 (2009)

Main conclusion

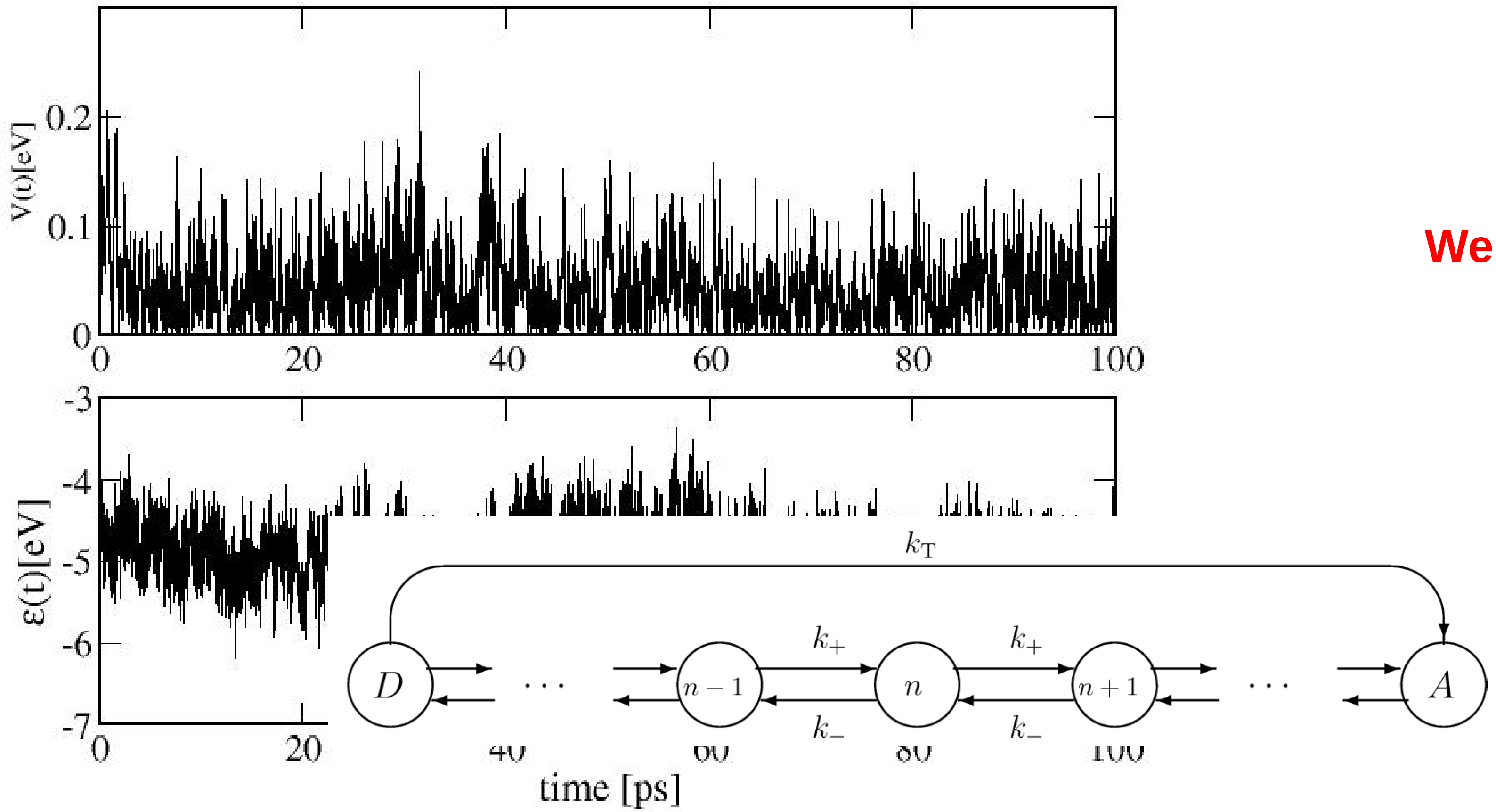
- Possible to obtain effective eletronic parametrization **including** dynamical effects

-Formally „ab initio“ model Hamiltonians

→different charge migration scenarios (incoherent hopping, polarons, etc)

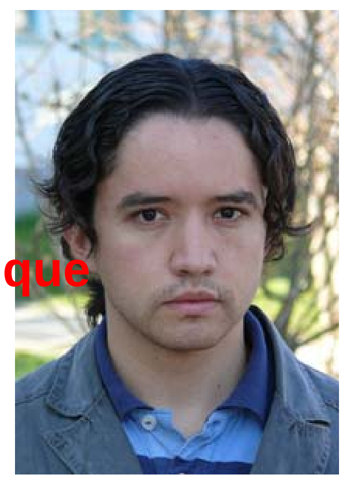
Where we are going…

Time-dependent Hamiltonians and master equation
→ Using parametrizations from MD simulations + incoherent transport
→ Realistic (experimentally relevant sequences, DNA-NP hybrids)



Wei Tu

Pedro Manrique

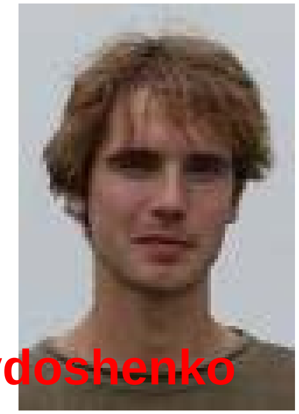


Collaborators:

TU-Dresden

Gianaurelio Cuniberti

Myeong Lee



Stas Avdoshenko

Wei Tu

TU Braunschweig

Marcus Elstner

Tomas Kubar

Benjamin Woiczikowski

Rodrigo Caetano
Univ. Maceio, Brasil

Funding

European Union

German Research Foundation - DFG

Deutsche Forschungsgemeinschaft DFG

Bundesministerium für Bildung und Forschung -BMBF

Bundesministerium für Bildung und Forschung