

# Solvent fluctuations drive the hole transfer in DNA

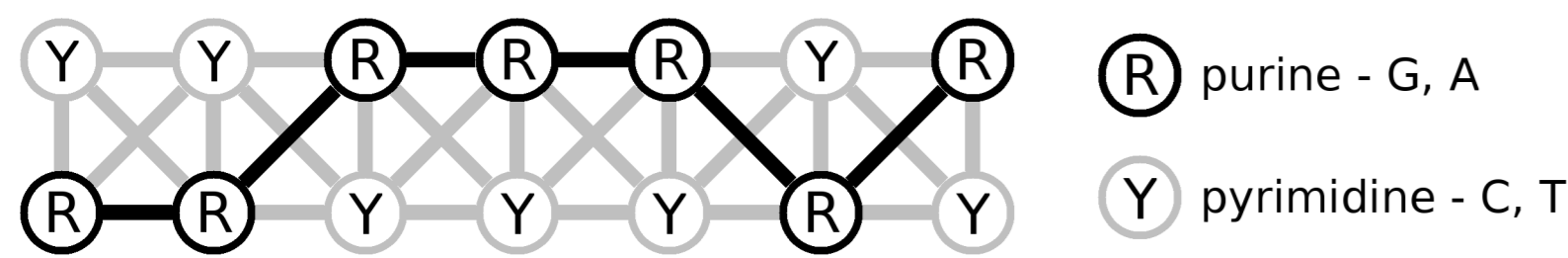
Tomáš Kubař, Ben Woiczikowski and Marcus Elstner

Institute of Physical and Theoretical Chemistry, Technische Universität Braunschweig

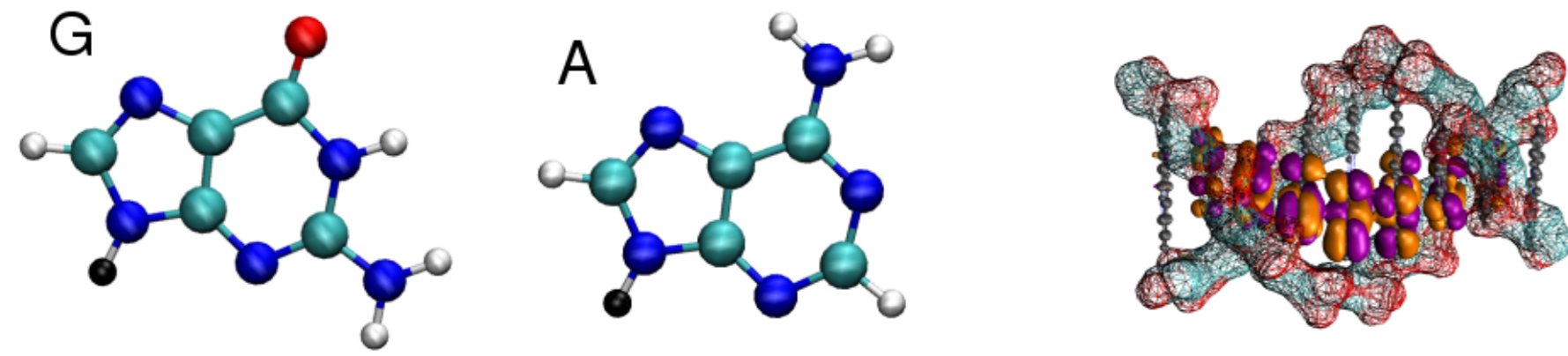


## Transfer of charge

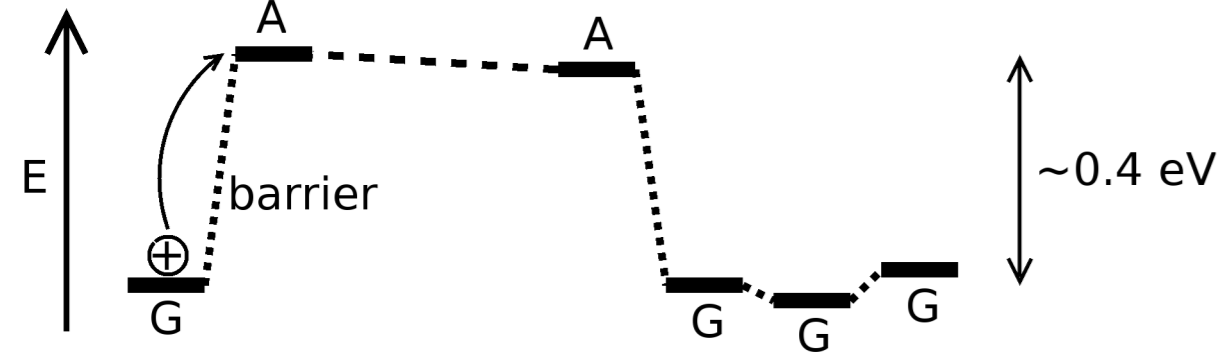
- ▶ Through double-stranded DNA – via the nucleobases



- ▶ Transport of positive charge – **hole**
- ▶ Electron donors with small IP required:



- ▶ Transfer of hole between G's across A-bridges



- ▶ **Charge-transfer parameters** using HOMO of bases:  
 $\epsilon_i = \langle \phi_i | \hat{H} | \phi_i \rangle$  – site energy / ionization potential  
 $T_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$  – electronic coupling

## Multi-scale computational scheme

### 1. Classical MD simulation

- ▶ Generate structures, sampling of the ensemble
- ▶ DNA backbone and the solvent included
- ▶ Amber force field, Gromacs package

### 2. Calculation of charge-transfer parameters

- ▶ For structures generated in the classical MD
- ▶ SCC-DFTB – approximative DFT, very efficient
- ▶ QM/MM implementation – environment included  
 → coarse-grained Hamiltonian for hole transfer

### 3. Integration of time-dependent Schrödinger eqn

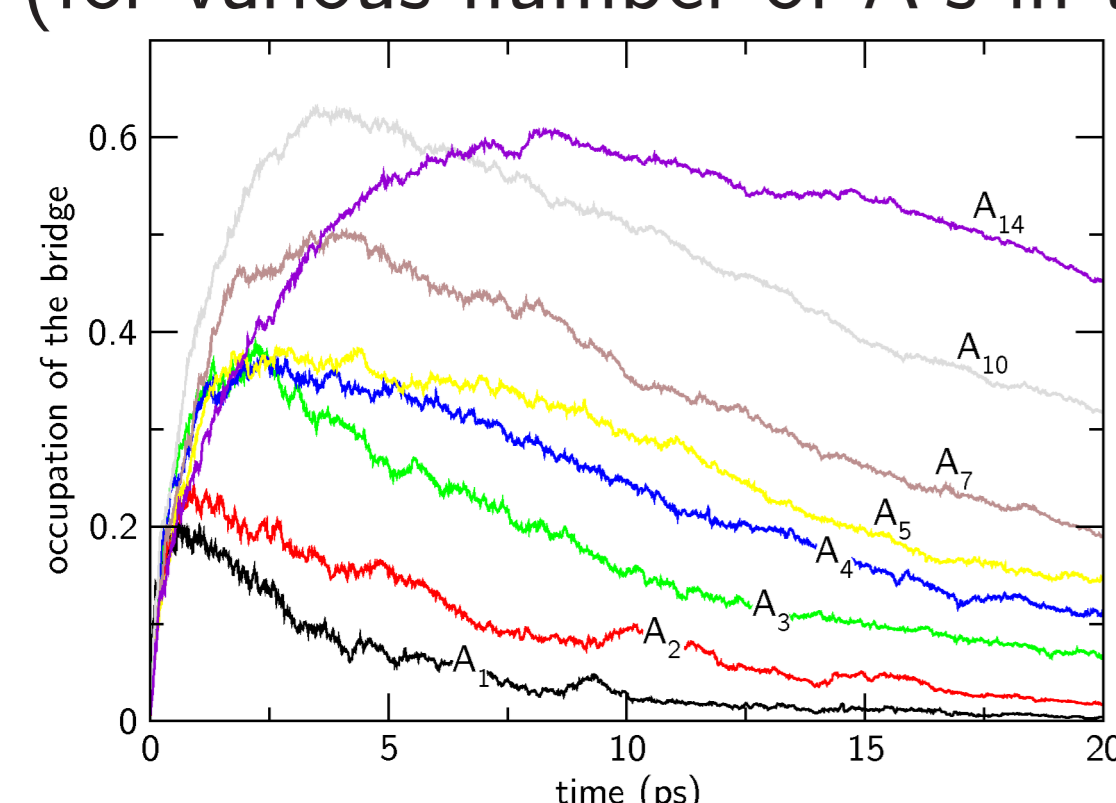
$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi$$

- ▶ Using the coarse-grained Hamiltonian
- ▶ Runge-Kutta predictor-corrector integrator (RKsuite)
- ▶ negative imag. potential to model the final oxidation

→ **Dynamics of a hole coupled to classical MD**

## Mechanism of hole transfer

- ▶ **Tunneling** – proposed for short bridges – one-step process through the barrier
- ▶ **Hopping** – assumed active in long bridges – consecutive hops of the hole between nucleobases
- ▶ Magnitude of charge present on the bridge: (for various number of A's in the bridge)



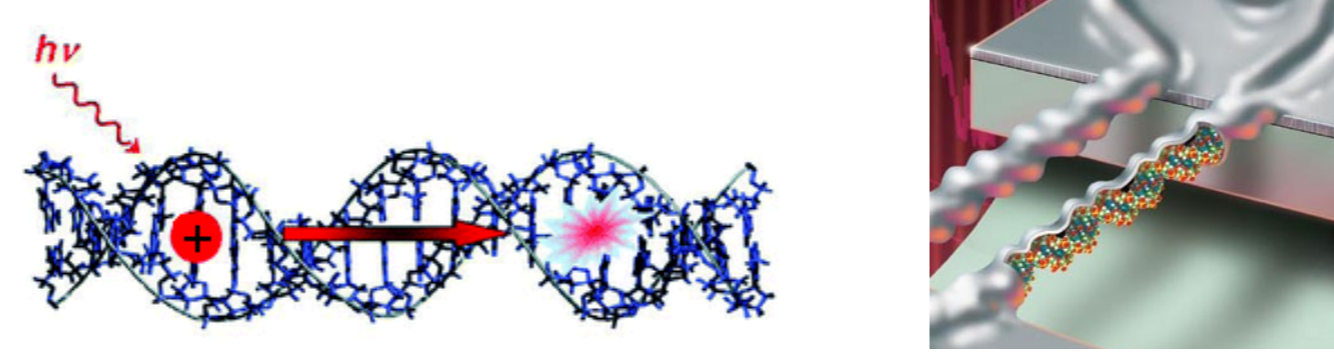
- significant already in short bridges
- **hopping** may be operative at all bridge lengths
- ▶ Interaction charge ··· solvent not yet described – may alter the results slightly

## References

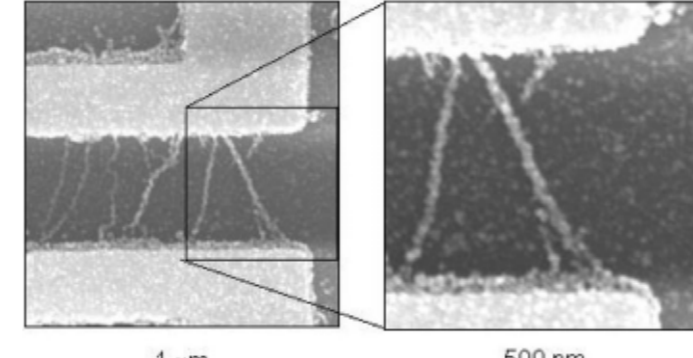
- ▶ TK, BW, G. Cuniberti, ME: Efficient calculation of charge-transfer matrix elements for hole transfer in DNA. JPCB, 112, 7937 (2008).
- ▶ TK, ME: What governs the charge transfer in DNA? The role of water and counterions. JPCB, 112, 8788 (2008).
- ▶ TK, ME: Solvent Reorganization Energy of Hole Transfer in DNA. JPCB, DOI: 10.1021/jp901888r (2009).
- ▶ TK, ME: Solvent fluctuations drive the hole transfer in DNA: a mixed quantum-classical study. JACS, submitted (2009).
- ▶ Long-range charge transfer in DNA. Top. Cur. Chem. 236, 237 (2004).

## Conductivity of DNA

- ▶ Significance
  - ▶ biology (DNA damage and repair)
  - ▶ nano-electronics



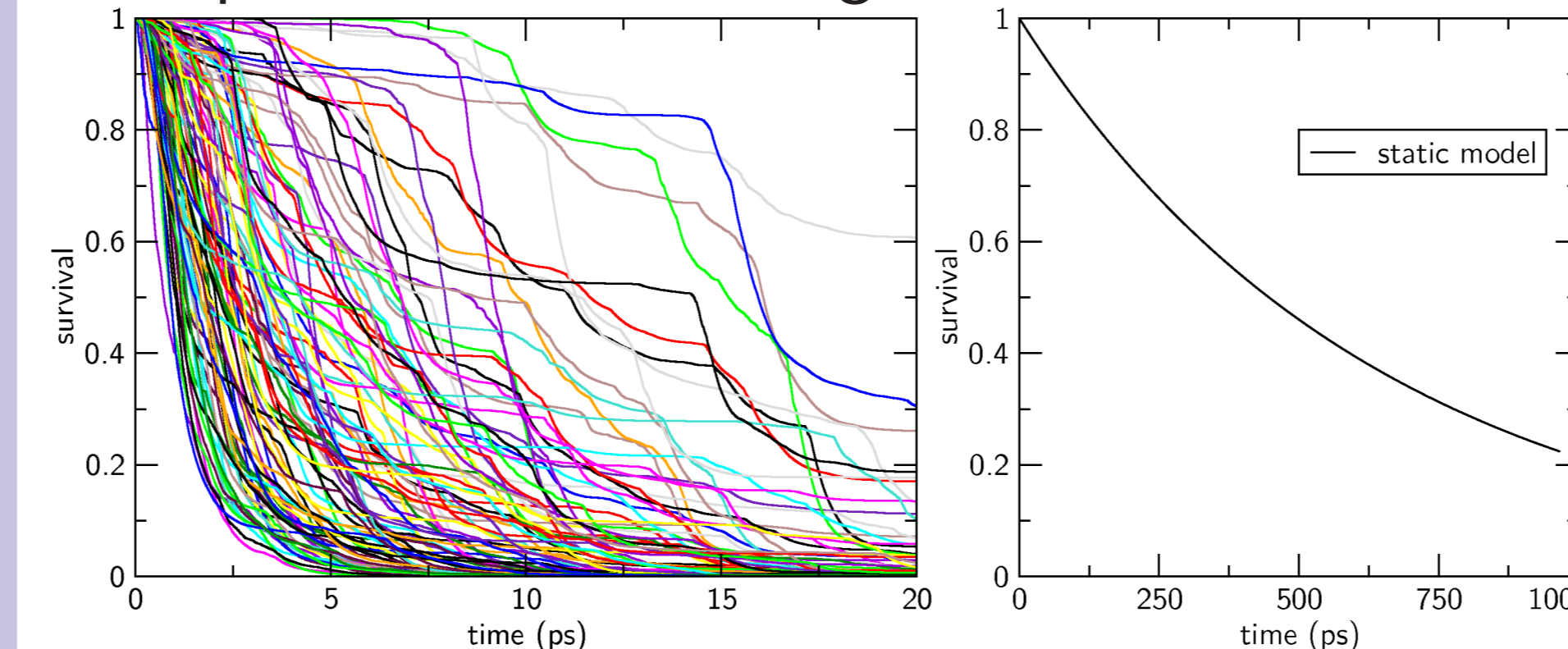
- ▶ Contradictory experimental findings
  - ▶ insulator, semi-conductor, metallic-like conductor
  - ▶ probably deviations in experimental setup
  - ▶ sensitivity to DNA structure & the environment



- ▶ Can molecular modeling help?
  - ▶ Static approaches often used
  - ▶ This work – multi-scale scheme involving MD simulation

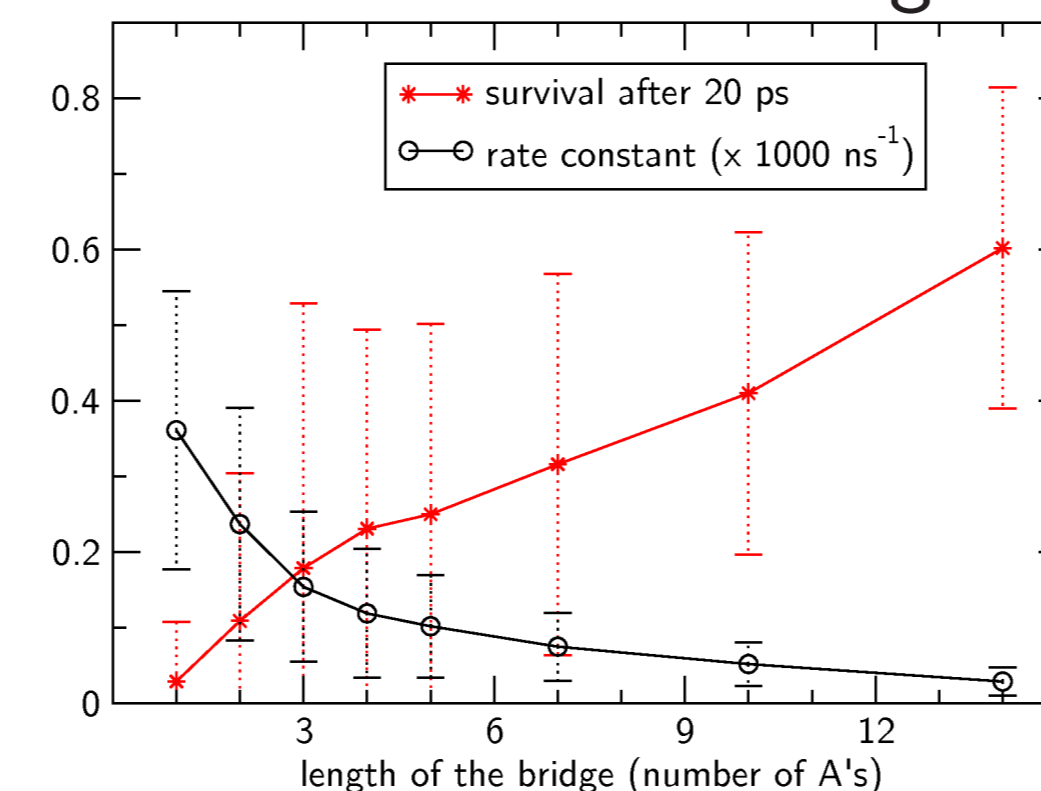
## Rate of hole transfer

- ▶ The part of hole remaining in **G1-A-G-G-G**:



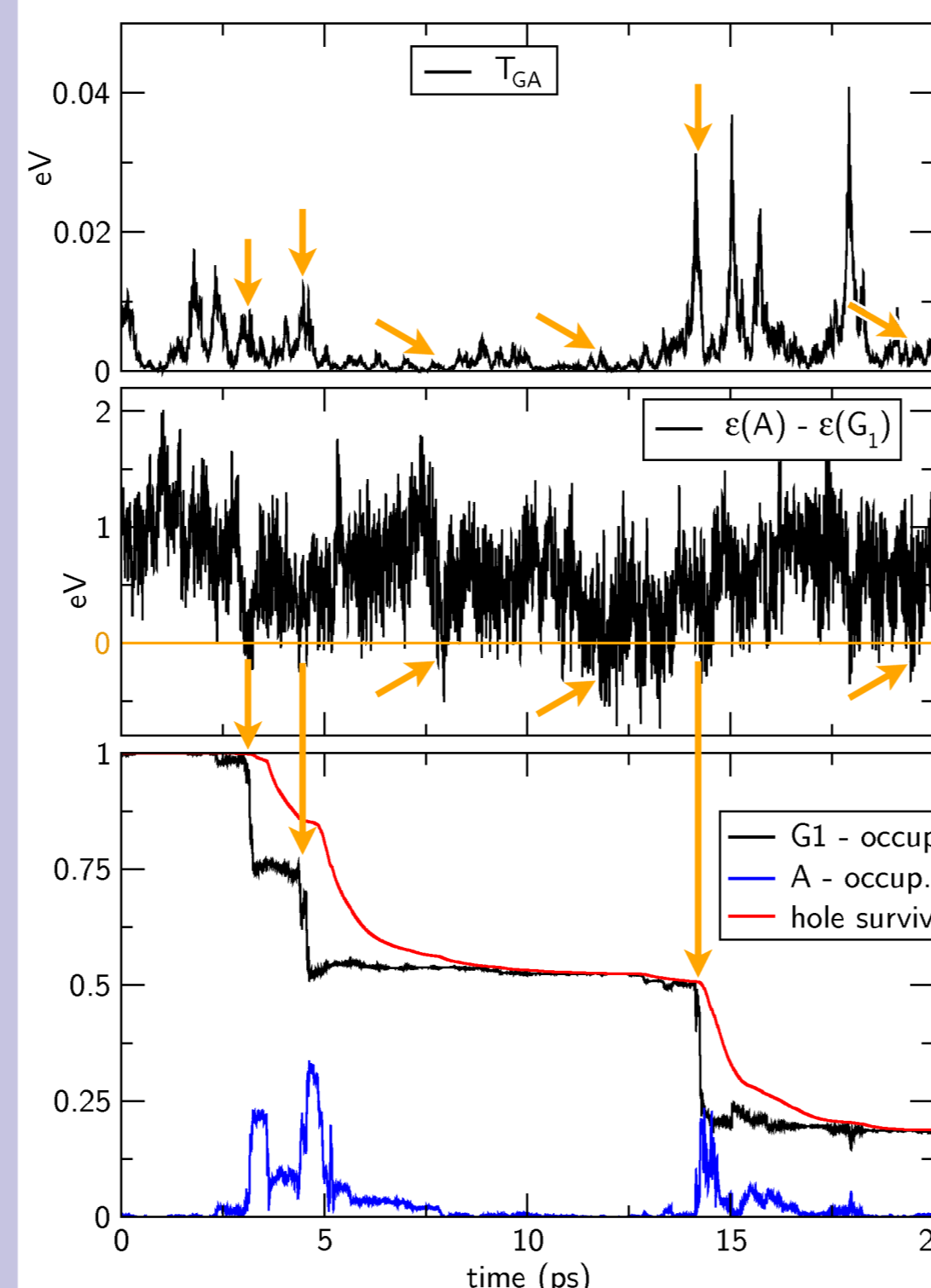
- ▶ Large variance of rate among individual simulations
- ▶  $\approx 100\times$  faster than with the static model
  - **dynamic energy profile** required
  - transfer suppressed by constant parameters

- ▶ Rate decreases with the length of bridge:



## Microscopic view of the transfer

- ▶ A 'slow' example of simulation of hole transfer in **G1-A-G-G-G**



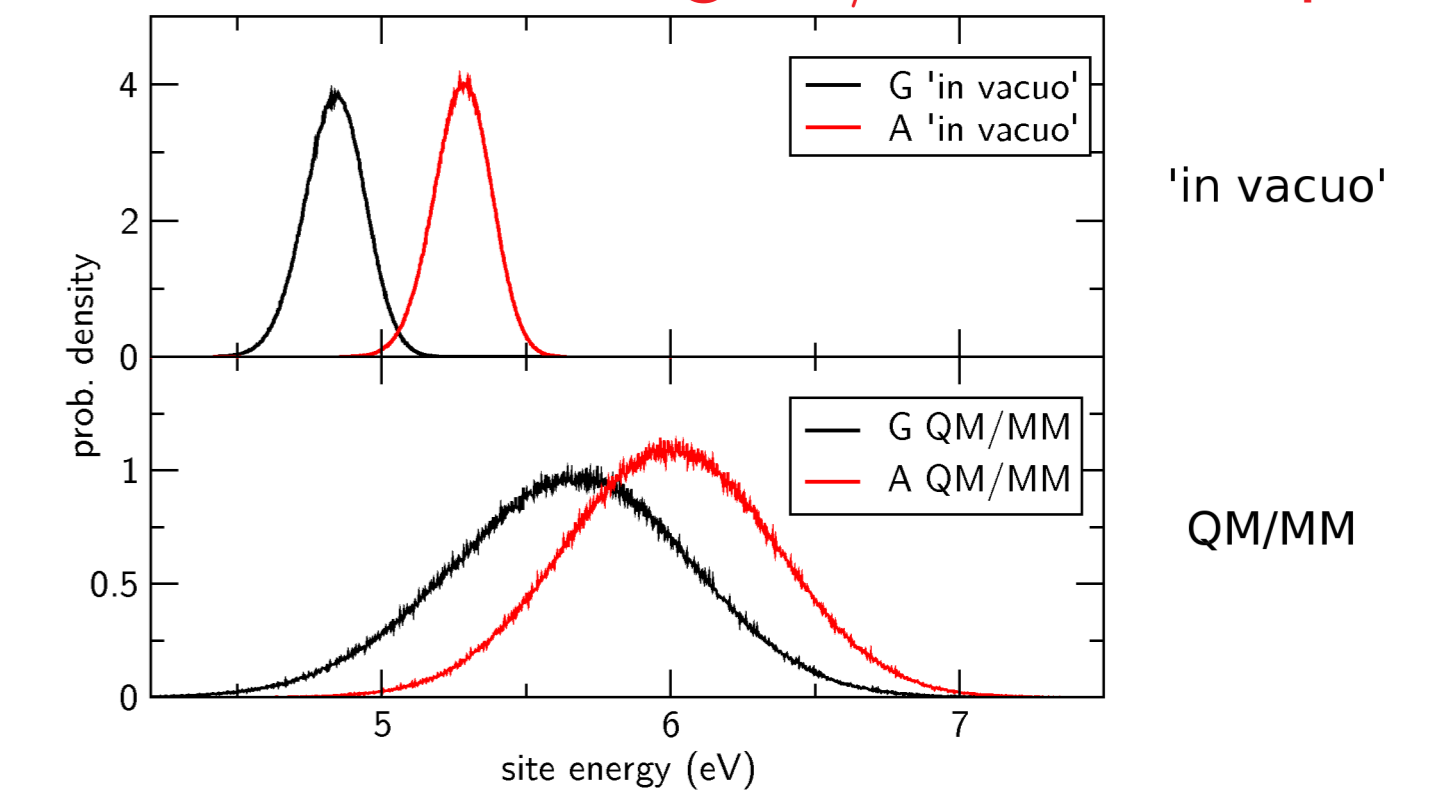
- ▶ **electronic coupling** fluctuations due to DNA structure
- ▶ **barrier height** fluctuations largely due to the solvent
- ▶ **several events of hole transfer** from G1 to A
- ▶ **conditions:**
  1. vanishing barrier
  2. non-zero coupling

## Work in progress

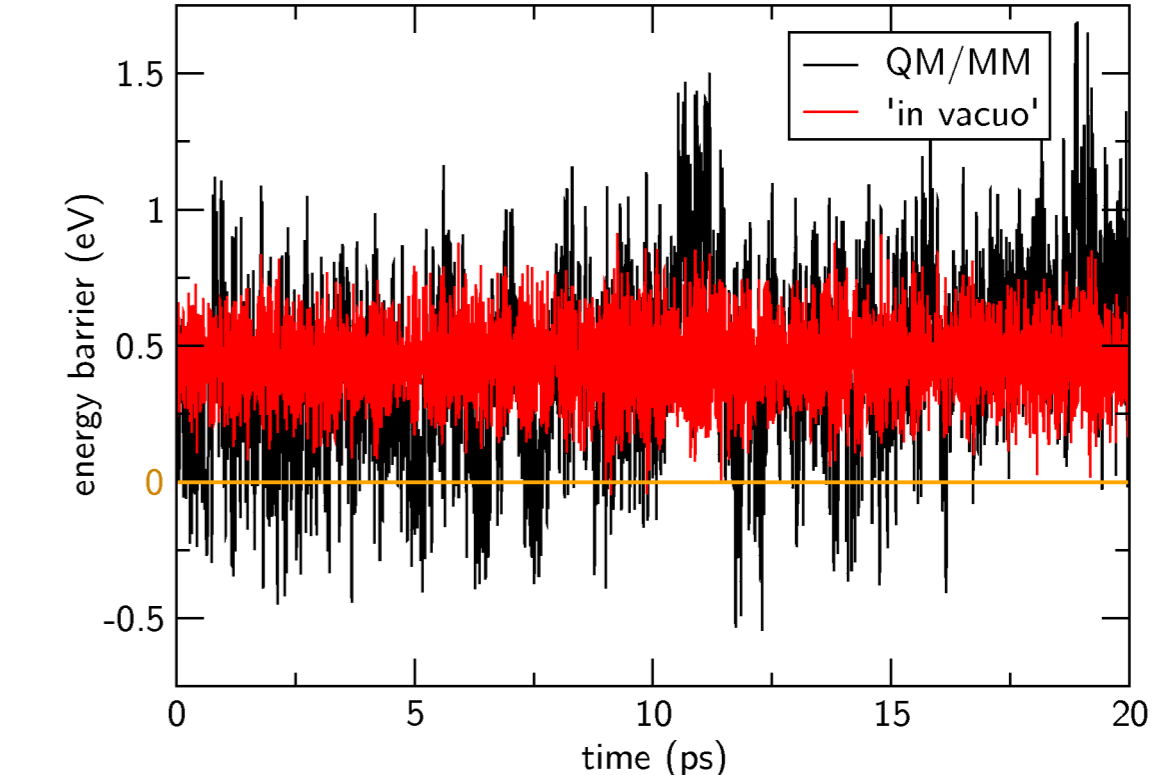
- ▶ **Mapping of the hole charge onto nucleobases**
- ▶ TDSE integration coupled with the classical MD (atom charges being modified in every MD step)
- ▶ Response of environment to the charge of hole and its varying distribution (polaron)
- ▶ Slower rate of transfer expected

## Effect of environment

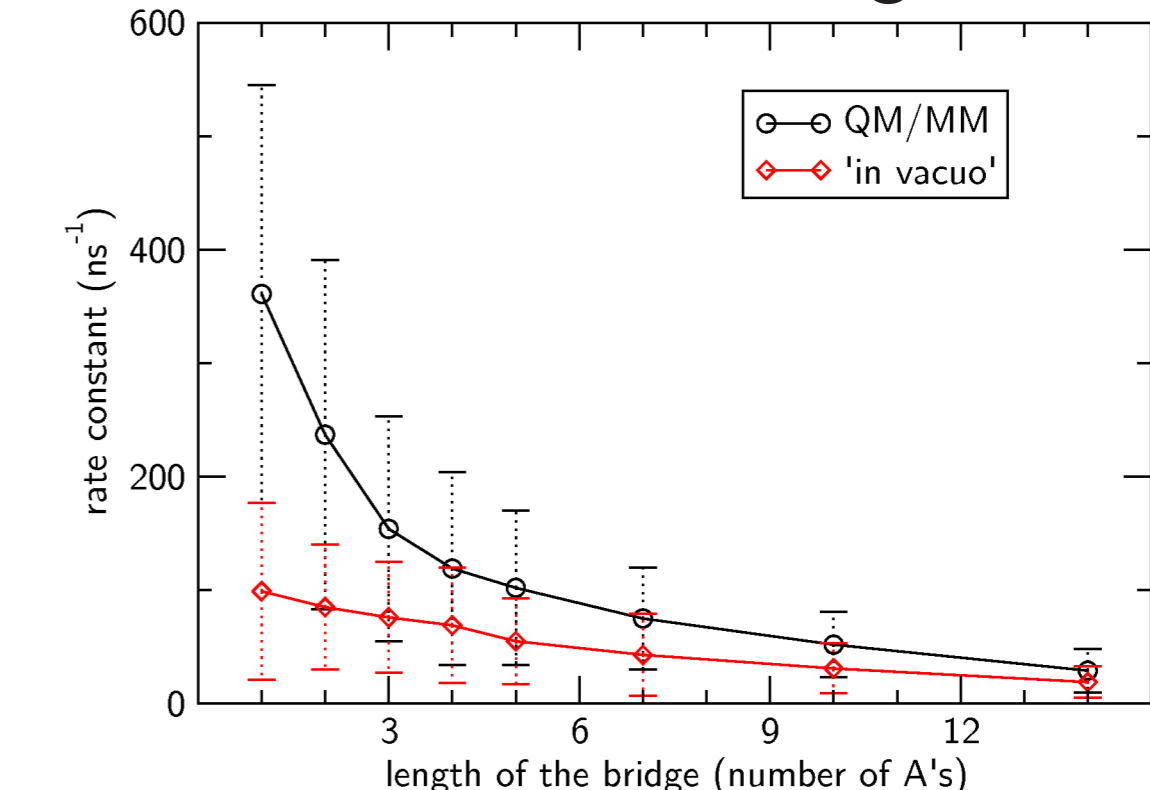
- ▶ Induction of electric field on the nucleobases
- ▶ Influence on **site energies / ionization potentials:**



→ large fluctuation of the **barrier height**



- ▶ Neglect of environment → **slower transfer rates** due to the barrier vanishing less frequently:



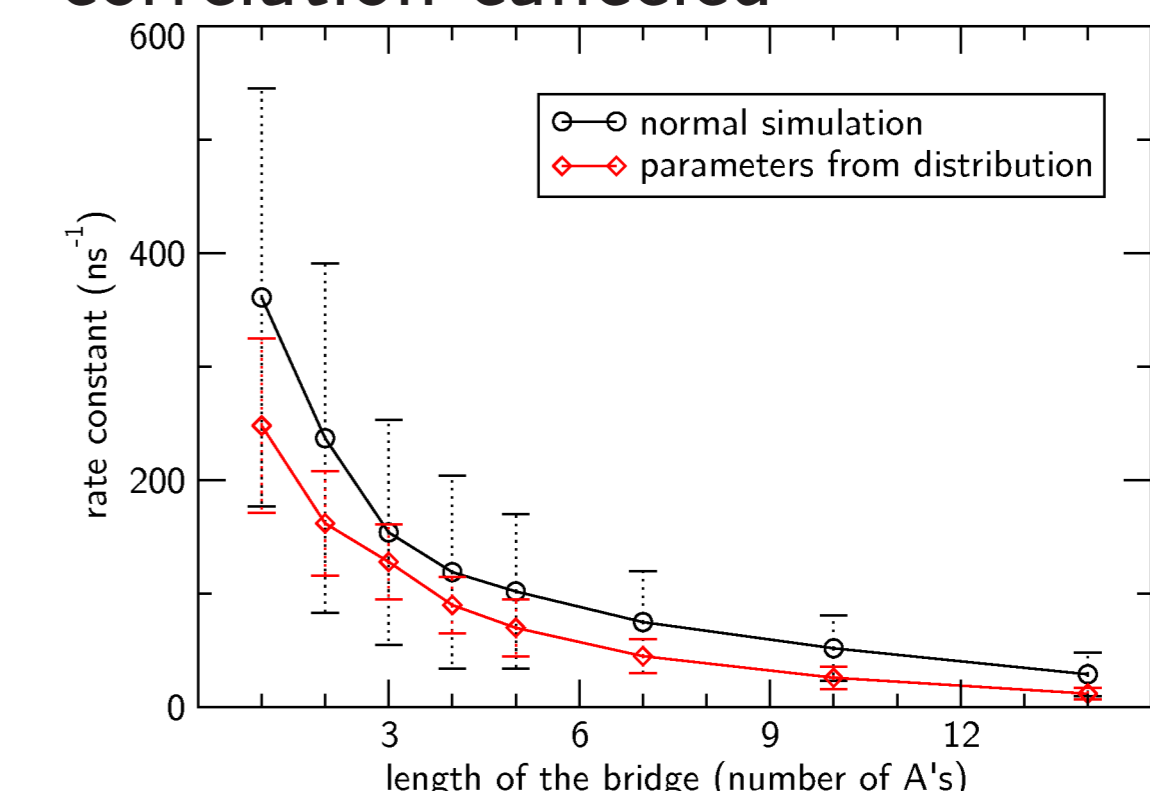
- ▶ No effect of solvent on **electronic couplings** (driven by the structure of DNA)

## Correlation of site energies

- ▶ Site energies of neighboring nucleobases **correlated** ( $\rho = 0.7$  with 1<sup>st</sup> neighbor, 0.3 with 2<sup>nd</sup> neighbor) → domains of synchronized site energies

### ▶ Stochastic model

- parameters drawn from distributions randomly
- correlation canceled



- slower rates obtained
- ▶ Correlations → **increased transfer efficiency** – up to 50 % difference (long DNA strands)
- ▶ Electronic couplings – no correlations observed

## Key observations

- ▶ Dynamics of DNA structure controls el. couplings
- ▶ The solvent drives the energetics of hole transfer
- ▶ The neglect of solvent decelerates the transfer
- ▶ Charge-transfer-active states of the DNA strand – those with vanishing energy barrier
- ▶ Hopping observed rather than tunnelling – non-zero occupation of the bridge by the hole

## Acknowledgment

This work has been supported by the Deutsche Forschungsgemeinschaft. SPP 1243 Quantum transport at the molecular scale (Project DFG-EL 206/5-1)