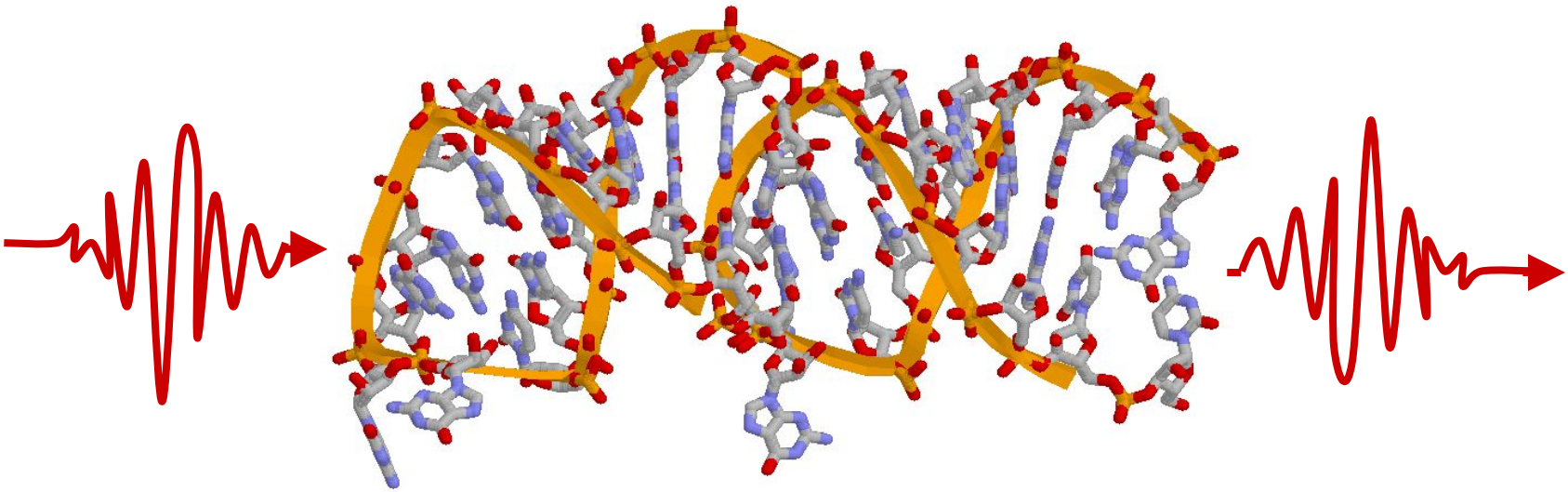
Atomistic DNA simulations: charge transfer in solution and through bio-nano contacts



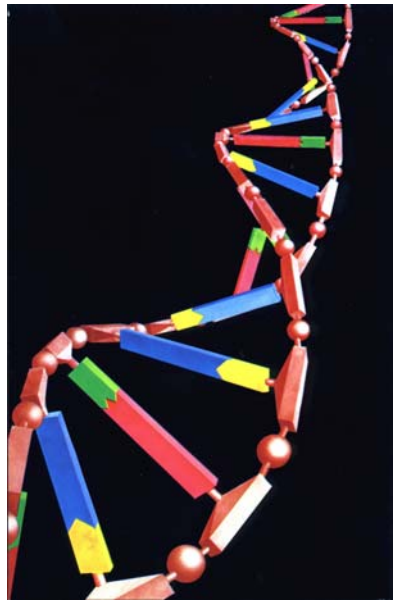
Thorsten Koslowski
Institut für Physikalische Chemie,
Universität Freiburg, Germany

Why charge transfer ?

- Fundamental processes of life:
  - photosynthesis
  - respiration
  - oxidative stress
  - mutagenesis
- transport and conductivity
- electrochemistry, corrosion
- nanoelectronics
- (Bio)sensors
- organic photovoltaics

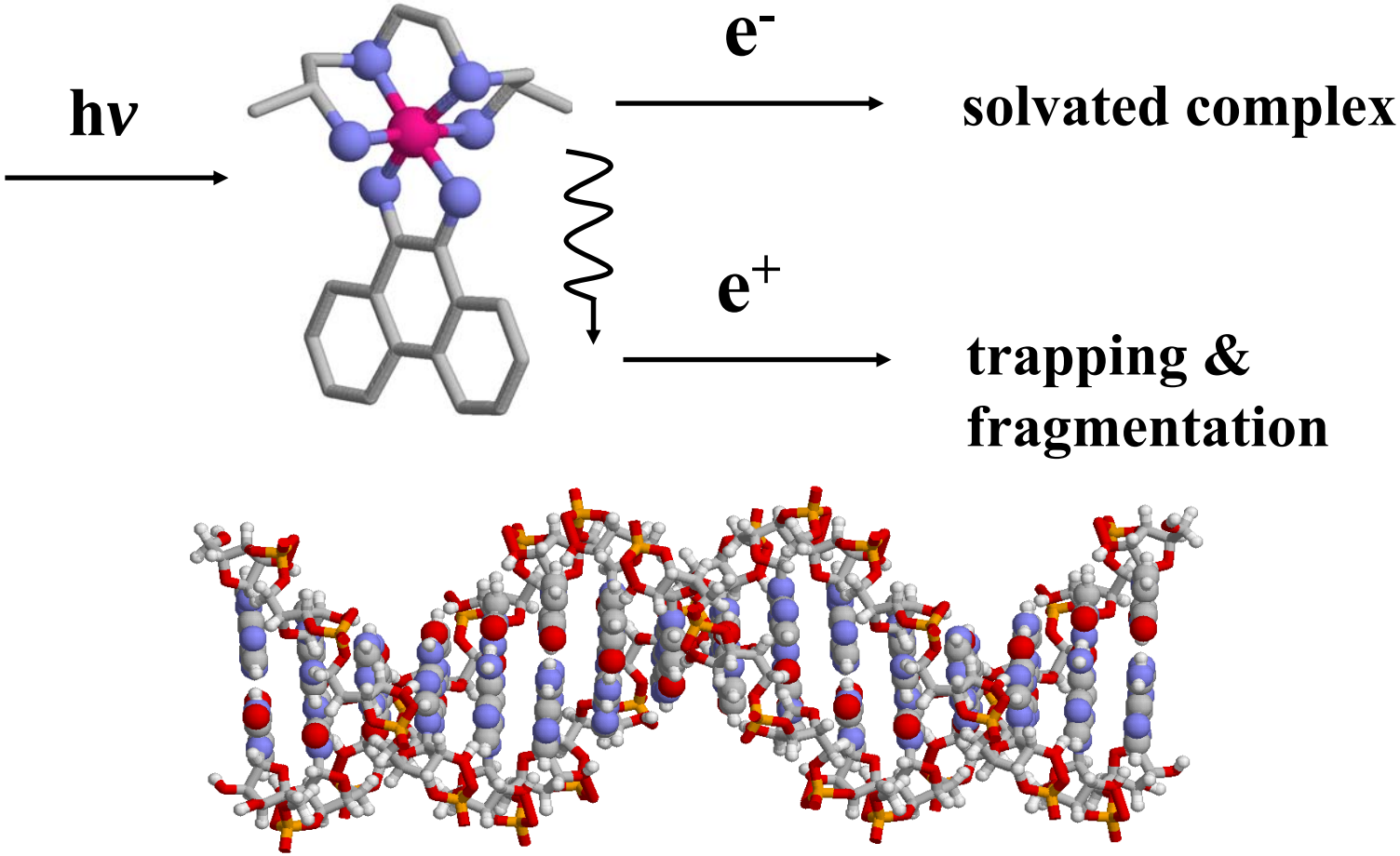
Hölldobler/Wilson

GEO



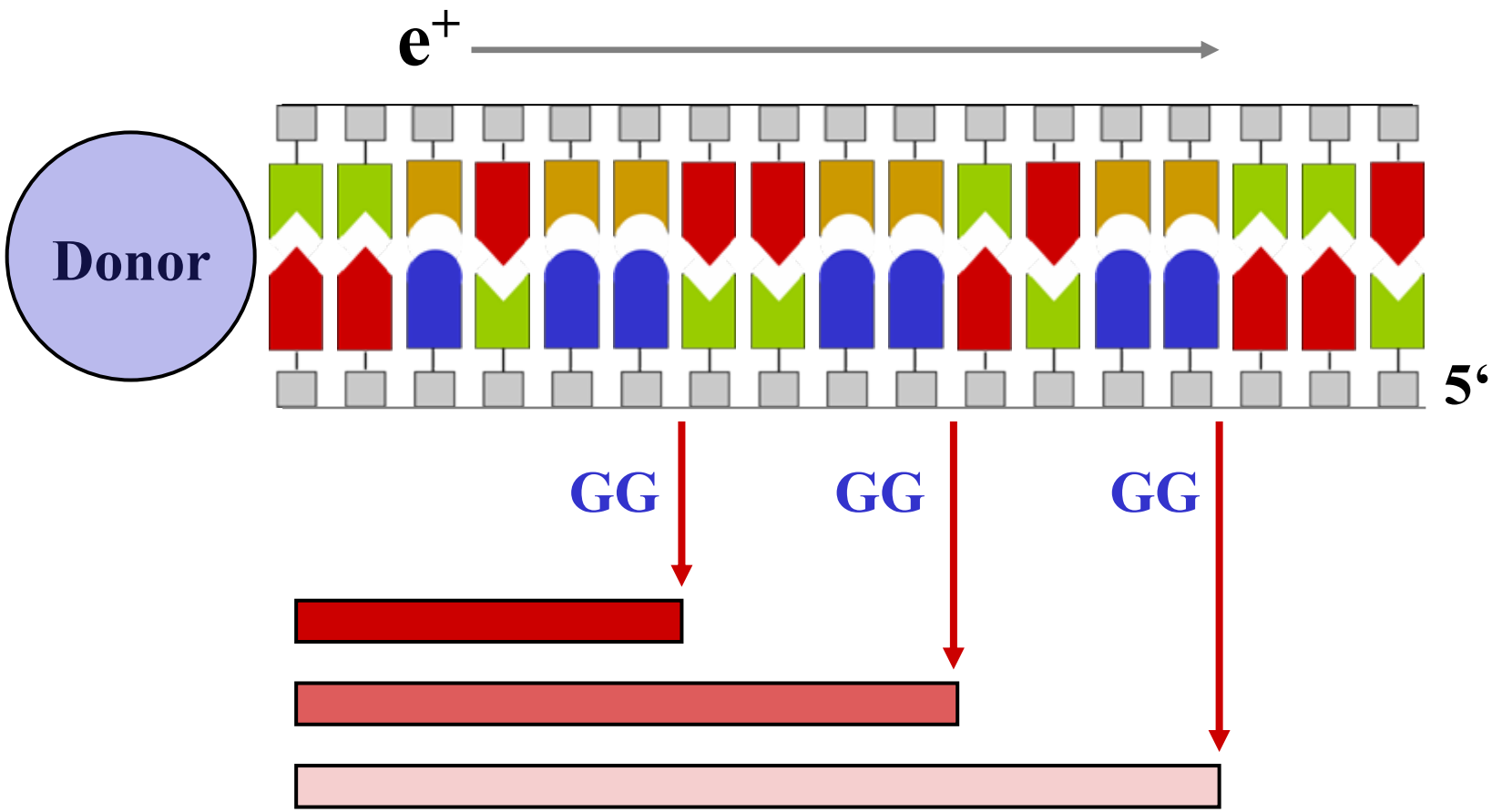
DNA charge transfer experiments

DNA charge transfer experiments in chemistry



Giese, Barton, Michel-Beyerle, Schuster, Carell, Wagenknecht, …

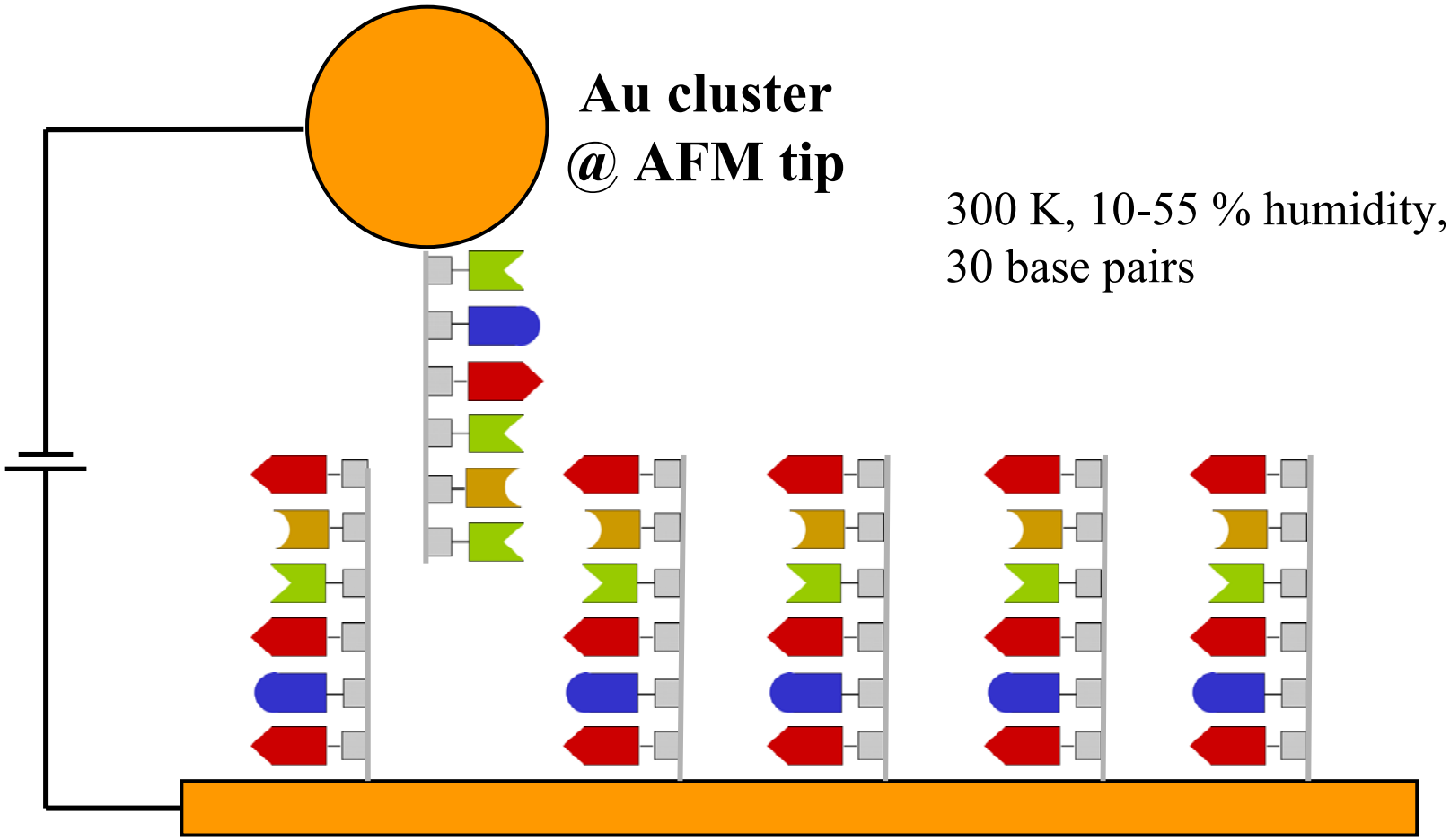
Trapping and fragmentation at multiple G sites



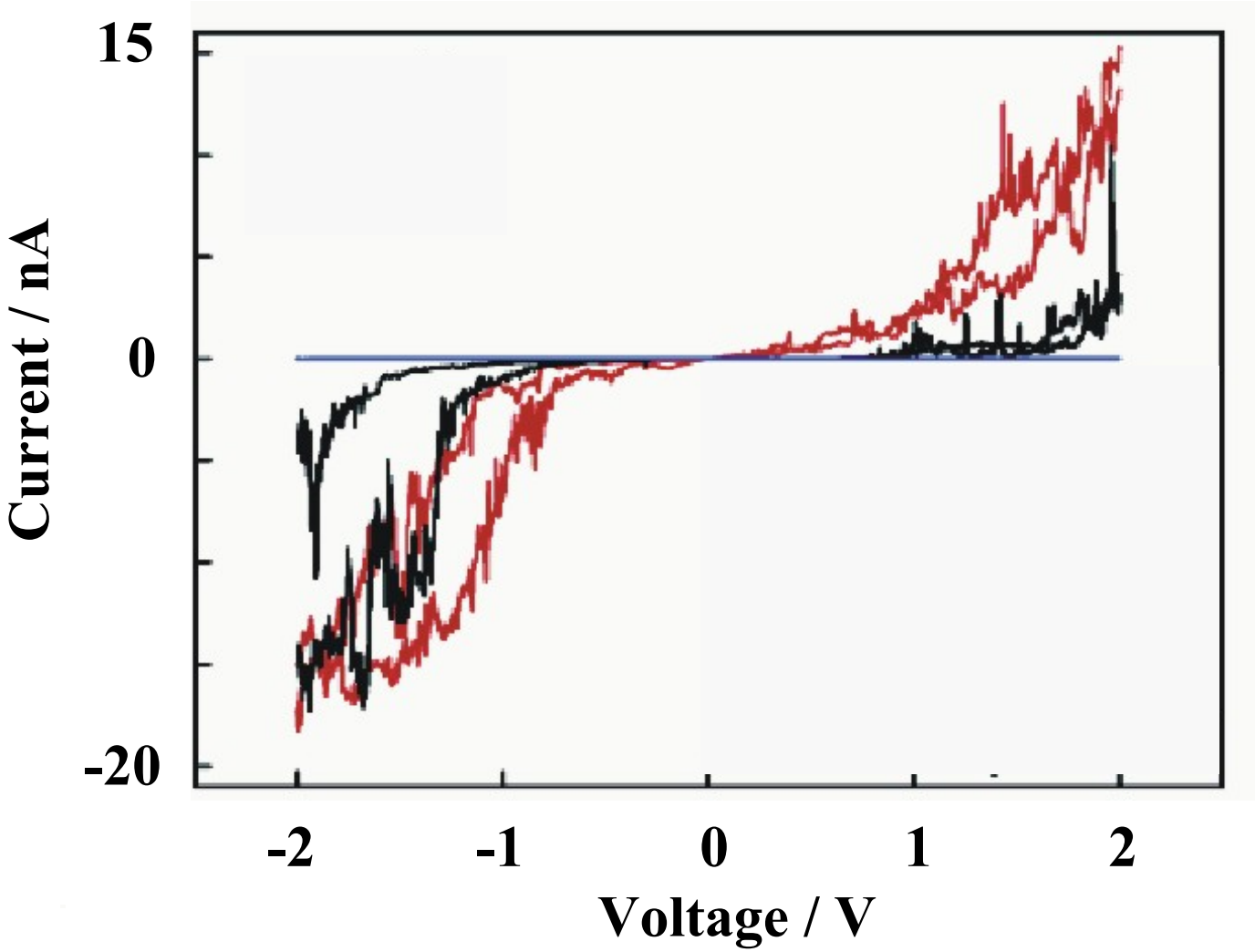
The fragment size distribution reflects the reaction kinetics

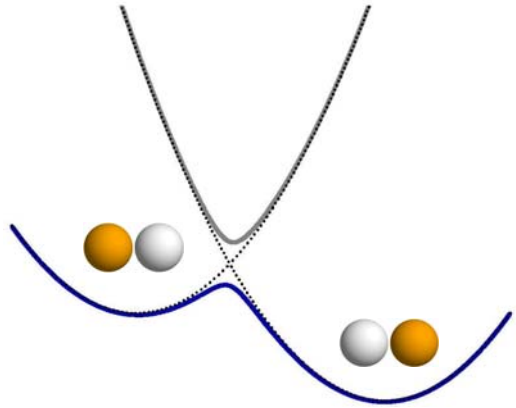
Nanoscopic conductivity setups

e.g. Porath et al., PNAS 102, 11589 (2004)



DNA: metal, semiconductor or insulator ?

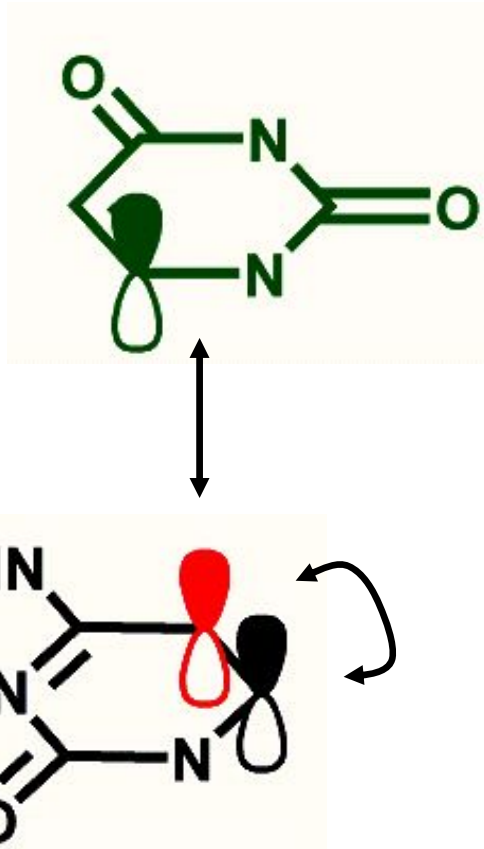




Theory I: model Hamiltonian and variational approach

The model: chemical bond

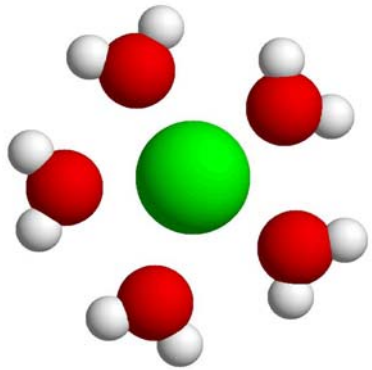
- atomistic LCAO picture
- nucleobase π orbital basis only
- Slater-Koster rules
- chemical specifity (N,C,O)
- *ab initio* DFT parametrization

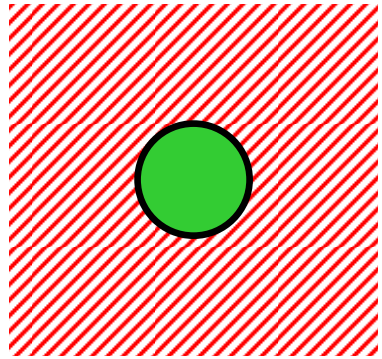


Outer sphere reorganization

solvated ion

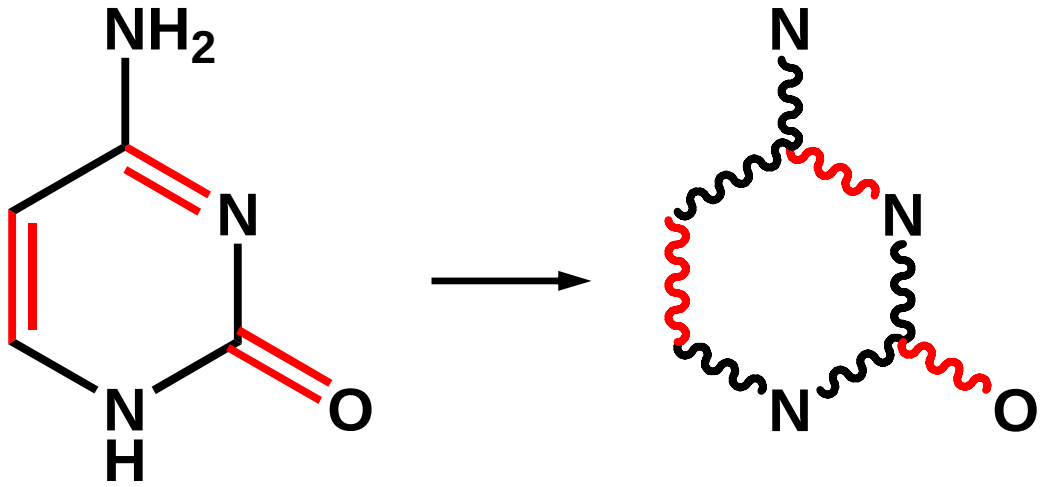
hard sphere in a dielectric continuum





$$\lambda_{out} \simeq \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{\epsilon_s}-\frac{1}{\epsilon'}\right)\sum_i \frac{\Delta z_i^2}{\sigma_i} = -\sum_i U_i(n_i-\bar{n}_{i,0})^2$$

Inner sphere: Su-Schrieffer-Heeger model



$$\hat{V} = \sum_{\langle ij \rangle} \frac{k}{2} x_{ij}^2 - \sum_{\langle ij \rangle \sigma} [t_0 - \alpha x_{ij}](a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma})$$

Resulting polaron-transformed electronic mean-field Hamiltonian

less corrections for counting the interactions twice:

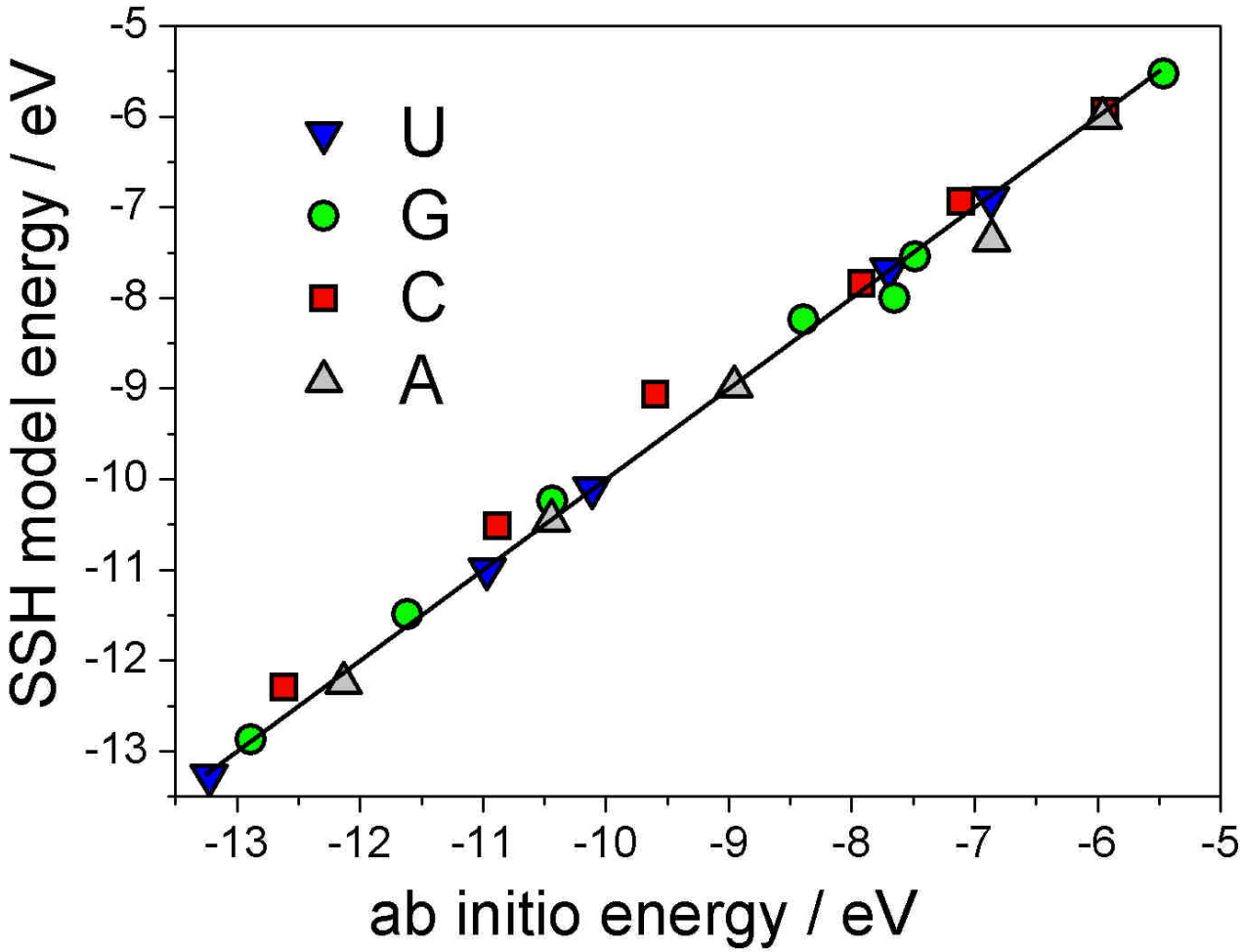
$$\hat{H} = -\sum_{ij}(t_{ij} + 4U_{ij}\bar{n}_{ij})a_i^\dagger a_j - 2\sum_i U_i n_i(\bar{n}_i - \bar{n}_{i,0})$$

chemical bond

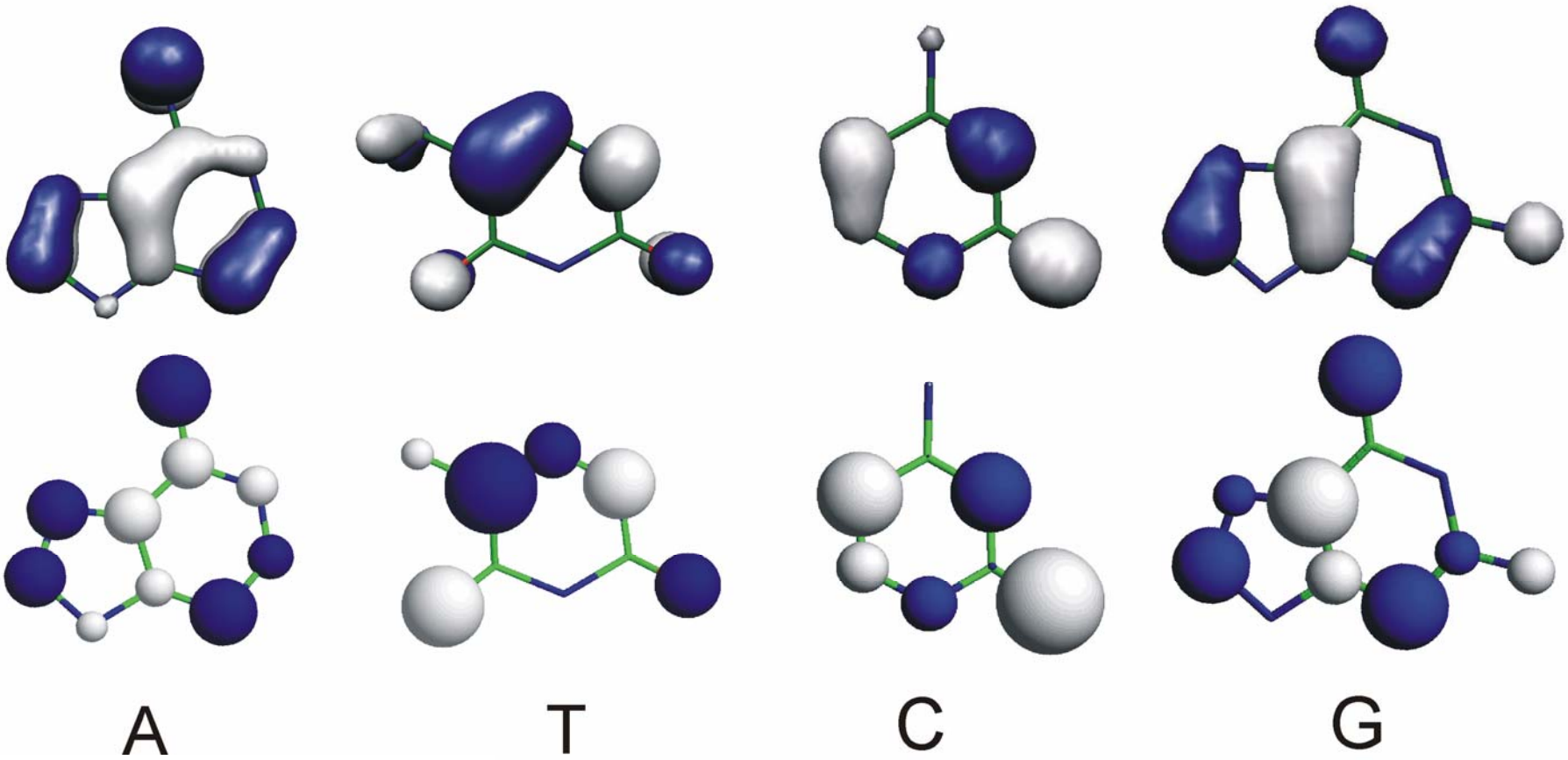
vibronic coupling

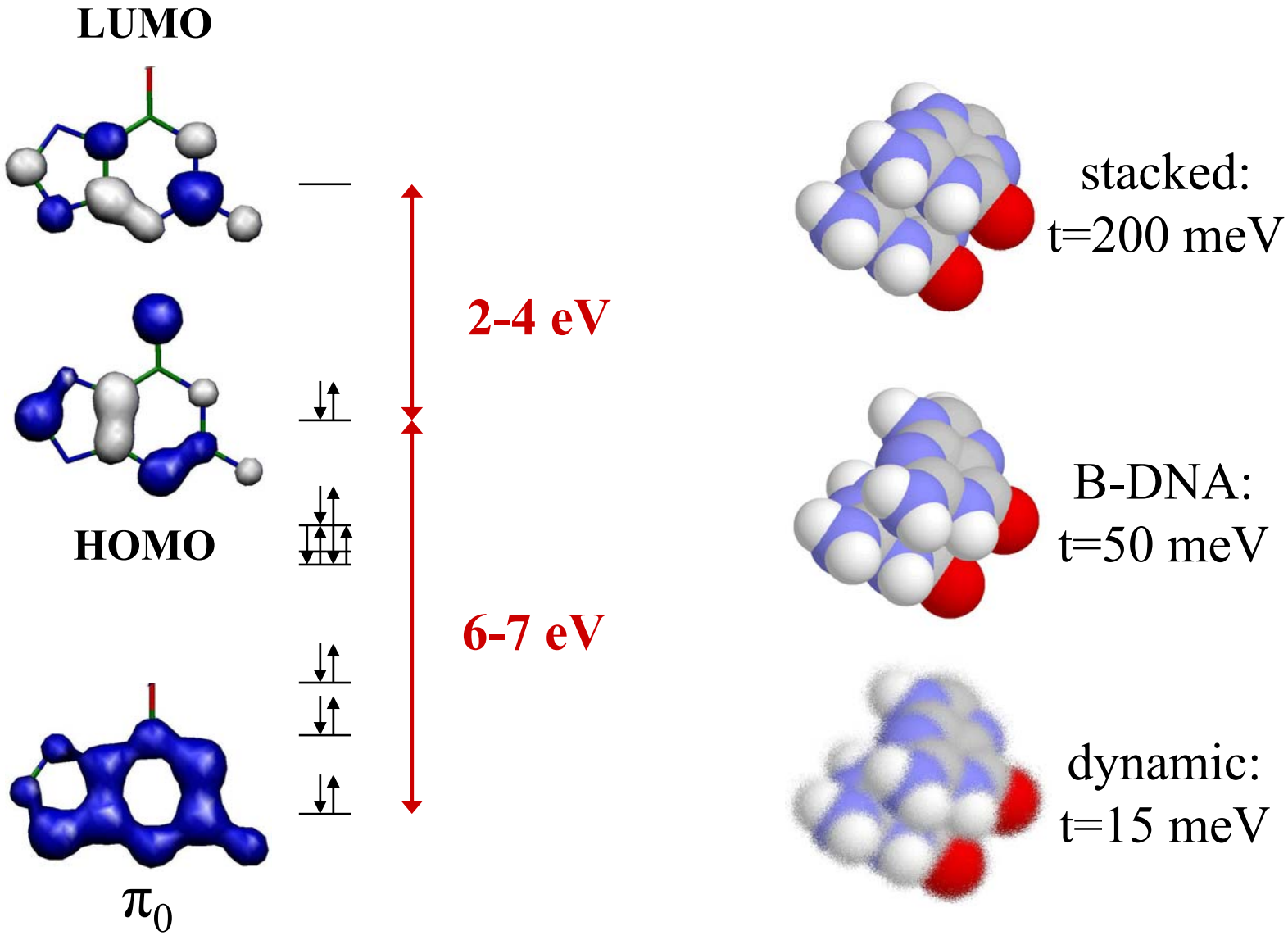
solvent polarization

Parametrization: π orbital energy levels

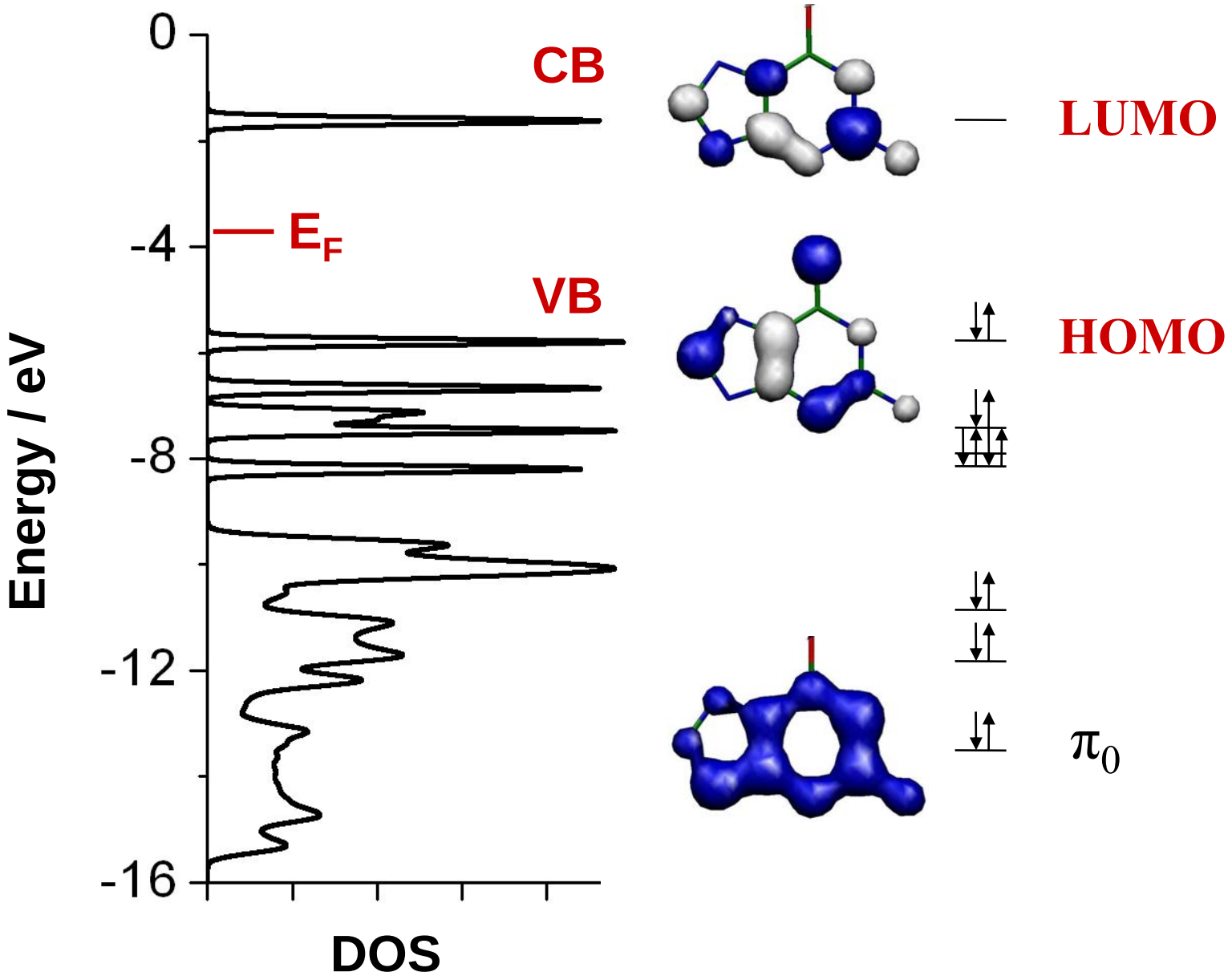


Test of the parametrization: *ab initio* HOMOs and SSH model HOMO coefficients

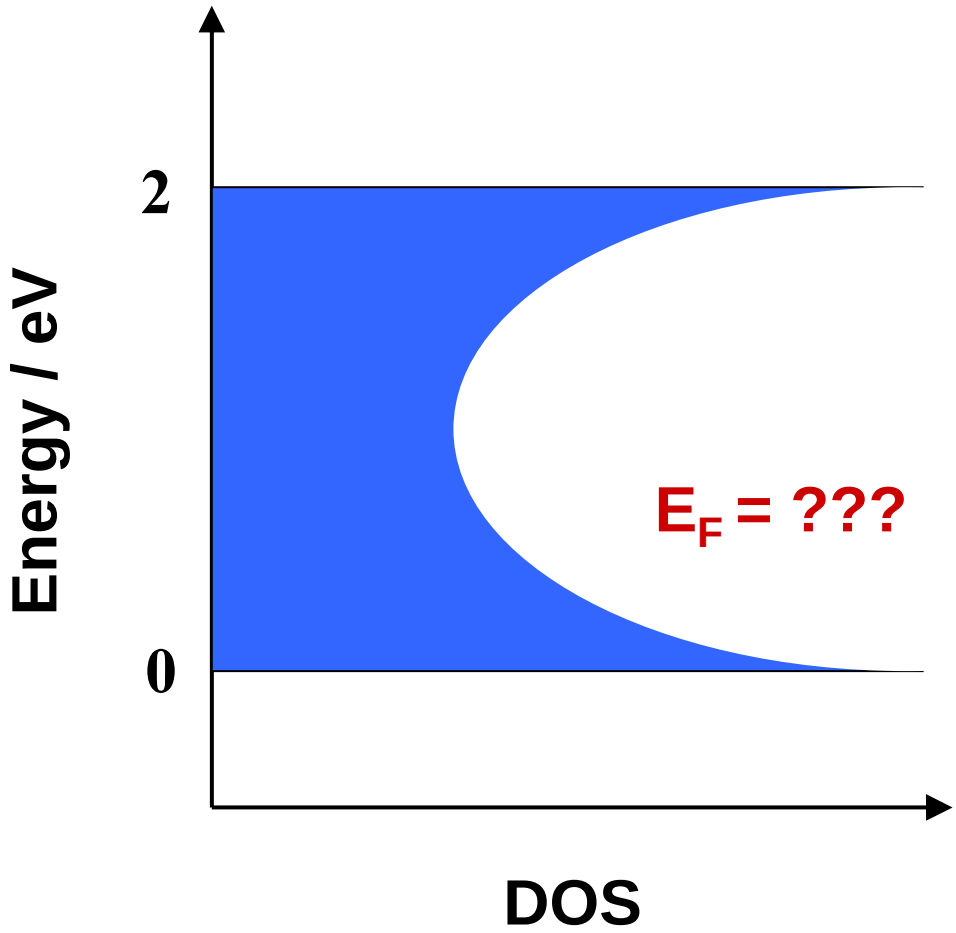




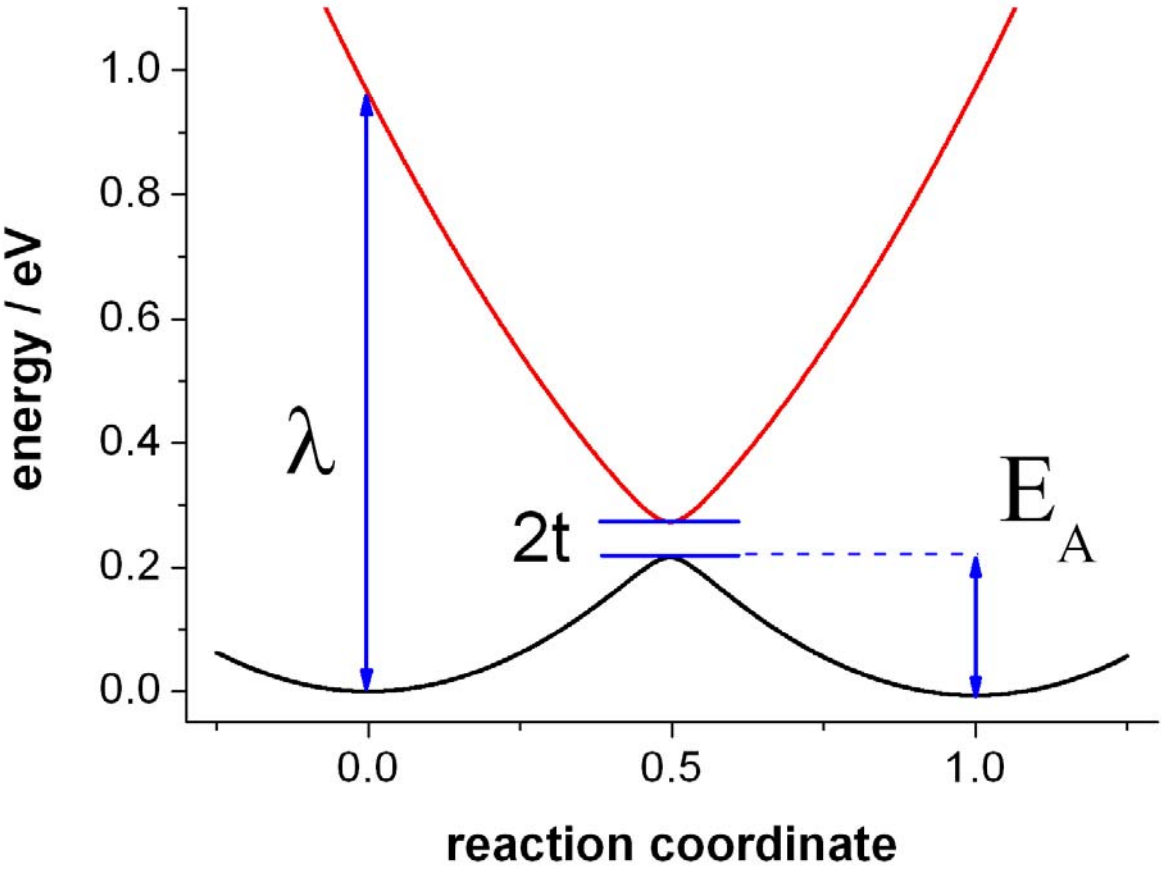
intrabase = bonding >> **inter**base = banding


0
-4
-8
-12
-16
Energy / eV
DOS
CB
VB
E_F
LUMO
HOMO
π_0

As opposed to:



Solving the SSH+U Hamiltonian: energy profile for G-A-G charge transfer



From energies to reaction rates: Marcus‘ theory

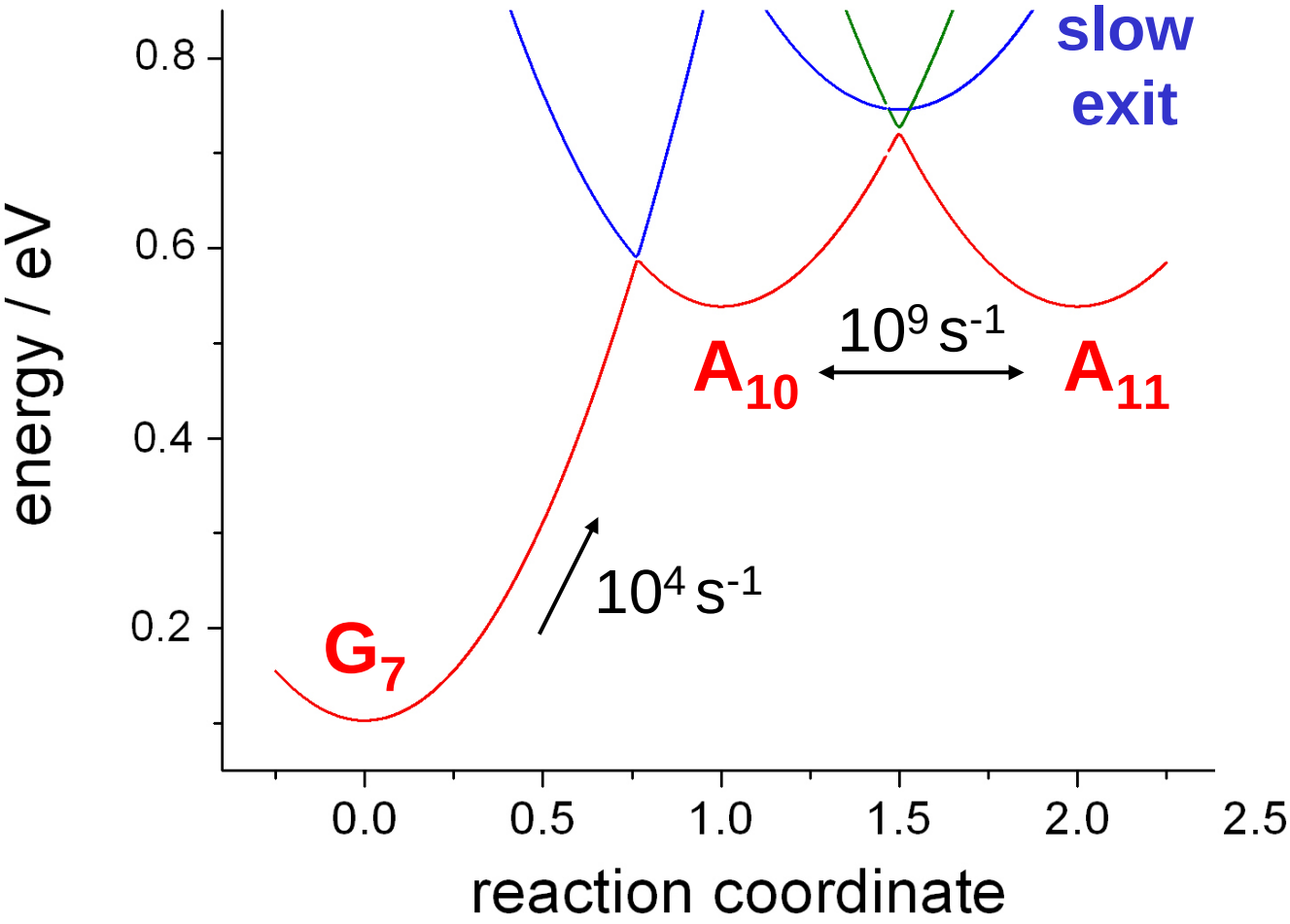
Large *t*, adiabatic, self-exchange:

$$k_{CT} = k_0 \exp\left(-\frac{E_A}{k_B T}\right)$$

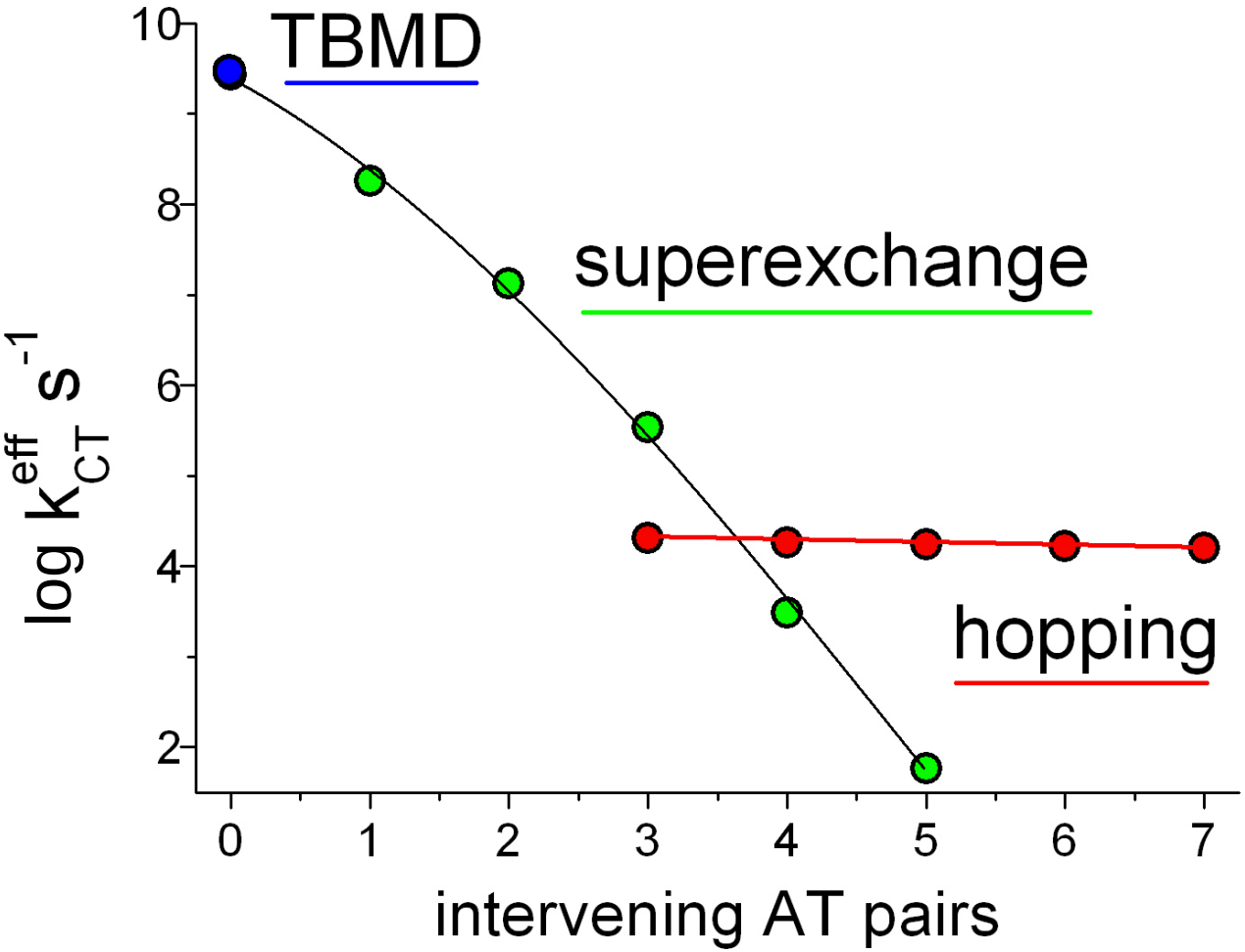
Small *t*, diabatic, self-exchange:

$$k_{CT} = \frac{t^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{E_A}{k_B T}\right)$$

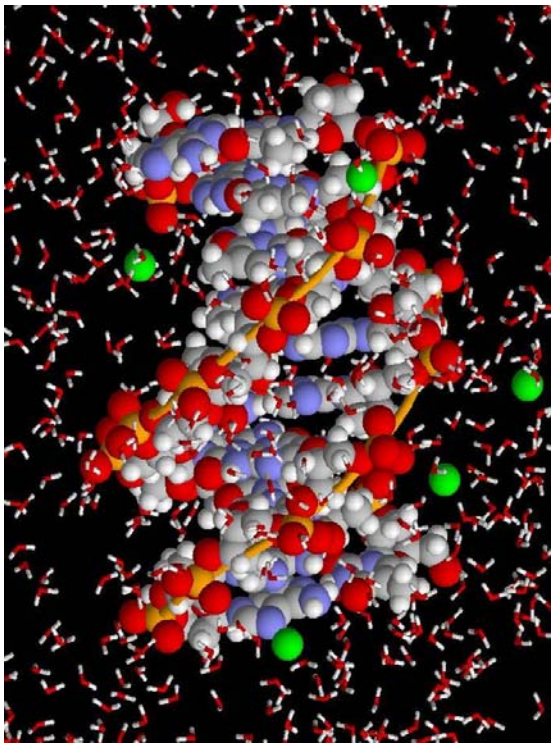
Adenine-adenine hopping



GG charge transfer kinetics for idealized systems

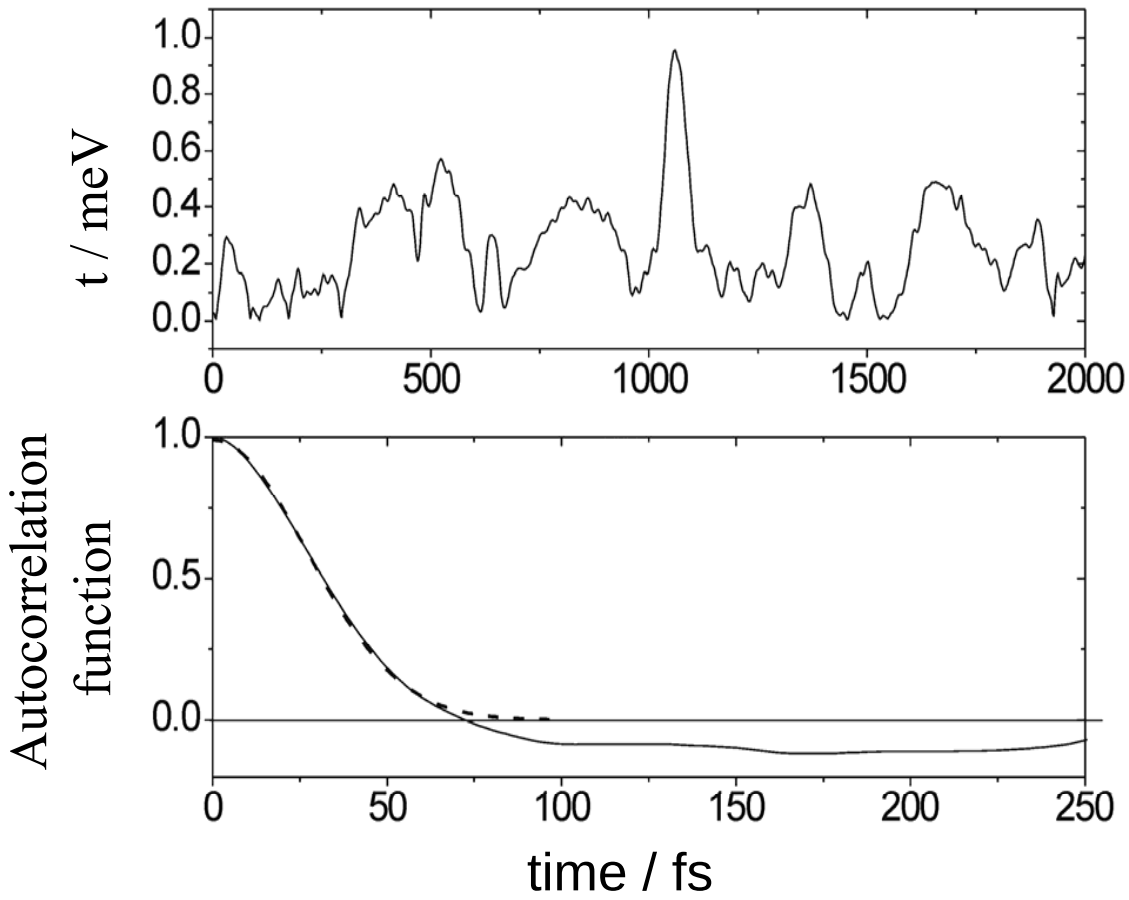


Theory II: MD simulation snapshots as input to the electronic structure theory



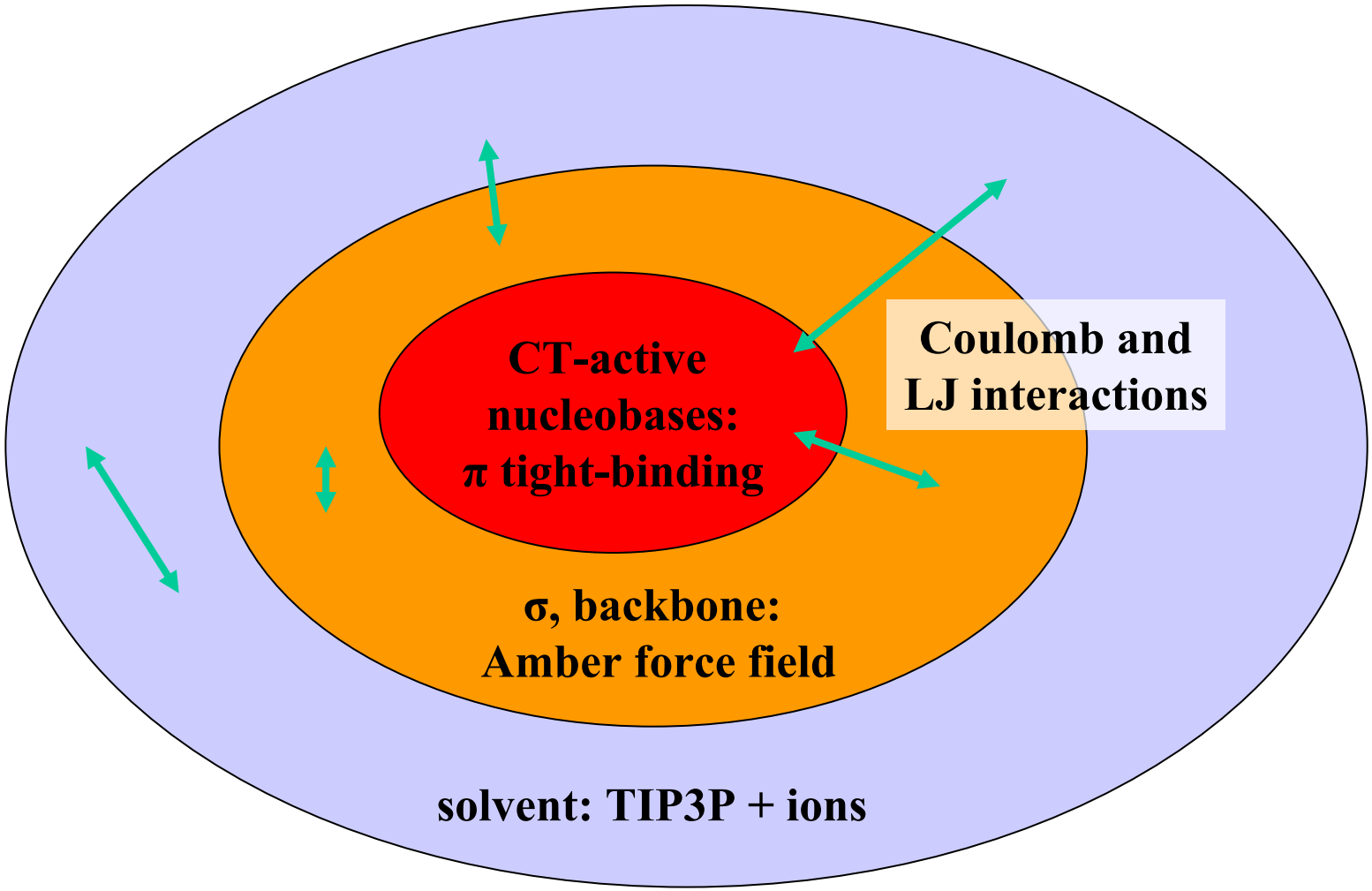
- Amber 8 modelling suite
- TIP3P water model
- 10-14 base pairs
- 16 Å water shell
- Na^+ counterions
- proper equilibration
- 10 ns simulation time
- SSH+U model post-processing

Note: **HOLE ≠ HOMO**

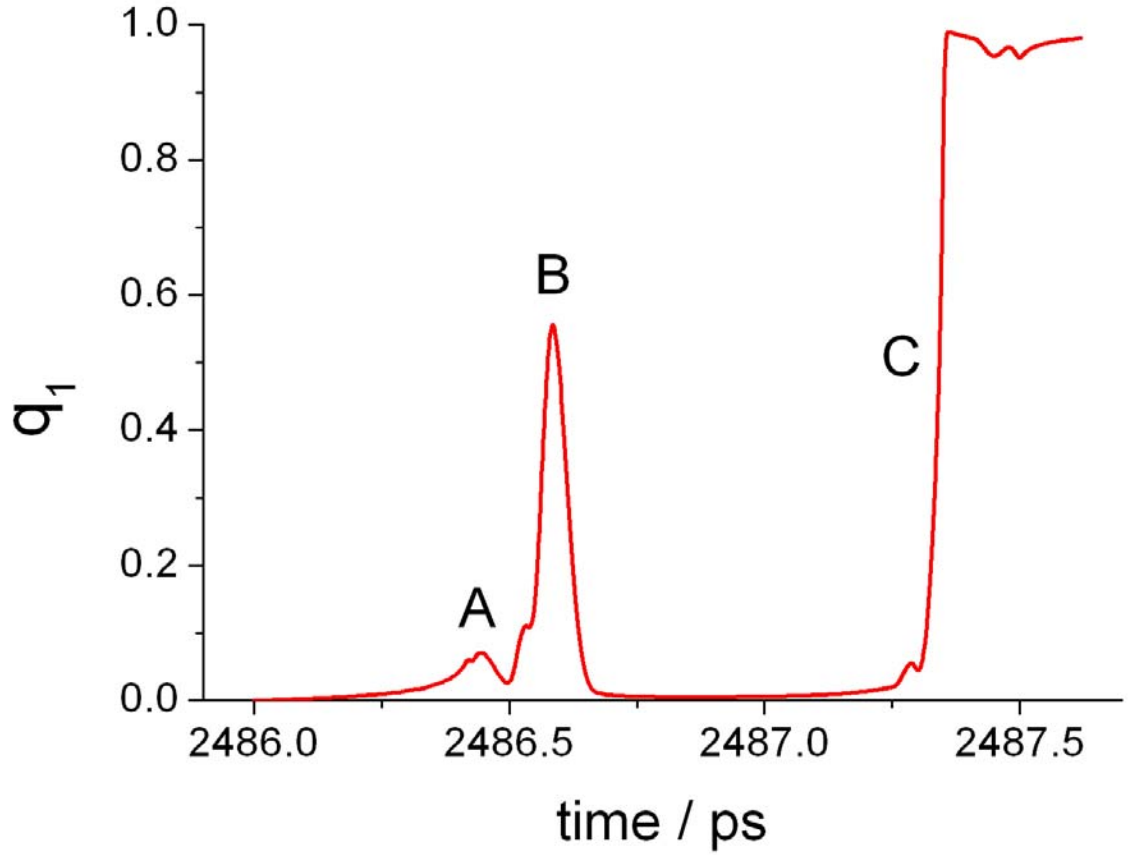


- k_{CT} fluctuates by one order of magnitude
- characteristic autocorrelation time: 30 fs
- elimination of conductivity bottlenecks is faster than CT

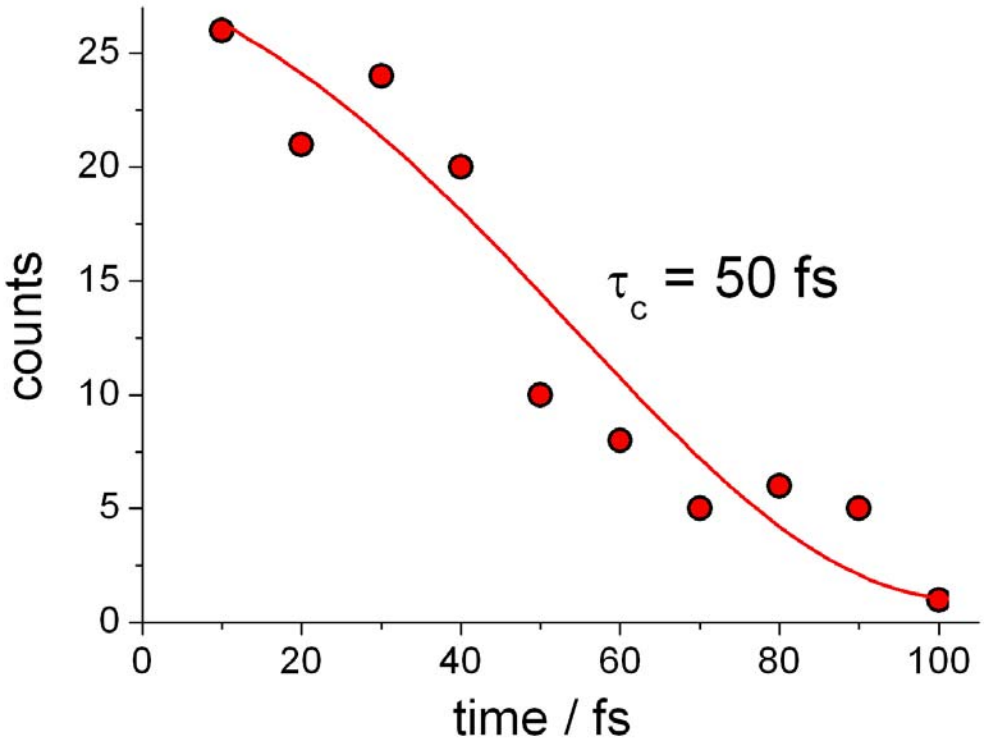
Theory III: direct adiabatic TBMD simulation



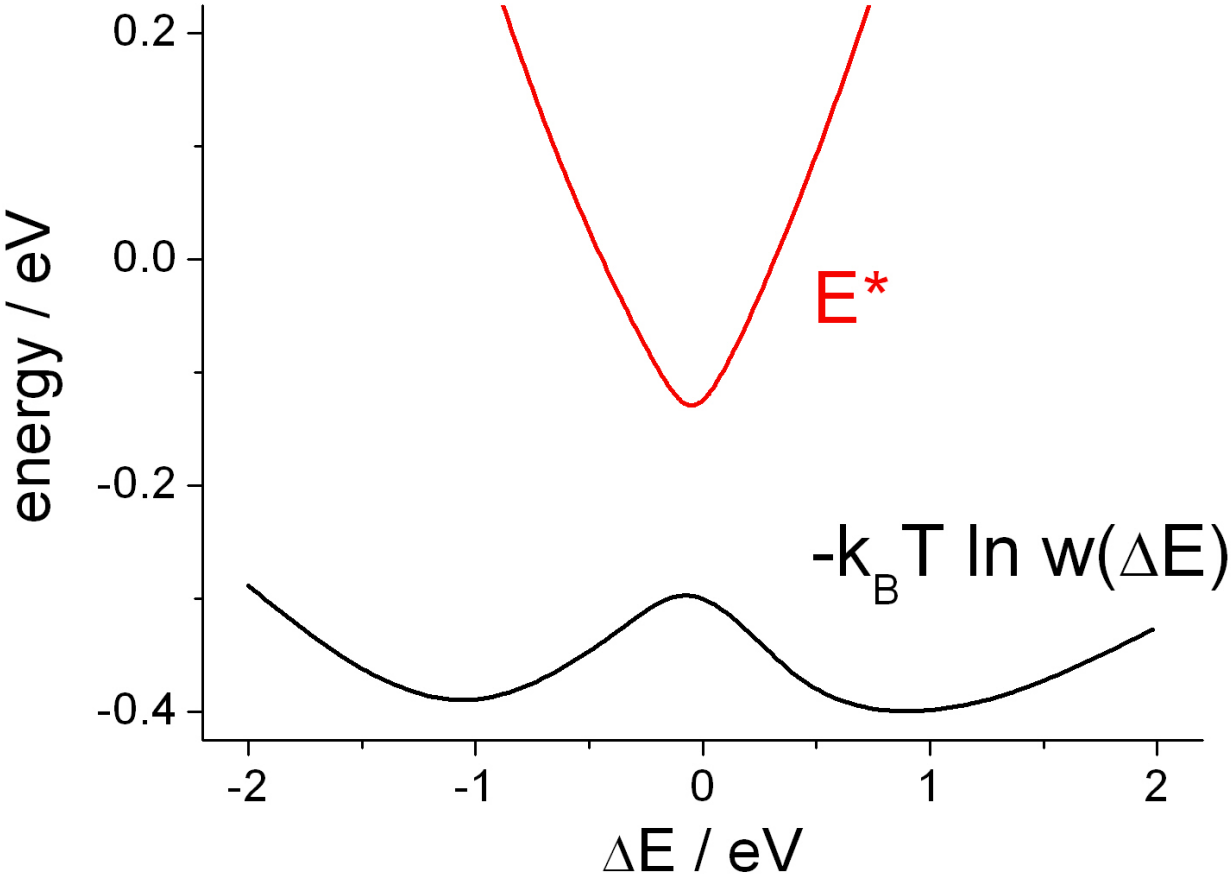
Charge transfer trajectories (A_4AAA_4, A_4GGA_4)
total of 100 ns simulation time per system



Rapid back transfer for 50 % of the hops



Potentials of mean force permit comparison to Marcus‘ theory characteristic energies



Numerical results

CT	AA	GG
t / eV	0.10	0.07
λ / eV	1.08	1.16
E_A / eV	0.09	0.12
k_{CT} / ns^{-1}	4.1	1.3

Theory IV: Transport through DNA nanocontacts

Intersite hopping rates

$$k_{ij} = \frac{t^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\exp\left(-\frac{(\Delta G^0 + U_j - U_i + \lambda)^2}{4\lambda k_B T}\right)$$

t, λ, ΔG^0: eSSH-Model; $U_i = E_z\, d_i$ potential at site i

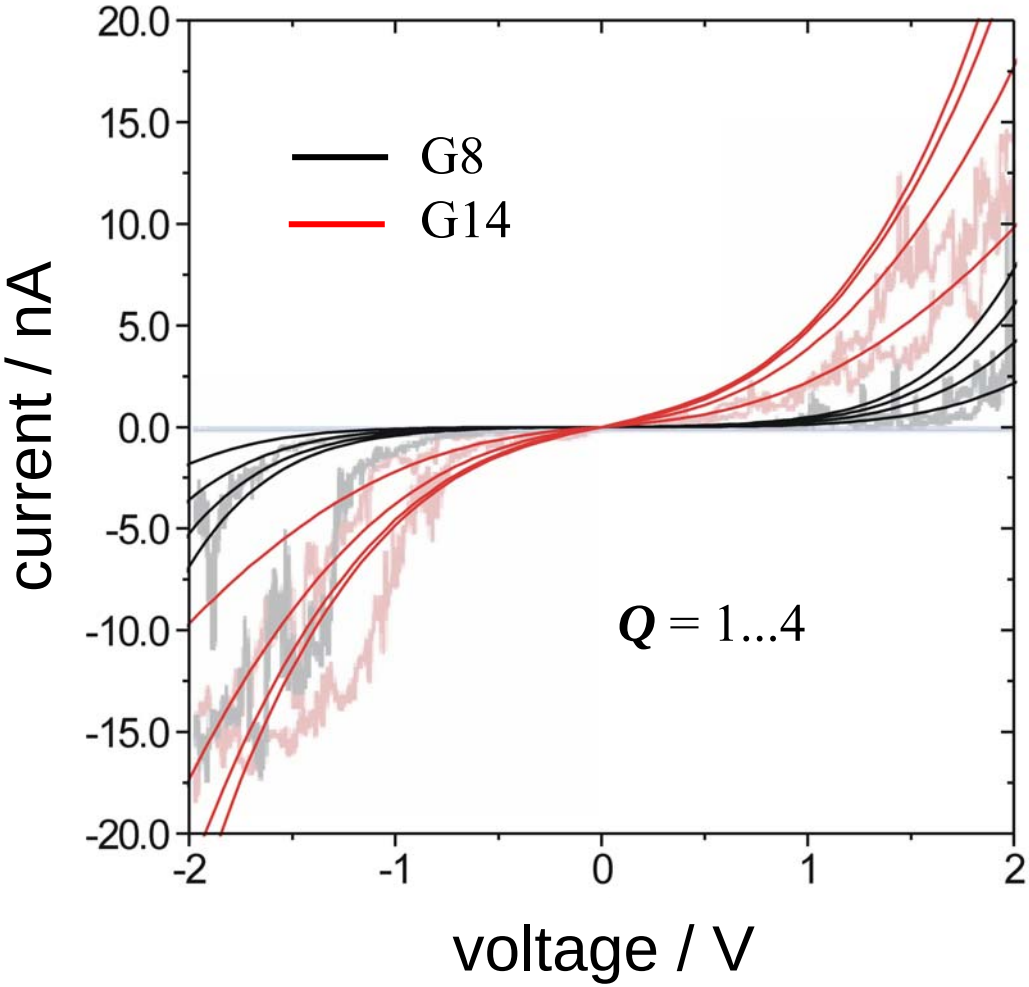
Master equations at stationarity:

$$\sum_{j \neq i}\left[k_{ij}\, p_i (1 - p_j) - k_{ji}\, p_j (1 - p_i)\right] = 0$$

Additional assumptions:

- ideal contact to the gold surface
- fixed number of charges: $Q = \sum p_i$
- smaller reorganization energy compared to solvated systems

I-V-Curves


20.0
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-20.0
-2
-1
0
1
2
current / nA
voltage / V
G8
G14
Q = 1...4

Conclusions

- chemically specific, atomistic model of DNA charge transfer
- variational approach, MD+SSH+U, QM/MD
- unified atomistic description of tunneling, hopping, and transport through nanojunctions

References

T. Cramer, S. Krapf, T. Koslowski, DNA Charge transfer: an atomistic model,
J. Phys. Chem. B, 108, 11812 (2004) (original model, variational approach)

T. Cramer, T. Steinbrecher, A. Labahn, T. Koslowski, Electronic and dynamic aspects of DNA charge transfer, PCCP 7, 4039 (2005) (MD + quantum mechanical postprocessing)

T. Steinbrecher, D. A. Case, T. Koslowski, Direct simulation of electron transfer reactions in DNA radical cations, J. Phys. Chem. B **112**, 16935 (2008) (true QM/MD simulation of charge transfer)

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T. Cramer, A. Volta, A. Blumen, T. Koslowski, Theory and simulation of DNA charge transfer: from junctions to networks, J. Phys. Chem. B 108, 16586 (2004) (application to nano-sized DNA objects)

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G. Rink, Y. Kong, T. Koslowski, Theory and simulation of charge transfer through DNA - nanotube contacts, Chem. Phys. 327, 98 (2006)

Co-Workers

Dr. Tobias Cramer
Sebastian Krapf
Fabian Burggraf
Sandra Kruse
Dr. Gundi Rink
Dr. Nadine Utz
Dr. Christian Wittekindt

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Cooperations

L. Mühlbacher, A. Blumen, Theoretical Physics
Th. Friedrich, Biochemistry
D. Case, T. Steinbrecher, Rutgers U
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