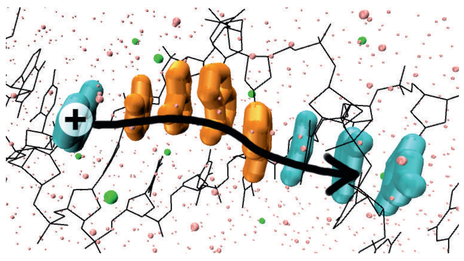

Non-adiabatic simulation of charge transfer in biomolecules

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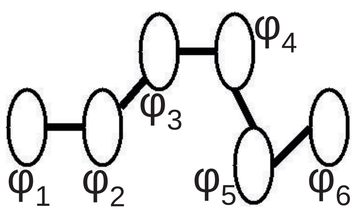
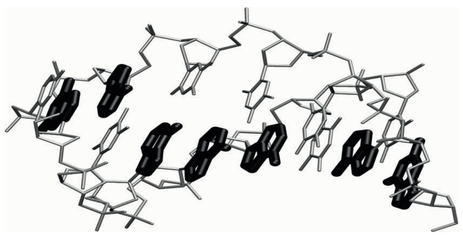
Coarse-graining – charge carriers

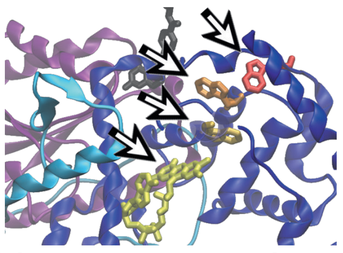
in general



nucleobases



AA side chains



Excess charge (electron / hole) – described with a wave packet

$\Psi = a_1\varphi_1 + a_2\varphi_2 + a_3\varphi_3 + \ldots = (a_1, a_2, a_3, \ldots)$

Charge on a carrier: $q_i = |a_i|^2 \cdot Q$ Total charge: $Q = \sum_i q_i$

Coarse-grained Hamiltonian

$$\begin{matrix} \varepsilon_1 & T_{12} & T_{13} & \ldots & T_{1n} \\ T_{21} & \varepsilon_2 & T_{23} & \ldots & T_{2n} \\ T_{31} & T_{32} & \varepsilon_3 & \ldots & T_{3n} \\ \ldots & & & & \\ T_{n1} & T_{n2} & T_{n3} & \ldots & \varepsilon_n \end{matrix}$$

site energy ε_i
– ionization potential (hole xfer)
– electron affinity (electron xfer)

electronic coupling T_{ij}
– approximated by Hamiltonian elements between HOMOs/LUMOs

evaluated with quantum chemistry
SCC-DFTB – efficient approx. DFT

Key ideas

2nd-order expansion of energy in density

$E = E_0 + E_1 + E_2$

E_0 – energy of neutral system

$E_1 = \sum_i a_i^* a_i \cdot \varepsilon_i + \sum_{i \neq j} a_i^* a_j \cdot T_{ij}$
– includes within ε_i the interaction of charge with environment

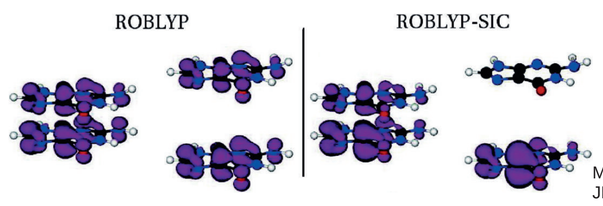
$E_2 = \sum_i q_i^2 \cdot U_i + \sum_{i \neq j} q_i q_j / R_{ij}$
– involves the Hubbard parameter U (chemical hardness of charge carriers)

Self-interaction error

pronounced for radical systems in DFT
correction – scaling with a constant < 1

$E_2' = C \cdot E_2 \quad C \approx 0.2$

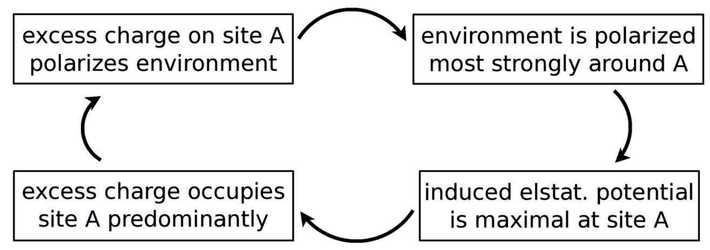
– improves the distribution of charge



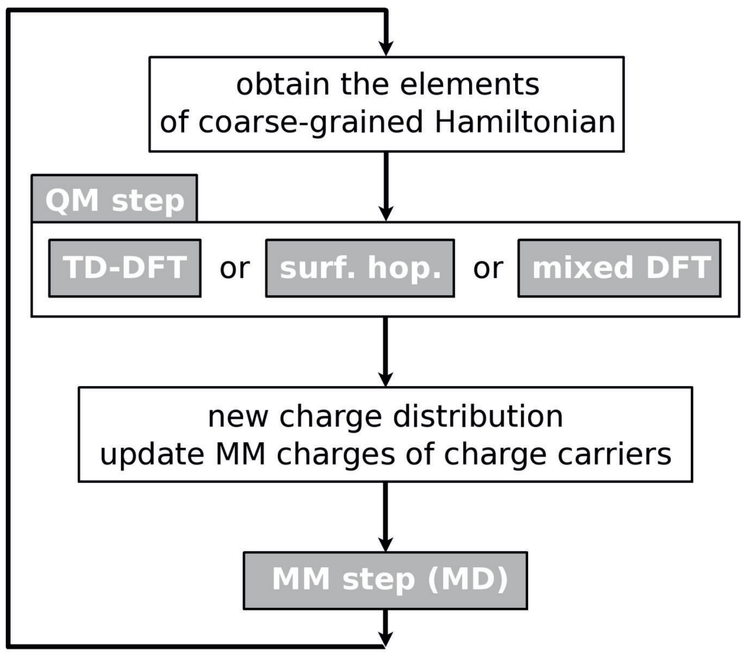
Mantz et al. 2007, JPCA 111, 105-112.

Interaction of charge with environment

Hamiltonian evaluated with QM/MM
– environment involved as point charges
E_1 contains the contribution "$\Delta E_{QM/MM}$"



Multi-scale simulation scheme



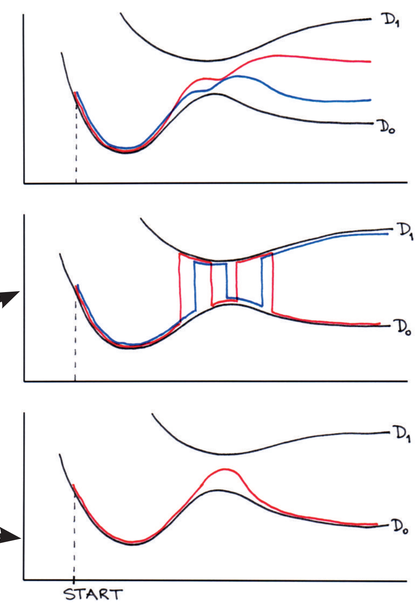
i) Classical MD simulation describes the entire molecular system
ii) Quantum chemistry » coarse-grained Hamiltonian
iii) Propagation of excess charge with this Hamiltonian

Propagation – various non-adiabatic schemes:

TD-DFT based – Ehrenfest dynamics:
numerical solution of time-dep. Schrödinger eqn.

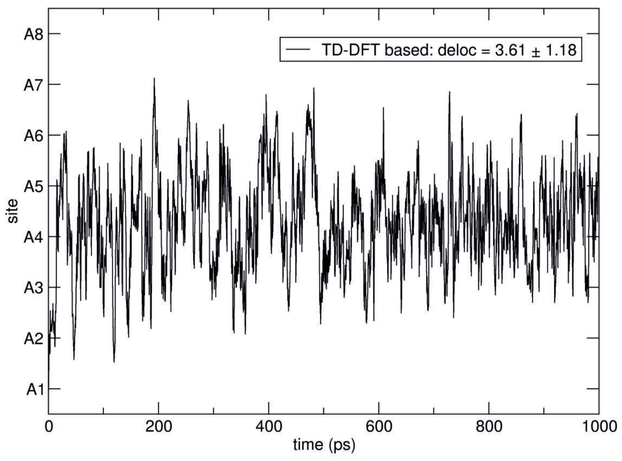
Surface hopping:
SCF procedure with diagonalization of Hamiltonian
+ simple diabatic surface hopping

Mixed DFT:
SCF procedure with diagonalization of Hamiltonian
+ mixing of eigenstates with Fermi–Dirac distrib.

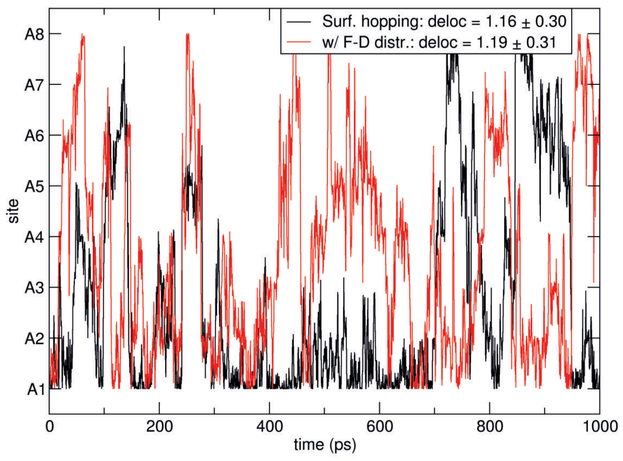


Application – hole transfer in poly(A) DNA

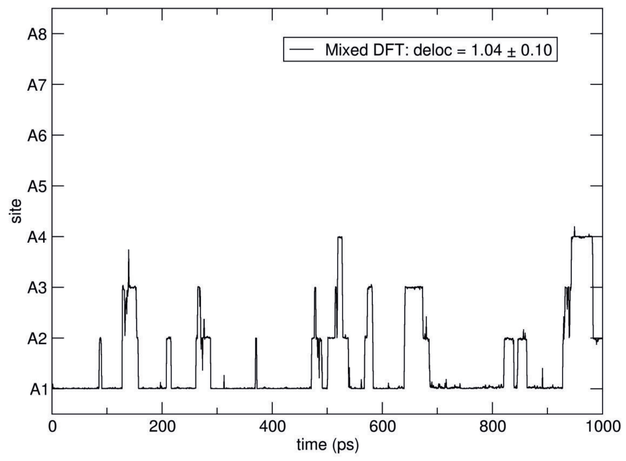
TD-DFT based simulation
Strongly delocalized hole is flowing along the strand



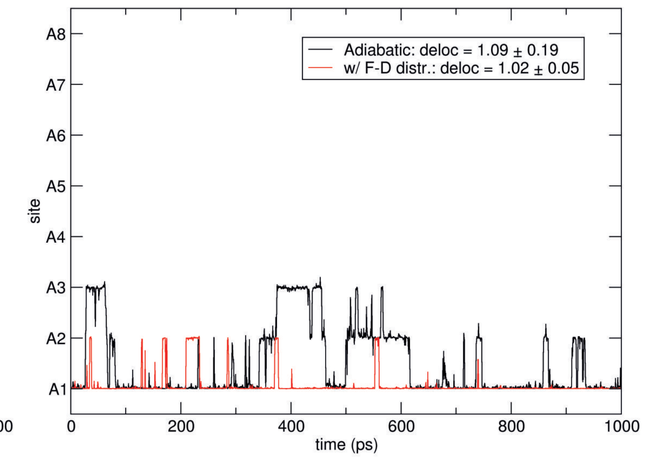
Surface hopping
Spatially confined hole is transferring along the strand



Mixing of states w/ F-D distro
Even more confined hole is transfering more slowly



"Standard" adiabatic QM/MM
Confined hole, slow xfer
Difficult convergence!



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