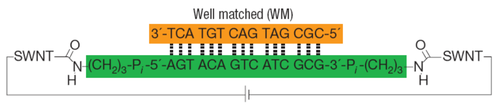
Electronic Properties of DNA-CNT molecular junctions

M. Lee , S. Avdoshenko, R. Gutierrez, and G. Cuniberti

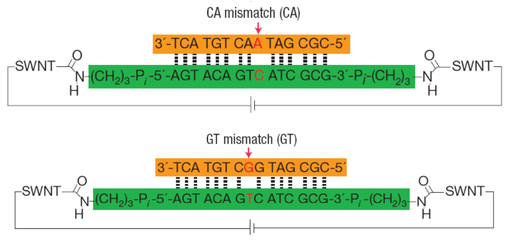
Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, D-01062 Dresden, Germany.

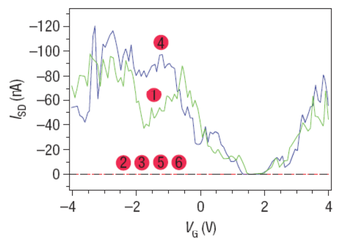
Motivation:

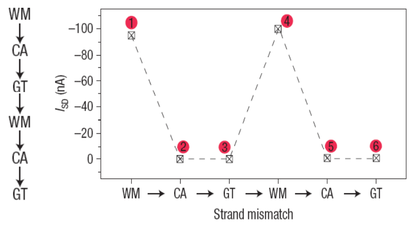
- Electrical detection of point mutations in DNA possible?
- Develop effective approach to combine dynamics and transport



Conductivity of a single DNA duplex bridging a carbon nanotube gap
X. Guo *et al. Nat. Nanotech.* ***3***, 163 (2008)



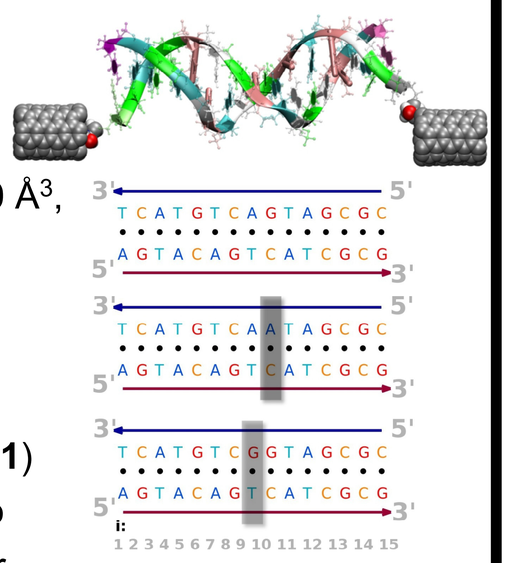




Simulation strategy: Molecular dynamics (MD) coupled to electronic structure calculations

MD simulation set-up:

- AMBER10 package, NVT thermostat, 0.5 fs time step
- AMBER99 force field used for the sp^2 carbon atoms of the CNT
- 70,000 atoms, TIP3P water box 70×70×120 Å^3, 28 Na+ ions neutralize the simulation box.



Snapshot of the CNT-DNA system (upper panel), the well-matched sequence and the sequences with mismatches

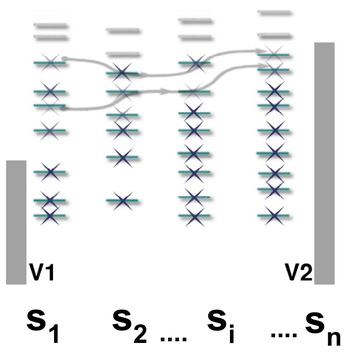
Electronic structure calculation*:*

- Use QM/MM approach in **Amber10** package
- QM method: semi-empirical Hamiltonian (**AM1**)
- Fragment molecular orbital method is used to obtain effective on-site energies $\varepsilon_i(t)$ and inter-fragment transfer integrals $T_{ij}(t)$ along the MD trajectory

Fragment Molecular Orbitals (FMO) technique[1]

- **H(A^0 B^0):** Fock matrix for isolated fragments (nucleotides pairs) **A^0** and **B^0**
- **H(AB):** Fock matrix for fragments **AB** embedded in the simulation box

Optimal transport pathway (relevant molecular orbital subspace)



- Mapping onto effective Hamiltonian (linear chain) with time-dependent parameters

$$H_t = \sum_i \varepsilon_i(t) c_i^+ c_i + \sum_{i,j} T'_{ij}(t) c_i^+ c_j$$

$$\varepsilon_i(t) = \left\langle \Phi_i^{MO}(t) | H | \Phi_i^{MO}(t) \right\rangle \qquad T_{ij}(t) = \left\langle \Phi_{A^i}^{MO}(t) | H_{A^i B^j}(t) | \Phi_{B^j}^{MO}(t) \right\rangle$$

$$\Phi_i^{MO}(t) = \sum C_i^{\mu}(t) \varphi_{\mu}^{AO} \qquad T'_{ij}(t) = S_{AO}^{-1/2} T_{ij}(t) S_{AO}^{1/2}$$

Transport properties:

- Time-dependent transmission function *T(E,t)*

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

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

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

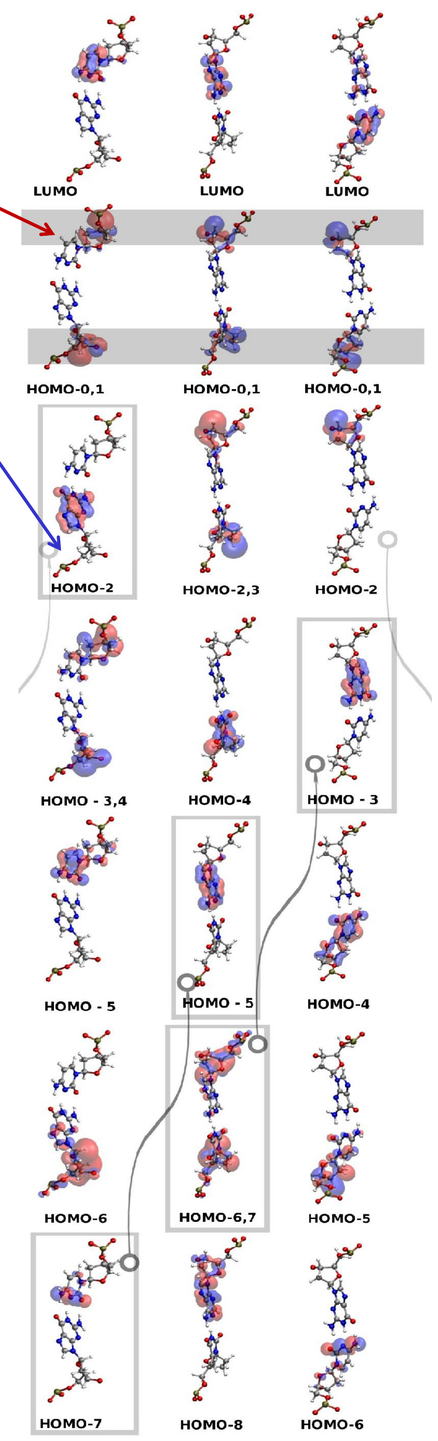
Time-averaged transmission

$$T(E) = \frac{1}{t_{MD}} \sum_i T(E, t = t_i)$$

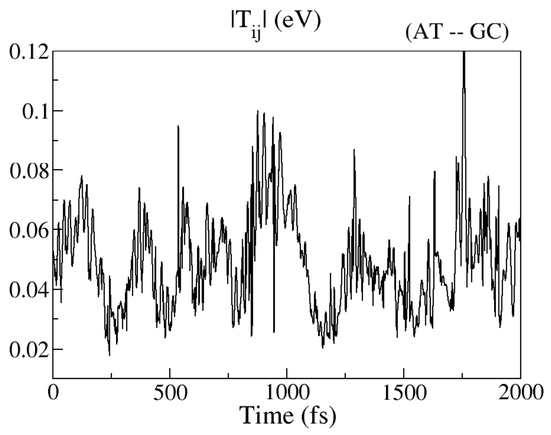
Results: DNA coupled to CNT electrodes

Time-dependent e-structure and orbitals

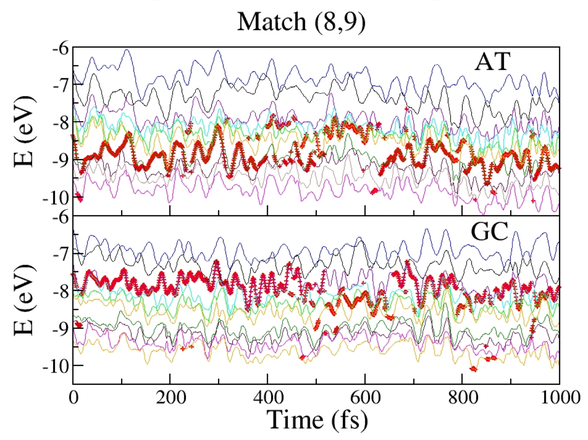
HOMO, HOMO-1 orbitals are mainly **localized on backbones, hopping** very small (~1 meV) → relevant orbitals for hole transport **below the HOMO level**



Effective hopping integral T_{ij} between the AT- and GC fragments

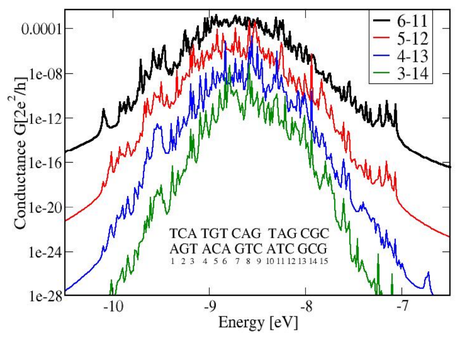


Effective onsite energy ε_i time series at site 8 (AT base pair) and 9 (GC base pair) for the interval [HOMO,HOMO-10]

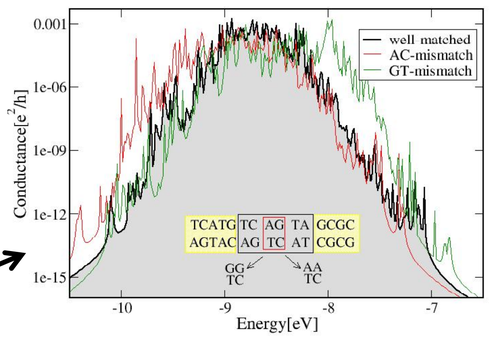


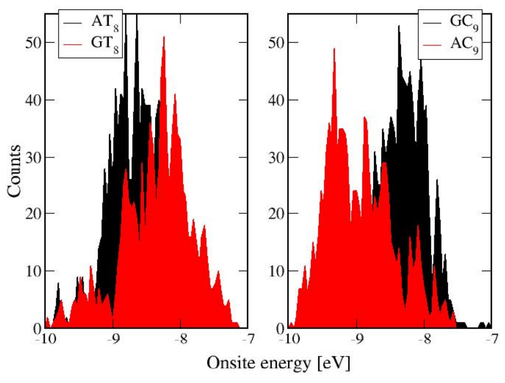
Results: Charge transport

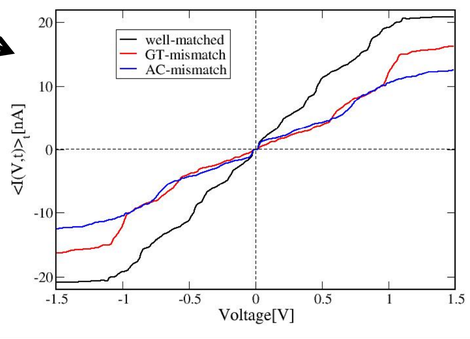
Conductance calculations with an increasing number of sites around the base pair region where mismatches are introduced



Histograms drawn from the time series showing the energy shifts due to introducing a mismatch **AT→GT** at chain site 8 resp. **GC→AC** at chain site 9

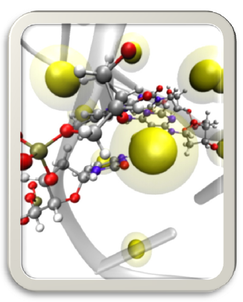






References:

1. Kitaura & Morokuma, J.Quantum Chem.**10**,325 (1976); T. Kubar, et al., J. Phys. Chem. B **112**, 7937 (2008**)**
2. P. B. Woiczikowski, T. Kubar, R. Gutierrez, R. A. Caetano, G. Cuniberti, and M. Elstner, J. Chem. Phys. **130,** 215104 (2009)
3. R. Gutierrez, R. A. Caetano, B. P. Woiczikowski, T. Kubar, M. Elstner, and G. Cuniberti, Phys. Rev. Lett. **102**, 208102 (2009)



Conclusions and Outlook

- Dynamical fluctuations included in efficient computational scheme
- Mapping of complex electronic structure onto effective model
- Differences between matched and mismatched sequences less dramatic than in experiment → improve e-structure methodology
- **Open**: Decoherence effects should be included (real-time charge propagation or coupling to dissipative environments)