Calculation of inter-molecular transition rates depending on structural parameters with DFTB

Fabian Teichert[1], Robin Silligmann[1], Florian Günther[2,3], Angela Thränhardt[1]

[1] Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany
[2] Departamento de Física, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista "Júlio de Mesquita Filho", Rio Claro, Brazil
[3] Instituto de Física de São Carlos, Universidade de São Paulo (USP), São Carlos, Brazil

**TECHNISCHE UNIVERSITÄT CHEMNITZ**

Motivation

- Organic semiconductors: new materials with interesting properties, many possibilities for improvements
- Example application: Organic solar cells – elastic, flexible, light, efficient to produce, cheap, adjustable electrical properties over a wide range
- Simulation of electronic properties: charge transport between organic molecules
- Quantum mechanical calculation of transfer rates → Basis for consecutive Monte-Carlo simulation of hopping processes
- Determination of the influence of geometric disorder → statistically averaged transfer rate
- System of interest: zinc porphyrine [1] as donor material
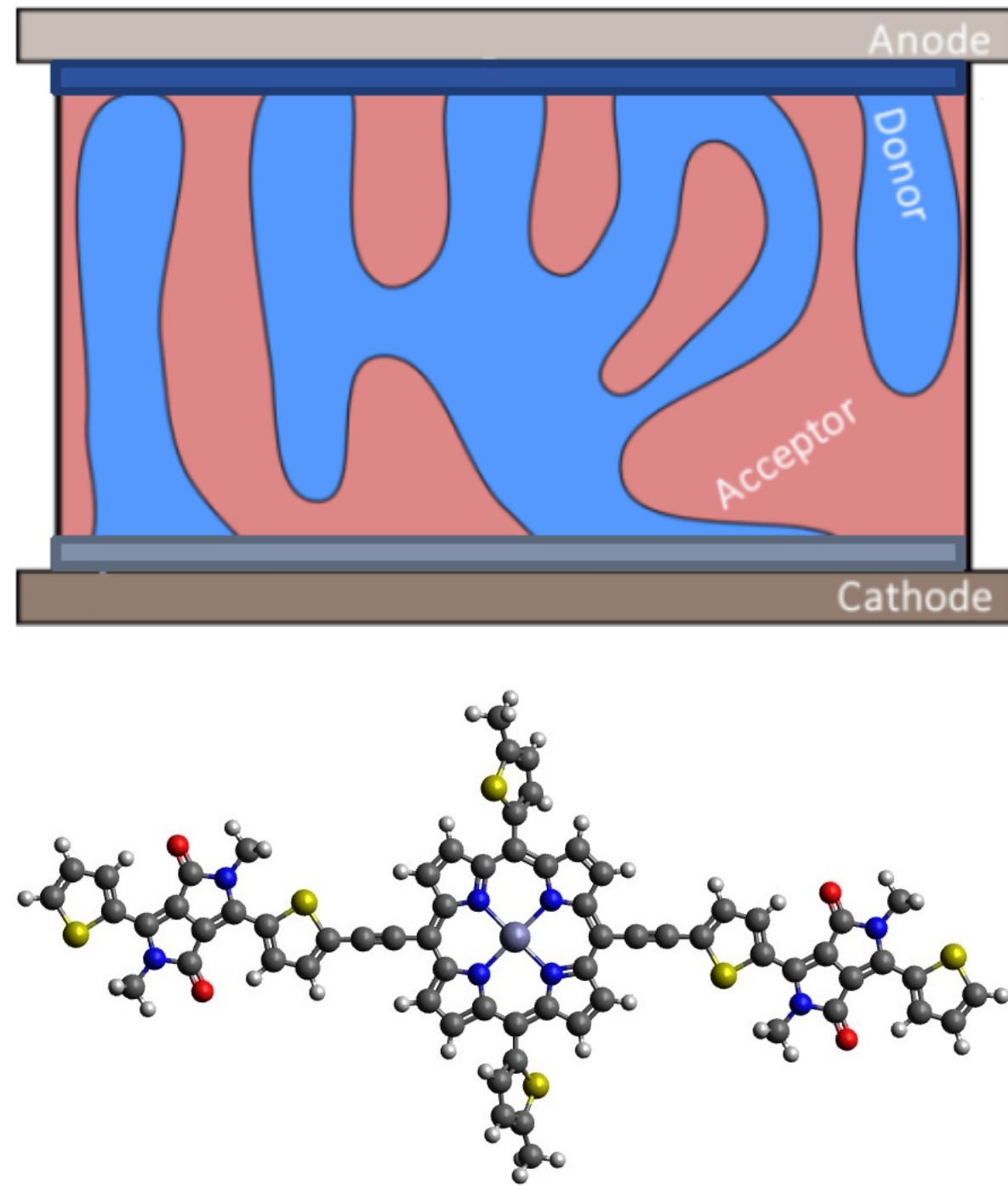
Theoretical background

Marcus transfer theory:
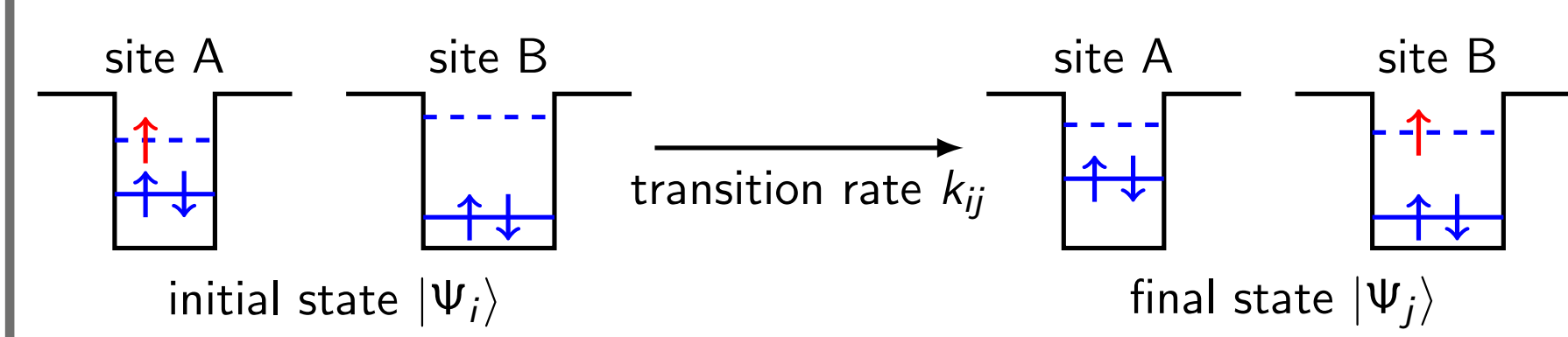
$$k_{ij} = \frac{|H_{ij}|}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta E - \lambda)^2}{4\lambda k_B T}\right)$$
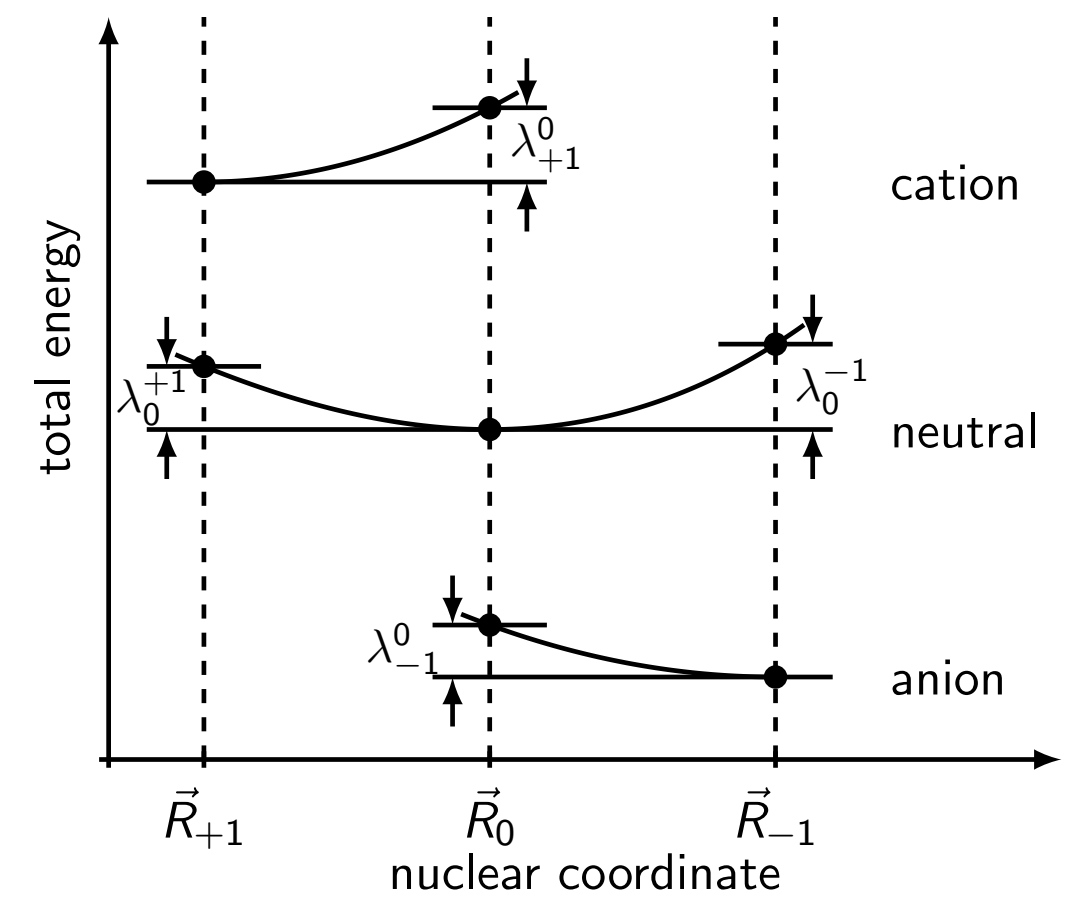
ΔE ... energy difference between two states
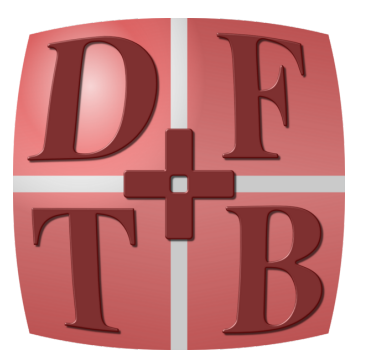λ ... reorganisation energy
$|H_{AB}| = \langle \varphi^A | H_{AB} | \varphi^B \rangle$ ... Hamiltonian coupling element

Density-functional-based tight binding (DFTB):

$$\hat{H}|\varphi_i^\alpha\rangle = \epsilon |\varphi_i^\alpha\rangle \quad \text{with} \quad H_{ij} = \begin{cases} \epsilon^{\text{atom}}: & i = j \\ \langle \varphi_i^\beta | \hat{T} + V^\alpha[n^\alpha + n^\beta] | \varphi_i^\alpha \rangle : & \alpha \neq \beta \\ 0: & \text{otherwise} \end{cases}$$

Software: dftb+, skprogs [2]

DFTB parameter sets

- Parameters available, but not suitable for the evaluation of coupling element and for van-der-Waals-bonded systems → new parameters neccessary
- Standard: compressed basis set for faster convergence:
$$\left[\hat{T} + \hat{V} + \left(\frac{r}{r_0}\right)^n\right]|\varphi_i^\alpha\rangle = \tilde{\epsilon}|\varphi_i^\alpha\rangle$$
- Underestimation of Hamiltonian and overlap matrix elements by up to 2 orders of magnitude
- Non-compressed parameters for $|H_{AB}|$ needed
- Electronic parameters created using skprogs
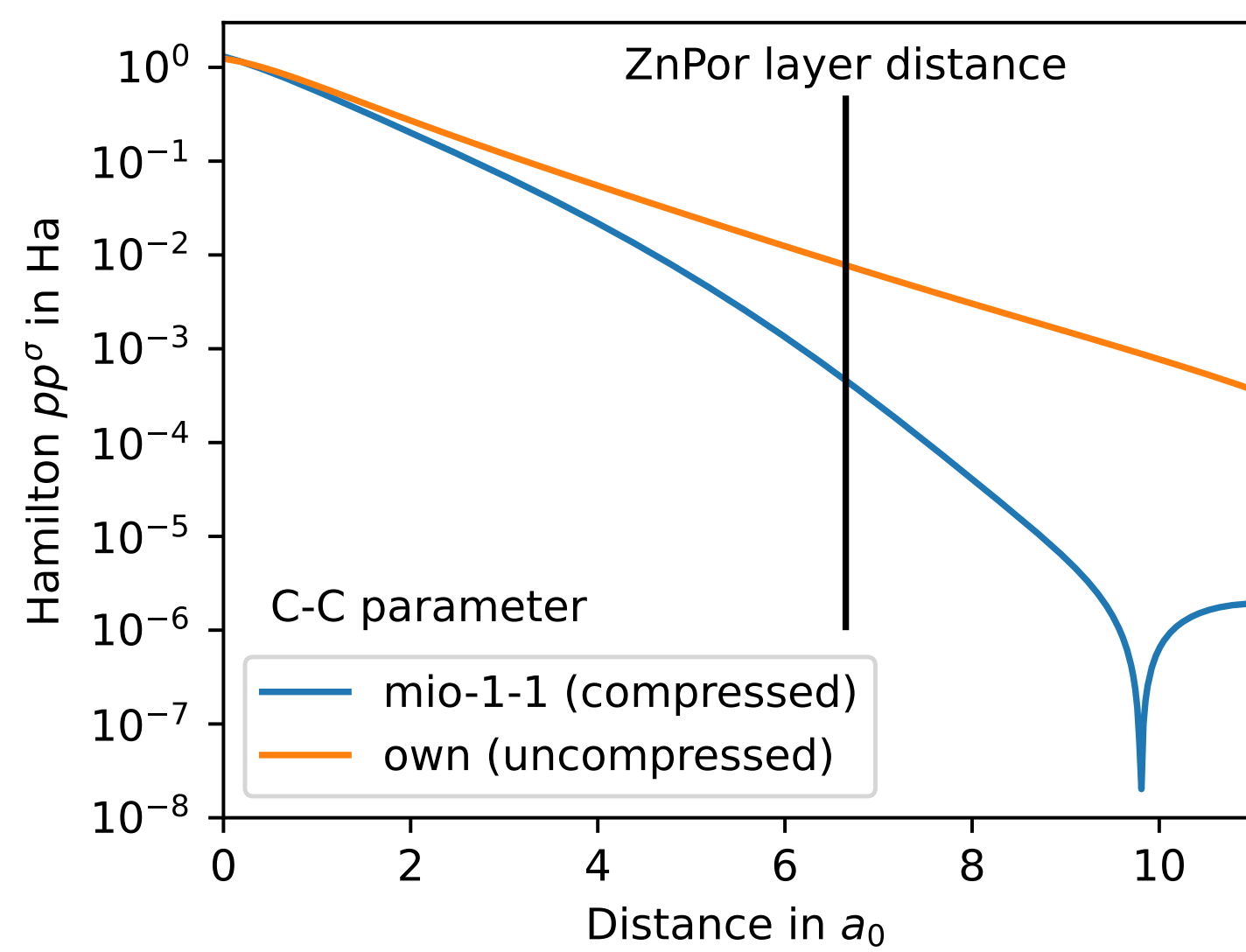
Validation of coupling element

- Test system: Two pi-stacked thiophenes
- Thiophene molecules rotated/shifted
- Correct qualitative trends
- Slightly smaller values (factor 0.8)
- HOMO: anti-symmetric → 0 at 90°
- LUMO: symmetric → maximum at 90°
- Reference data: DFT + PBE + TZDP [3]
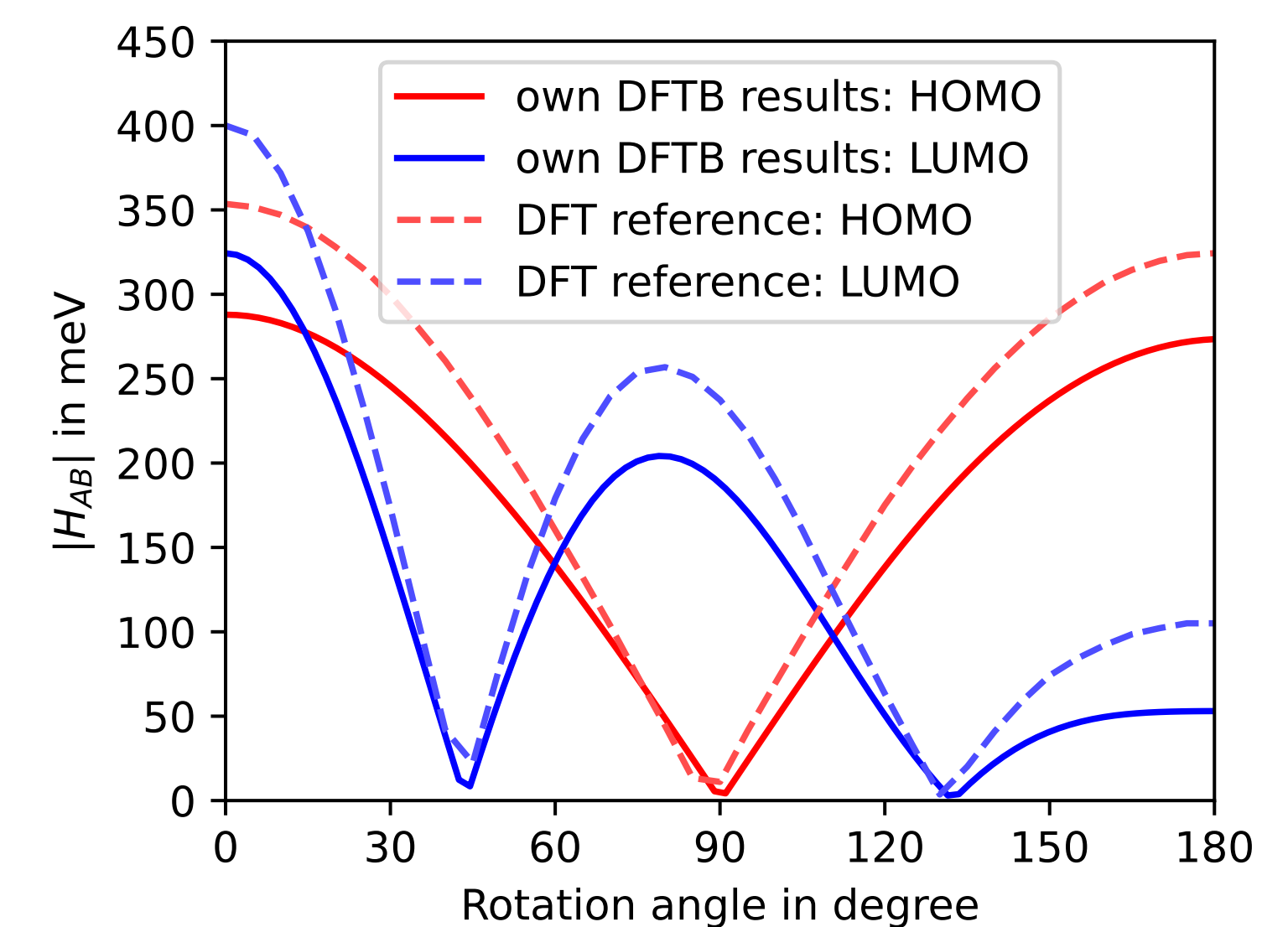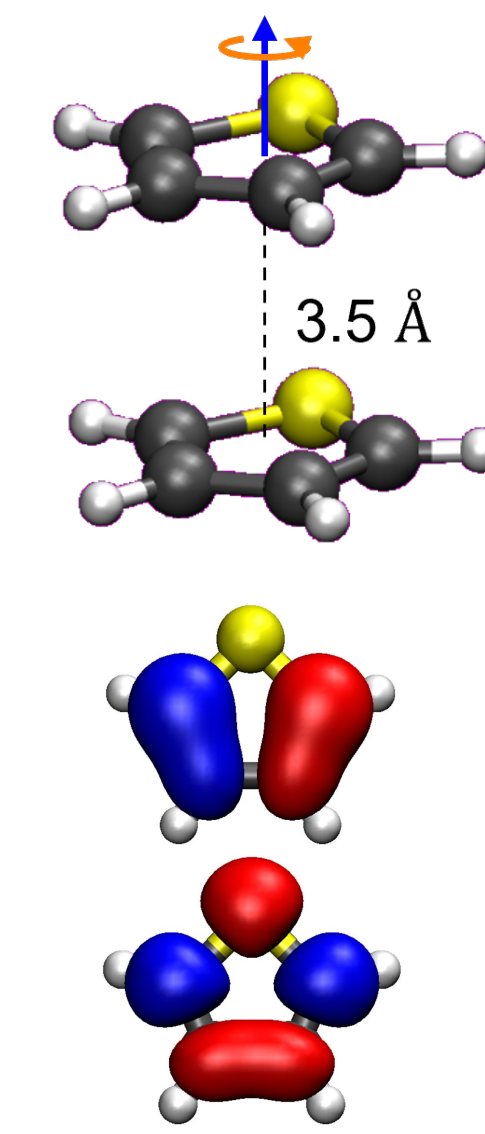
Zinc porphyrine: reorganisation energy

- Internal degrees of freedom of planar configuration:
  A ... Rotation of outer thiophene rings (1 & 2)
  B ... Rotation of inner thiophene rings (3 & 4)
  C ... Rotation of whole lateral side group (5 & 6)
 D ... Rotation of lateral side thiophene rings (7)
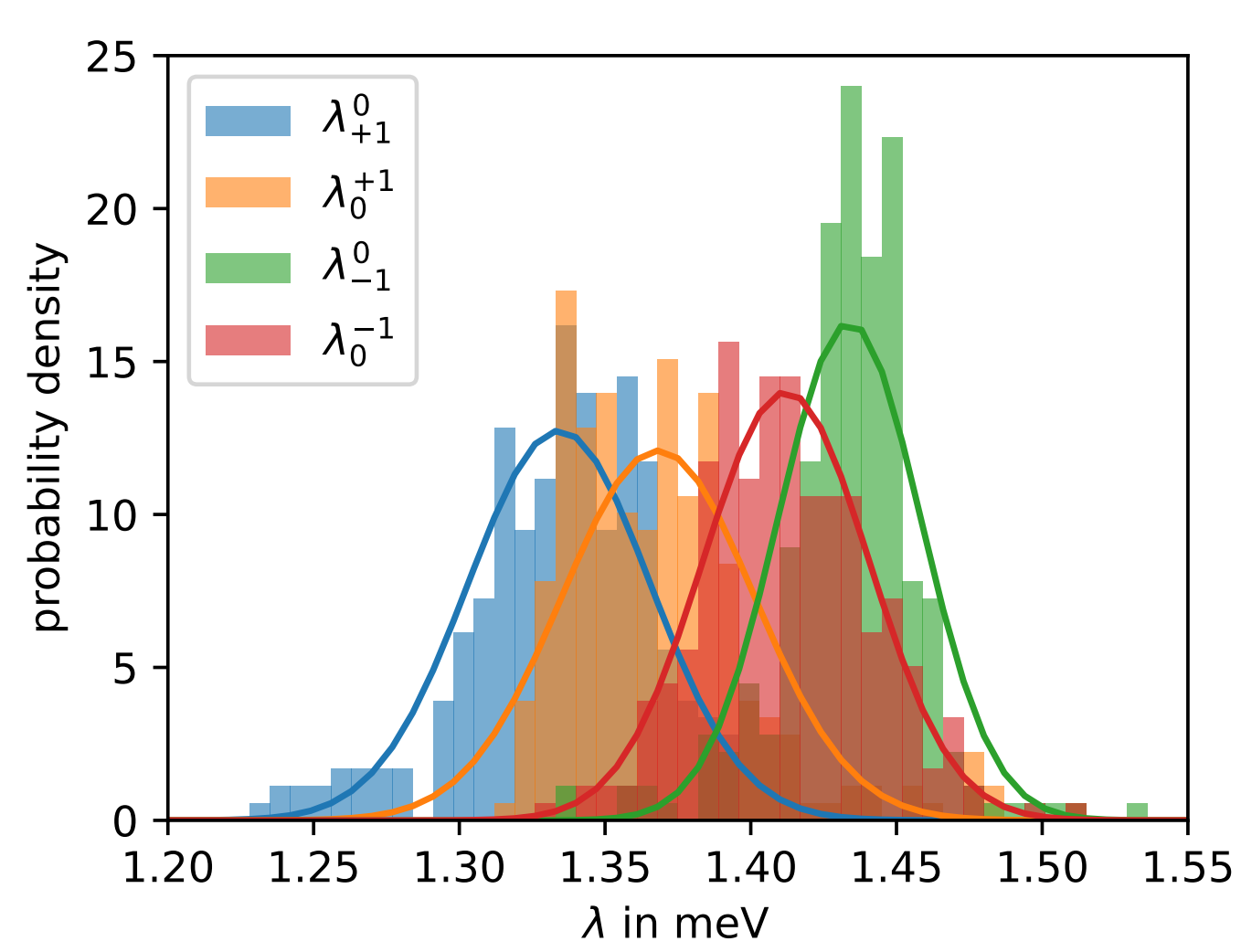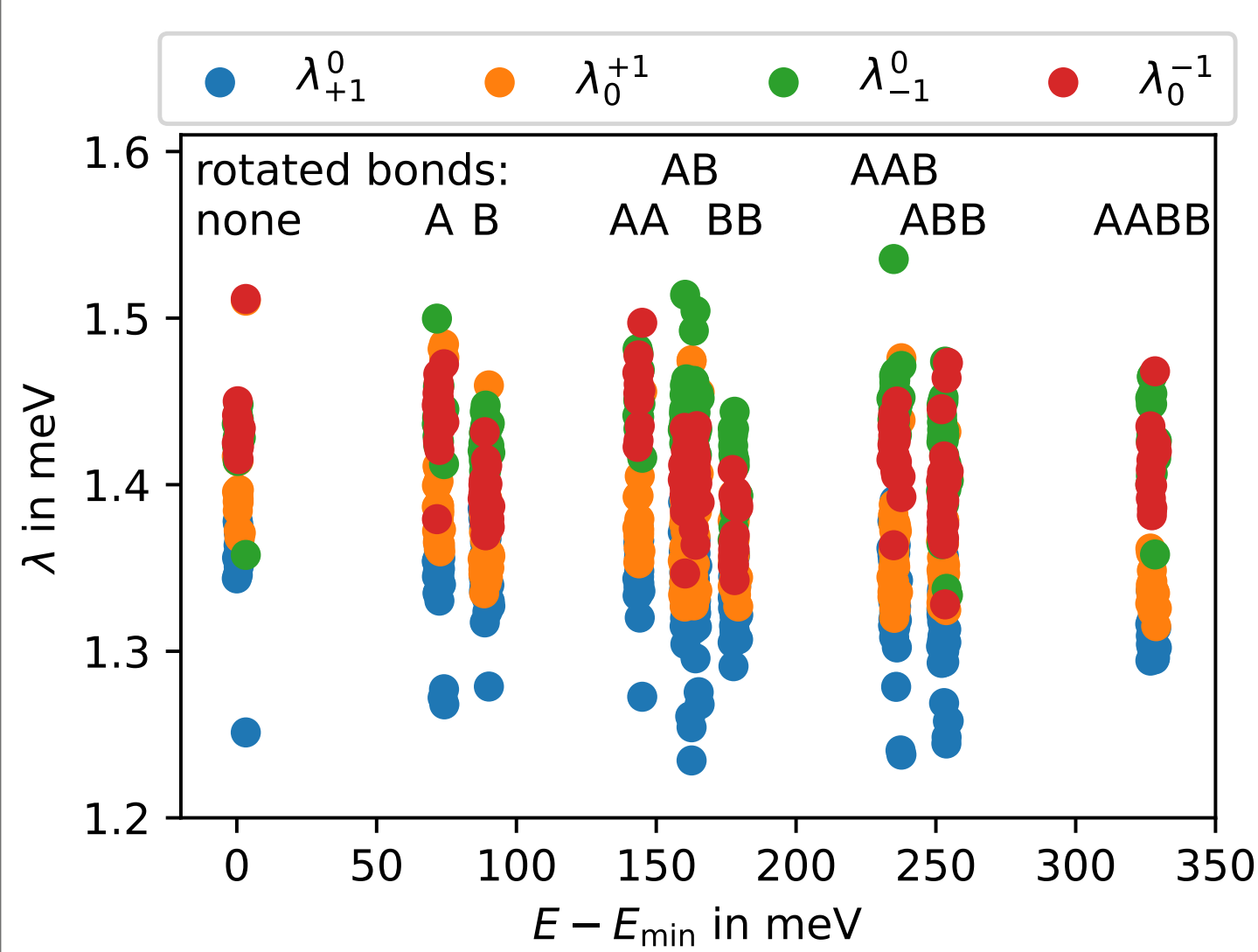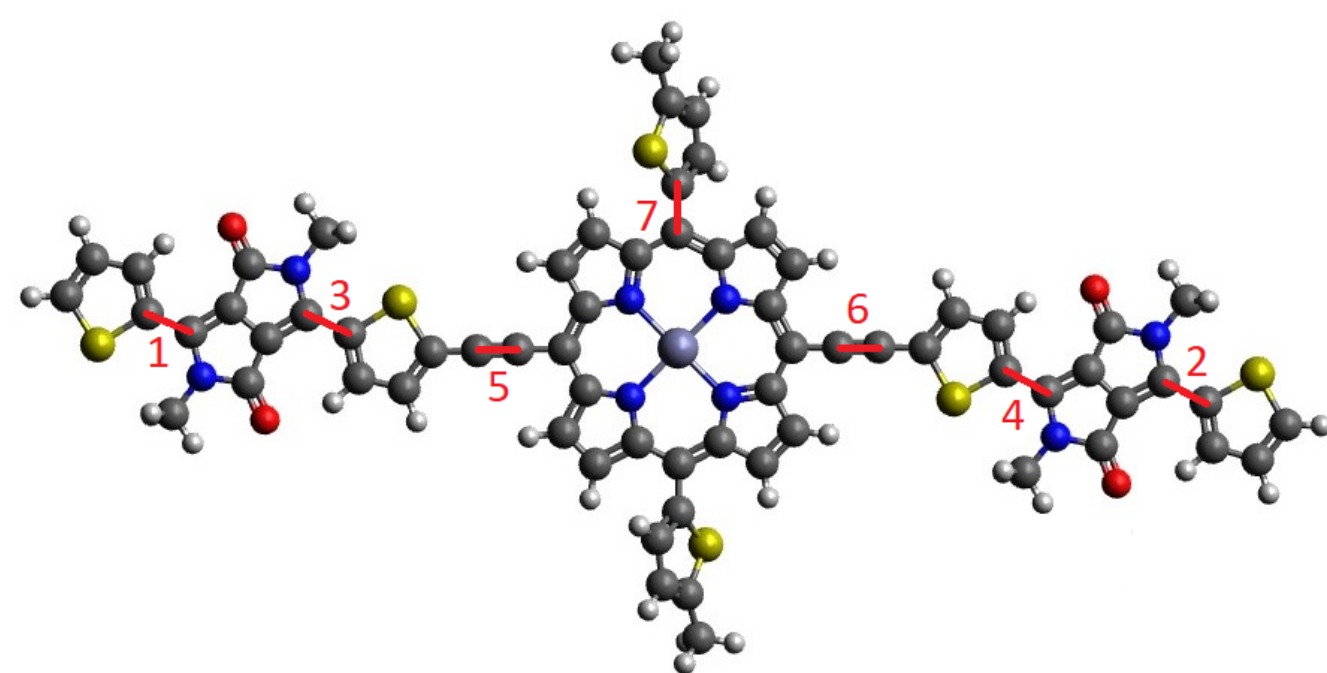
- Minimum energy if all sulfur away from oxygen
- ~ 80 meV higher energy for each rotated thiophene
- Sub sets: rotation of outer (71 meV) vs. inner thiophene (88 meV)
- Rotation C & D (5-7): no influence on total energy, but on reorganisation energy
- Very tiny reorganisation energy due to strong delocalization of additionl charge: $\lambda = (1.2 \dots 1.5)$ meV
- Reorganisation energy for hole transport higher than for electron transport

Zinc porphyrine: Hamiltonian coupling element

- Two stacked zinc porphyrine molecules
- Additional geometric degrees of freedom, so far obtained for most stable configurations:
  - In-plane shift in two directions
  - In-plane rotation
  - Out-off plane tilt
- Most stable binding positions at ±5 Å y shift
- Min 1: Porphyrine 6-rings above each other, strong pi-pi interaction between thiophene rings
- Min 2: Zn above acetylene group (C-C triple bond), pos./neg. partial charges stacked, small interaction between thiophene rings
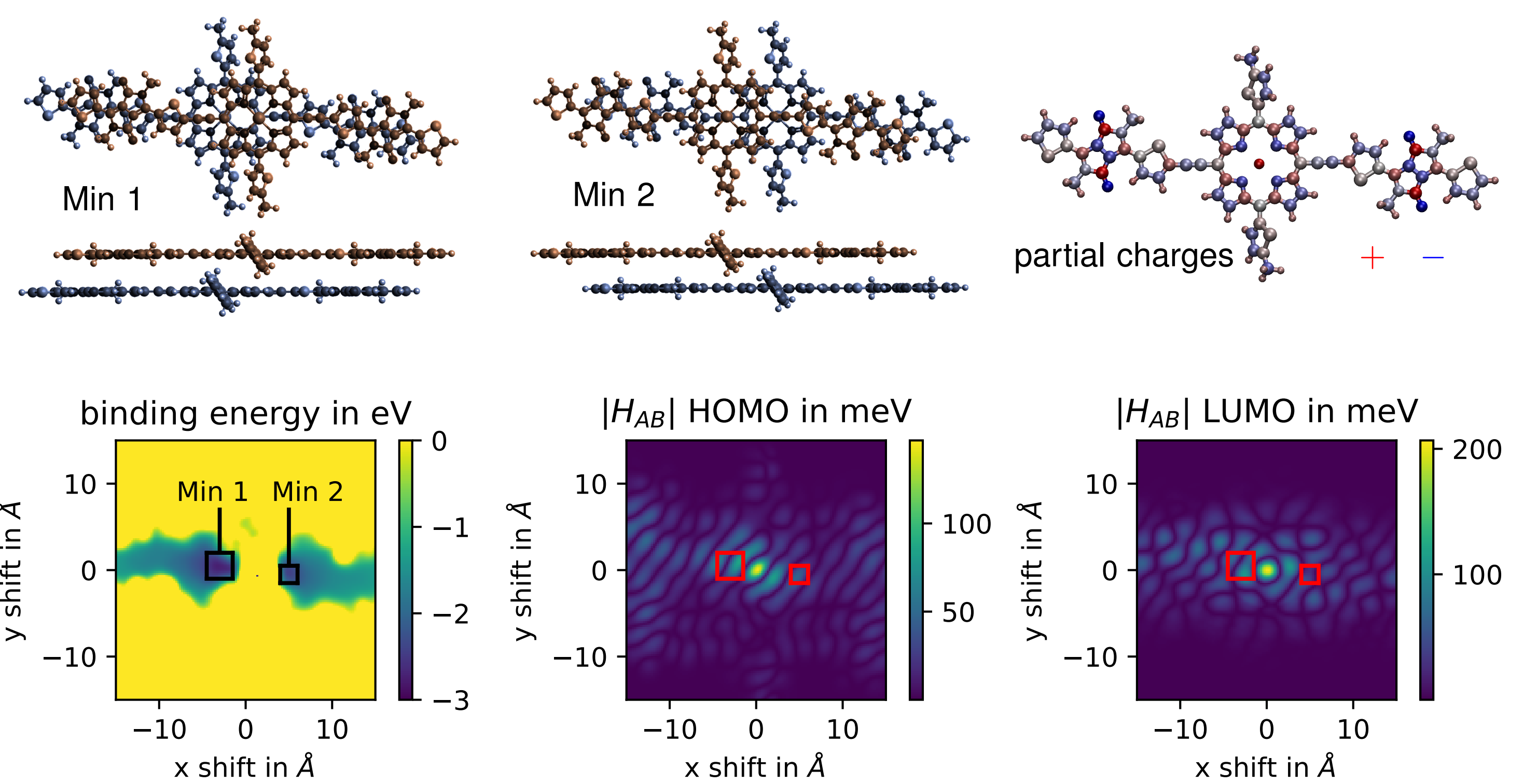
- Very strong fluctuations of Hamiltonian coupling elements
- Reason: antisymmetric nodes in HOMO/LUMO states overlap with symmetric regions → $|H_{AB}| = 0$ → many points with vanishing resp. very tiny $|H_{AB}|$
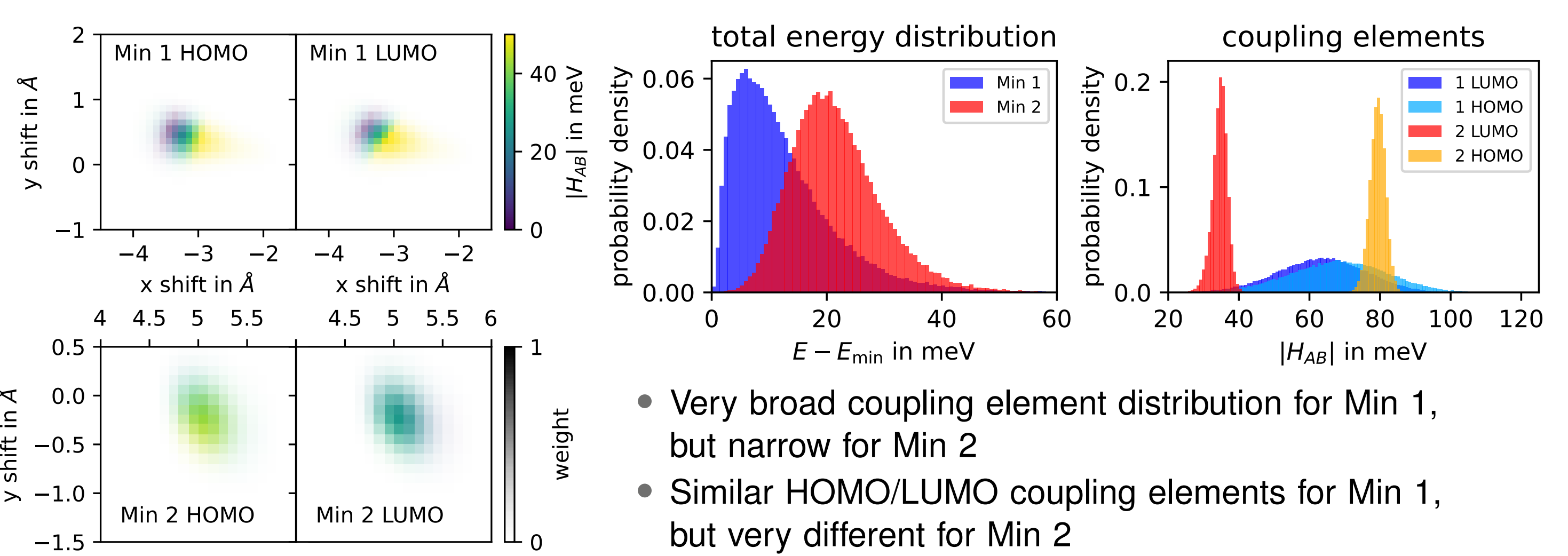
- Very broad coupling element distribution for Min 1, but narrow for Min 2
- Similar HOMO/LUMO coupling elements for Min 1, but very different for Min 2

Conclusion

- Reorganisation energy for hole transport higher than for electron transport
- Very strong fluctuations of Hamiltonian coupling elements
- Mean geometry not sufficient → statistical analyis necessary

References

[1] J. Am. Chem. Soc. 137, 7282–7285 (2015)
[2] J. Chem. Phys. 152, 124101 (2020)
[3] F. Günther: "Theoretical Studies of Structural and Electronic Properties of Donor-Acceptor Polymers" (2018)

IFSC UNIVERSITY OF SÃO PAULO — São Carlos Institute of Physics

www.tu-chemnitz.de/physik
www.tu-chemnitz.de/physik/TPSM
www.ifsc.usp.br

fabian.teichert@physik.tu-chemnitz.de
florian.gunther@unesp.br