# Analysis of Excited-State Computations: Turning Numbers into Chemical Insight

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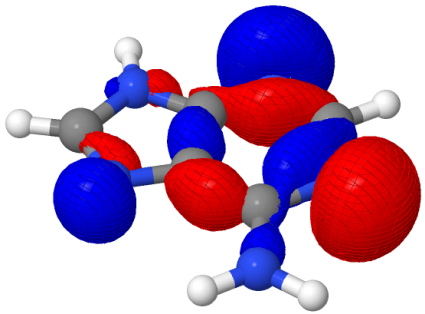
# Introduction

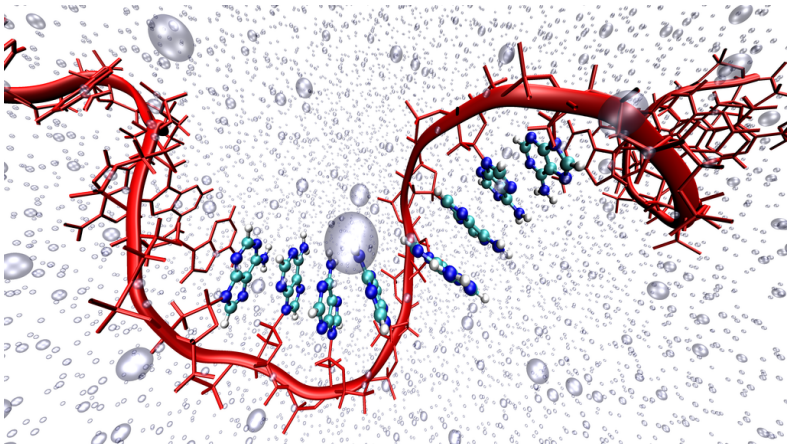
## Computational Photochemistry

- Accurate numbers
- ☺ *Quantum chemical methods*:
  Semi-emp., TDDFT, CC, ADC, CASSCF, DMRG, CASPT2, MR-CI, ...
- ☺ *Environmental models*: QM/MM, PCM, density embedding, ...
- ☺ *Algorithmic efforts*: Linear scaling, density fitting, parallelization, GPUs, ...
- Comparison to experiment
- ☺ *Linear and non-linear optical properties*
- Chemical insight

☹ **Look at the HOMO and LUMO**



# DNA

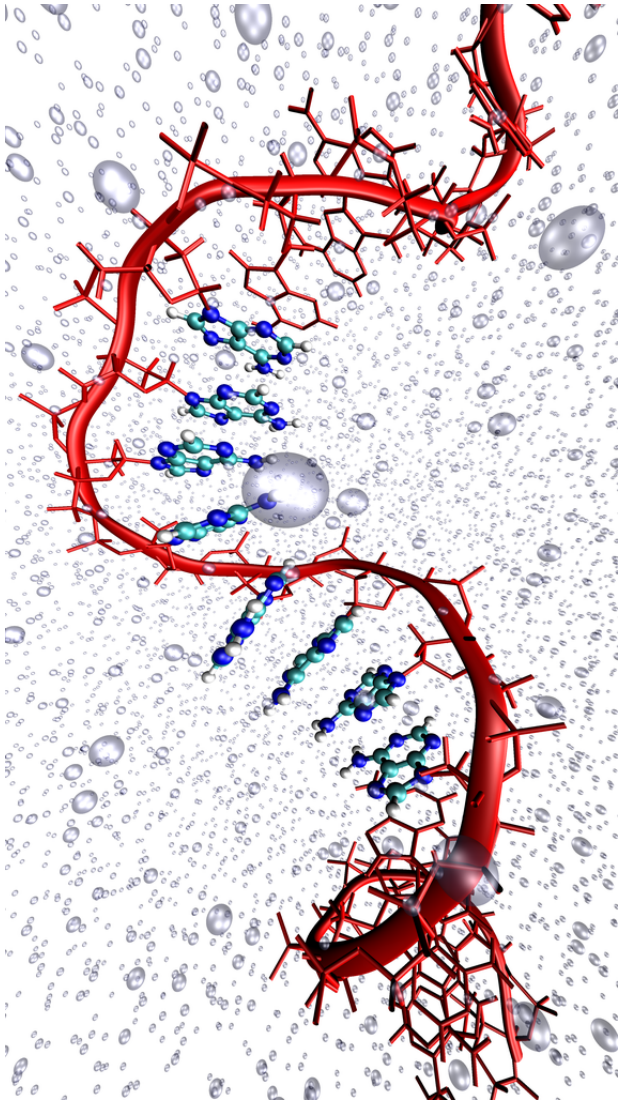


# Conjugated Polymers

# DNA

**Photophysics** of DNA

- ? How is UV light absorbed by interacting nucleobases
  - Localized excitations
  - Collective excitations
- → Excitons
  - Charge transfer states

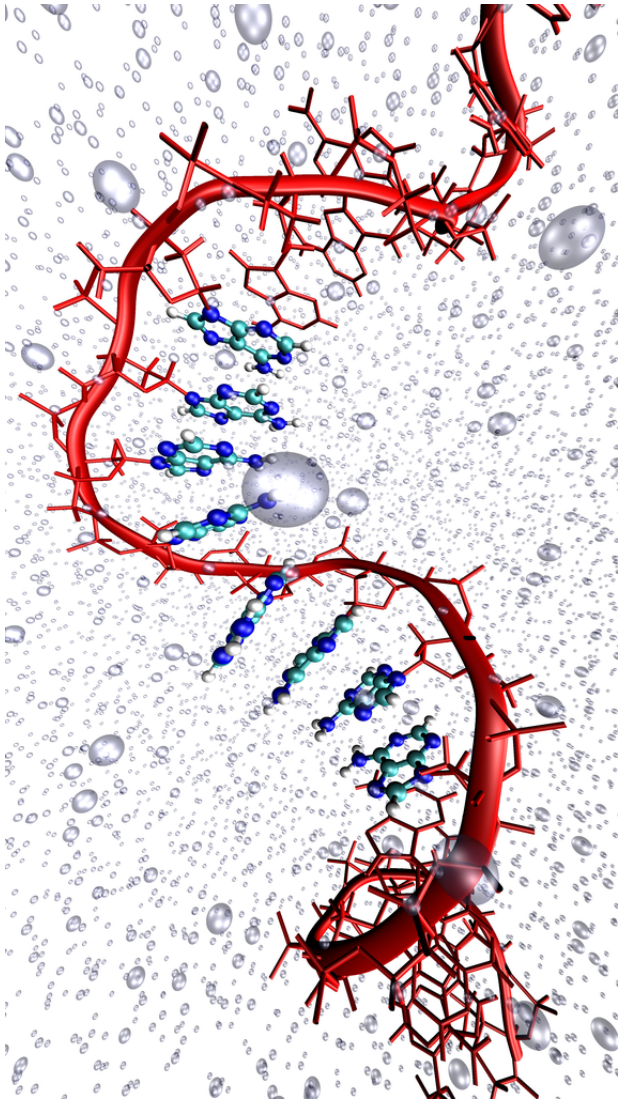


# DNA

## Polyadenine (single stranded)

- QM/MM calculation
  - 8 nuclebases in the QM region
- CAM-B3LYP/SV(P) excitation energies
  - GPU-based `Terachem` code
- **100** MD snapshots $\times$ **60** excited states

☹ How do we analyze **6000** excited states?



[1] J. J. Nogueira, FP, L. González *Chem. Sci.* **2017**, 8, 5682.

# DNA

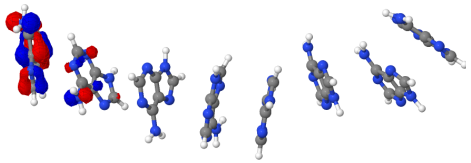
## Leading configurations

- $S_1$ state
  - H-2 → L+1 (-0.70)
  - H-2 → L (-0.47)
  - H-2 → L+10 (0.29)
- $S_2$ state
  - H-2 → L+10 (-0.45)
  - H-2 → L+1 (-0.40)
  - H-2 → L+2 (0.35)

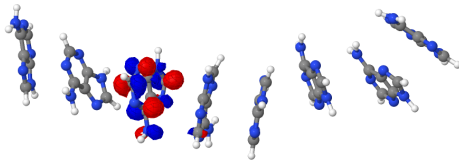
☹ Tedious **work**

☹ Possible **ambiguities**

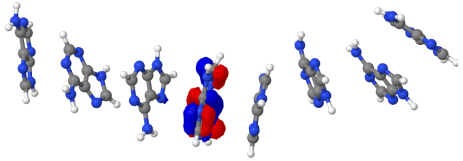
## Canonical orbitals



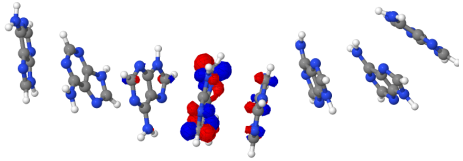
HOMO



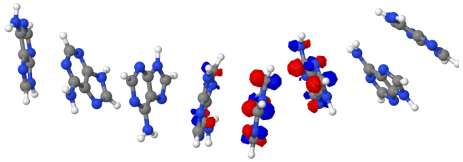
L (LUMO)



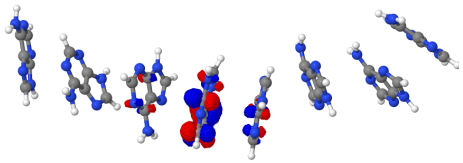
H-2



L+1



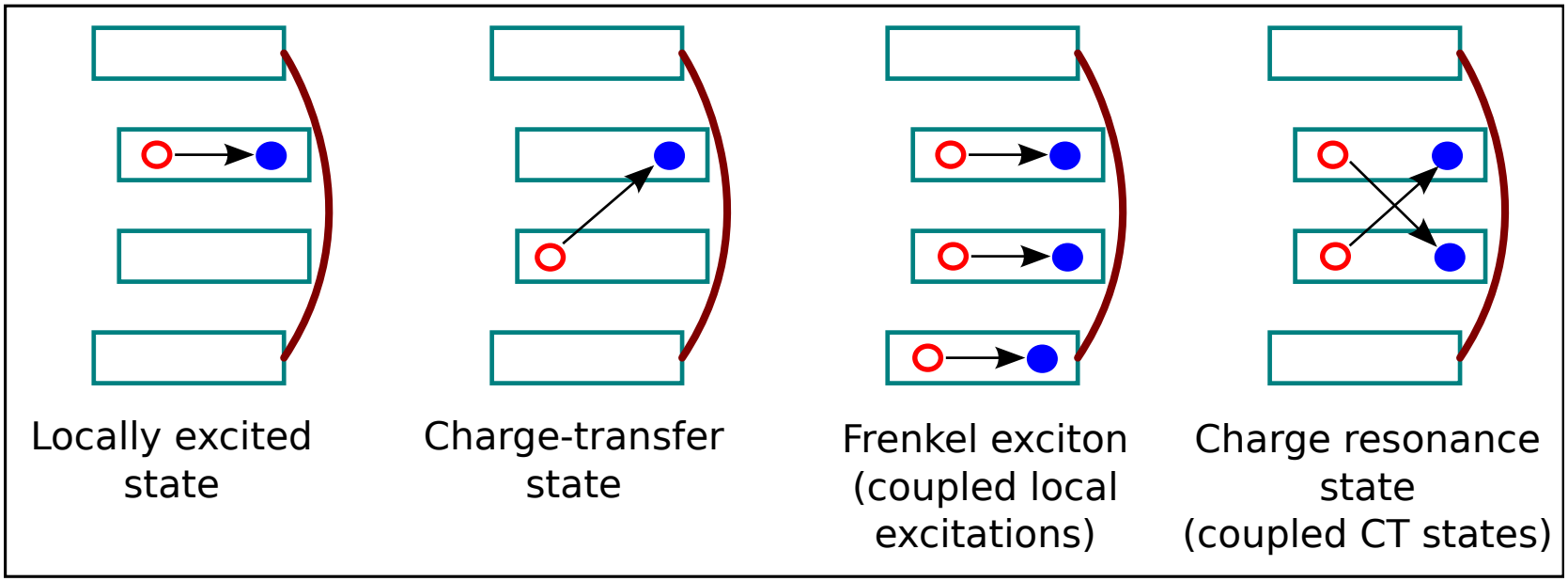
L+2



L+10

# DNA

- Excited states in multichromophoric systems




- Where the excitation comes from - "hole"
- Where the excitation goes to - "electron"

- Connection between **electron** and **hole** decisive

! *2-dimensional* picture

# Quantitative Description

## Transition density matrix (1TDM)

$$D^{0I}_{\mu\nu} = \langle \Psi_0 | \hat{a}^\dagger_\mu \hat{a}_\nu | \Psi_I \rangle$$

$\Psi_0, \Psi_I$ Ground and excited state wavefunctions

$\hat{a}^\dagger_\mu, \hat{a}_\nu$ **Creation** and **annihilation** operators

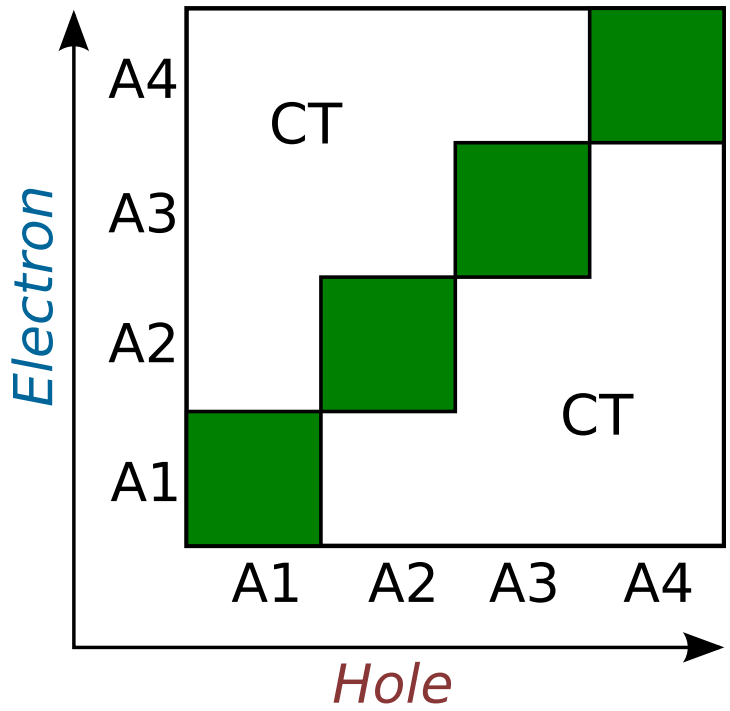
- 2-dimensional population analysis

$\rightarrow$ **Charge transfer numbers** $\Omega_{AB}$

- Consider individual adenine molecules A1, A2, A3, A4, ...

- Locally excited contributions (diagonal)
- CT contributions (off-diagonal)

Transition density matrix

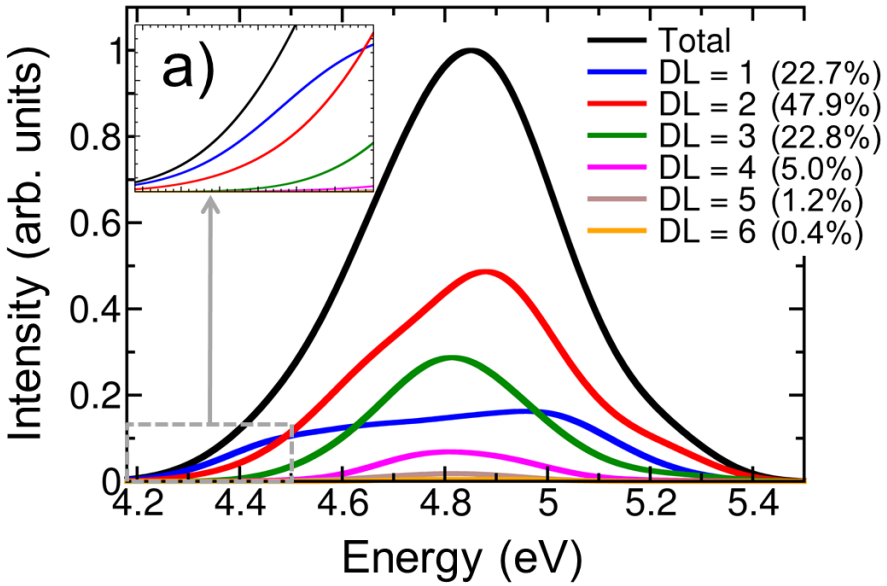


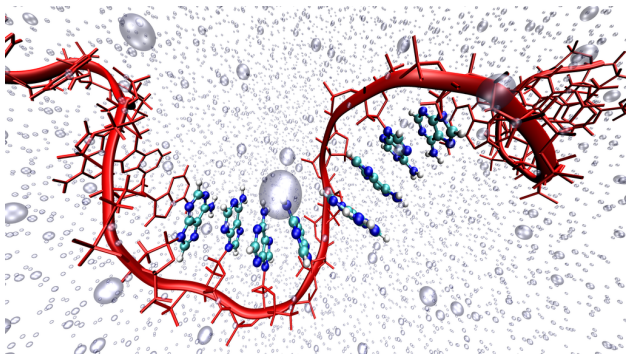

[1] FP, H. Lischka *JCTC* **2012**, 8, 2777.
[2] FP, M. Wormit, A. Dreuw *JCP* **2014**, 141, 024106.

# Polyadenine

**Delocalization length** (DL)

- Decomposition of the spectrum
  - Analysis of 6000 excited states
- Main contribution: DL=2
  - Nearest neighbor interactions
- Additionally: DL=1, DL=3
- No significant contributions $> 4$



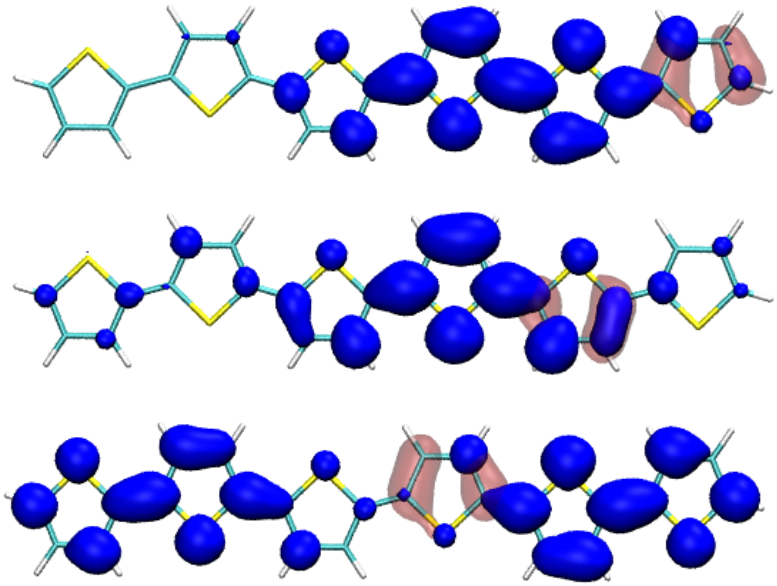



[1] J. J. Nogueira, FP, L. González *Chem. Sci.* **2017**, 8, 5682.

## DNA

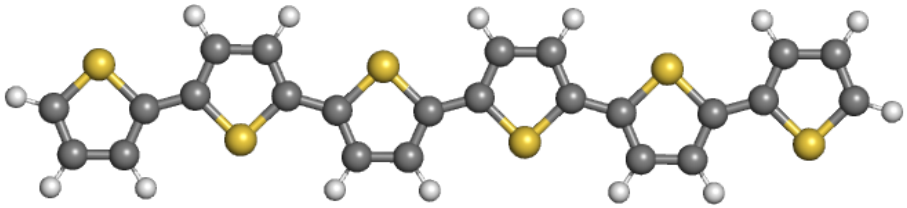


## Conjugated Polymers



# Oligothiophene

- Oligothiophene



  - Prototypical conjugated polymer

- CAM-B3LYP computations

(?) How to analyse the states

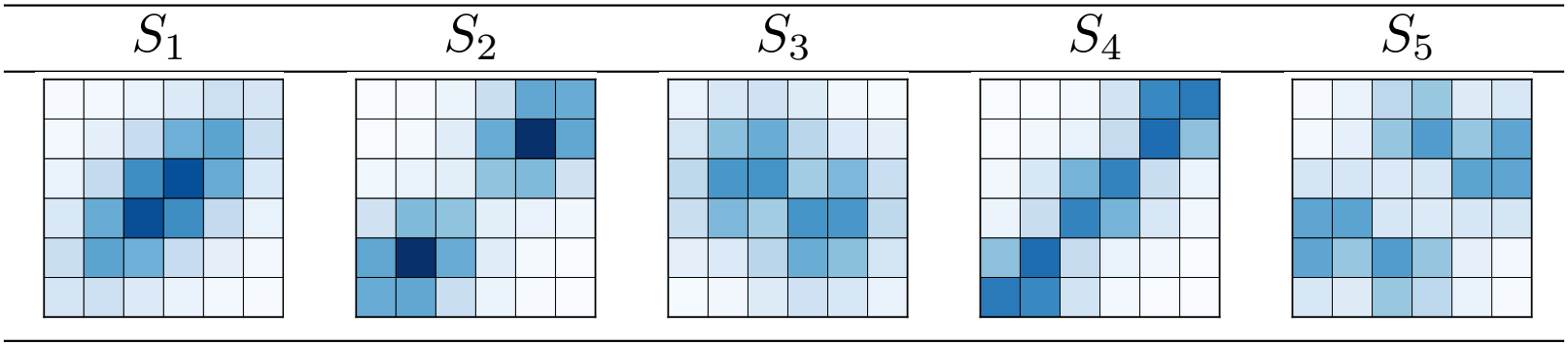
(☹) Just many delocalized $\pi$ and $\pi^*$ orbitals

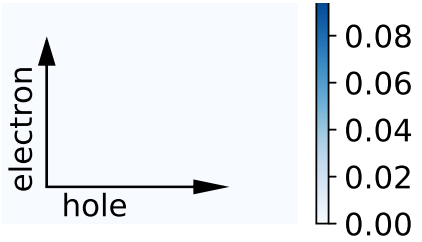
- Plot matrix of CT numbers

→ **Electron-hole correlation plot**

# Oligothiophene

## Electron-hole correlation plots




- ▶ Excitonic structure visible
- \- Different nodal planes
- ? More intuitive visualization

# Conditional densities

## Transition density matrix (real space)

$$\gamma^{0I}(r_h, r_e) = \sum_{\mu\nu} D^{0I}_{\mu\nu} \chi_\mu(r_h) \chi_\nu(r_e)$$

$\gamma^{0I}(r_h, r_e)$ Transition density matrix (real space)

$D^{0I}_{\mu\nu}$ Transition density matrix (matrix representation)

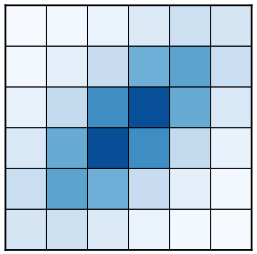
$\chi_\mu$ Atomic orbital

## Conditional density for the excited electron

$$\rho_e^{h:A}(r_e) = \int_A \gamma^{0I}(r_h, r_e)^2 \mathrm{d}r_h$$

$\rho_e^{h:A}(r_e)$ Conditional density for the hole localized on fragment $A$

# Conditional densities



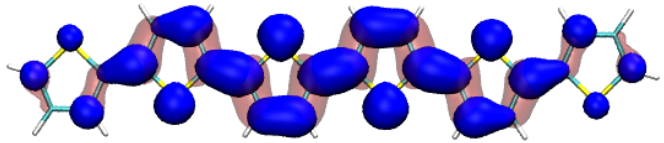
## $S_1$ state

- Overall electron and hole densities **delocalized**
- Conditional electron density **follows** hole

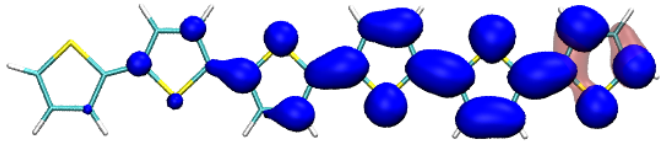
## *Further statistics*[1,2]

- Average e-h separation **5.7 Å**
- e-h correlation coeff. **0.45**

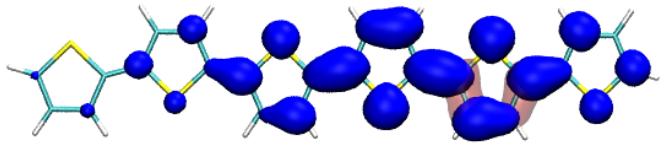
$\rho_e / \rho_h$



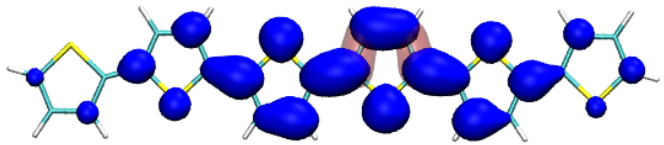
$\rho_e^{h:1} / \rho_h^{h:1}$



$\rho_e^{h:2} / \rho_h^{h:2}$

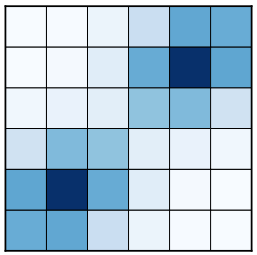


$\rho_e^{h:3} / \rho_h^{h:3}$



[1] S. A. Bäppler, FP, M. Wormit, A. Dreuw *PRA* **2014**, 90, 052521.
[2] FP, B. Thomitzni et al. *JCC* **2015**, 36, 1609.

# Conditional densities



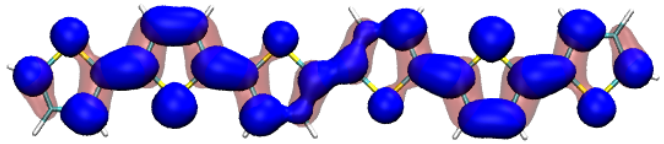
## $S_2$ state

- Overall electron and hole densities similar to $S_1$
- **Stronger correleations** between electron and hole

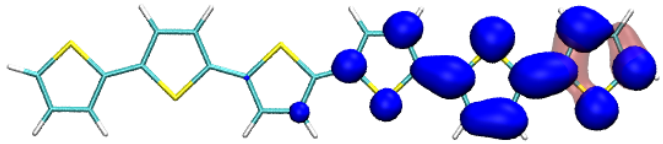
## *Further statistics*

- Average e-h separation **4.9 Å**
- e-h correlation coeff. **0.74**

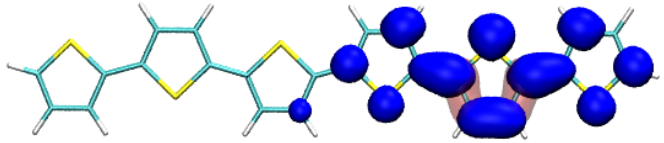
$\rho_e / \rho_h$



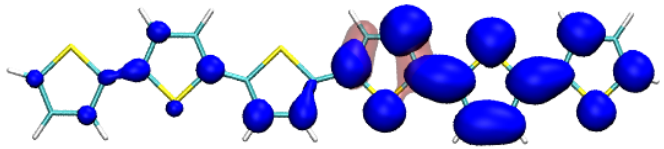
$\rho_e^{h:1} / \rho_h^{h:1}$



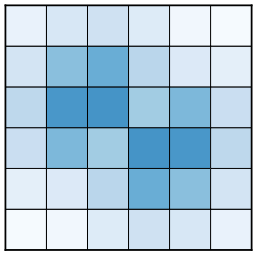
$\rho_e^{h:2} / \rho_h^{h:2}$



$\rho_e^{h:3} / \rho_h^{h:3}$



# Conditional densities



## $S_3$ state

- **Negative correleations** between electron and hole

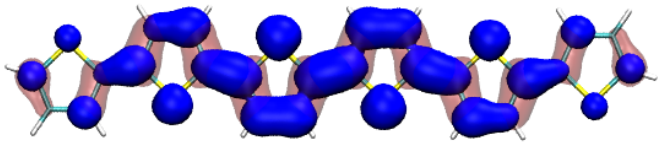
$\rightarrow$ Large e-h separation

- Nodal plane on **probe** thiophene

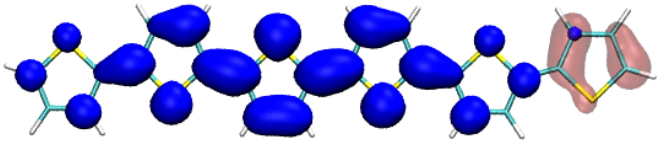
## *Further statistics*

- Average e-h separation **8.9 Å**
- e-h correlation coeff. **-0.24**

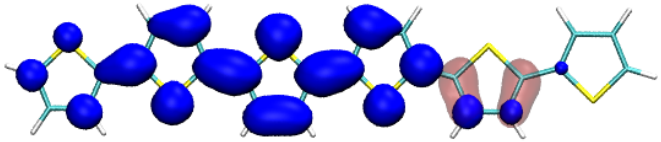
$\rho_e / \rho_h$



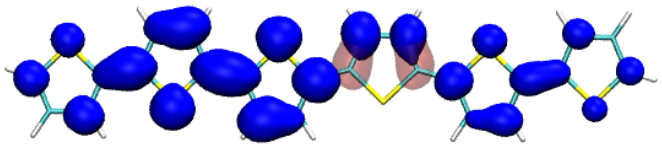
$\rho_e^{h:1} / \rho_h^{h:1}$



$\rho_e^{h:2} / \rho_h^{h:2}$



$\rho_e^{h:3} / \rho_h^{h:3}$



# Conclusions

Analysis of excited state wavefunctions

- DNA
  - **Automatic** analysis of thousands of states
  - **Rigorous** classification: delocalization, CT character
- Conjugated polymers
  - Visualization of **excitonic structure**
  - **Consistent picture** between correlation plots, conditional densities, and quantitative descriptors

# Recent Applications

- **DNA**
  - J. J. Nogueira, FP, L. González *Chem. Sci.* **2017**, 8, 5682.
- **Conjugated polymers**
  - S. A. Mewes, J.-M. Mewes, A. Dreuw, FP *PCCP* **2016**, 18,2548.
  - S. A. Mewes, FP, A. Dreuw *JPCL* **2017**, 8,1205.
- **Transition metal complexes**
  - S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González *CCR* **2018**, 361, 74.

→ *Talk OP68* by Pedro Sánchez-Murcia

# Software

Extended *wavefunction analysis toolbox*.

`TheoDORE` - **Theo**retical **D**ensity, **O**rbital **R**elaxation and **E**xciton analysis[1]

- Program package for wavefunction analysis
- Interfaces to various quantum chemistry programs:
  `Columbus`, `Turbomole`, `Orca`, `GAMESS`, `Gaussian`, `ADF`, `Terachem`, ...
- Open-source

`libwfa` - An open-source wavefunction analysis tool library[2]

- `Q-Chem`: Single-reference methods
- `MOLCAS`: Multireference methods

[1] `http://theodore-qc.sourceforge.net`
[2] `https://github.com/libwfa/libwfa`

# Acknowledgements

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Vienna Scientific Cluster

FWF

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