A toolbox for analysing structure-property relationships in functional molecules interacting with light

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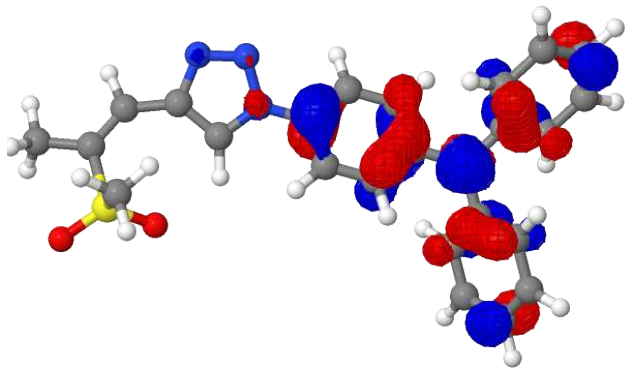
Introduction

Computational Photochemistry

- Accurate numbers
- ☺ *Quantum chemical methods*:
  TDDFT, CC, ADC, CASSCF, DMRG, MRCI, CASPT2
- ☺ *Multiscale models*: QM/MM, PCM, density embedding, ...
- ☺ *Algorithmic efforts*: Linear scaling, density fitting, parallelization, GPUs, ...
- Comparison to experiment
- ☺ *Linear* and *non-linear* optical properties
- ☺ *Static* and *time-resolved* experiments
- Chemical insight
- ☹ **Look at some blobs of colour**



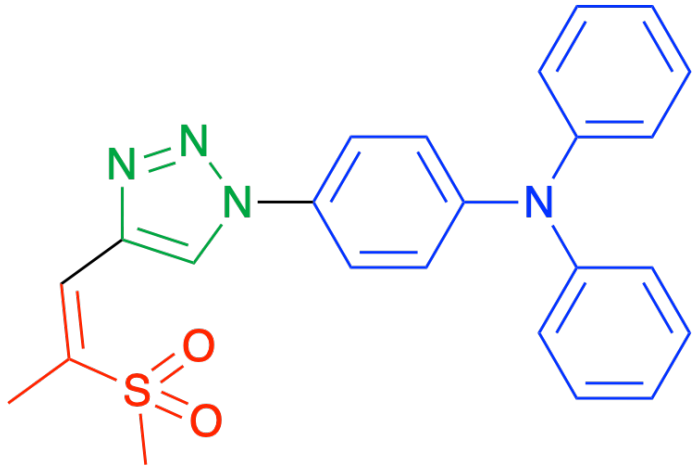
Computational Photochemistry

- ? Can we assign **excited-state character** in a **completely automated** way
  - Save time and analyse **larger data sets**
  - Remove **personal bias**
  - → Detailed analysis of **structure-property relationships** in functional molecules

- ? Can we learn about physics **beyond the MO picture**
  - Cross-links to other models
  - → Exciton theory
  - → Valence-bond theory

Push-pull systems

- Typical push-pull chromophore
  - ZMSO$_2$M-TPA
- Correlated ab initio computations
  - RI-CC2
  - Turbomole

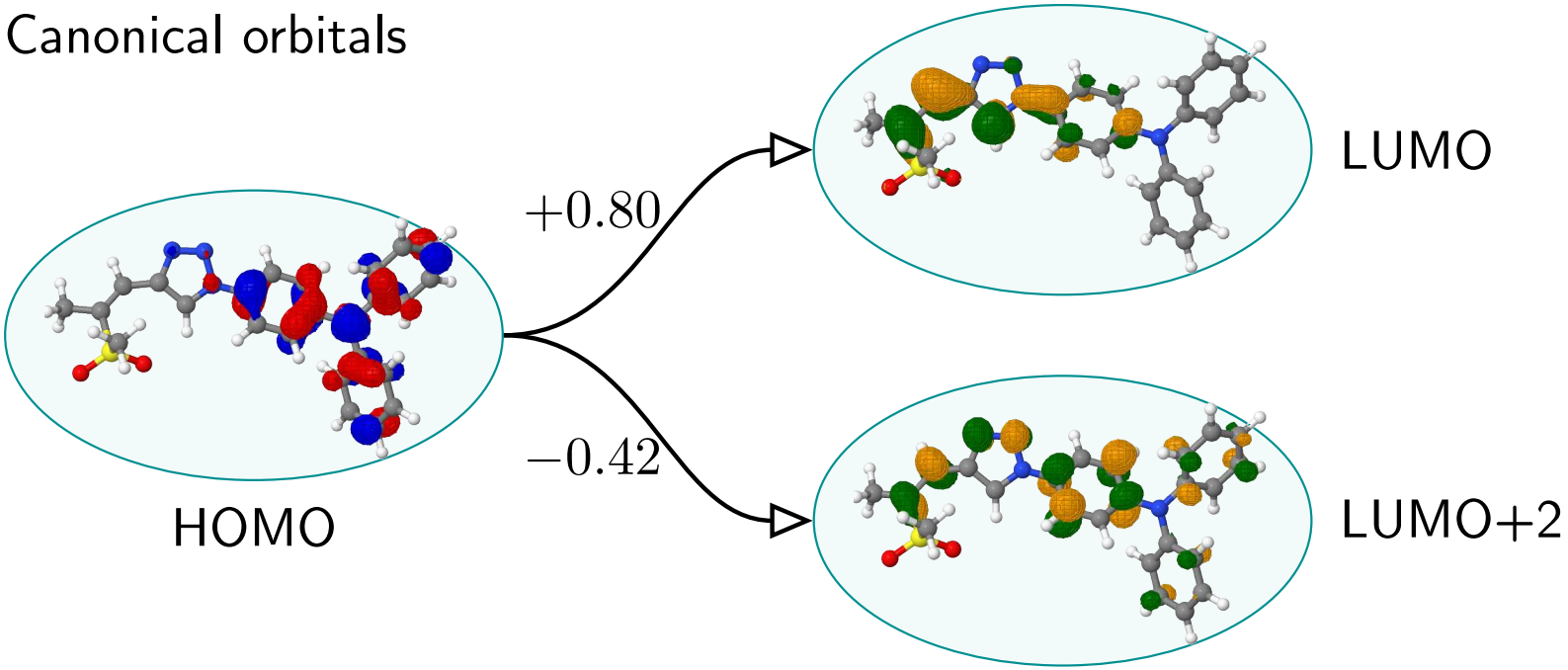


[1] P. Kautny, F. Glöcklhofer, T. Kader, J.-M. Mewes, B. Stöger, J. Fröhlich, D. Lumpi, FP, *PCCP* **2017**, 19, 18055.

[2] FP, *ChemRxiv* **2019**, DOI: 10.26434/chemrxiv.11395314.

$ZMSO_2M$-TPA

- First excited state (S_1)
  - Canonical orbitals



? How much charge transfer is there?

? What is the role of the second orbital?

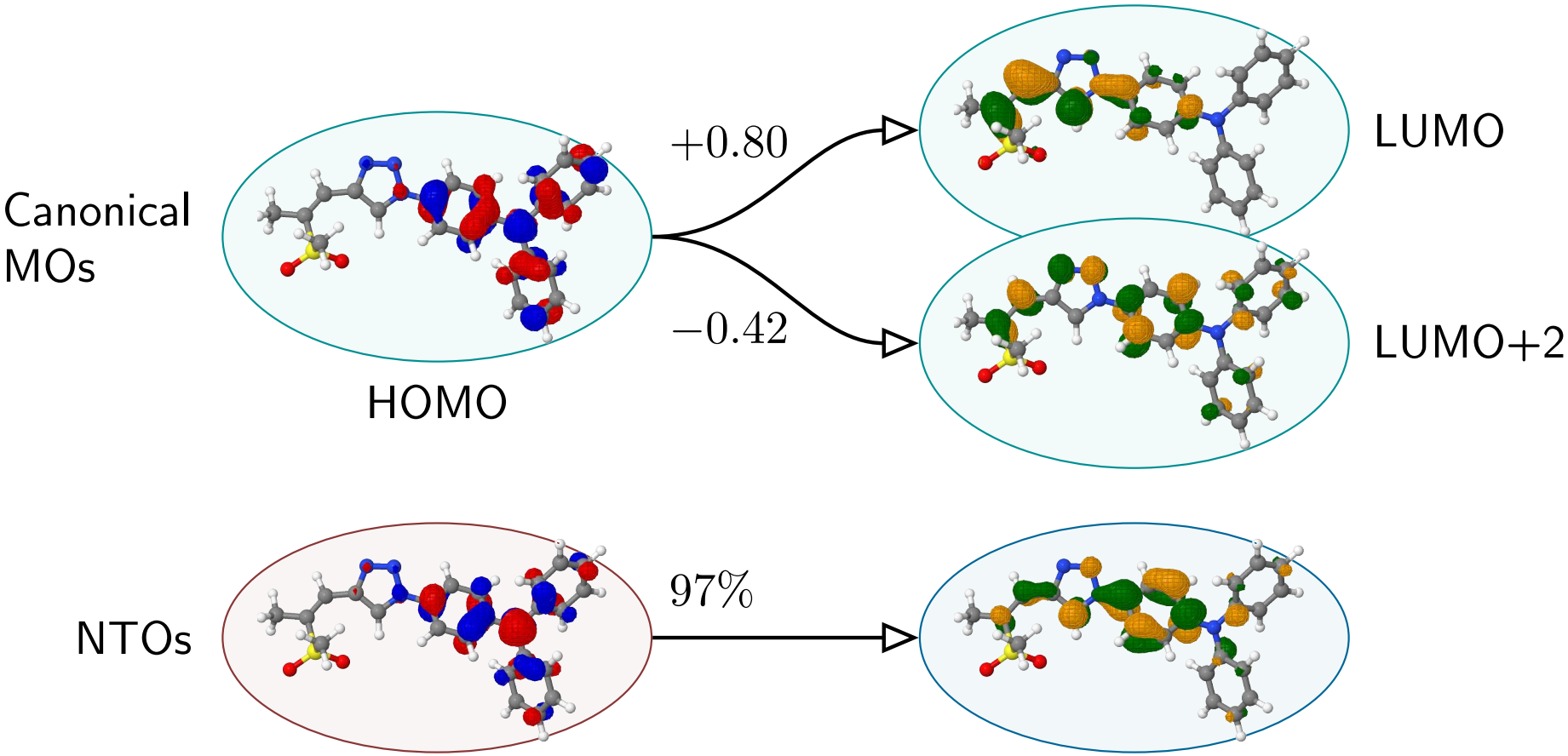
Compact Visualization

- **Natural transition orbitals**
  - Singular value decomposition of the transition density matrix

→ Compact representation of the excitation process

[1] R. L. Martin, *JCP* **2003**, 118, 11.
[2] FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

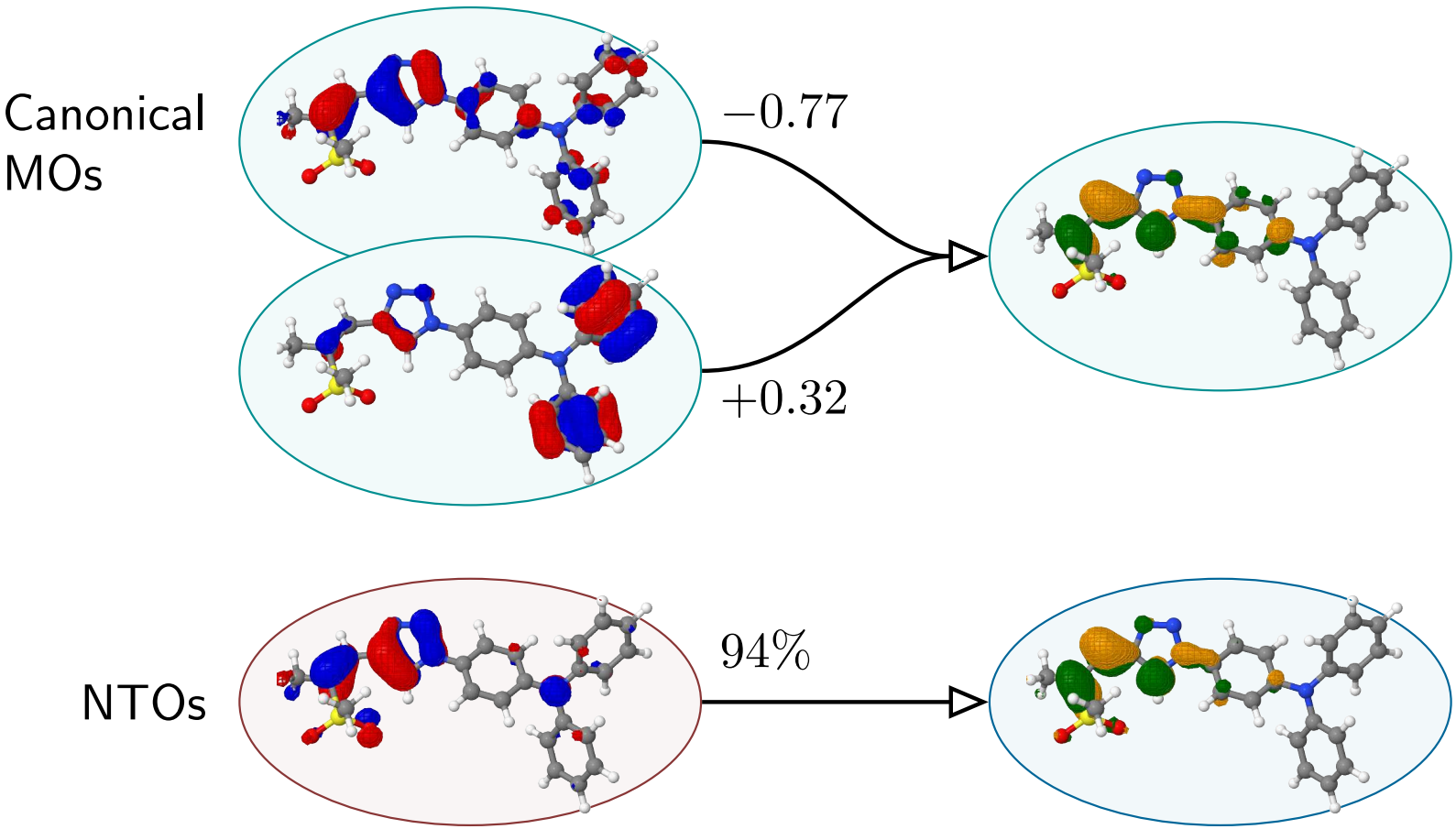
Natural transition orbitals – S_1



- Only one orbital-pair decisive
- ⓘ Shape quite different (interference)

→ **Reduced charge transfer** as opposed to HOMO-LUMO transition

Natural transition orbitals – S_7



- Again **non-trivial interference** effects

Natural transition orbitals

- **Natural transition orbitals**
- ☺ Well-defined and compact description
- ☹ Manual inspection still necessary

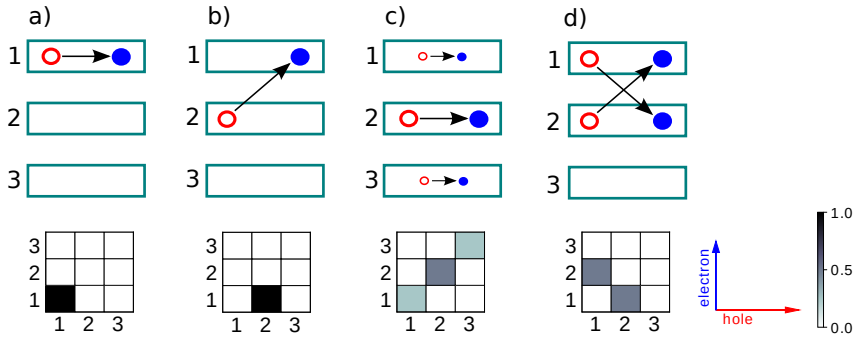
- ? Can we automate the analysis process

Charge-transfer numbers

- Excited state interpreted as a correlated **electron-hole** pair
  - Molecule divided into **fragments**
- Analysis of the **mutual** probability distribution of **electron** and **hole**

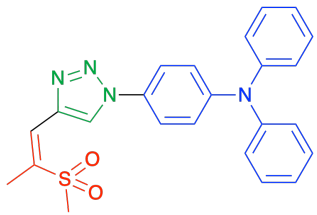
→ **Charge-transfer numbers** Ω_{AB}

  - Ω_{AB} – probability of $A \to B$ charge transfer
  - Ω_{AA} – probability of local excitation on fragment A



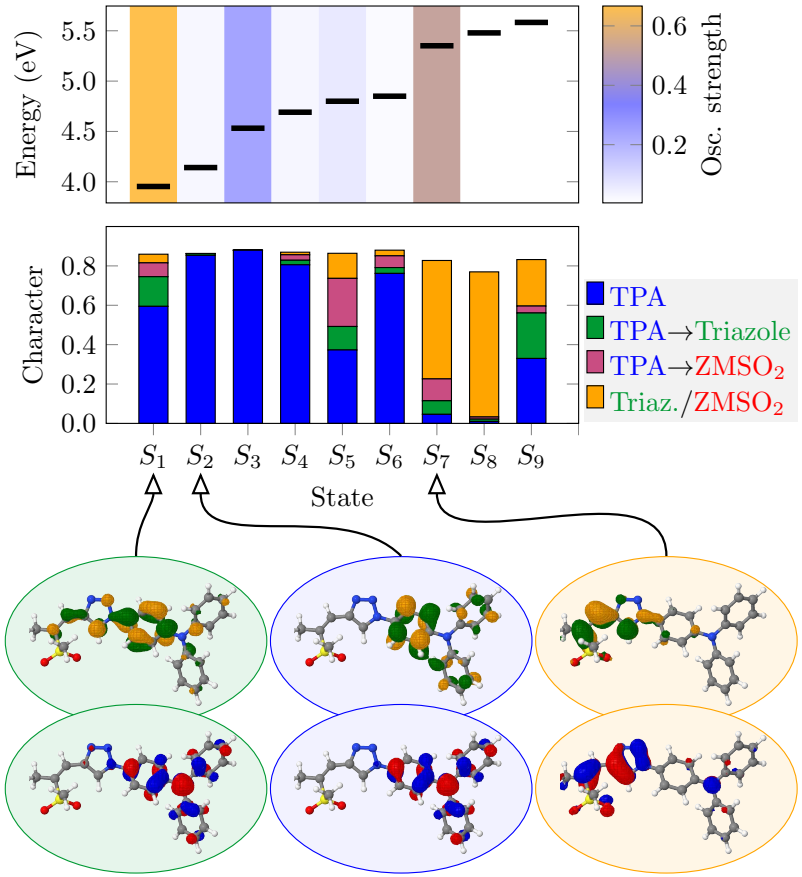
a) Local excitation
b) Charge-transfer state
c) Delocalised exciton
d) Charge-resonance state

[1] A. V. Luzanov and O. A. Zhikol, *IJQC* **2010**, 110, 902.
[2] FP, H. Lischka, *JCTC* **2012**, 8, 2777.
[3] FP, *ChemRxiv* **2019**, DOI: 10.26434/chemrxiv.11395314.



- **Automatic assignment** of state character
  - Localisation and charge transfer

☺ Ready to address question of interest[2,3]
  - Structure-property relations
  - Substitution patterns
  - Solvation



[1] FP, *ChemRxiv* **2019**, DOI: 10.26434/chemrxiv.11395314.
[2] P. Kautny, F. Glöcklhofer, et al., *PCCP* **2017**, 19, 18055.
[3] F. Glöcklhofer, A. Rosspeintner, et al., *Mol. Syst. Des. Eng.* **2019**, 4, 951.

Conjugated Polymers

- Excited states of conjugated polymers
  - Many electronic configurations

? Can we **visualise** the ensuing **electron correlation** effects

→ **Conditional electron densities**

[1] FP, *ChemPhotoChem* **2019**, 3, 702.

Conditional densities

Conditional density for the excited electron

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

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

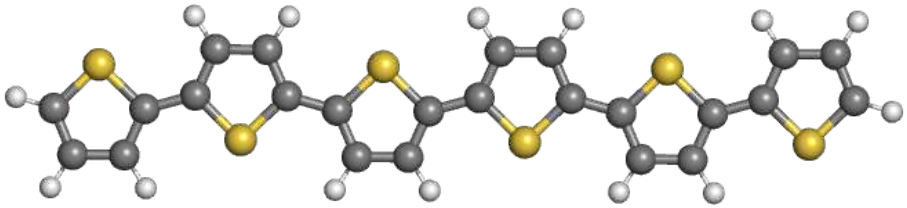
$\rho_e^{h:A}(r_e)$ Conditional **electron** density for the **hole** localized on fragment A

- Evaluated through multiplication of matrix blocks

[1] FP, *ChemPhotoChem* **2019**, 3, 702.

Oligothiophene

- Oligothiophene

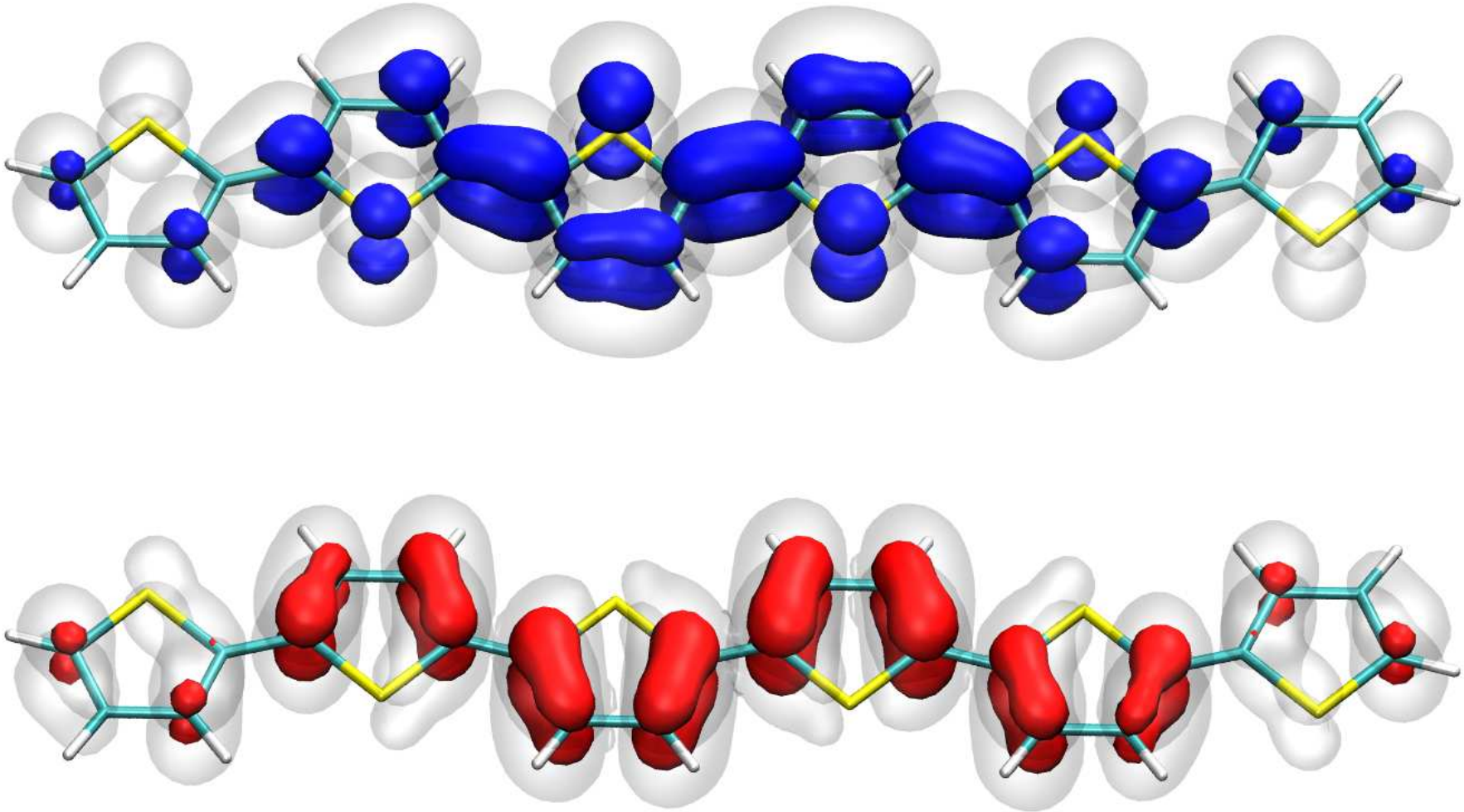


  - Prototypical conjugated polymer

- CAM-B3LYP computations

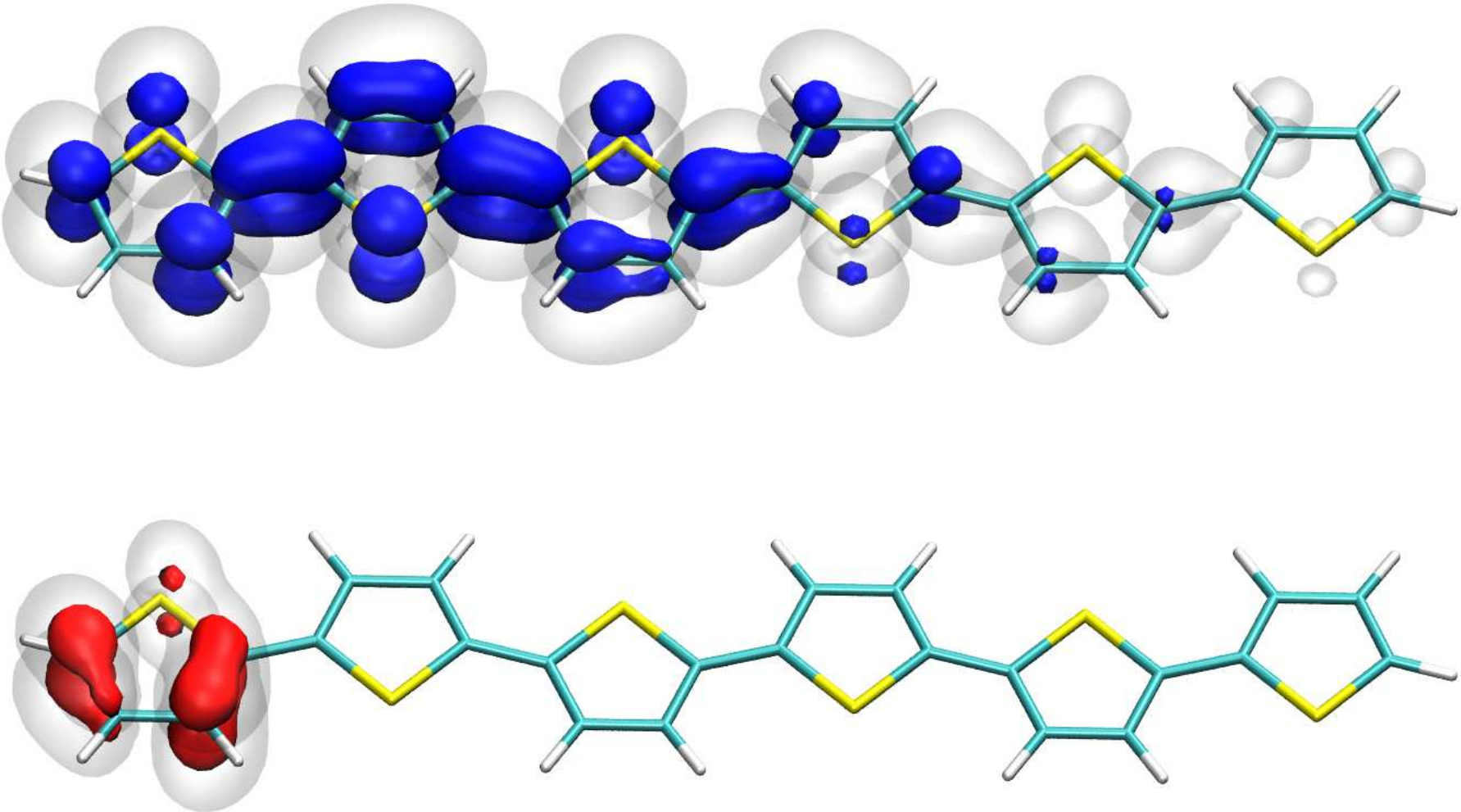
Oligothiophene

- S_1 state
  - Overall **hole** and **electron** densities



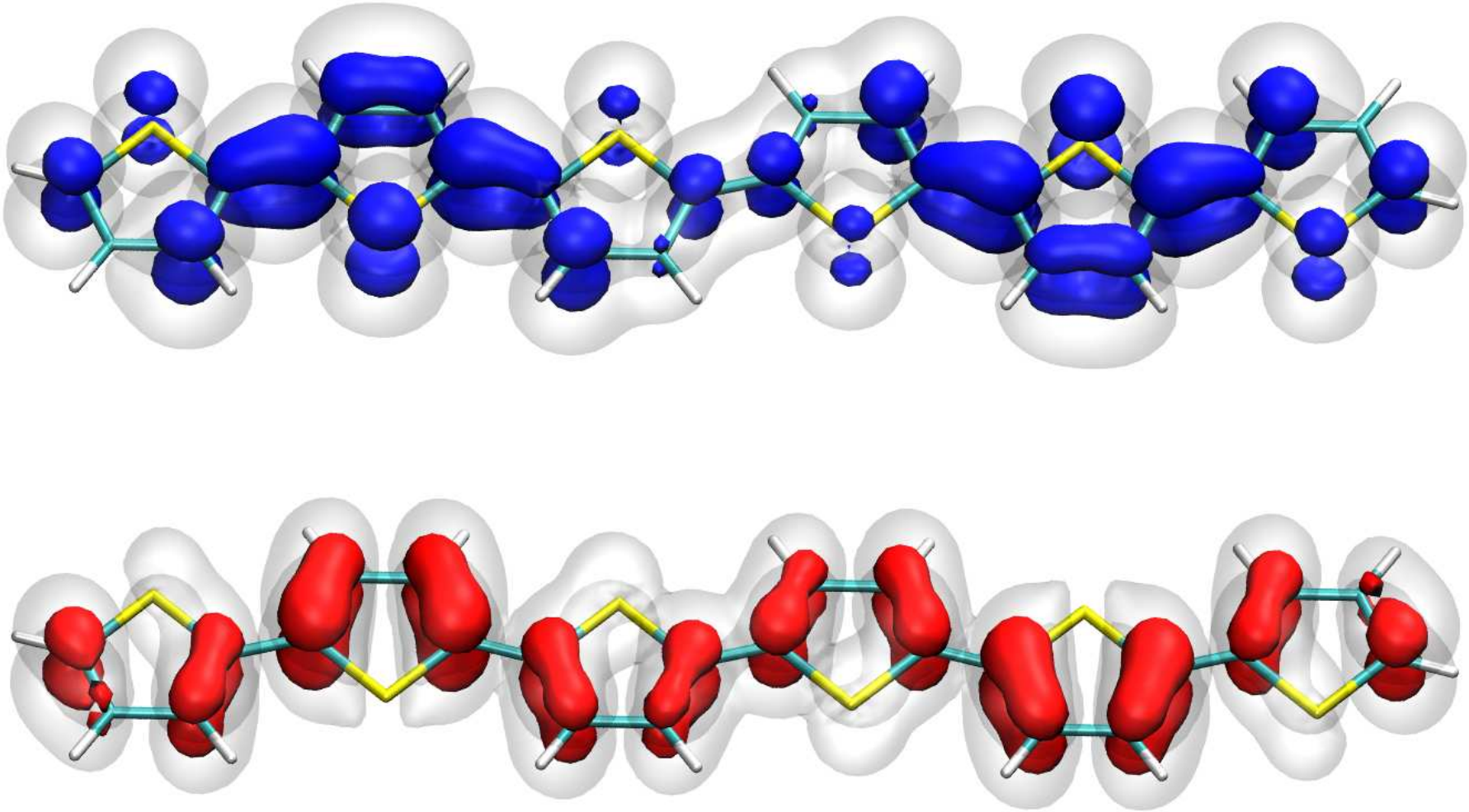
Oligothiophene

- S_1 state
  - **Conditional densities**



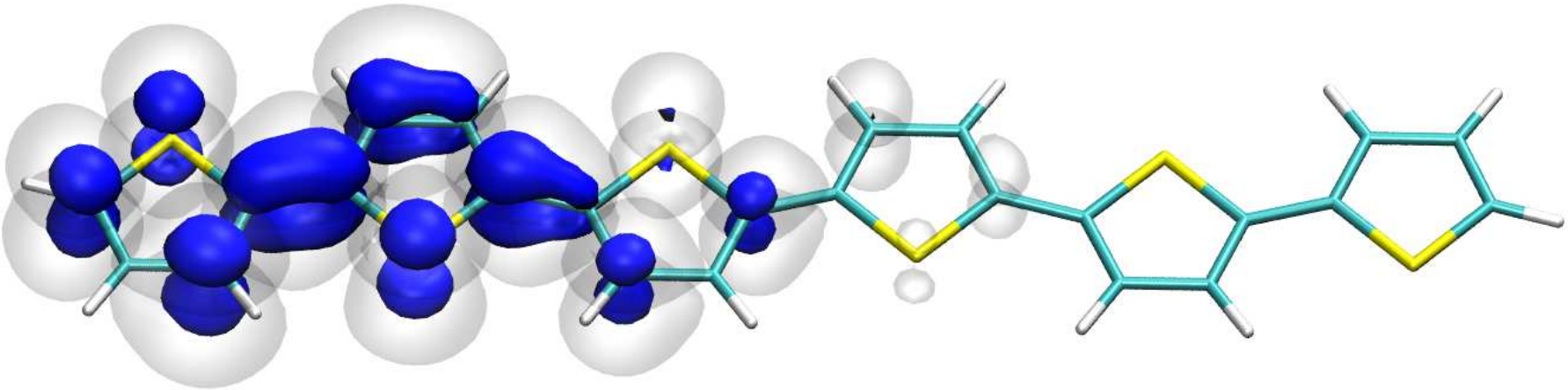
Oligothiophene

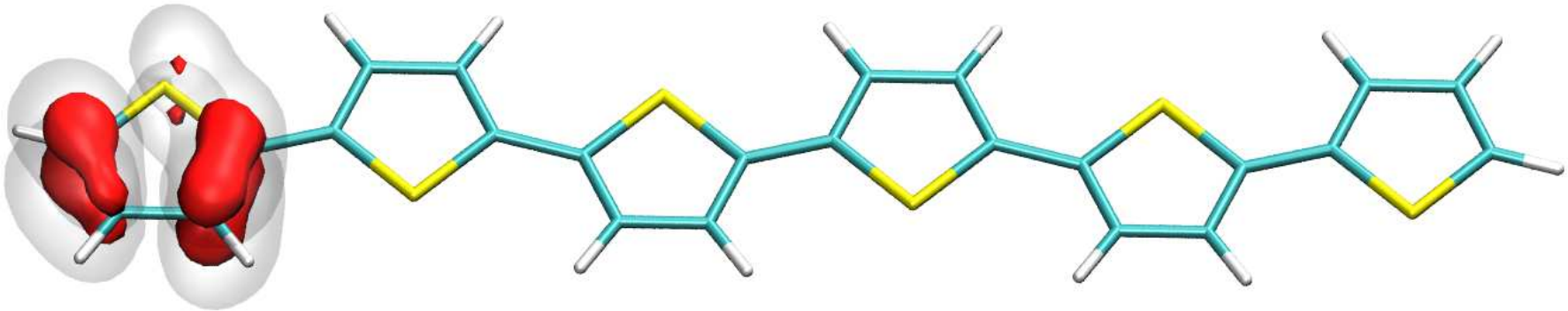
- S_2 state
  - Overall **hole** and **electron** densities



Oligothiophene

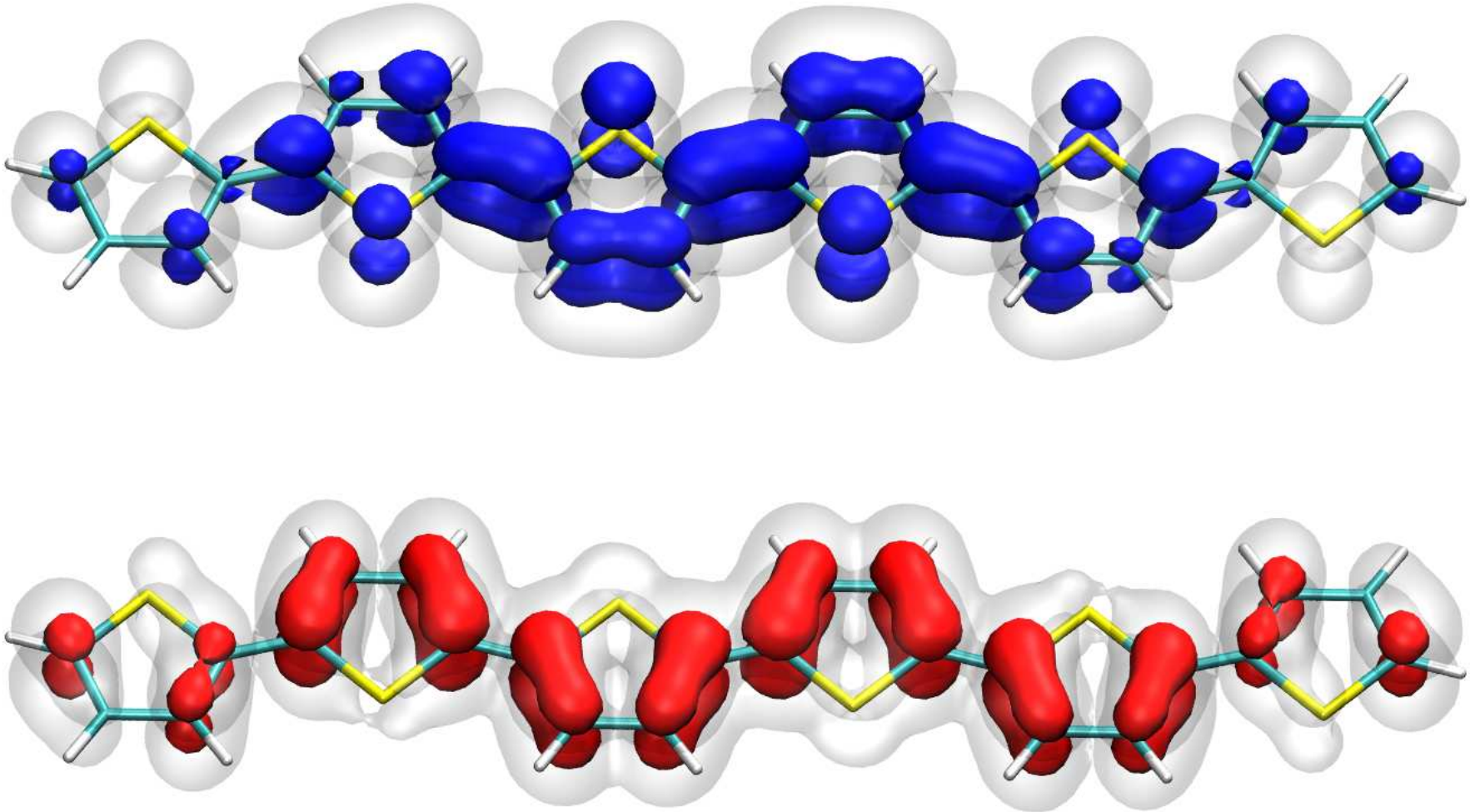
- S_2 state
  - **Conditional densities**





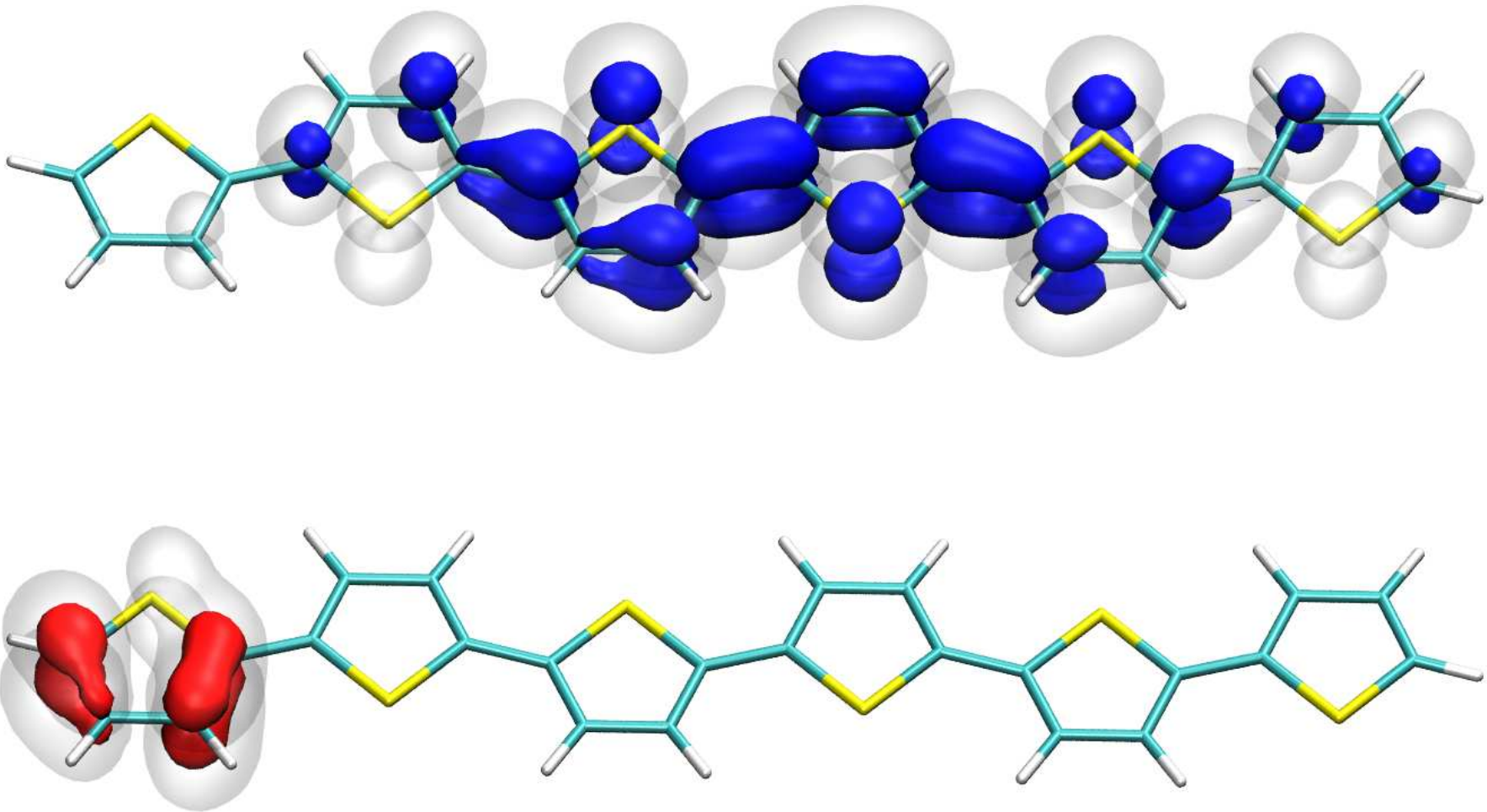
Oligothiophene

- S_3 state
  - Overall **hole** and **electron** densities



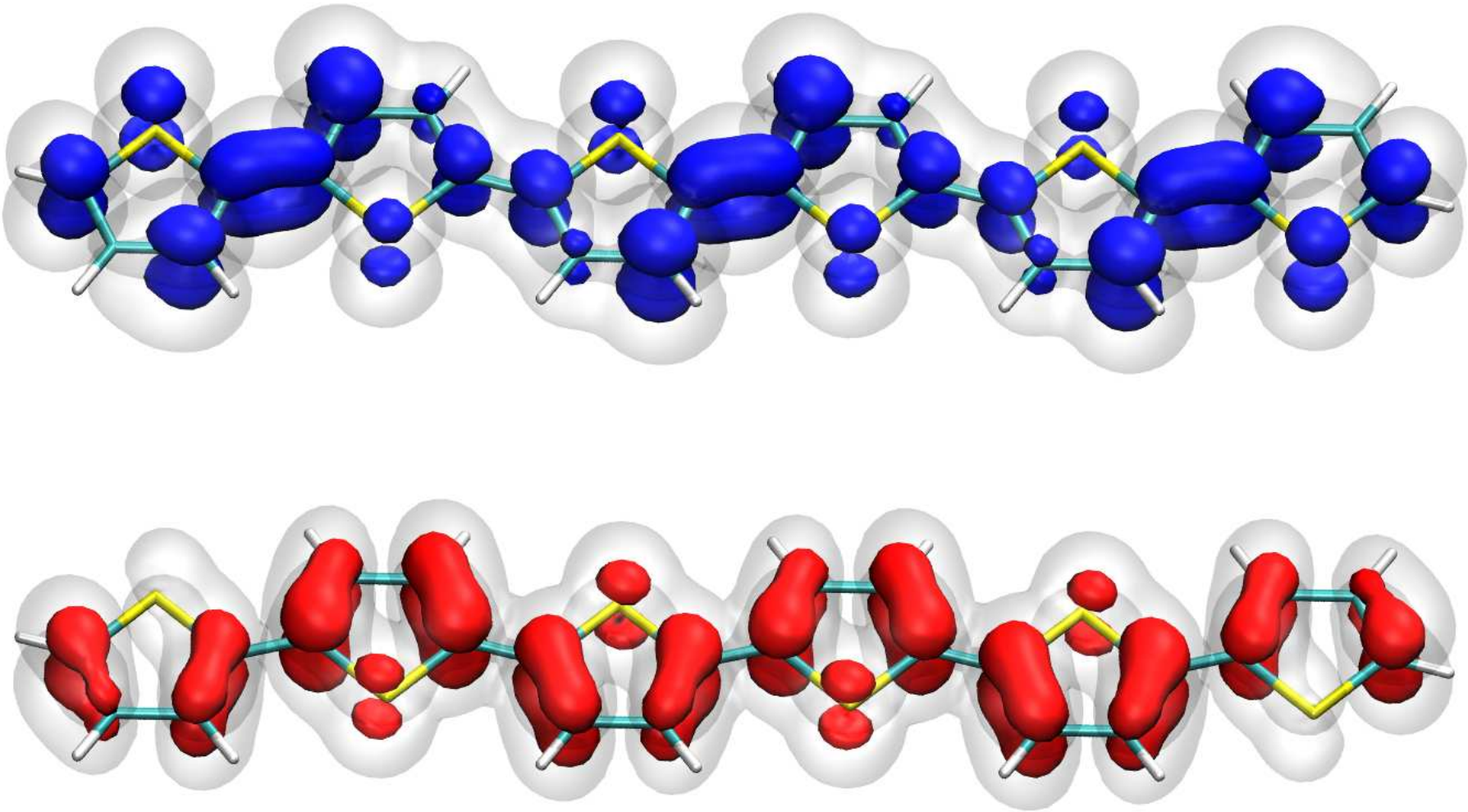
Oligothiophene

- S_3 state
  - **Conditional densities**



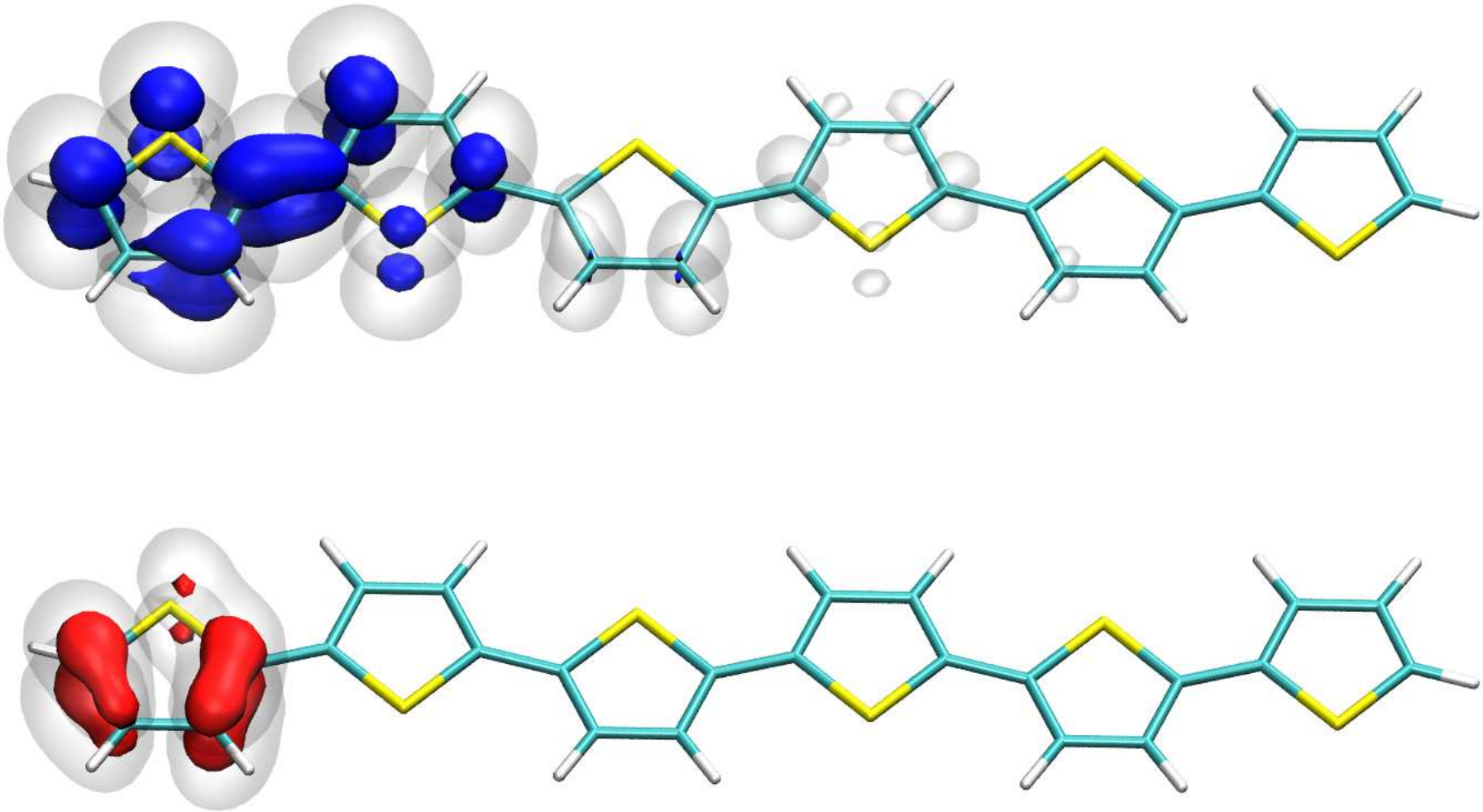
Oligothiophene

- S_4 state
  - Overall **hole** and **electron** densities



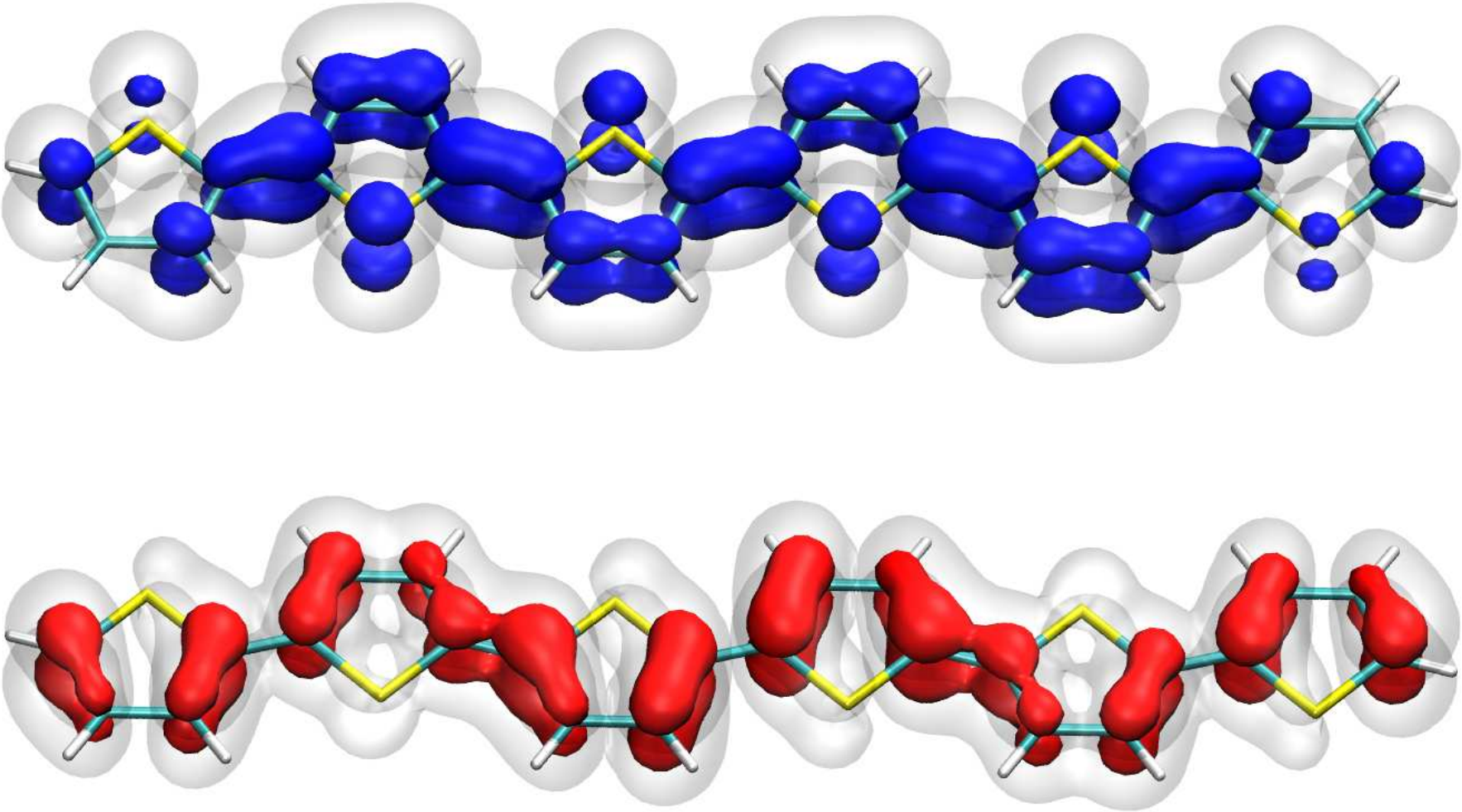
Oligothiophene

- S_4 state
  - **Conditional densities**



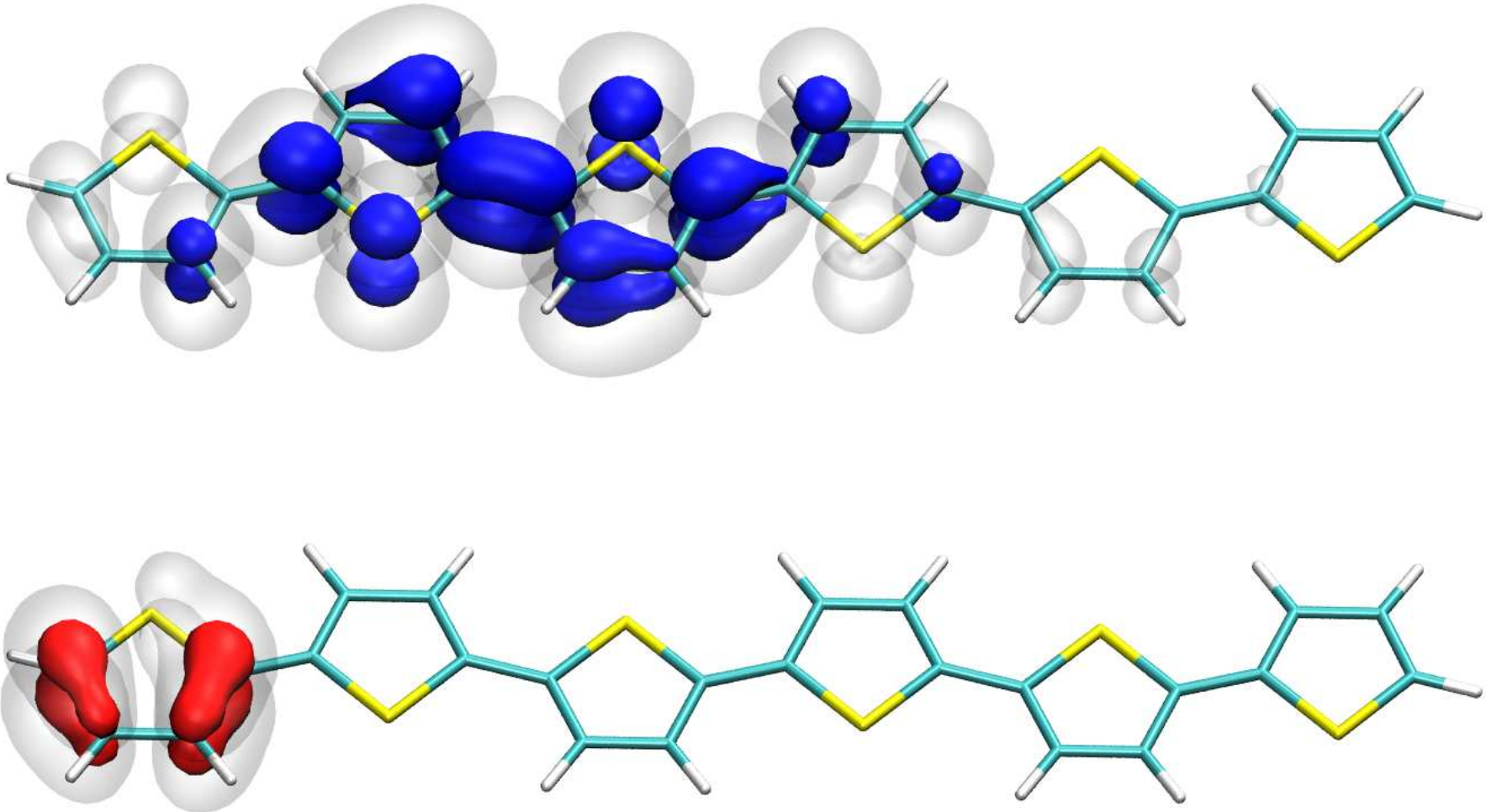
Oligothiophene

- S_5 state
  - Overall **hole** and **electron** densities



Oligothiophene

- S_5 state
  - **Conditional densities**



Conclusions

- **Automated assignment** of excited-state character
  - Push-pull systems ✓
  - Transition metal complexes ✓
  - Rydberg vs valence states ✓
- (?) $n\pi*$ vs $\pi\pi^*$

- **Conditional electron/hole densities**
  - **Excitons** in conjugated polymers ✓
  - **Valence-bond** picture: Ionic/covalent (+/-) states ✓

(?) Extension to other kinds of pair-distributions

→ Electron pair density

→ Green's functions

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`: ADC, EOM-CC, TDDFT
- `MOLCAS`: CASSCF, MS-CASPT2
- `CFOUR`

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

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Slides available at: https://fplasser.sci-public.lboro.ac.uk