Analysis of Transition Metal Complex Excited States: Turning Numbers into Chemical Insight

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Loughborough University

Introduction

Computational Photochemistry

- Accurate numbers
- Comparison to experiment
- Chemical insight

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- ☺ *Quantum chemical methods*:
  Semi-emp., TDDFT, CC, ADC, CASSCF, **DMRG**, **QMC**, CASPT2, ...
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- ☺ *Linear* and *non-linear* optical properties
- ☺ *Static* and *time-resolved* experiments
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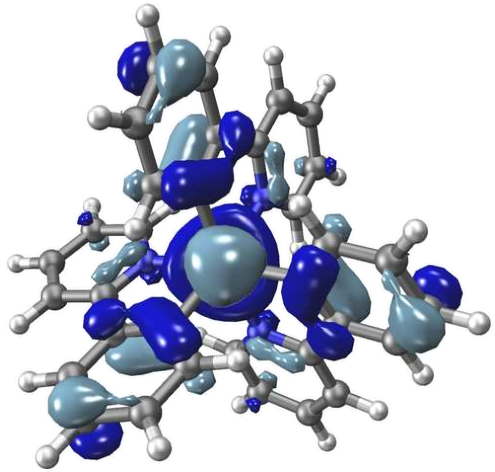
☹ **Look at some blobs of colour**



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→ Benchmark computational methods

Outline

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Ir(ppy)$_3$

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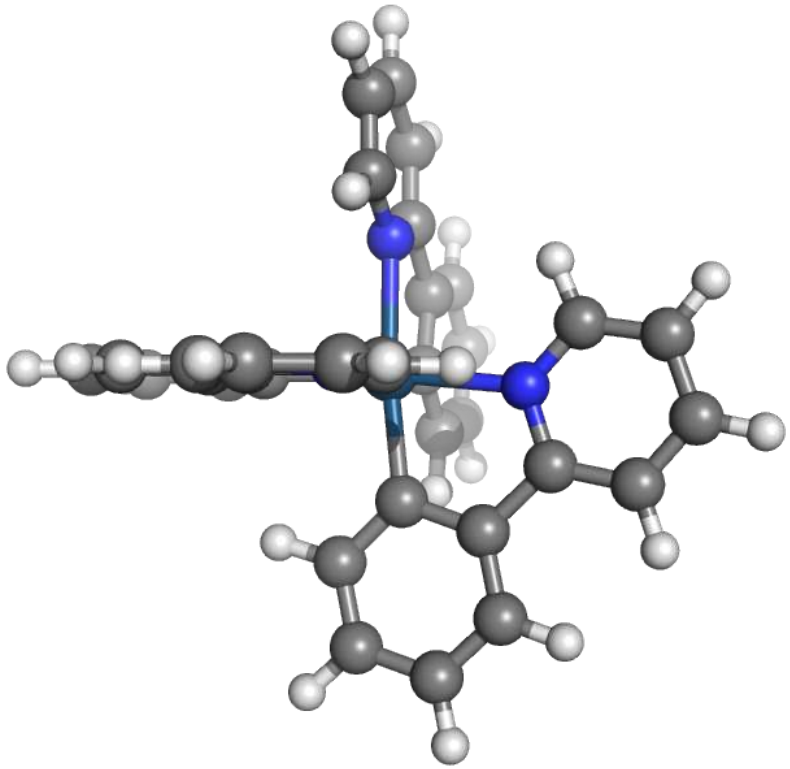
- Highly phosphorescent complex[1]
- **Interplay** of IL and MLCT states decisive for emission[2]
  - **MLCT** $\rightarrow$ spin-orbit coupling $\rightarrow$ phosphorescence
  - **IL** $\rightarrow$ exchange splitting $\rightarrow$ low-energy triplets



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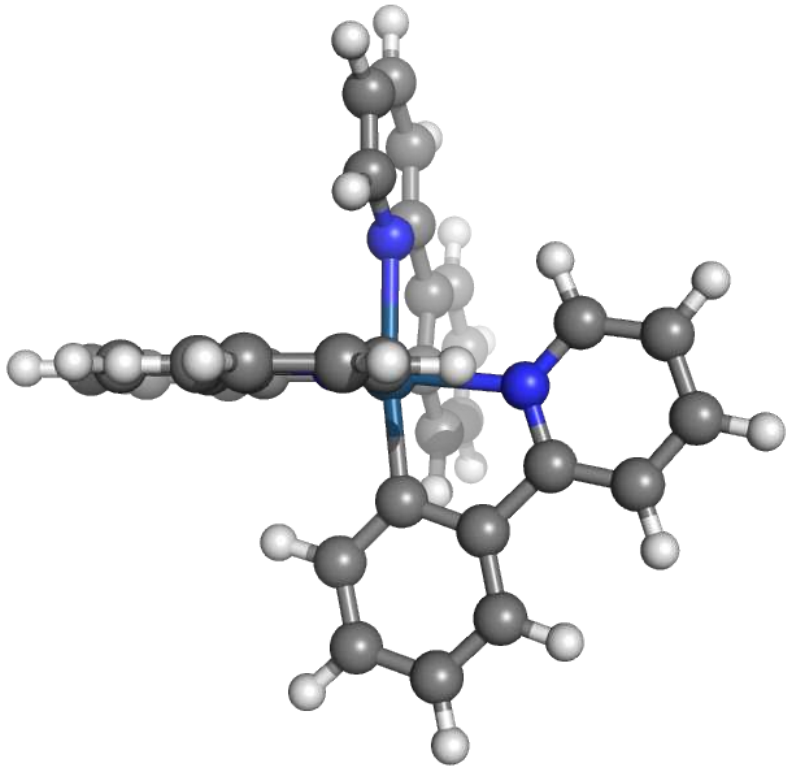
? How to quantify



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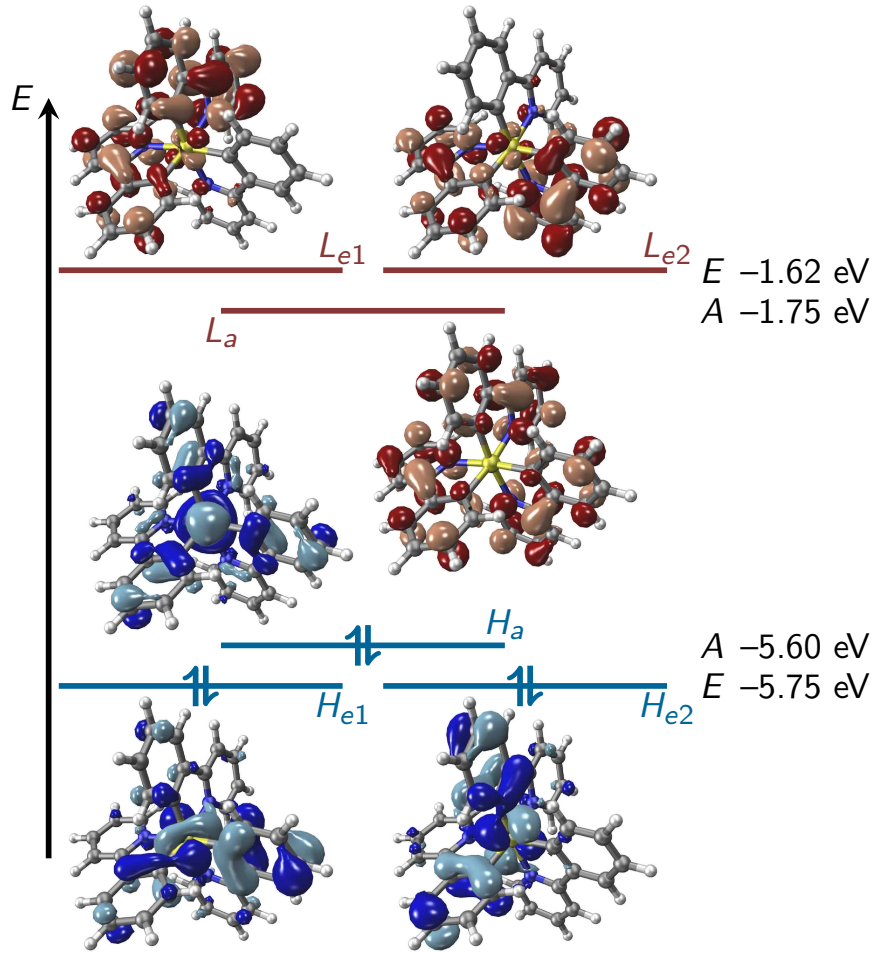
Frontier orbitals

- DFT/B3LYP
- **Occupied** orbitals
  - Mixture metal-d/ligand-π
- **Virtual** orbitals
  - Ligand-π^*



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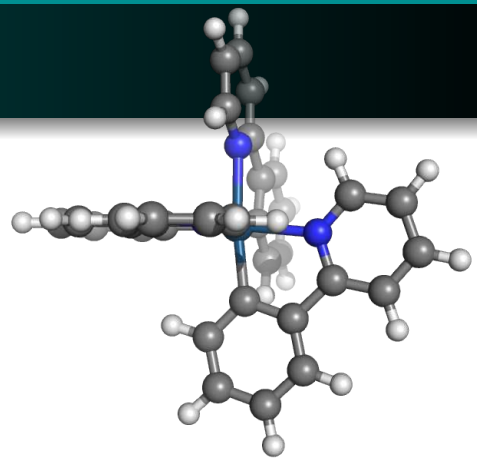


Lowest triplet states

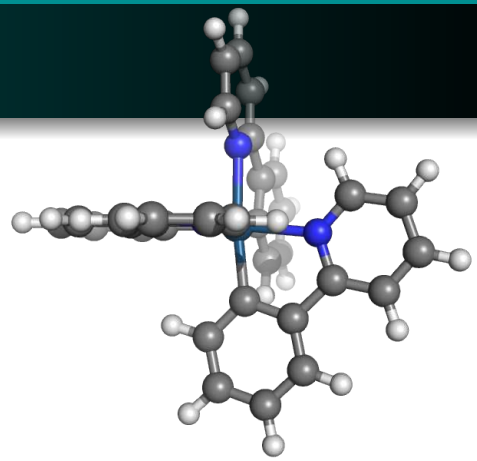
- TDDFT/B3LYP

	E (eV)	Sym.	Leading excitations		
T_1	2.89	A	$+0.85H_aL_a$	$+0.32H_{e1}L_{e2}$	$+0.32H_{e2}L_{e1}$
T_2	2.93	E	$+0.58H_aL_{e1}$	$+0.49H_aL_{e2}$	
T_3	2.93	E	$+0.58H_aL_{e2}$	$-0.49H_aL_{e1}$	
T_4	3.17	A+E	$+0.48H_{e1}L_{e1}$	$+0.44H_{e2}L_{e1}$	$+0.41H_{e1}L_a$
T_5	3.17	A+E	$+0.56H_{e2}L_a$	$+0.46H_{e2}L_{e2}$	$-0.42H_{e2}L_{e1}$
T_6	3.17	A+E	$-0.56H_{e1}L_a$	$+0.53H_{e1}L_{e2}$	$+0.45H_aL_{e2}$

- Metal-d/ligand-$\pi \rightarrow$ ligand-π^* excitations

$\rightarrow$ Mixture: MLCT, IL, LLCT

Frontier orbitals



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☹ Tedious **work**, possible **ambiguities**

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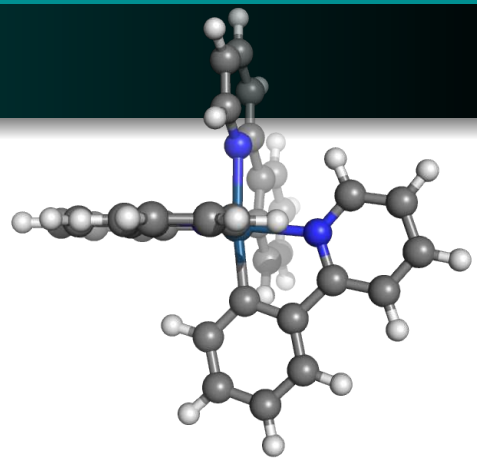

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? Different graphical representation

Natural Transition Orbitals

1-electron transition density matrix

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

$\hat{a}^\dagger_\mu$ Creation operator

$\hat{a}_\nu$ Annihilation operator

$D^{0I}_{\mu\nu}$ Matrix representation of the 1TDM

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Natural transition orbitals — Singular value decomposition

$$\mathbf{D}^{0I} = \mathbf{U} \times \mathrm{diag}\left(\sqrt{\lambda_1}, \sqrt{\lambda_2}, \ldots\right) \times \mathbf{V}^{\mathrm{T}}$$

$\mathbf{U}$ **Hole** orbital coefficients

λ_i Transition amplitudes

$\mathbf{V}$ **Electron** orbital coefficients

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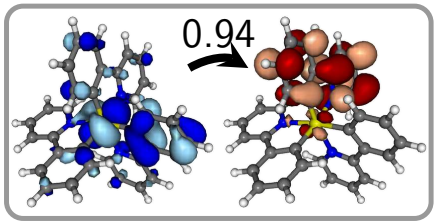
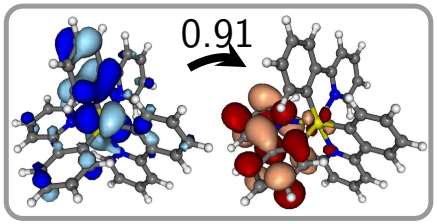
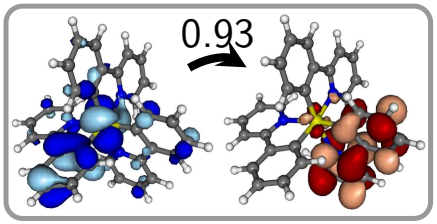
Natural transition orbitals



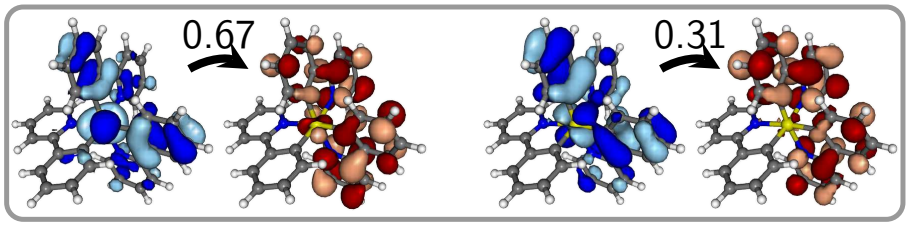
T_4 3.17 eV (1.11)



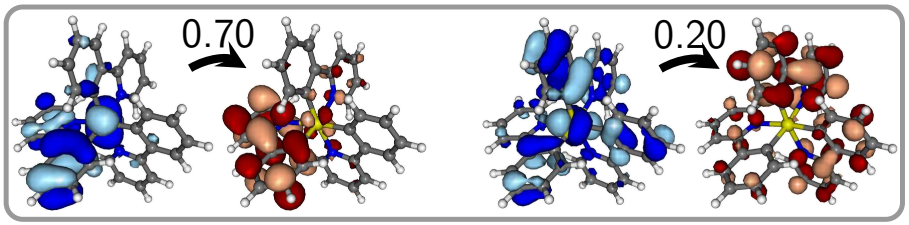
T_5 3.17 eV (1.17)



T_6 3.17 eV (1.13)



T_2 2.93 eV (1.82)



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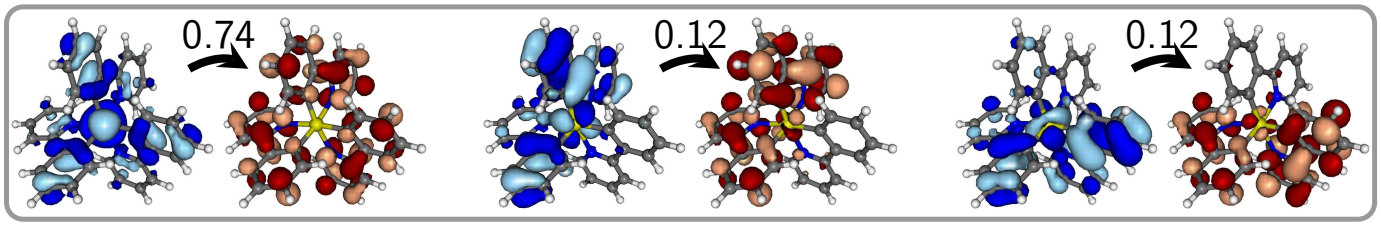

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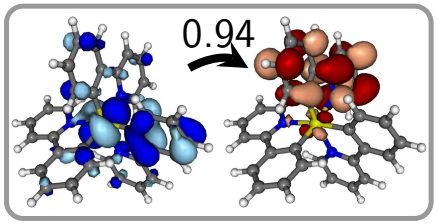
- Clear differences visible

→ More **IL** for $T_1 - T_3$, more **LLCT** for $T_4 - T_6$

Natural transition orbitals



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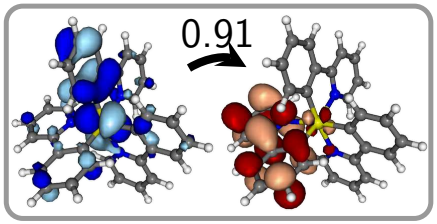

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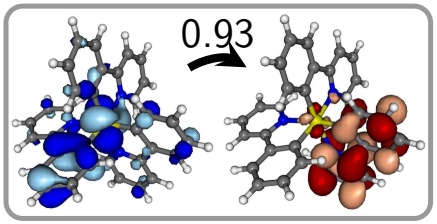

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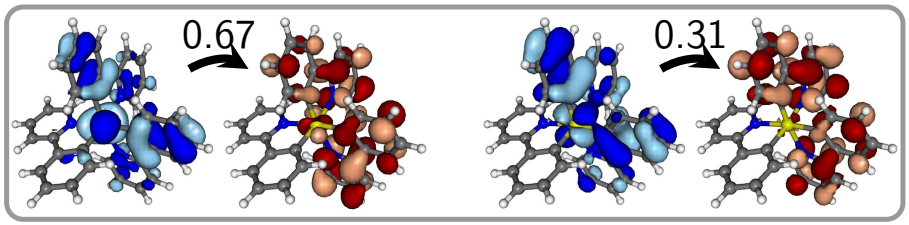

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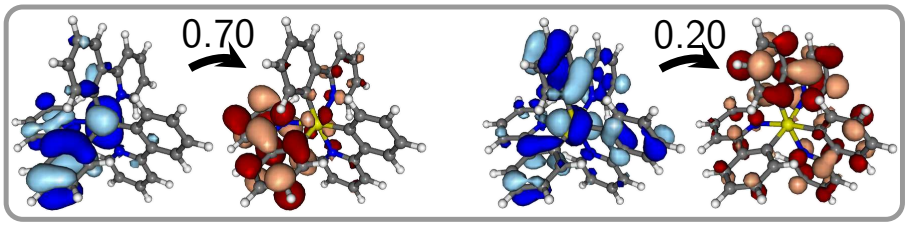

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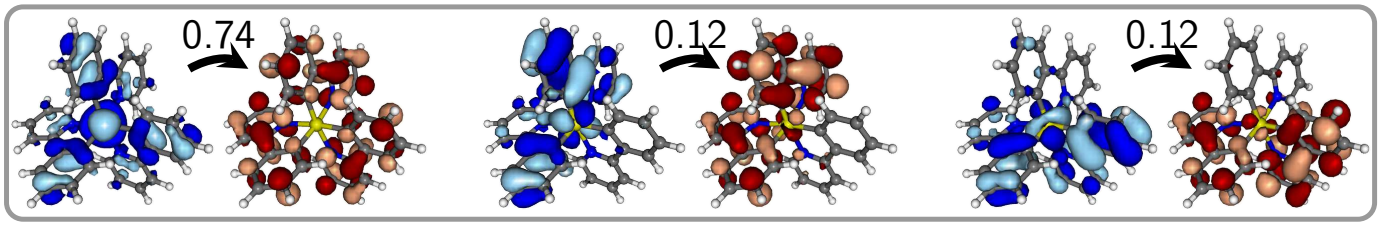

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- Clear differences visible

→ More **IL** for $T_1 - T_3$, more **LLCT** for $T_4 - T_6$

? Quantitative description

Charge Transfer Numbers

- Summation over **squared 1TDM elements**

Charge transfer numbers

$$\Omega_{AB} = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in B} |\tilde{D}^{0I}_{\mu\nu}|^2$$

$\tilde{D}^{0I}_{\mu\nu}$	Element of the 1TDM after Löwdin orthogonalisation
Ω_{AA}	Weight of local excitations on fragment A
$\Omega_{AB}, A \neq B$	Amount of charge transfer from A to B

- **Fragment** definition
  - Central metal + ligands: Ir, L^1, L^2, L^3

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

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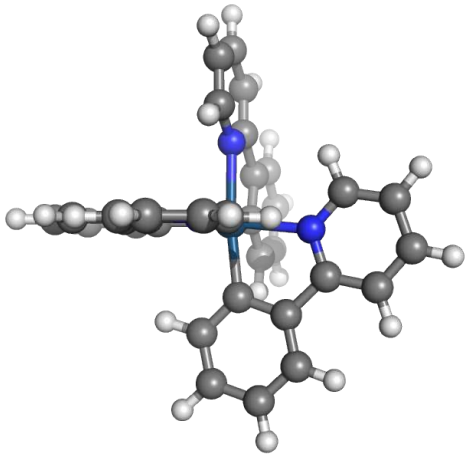


- $T_1 - T_3$
  - $L^i \rightarrow L^i$ (IL)
  - Ir$\rightarrow L^i$ (MLCT)
- $T_4 - T_6$
  - Ir$\rightarrow L^i$ (MLCT)
  - $L^i \rightarrow L^j$ (LLCT)

(d) T_4 (3.17 eV)

Ir	L^1	L^2	L^3
1	0	0	15
0	0	1	7
1	0	1	22
2	1	2	46

(e) T_5 (3.17 eV)

Ir	L^1	L^2	L^3
1	1	22	0
1	1	14	1
0	1	6	0
2	3	45	2

(f) T_6 (3.17 eV)

Ir	L^1	L^2	L^3
0	7	1	0
1	22	1	1
0	14	1	1
2	46	3	1

(b) T_2 (2.93 eV)

Ir	L^1	L^2	L^3
1	2	0	24
0	2	0	2
1	29	0	2
2	19	1	16

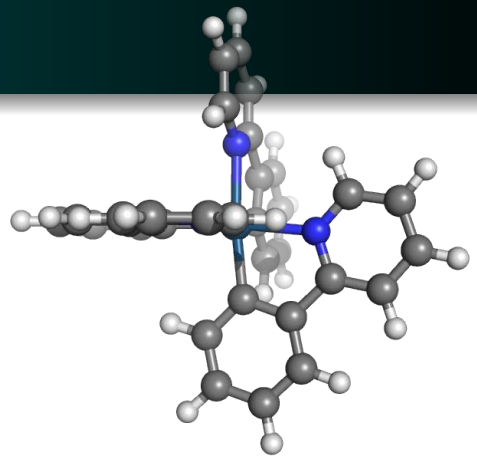
(a) T_1 (2.89 eV)

Ir	L^1	L^2	L^3
0	2	2	16
0	2	16	2
0	16	2	2
1	13	13	13

(c) T_3 (2.93 eV)

Ir	L^1	L^2	L^3
1	1	3	11
1	1	35	1
0	7	2	1
2	5	23	8

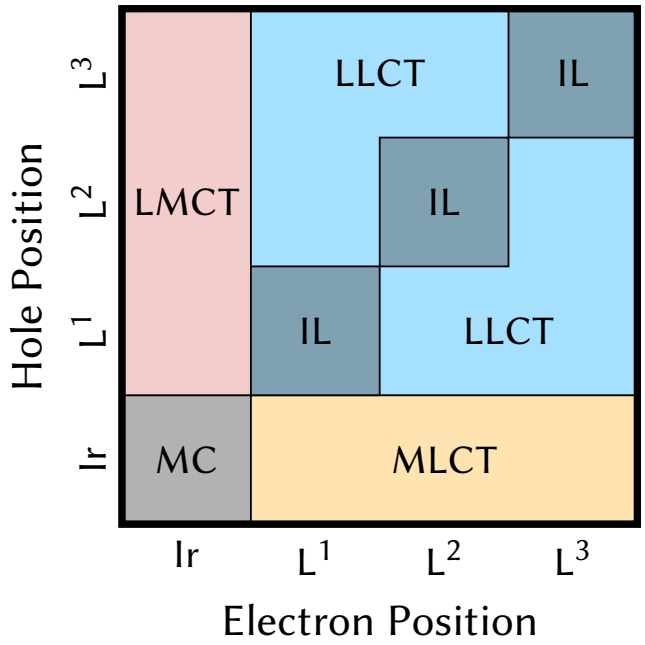
Charge Transfer Numbers



- General classification
  - Different formal state characters correspond to different Ω_{AB} elements

→ Automatic **classification** of state character

→ Quantification of **state mixing**



[1] FP, A. Dreuw, *JPCA* **2015**, 119,1023.

[2] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

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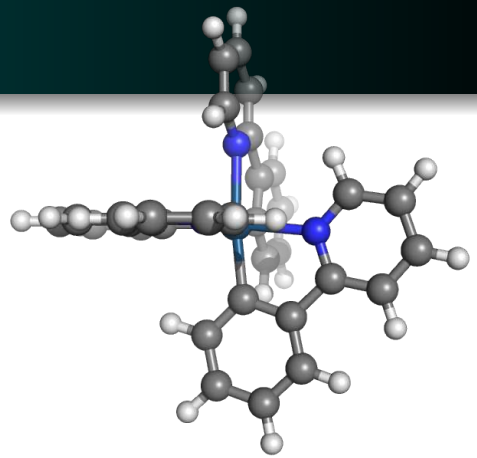

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	E (eV)	Sym.	State character	
T_1	2.89	A	49% **IL**	38% **MLCT**
T_2	2.93	E	53% **IL**	35% **MLCT**
T_3	2.93	E	53% **IL**	35% **MLCT**
T_4	3.17	A+E	49% **MLCT**	31% **LLCT**
T_5	3.17	A+E	50% **MLCT**	31% **LLCT**
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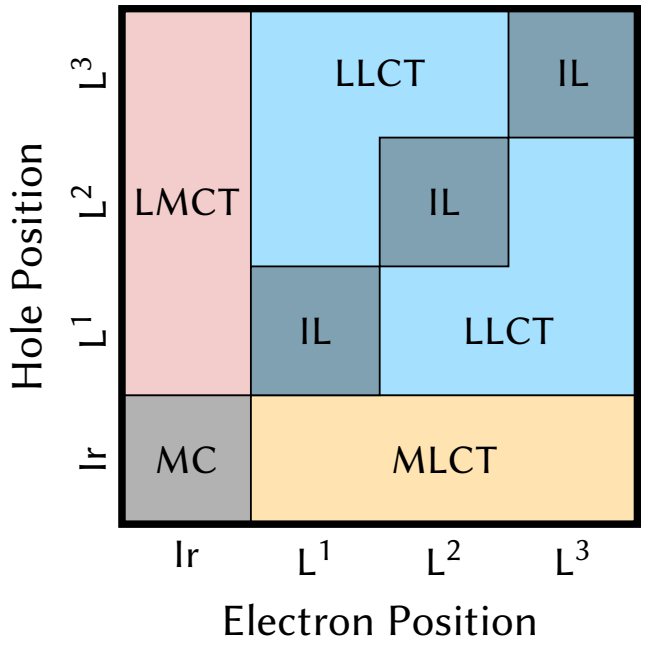

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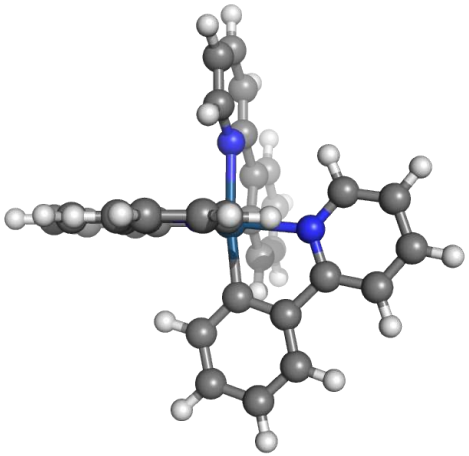
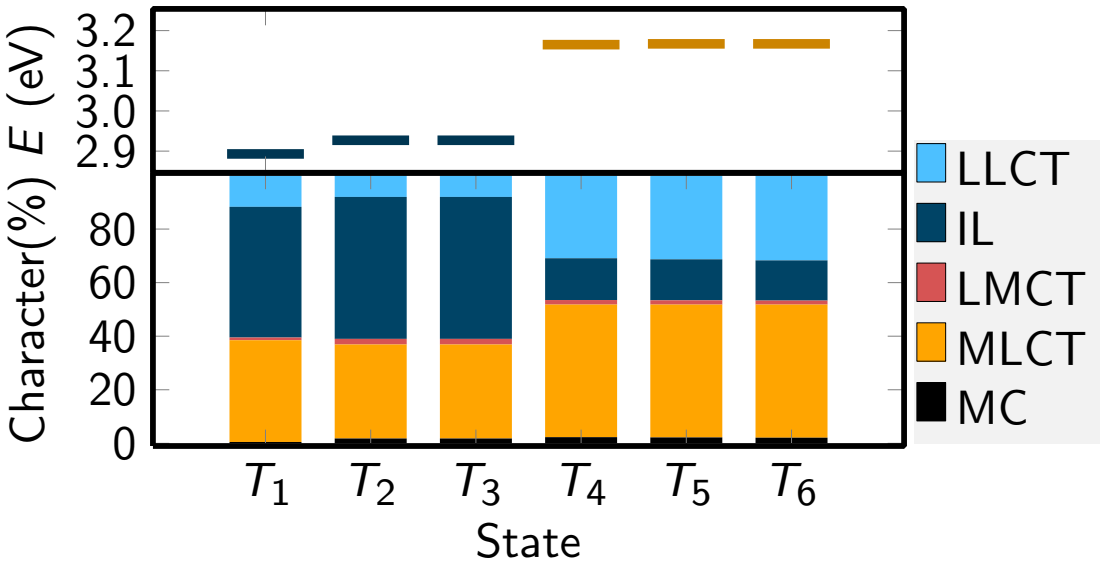


- Compact graphical depiction



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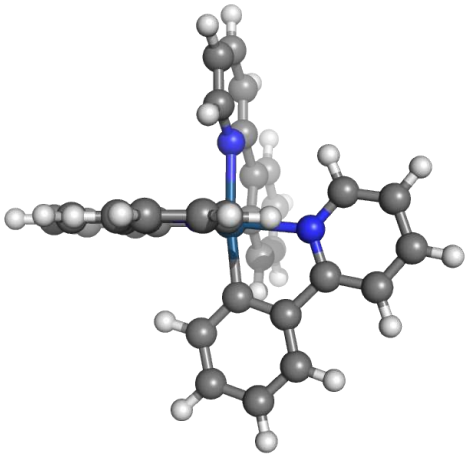

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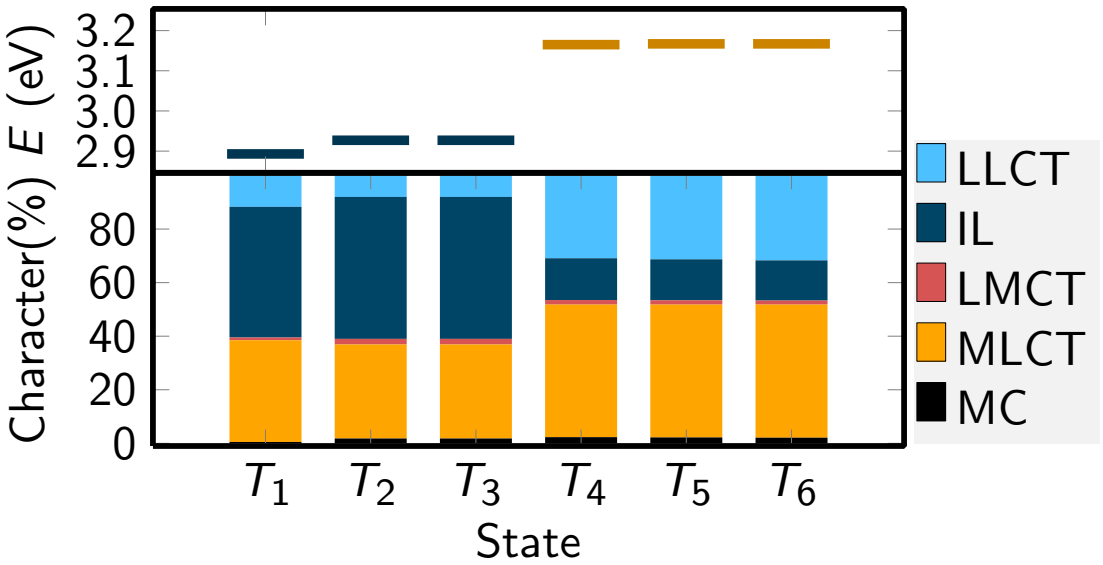


? Can we avoid the fragment definition

Exciton Analysis

Exciton analysis

- Interpret the 1TDM as the wavefunction χ_{exc} of the electron-hole pair
- Use as a basis for analysis

Exciton wavefunction

$$\chi_{exc}(x_h, x_e) = \sum_{\mu\nu} D^{0I}_{\mu\nu} \chi_\mu(x_h) \chi_\nu(x_e)$$

$D^{0I}_{\mu\nu}$ Matrix representation of the 1TDM

$\chi\mu$ Atomic orbital

x_h, x_e Coordinates of the **excitation hole** and the **excited electron**

.

[1] S. A. Bäppler, FP, M. Wormit, A. Dreuw, *Phys. Rev. A* **2014**, 90, 052521.

Exciton Analysis

Operator expectation value

$$\left\langle \hat{O} \right\rangle = \frac{\langle \chi_{exc} | \hat{O} | \chi_{exc} \rangle}{\langle \chi_{exc} | \chi_{exc} \rangle}$$

Exciton size

$$d_{exc}{}^2 = \left\langle (r_e - r_h)^2 \right\rangle$$

- Average separation of the electron and hole quasi-particles
- Evaluated using **analytic integration** techniques

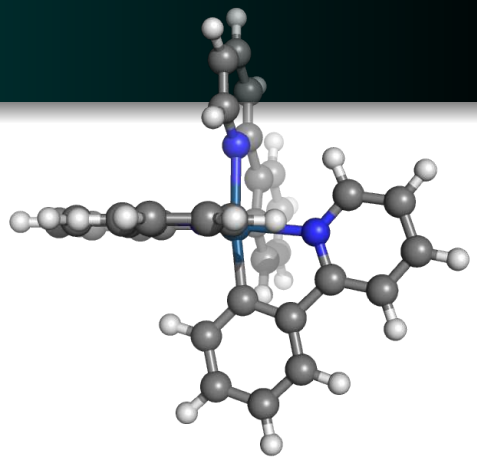
☺ No fragment definition

☺ No population analysis

☺ Works also for centrosymmetric systems

[1] S. A. Bäppler, FP, M. Wormit, A. Dreuw, *Phys. Rev. A* **2014**, 90, 052521.

Exciton size

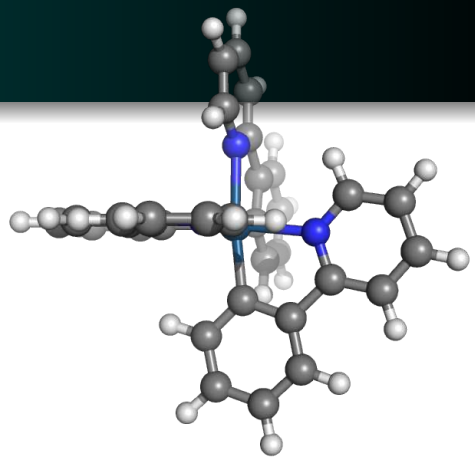


- TDDFT/B3LYP
  - Ir(ppy)$_3$

	E (eV)	State character		d_{exc} (Å)
$2^3A\ (T_1)$	2.74	49% **IL**	38% **MLCT**	4.07
$1^3E\ (T_2, T_3)$	2.77	51% **IL**	37% **MLCT**	3.94
$3^3A\ (T_4)$	2.97	49% **MLCT**	29% **LLCT**	4.40
$2^3E\ (T_5, T_6)$	2.98	48% **MLCT**	31% **LLCT**	4.50
$3^3E\ (T_7, T_8)$	3.10	48% **MLCT**	38% **LLCT**	5.03
$4^3A\ (T_9)$	3.14	47% **MLCT**	38% **LLCT**	5.05

- Smaller exciton size $\rightarrow$ less CT character

Exciton size



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- Smaller exciton size $\rightarrow$ less CT character
- ? What is really going on

Electron/hole densities

Density for the excited electron / excitation hole

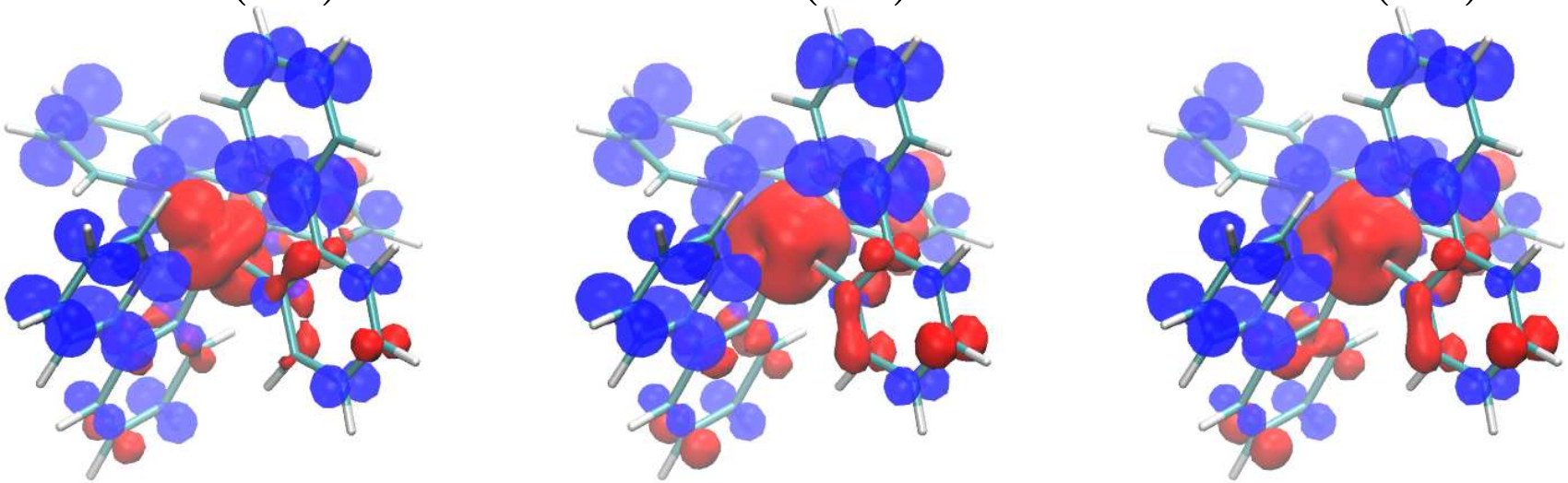
$$\rho_e(r_e) = \int \gamma^{0I}(r_h, r_e)^2 \mathrm{d}r_h$$

$$\rho_h(r_h) = \int \gamma^{0I}(r_h, r_e)^2 \mathrm{d}r_e$$

- Equivalent to weighted sums over NTOs

Electron/hole densities

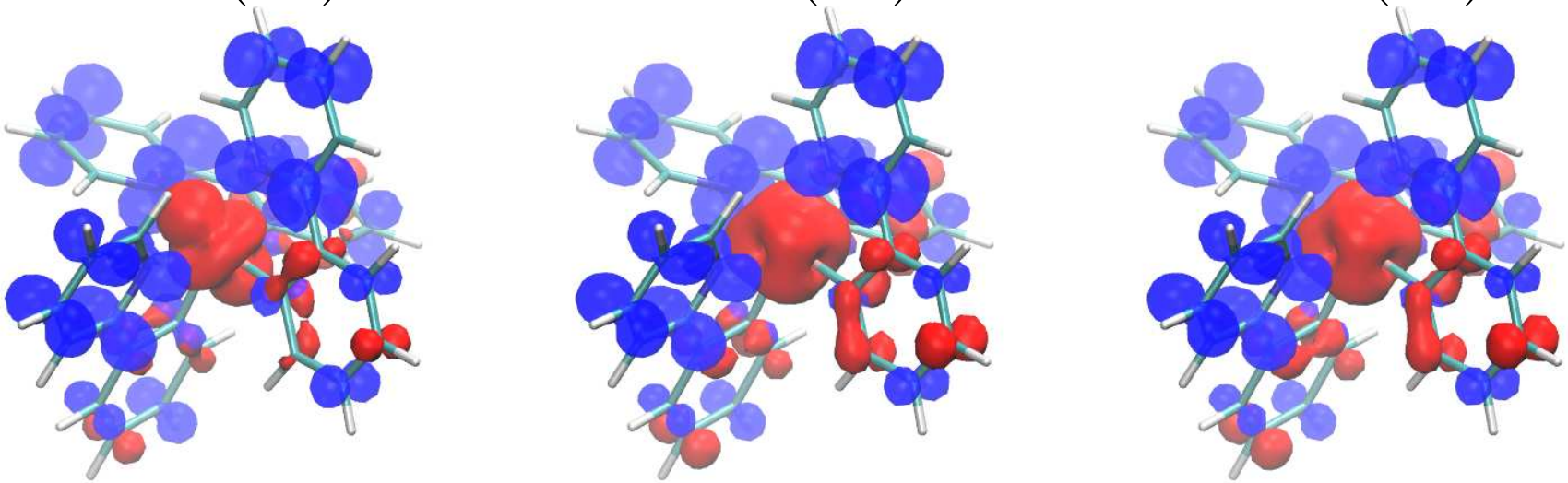
$2^3A\ (T_1)$ $3^3A\ (T_4)$ $4^3A\ (T_9)$



- **Hole** density → centered around Ir
  - Some contributions on phenyl
- **Electron** density → delocalized
  - Mostly on pyridine groups

Electron/hole densities

$2^3A\ (T_1)$ $3^3A\ (T_4)$ $4^3A\ (T_9)$



- **Hole** density → centered around Ir
  - Some contributions on phenyl
- **Electron** density → delocalized
  - Mostly on pyridine groups
- ? Can we learn more

Conditional densities

Conditional density for the excited electron

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

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

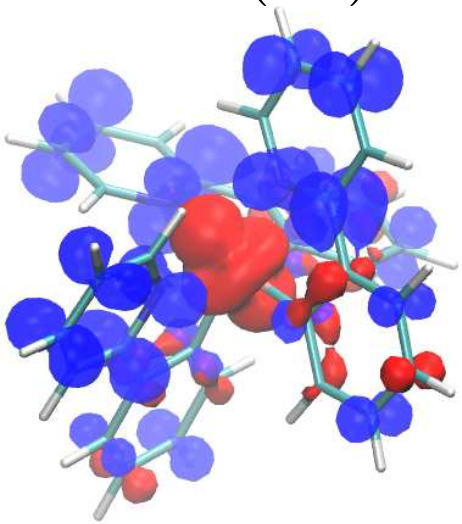
- Evaluated through multiplication of matrix blocks

[1] FP, *ChemPhotoChem* **2019**, DOI: 10.1002/cptc.201900014.

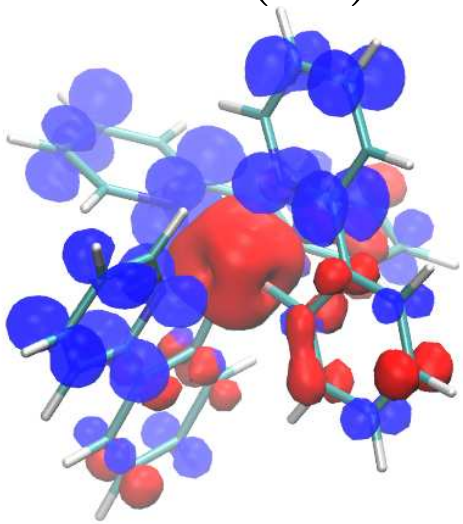
Conditional electron/hole densities

- **Electron** fixed on the ligand in the back

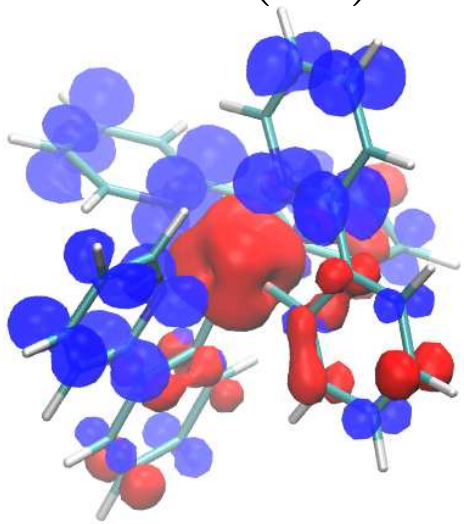
$2^3A\ (T_1)$



$3^3A\ (T_4)$



$4^3A\ (T_9)$



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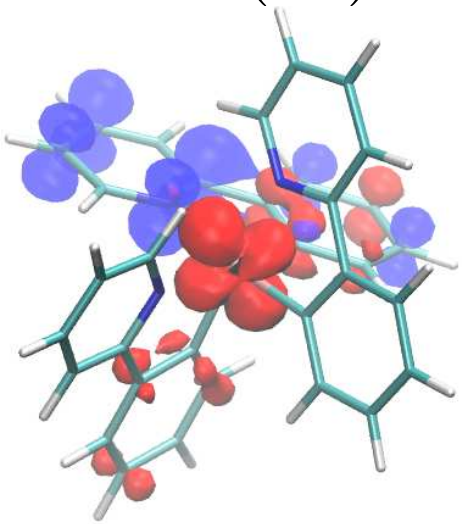
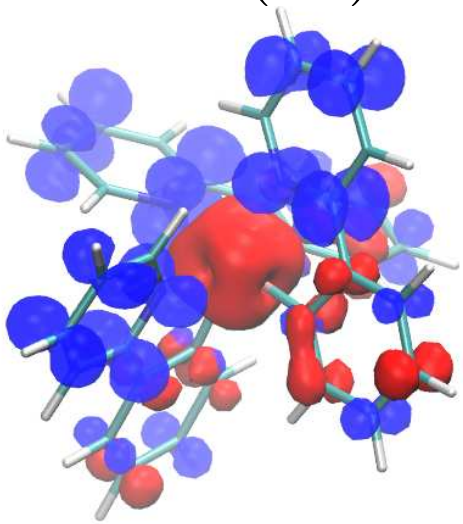


$3^3A\ (T_4)$



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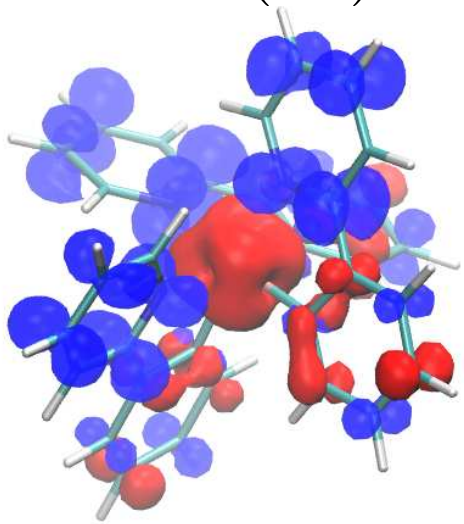

Conditional electron/hole densities

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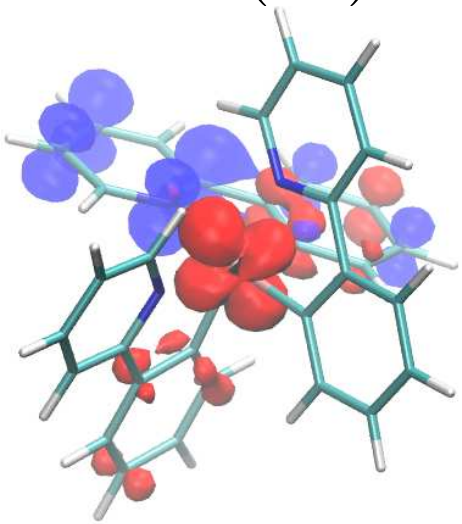
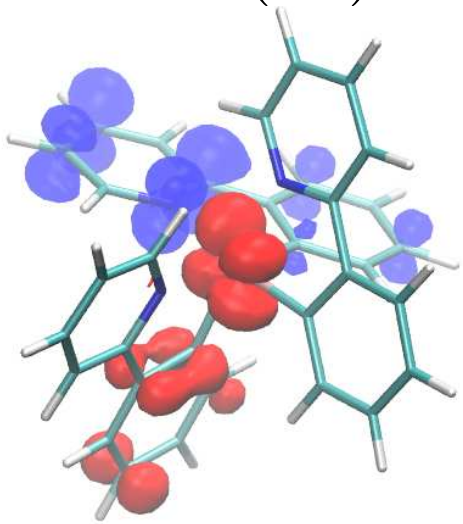
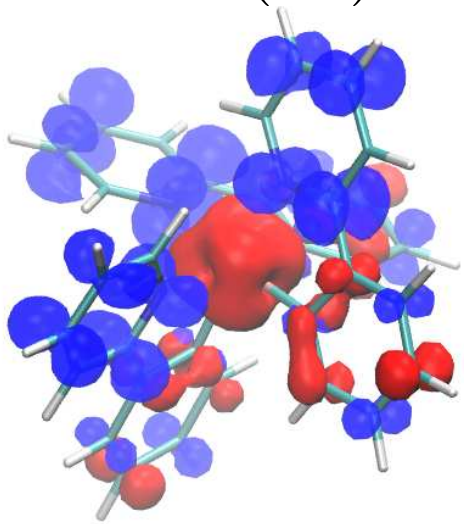


$3^3A\ (T_4)$



$4^3A\ (T_9)$



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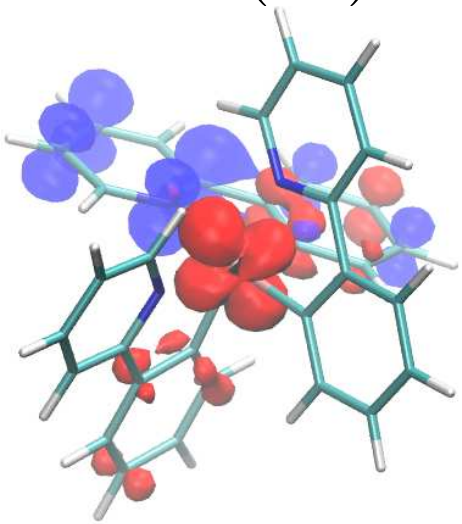

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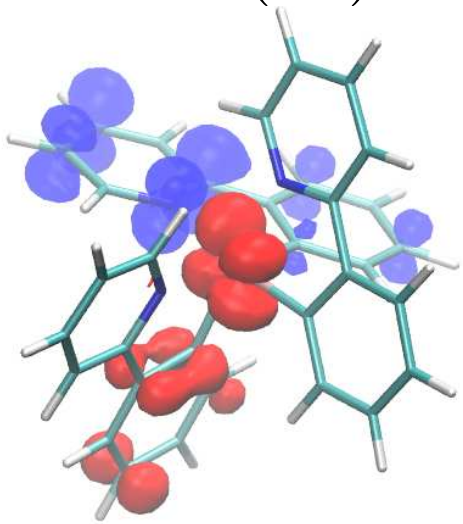

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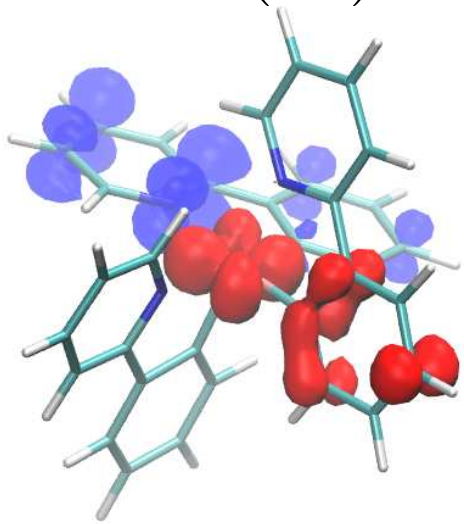

Conditional electron/hole densities

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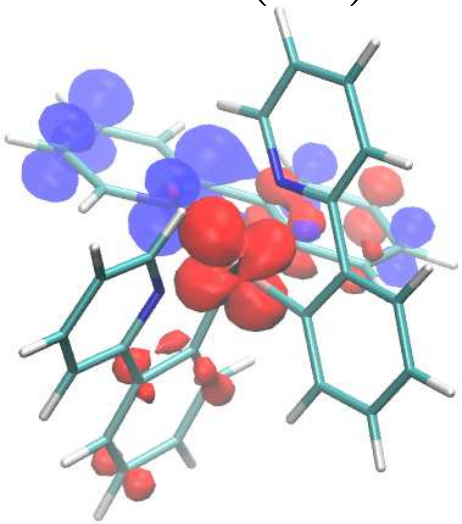
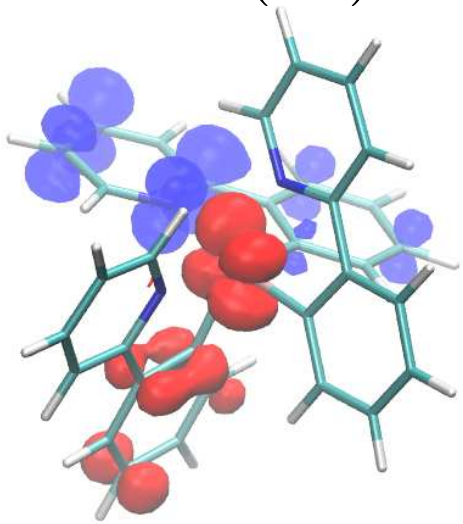


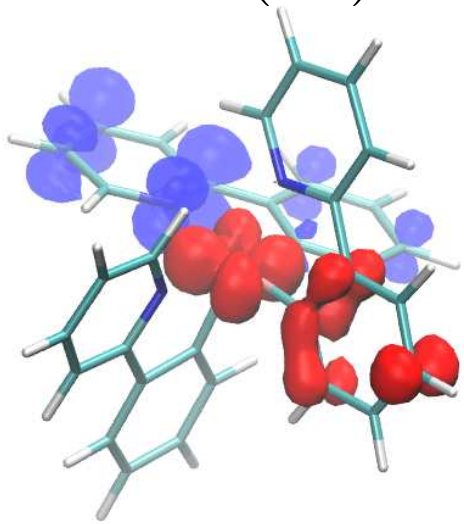
Intraligand

$3^3A\ (T_4)$



"Corner" CT

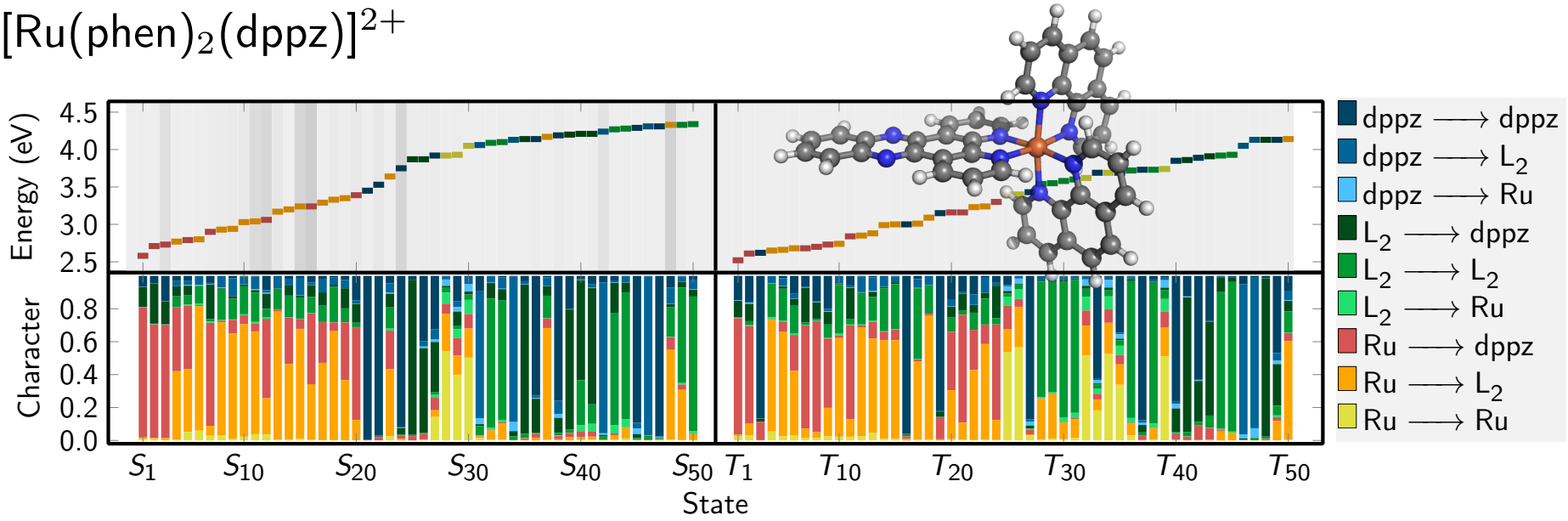
$4^3A\ (T_9)$



"Straight" CT

Outline

$[Ru(phen)_2(dppz)]^{2+}$



[1] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

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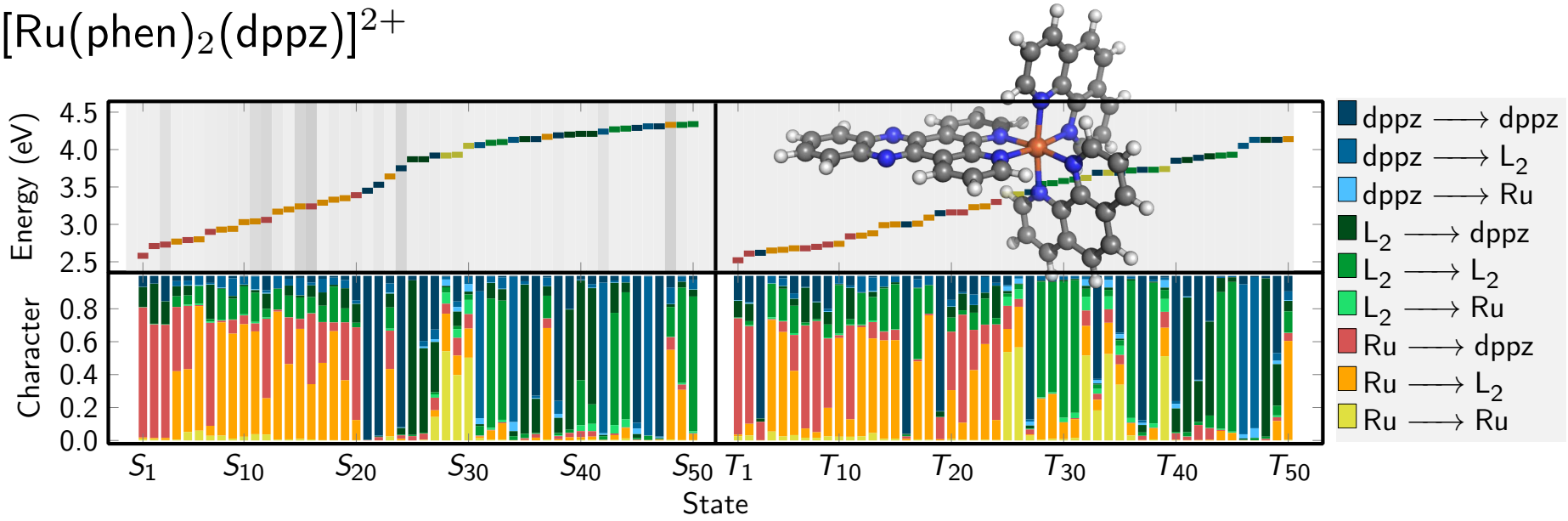
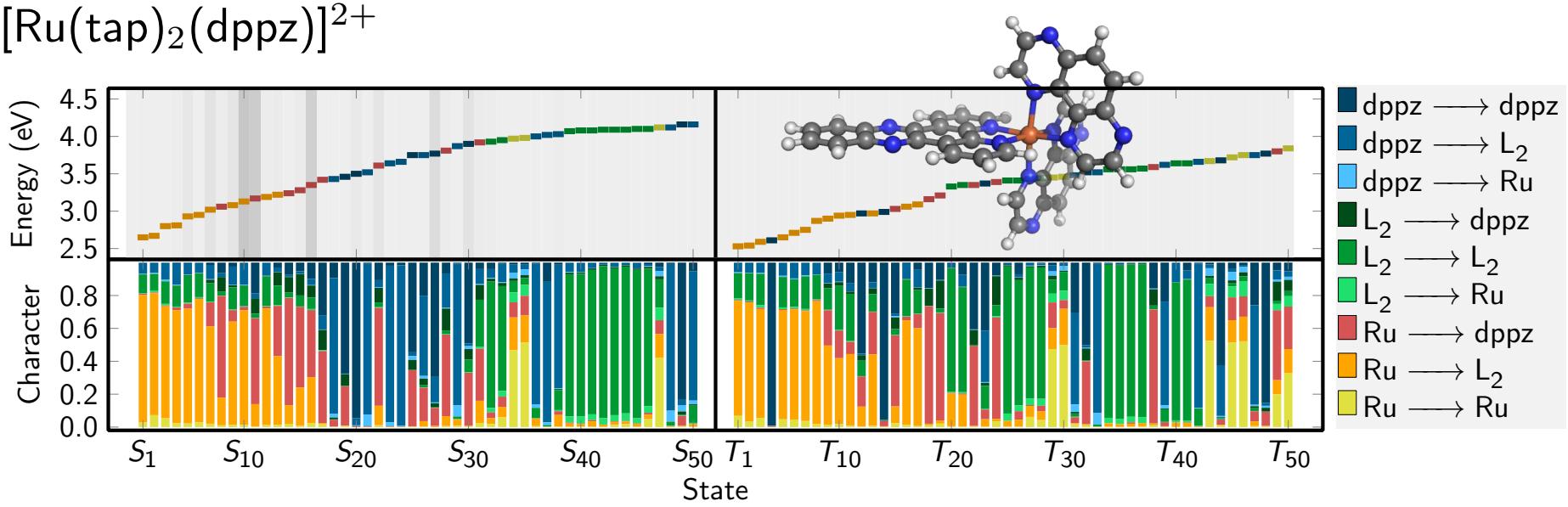
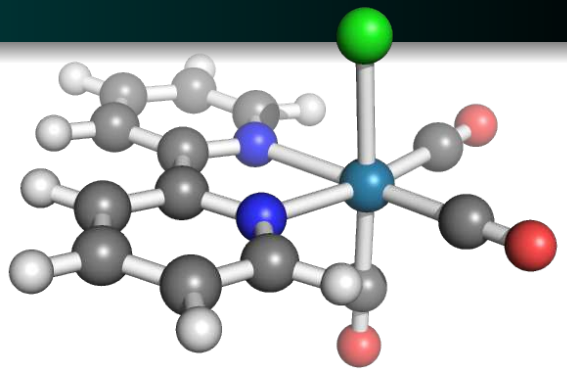


$[Ru(tap)_2(dppz)]^{2+}$

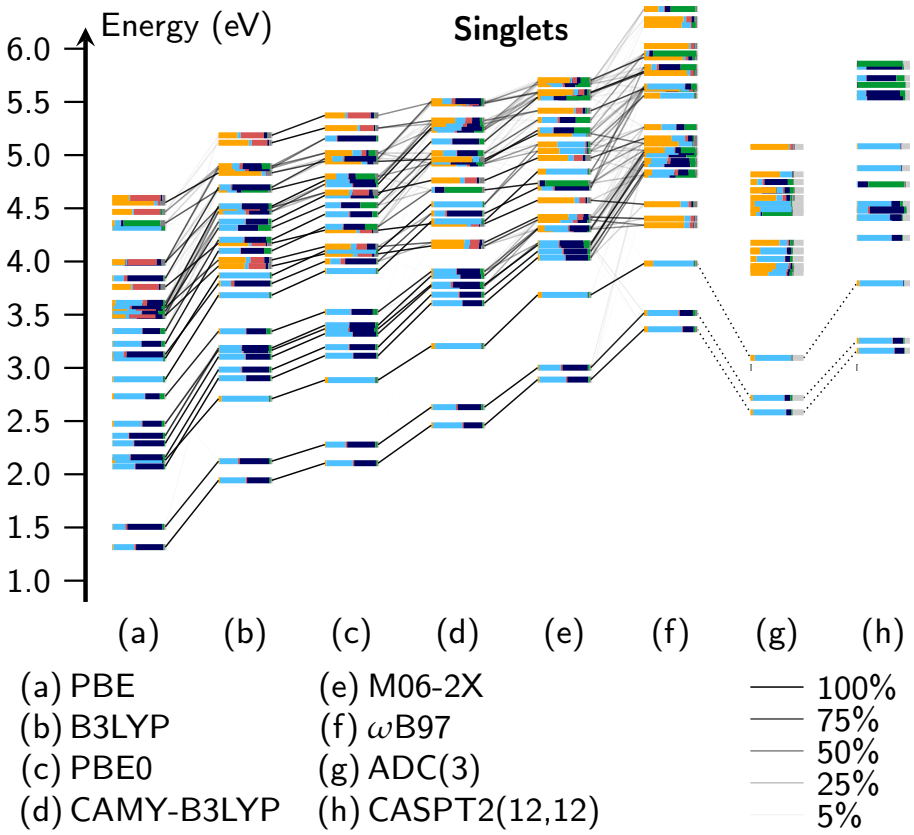


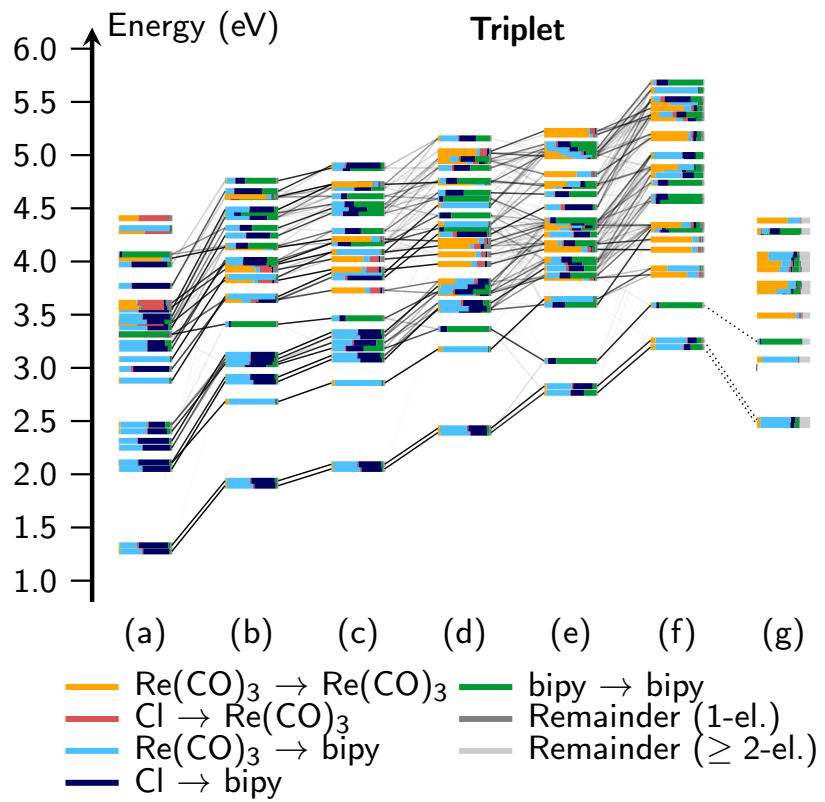
[1] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

Method evaluation



- Re(Cl)(CO)$_3$(bipy)
  - Comparison of TDDFT and wavefunction based methods

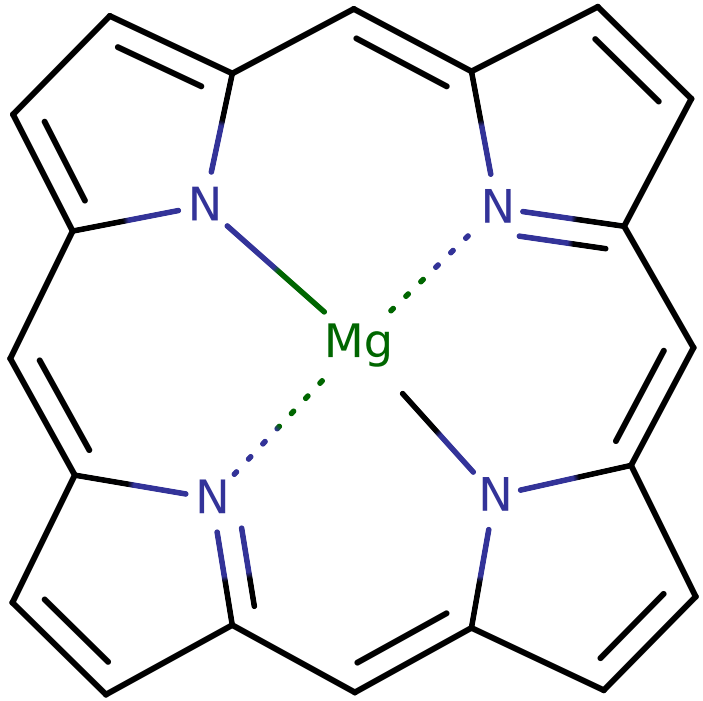




[1] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

Porphyrin

- Mg porphyrin
- Comparison of different methods
  - ADC, EOM-CC
  - TDDFT
- Energies, oscillator strengths
- Exciton sizes, electron-hole correlation coefficents



[1] S. A. Mewes, FP, A. Krylov, A. Dreuw, *JCTC* **2018**, 14, 710.

Exciton Analysis

Electron-hole correlation coefficient

$$R_{eh} = \frac{\mathrm{COV}(r_h, r_e)}{\sigma_h \sigma_e}$$

- Interpret electron-hole distribution as a distribution of two random variables

→ Compute **correlation coefficient**

- Interpretation
  - $R_{eh} \approx 0 \rightarrow$ Electron and hole are independent
  - $R_{eh} > 0 \rightarrow$ Bound exciton (Coulomb **attraction**)
  - $R_{eh} < 0 \rightarrow$ Dynamic avoidance (exchange **repulsion**)

[1] FP, B. Thomitzni, S. Bäppler, J. Wenzel, D. Rehn, M. Wormit, A. Dreuw, *JCC* **2015**, 36, 1609.

Porphyrin

- First excited Q state
- Compare energies, f_{osc}, d_{exc} and R_{eh}
  - Main qualitative difference: R_{eh}

Method	ΔE (eV)	f_{osc}	d_{exc} (Å)	R_{eh}
exp.	2.07[a]			
ADC(3)/SV(P)	**1.996**	0.008	4.58	0.179
ADC(2)/SV(P)	2.382	0.007	4.64	0.169
EOM-CCSD/SV(P)	2.344	0.001	4.58	0.167
EOM-CCSD/cc-pVDZ	2.345	0.007	4.62	0.158
EOM-CCSD/cc-pVTZ	2.302	0.007	4.65	0.158
BLYP/SV(P)	2.265	0	**5.17**	**−0.048**
B3LYP/SV(P)	2.388	0.001	**5.03**	**0.012**
CAM-B3LYP/SV(P)	2.423	0.004	4.81	0.090
CIS/SV(P)	2.432	0.038	4.68	0.160

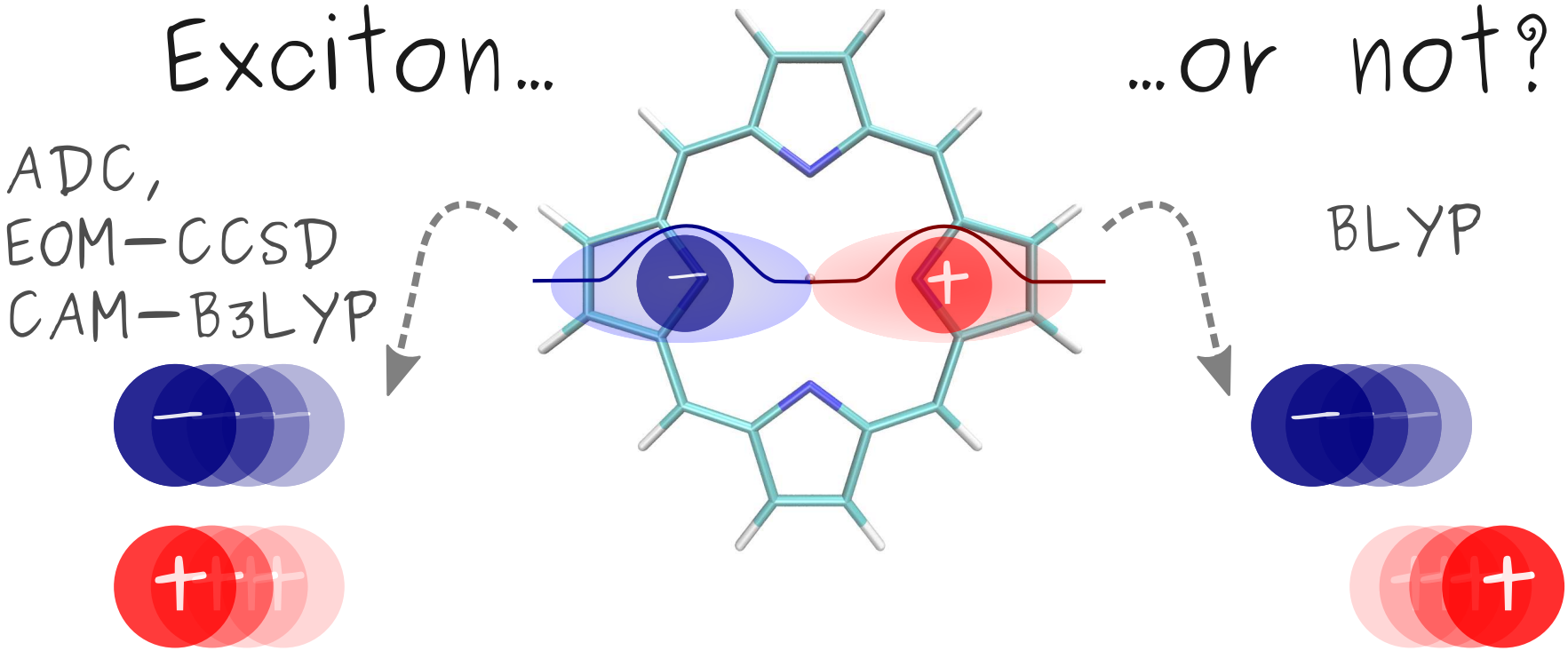
[1] S. A. Mewes, FP, A. Krylov, A. Dreuw, *JCTC* **2018**, 14, 710.

Porphyrin

Method	state	ΔE (eV)	f_{osc}	d_{exc} (Å)	R_{eh}
exp.	Q	2.07[a]			
BLYP	S_1	2.271	0	**5.20**	**−0.046**
B3LYP	S_1	2.393	0	5.05	0.011
CAM-B3LYP	S_1	2.430	0.001	4.83	0.088
ADC(2)[b]	1^1B_{2u}	2.382	0.007	4.64	0.136
exp.	B	3.05[a]			
BLYP	S_3	3.156	0.016	**5.55**	**−0.101**
B3LYP	S_4	**3.676**	0.110	5.14	0.038
CAM-B3LYP	S_3	**4.098**	1.123	4.65	0.172
ADC(2)[b]	2^1B_{2u}	3.487	1.357	4.88	0.075
exp.	N	3.97[a]			
BLYP	S_{10}	**3.441**	0.064	**5.47**	**−0.059**
B3LYP	S_8	3.947	0.593	5.04	0.042
CAM-B3LYP	S_7	**4.402**	0.992	4.93	0.092
ADC(2)[b]	3^1B_{2u}	3.993	0.007	4.89	0.105

[1] S. A. Mewes, FP, A. Krylov, A. Dreuw, *JCTC* **2018**, 14, 710.

Porphyrin



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Summary - Transition metal complexes

- **Automatic assignment** of excited states

→ High-throughput analysis

[1] J. J. Nogueira, FP, L. González, *Chem. Sci.* **2017**, 8, 5682.
[2] S. A. Mewes, FP, A. Dreuw, *JPCL* **2017**, 8,1205.

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- Similar: Analysis of excitonic delocalisation and charge transfer for **interacting chromophores**[1]

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- **Benchmarking** of computational methods

→ Reveals some *inconvenient truths*

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- Similar: Analysis of excitonic delocalisation and charge transfer for **interacting chromophores**[1]

- **Benchmarking** of computational methods

→ Reveals some *inconvenient truths*

- Consistent with expectations for TDDFT[2]

[1] J. J. Nogueira, FP, L. González, *Chem. Sci.* **2017**, 8, 5682.
[2] S. A. Mewes, FP, A. Dreuw, *JPCL* **2017**, 8,1205.

Outline

Outlook

- Excited states of conjugated polymers
  - Many electronic configurations

[1] FP, *ChemPhotoChem* **2019**, DOI: 10.1002/cptc.201900014.

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

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Outlook

- Excited states of conjugated polymers
  - Many electronic configurations

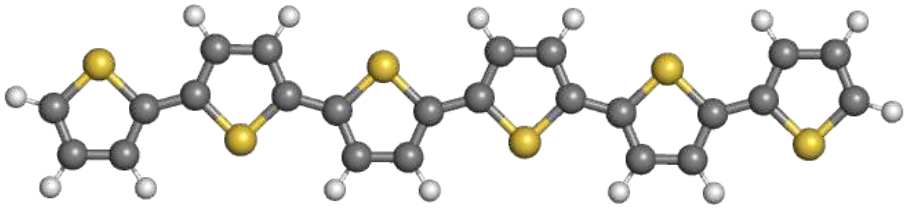
? Can we **visualise** the ensuing **electron correlation** effects

→ **Conditional electron densities**

[1] FP, *ChemPhotoChem* **2019**, DOI: 10.1002/cptc.201900014.

Oligothiophene

- Oligothiophene

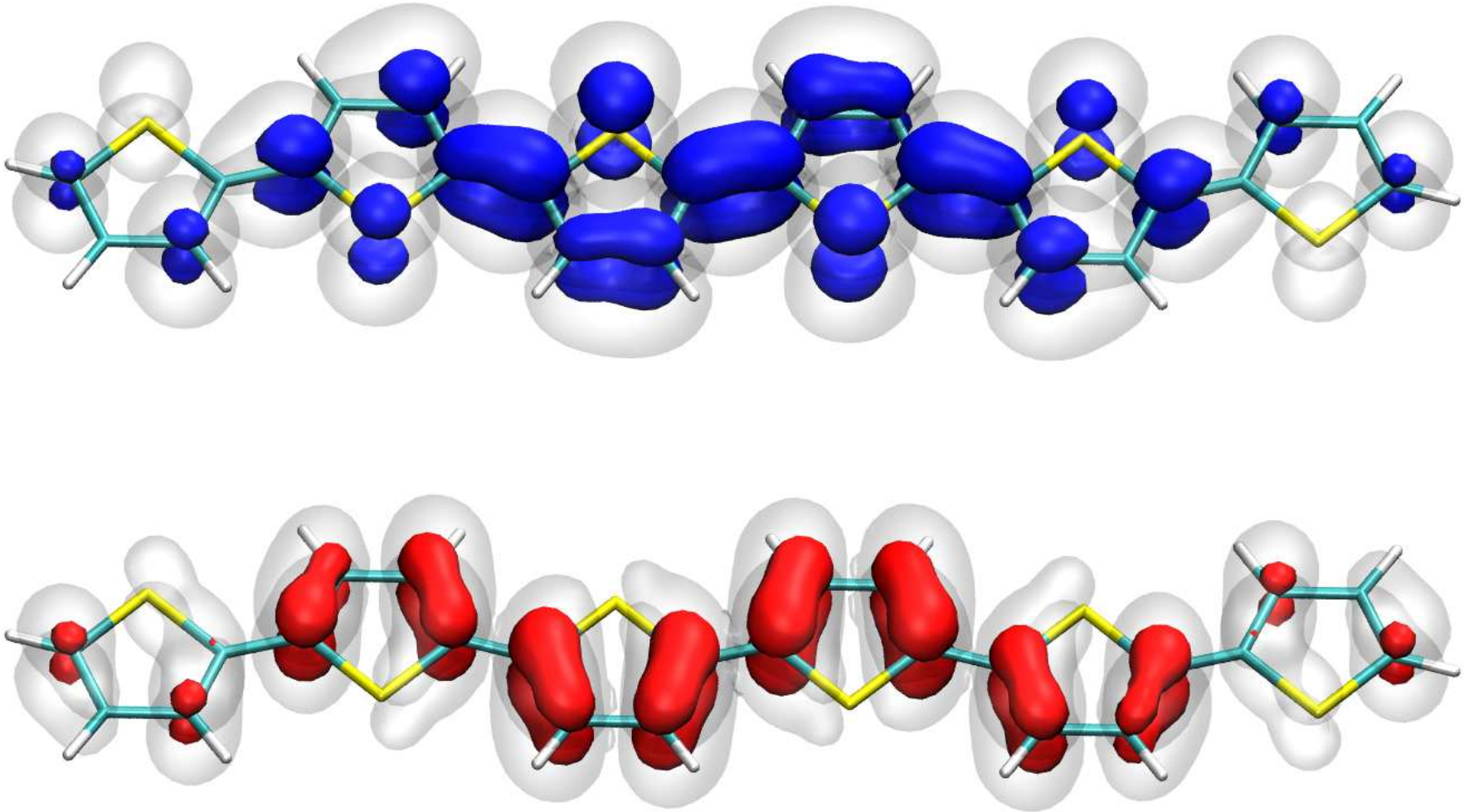


  - Prototypical conjugated polymer

- CAM-B3LYP computations

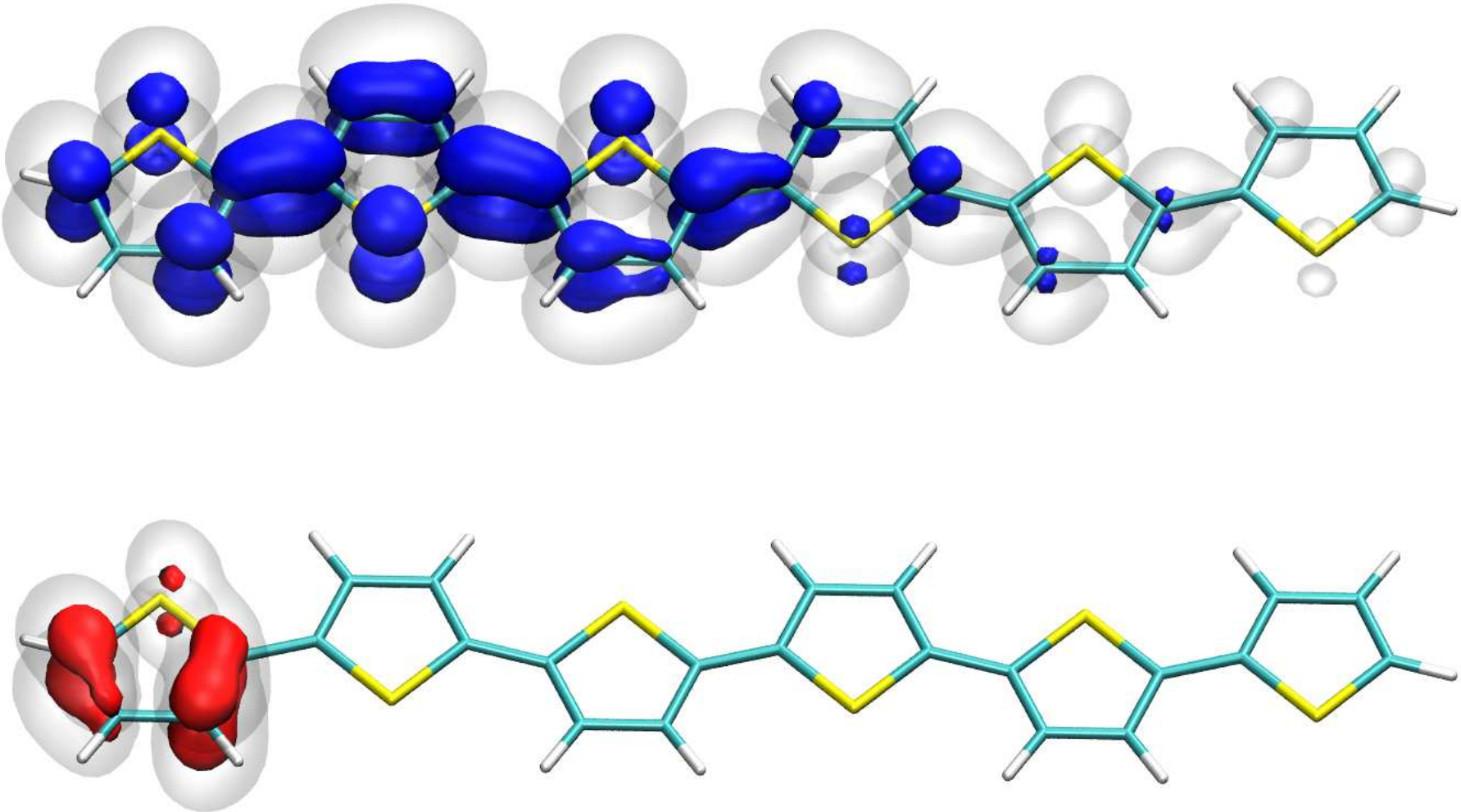
Oligothiophene

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



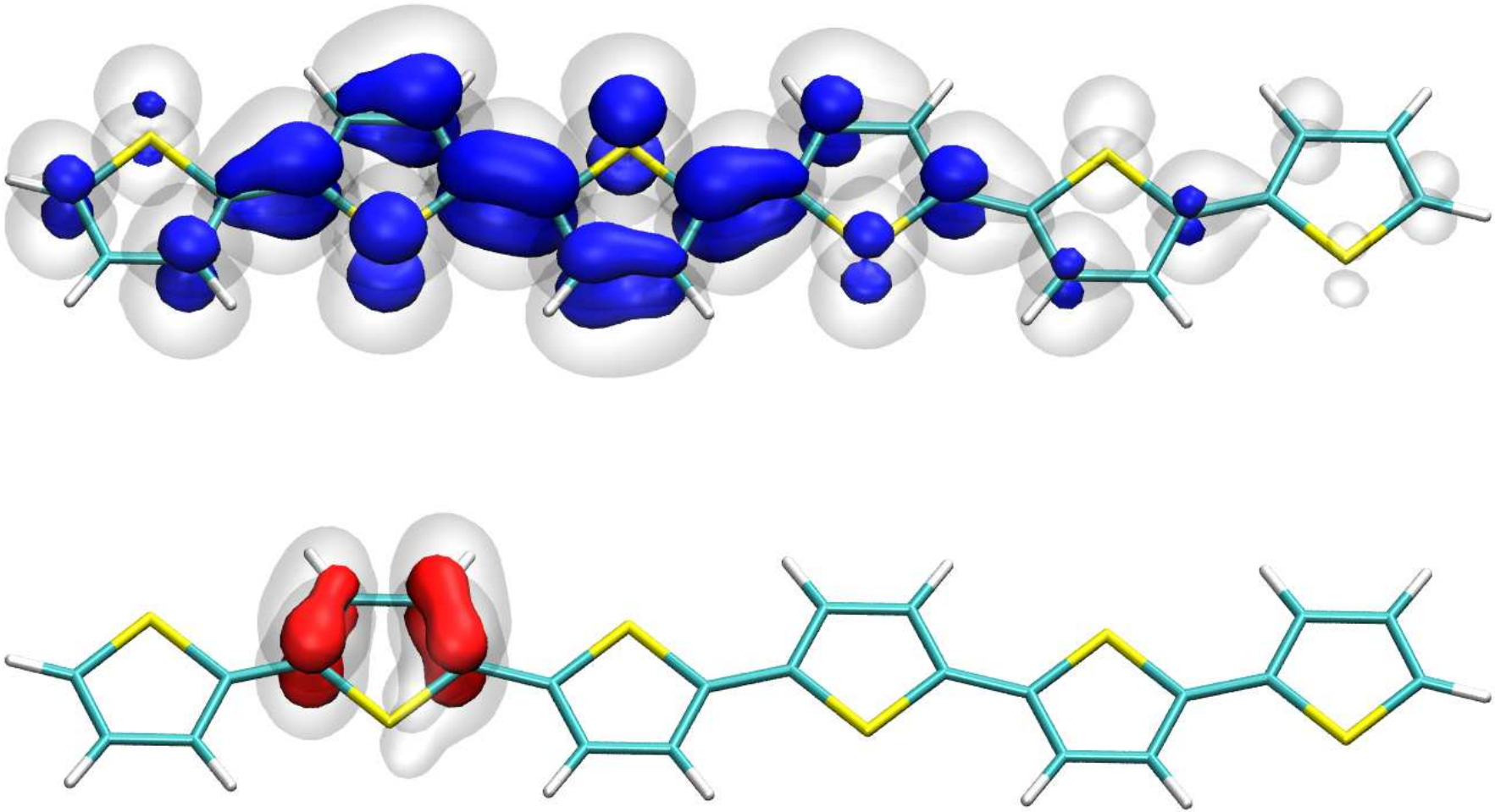
Oligothiophene

- S_1 state
  - **Conditional densities**



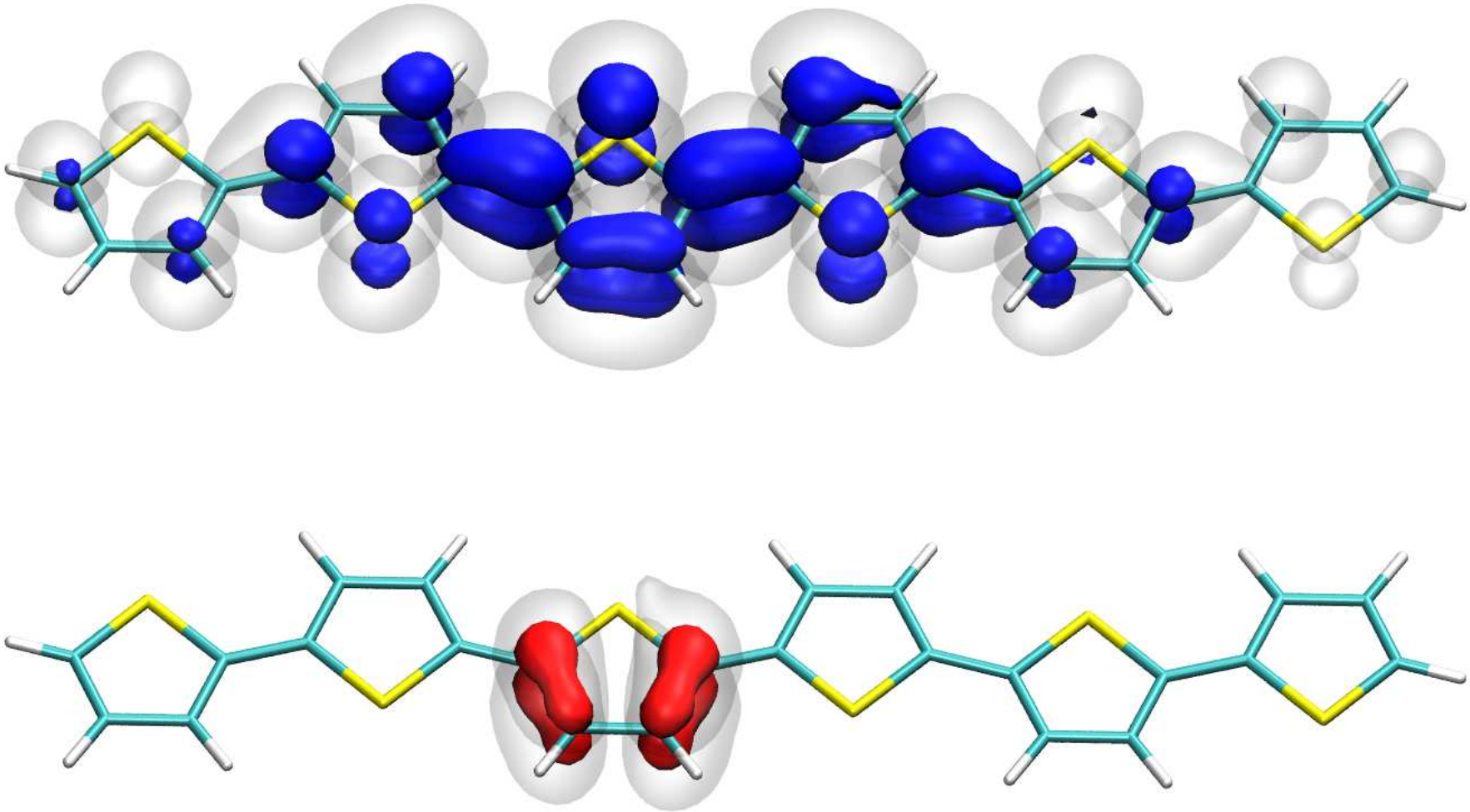
Oligothiophene

- S_1 state
  - **Conditional densities**



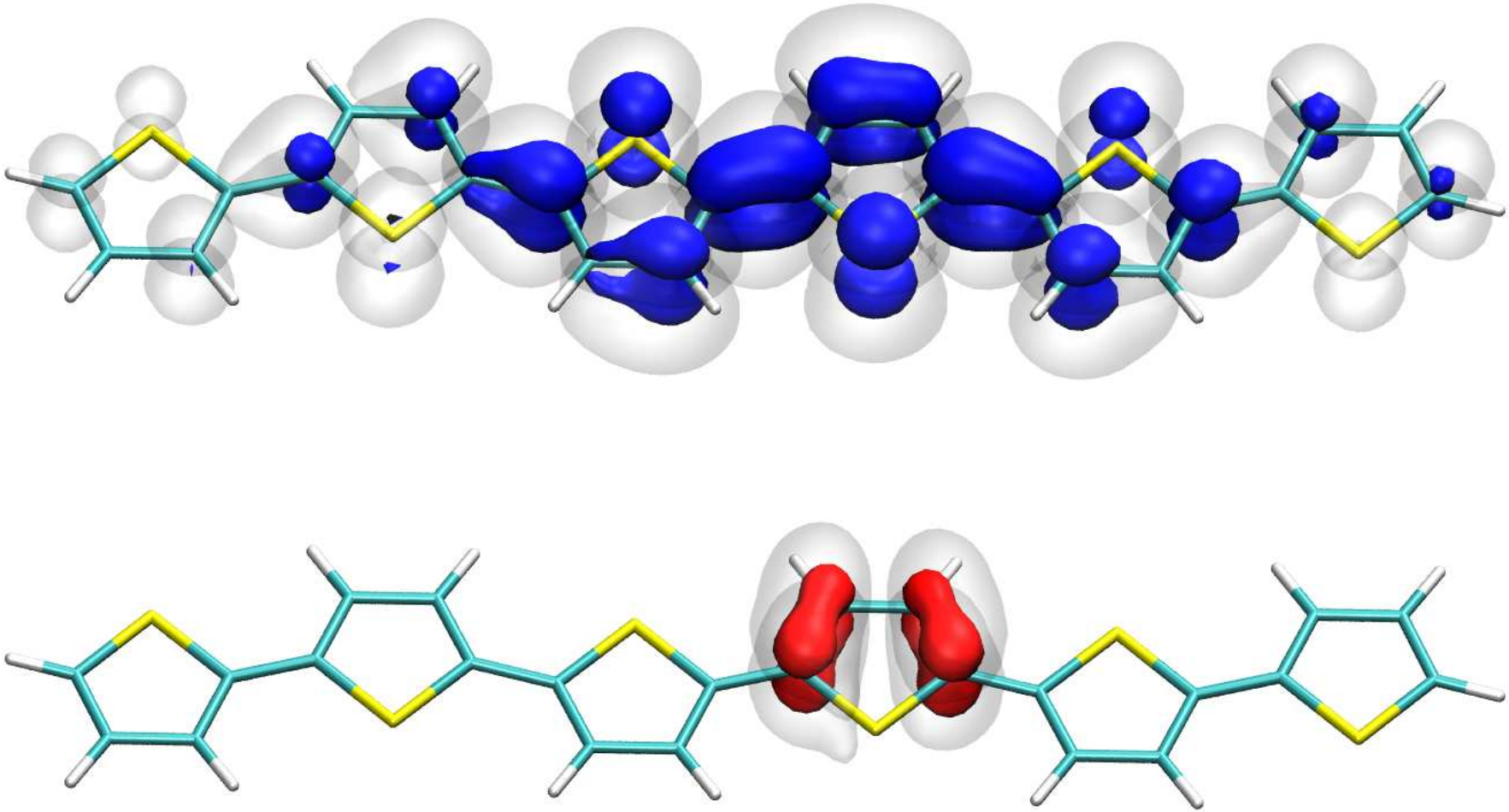
Oligothiophene

- S_1 state
  - **Conditional densities**



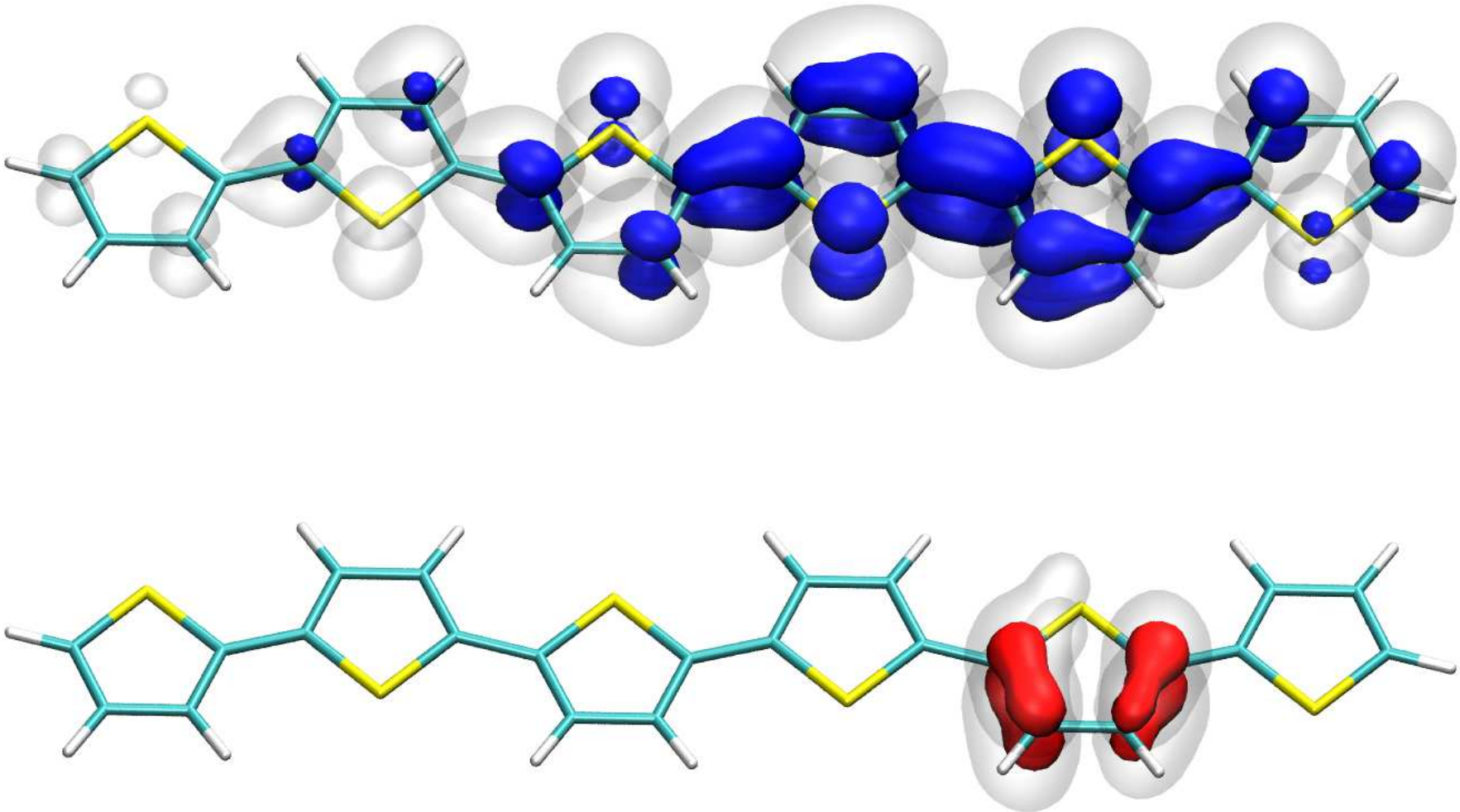
Oligothiophene

- S_1 state
  - **Conditional densities**



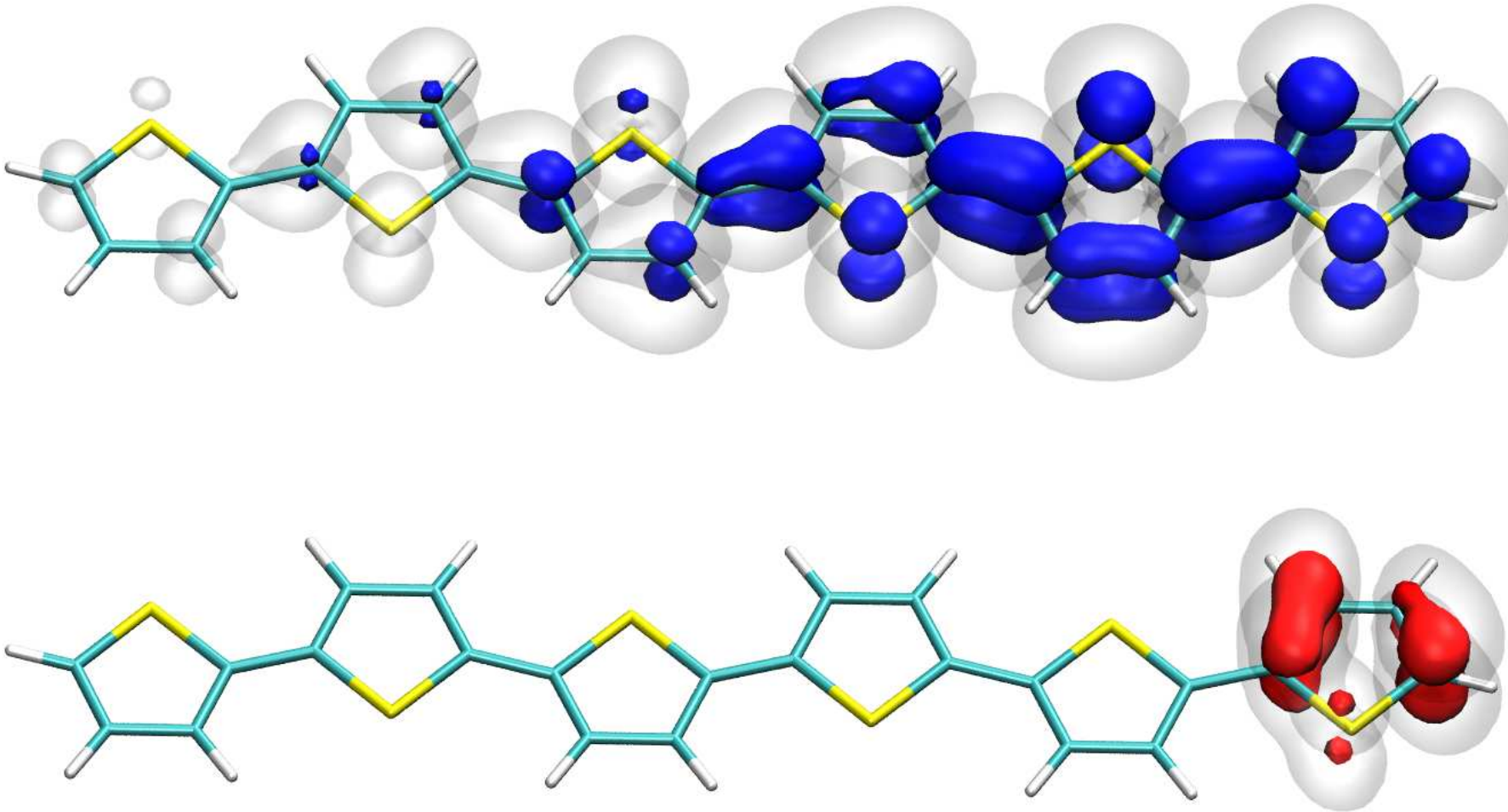
Oligothiophene

- S_1 state
  - **Conditional densities**



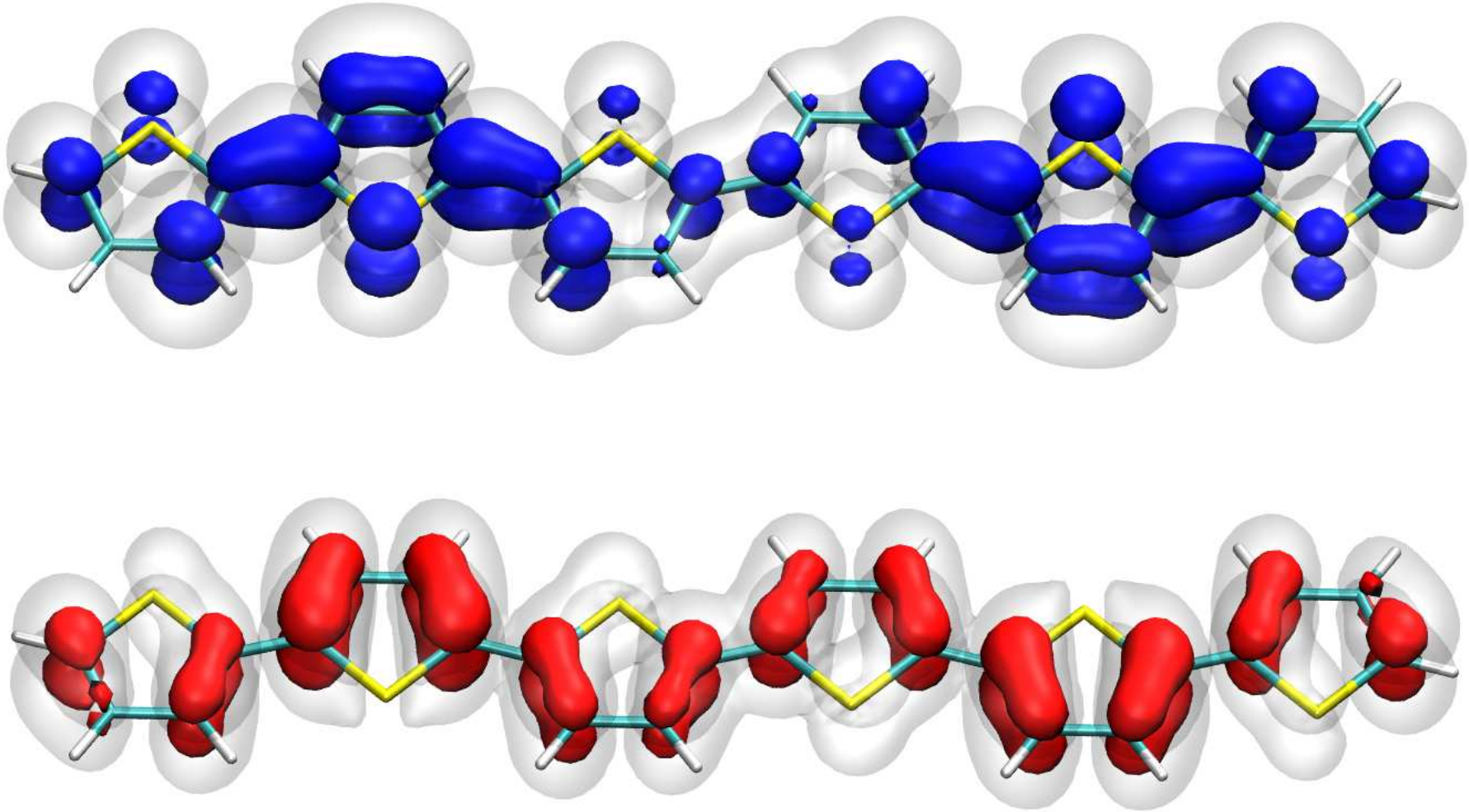
Oligothiophene

- S_1 state
  - **Conditional densities**



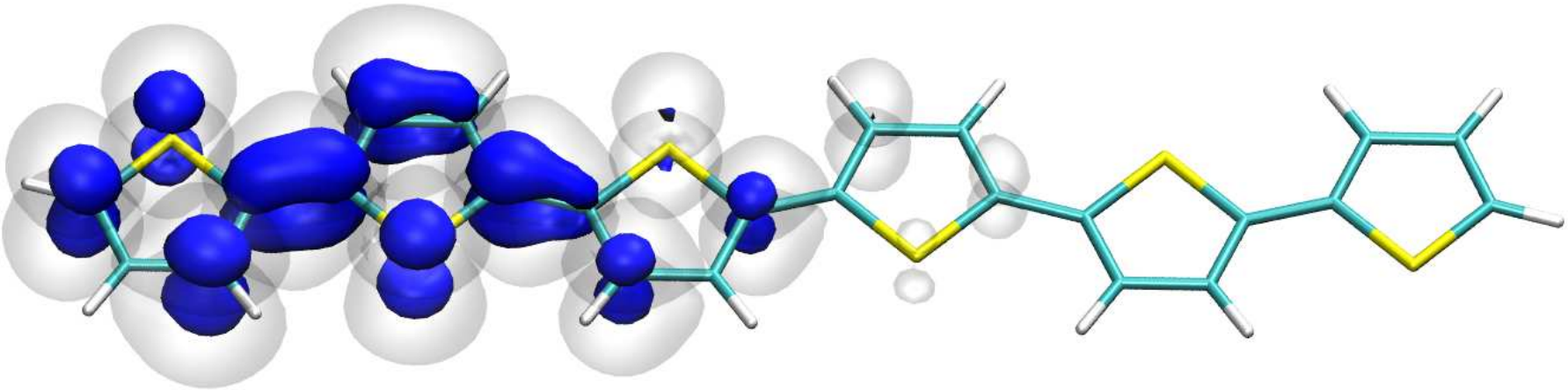
Oligothiophene

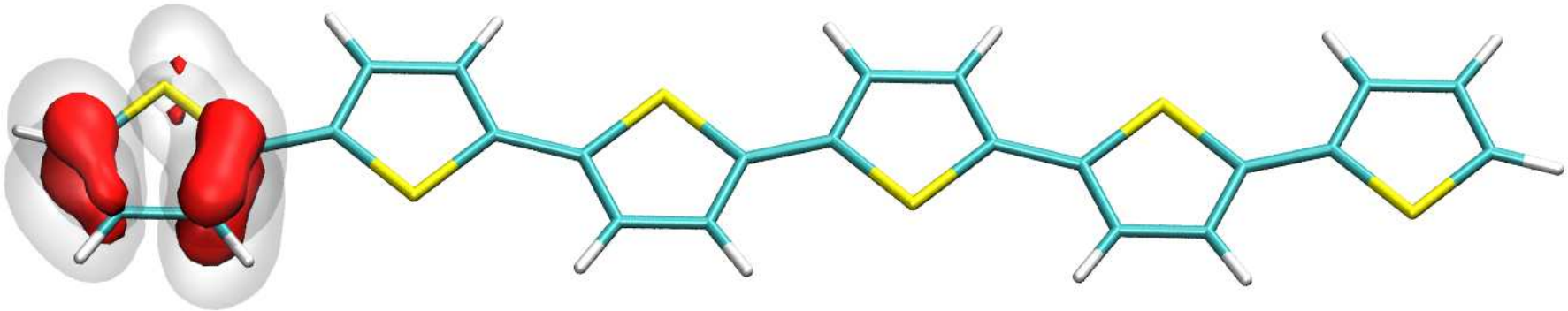
- S_2 state
  - Overall **hole** and **electron** densities



Oligothiophene

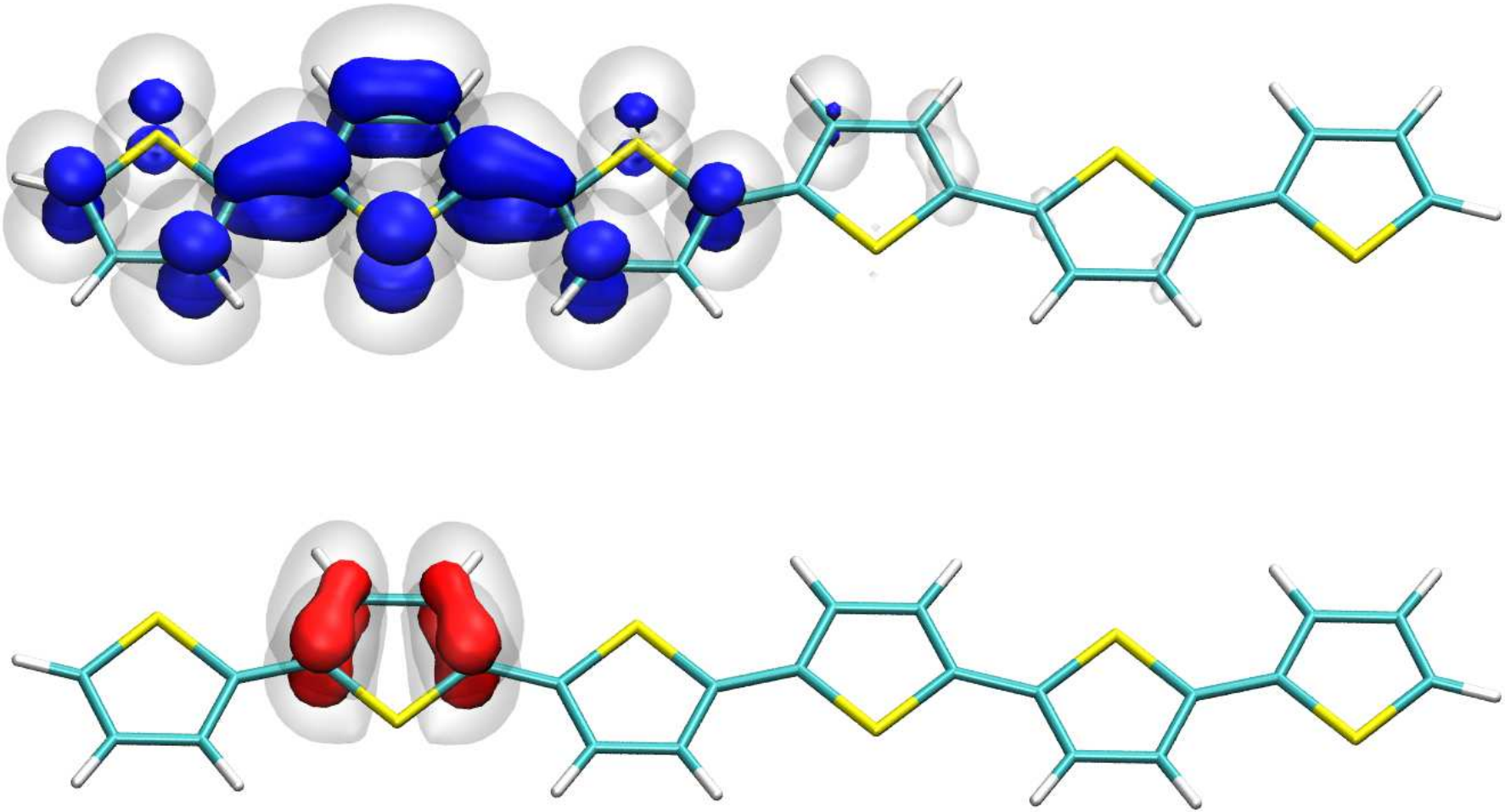
- S_2 state
  - **Conditional densities**





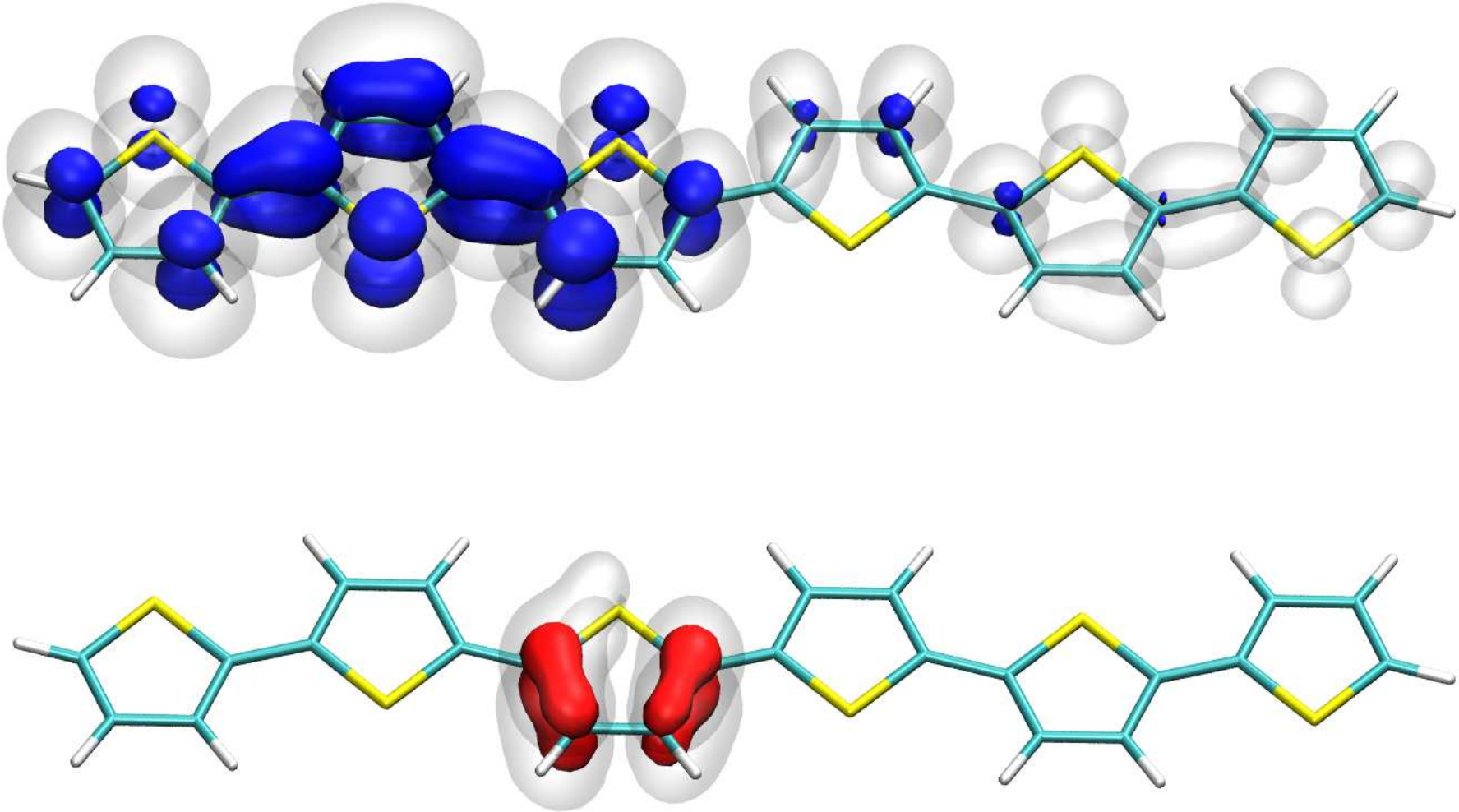
Oligothiophene

- S_2 state
  - **Conditional densities**



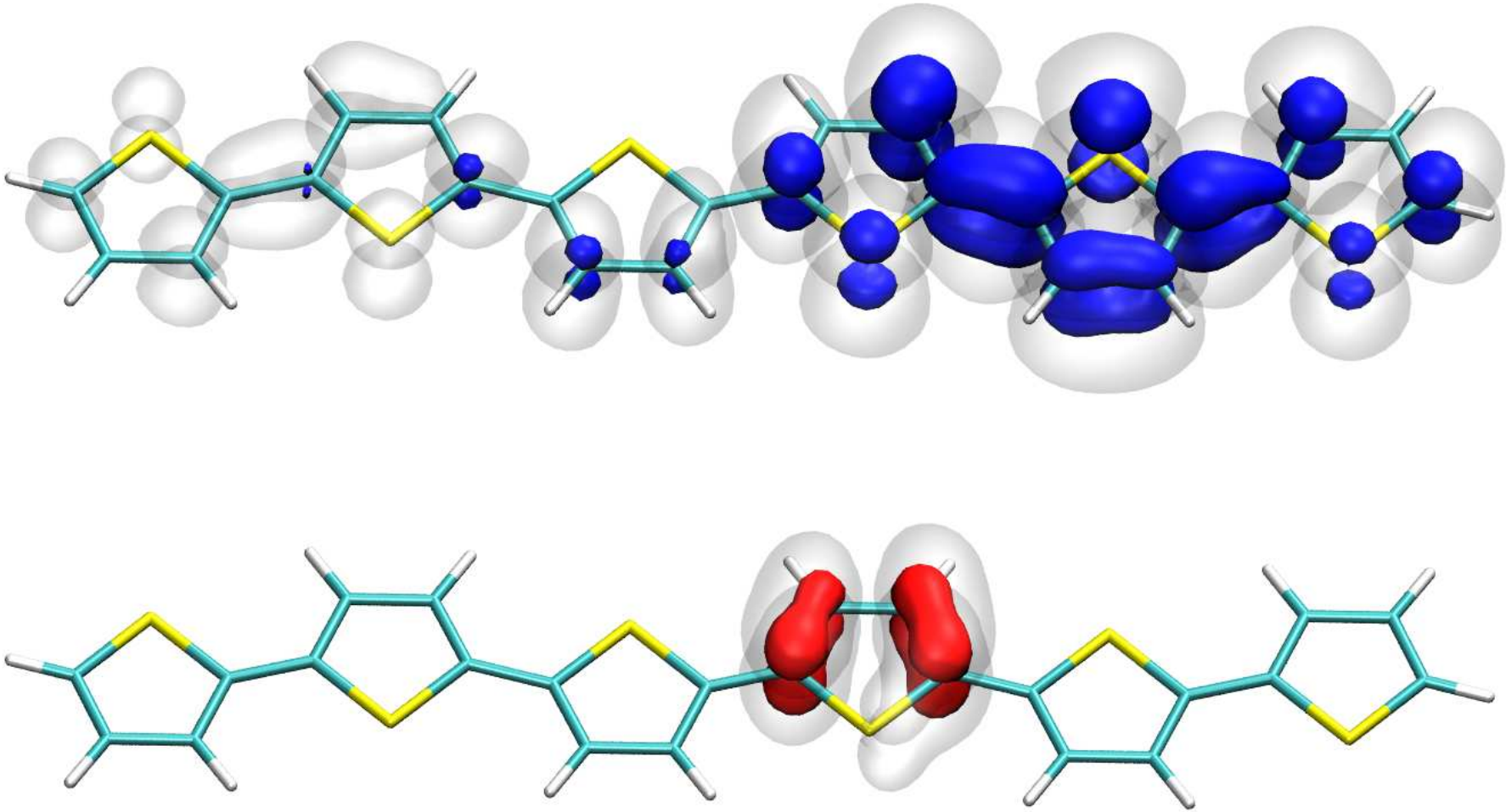
Oligothiophene

- S_2 state
  - **Conditional densities**



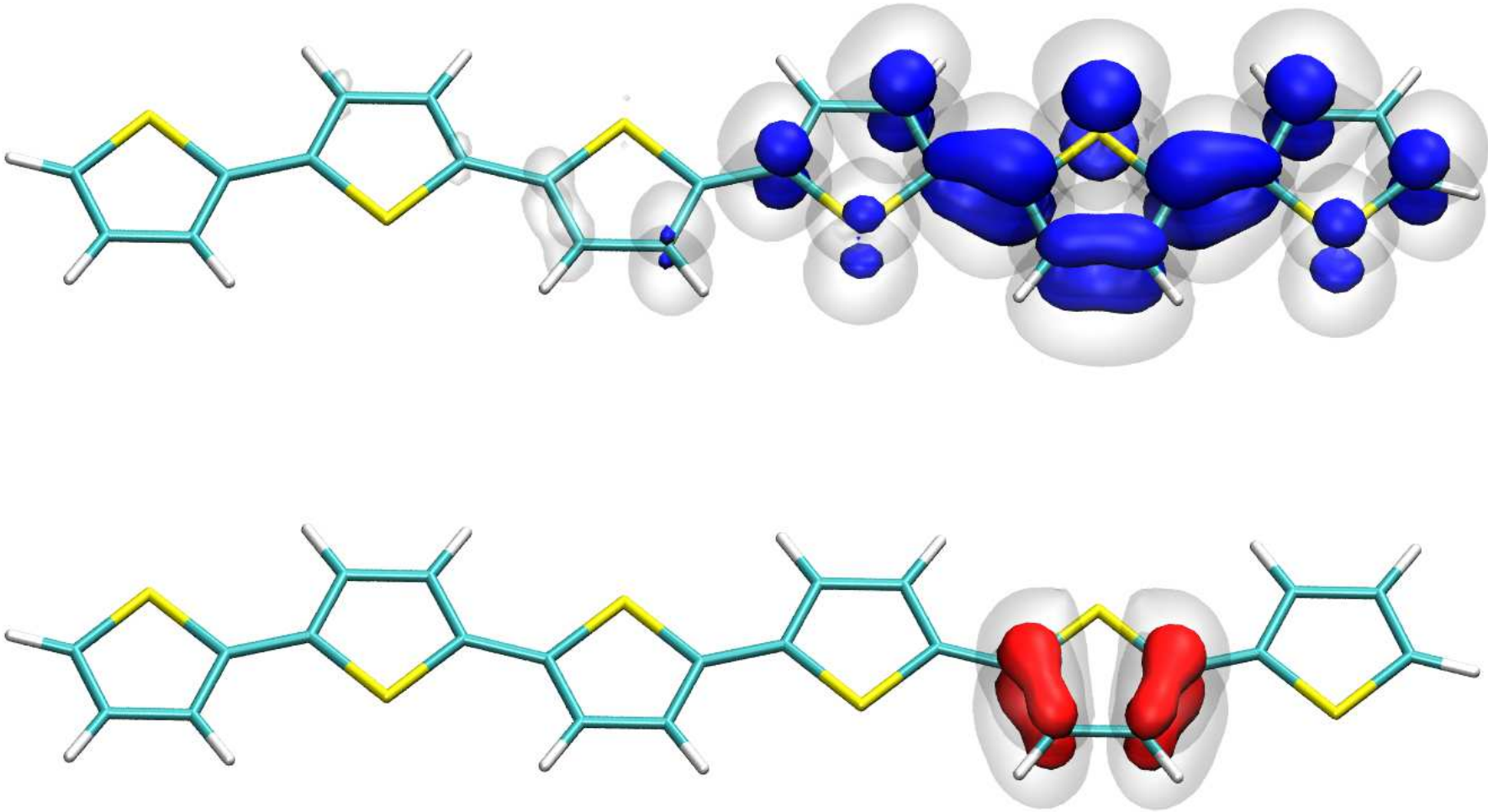
Oligothiophene

- S_2 state
  - **Conditional densities**



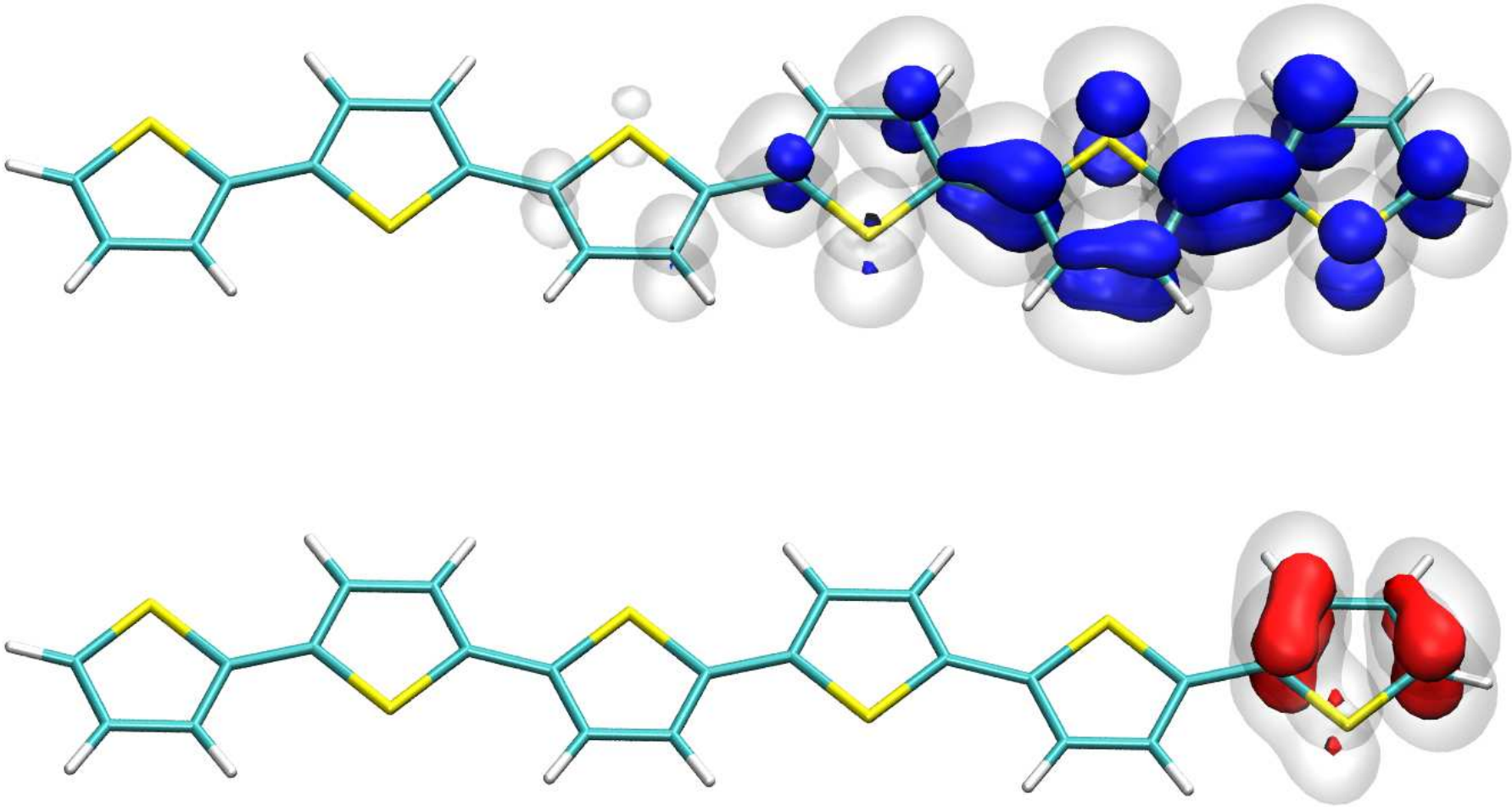
Oligothiophene

- S_2 state
  - **Conditional densities**



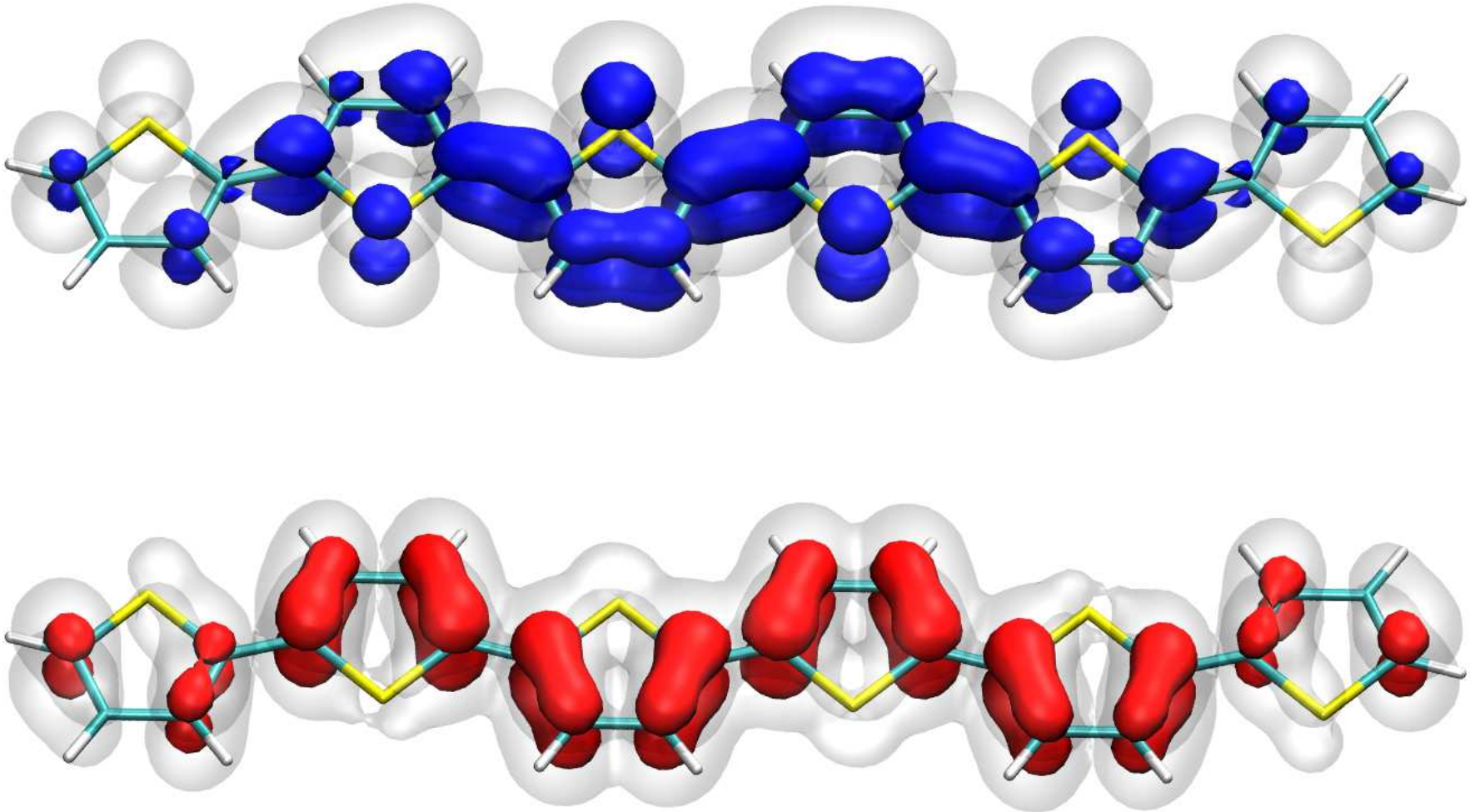
Oligothiophene

- S_2 state
  - **Conditional densities**



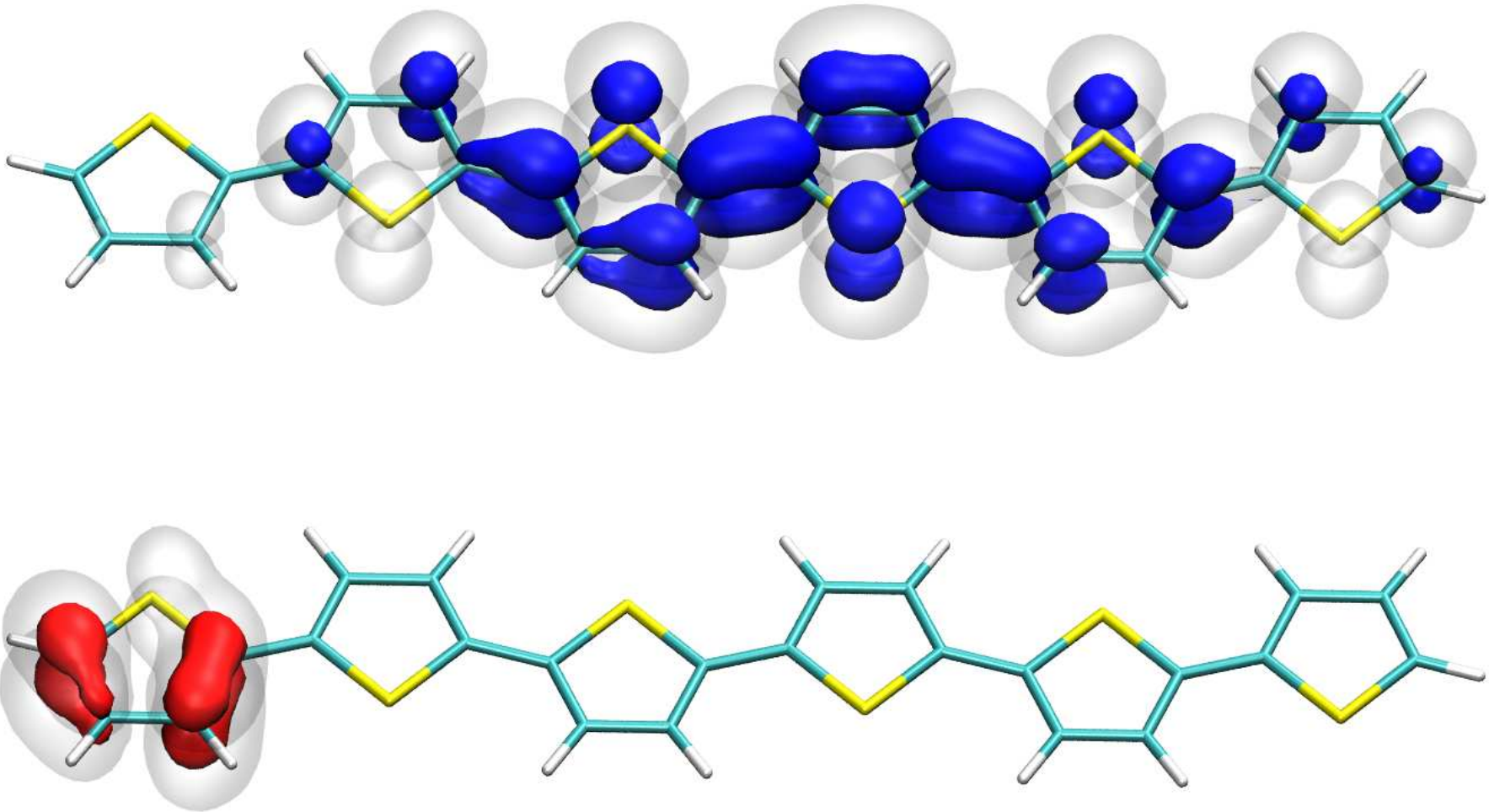
Oligothiophene

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



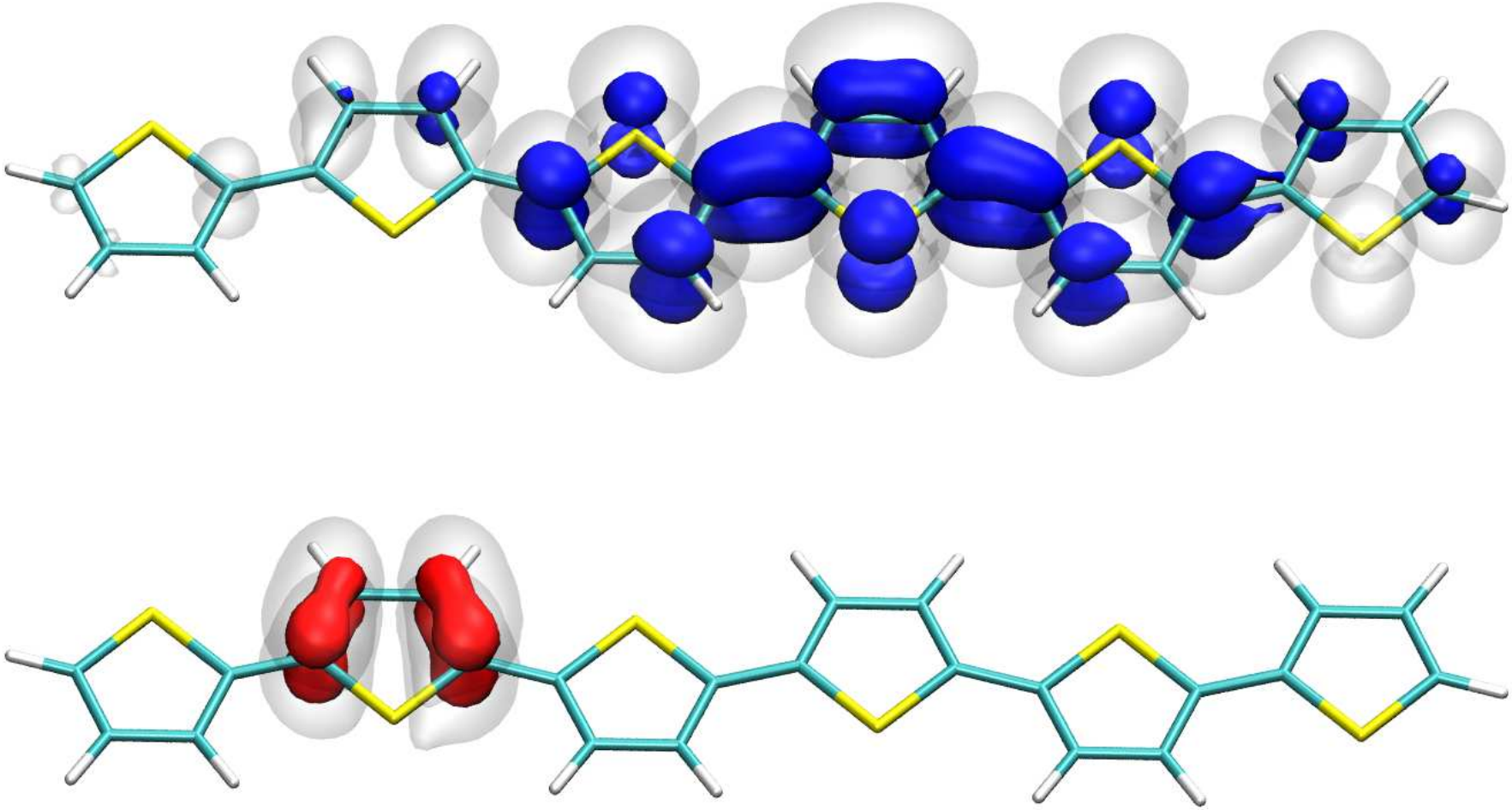
Oligothiophene

- S_3 state
  - **Conditional densities**



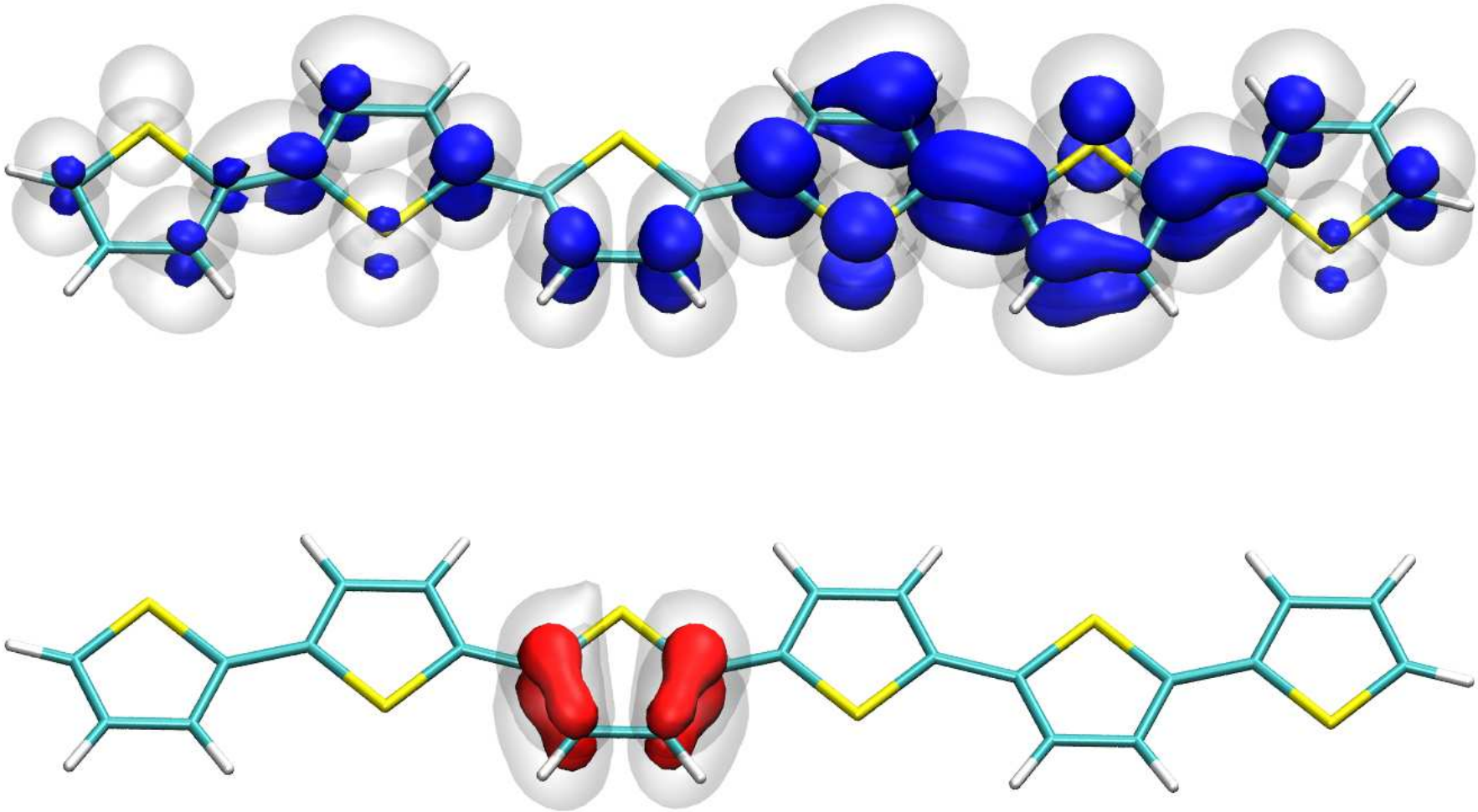
Oligothiophene

- S_3 state
  - **Conditional densities**



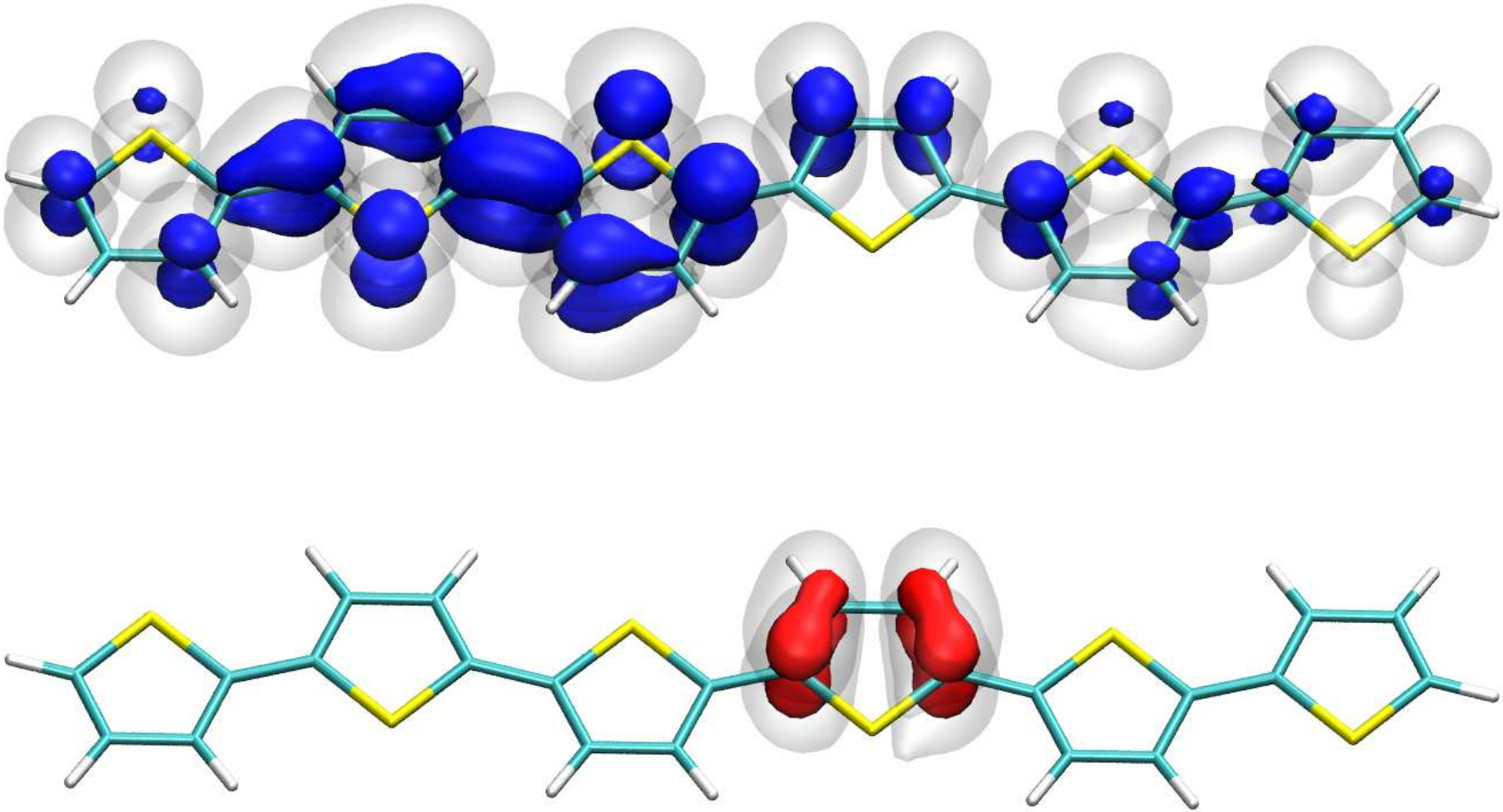
Oligothiophene

- S_3 state
  - **Conditional densities**



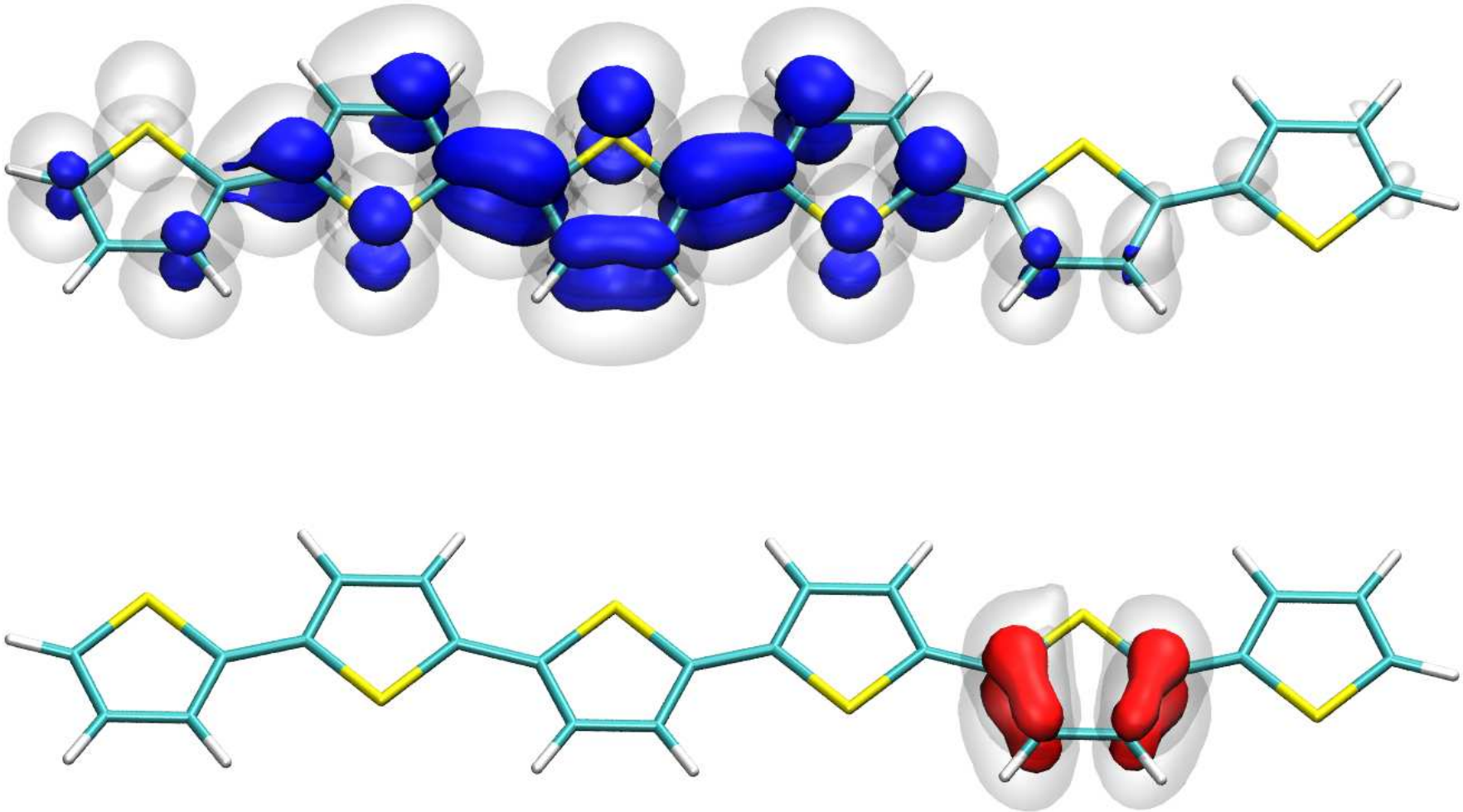
Oligothiophene

- S_3 state
  - **Conditional densities**



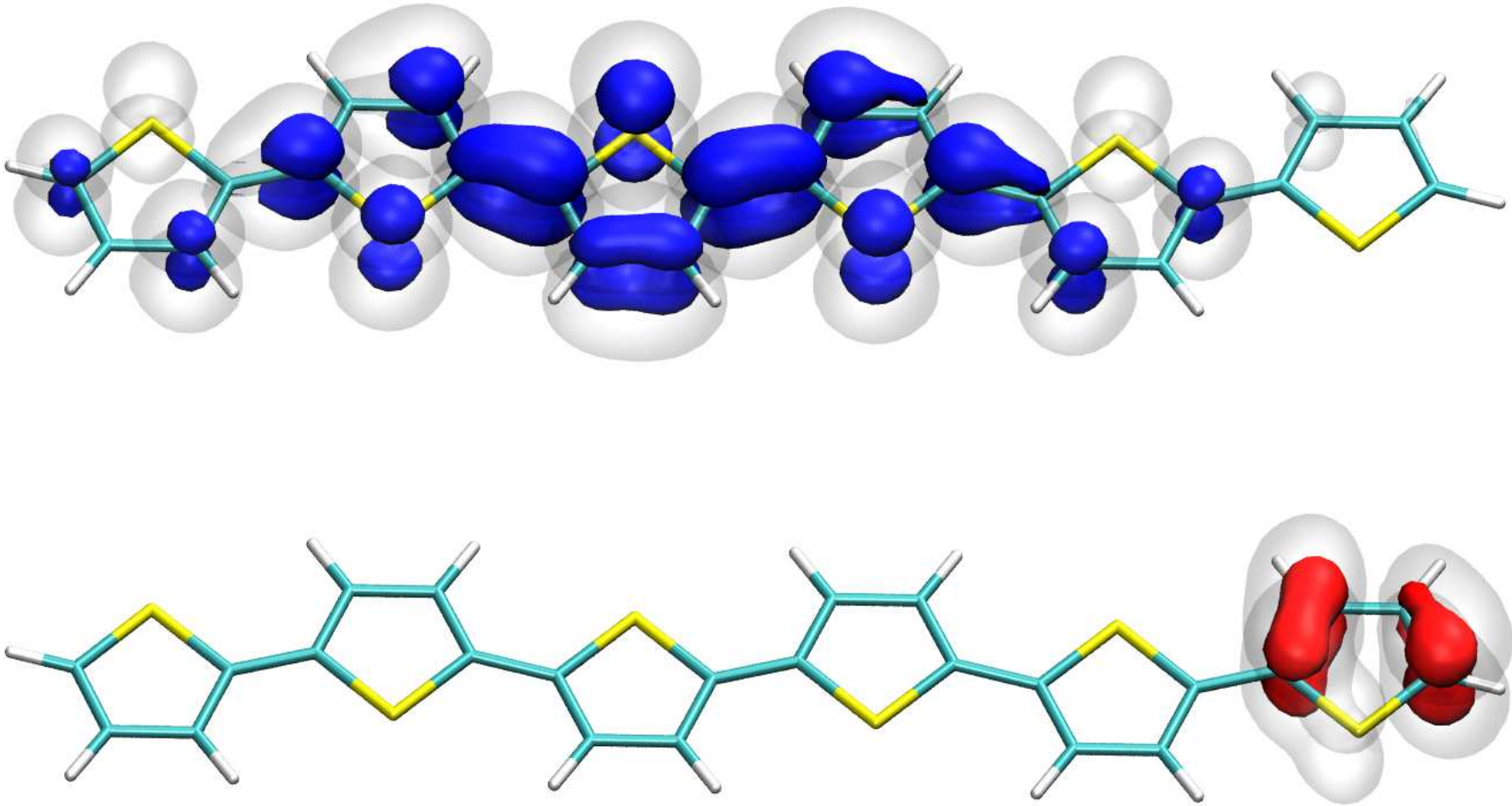
Oligothiophene

- S_3 state
  - **Conditional densities**



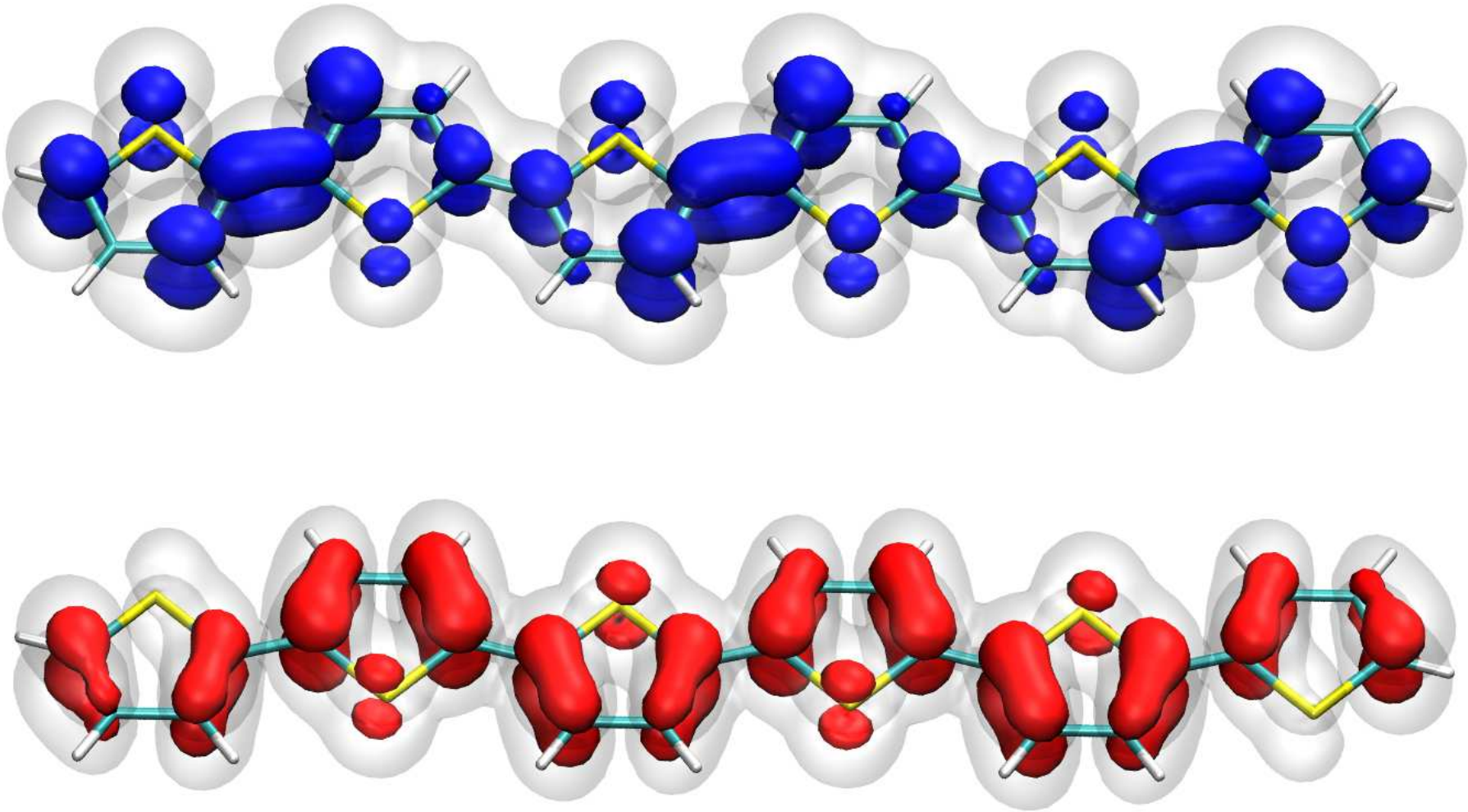
Oligothiophene

- S_3 state
  - **Conditional densities**



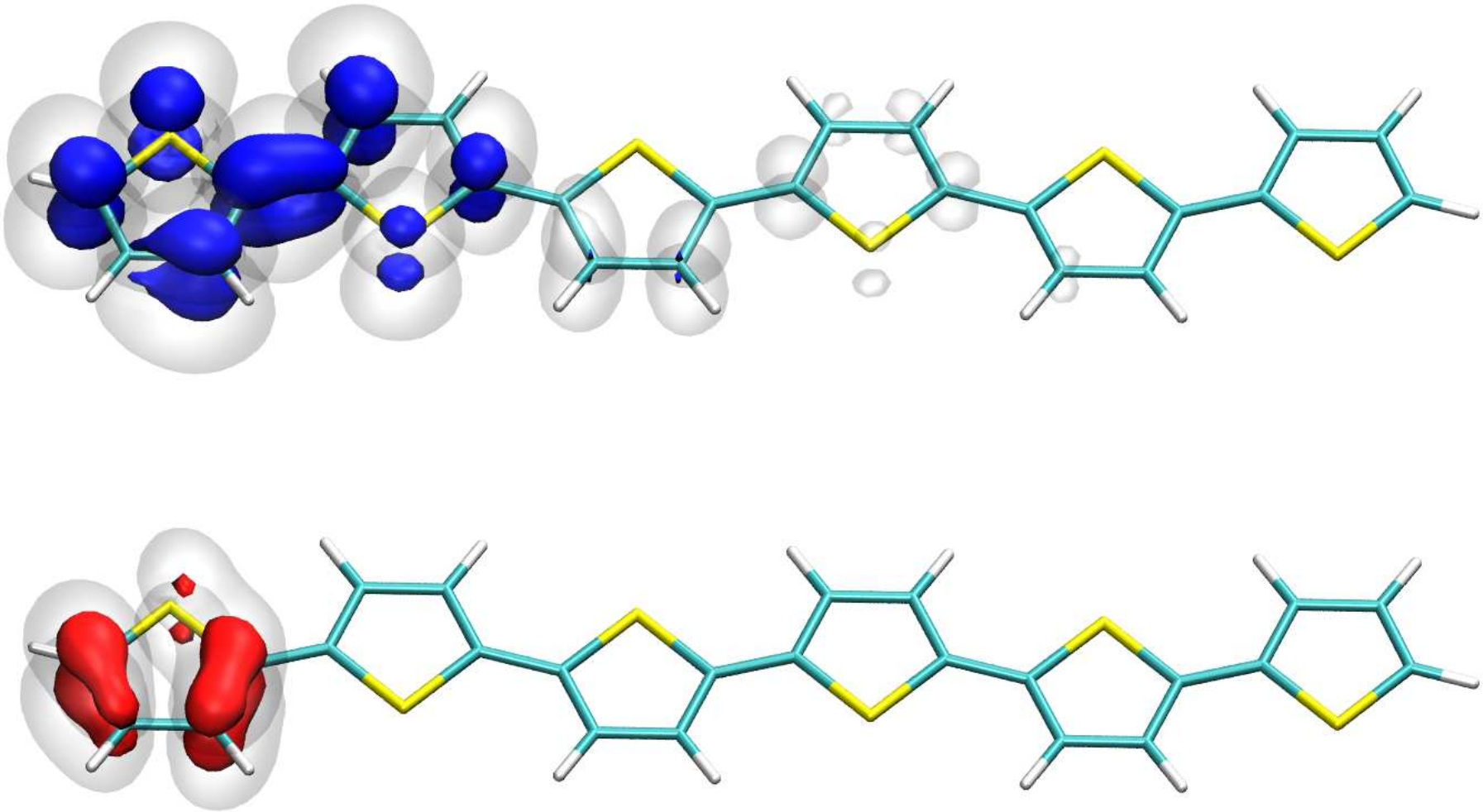
Oligothiophene

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



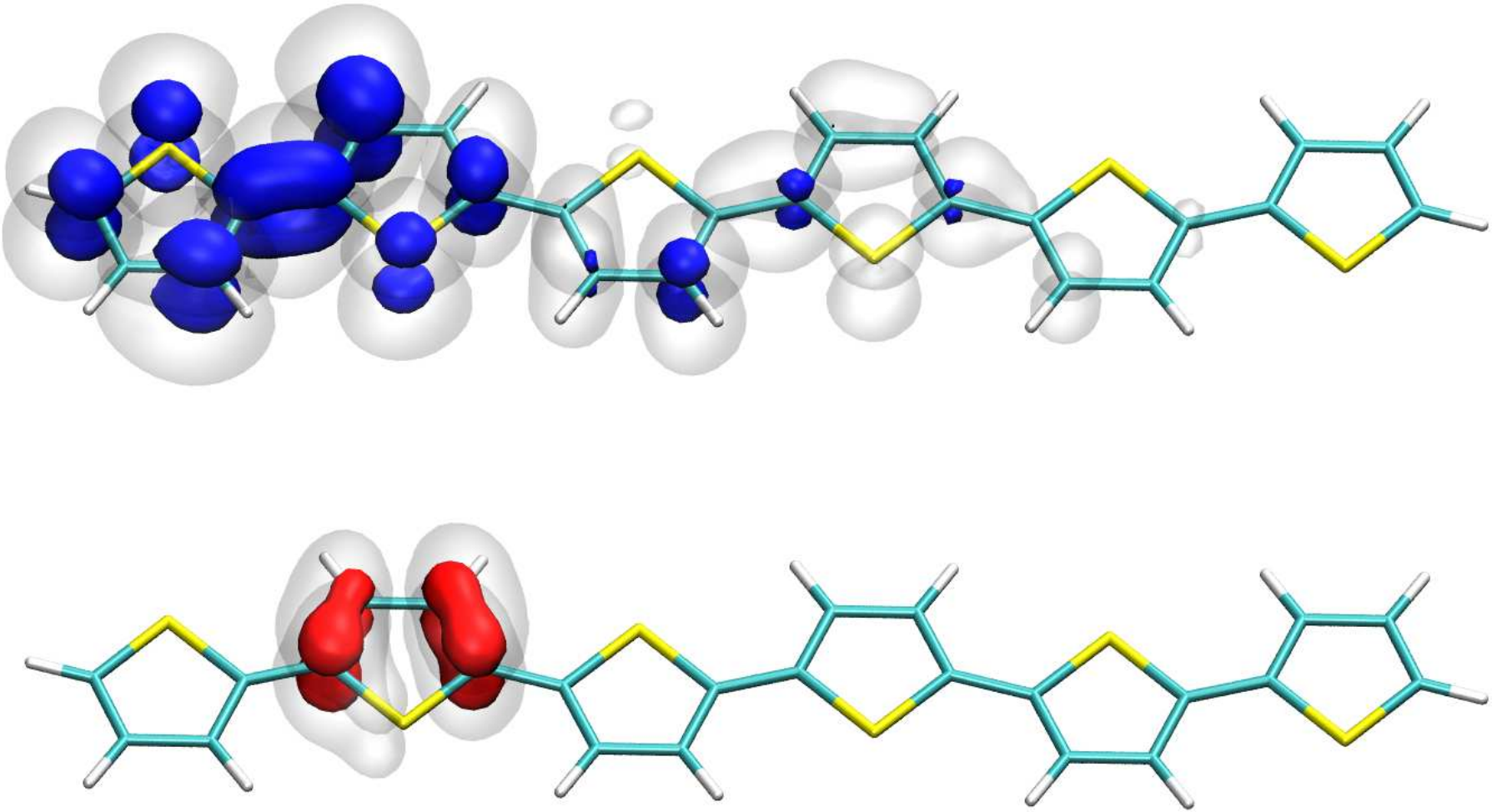
Oligothiophene

- S_4 state
  - **Conditional densities**



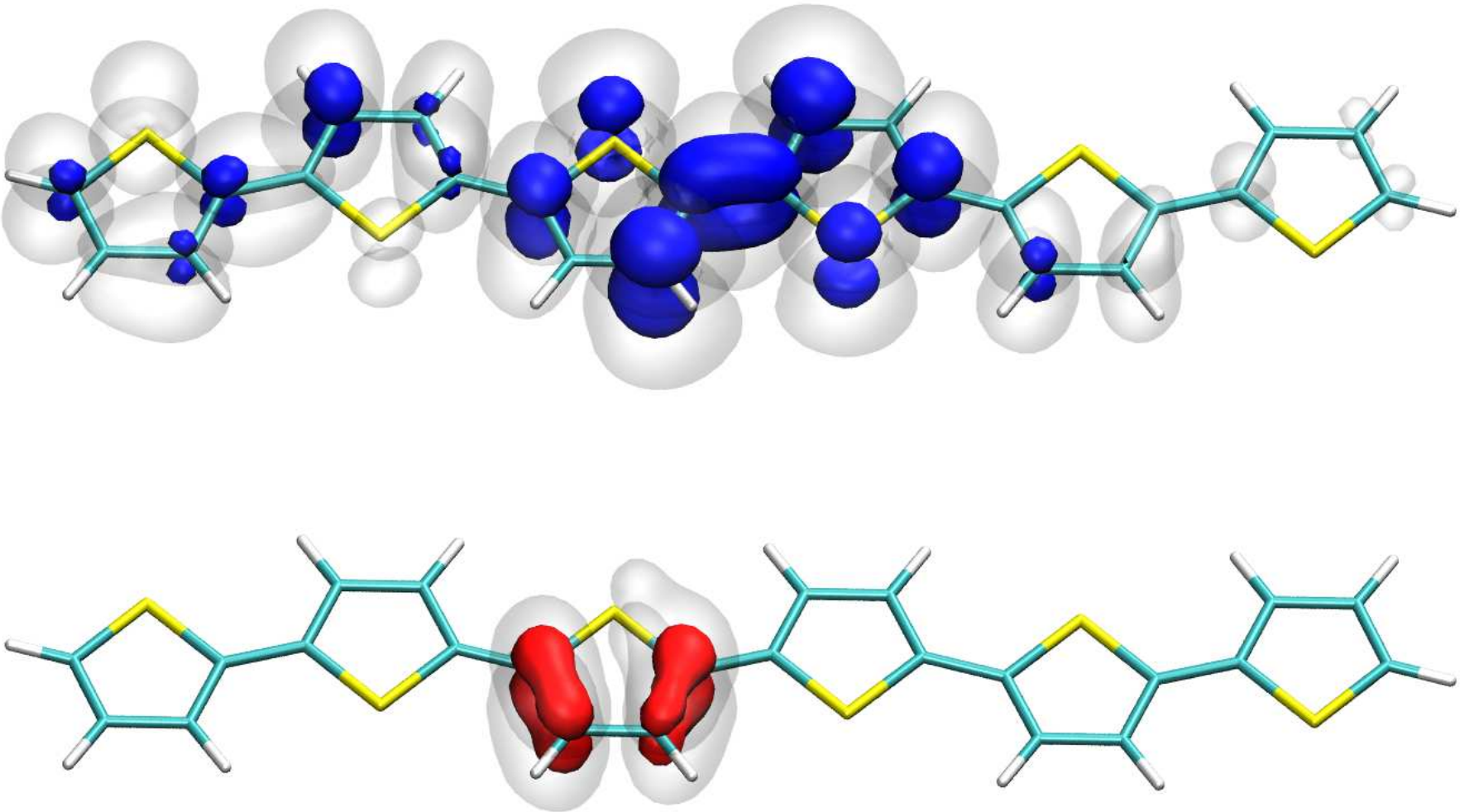
Oligothiophene

- S_4 state
  - **Conditional densities**



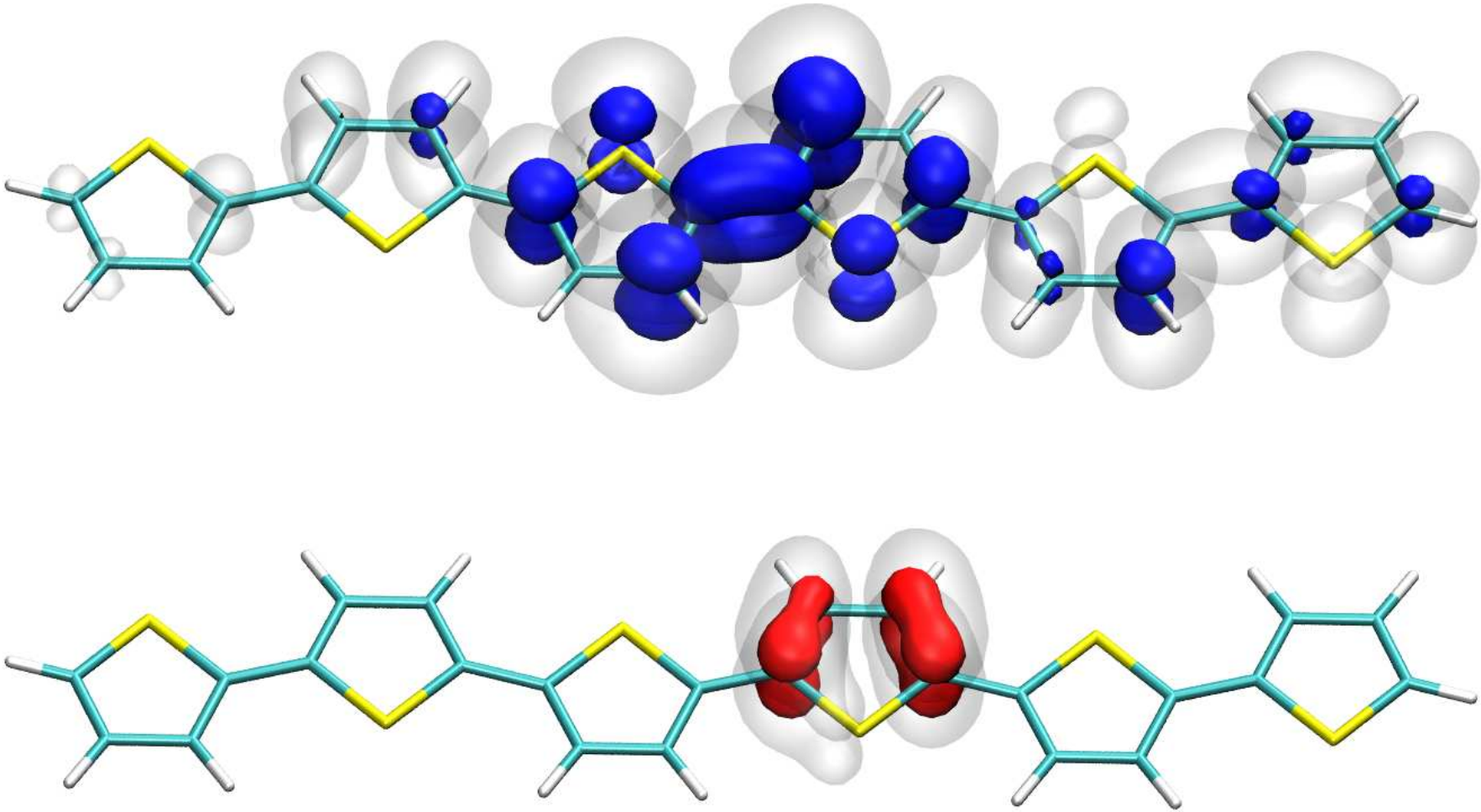
Oligothiophene

- S_4 state
  - **Conditional densities**



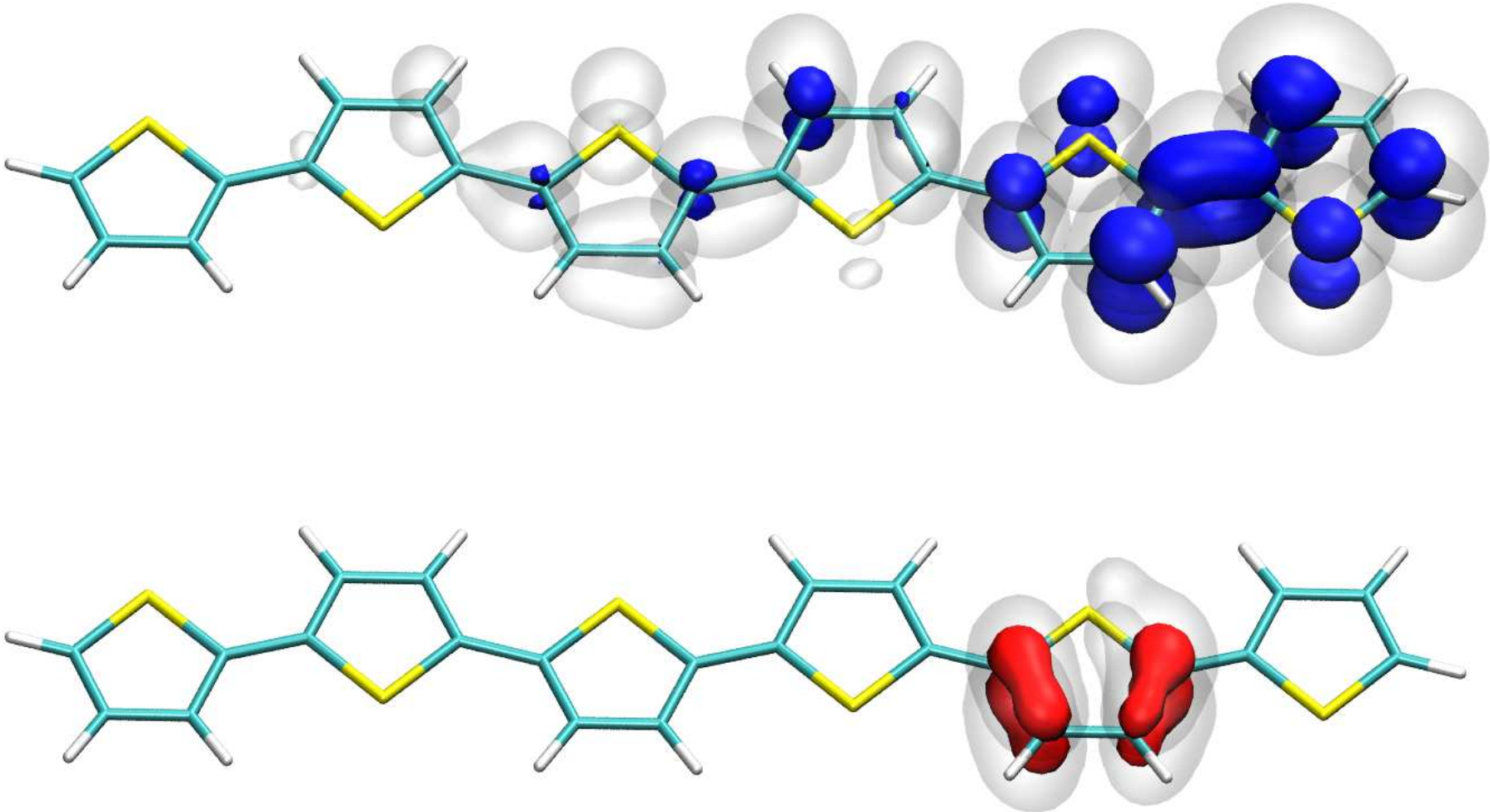
Oligothiophene

- S_4 state
  - **Conditional densities**



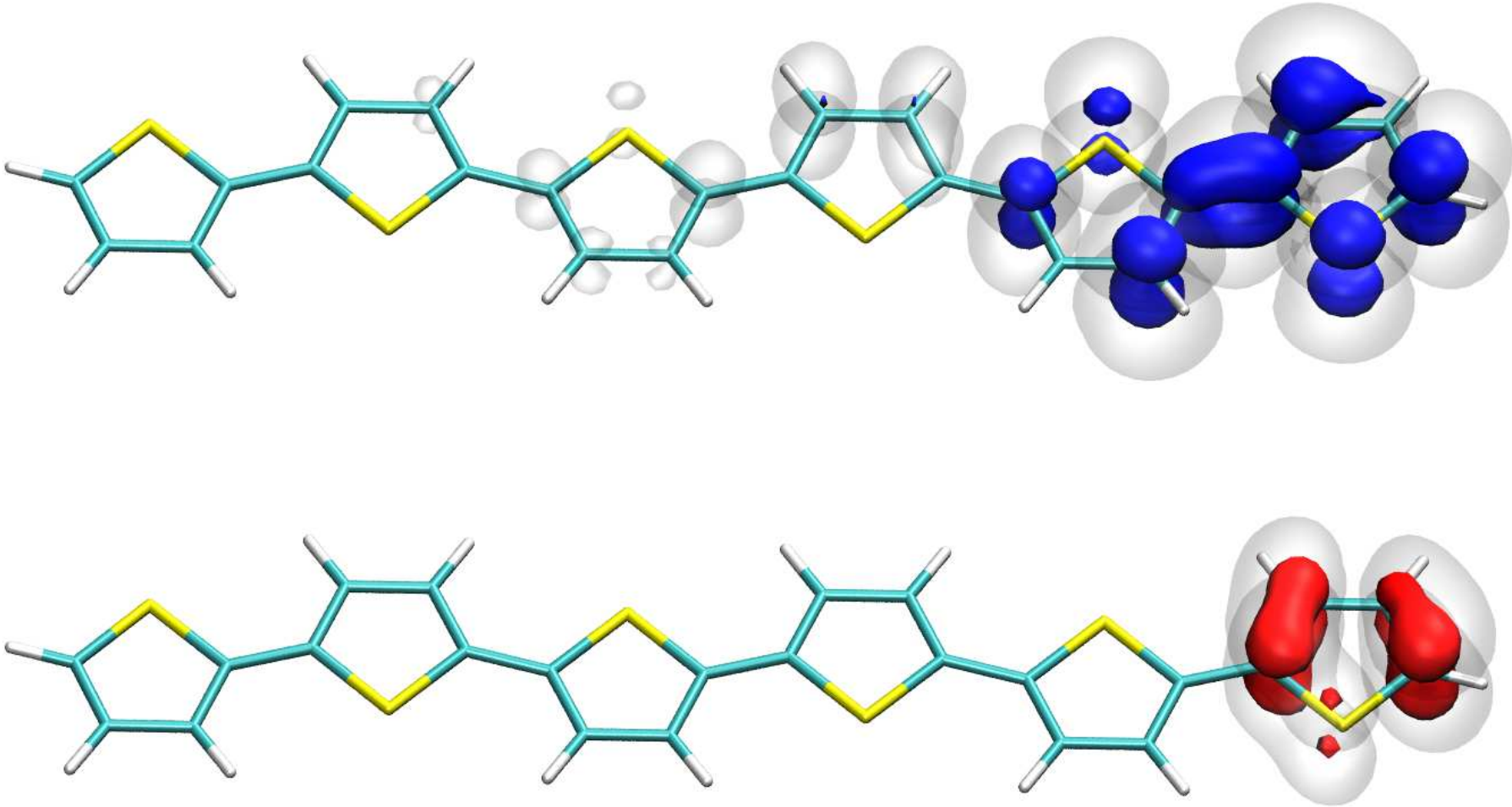
Oligothiophene

- S_4 state
  - **Conditional densities**



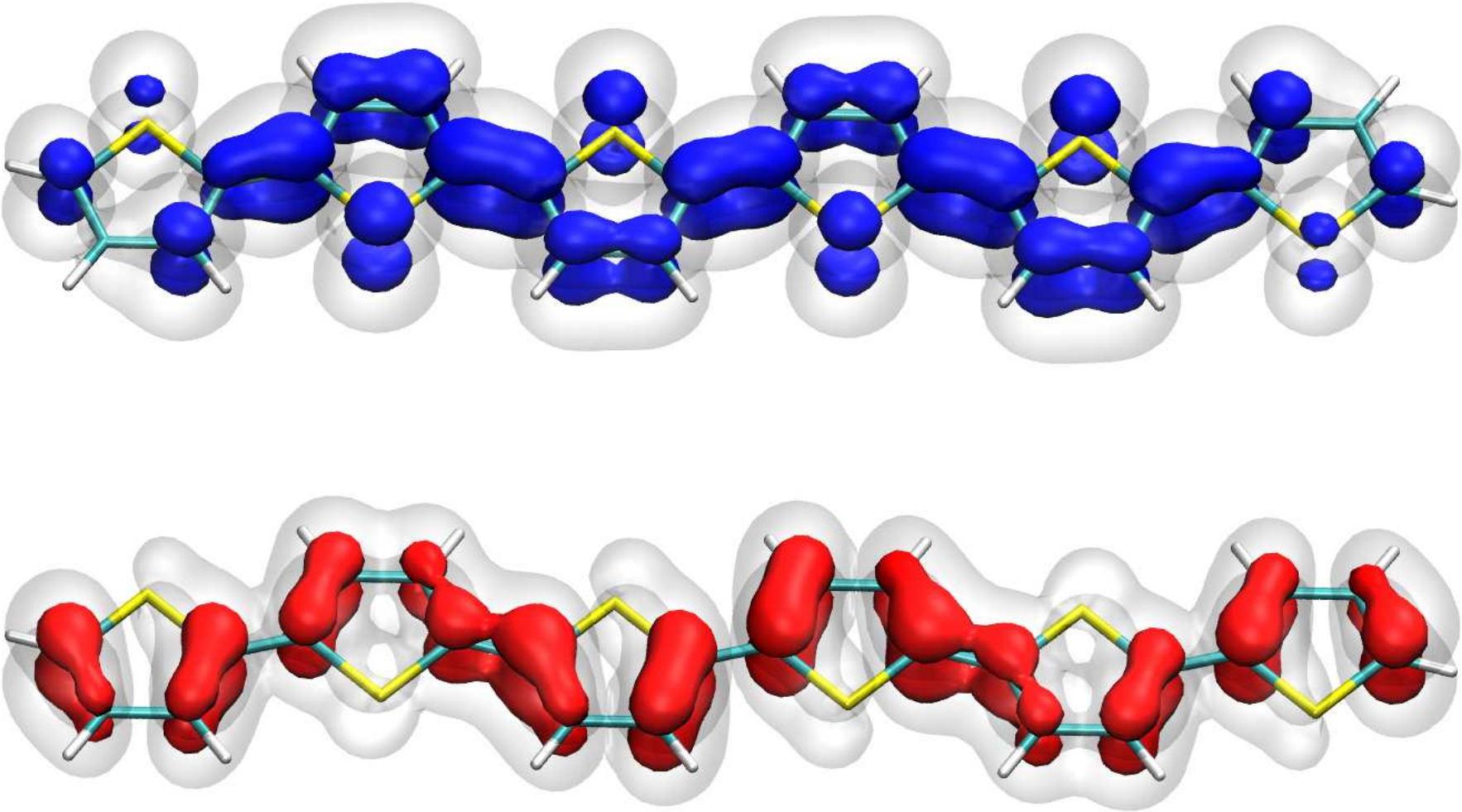
Oligothiophene

- S_4 state
  - **Conditional densities**



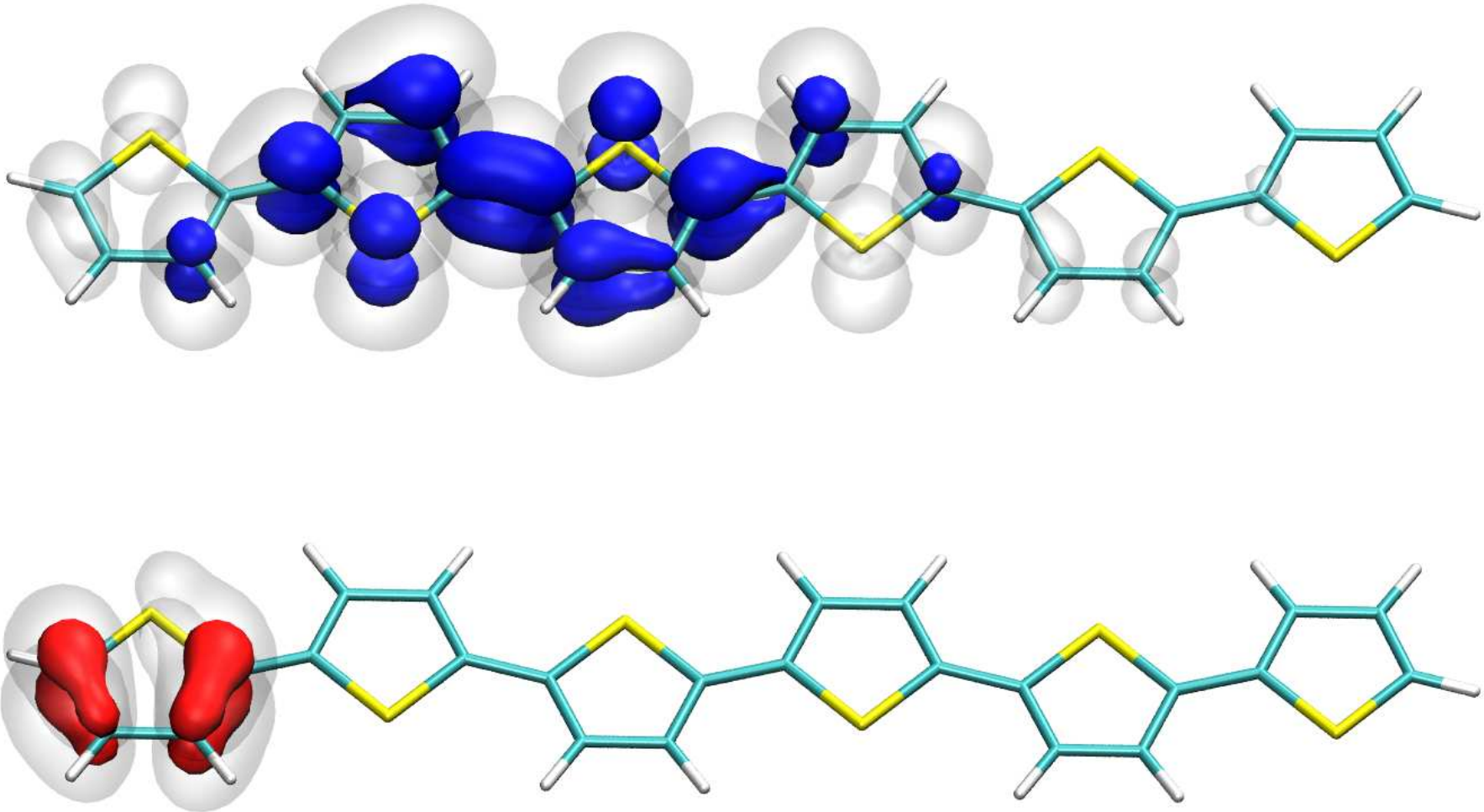
Oligothiophene

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



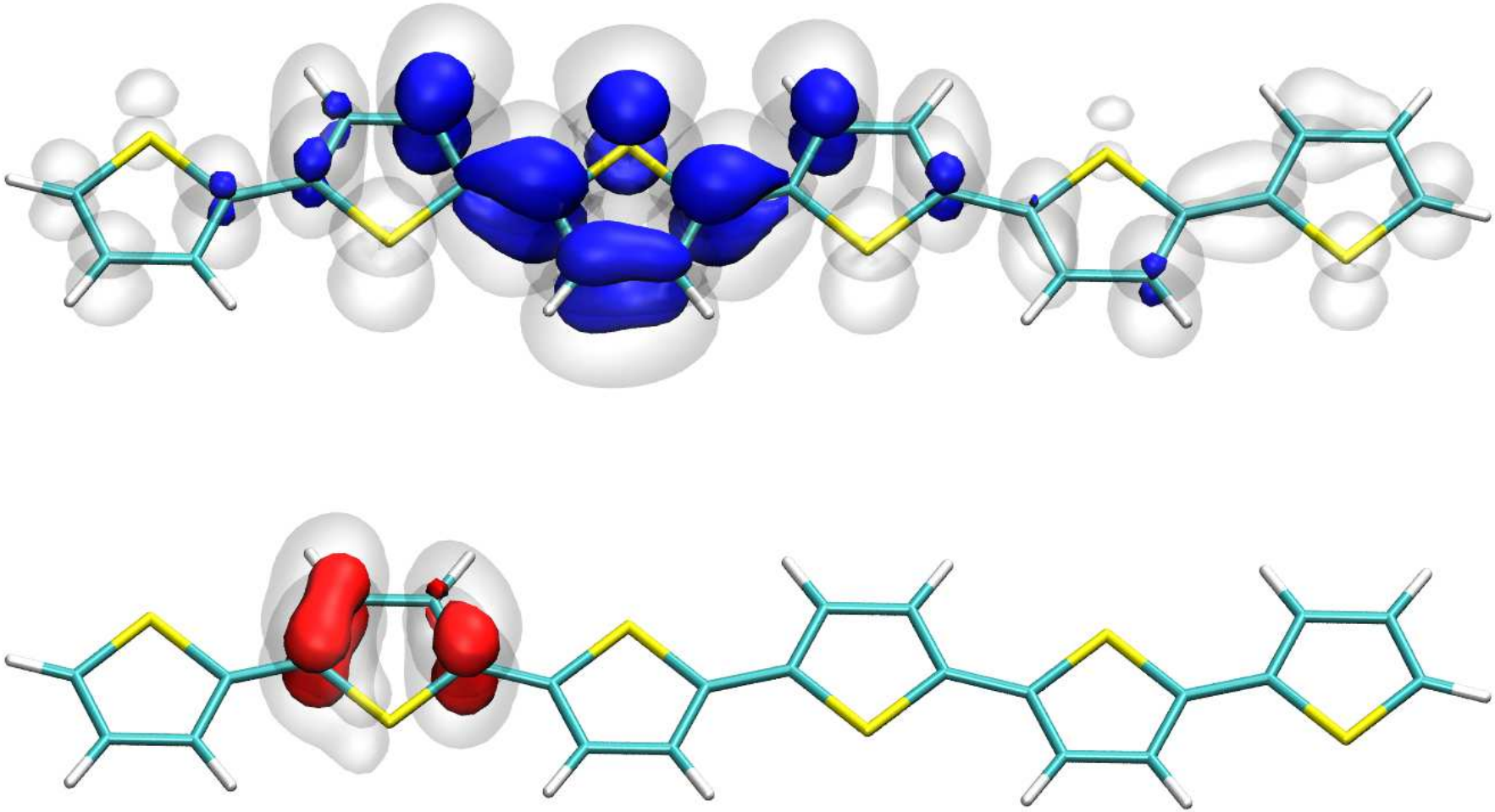
Oligothiophene

- S_5 state
  - **Conditional densities**



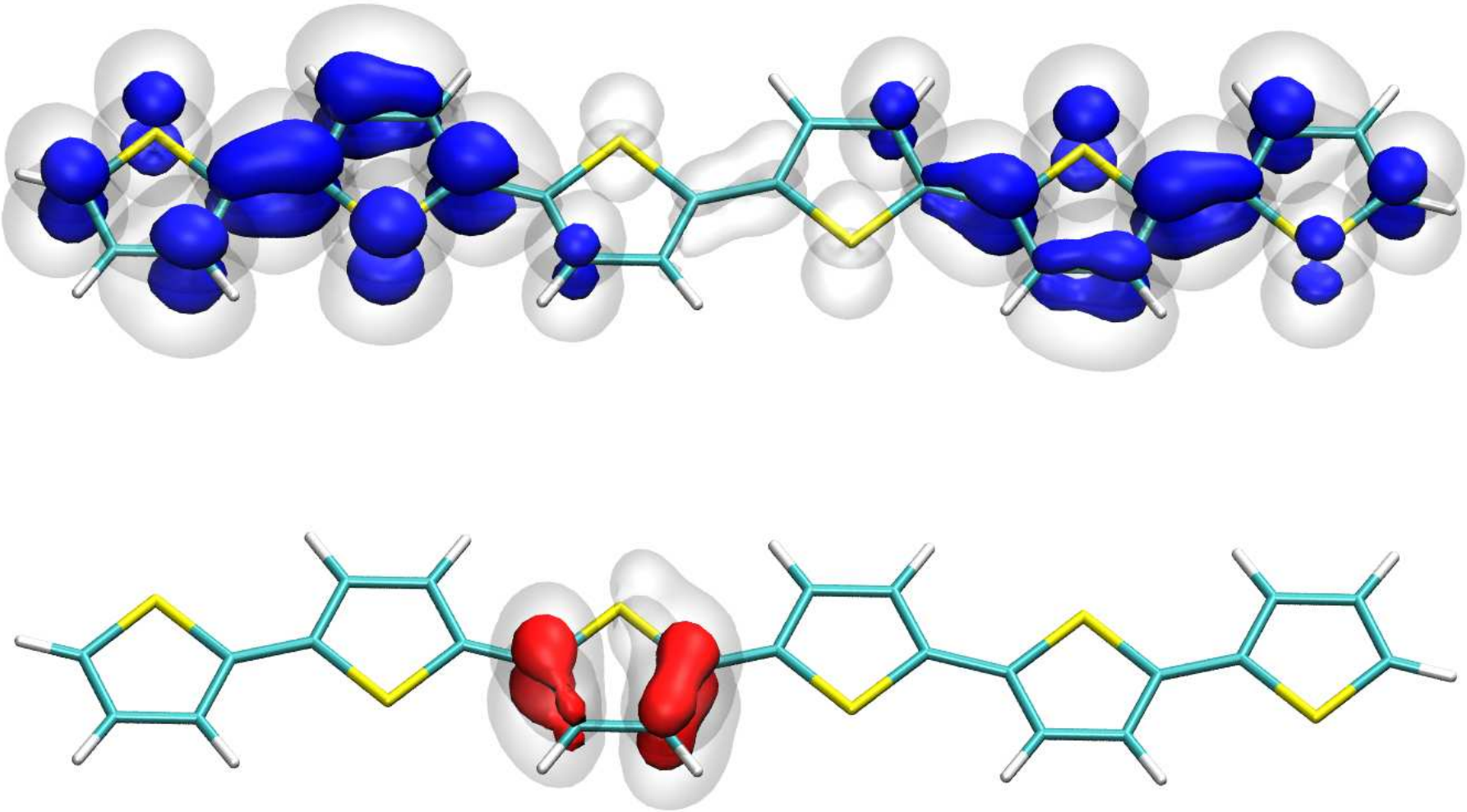
Oligothiophene

- S_5 state
  - **Conditional densities**



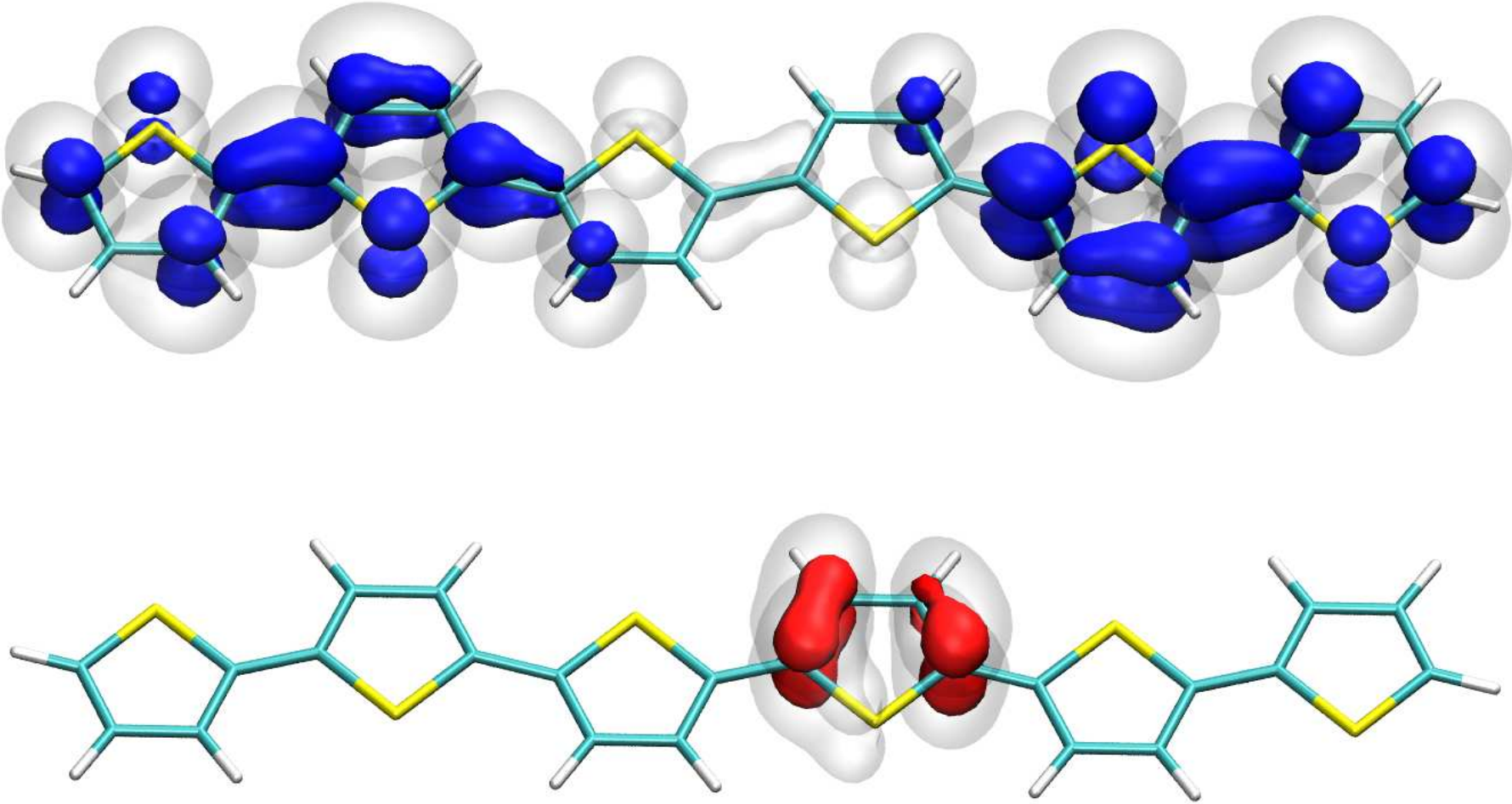
Oligothiophene

- S_5 state
  - **Conditional densities**



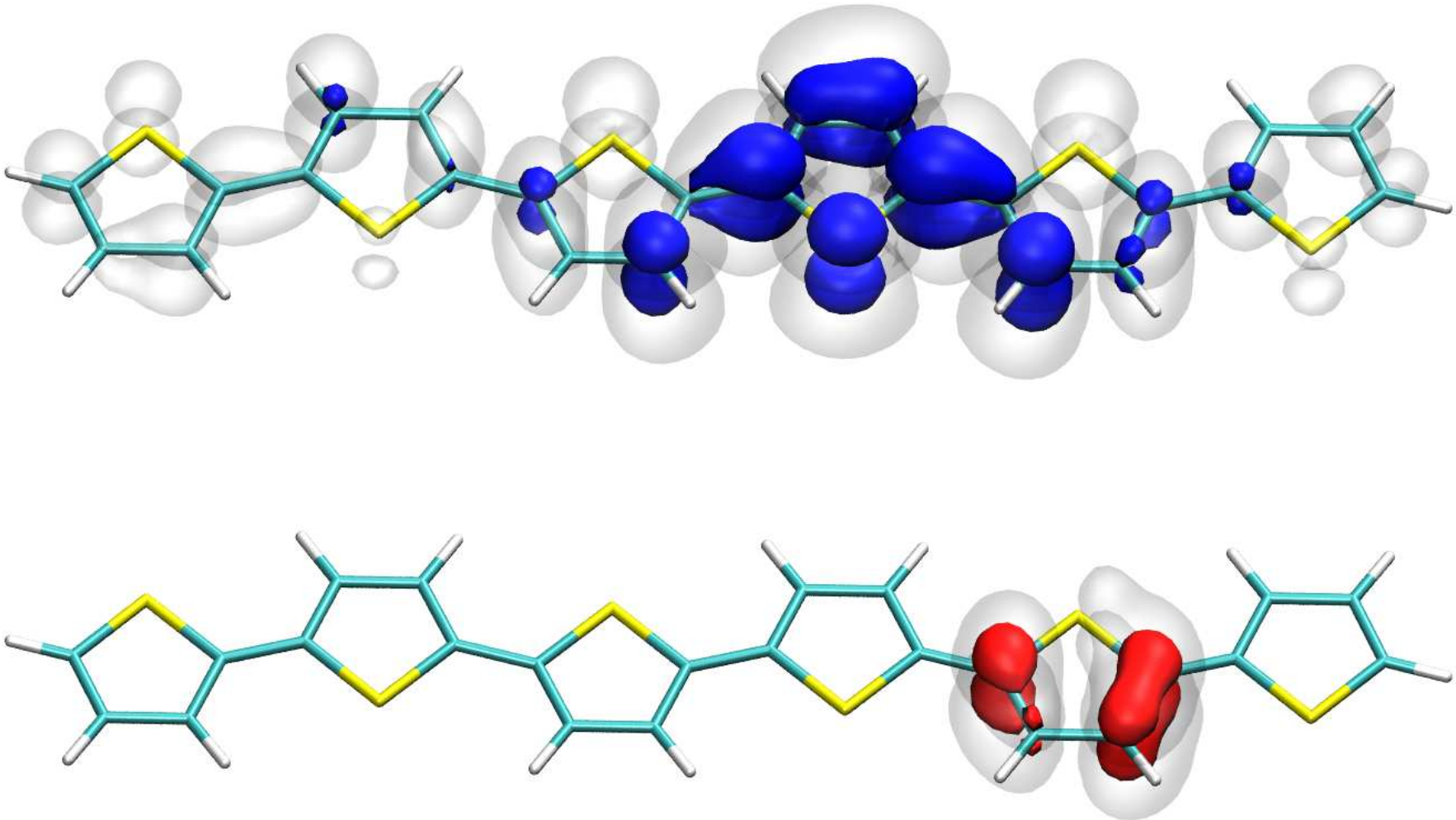
Oligothiophene

- S_5 state
  - **Conditional densities**



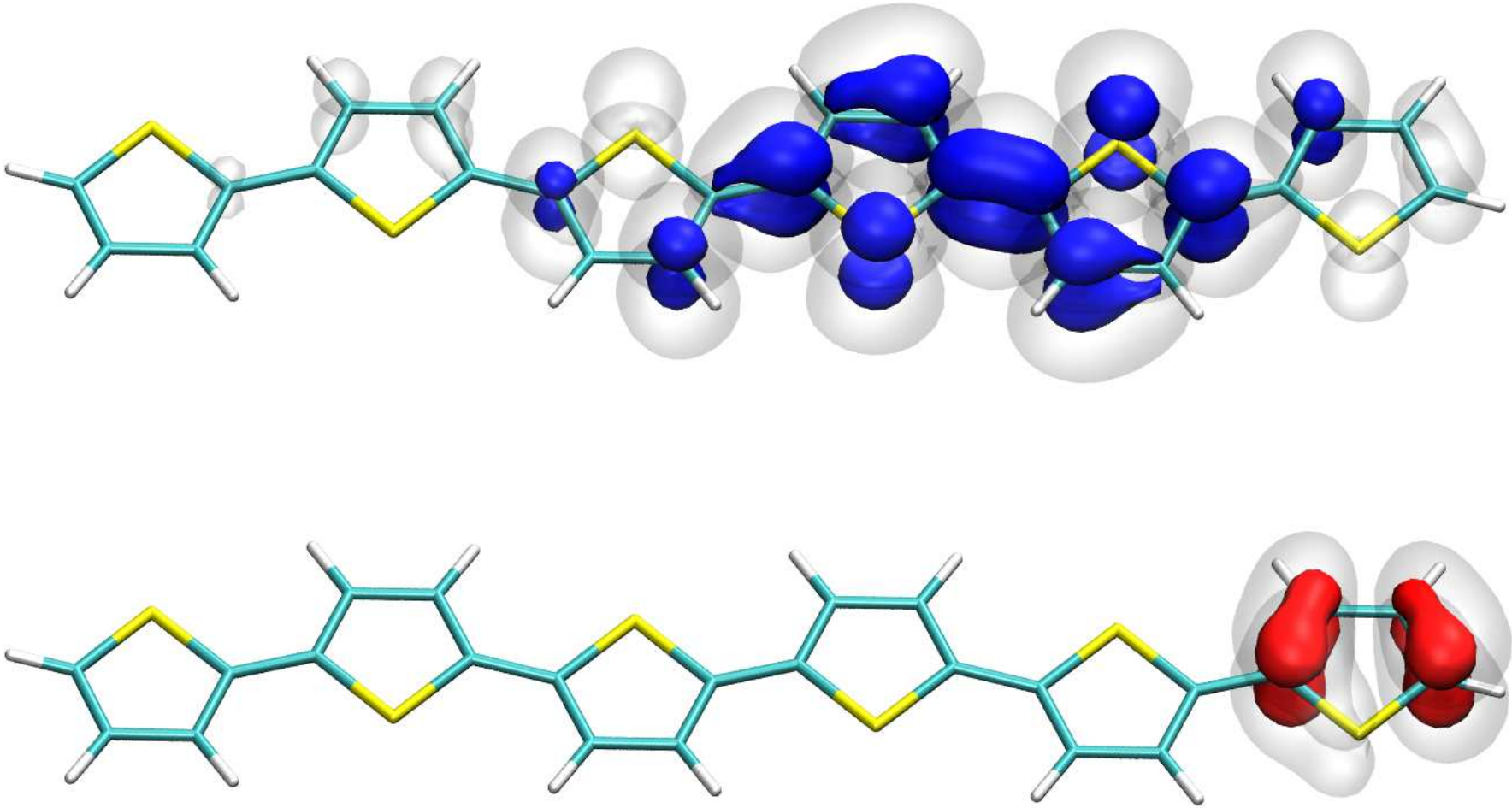
Oligothiophene

- S_5 state
  - **Conditional densities**



Oligothiophene

- S_5 state
  - **Conditional densities**



Conditional Densities

- Conditional electron/hole densities

→ A new way to visualise strong correlation

- **Conjugated polymers**
- Ionic/covalent (+/-) states in **alternant hydrocarbons**

[1] FP, *ChemPhotoChem* **2019**, DOI: 10.1002/cptc.201900014.

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`
  `DFT/MRCI`?
- 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