Detailed Insight into Exciton Wavefunctions from Quantum Chemistry Computations

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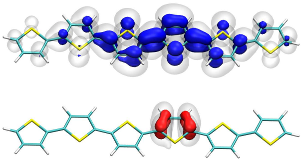
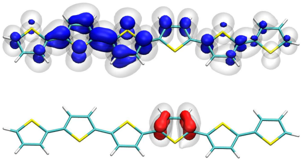
Felix Plasser

Department of Chemistry, Loughborough University





CECAM, 16 December 2021

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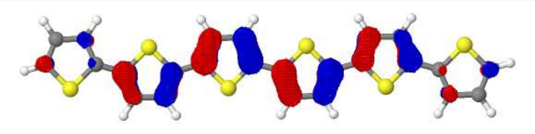
Motivation

Computational Science – Exciton Dynamics

- ▶ Accurate description
- ☺ Exciton-phonon coupling
- ☺ Exciton-exciton interactions
- ☺ Polaritons
- ☺ Transport processes
- ☺ Recombination

- ▶ Insight
- ☹ **Look at some blobs of colour**



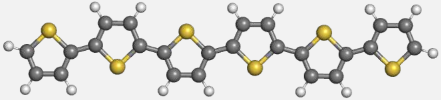
Exciton wavefunctions

? How to understand with **correlated exciton wavefunctions**

- Visualisation via electron-hole correlation plots
- Visualisation in real space
- Quantitative representation

Oligothiophene

- Oligothiophene



  - Prototypical conjugated polymer

- TDDFT/CAM-B3LYP computations

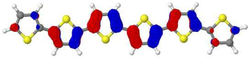
? How to analyse the states

Molecular orbital (MO) picture

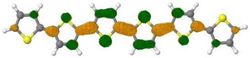
- Standard picture
- → State represented via linear combination of MO transitions
- ☹ Just many delocalized π and π^* orbitals
- ? Meaning of +/−
- ! We need a different way to think about this

TDDFT output

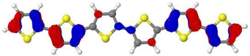
State	ΔE	Contribution
$S_1(1^1B_u)$	2.92	$0.94\ \mathrm{hl} + 0.28\ \mathrm{h_1l_1}$
$S_2(2^1A_g)$	3.77	$0.73\ \mathrm{hl_1} + 0.60\ \mathrm{h_1l}$
$S_3(3^1A_g)$	4.12	$-\ 0.58\ \mathrm{hl_1} + 0.72\ \mathrm{h_1l}$
$S_4(2^1B_u)$	4.44	$0.68\ \mathrm{hl_2} - 0.54\ \mathrm{h_1l_1} + 0.29\ \mathrm{h_2l}$
$S_5(3^1B_u)$	4.73	$-\ 0.50\ \mathrm{hl_2} - 0.30\ \mathrm{h_1l_1} + 0.71\ \mathrm{h_2l}$



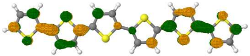
HOMO (h)



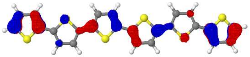
LUMO (l)



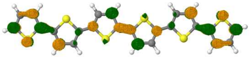
HOMO-1 ($\mathrm{h_1}$)



LUMO+1 ($\mathrm{l_1}$)



HOMO-2 ($\mathrm{h_2}$)

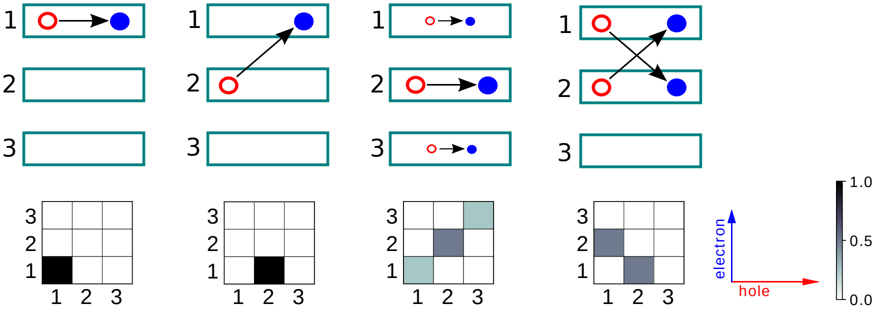


LUMO+2 ($\mathrm{l_2}$)

Electron-hole picture

- Excitation viewed as **electron**-**hole** pair
- (!) *2-dimensional* correlated picture
- (?) How do we construct the **two-body exciton wavefunction**

Excitation in multichromophoric system



[1] FP, *JCP* **2020**, 152, 084108.

Quantitative Description

Transition density matrix (1TDM)

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

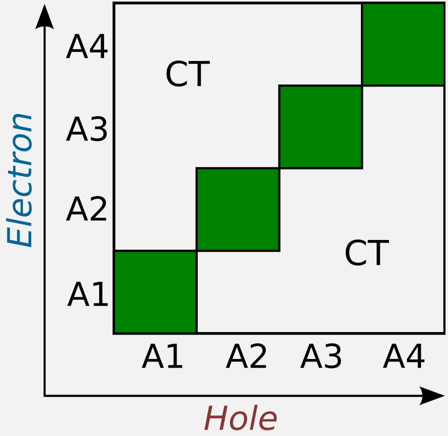
Ψ_0, Ψ_I Ground and excited state wavefunctions

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

- 1TDM interpreted as matrix representation of exciton wavefunction
- 2-dimensional population analysis
  - **Charge transfer numbers** Ω_{AB}

→ Electron-hole correlation plot

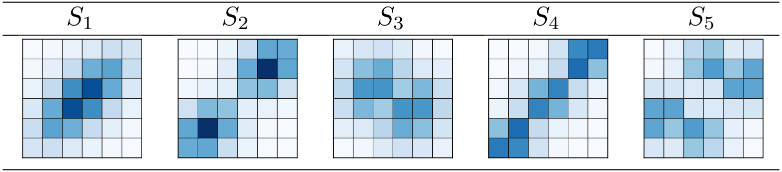
Transition density matrix

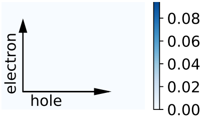


[1] FP, H. Lischka, *JCTC* **2012**, 8, 2777.
[2] FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

Oligothiophene

Electron-hole correlation plots





- ▶ Excitonic structure visible
- → **Hydrogen atom in a box**
- ? More intuitive visualization

Conditional densities

Exciton wavefunction

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

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

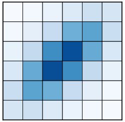
χ_μ Atomic orbital

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

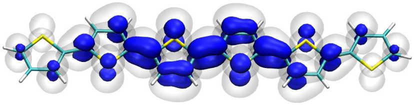
Conditional densities



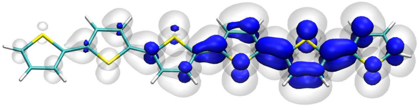
S_1 **state**

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

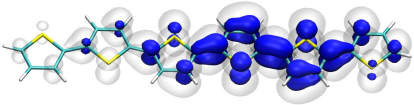
ρ_e



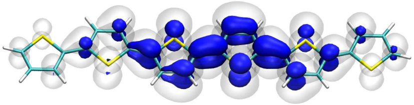
$\rho_e^{h:1}$



$\rho_e^{h:2}$



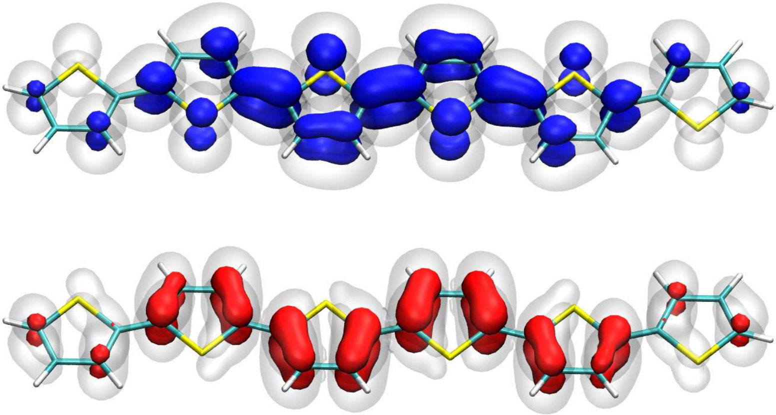
$\rho_e^{h:3}$



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

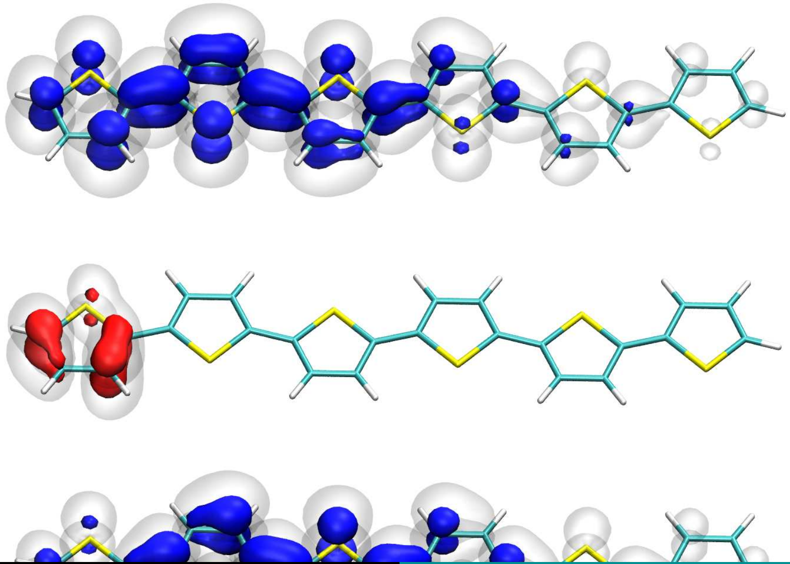
Oligothiophene

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



Oligothiophene

- S_1 state
  - **Conditional densities**



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

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

Operator expectation value

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

→ Evaluate using **analytic integration** techniques

.

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

Exciton Analysis

Exciton size

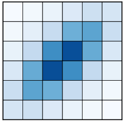
Exciton size

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

- Average separation of the electron and hole quasi-particles
- ☺ No fragment definition
- ☺ No population analysis

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

Conditional densities



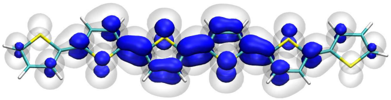
S_1 state

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

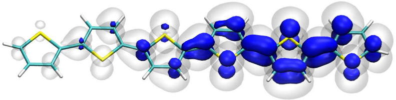
Exciton analysis[1,2]

- $d_{exc} =$ **5.7 Å**
- e-h correlation coeff. **0.45**

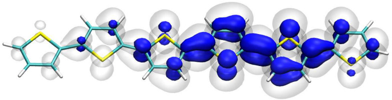
ρ_e / ρ_h



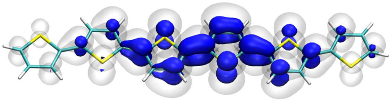
$\rho_e^{h:1} / \rho_h^{h:1}$



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

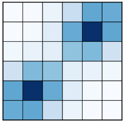


$\rho_e^{h:3} / \rho_h^{h:3}$



[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



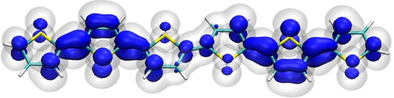
S_2 state

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

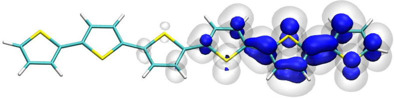
Exciton analysis

- $d_{exc} =$ **4.9 Å**
- e-h correlation coeff. **0.74**

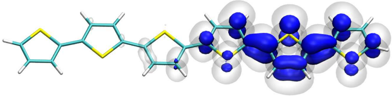
ρ_e / ρ_h



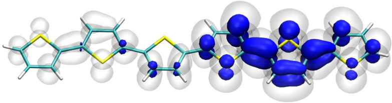
$\rho_e^{h:1} / \rho_h^{h:1}$



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

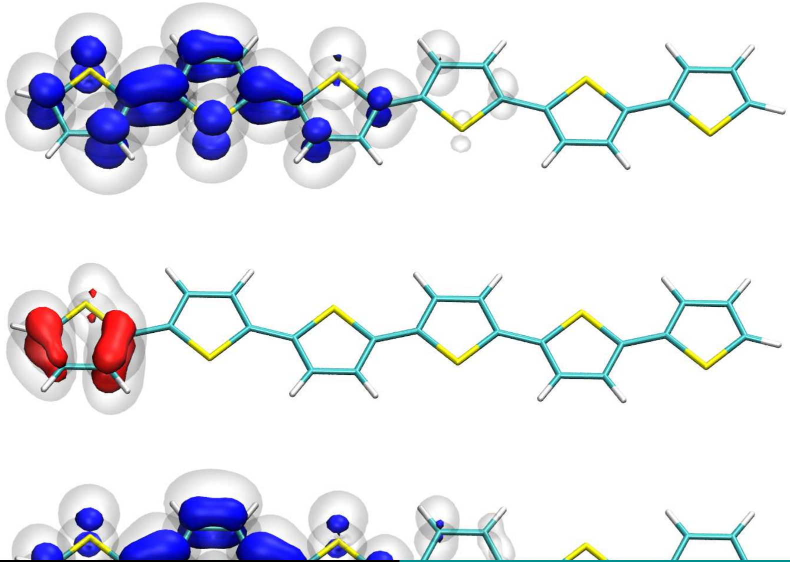


$\rho_e^{h:3} / \rho_h^{h:3}$

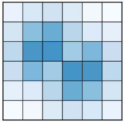


Oligothiophene

- S_2 state
  - Conditional densities



Conditional densities



S_3 state

- **Negative correleations** between electron and hole
- → Large e-h separation
- Nodal plane on **probe** thiophene

Exciton analysis

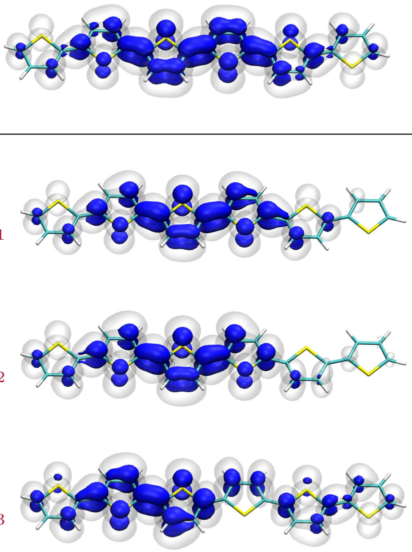
- $d_{exc} =$ **8.9 Å**
- e-h correlation coeff. **-0.24**

ρ_e / ρ_h

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

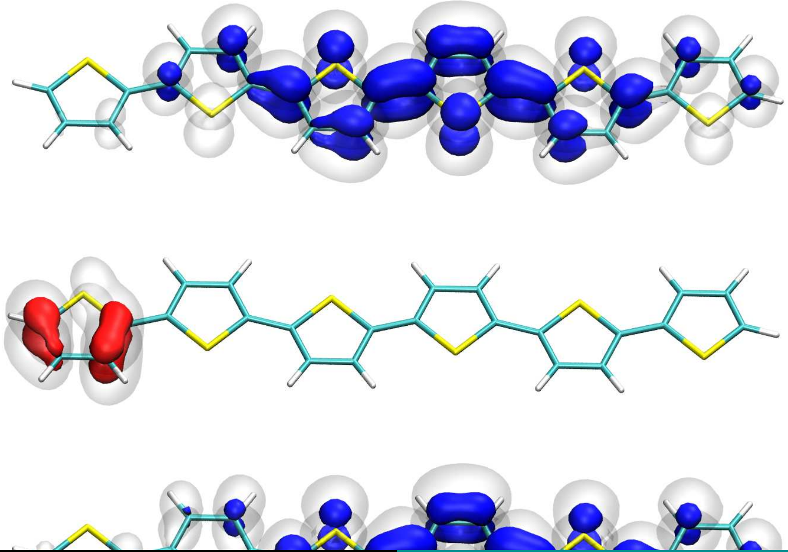
$\rho_e^{h:2} / \rho_h^{h:2}$

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



Oligothiophene

- S_3 state
  - **Conditional densities**



Conclusions

- Analysis of **correlated exciton wavefunctions**
  - Electron-hole correlation plots
  - Real-space picture of correlations
  - Quantitative analysis
  - Quantification of Coulomb/exchange contributions to excitation energy[1]
- Example applications – **Conjugated polymers**
  - Analysis of exciton bands in conjugated polymers[2]
  - Exciton size and binding energy limitations[3]
  - Problems in the TDDFT description of conjugated polymers[4]
- **Other examples**
  - Interacting chromophores, push-pull systems, transition metal complexes, ...
  - Rydberg states, double excitations, ...

[1] P. Kimber, FP, *PCCP* **2020**, 22, 6058.
[2] S. A. Mewes, J.-M. Mewes, A. Dreuw, FP, *PCCP* **2016**, 18, 2548.
[3] S. Kraner, R. Scholz, FP, C. Koerner, K. Leo, *JCP* **2015**, 143, 244905.
[4] S. A. Mewes, FP, A. Dreuw, *JPCL* **2017**, 8, 1205.

Software

Extended *wavefunction analysis toolbox*.

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

- Program package for wavefunction analysis

→ Excitons and more ...

- Interfaces to various quantum chemistry programs:
  `Columbus, Turbomole, Orca, GAMESS, Gaussian, ADF, Terachem, DFT-MRCI, ONETEP`
- Open-source

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

- `Q-Chem`: ADC, EOM-CC, TDDFT
- `OpenMolcas`: CASSCF, MS-CASPT2
- `CFOUR`

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

Further reading

- **Intro for practical computations**[1]
  - User friendly analysis tools

→ Plotting

→ Rigorous and **quantitative** analysis of trends

- **Chemical theory**[2]
  - Learn about nature and/or quantum chemical methods
  - New **qualitative** insight

[1] FP, *JCP* **2020**, 152, 084108.
[2] P. Kimber, FP, *PCCP* **2020**, 22, 6058.

Acknowledgements

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