New Tools for Computational Photochemistry: Wavefunction Analysis and Dynamics

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Marseille, 11 April 2019

Montpellier, 12 April 2019

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Introduction

Computational Photochemistry

- Going beyond standard quantum chemistry

? What really happens to the **electrons** after photoexcitation

→ Wavefunction analysis

Columbus | Q-CHEM A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY | OPEN CAS | TheoDORE

? **Time-resolved** description

→ Nonadiabatic dynamics

NX newtonx.org | SHARC2.0

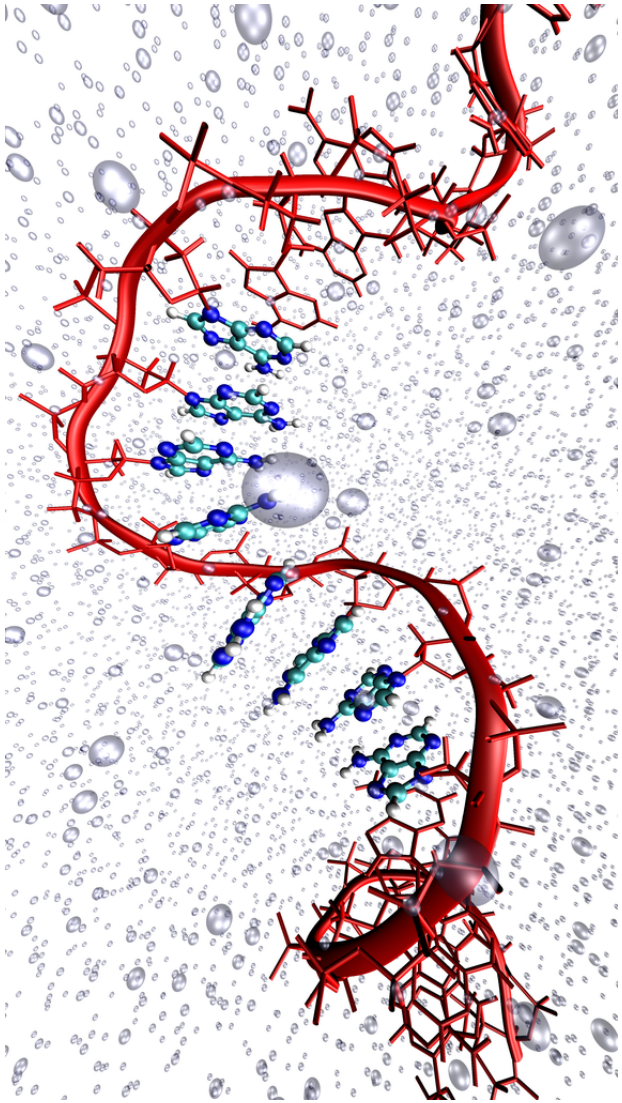
DNA

Photophysics of interacting nucleobases

- ? What happens after DNA is excited by UV light
  - Energy transfer[1]
  - Electron transfer and exciplex formation[2]

Starting point: **UV absorption**

- Localized/delocalized excitations
- Charge transfer states



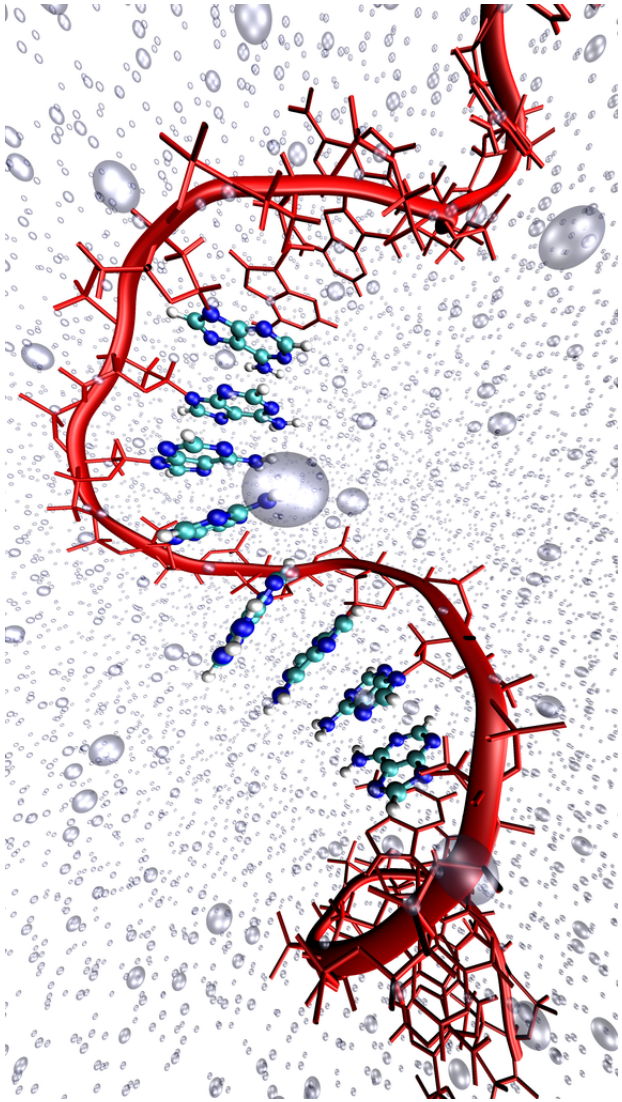
[1] D. Onidas, T. Gustavsson, E. Lazzarotto, D. Markovitsi, *PCCP* **2007**, 9, 5143.
[2] T. Takaya, C. Su, et al., *PNAS* **2008**, 105, 10285.

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 × **60** excited states

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



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

DNA

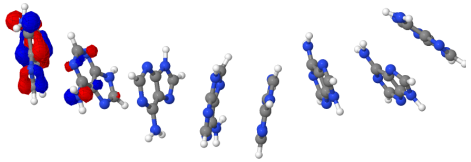
Leading configurations

- 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)

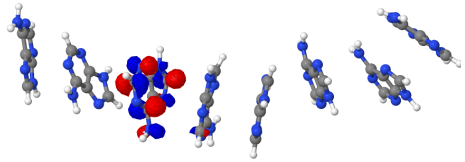
☹ Tedious **work**

☹ Possible **ambiguities**

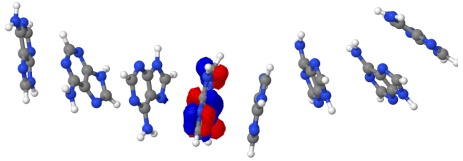
Canonical orbitals



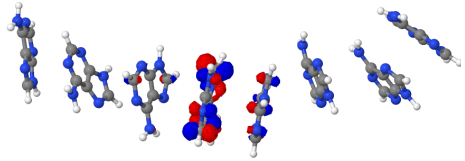
HOMO



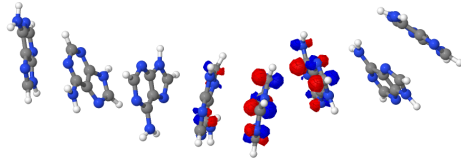
L (LUMO)



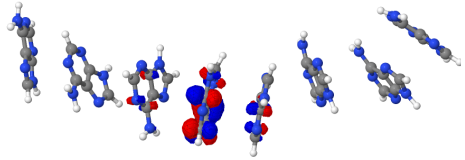
H-2



L+1



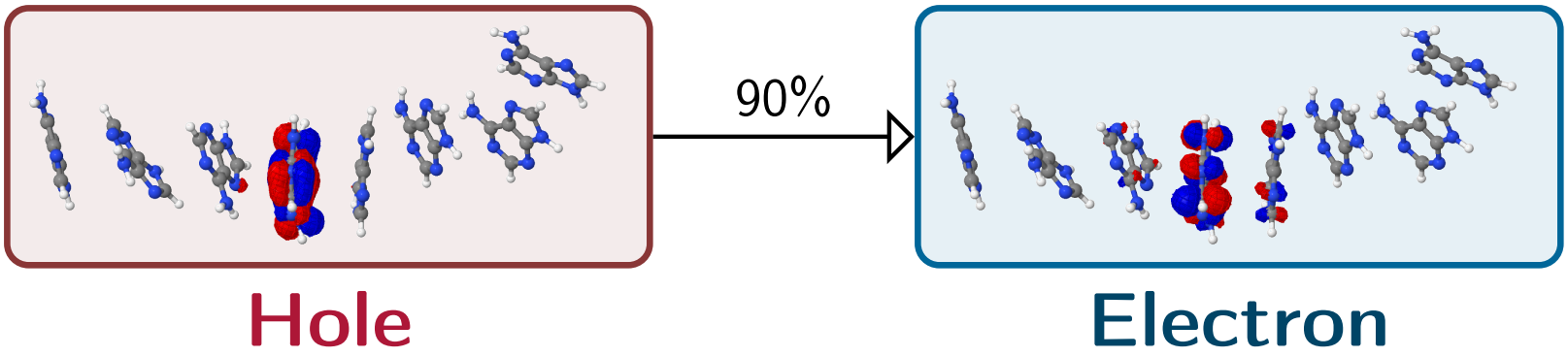
L+2



L+10

Compact Visualization

- Natural transition orbitals[1]
  - Singular value decomposition of the transition density matrix
- S_1 state
  - *Locally excited state (L_a)*
  - Only one important configuration



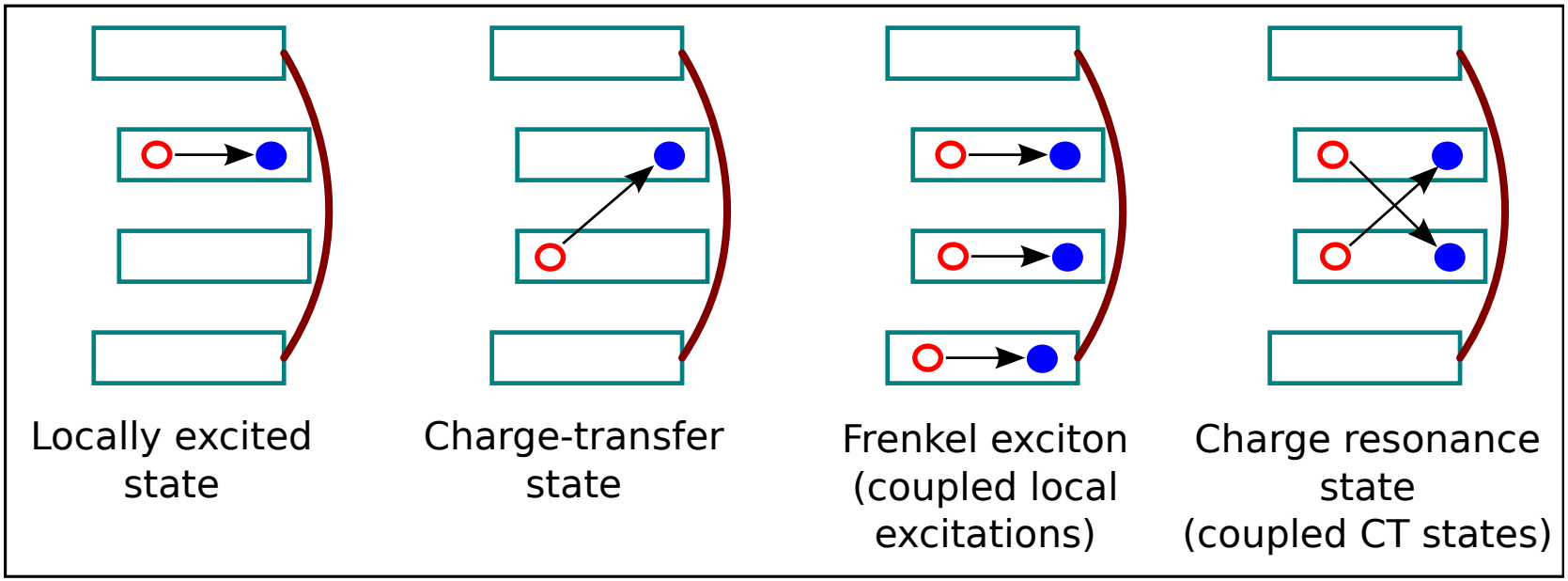
☺ Resolves (some) **ambiguities**

☹ Still tedious **work**

[1] R. L. Martin, *J. Chem. Phys.* **2003**, 118, 11.

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)

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

Ψ_0, Ψ_I Ground and excited state wavefunctions

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

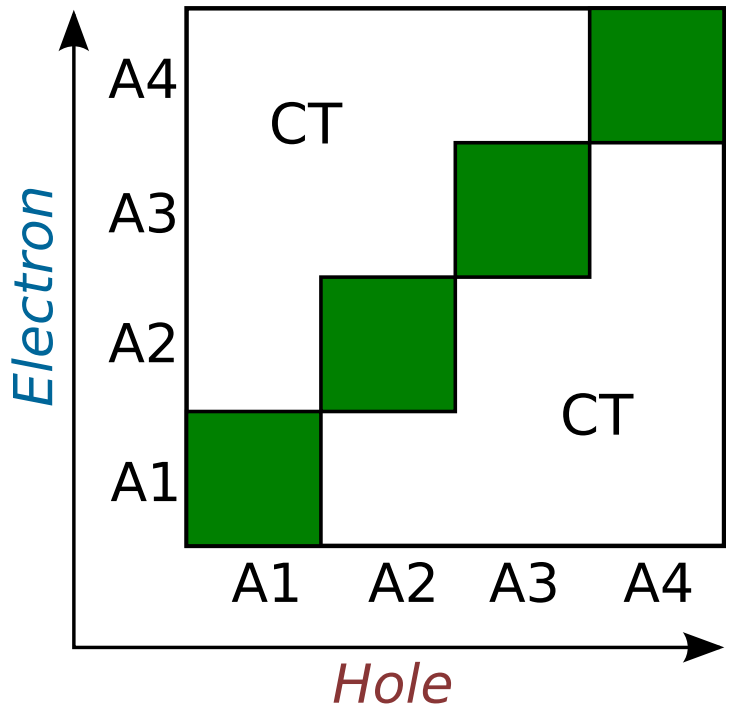
- 2-dimensional population analysis

→ **Charge transfer numbers** Ω_{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.

Statistical Analysis

- Delocalization length
- (?) How many fragments contribute to the excitation
- → Count the number of non-vanishing Ω_{AB} values

Delocalization Length

$$\mathrm{DL} = \frac{\Omega^2}{\sum_A \left(\sum_B \frac{\Omega_{AB}+\Omega_{BA}}{2}\right)^2}$$

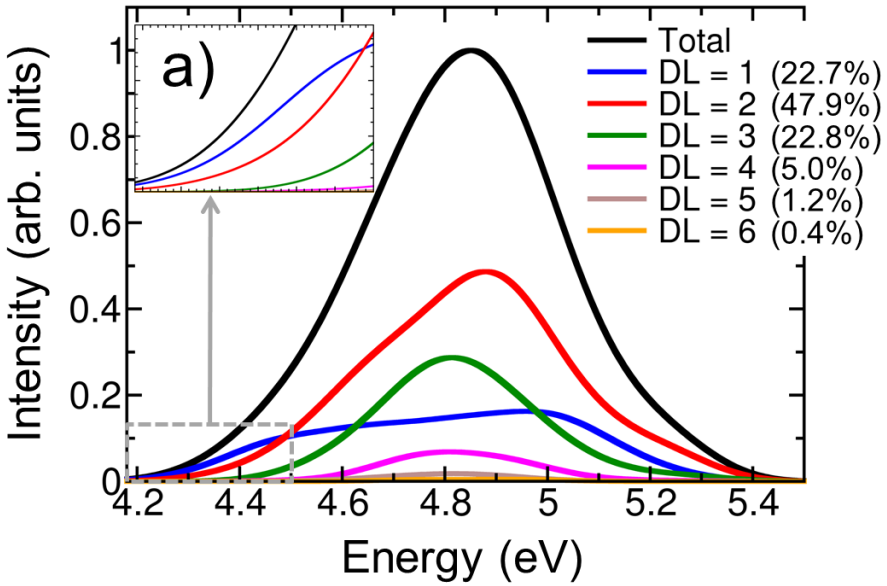
DL=1 Locally excited state (only one molecule involved)

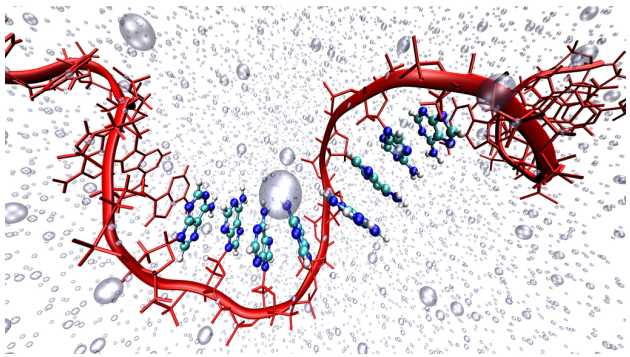
DL>1 Delocalized exciton or charge transfer state

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.

Polyadenine

Charge transfer (CT)

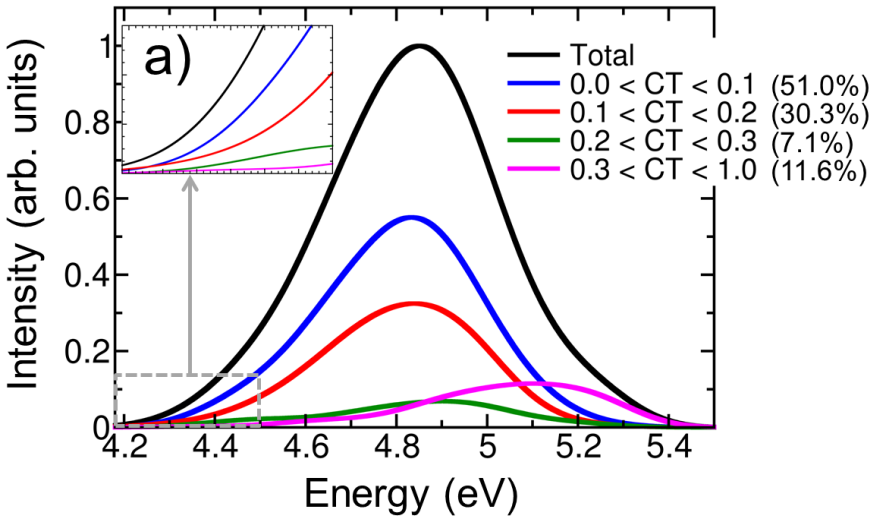
- Local and Frenkel exciton states (CT< 0.1)

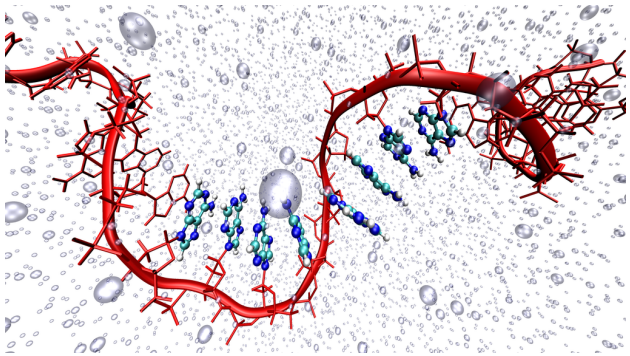
→ 51% of the spectral intensity

→ CT admixture for remaining states

- States with significant CT character (CT> 0.3)

→ Low intensity, high energies





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

Ionic and covalent states

- Excited states in **polyenes** and **polyacenes** come in two flavours[1]

→ **+ states** and **− states**

  - *Reason*: Quasidegeneracies of orbital transitions

- Interpretation as **ionic** and **covalent** states within **valence bond theory**[2]
  - **Ionic** configuration: $|\chi_A\bar{\chi}_A| - |\chi_B\bar{\chi}_B|$
  - **Covalent** configuration: $|\chi_A\bar{\chi}_B| - |\bar{\chi}_A\chi_B|$

(!) Fundamental property of electronic states

[1] R. Pariser, *J. Chem. Phys* **1956**, 24, 250.
[2] K. Schulten, I. Ohmine, and M. Karplus, *J. Chem. Phys* **1976**, 64, 4422.

Methodological implications

☹ Ionic states cause **problems for CASSCF**

→ Energies overestimated by > 1 eV

- B. O. Roos et al., *Chem. Phys. Lett.* **1992**, 192, 5.
- E. R. Davidson, *J. Phys. Chem.* **1996**, 100, 6161.
- C. Angeli, *J. Comput. Chem.* **2009**, 30, 1319.

→ **Dynamic σ polarisation** effects

- H. Lischka et al., *Chem. Rev.* **2018**, 118, 7293.

☹ Ionic states behave like **hidden charge-transfer states with TDDFT**

→ Energies too low

- S. Grimme, M. Parac, *ChemPhysChem* **2003**, 4, 292.
- R. M. Richard, J. M. Herbert, *J. Chem. Theory Comput.* **2011**, 7, 1296.

State of the art

- How do we characterise ionic and covalent states?
- VB wavefunctions **constructed** using **dedicated valence-bond protocols**

→ CASVB,[1] orthogonal VB,[2] VBSCF[3]

→ Specific and involved computational methods

(?) Can we **reconstruct** ionic and covalent character from the **wavefunctions**

→ Application of **standard quantum chemistry** methods

[1] K. Hirao, H. Nakano, and K. Nakayama. J., *Chem. Phys.* **1997**, 107, 9966.
[2] C. Angeli, R. Cimiraglia and J. P. Malrieu, *Mol. Phys.* **2013**, 111, 1069.
[3] J. Gu, W. Wu, D. Danovich, R. Hoffmann, Y. Tsuji, and S. Shaik., *JACS* **2017**, 139, 9302.

Naphthalene

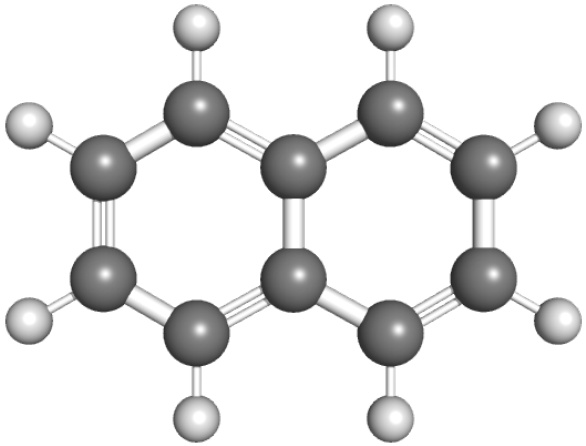
- Napthalene molecule
- Vertical excitations
  - ADC(2)/def-SV(P) level

- **Three types** of labels:

→ Multiplicity, irrep, +/−

- **Bright states**

→ Singlet, u, +



Term	ΔE	f
$^3B_{2u}^+$	3.26	-
$^3B_{3u}^+$	4.39	-
$^1B_{3u}^-$	4.49	0.0002
$^3B_{1g}^+$	4.66	-
$^3B_{2u}^+$	4.90	-
$^1B_{2u}^+$	5.01	0.11
$^3B_{3u}^-$	5.14	-
$^3A_g^+$	5.80	-
$^1A_g^-$	6.34	-
$^1B_{3u}^+$	6.37	1.52
$^1B_{1g}^-$	6.42	-
$^3B_{1g}^-$	6.63	-
$^1B_{2u}^+$	6.67	0.31

Napthalene B_{3u} states

- Focus on B_{3u} states
- All have the same orbital transitions
  - HOMO$-1 \rightarrow$ LUMO and HOMO $\rightarrow$ LUMO$+1$

(!) Only difference: **signs**

B3u states

$$
\begin{aligned}
{}^1B_{3u}^{\pm} &= \frac{1}{2}\left(\left(\Phi_{H1,\alpha}^{L,\alpha} + \Phi_{H1,\beta}^{L,\beta}\right) \pm \left(\Phi_{H,\alpha}^{L1,\alpha} + \Phi_{H,\beta}^{L1,\beta}\right)\right) \\
{}^3B_{3u}^{\pm} &= \frac{1}{2}\left(\left(\Phi_{H1,\alpha}^{L,\alpha} - \Phi_{H1,\beta}^{L,\beta}\right) \pm \left(\Phi_{H,\alpha}^{L1,\alpha} - \Phi_{H,\beta}^{L1,\beta}\right)\right)
\end{aligned}
$$

- Different **signs** lead to different **superpositions**

(?) How to analyse

Napthalene B_{3u} states

- Detailed energetics

Config.	ADC(0)	State	ADC(1)	ADC(2)	ADC(3)
$\Phi_{H,\alpha}^{L1,\alpha}$	11.014	${}^3B_{3u}^+$	4.24	4.39	3.91
$\Phi_{H,\beta}^{L1,\beta}$	11.014	${}^1B_{3u}^-$	5.27	4.49	4.16
$\Phi_{H1,\alpha}^{L,\alpha}$	11.027	${}^3B_{3u}^-$	4.91	5.14	4.88
$\Phi_{H1,\beta}^{L,\beta}$	11.027	${}^1B_{3u}^+$	7.23	6.37	6.41

? Why are the singlet and triplet **− states** similar in energy

? Why is there a large gap between the singlet and triplet **+ states**

Napthalene B_{3u} states

B3u states

$$
\begin{aligned}
{}^1B_{3u}^{\pm} &= \frac{1}{2}\left(\left(\Phi_{H1,\alpha}^{L,\alpha} + \Phi_{H1,\beta}^{L,\beta}\right) \pm \left(\Phi_{H,\alpha}^{L1,\alpha} + \Phi_{H,\beta}^{L1,\beta}\right)\right) \\
{}^3B_{3u}^{\pm} &= \frac{1}{2}\left(\left(\Phi_{H1,\alpha}^{L,\alpha} - \Phi_{H1,\beta}^{L,\beta}\right) \pm \left(\Phi_{H,\alpha}^{L1,\alpha} - \Phi_{H,\beta}^{L1,\beta}\right)\right)
\end{aligned}
$$

- Exactly the same **canonical orbitals** (*in the PPP description*)
- Same **density matrices**

→ Same densities

→ Same difference densities, attachment-detachment densities

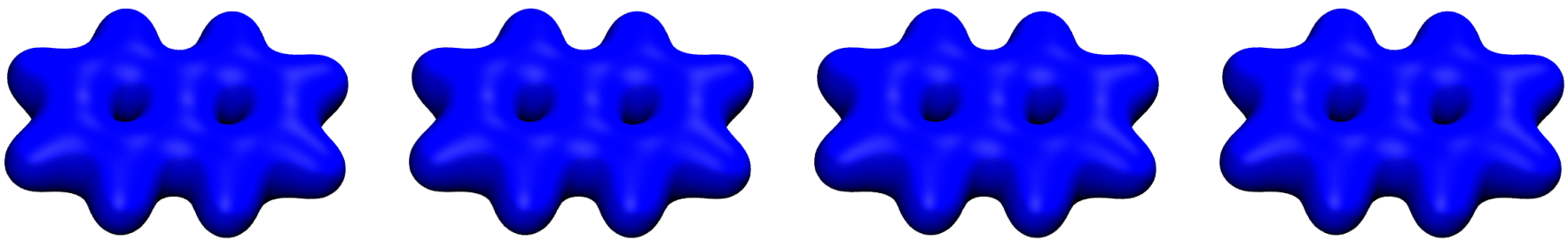
→ Same natural orbitals

- Same **natural transition orbitals**

ⓘ Only difference: **signs**

Napthalene B_{3u} states

- ADC(2) densities

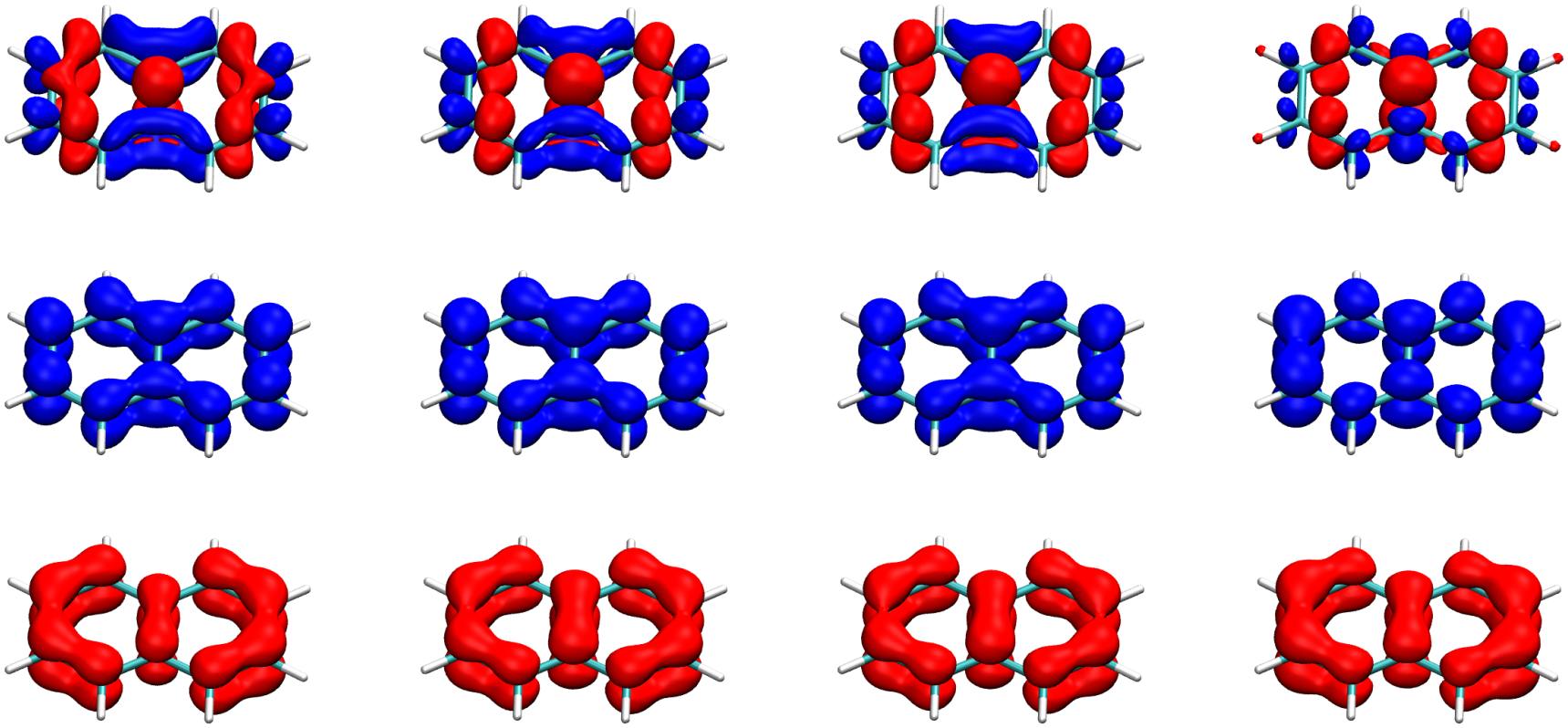


$^3B_{3u}^+$ $^1B_{3u}^-$ $^3B_{3u}^-$ $^1B_{3u}^+$

ⓘ The **ground state** density contains all physically relevant information **but we do not know how to extract it**

Napthalene B_{3u} states

- ADC(2) difference, **attachment**, **detachment**[1] densities



$^3B_{3u}^+$ $^1B_{3u}^-$ $^3B_{3u}^-$ $^1B_{3u}^+$

[1] M. Head-Gordon et al., *JPCA* **1995**, 99, 14261.

The major analysis methods fail!

What do we do?

Transition density matrix

Transition density matrix (1TDM)

$$\gamma_{0I}(r_h, r_e) = \langle \Psi_0 | \hat{a}_p^\dagger \hat{a}_q | \Psi_I \rangle \phi_p(r_h) \phi_q(r_e)$$

Ψ_0, Ψ_I Ground and excited state wavefunctions

$\hat{a}_p^\dagger, \hat{a}_q$ **Creation** and **annihilation** operators

ϕ_p, ϕ_q Molecular orbitals

r_h, r_e Coordinates of the **hole** and **electron**

- Ground and excited state connected via **a matrix element**

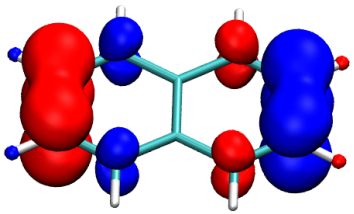
Transition density

$$\rho_{0I}(r) = \gamma_{0I}(r, r)$$

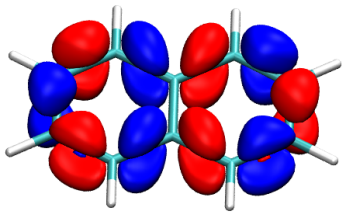
[1] FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024107.

Napthalene B_{3u} states

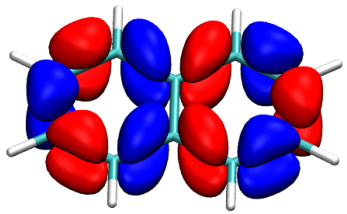
- ADC(2) **transition densities**
  - *For triplets:* Spin-difference transition densities



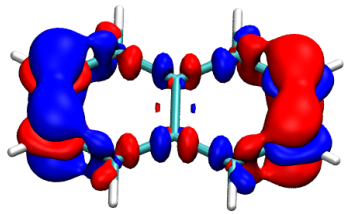
$^3B_{3u}^+$



$^1B_{3u}^-$



$^3B_{3u}^-$



$^1B_{3u}^+$

☺ +/− assignment clear → **+ on atoms**, **− on bonds**

- Strong transition moment for $^1B_{3u}^+$

! Most important **physically observable** derives from the **transition density**

? What about the energies

CIS excitation energy

$$\Delta E = \sum_{ia} |C_{ia}|^2(\epsilon_a - \epsilon_i) + \iint \frac{\rho_{0I}(r_h)\rho_{0I}(r_e)}{r_{he}} dr_h dr_e - \iint \frac{|\gamma_{0I}(r_h, r_e)|^2}{r_{he}} dr_h dr_e$$

C_{ia} CI coefficient

ϵ_i Orbital energy

Hartree-Fock	**Coulomb/Hartree**	**Exchange**
Electron/hole	**Exchange repulsion**	**Coulomb attraction Exciton binding**
Applicability	**Only for singlets**	**Singlets and triplets**
TDDFT	**Included**	**Non-local X**
Type	**One-body interaction**	**Two-body term**

CIS excitation energy

$$\Delta E = \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + \iint \frac{\rho_{0I}(r_h)\rho_{0I}(r_e)}{r_{he}} dr_h dr_e - \iint \frac{|\gamma_{0I}(r_h, r_e)|^2}{r_{he}} dr_h dr_e$$

- Excitation involving only two orbitals o, v

$\rightarrow$ $\gamma_{0I}(r_h, r_e) = o(r_h)v(r_e)$

$\rightarrow$ $\rho_{0I}(r) = o(r)v(r)$

CIS excitation energy - two orbitals

$$\Delta E = \epsilon_v - \epsilon_o + (ov|ov) - (oo|vv)$$

- Non-trivial terms only if **electron-hole entanglement**[1] is present

[1] FP, *JCP* **2016**, 144, 194107.

CIS excitation energy

$$\Delta E = \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + \iint \frac{\rho_{0I}(r_h)\rho_{0I}(r_e)}{r_{he}} dr_h dr_e - \iint \frac{|\gamma_{0I}(r_h, r_e)|^2}{r_{he}} dr_h dr_e$$

State	ADC(1)	ADC(2)	ADC(3)
$^3B_{3u}^+$	4.24	4.39	3.91
$^1B_{3u}^-$	5.27	4.49	4.16
$^3B_{3u}^-$	4.91	5.14	4.88
$^1B_{3u}^+$	7.23	6.37	6.41

- Highest energy for $^1B_{3u}^+$ – exchange repulsion
- What about the other states
- ? How to analyse $\gamma_{0I}(r_h, r_e)$

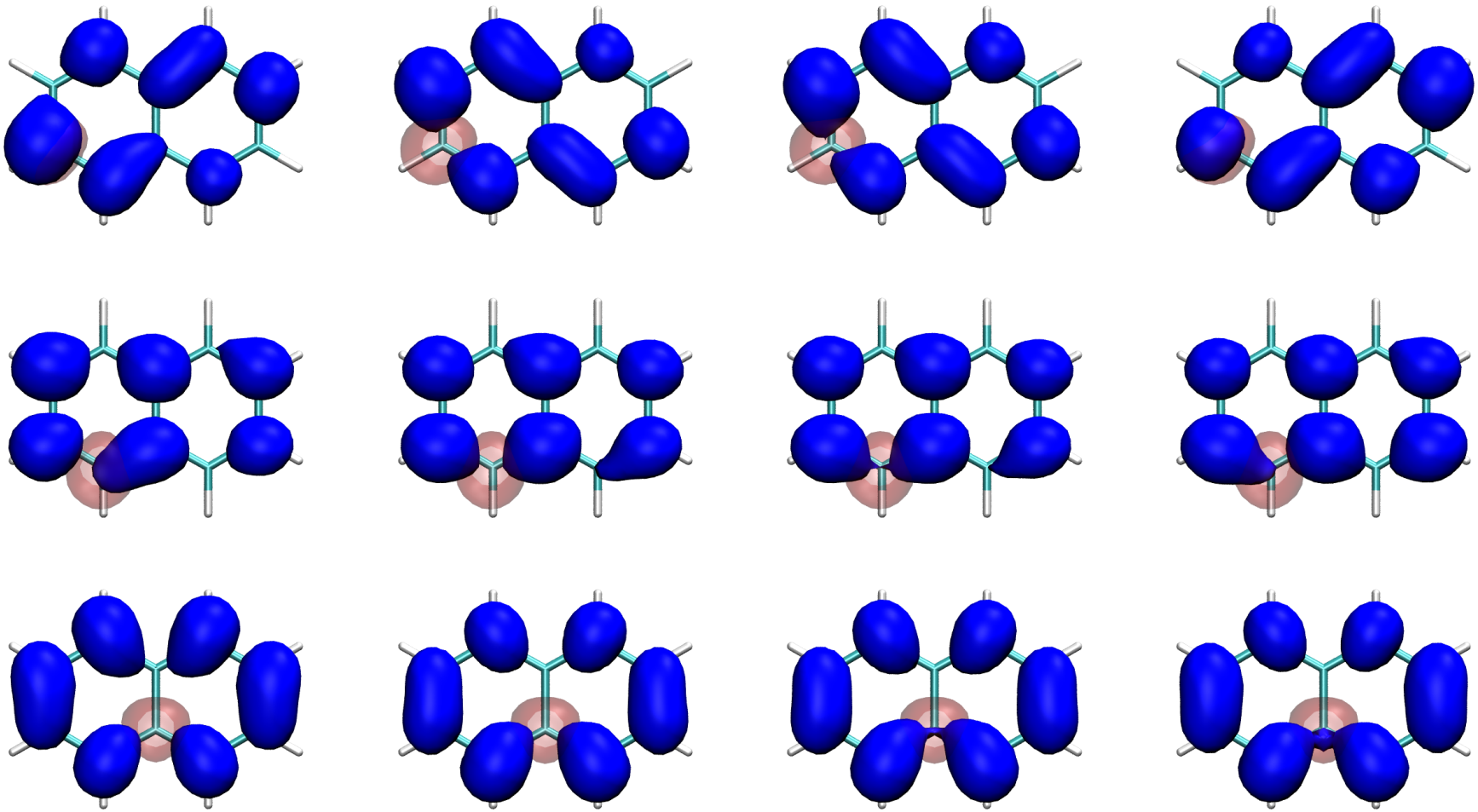
Conditional density for the excited electron

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

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

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

Conditional densities



$^3B_{3u}^+$ $^1B_{3u}^-$ $^3B_{3u}^-$ $^1B_{3u}^+$

Energetics

- **Ionic + states**: Enhanced electron-hole overlap

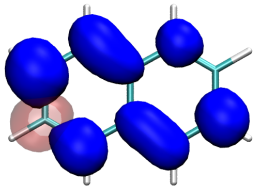
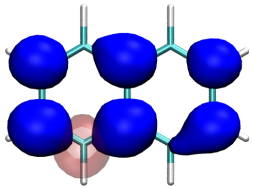
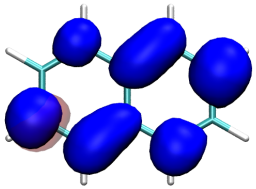
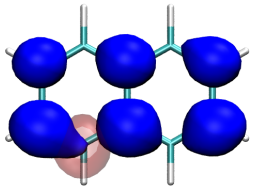
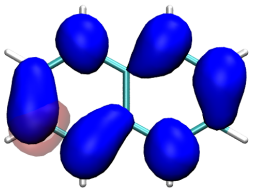
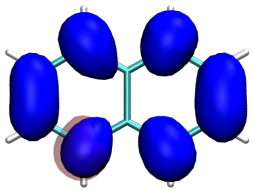
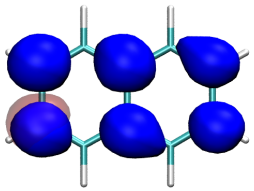
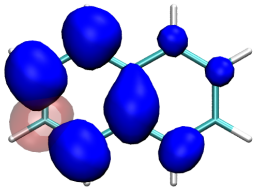
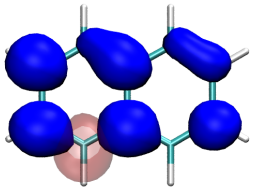
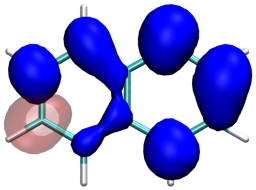
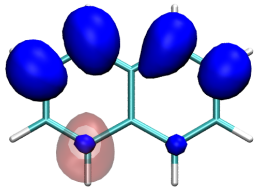
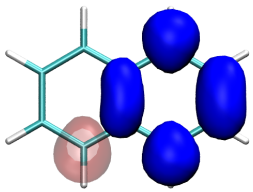
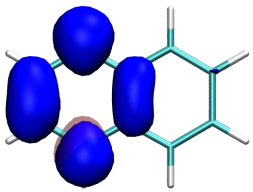
→ **More** exchange repulsion and Coulomb attraction

- **Covalent − states**: Enhanced electron-hole overlap

→ **Less** exchange repulsion and Coulomb attraction

State	ADC(1)	ADC(2)	ADC(3)
$^3B_{3u}^+$	4.24	4.39	3.91
$^1B_{3u}^-$	5.27	4.49	4.16
$^3B_{3u}^-$	4.91	5.14	4.88
$^1B_{3u}^+$	7.23	6.37	6.41

Naphthalene - Singlet States

$\rho_e^{h:2}/\rho_h^{h:2}$	$\rho_e^{h:1}/\rho_h^{h:1}$	$\rho_e^{h:2}/\rho_h^{h:2}$	$\rho_e^{h:1}/\rho_h^{h:1}$
			
$1^1B_{3u}^-$, 4.49 eV		$1^1B_{3u}^+$, 6.37 eV	
			*Vanishing*
$1^1B_{2u}^+$, 5.01 eV		$2^1B_{2u}^+$, 6.67 eV	
			
$1^1A_g^-$, 6.34 eV		$2^1A_g^-$, 7.49 eV	
Vanishing 		*Vanishing* 	
$1^1B_{1g}^-$, 6.42 eV		$1^1B_{1g}^+$, 7.00 eV	

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

- Alternative
- Use **CT measure**[1]
  - Weight of all the charge-transfer contributions between atoms

→ Automatised analysis possible

- *CT=0.9* for simple delocalised transition over 10 atoms
  - *CT<0.9* for **ionic + states**
  - *CT>0.9* for **covalent − states**

- Singlets prefer −

→ Exchange repulsion dominant

- Triplets prefer +

→ Only Coulomb attraction

Term	ΔE	f	CT
$^3B_{2u}^+$	3.26	-	**0.627**
$^3B_{3u}^+$	4.39	-	**0.836**
$^1B_{3u}^-$	4.49	0.0002	**0.980**
$^3B_{1g}^+$	4.66	-	**0.621**
$^3B_{2u}^+$	4.90	-	**0.776**
$^1B_{2u}^+$	5.01	0.11	**0.874**
$^3B_{3u}^-$	5.14	-	**0.975**
$^3A_g^+$	5.80	-	**0.723**
$^1A_g^-$	6.34	-	**0.979**
$^1B_{3u}^+$	6.37	1.52	**0.911**
$^1B_{1g}^-$	6.42	-	**0.995**
$^3B_{1g}^-$	6.63	-	**0.993**
$^1B_{2u}^+$	6.67	0.31	**0.844**

[1] FP, H. Lischka, *JCTC* **2012**, 8, 2777.
[2] FP, *ChemPhotoChem* **2019**, DOI: 10.1002/cptc.201900014.

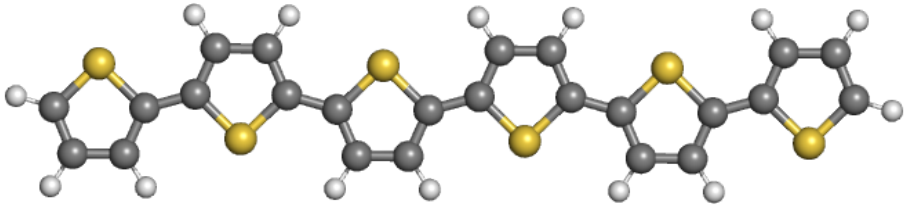
Physical Observability

- Knowledge of the **transition density** allows us to make testable predictions about the **absorption strengths**
- Knowledge of the **transition density matrix** allows us to make testable predictions about the **absorption strengths** and **relative energies**
- The **density** does **not** tell us anything at all about the **absorption strengths** and **relative energies**

? Is the transition density matrix **physically observable**?

Oligothiophene

- Oligothiophene



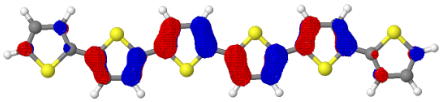
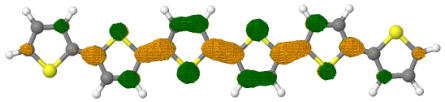
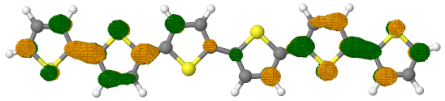
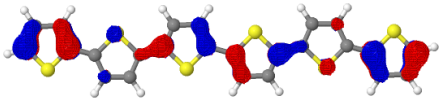
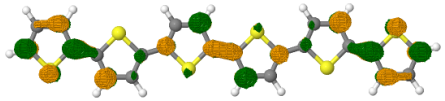
  - Prototypical conjugated polymer

- CAM-B3LYP computations

? How to analyse the states

Oligothiophene

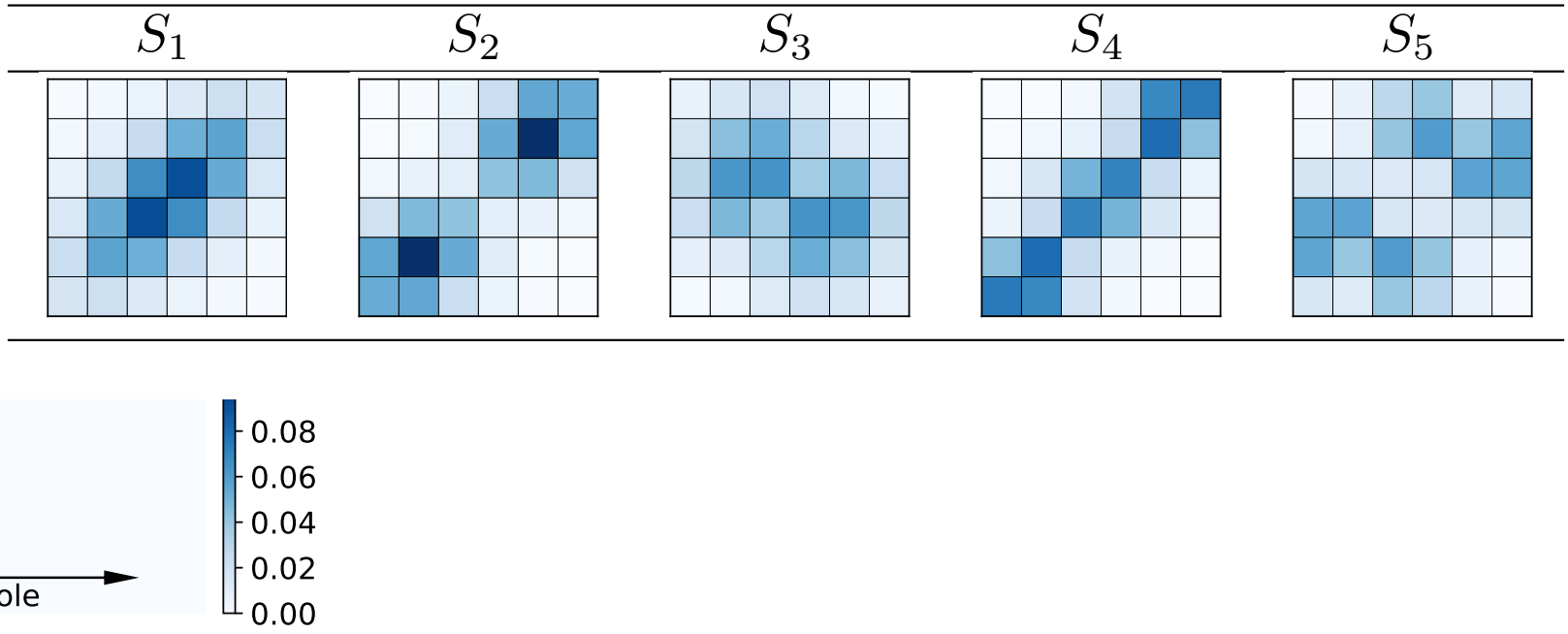
State	ΔE	Contribution
$S_1(1^1B_u)$	2.92	0.94 hl + 0.28 h_1l_1
$S_2(2^1A_g)$	3.77	0.73 hl_1 + 0.60 h_1l
$S_3(3^1A_g)$	4.12	− 0.58 hl_1 + 0.72 h_1l
$S_4(2^1B_u)$	4.44	0.68 hl_2 − 0.54 h_1l_1 + 0.29 h_2l
$S_5(3^1B_u)$	4.73	− 0.50 hl_2 − 0.30 h_1l_1 + 0.71 h_2l

h		l	
h_1		l_1	
h_2		l_2	

- ☹ Just many delocalized π and π^* orbitals
- ? Meaning of $+/-$
- ▶ 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)

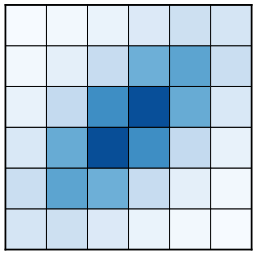
χ_μ Atomic orbital

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

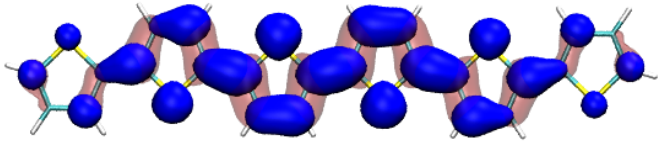
Conditional densities



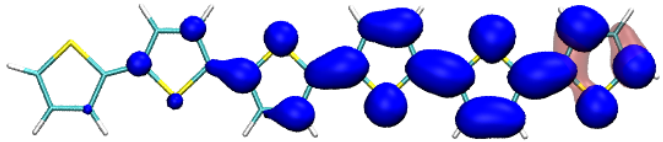
S_1 state

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

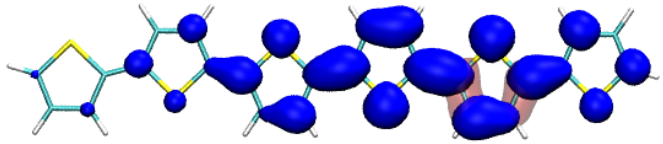
ρ_e / ρ_h



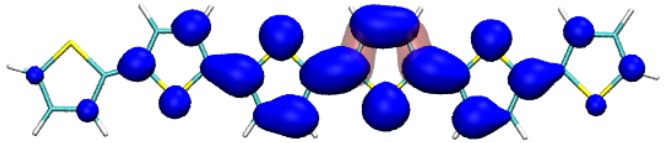
$\rho_e^{h:1} / \rho_h^{h:1}$



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



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



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

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

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

Operator expectation value

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

$\rightarrow$ Evaluate using **analytic integration** techniques

.

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

Exciton Analysis

Exciton size

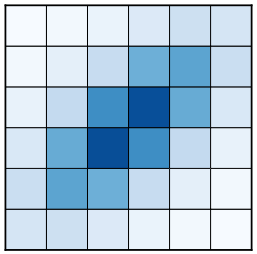
Exciton size

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

- 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



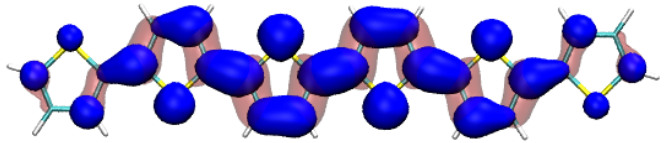
S_1 state

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

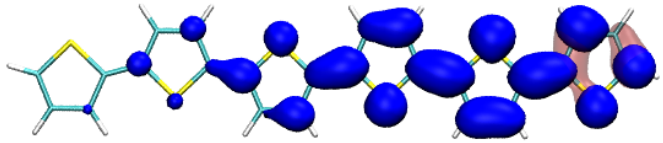
Further statistics[1,2]

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

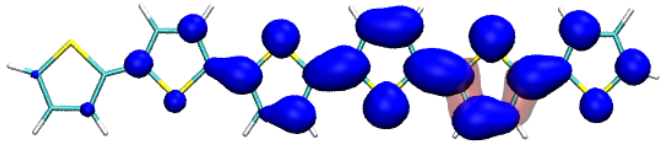
ρ_e / ρ_h



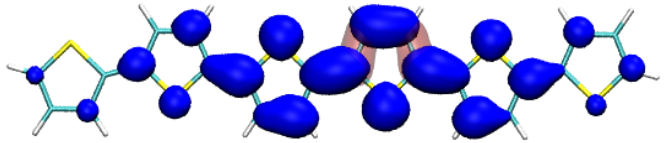
$\rho_e^{h:1} / \rho_h^{h:1}$



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

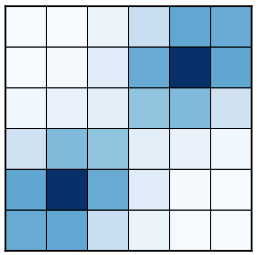


$\rho_e^{h:3} / \rho_h^{h:3}$



[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



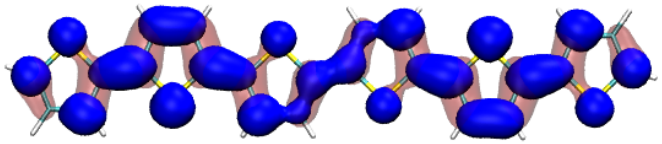
S_2 state

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

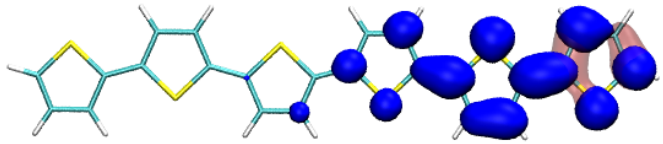
Further statistics

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

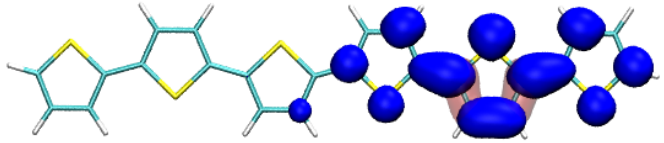
ρ_e / ρ_h



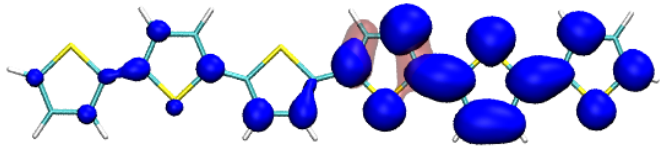
$\rho_e^{h:1} / \rho_h^{h:1}$



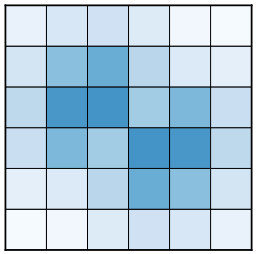
$\rho_e^{h:2} / \rho_h^{h:2}$



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



Conditional densities



S_3 state

- **Negative correleations** between electron and hole

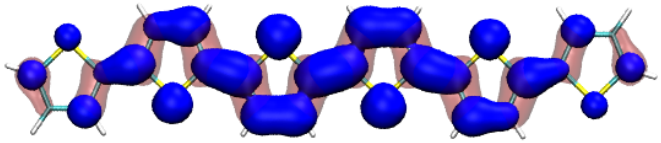
$\rightarrow$ Large e-h separation

- Nodal plane on **probe** thiophene

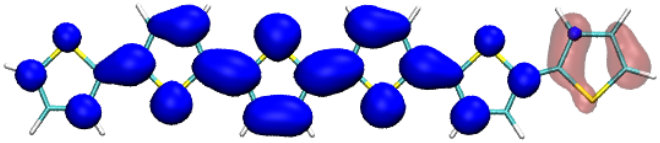
Further statistics

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

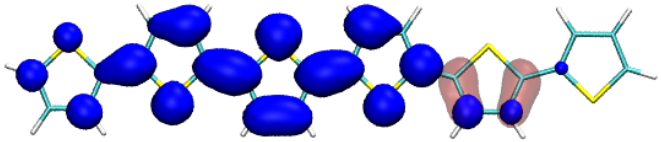
ρ_e / ρ_h



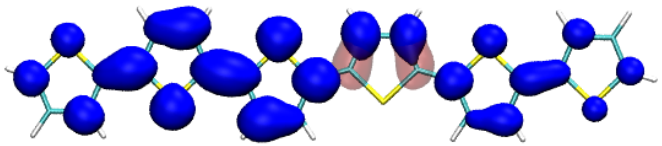
$\rho_e^{h:1} / \rho_h^{h:1}$



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



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



Summary

- Excited state **wavefunction analysis** tools
  - Visualization
  - Quantitative analysis

→ Automatization

→ Rigorous discussion

→ **New qualitative insight**

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`

Nonadiabatic dynamics

- ? How can we extend the scope of nonadiabatic dynamics methods
  - New electronic structure methods
  - Speed up the computation of nonadiabatic interaction terms
  - Application of model potentials

Electronic structure

- ? What **electronic structure method** should we use
  - Multireference theory[1]
  - ☹ Difficult to use
  - ☹ Computationally expensive
  - Time-dependent density functional theory
  - ☹ Dependence on functionals
  - Correlated single-reference methods
  - ADC(2) / CC2
  - ☺ Easy, cheap, well-defined

[1] H. Lischka et al., *Chem. Rev.* **2018**, 118, 7293–7361.

ADC(2)/CC2

- ADC(2)/CC2 dynamics
- `Turbomole/NX` interface[1]
  - **Nonadiabatic coupling** through **overlaps of approximate wavefunctions**

→ Internal conversion processes

- `Turbomole/SHARC` interface[2]
  - **Spin-orbit coupling** through `Turbomole/ORCA` interface

→ Intersystem crossing + internal conversion

[1] FP, R. Crespo-Otero, M. Pederzoli, et al., *JCTC* **2014**, 10, 1395.
[2] S. Mai, FP, M. Pabst, F. Neese, A. Köhn, L. González, *JCP* **2017**, 147, 184109.

Overlaps

Wave function overlaps

$$S_{IJ} = \langle \Psi_I(\mathbf{R}) | \Psi_J(\mathbf{R}') \rangle$$

Many-electron wave functions

- Expansion into Slater determinants

$$|\Psi_I\rangle = \sum_{k=1}^{n_{CI}} d_{kI} \, |\Phi_k\rangle$$

- Expansion into MOs
  - α and β spin

$$|\Phi_k\rangle = |\varphi_1 \cdots \varphi_{n_\alpha} \bar{\varphi}_{n_\alpha+1} \cdots \bar{\varphi}_n|$$

Overlaps

- Overlap as double sum over Slater determinant overlaps

$$S_{IJ} = \langle \Psi_I | \Psi'_J \rangle = \sum_{k=1}^{n_{CI}} \sum_{l=1}^{n'_{CI}} d_{kI} d'_{lJ} \langle \Phi_k | \Phi'_l \rangle$$

- Computed as determinant over MO overlaps
  $\langle \Phi_k | \Phi'_l \rangle =$

$$\begin{vmatrix} \langle \varphi_1 | \varphi'_1 \rangle & \cdots & \langle \varphi_1 | \varphi'_{n_\alpha} \rangle & & \\ \vdots & \ddots & \vdots & & \\ \langle \varphi_{n_\alpha} | \varphi'_1 \rangle & \cdots & \langle \varphi_{n_\alpha} | \varphi'_{n_\alpha} \rangle & & \\ & & & & \\ & \mathbf{0} & & & \\ & & & & \\ & & & \langle \bar{\varphi}_{n_\alpha+1} | \bar{\varphi}'_{n_\alpha+1} \rangle & \cdots & \langle \bar{\varphi}_{n_\alpha+1} | \bar{\varphi}'_{l(n)} \rangle \\ & & & \vdots & \ddots & \vdots \\ & & & \langle \bar{\varphi}_n | \bar{\varphi}'_{n_\alpha+1} \rangle & \cdots & \langle \bar{\varphi}_n | \bar{\varphi}'_n \rangle \end{vmatrix}$$

- **Formal scaling**: $\mathcal{O}(n_{CI} n'_{CI} n_{el}^3)$
- Simplifications?

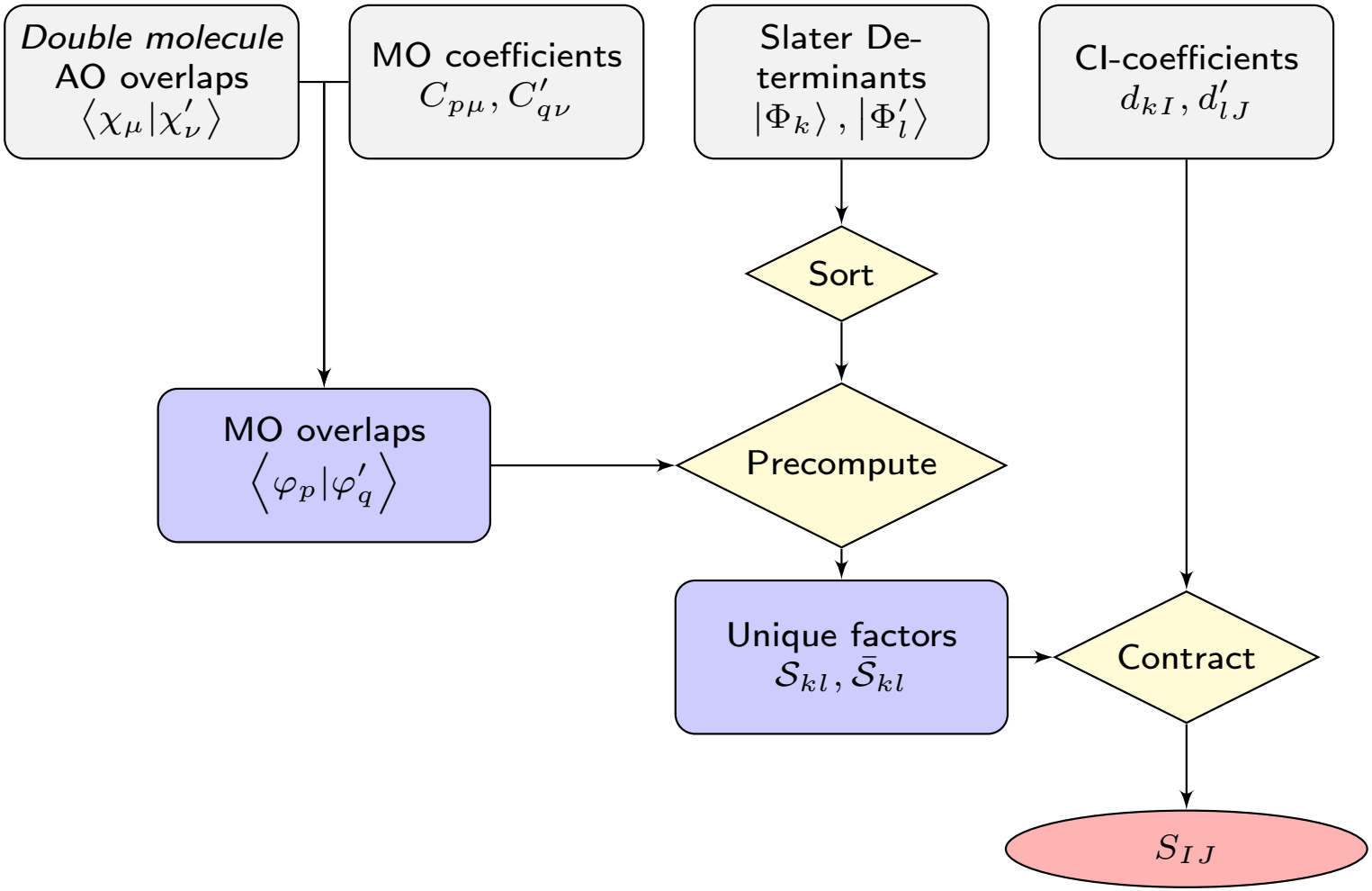
Overlaps

- Two independent factors for α and β spin

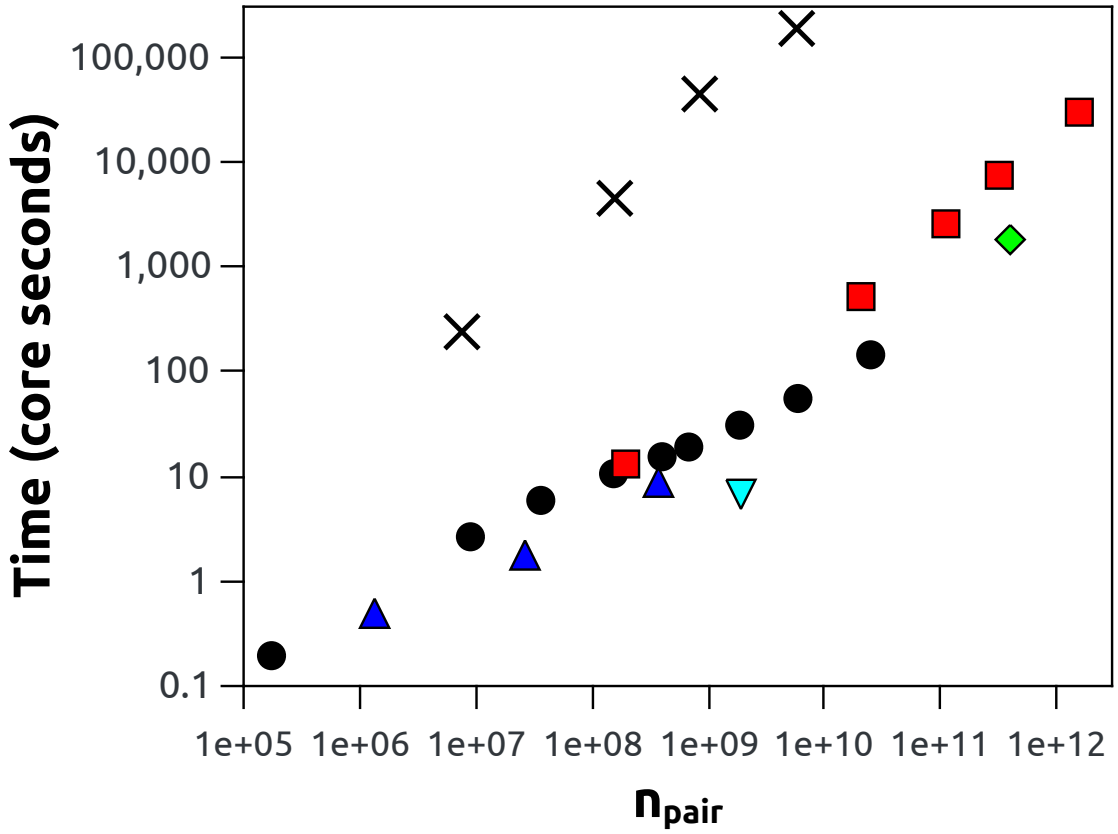
$$\langle \Phi_k | \Phi'_l \rangle = \begin{vmatrix} \langle \varphi_1 | \varphi'_1 \rangle & \cdots & \langle \varphi_1 | \varphi'_{n_\alpha} \rangle \\ \vdots & \ddots & \vdots \\ \langle \varphi_{n_\alpha} | \varphi'_1 \rangle & \cdots & \langle \varphi_{n_\alpha} | \varphi'_{n_\alpha} \rangle \end{vmatrix} \times \begin{vmatrix} \langle \bar{\varphi}_{n_\alpha+1} | \bar{\varphi}'_{n_\alpha+1} \rangle & \cdots & \langle \bar{\varphi}_{n_\alpha+1} | \bar{\varphi}'_{l(n)} \rangle \\ \vdots & \ddots & \vdots \\ \langle \bar{\varphi}_n | \bar{\varphi}'_{n_\alpha+1} \rangle & \cdots & \langle \bar{\varphi}_n | \bar{\varphi}'_n \rangle \end{vmatrix} = \mathcal{S}_{\mathbf{kl}} \bar{\mathcal{S}}_{\mathbf{kl}}$$

- Spin-factors reappear
- **Strategy**: Precompute and store these factors

Overlaps


Double molecule
AO overlaps
$\langle \chi_\mu | \chi'_\nu \rangle$
MO coefficients
$C_{p\mu}, C'_{q\nu}$
Slater Determinants
$|\Phi_k\rangle, |\Phi'_l\rangle$
CI-coefficients
d_{kI}, d'_{lJ}
Sort
MO overlaps
$\langle \varphi_p | \varphi'_q \rangle$
Precompute
Unique factors
$\mathcal{S}_{kl}, \bar{\mathcal{S}}_{kl}$
Contract
S_{IJ}

Performance



- Uniform performance
  - Over 7 orders of magnitude in problem size
  - For various wave function models
- 2-3 orders of magnitude faster than previous code (X)

Overlaps

- Integration into the SHARC dynamics code[1]
- Interface to various electronic structure codes

Multireference methods	Columbus, Molcas
Time-dependent DFT	ADF, Dalton, Gaussian
Coupled cluster	Turbomole

- Photoelectron spectra / Dyson orbitals[2]
- Wave function analysis[3]

[1] FP, M. Ruckenbauer, S. Mai, M. Oppel, P. Marquetand, L. González, *JCTC* **2016**, 12, 1207.
[2] M. Ruckenbauer, S. Mai, P. Marquetand, L. González, *Sci. Rep.* **2016**, 6, 35522.
[3] F. Plasser, L. González, *J. Chem. Phys.* **2016**, 145, 021103.

Formalism

Linear Vibronic Coupling Model

$$\mathbf{H}_{el} = V_0 \mathbf{1} + \mathbf{W}$$

$\mathbf{H}_{el}$ *Diabatic* Hamiltonian matrix

V_0 (Harmonic) ground state potential - *the same* for all states

$\mathbf{W}$ Coupling terms - *different* among states

- Separation of ground- and excited state contributions
- Construction possible from computations at one geometry

Formalism

Intrastate coupling terms

$$W^{n,n} = \epsilon_n + \sum_i \kappa_i^{(n)} Q_i \qquad \kappa_i^{(n)} = \langle \Psi_n | \frac{\partial \hat{H}_{el}}{\partial Q_i} | \Psi_n \rangle$$

ϵ_n Constant term - *vertical excitation energy*

$\kappa_i^{(n)}$ Intrastate coupling term for state n and mode i - *gradient*

Q_i Normal mode displacement

Interstate coupling terms

$$W^{m,n} = \sum_j \lambda_j^{(m,n)} Q_j$$

$$\lambda_i^{(n,m)} = \langle \Psi_n | \frac{\partial \hat{H}}{\partial Q_i} | \Psi_m \rangle = (\epsilon_m - \epsilon_n) \langle \Psi_n | \partial Q_i | \Psi_m \rangle$$

$\lambda_i^{(n,m)}$ Interstate coupling term for states n, m and mode i - *nonad. coupling*, *wavefunction overlap* or *excited state Hessians*

Parameterisation

- If nonadiabatic coupling vectors are available available

→ All parameters from **one** single point computation at the Franck-Condon geometry

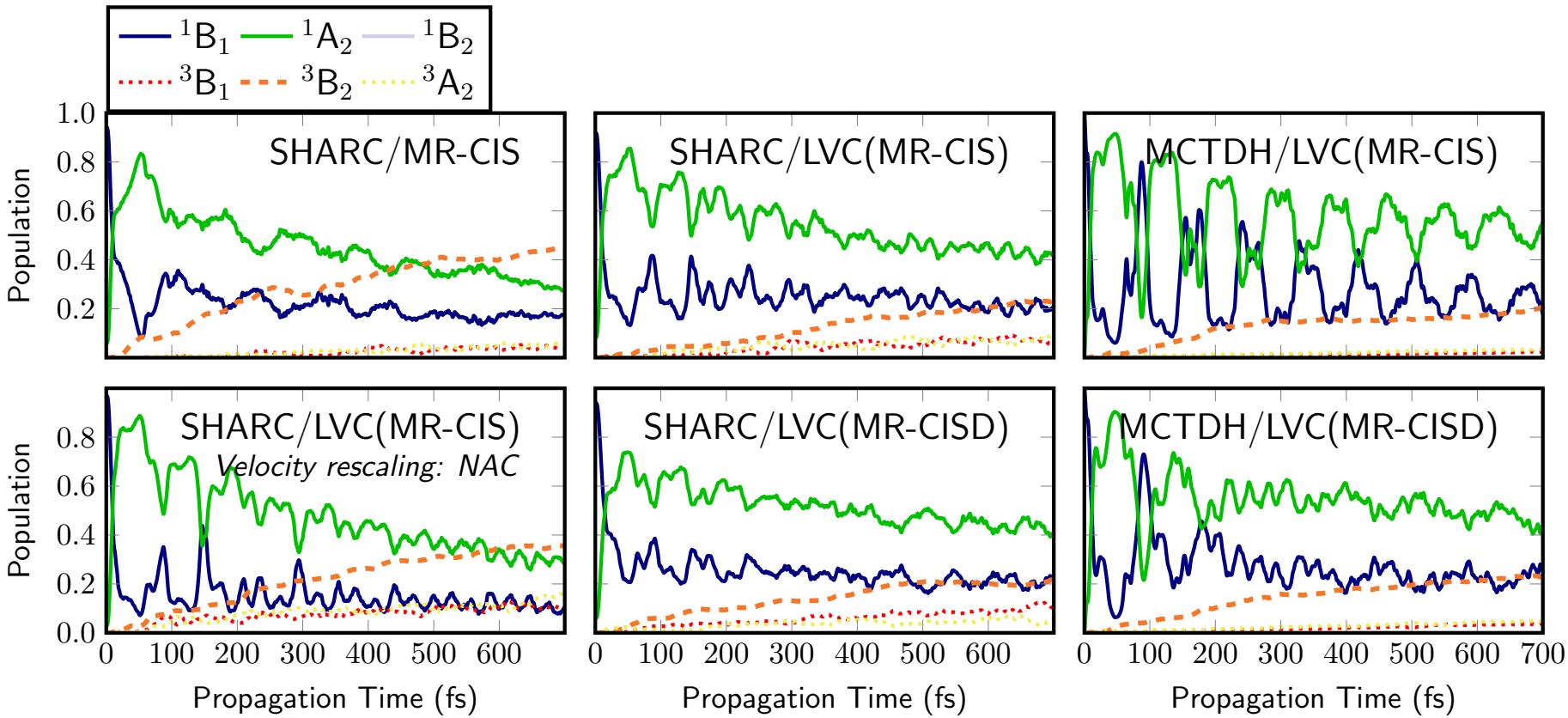
- With wavefunction overlaps

→ **3N** computations[1]

[1] M. Fumanal, F. Plasser, S. Mai, C. Daniel, E. Gindensperger, *JCP* **2018**, 148, 124119.

SO2

- Example SO_2



[1] FP, S. Gómez, M. F. S. J. Menger, S. Mai, L. González, *PCCP* **2019**, 21, 57.

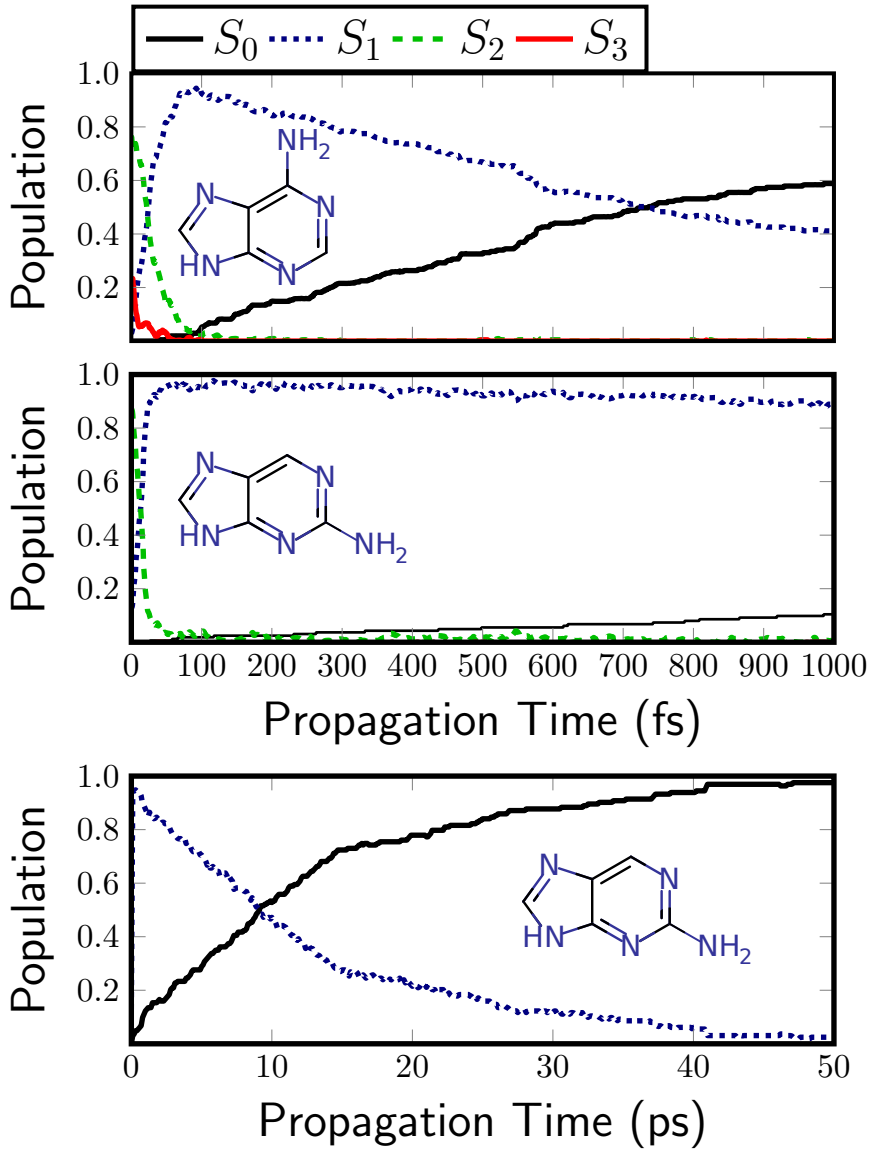
Adenine vs 2-aminopurine

- Comparison of adenine and 2-aminopurine
- Adenine

→ **Ultrafast decay**

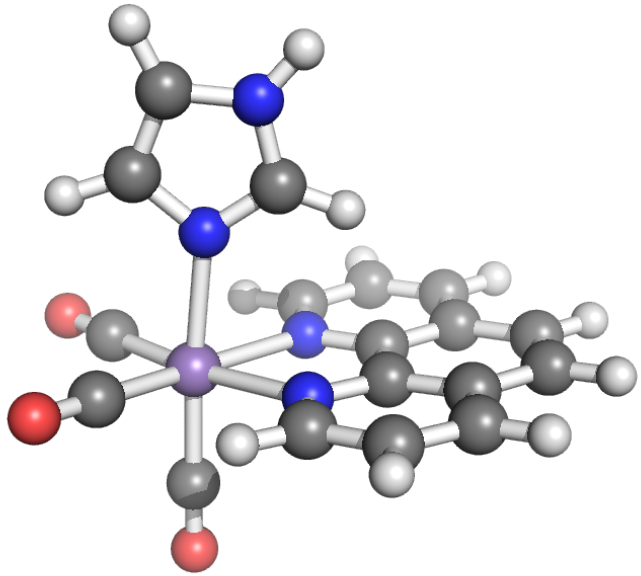
- 2-aminopurine

→ **Longer lifetime** in S_1



Method evaluation

- Compare MCTDH dynamics with surface hopping
- Potentials for Re complex
  - 15 modes
  - 2 singlets, 4 triplets
- Evaluate different methods



Method evaluation

- **Decoherence** corrections

→ Energy-based decoherence (EDC)[1]

→ Augmented fewest switches surface hopping (AFSSH)[2]

- **Momentum** rescaling

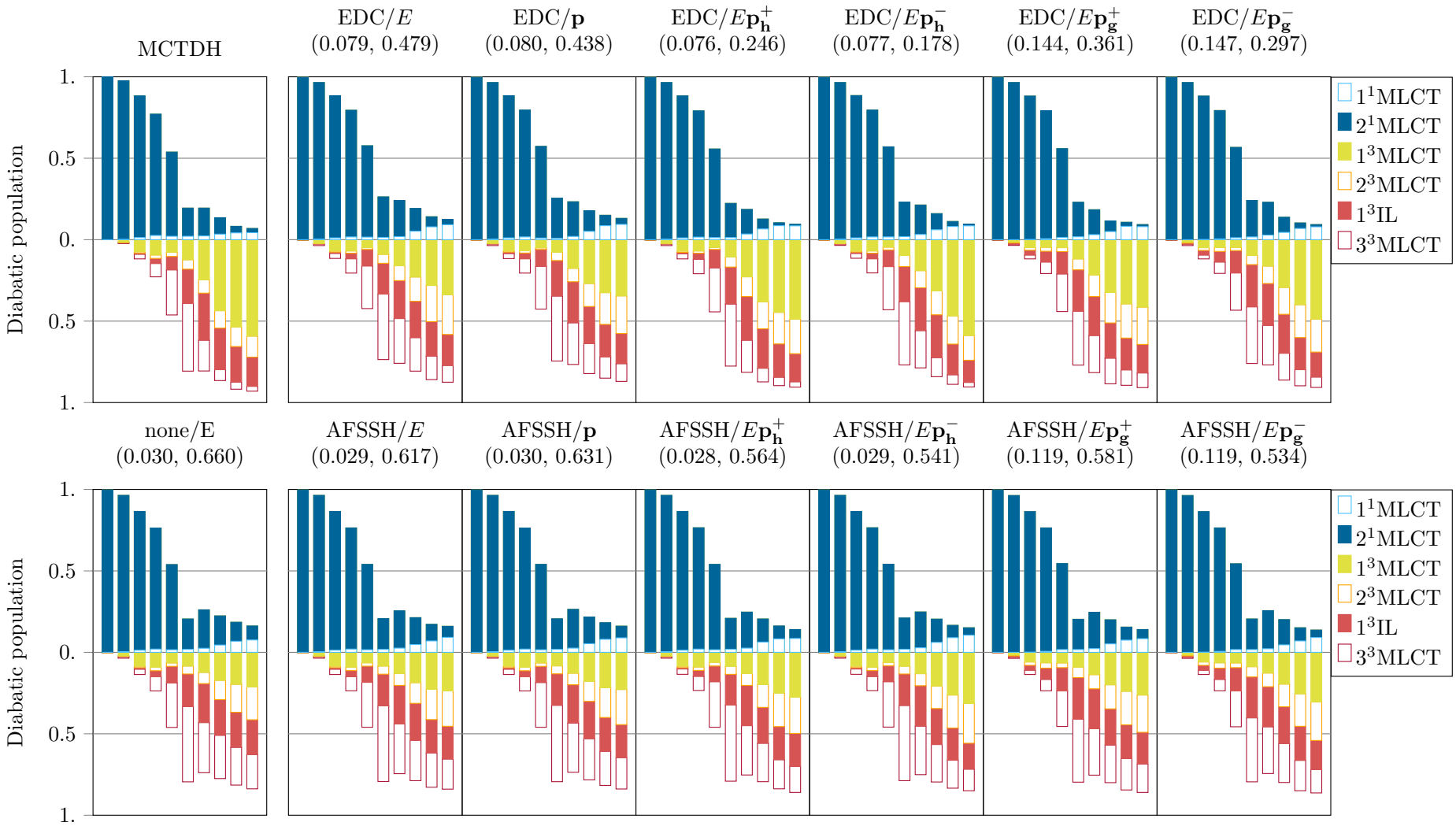
	Conserved quantity	Rescaling along
E	Energy	Momentum
$\mathbf{p}$	Momentum	None
$E\mathbf{p_h}$	Energy and momentum	NAC
$E\mathbf{p_g}$	Energy and momentum	Grad. diff.

- **Frustrated hops**[3]

→ +/−

[1] G. Granucci, M. Persico, *JCP* **2007**, 126, 1.
[2] A. Jain, E. Alguire, J. E. Subotnik, *JCTC* **2016**, 12, 5256.
[3] A. W. Jasper, D. G Truhlar, *CPL* **2003**, 369, 60.

- Population dynamics on a **logarithmic time scale**



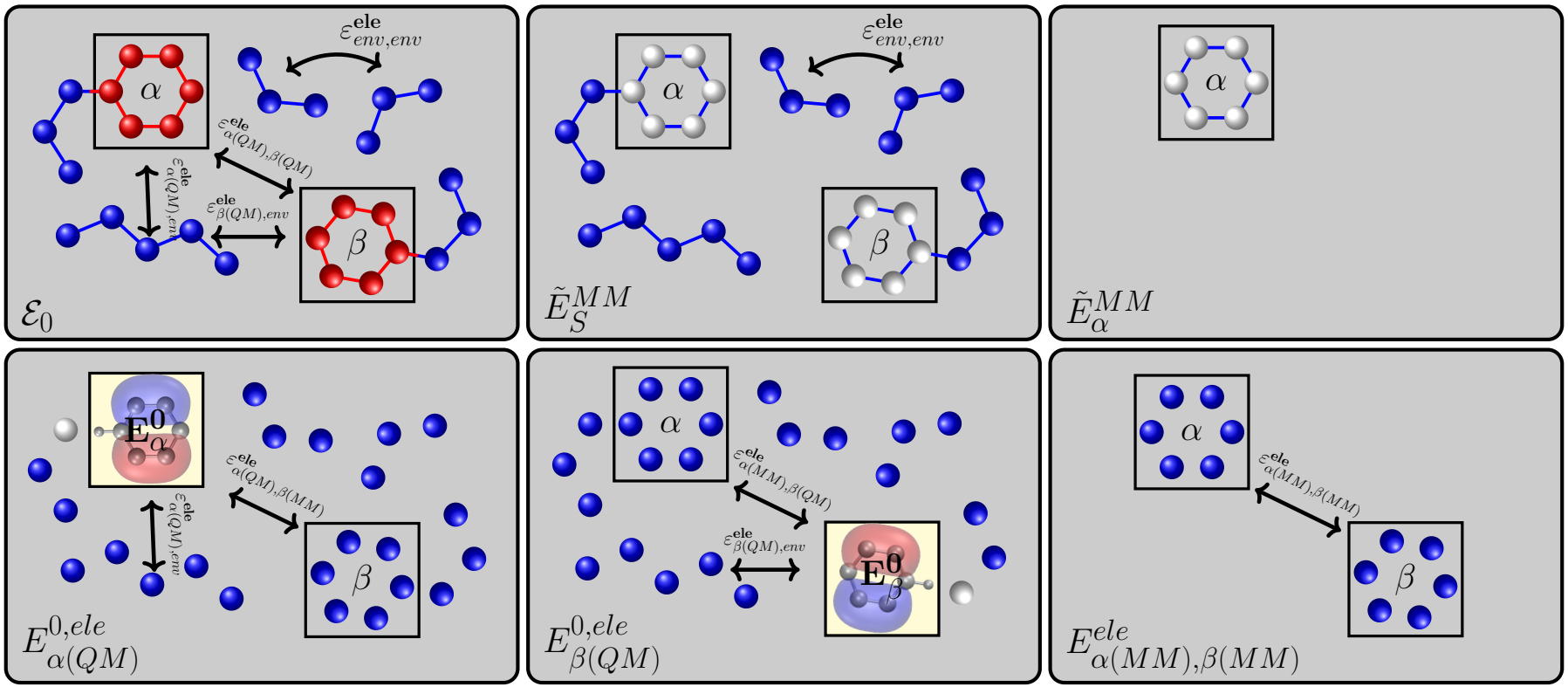
- Strong method dependence

→ Best results: EDC/$E\mathbf{p}_\mathbf{h}^-$

Exciton model

- QM/MM **exciton model**
  - Monomer calculations combined via exciton model
  - Electrostatic embedding scheme

→ Applied to surface hopping dynamics



[1] M. F. S. J. Menger, F. Plasser, B. Mennucci, L. González, *JCTC* **2018**, 14, 6139.

Summary

- Nonadiabatic dynamics
- Enhance applicability through small improvements
  - Dynamics at the ADC(2)/CC2 level
  - Wavefunction overlaps
  - Model potentials

Acknowledgements

Vienna
S. Mai
J. J. Nogueira
L. González

Heidelberg
S. A. Mewes
M. Wormit
A. Dreuw

Vienna/Lubbock/Tianjin
H. Lischka

Marseille
M. Barbatti

Strasbourg
C. Daniel

Pisa
B. Mennucci

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