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

Felix Plasser

Department of Chemistry, Loughborough University

Loughborough, 6 March 2018

Loughborough University

Introduction

Computational Chemistry / Photochemistry

- Accurate computations
- Comparison to experiment
- Chemical insight

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- ☺ *Quantum chemical methods*:
  Semi-emp., TDDFT, CC, ADC, CASSCF, DMRG, CASPT2, MR-CI, ...

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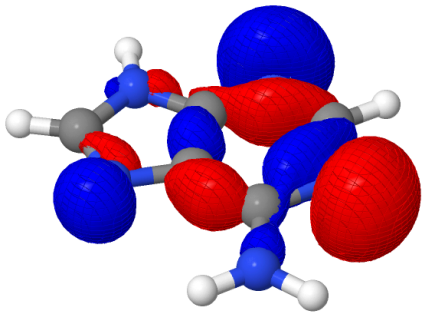
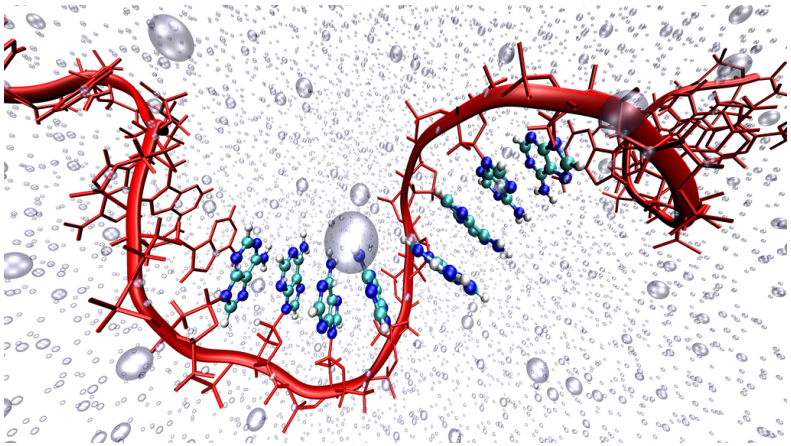
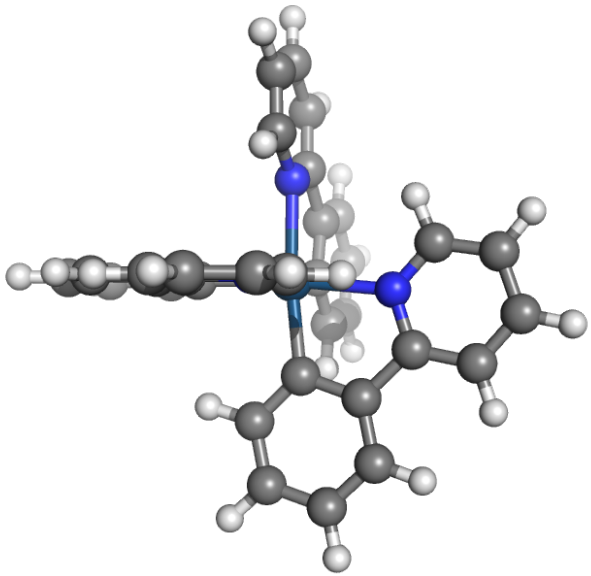
☹ **Look at the HOMO and LUMO**



DNA



Transition Metal Complexes



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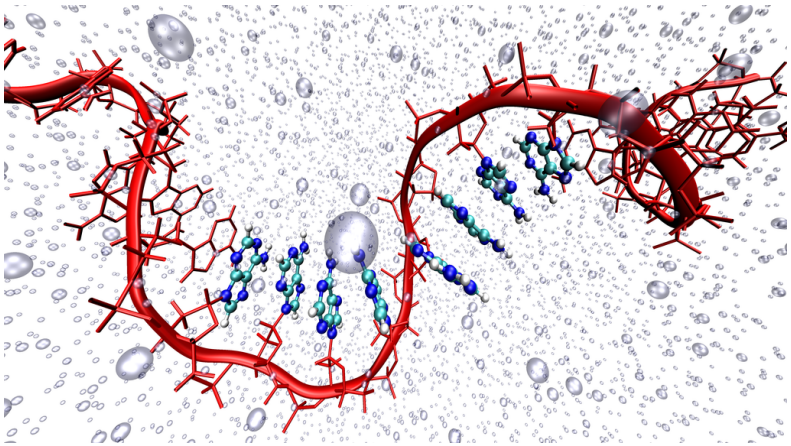

Transition Metal Complexes

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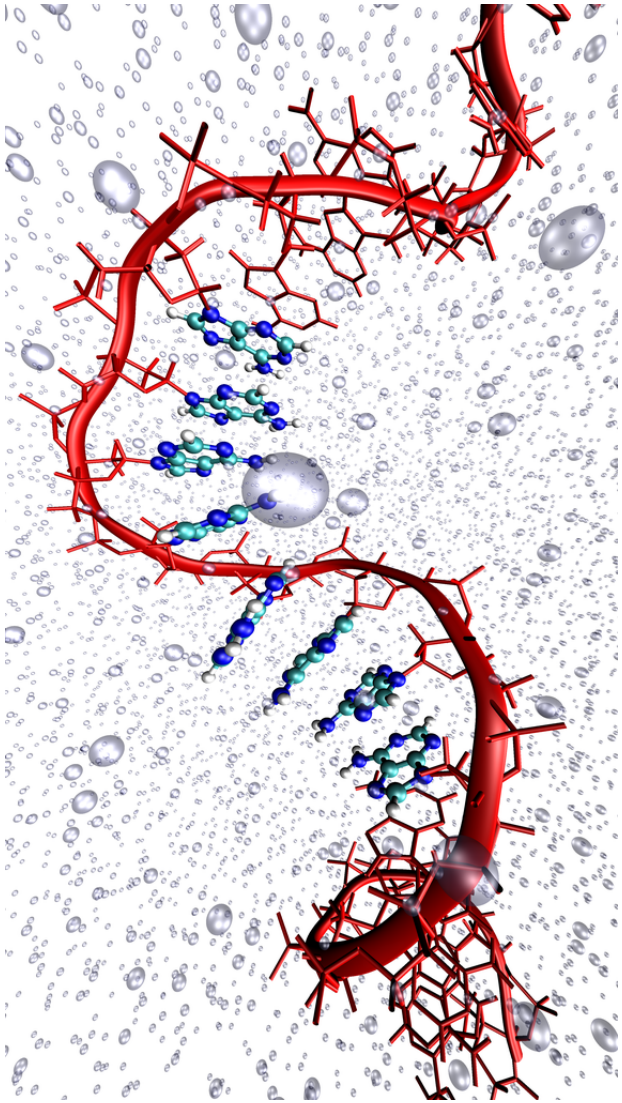
Photophysics of interacting nucleobases

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



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DNA

Photophysics of interacting nucleobases

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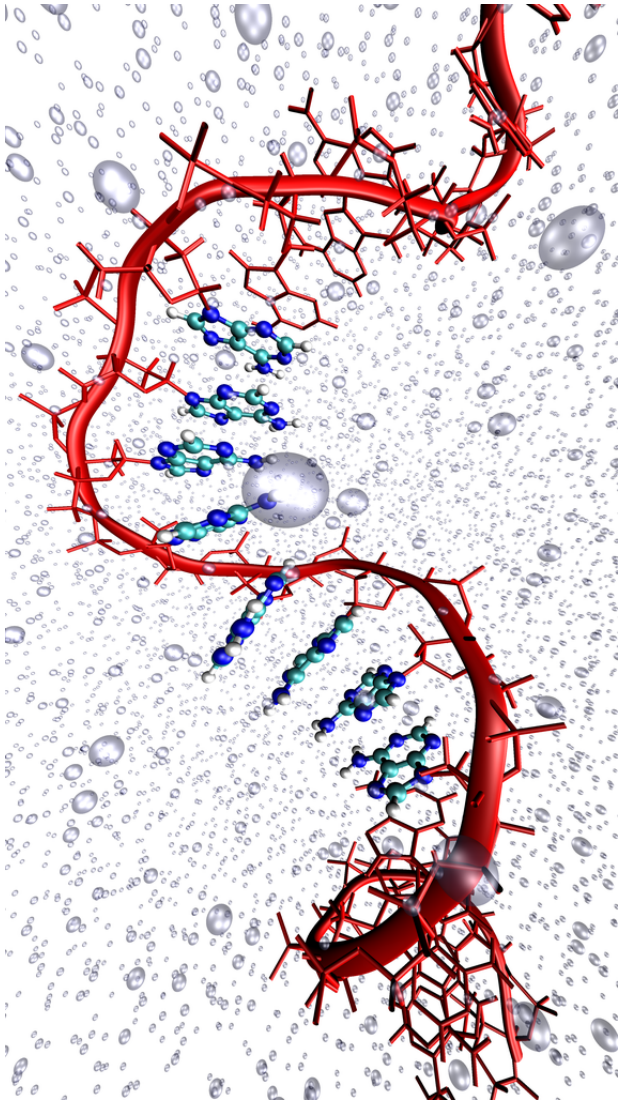
Starting point: **UV absorption**

- Localized/delocalized excitations
- Charge transfer states



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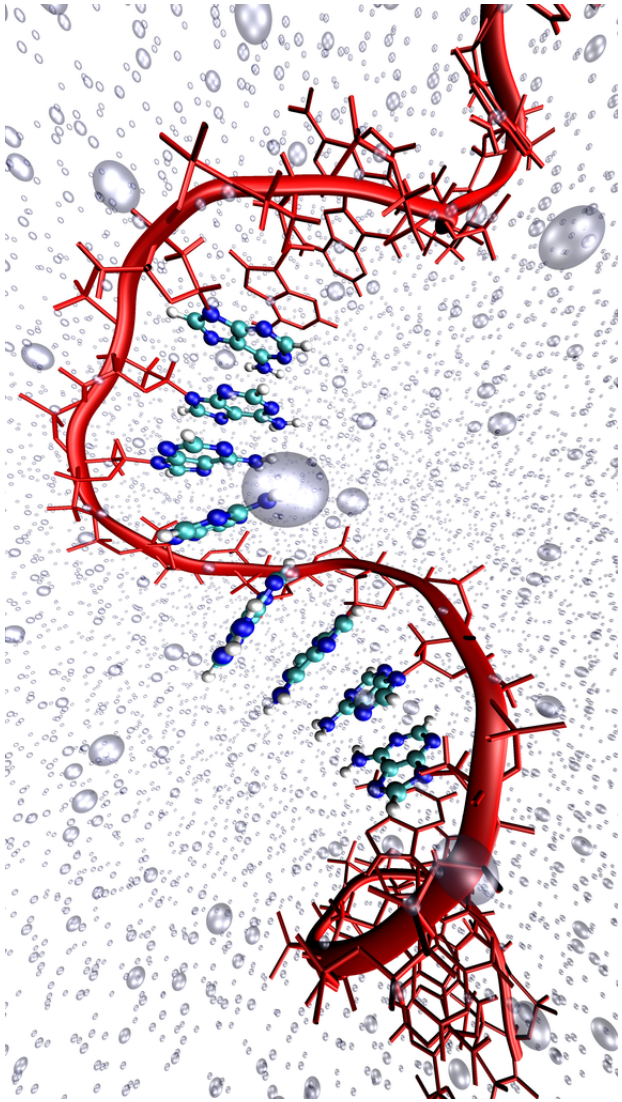
DNA

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



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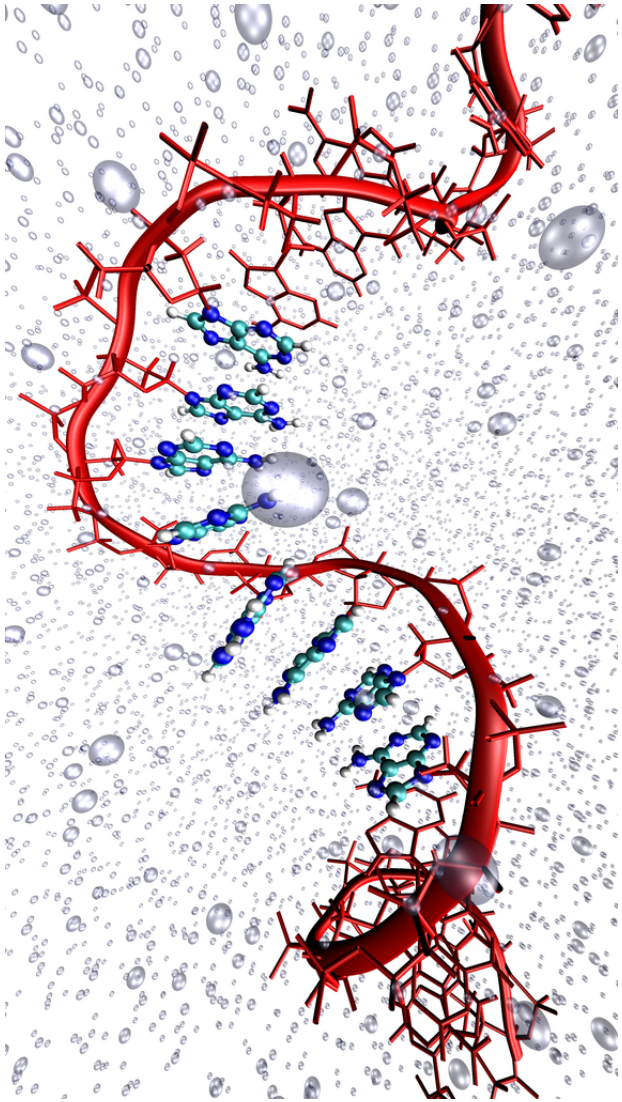
☹ How do we analyze **6000** excited states?



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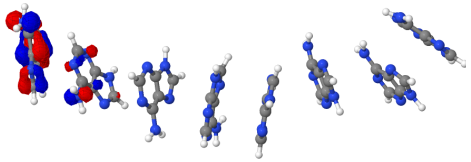
DNA

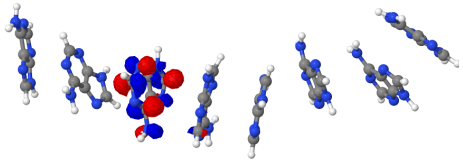
Leading configurations

- 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)

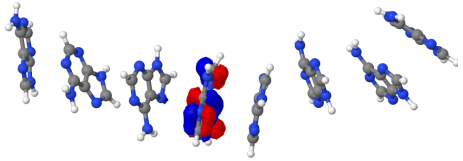
Canonical orbitals



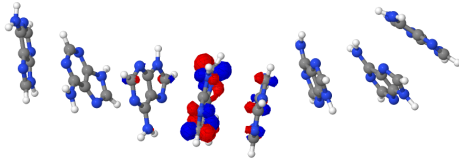
HOMO



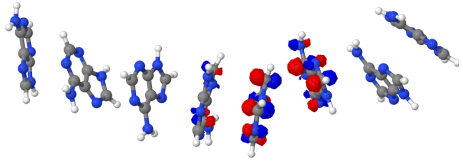
L (LUMO)



H-2



L+1



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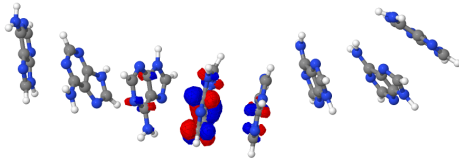

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☹ Tedious **work**

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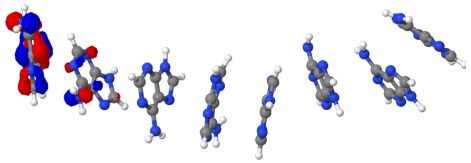

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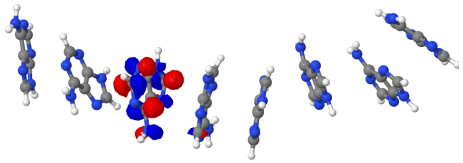

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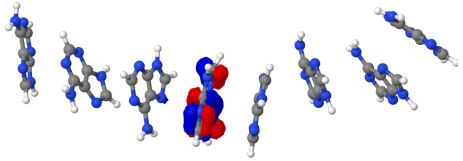

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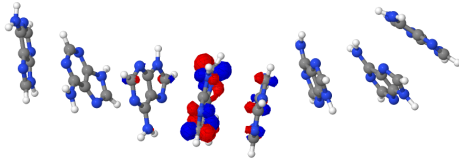

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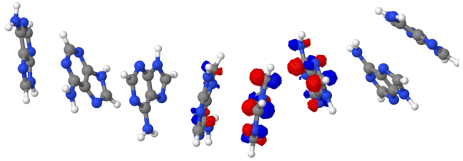

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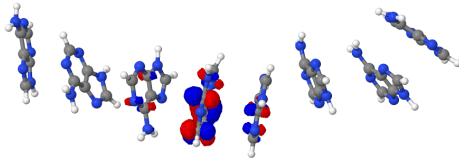

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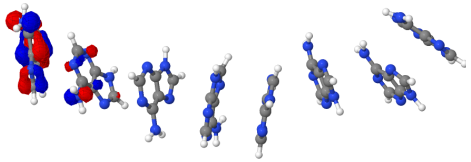

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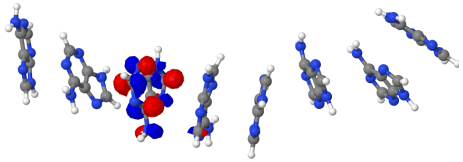

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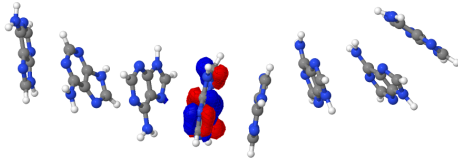

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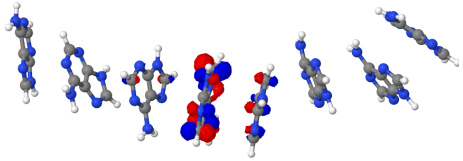

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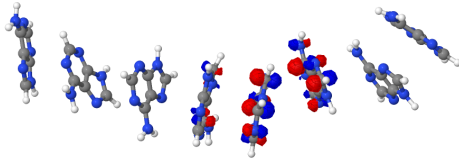

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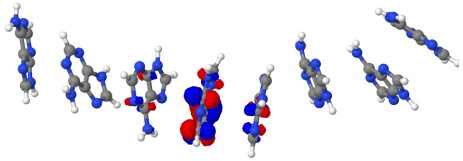

L+10

Compact Visualization

- Natural transition orbitals[1]
  - Singular value decomposition of the transition density matrix

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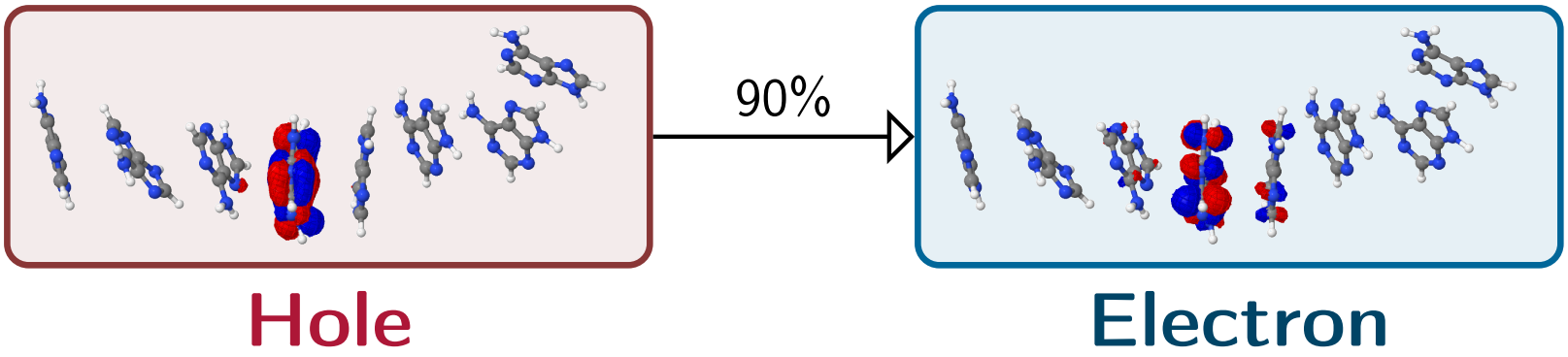
  - *Locally excited state (L_a)*
  - Only one important configuration



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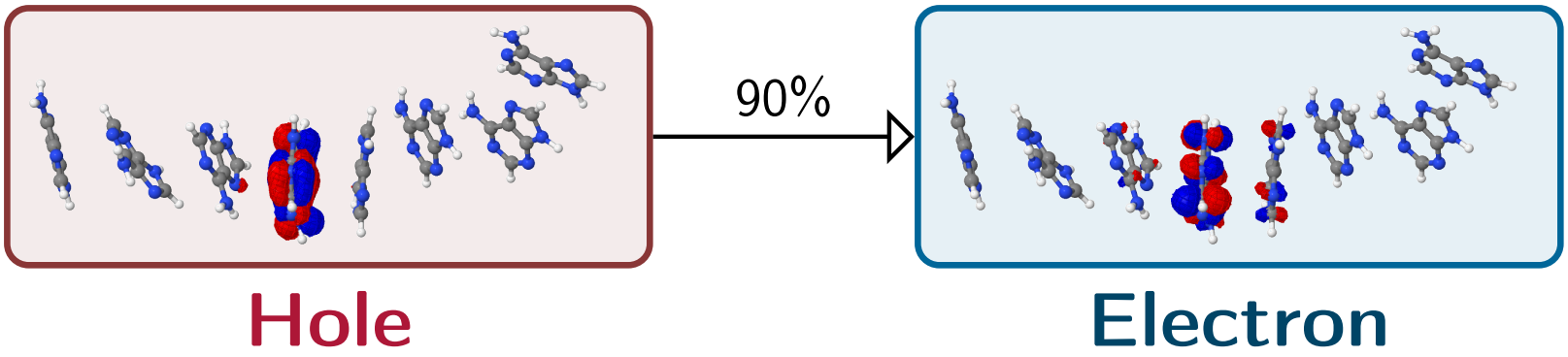

☺ Resolves (some) **ambiguities**

☹ Still tedious **work**

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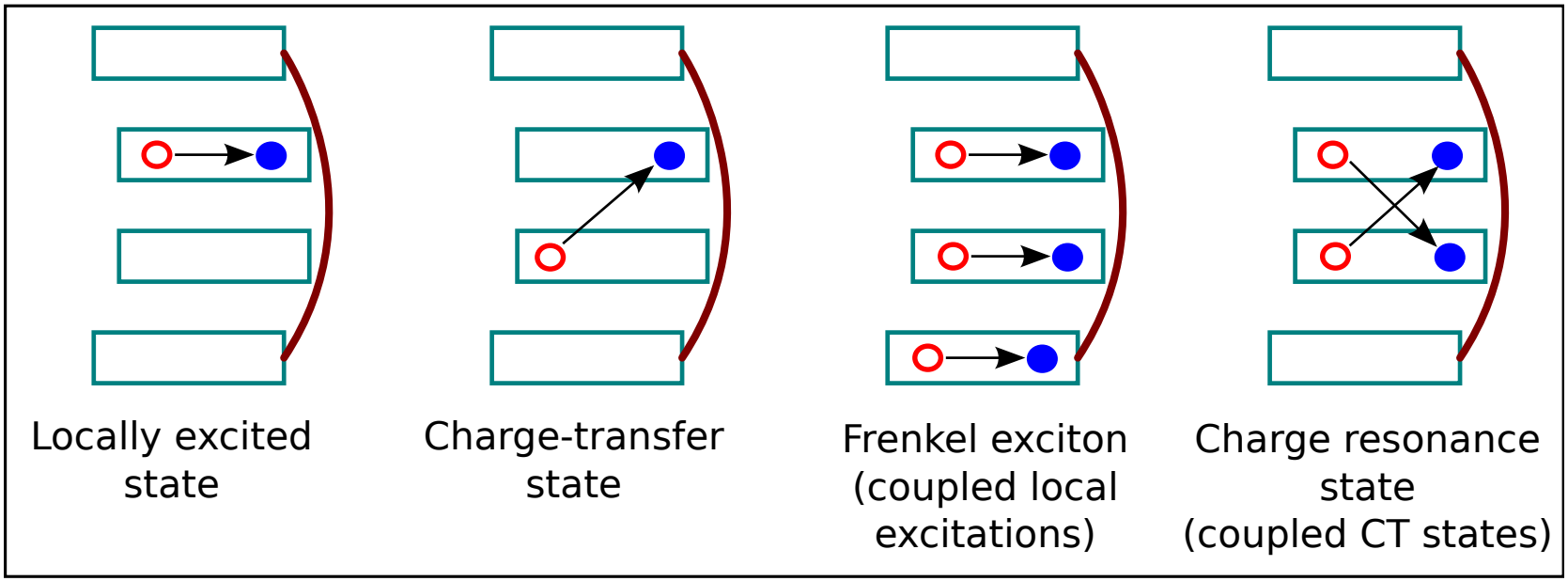
DNA

- Excited states in multichromophoric systems



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- Where the excitation goes to - "electron"

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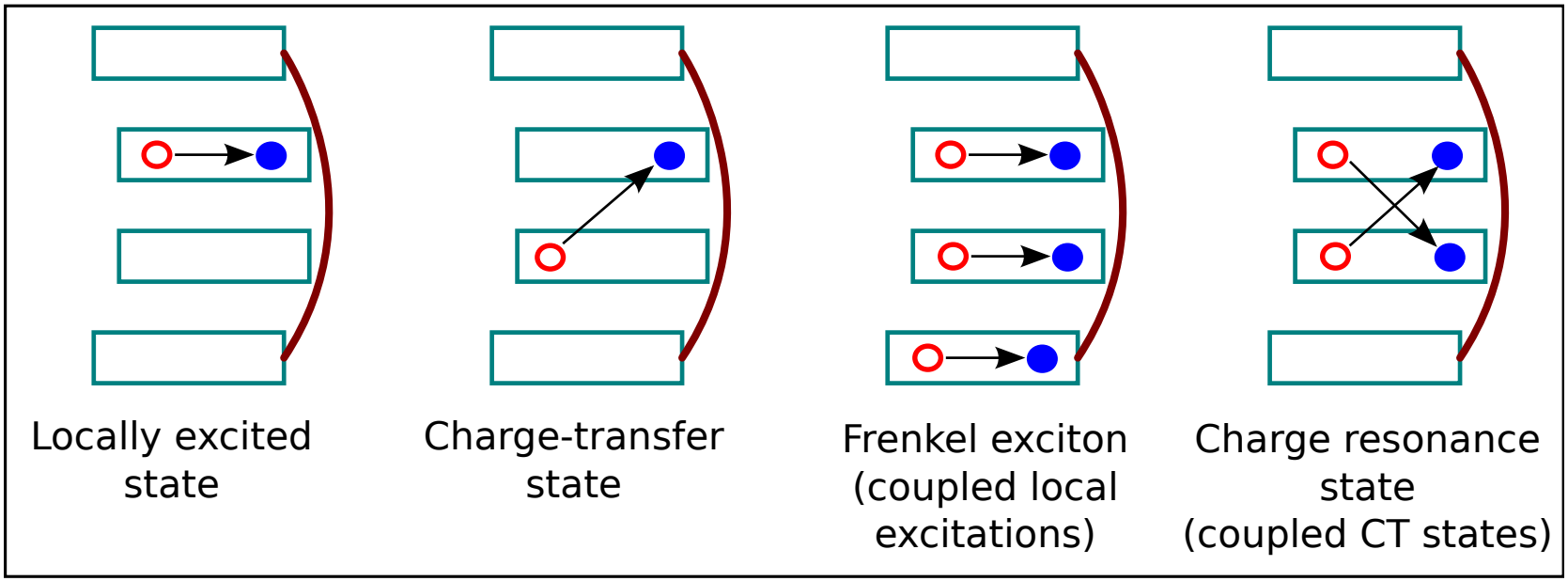

- Where the excitation comes from - "hole"
- Where the excitation goes to - "electron"

- 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

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

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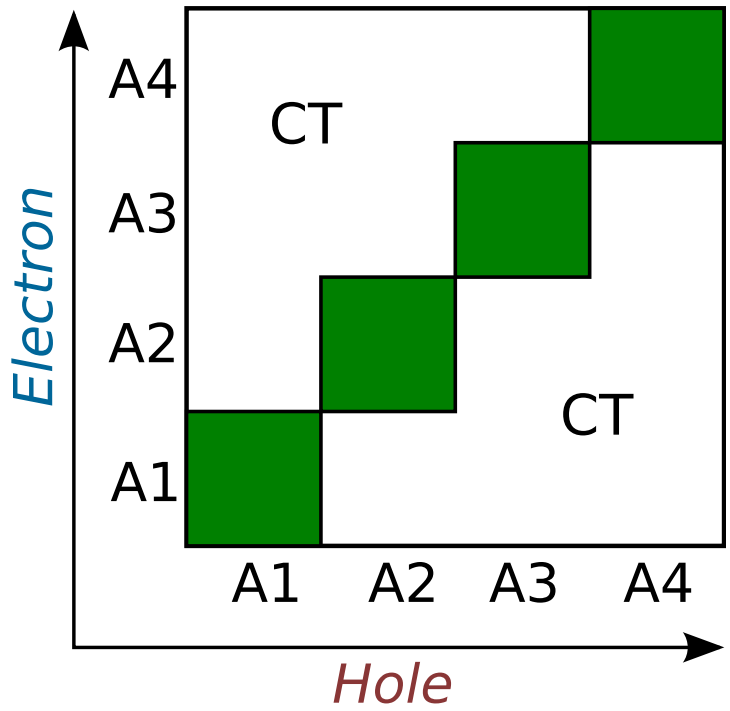

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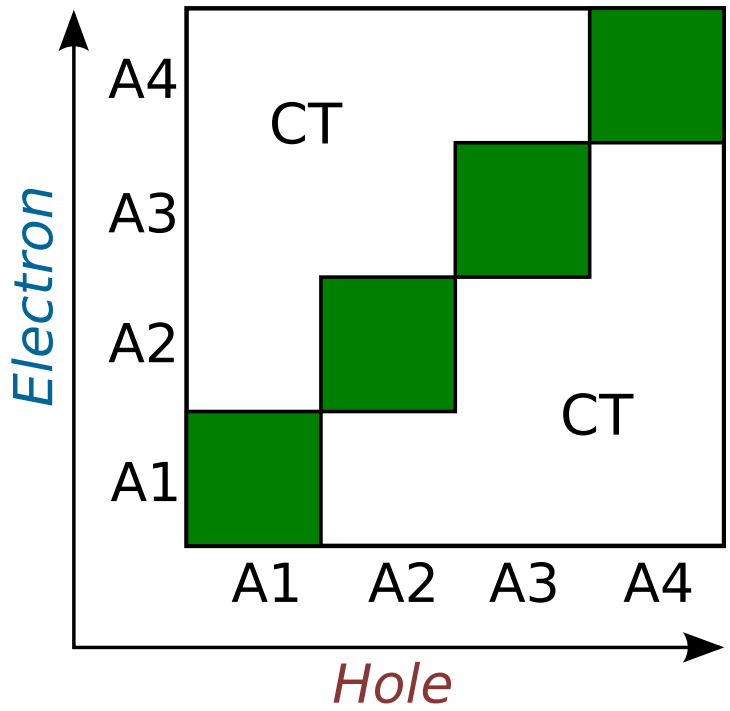
- Locally excited contributions (diagonal)
- CT contributions (off-diagonal)

Transition density matrix



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Statistical Analysis

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

Delocalization Length

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

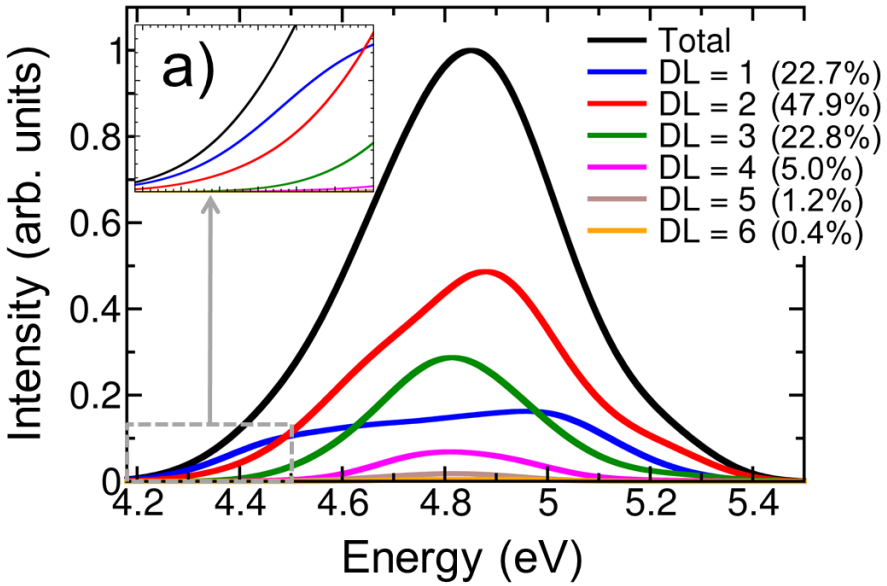
DL=1 Locally excited state (only one molecule involved)

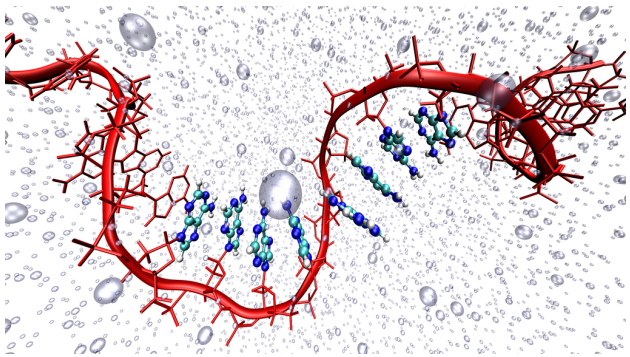
DL>1 Delocalized exciton or charge transfer state

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





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Statistical Analysis

Charge transfer character

$$\mathrm{CT} = \Omega^{-1} \sum_{B \neq A} \Omega_{AB} \qquad \Omega = \sum_{A,B} \Omega_{AB}$$

CT=0 Locally excited state or Frenkel exciton

CT=1 Charge transfer or charge resonance state

Polyadenine

Charge transfer (CT)

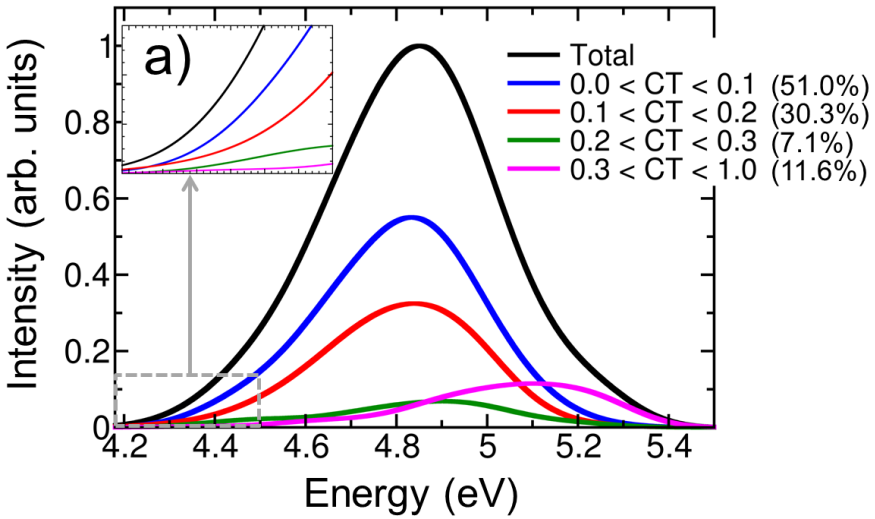
- Local and Frenkel exciton states (CT< 0.1)

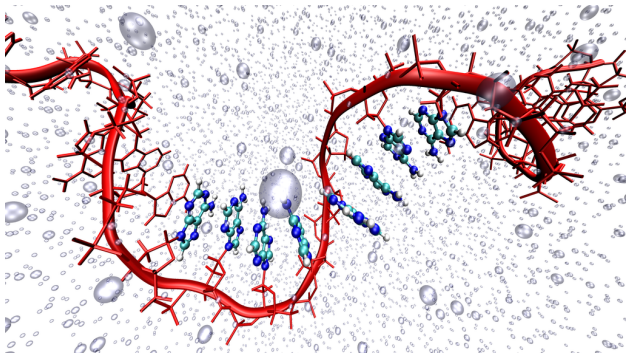
→ 51% of the spectral intensity

→ CT admixture for remaining states

- States with significant CT character (CT> 0.3)

→ Low intensity, high energies





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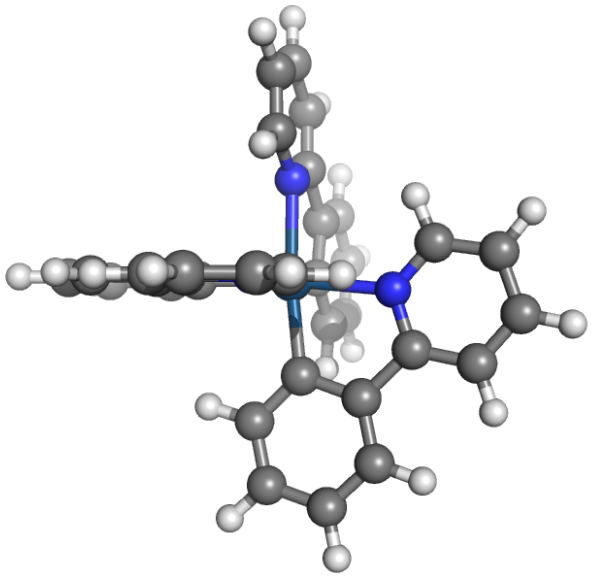
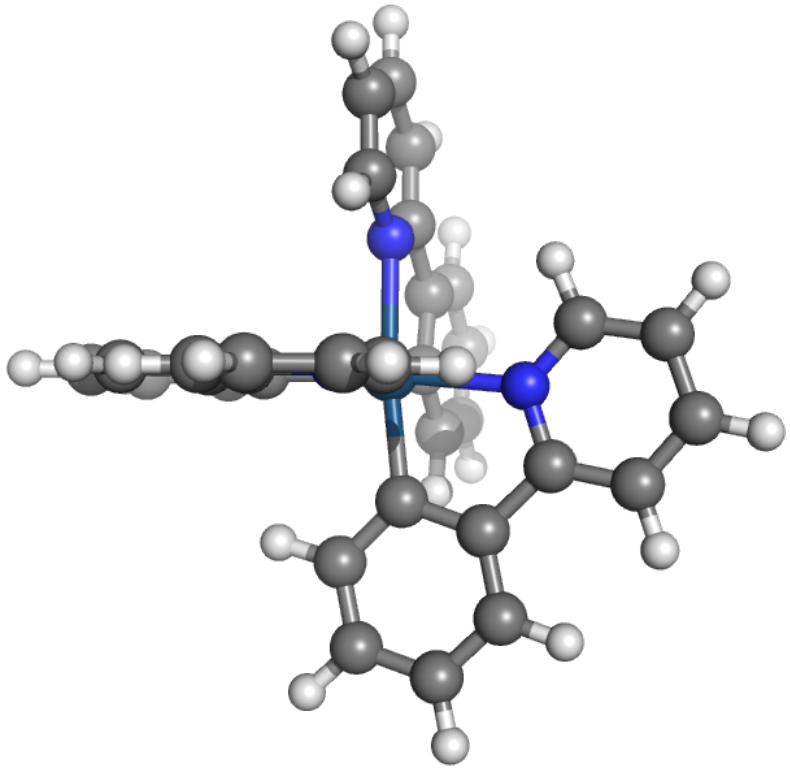


$Ir(ppy)_3$

$Ir(ppy)_3$

- Highly phosphorescent complex[1]
- **Interplay** of LC and MLCT states decisive for flourescence[2]
  - **MLCT** $\rightarrow$ relavistic effects $\rightarrow$ spin-orbit coupling
  - **LC** $\rightarrow$ low-energy triplets



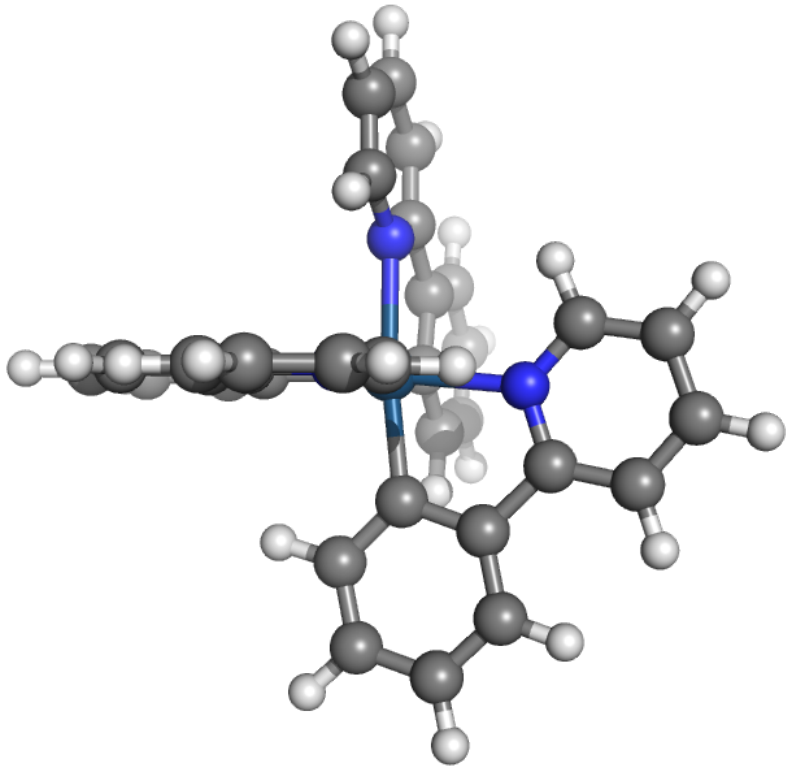
[1] K. Dedeian, P. I. Djurovich, et al. *Inorg. Chem.* **1991**, 30, 1685.
[2] B. Powell *CCR* **2015**, 295, 46.

$Ir(ppy)_3$

$Ir(ppy)_3$

- Highly phosphorescent complex[1]
- **Interplay** of LC and MLCT states decisive for flourescence[2]
  - **MLCT** $\rightarrow$ relavistic effects $\rightarrow$ spin-orbit coupling
  - **LC** $\rightarrow$ low-energy triplets

? How to quantify



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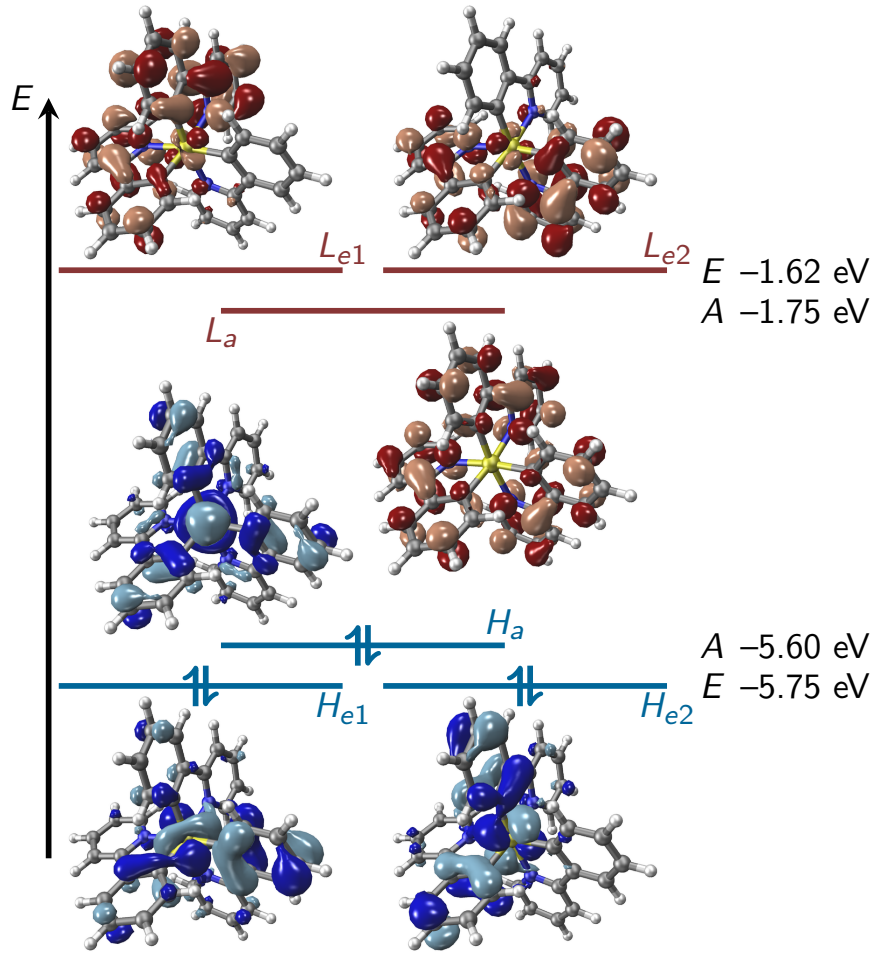
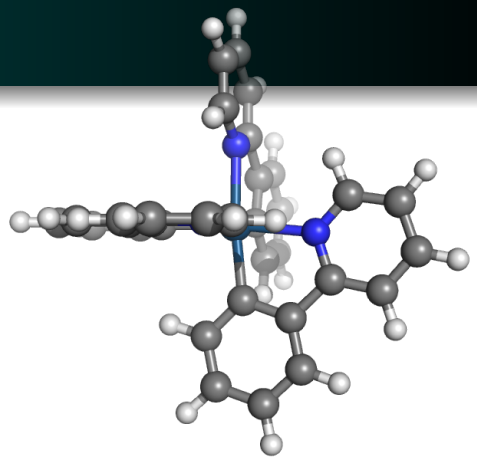
Frontier orbitals

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



Frontier orbitals



Lowest triplet states

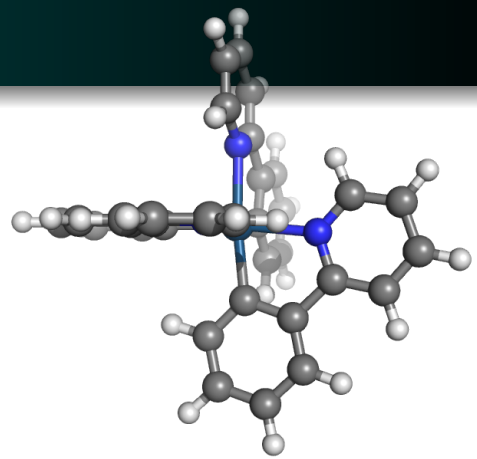
- TDDFT/B3LYP

	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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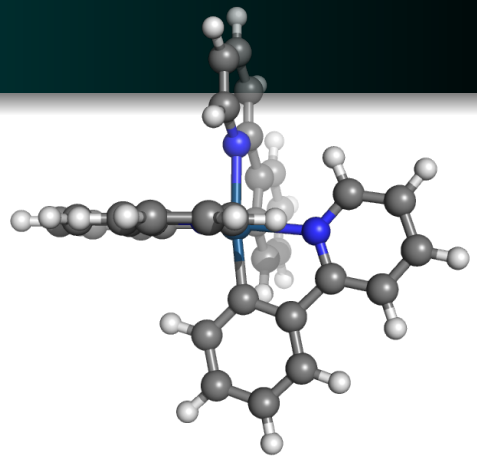
$\rightarrow$ Mixture: MLCT, IL, LLCT

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

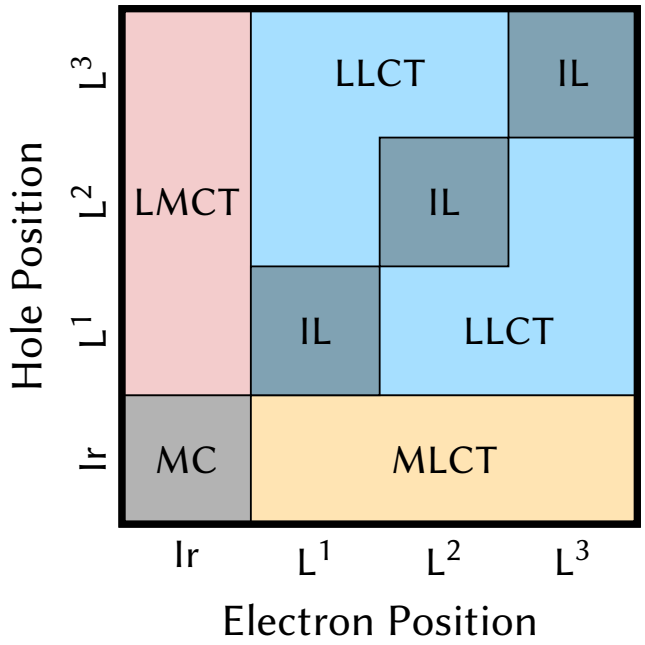
Charge Transfer Numbers



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

→ Automatic **classification** of state character

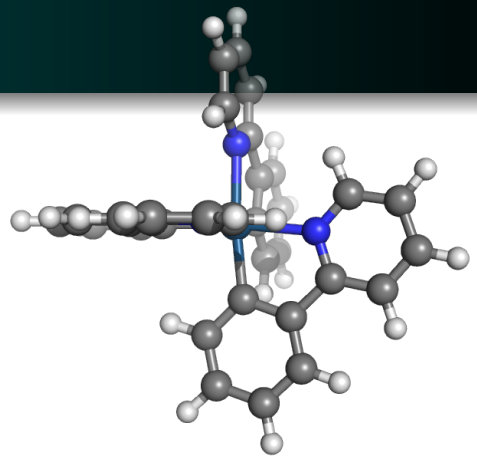
→ Quantification of **state mixing**



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

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

Charge Transfer Numbers



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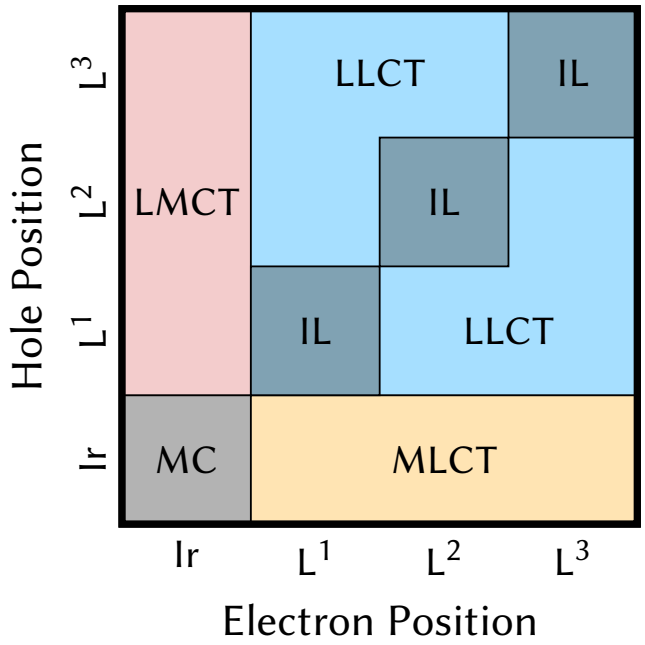

	E (eV)	Sym.	State character	
T_1	2.89	A	49% IL	38% MLCT
T_2	2.93	E	53% IL	35% MLCT
T_3	2.93	E	53% IL	35% MLCT
T_4	3.17	A+E	49% MLCT	31% LLCT
T_5	3.17	A+E	50% MLCT	31% LLCT
T_6	3.17	A+E	50% MLCT	32% LLCT

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

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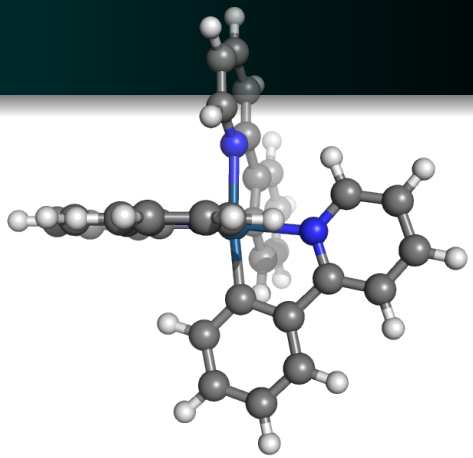
Charge Transfer Numbers



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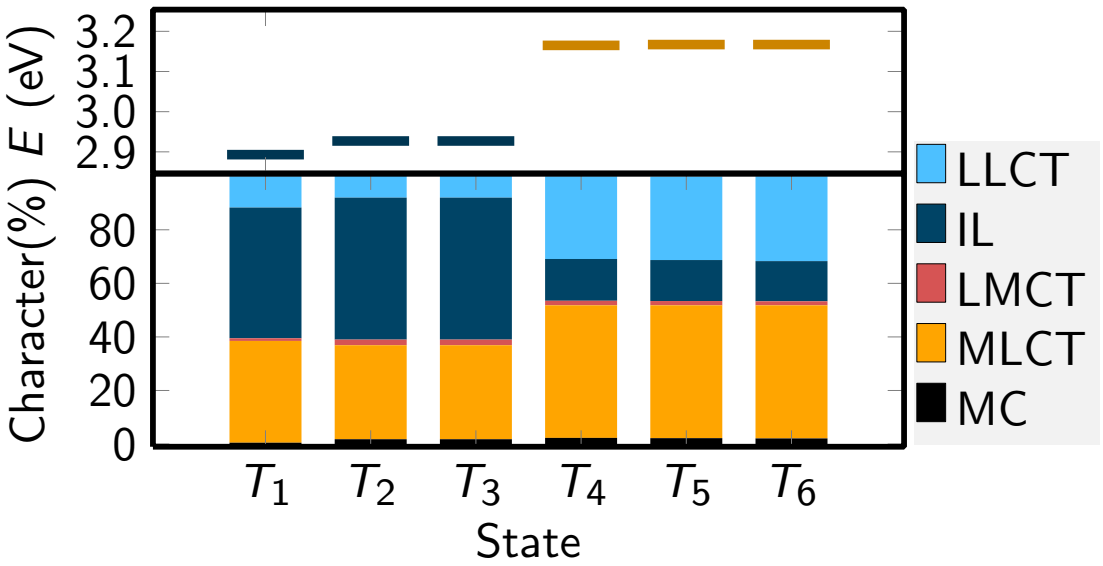
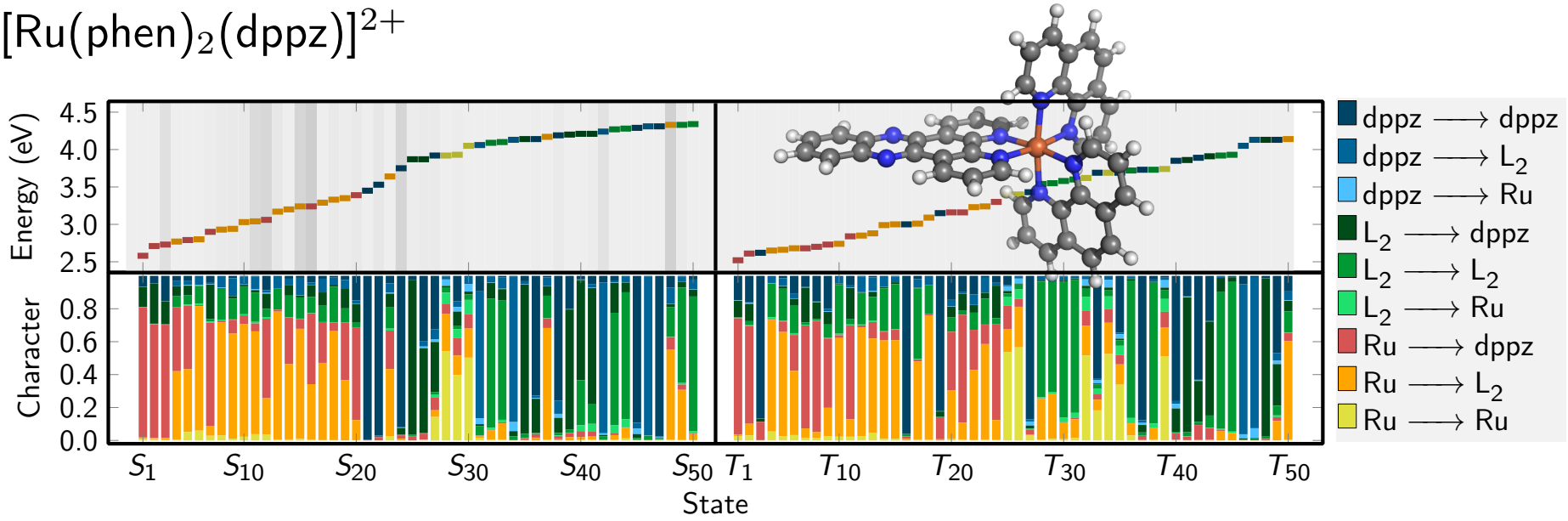
T_6	3.17	A+E	50% MLCT	32% LLCT

- Compact graphical depiction



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



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

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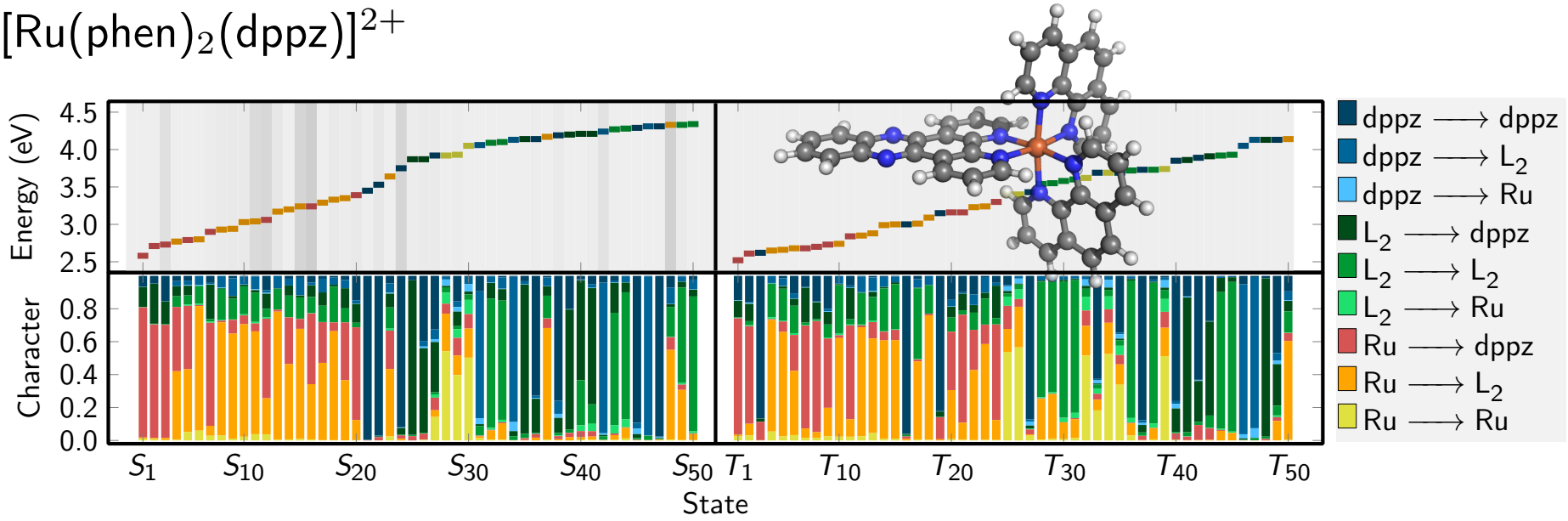
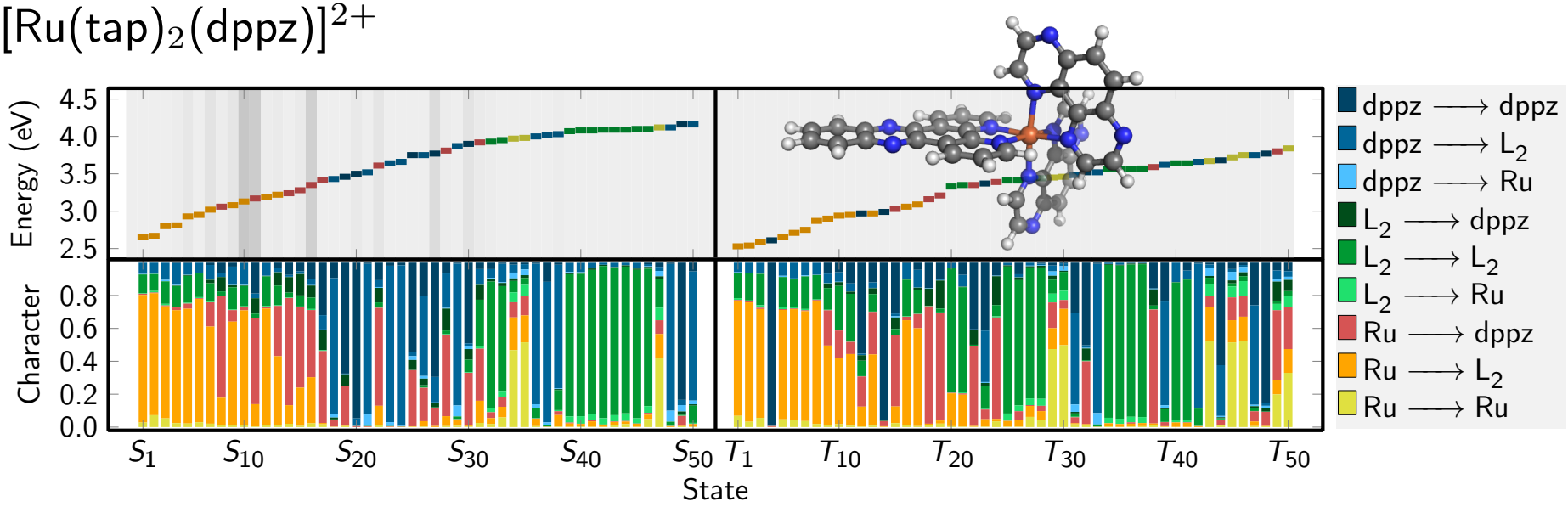


$[Ru(tap)_2(dppz)]^{2+}$



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

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

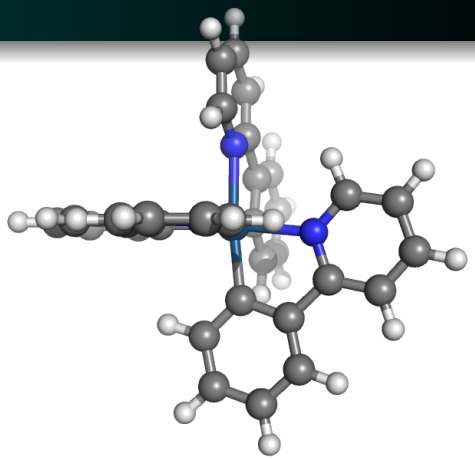
Exciton size

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

- 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.

Charge Transfer Numbers



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

	E (eV)	State character		d_{exc} (Å)
$^3A_2$	2.74	49% IL	38% MLCT	4.07
$^3E_1$	2.77	51% IL	37% MLCT	3.94
$^3A_3$	2.97	49% MLCT	29% LLCT	4.40
$^3E_2$	2.98	48% MLCT	31% LLCT	4.50
$^3E_3$	3.10	48% MLCT	38% LLCT	5.03
$^3A_4$	3.14	47% MLCT	38% LLCT	5.05

- Smaller exciton size $\rightarrow$ less CT character

Conclusions

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

→ Automatization

→ Rigorous discussion

Application areas

- **DNA**
- **Transition metal complexes**
- **Conjugated polymers**
  - S. A. Mewes, J.-M. Mewes, A. Dreuw, FP *PCCP* **2016**, 18,2548.
  - S. A. Mewes, FP, A. Dreuw *JPCL* **2017**, 8,1205.
- **Push-pull systems**
  - P. Kautny, F. Glöcklhofer, T. Kader, J. Mewes, B. Stöger, J. Fröhlich, D. Lumpi, FP *PCCP* **2017**, 19, 18055.
- **Polycyclic aromatic hydrocarbons**
  - FP, H. Pasalic et al. *ANIE* **2013**, 52, 2581.
  - A. Das, T. Müller, FP, H. Lischka *JPCA* **2016**, 120, 1625.

Software

Extended *wavefunction analysis toolbox*.

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

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

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

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

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

Acknowledgements

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

Strasbourg
C. Daniel

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S. A. Mewes
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H. Lischka

Loughborough University

ÖAW Österreichische Akademie der Wissenschaften

Alexander von Humboldt Stiftung/Foundation

Vienna Scientific Cluster

FWF

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