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

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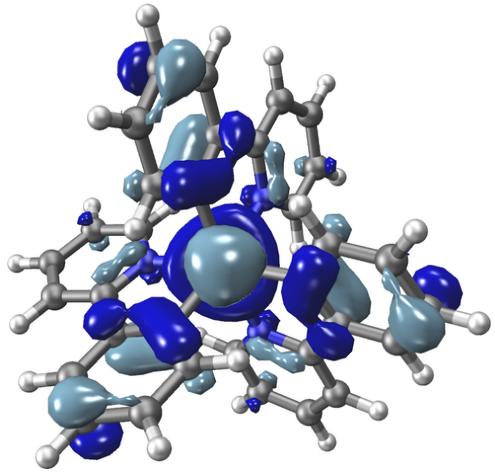
Introduction

Computational Photochemistry

- Accurate numbers
- ☺ *Quantum chemical methods*:
  Semi-emp., TDDFT, CC, ADC, CASSCF, DMRG, CASPT2, MR-CI, ...
- ☺ *Environmental models*: QM/MM, PCM, density embedding, ...
- ☺ *Algorithmic efforts*: Linear scaling, density fitting, parallelization, GPUs, ...
- Comparison to experiment
- ☺ *Linear* and *non-linear* optical properties
- ☺ *Static* and *time-resolved* experiments
- Chemical insight

☹ **Look at the HOMO and LUMO**

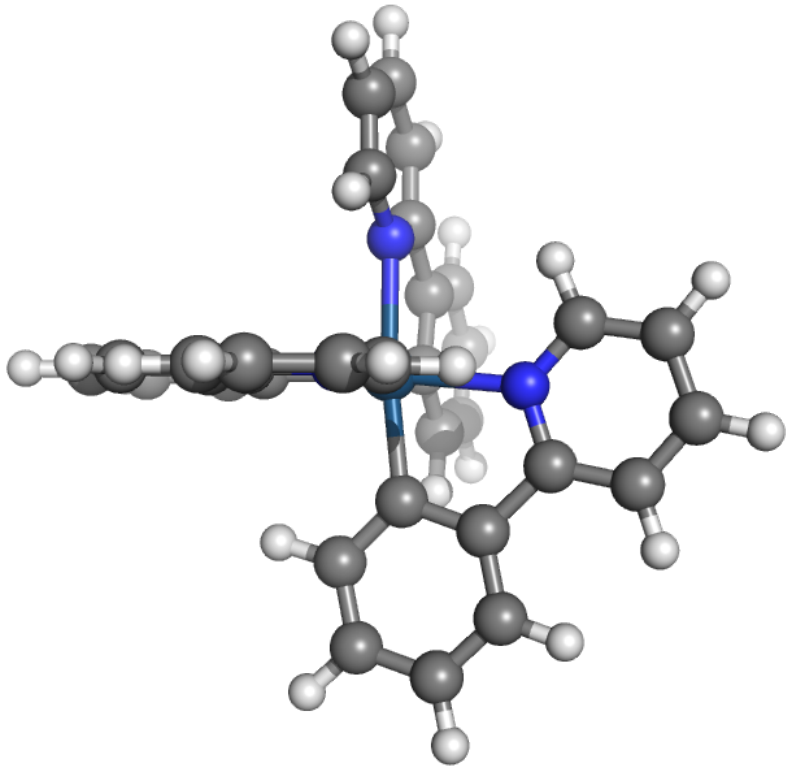


$Ir(ppy)_3$

$Ir(ppy)_3$

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

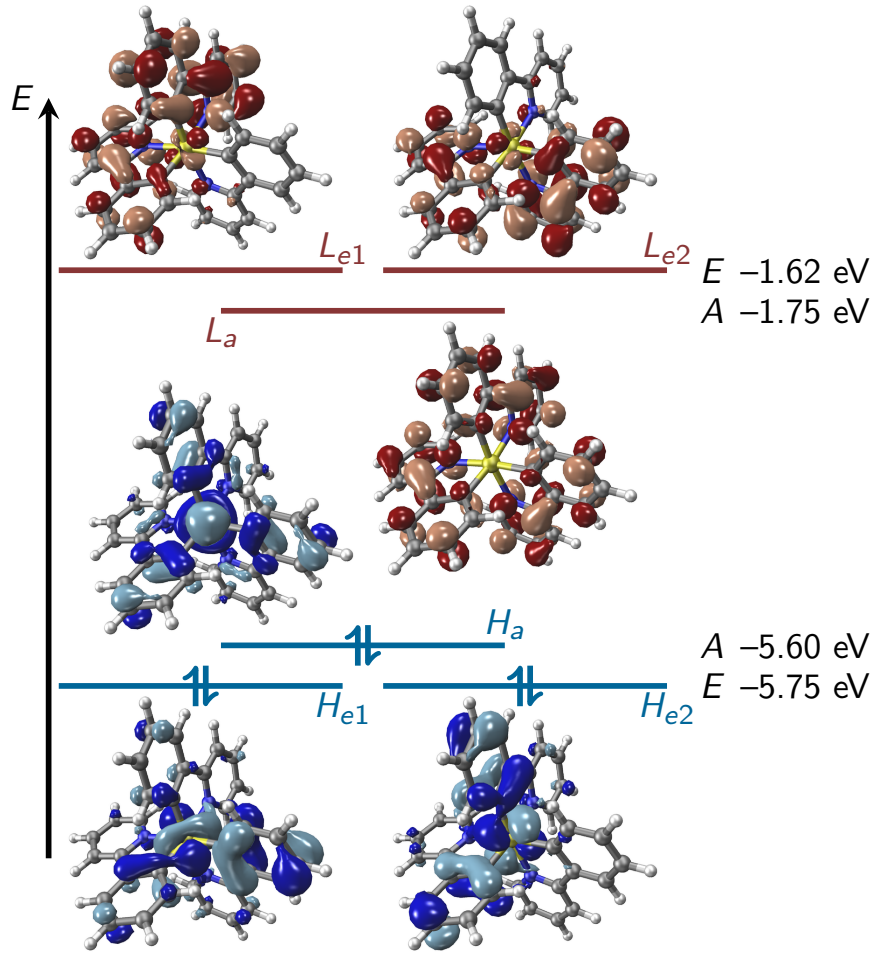
? How to quantify



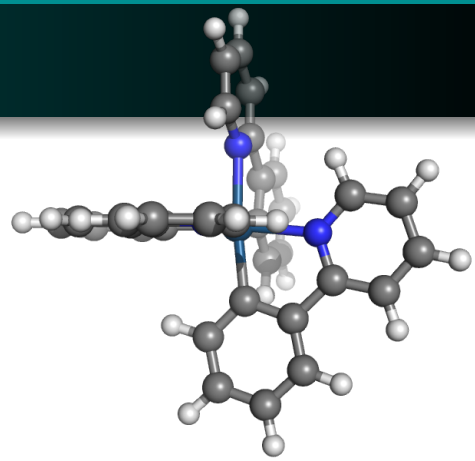
[1] K. Dedeian, P. I. Djurovich, et al., *Inorg. Chem.* **1991**, 30, 1685.
[2] B. Powell, *CCR* **2015**, 295, 46.

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

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

? 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

Natural transition orbitals — Singular value decomposition

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

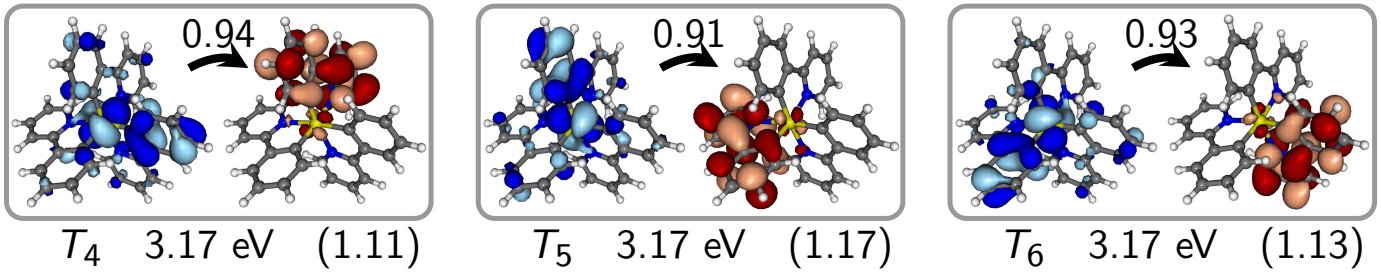
$\mathbf{U}$ **Hole** orbital coefficients

λ_i Transition amplitudes

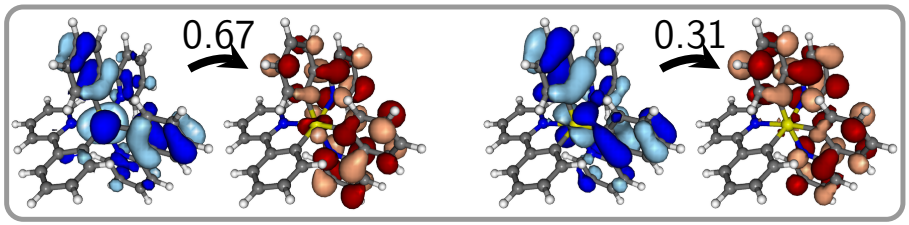
$\mathbf{V}$ **Electron** orbital coefficients

[1] R. L. Martin, *J. Chem. Phys.* **2003**, 11, 4775.

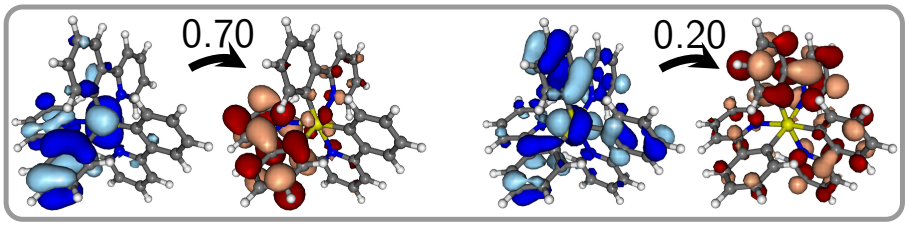
Natural transition orbitals



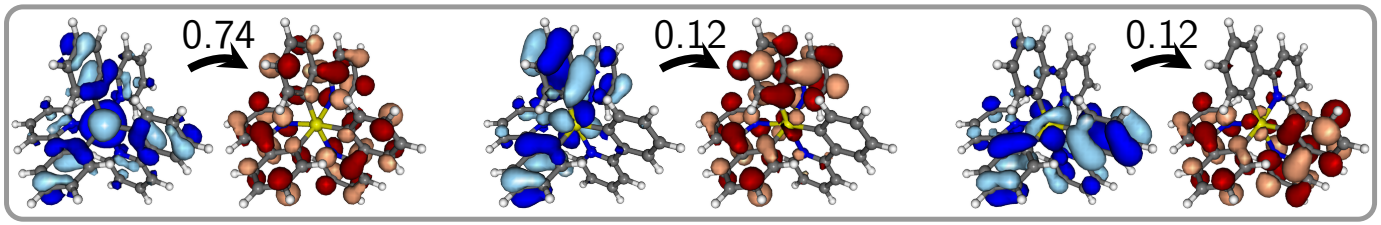
T_4 3.17 eV (1.11) T_5 3.17 eV (1.17) T_6 3.17 eV (1.13)



T_2 2.93 eV (1.82)



T_3 2.93 eV (1.81)



T_1 2.89 eV (1.73)

- 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

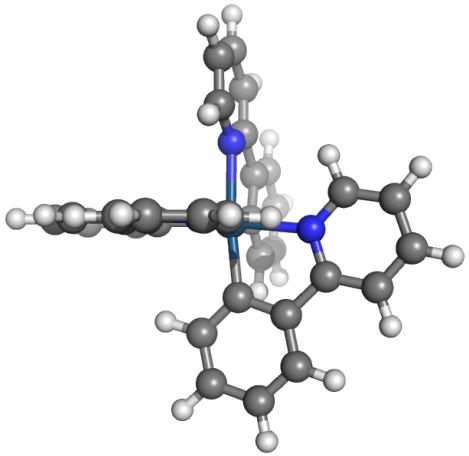
$$\Omega_{AB} = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in B} |\tilde{D}^{0I}_{\mu\nu}|^2$$

$\tilde{D}^{0I}_{\mu\nu}$	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.

Charge Transfer Numbers



- $T_1 - T_3$
  - $L^i \rightarrow L^i$ (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	L¹	L²	L³
1	0	0	15
0	0	1	7
1	0	1	22
2	1	2	46

(e) T_5 (3.17 eV)

Ir	L¹	L²	L³
1	1	22	0
1	1	14	1
0	1	6	0
2	3	45	2

(f) T_6 (3.17 eV)

Ir	L¹	L²	L³
0	7	1	0
1	22	1	1
0	14	1	1
2	46	3	1

(b) T_2 (2.93 eV)

Ir	L¹	L²	L³
1	2	0	24
0	2	0	2
1	29	0	2
2	19	1	16

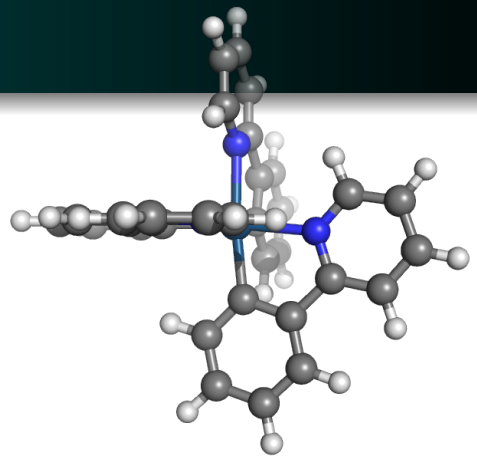
(a) T_1 (2.89 eV)

Ir	L¹	L²	L³
0	2	2	16
0	2	16	2
0	16	2	2
1	13	13	13

(c) T_3 (2.93 eV)

Ir	L¹	L²	L³
1	1	3	11
1	1	35	1
0	7	2	1
2	5	23	8

Charge Transfer Numbers

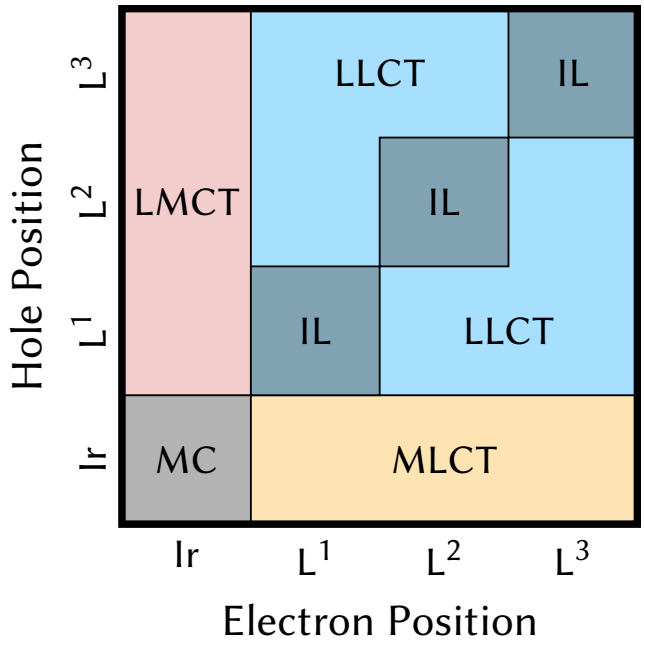


- General classification
  - Different formal state characters correspond to different Ω_{AB} elements

→ Automatic **classification** of state character

→ Quantification of **state mixing**

	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.

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

Charge Transfer Numbers

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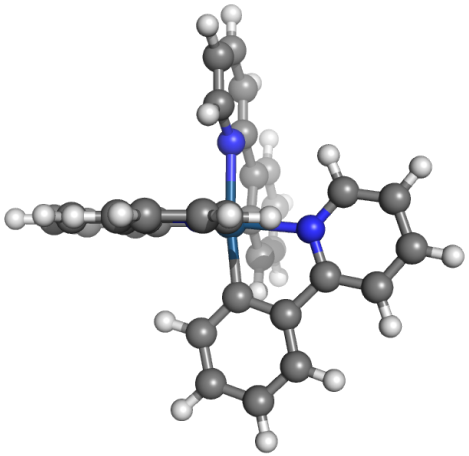
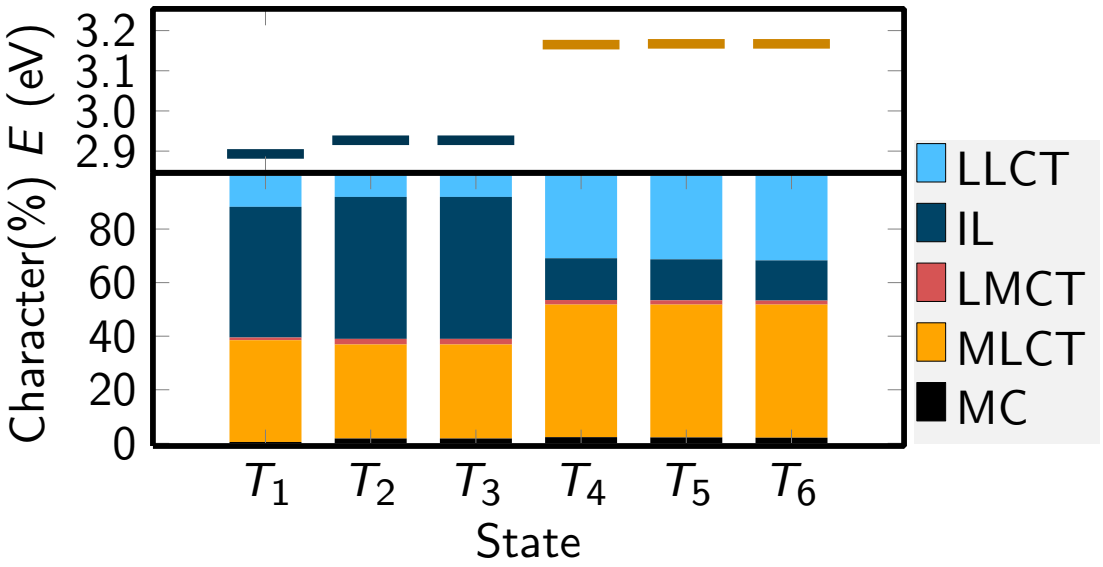
T_4	3.17	A+E	49% MLCT	31% LLCT
T_5	3.17	A+E	50% MLCT	31% LLCT
T_6	3.17	A+E	50% MLCT	32% LLCT



- Compact graphical depiction



? 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

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

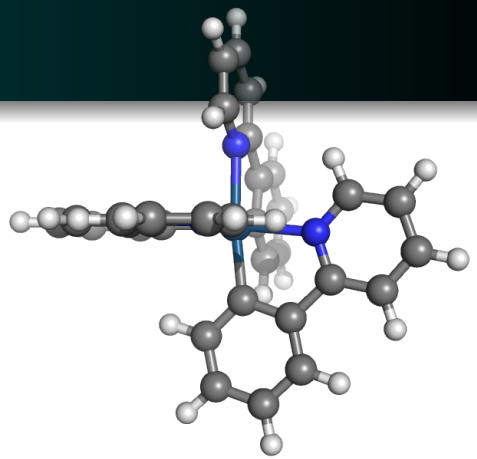
Exciton size

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

- Average separation of the electron and hole quasi-particles
- Evaluated using **analytic integration** techniques
- ☺ No fragment definition
- ☺ No population analysis

[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
- ? What is really going on

Electron/hole densities

Density for the excited electron / excitation hole

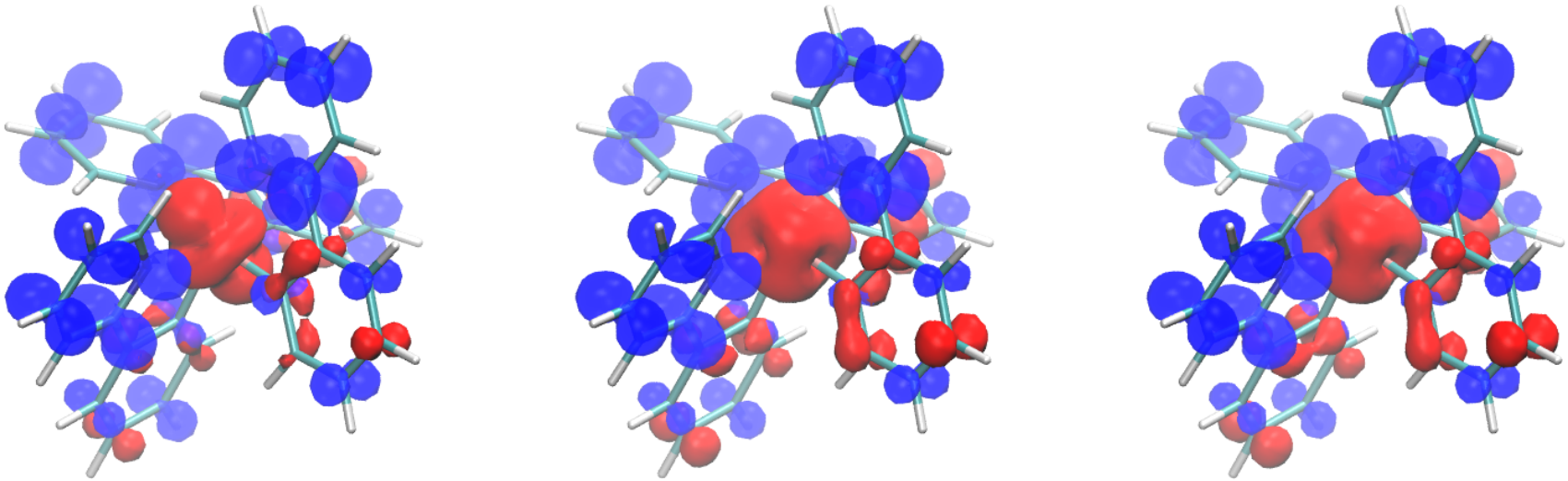
$$\rho_e(r_e) = \int \gamma^{0I}(r_h, r_e)^2 \mathrm{d}r_h$$

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

- Equivalent to weighted sums over NTOs

Electron/hole densities

2^3A 3^3A 4^3A



- **Hole** density → centered around Ir
- **Electron** density → delocalized

? Can we learn more

Conditional densities

Conditional density for the excited electron

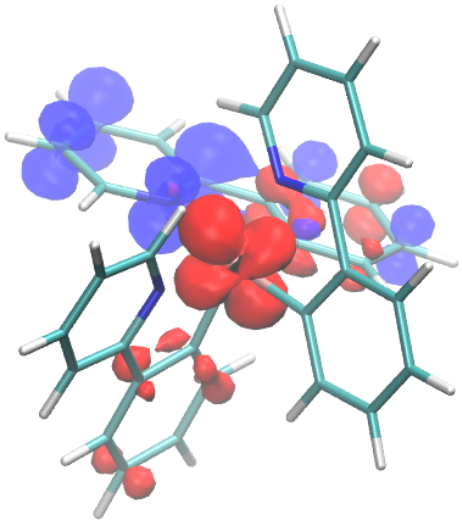
$$\rho_e^{h:A}(r_e) = \int_A \gamma^{0I}(r_h, r_e)^2 \mathrm{d}r_h$$

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

- Evaluated through multiplication of matrix blocks

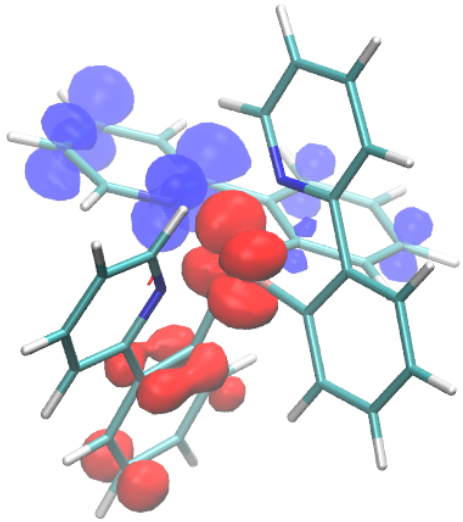
Conditional electron/hole densities

2^3A



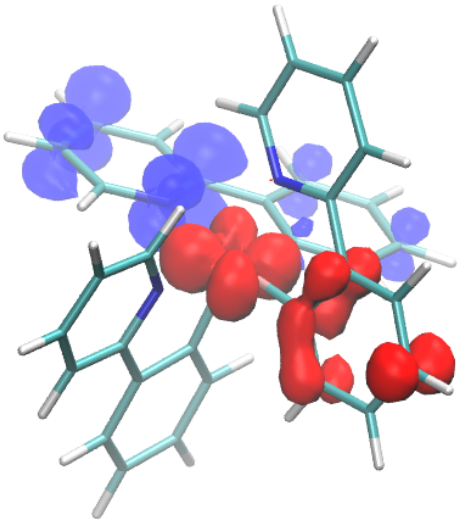
Local

3^3A



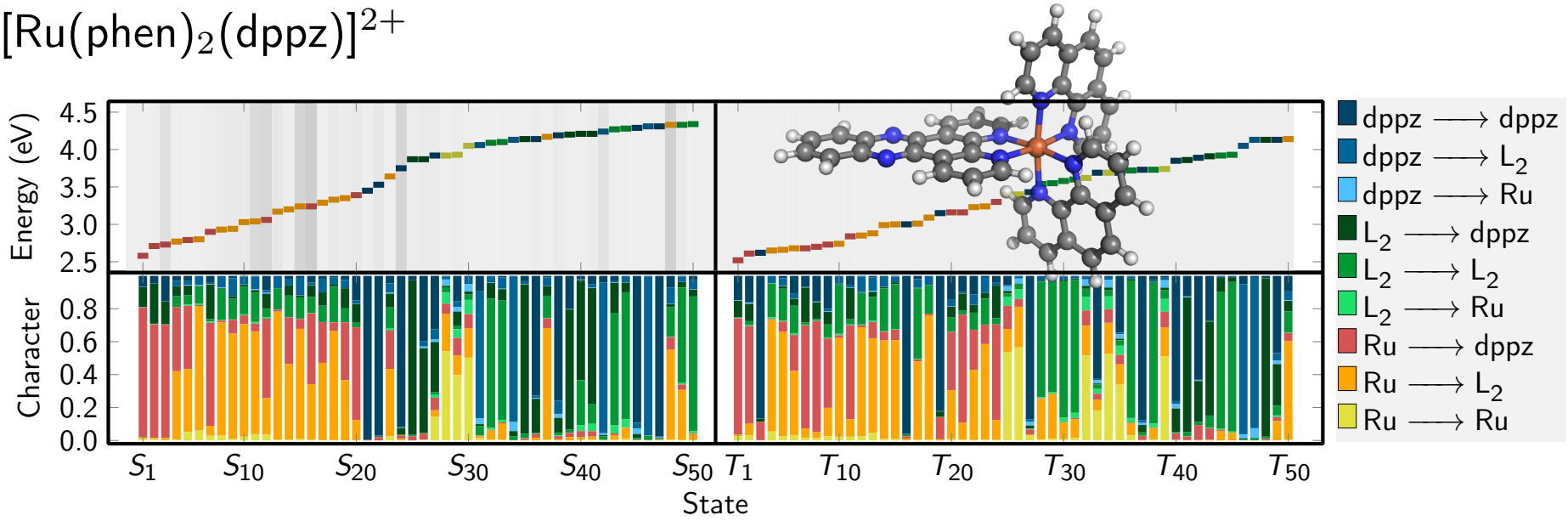
"Corner" CT

4^3A

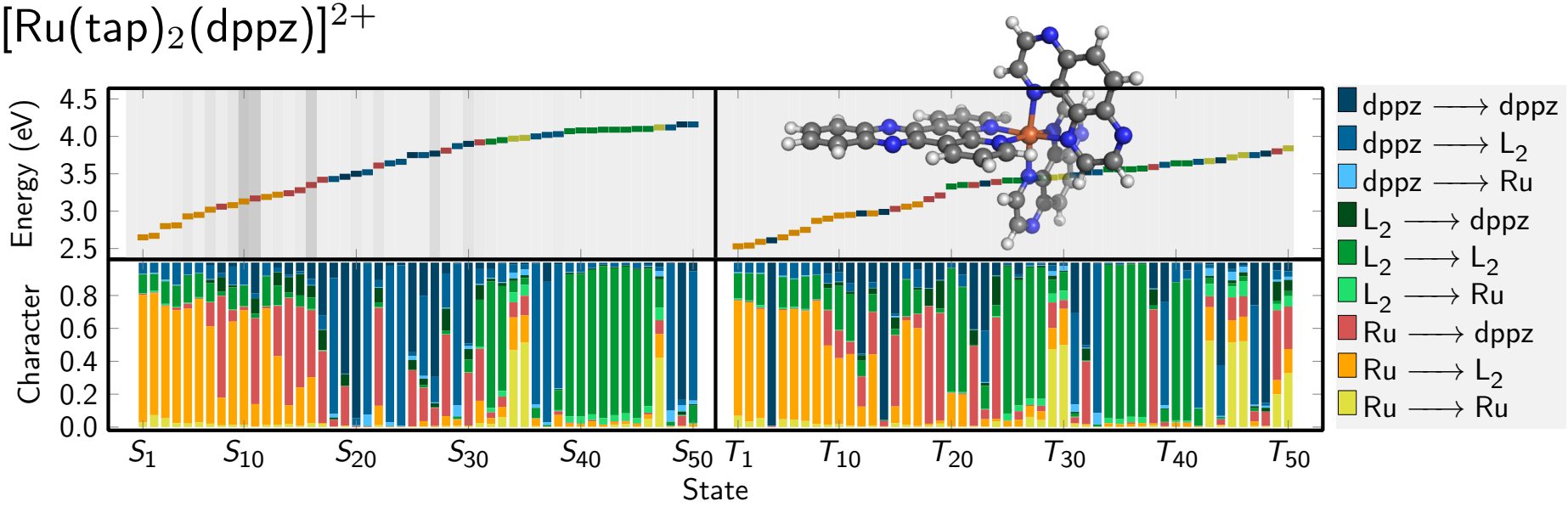


"Straight" CT

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

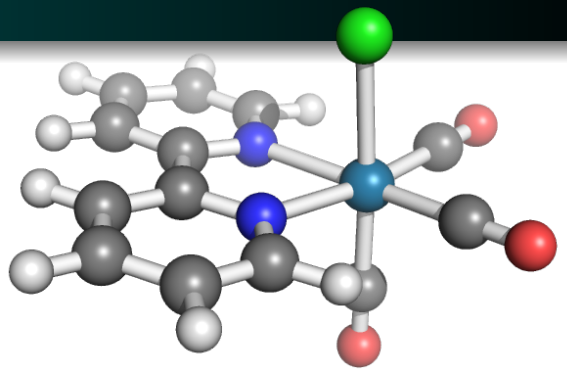


$[Ru(tap)_2(dppz)]^{2+}$

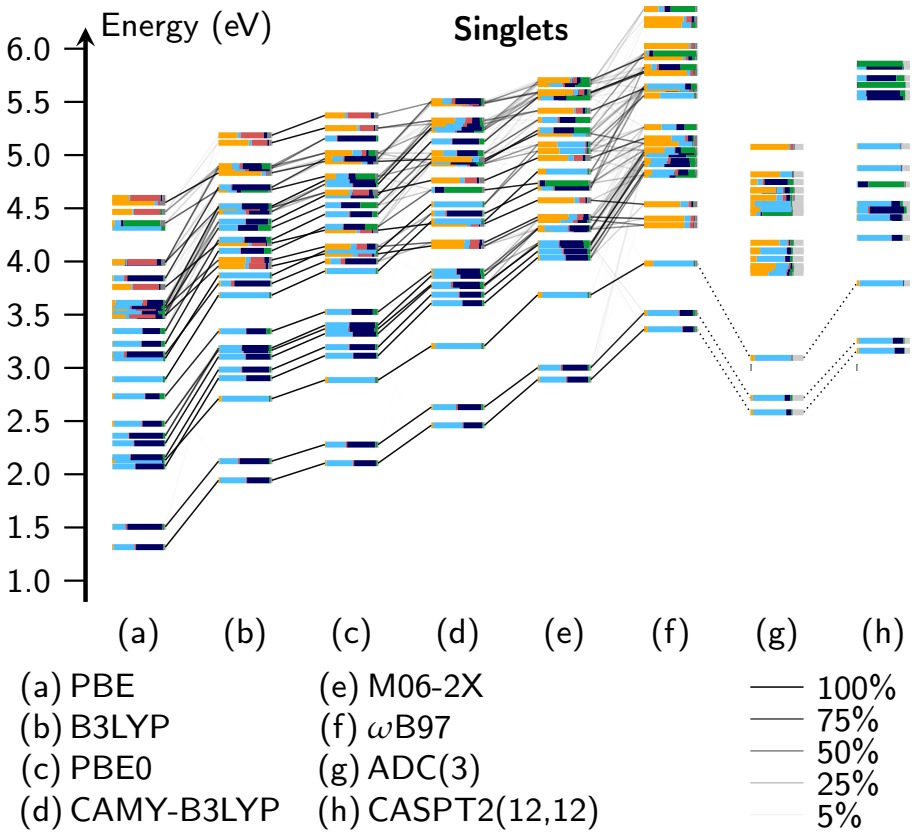


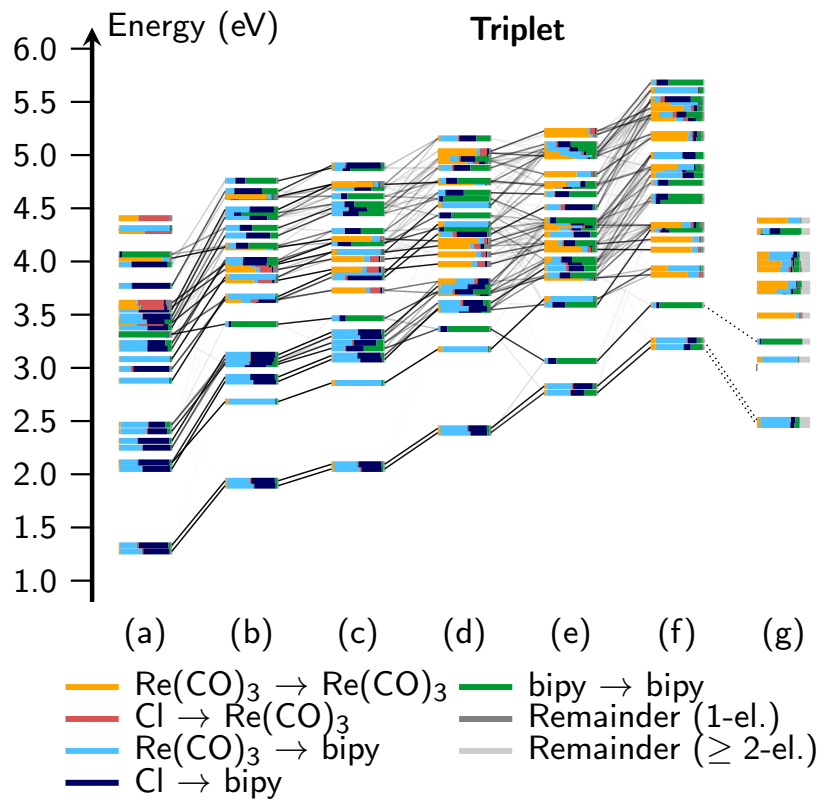
[1] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

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.

Conclusions

- Excited state **wavefunction analysis** tools
- Visualization
  - Natural transition orbitals
  - *Conditional electron densities*
- Quantitative analysis
  - Charge transfer numbers

→ Automatization

→ Rigorous discussion

- Implementation through **matrix operations**

→ Fast

Application areas

- **Transition metal complexes**
  - FP, A. Dreuw, *JPCA* **2015**, 119, 1023.
  - S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

→ *Talk*: Leticia González

→ *Poster*: Pedro Sánchez-Murcia

- **DNA**
  - J. J. Nogueira, FP, L. González, *Chem. Sci.* **2017**, 8, 5682.
- **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.

- **Method evaluation**
  - FP, S. A. Mewes, A. Dreuw, L. González, *JCTC* **2017**, 13, 5343.
  - S. A. Mewes, FP, A. Krylov, A. Dreuw, *JCTC* **2018**, 14, 710.

Software

Extended *wavefunction analysis toolbox*.

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

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

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

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

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

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H. Lischka

Loughborough University

Alexander von Humboldt
Stiftung/Foundation

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