# New Analysis Tools for Excited-State Quantum Chemistry: Turning Numbers into Chemical Insight
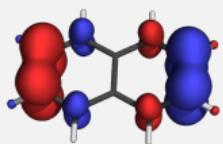
Felix Plasser

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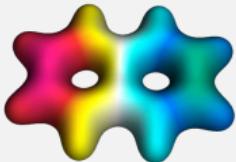
VISTA – 17 December 2020
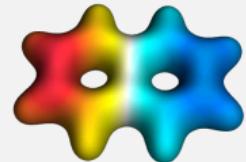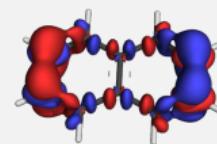
Loughborough University

Introduction

Computational Photochemistry

- ▶ Accurate numbers
- ☺ *Quantum chemical methods*:
  TDDFT, CC, ADC, CASSCF, DMRG, MRCI, CASPT2
- ☺ *Multiscale 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 some blobs of colour**
- ☹ ... derived as **intermediates** in an **approximate theory**
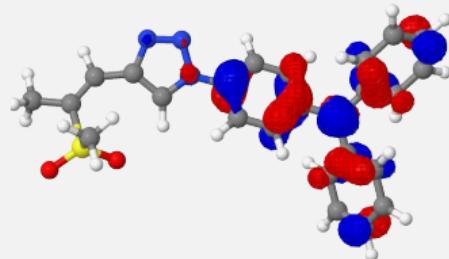
Computational Photochemistry

(?) Can we assign **excited-state character** in a **completely automated** way
- Save time and analyse **larger data sets**
- Remove **personal bias**

(?) Can we learn about physics **beyond the MO picture**
- Cross-links to other models
→ **Valence-bond** theory
→ **Exciton** theory

Outline

1. Transition metal complexes
   → **Automatic assignment** of state character

2. Naphthalene
   → Connection to **valence-bond theory**

3. Conclusions

Rhenium complex

$Re(bpy)(CO)_3Cl$

- ▶ Well-studied complex[1]
- → Ultrafast intersystem crossing
- ⑦ Which types of states are involved

- ▶ MS-CASPT2 computations - `OpenMolcas`
  - CAS(12,12)
  - Cholesky decomposition
  - 19 singlets, 18 triplets

- ⚠ How do we characterise so many states

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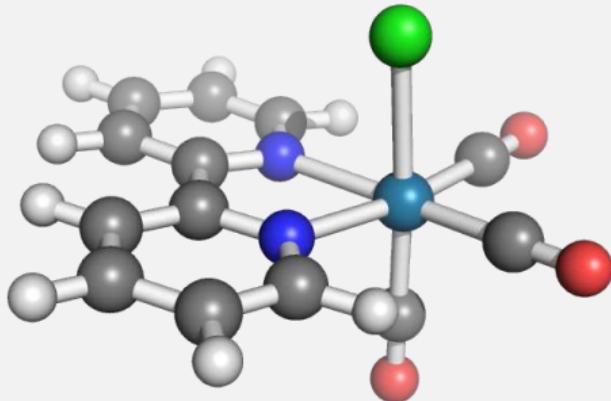
[1] J. Eng, C. Gourlaouen, E. Gindensperger, C. Daniel, *Acc. Chem. Res* **2015**, 48, 809.

Electron/hole densities

Transition density matrix (1TDM)

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

$$\gamma^{0I}(r_h, r_e) = \sum_{\mu\nu} D_{\mu\nu}^{0I}\chi_\mu(r_h)\chi_\nu(r_e)$$

Ψ_0, Ψ_I Ground and excited state wavefunctions
$\hat{a}_p^\dagger, \hat{a}_q$ **Creation** and **annihilation** operators
r_h, r_e Coordinates of **hole** and **electron**
χ_μ, χ_ν Basis functions

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 natural transition orbitals

Electron/hole densities

- Analysis of S_1 state
  - **Hole** on Re and Cl
  - **Electron** on bpy ligand

- ☺ Compact description
  - Well-defined for **exact solution**
- → Not *observable* but part of *physical reality*

- ☹ Still looking at blobs of colour

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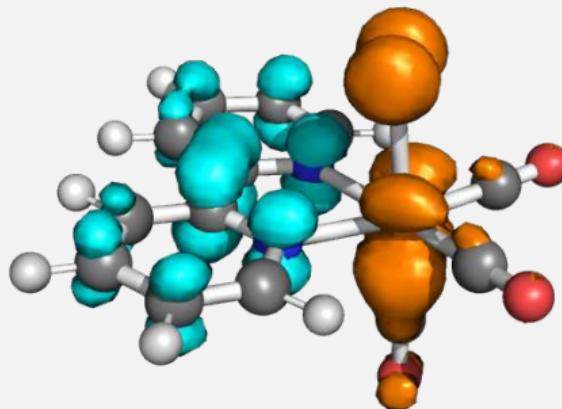
[1]I. Fdez. Galván, et al., *JCTC* **2019**, 15, 5925.

Charge Transfer Numbers

- ▶ General classification
  - Different formal state characters correspond to different blocks of the 1TDM

- ▶ Summation over these blocks
- → Automatic **classification** of state character
- → Quantification of **state mixing**

1TDM decomposition

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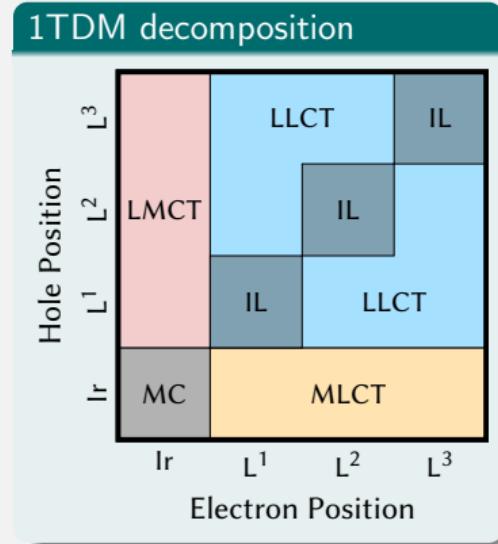
[1]FP, A. Dreuw, *JPCA* **2015**, 119,1023.
[2]S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

Fragment decomposition
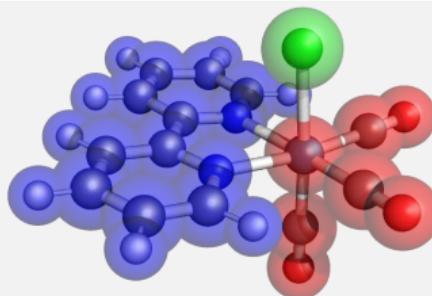
▶ Division into three fragments

 - Re(CO)$_3$, bpy, Cl

→ Quantify excitations between them

 - For **singlets** and **triplets**

▶ **Discussion**

→ More Cl→bpy for **singlets**

→ More bpy for **triplets**

Excited state analysis
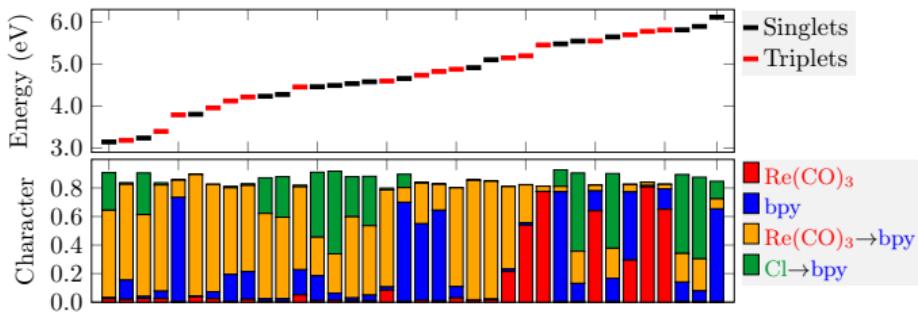
[1] I. Fdez. Galván, et al., *JCTC* **2019**, 15, 5925.

Fragment-based analysis

- ▶ Fragment-based analysis[1]
- ☺ State-character assignment by just pressing a button

- ☹ Definition of fragments not always obvious
- → Real-space analysis of 1TDM interpreted as *exciton wavefunction*[2]
- → Automatic assignment of fragments[3]

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[1]FP, *J. Chem. Phys* **2020**, 152, 084108.
[2]S. A. Bäppler, FP, M. Wormit, A. Dreuw, *Phys. Rev. A* **2014**, 90, 052521.
[3]S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. GonzÍez, *Coord. Chem. Rev.* **2018**, 361, 74–97.

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

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

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

χ_μ Atomic orbital

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

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[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

$$d_{h \to e} = \langle r_e - r_h \rangle$$

▶ Average (linear) separation of the electron and hole quasi-particles

- Evaluated using **analytic integration** techniques

☺ No fragment definition

☺ No population analysis

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[1]FP, et al., *J. Comput. Chem.* **2015**, 36, 1609.
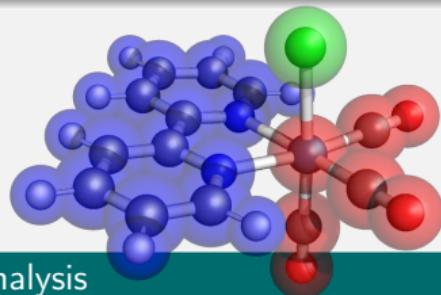
- **Consistent trends** between fragment-based and real-space analysis
- CT always larger for **singlets** than for **triplets** ($\times$)
- CT reduced by **orbital relaxation** ($\bullet$)

Excited state analysis
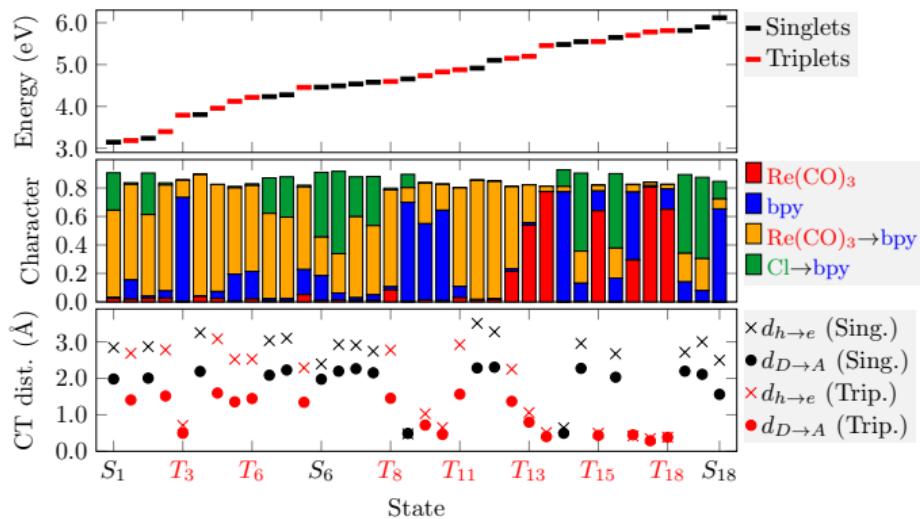
[1] I. Fdez. Galván, et al., *JCTC* **2019**, 15, 5925.

Outlook

- ▶ Ruthenium complexes - Ru(bpy)$_3$
- (?) How are the excited states affected by different substituents

- → Excited electron delocalisation (EEDL)
- → Substituent induced electron localisation (SIEL)

Ru complexes

(a) Excited electron delocalization? **EEDL$_n$**

EEDL$_1$ EEDL$_2$ EEDL$_3$

(b) Does R attract or repel the excited electron? **SIEL**

bpy$_1$-EWG   EWG   bpy$_1$-EDG   EDG

bpy$_3$ Ru   e⁻   e⁻   Ru   bpy$_3$

bpy$_2$ bpy$_2$

$-1 \leq$ SIEL$^{EWG} < 0$ $0.5 \geq$ SIEL$^{EDG} > 0$
ATTRACTION   **REPULSION**

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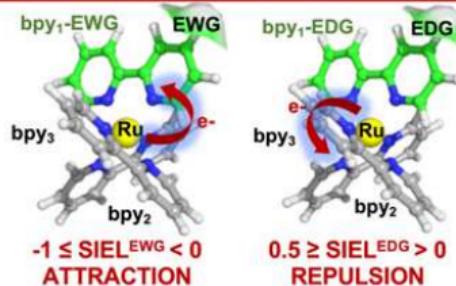
[1]P. A. Sánchez-Murcia, J. J. Nogueira, FP, L. González, *Chem. Sci.* **2020**, 331, 195–199.

N_2 splitting

Binuclear complexes

- ▶ Binuclear complexes
- → Used for N_2 splitting

- ▶ Assign excited-state character
- - Ligand-to-metal charge transfer (**LMCT**)
- - Metal-to-ligand charge transfer (**MLCT**)

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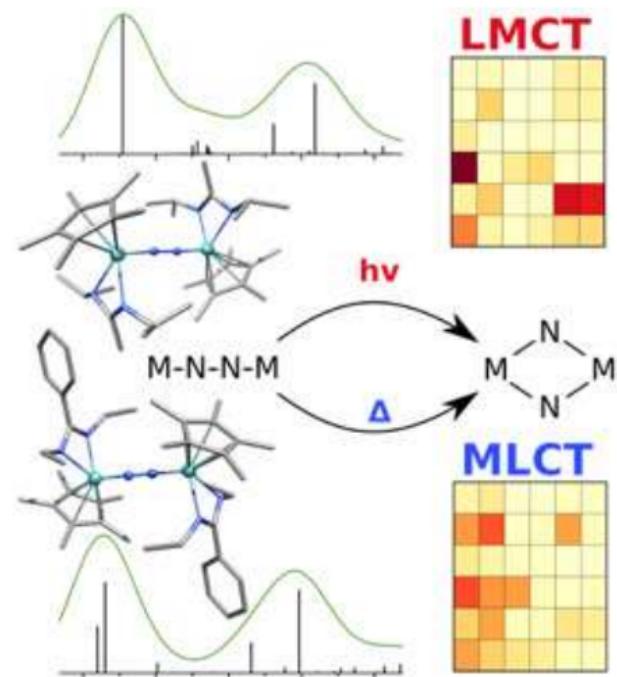
[1]S. Rupp, FP, V. Krewald, *Eur. J. Inorg. Chem* **2020**, 2020, 1506.

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

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[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

☹ Ionic L_a state behaves like a **hidden charge-transfer state 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

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[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)
  - Q-Chem

- ▶ **Three types** of labels → Multiplicity, irrep, +/−
- ▶ **Bright states** → Singlet, u, +

- (?) Difference between B_{3u} states
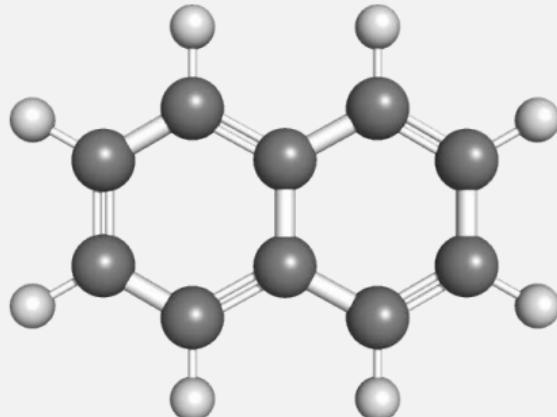
Excited states

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** $\rightarrow$ no use to look at the orbitals

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B3u states

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

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

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

(?) How to analyse

Napthalene B_{3u} states

B3u states

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

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

- ▶ Exactly the same **canonical orbitals** (*in the PPP description*)
- ▶ Same **one-electron density matrices**
- → Same densities
- → Same natural orbitals
- → Same difference densities, attachment-detachment densities
- ▶ Same **natural transition orbitals**

☺ Let's look at this with `libwfa`

Napthalene B_{3u} states

ADC(2) excited-state densities
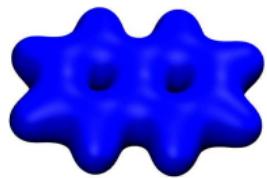
$$^3B_{3u}^+ \qquad\qquad ^1B_{3u}^- \qquad\qquad ^3B_{3u}^- \qquad\qquad ^1B_{3u}^+$$
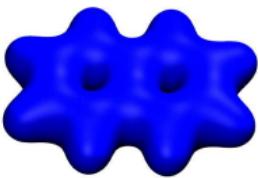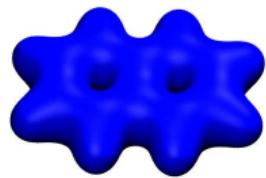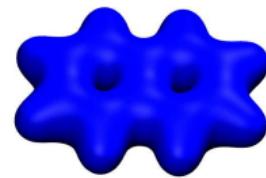
Napthalene B_{3u} states

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

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

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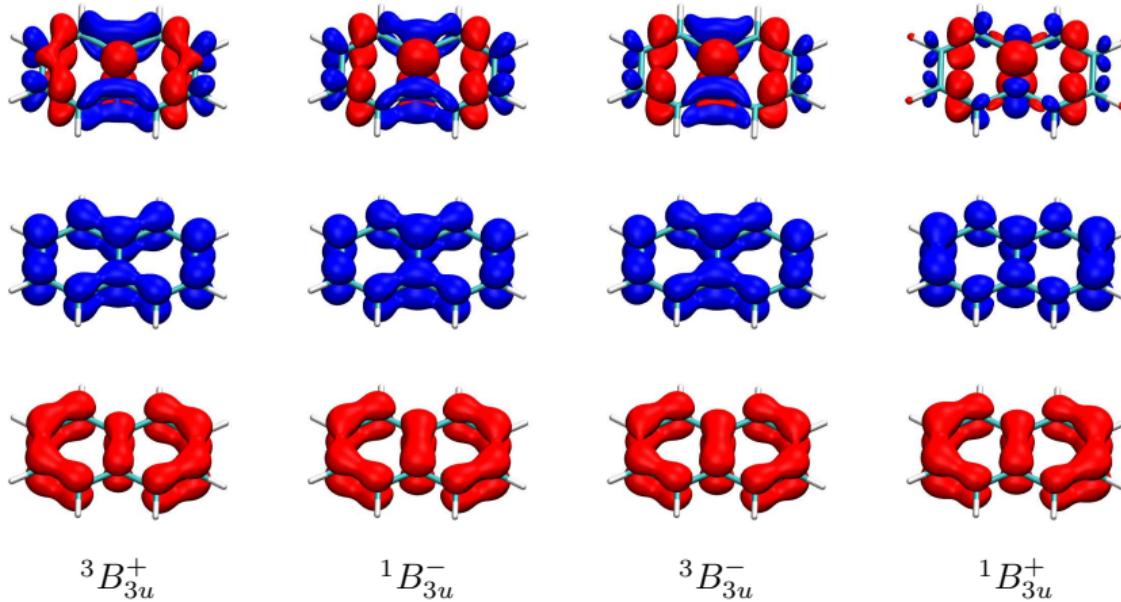
[1]M. Head-Gordon et al., *JPCA* **1995**, 99, 14261.

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

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

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

Napthalene B_{3u} states

▶ ADC(2) **transition densities**

- *For triplets:* Spin-difference transition densities
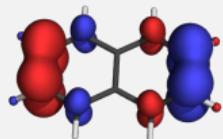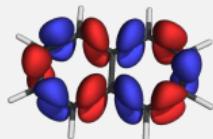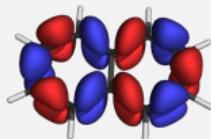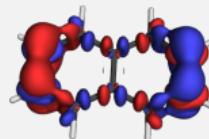
| ${}^3B_{3u}^+$ | ${}^1B_{3u}^-$ | ${}^3B_{3u}^-$ | ${}^1B_{3u}^+$ |

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

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

(?) What about the energies

(?) Why are there extra blobs for the ${}^1B_{3u}^+$ state

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**

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[1]P. Kimber, F. Plasser, *PCCP* **2020**, 22, 6058.

Exchange repulsion

$$\iint \frac{\rho_{0I}(r_h)\rho_{0I}(r_e)}{r_{he}} dr_h dr_e = \int \rho_{0I}(r_h) \int \frac{\rho_{0I}(r_e)}{r_{he}} dr_e dr_h = \left\langle \rho_{0I} \middle| \hat{V}\rho_{0I} \right\rangle$$

ρ_{0I}

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

$\hat{V}\rho_{0I}$

$\left\langle \rho_{0I} \middle| \hat{V}\rho_{0I} \right\rangle$ 4.9 eV   0.2 eV   0.4 eV   1.4 eV
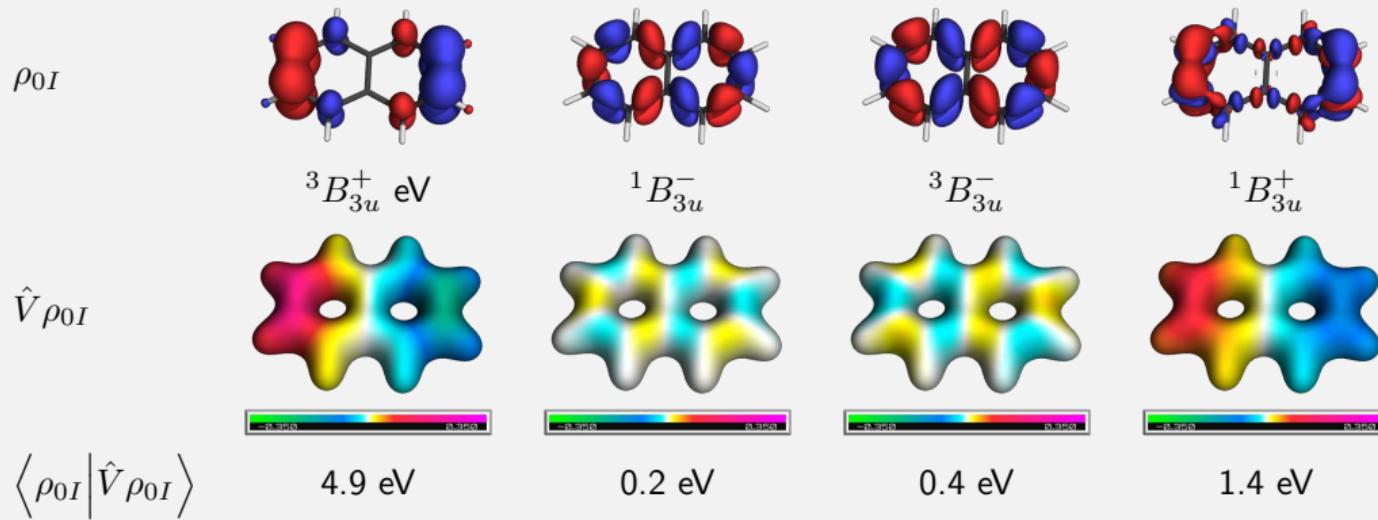
▶ Higher exchange repulsion for $^1B_{3u}^+$ than for $^1B_{3u}^- \rightarrow$ higher energy

▶ $\left\langle \rho_{0I} \middle| \hat{V}\rho_{0I} \right\rangle$ term lower for $^1B_{3u}^+$ than for $^3B_{3u}^+ \rightarrow \sigma$-polarisation

Conditional densities

Coulomb attraction

$$- \iint \frac{|\gamma_{0I}(r_h, r_e)|^2}{r_{he}} dr_h dr_e$$

▶ Non-local **two-body term**

(?) How to visualise

Conditional density for the excited electron

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

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

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

- ▶ **Covalent − states**: **Reduced** electron-hole overlap
- → **Less** exchange repulsion and Coulomb attraction
- ▶ **Ionic + states**: **Enhanced** electron-hole overlap
- → **More** exchange repulsion and Coulomb attraction

State	ΔE
$^3B_{3u}^+$	4.39
$^1B_{3u}^-$	4.49
$^3B_{3u}^-$	5.14
$^1B_{3u}^+$	6.37

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

$1^1B_{2u}^+$, 5.01 eV $2^1B_{2u}^+$, 6.67 eV *Vanishing*

$1^1A_g^-$, 6.34 eV $2^1A_g^-$, 7.49 eV

Vanishing $1^1B_{1g}^-$, 6.42 eV   *Vanishing* $1^1B_{1g}^+$, 7.00 eV

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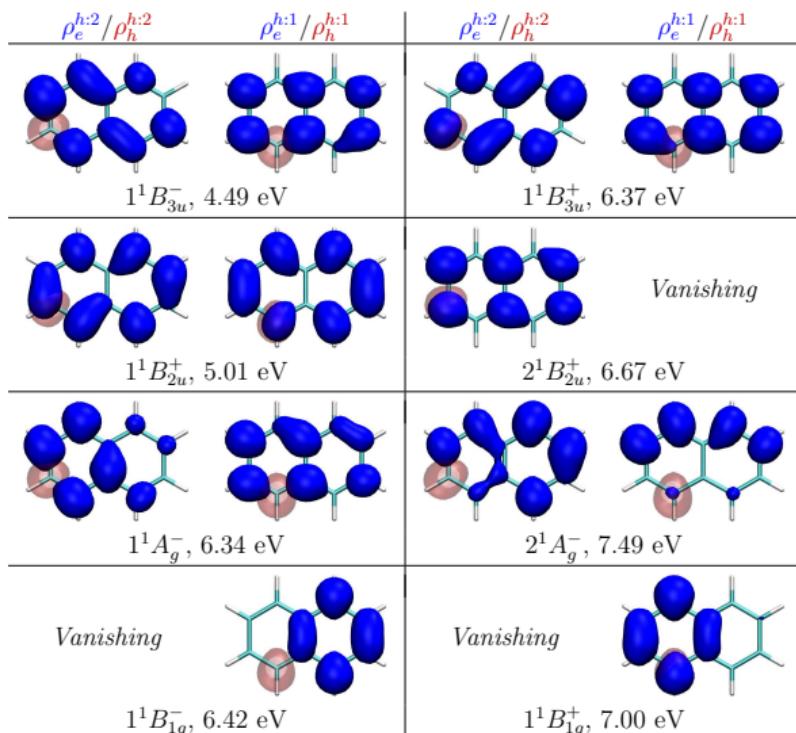
▶ Alternative

▶ Use **CT measure**[1]

- Weight of all the charge-transfer
  contributions between atoms

→ Automatised analysis possible

▶ $CT=0.9$ for simple fully 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**

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[1]FP, H. Lischka, *JCTC* **2012**, 8, 2777.
[2]FP, *ChemPhotoChem* **2019**, 3, 702.

Conclusions

▶ Extended *wavefunction analysis toolbox* for excited states and open shells

▶ **Automated assignment** of excited-state character
- Transition metal complexes
- Multichromophoric systems
- Push-pull systems
- Rydberg *vs* valence states
- Single *vs* double excitations
→ Use for *dynamics*, *extended sampling*, *method comparison*

▶ Deeper **physical insight**
- **Valence-bond** picture: Ionic/covalent (+/-) states
- **Excitons** in conjugated polymers

Further reading

▶ **Intro for practical computations**[1]
- User friendly analysis tools
$\rightarrow$ Plotting
$\rightarrow$ Rigorous and **quantitative** analysis of trends

▶ **Chemical theory**[2]
- Learn about nature and/or quantum chemical methods
- New **qualitative** insight
$\rightarrow$ Understanding of excitation energies via *partial densities* and their *ESPs*

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

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