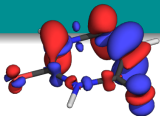


Understanding electronic excitation energies within and beyond the molecular orbital picture

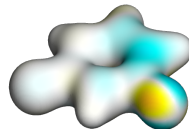
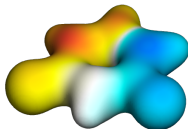


Felix Plasser



Department of Chemistry, Loughborough University

Groningen, 22 October 2019

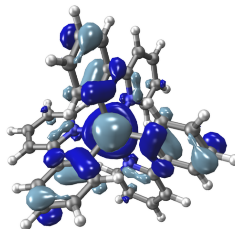


Loughborough
University

Introduction

Computational Photochemistry

- ▶ Accurate numbers
- 😊 *Quantum chemical methods*:
TDDFT, CC, ADC, CASSCF, CASPT2, DMRG, DFT-MRCI
- 😊 *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 some blobs of colour**



Molecular orbitals

Frontier molecular orbitals

- 😊 An **abstract quantum mechanical** concept in wide use
- 😊 High **predictive power** for practising chemists
- 😞 **Not well-defined** for arbitrary wavefunctions
 - MO shapes and energies depend on the level of theory / density functional
- Use *general* orbital transformations: NOs, NTOs, ...
- 😞 **Not the whole story**

Molecular orbitals

☹ Not the whole story

- ▶ Difference between **singlet** and **triplet** states
 - Exchanges splitting
- ▶ **Charge transfer** states
 - Energy for separating the charges
- ▶ **Excitons** in large molecules
 - Dynamic electron-hole attraction
- ▶ Multiconfigurational excited states
 - **ionic** vs **covalent** wavefunction character

❓ How can we go beyond orbitals?

CIS

- ▶ MO energies → **zero-order** description
- ▶ Move to first order
- Configuration interaction singles (**CIS**)
 - Same energies as CCS and ADC(1)
 - Same structure as TDDFT, Bethe-Salpeter equation
- Physics of a **correlated electron-hole pair**
- ▶ *Strategy*: Right down equations - then interpret them

CIS

Excited-state wavefunction

$$|\Psi_I\rangle = \sum_{ia} C_{ia} \hat{a}_a^\dagger \hat{a}_i |\Phi_0\rangle$$

C_{ia} CI-coefficient

$\hat{a}_a^\dagger$ Creation operator for virtual orbital ϕ_a

$\hat{a}_i$ Annihilation operator for occupied orbital ϕ_i

$|\Phi_0\rangle$ Single determinant ground state

Hamiltonian

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} (pq|rs) \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q$$

h_{pq} Element of one-electron Hamiltonian

$(pq|rs)$ Two-electron repulsion integral

Excited-state energy

$$E_I = \langle \Psi_I | \hat{H} | \Psi_I \rangle = \sum_{iajb} C_{ia} C_{jb} \sum_{pq} h_{pq} \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{a}_p^\dagger \hat{a}_q \hat{a}_b^\dagger \hat{a}_j | \Phi_0 \rangle + \\ \frac{1}{2} \sum_{iajb} C_{ia} C_{jb} \sum_{pqrs} (pq|rs) \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \hat{a}_b^\dagger \hat{a}_j | \Phi_0 \rangle$$

☹ So many terms

► Clear rules for evaluation

- $\hat{a}_i^\dagger | \Phi_0 \rangle = 0$ and $\hat{a}_a | \Phi_0 \rangle = 0$
- Anticommutation relations: $\hat{a}_p^\dagger \hat{a}_q = \delta_{pq} - \hat{a}_q \hat{a}_p^\dagger$

→ Creation and annihilation operators have to come in pairs

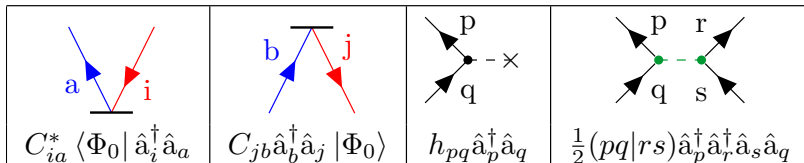
① Connect the creation and annihilation operators in all possible ways

Excited-state energy

$$E_I = \langle \Psi_I | \hat{H} | \Psi_I \rangle = \sum_{iajb} C_{ia} C_{jb} \sum_{pq} h_{pq} \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{a}_p^\dagger \hat{a}_q \hat{a}_b^\dagger \hat{a}_j | \Phi_0 \rangle + \frac{1}{2} \sum_{iajb} C_{ia} C_{jb} \sum_{pqrs} (pq|rs) \langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \hat{a}_b^\dagger \hat{a}_j | \Phi_0 \rangle$$

► Representation through diagrams¹

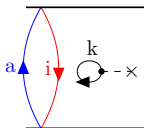
- Creation and annihilation operators → *arrows*
- Operators → *dots*
- bra and ket states → *horizontal lines*



☺ Let's connect the dots!

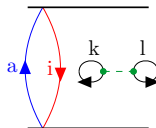
¹I. Shavitt, R. J. Bartlett, *Many-Body Methods in Chem. and Phys.* **2009**, Cam. Mol. Sci.

1-Electron

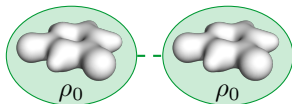


$$\underbrace{\sum_{ia} |C_{ia}|^2}_{=1} \sum_k h_{kk}$$

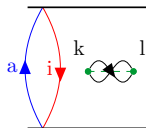
Coulomb



$$\frac{1}{2} \sum_{kl} (kk|ll) = \frac{1}{2} (\rho_0|\rho_0)$$



Exchange



$$-\frac{1}{2} \sum_{kl} (kl|lk) = -\frac{1}{2} \langle \gamma_0 | \gamma_0 \rangle$$

$$\approx -\frac{1}{2} \sum_k (kk|kk)$$

Ground-state energy

$$E_0 = \sum_k h_{kk} + \frac{1}{2} (\rho_0|\rho_0) - \frac{1}{2} \langle \gamma_0 | \gamma_0 \rangle$$

Density matrix

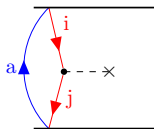
Ground-state density

$$\begin{aligned}\rho_0(r) &= \sum_{k \in \text{occ}} \phi_k(r)^2 \\ \frac{1}{2} \sum_{kl} (kk|ll) &= \frac{1}{2} \sum_{kl} \iint \frac{\phi_k(r_1)^2 \phi_l(r_2)^2}{r_{12}} dr_1 dr_2 \\ &= \frac{1}{2} \iint \frac{\rho_0(r_1) \rho_0(r_2)}{r_{12}} dr_1 dr_2 = \frac{1}{2} (\rho_0 | \rho_0)\end{aligned}$$

Ground-state density matrix

$$\begin{aligned}\gamma_0(r_1, r_2) &= \sum_{k \in \text{occ}} \phi_k(r_1) \phi_k(r_2) \\ \frac{1}{2} \sum_{kl} (kl|lk) &= \frac{1}{2} \iint \frac{|\gamma_0(r_1, r_2)|^2}{r_{12}} dr_1 dr_2 = \frac{1}{2} \langle \gamma_0 | \gamma_0 \rangle\end{aligned}$$

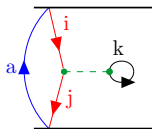
1-Electron



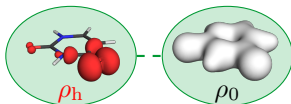
$$-\sum_{a ij} C_{ia}^* C_{ja} h_{ji}$$

$$= -\sum_{ij} D_{ij}^h h_{ij}$$

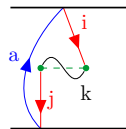
Coulomb



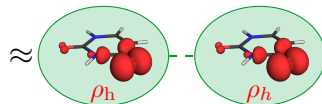
$$-\sum_{ijk} D_{ij}^h (ji|kk) = -(\rho_h|\rho_0)$$



Exchange



$$\sum_{ijk} D_{ij}^h (jk|ki) = \langle \gamma_h | \gamma_0 \rangle$$



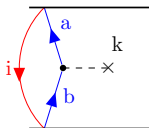
Energy of the excitation hole

$$-\sum_{ij} D_{ij}^h h_{ij} - (\rho_h|\rho_0) + \langle \gamma_h | \gamma_0 \rangle = -\sum_{ia} |C_{ia}|^2 \epsilon_i$$

ϵ_i Energy of occupied orbital ϕ_i

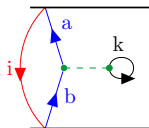
D_{ij}^h Hole density matrix

1-Electron

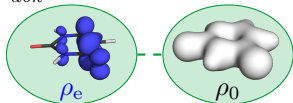


$$\sum_{ab} D_{ab}^e h_{ab}$$

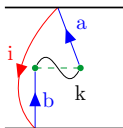
Coulomb



$$\sum_{abk} D_{ab}^e (ab|kk) = (\rho_e|\rho_0)$$



Exchange



$$-\sum_{abk} D_{ab}^e (kb|ak) = -\langle \gamma_e | \gamma_0 \rangle$$

$$\approx 0$$

Energy of the excited electron

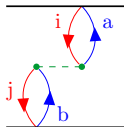
$$\sum_{ab} D_{ab}^e h_{ab} + (\rho_e|\rho_0) - \langle \gamma_e | \gamma_0 \rangle = + \sum_{ia} |C_{ia}|^2 \epsilon_a$$

ϵ_a Energy of virtual orbital ϕ_a

D_{ij}^e Electron density matrix

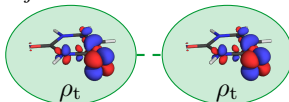
1-Electron

Coulomb

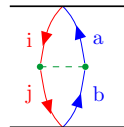


0

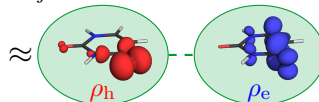
$$\sum_{abij} C_{ia} C_{jb} (j\bar{b}|a\bar{i}) = (\rho_t|\rho_t)$$



Exchange



$$-\sum_{abij} C_{ia} C_{jb} (j\bar{i}|a\bar{b}) = -\langle \gamma_t | \gamma_t \rangle$$



Electron-hole interactions

$$(\rho_t|\rho_t) - \langle \gamma_t | \gamma_t \rangle \approx (\rho_t|\rho_t) - (\rho_h|\rho_e)$$

Transition density matrix

Transition density matrix

$$D_{pq}^t = \langle \Psi_0 | \hat{a}_p^\dagger \hat{a}_q | \Psi_I \rangle$$

$$\gamma_t(r_h, r_e) = \sum_{pq} D_{pq}^t \phi_p(r_h) \phi_q(r_e)$$

r_h Coordinate of the excitation **hole**

r_e Coordinate of the excited **electron**

Transition density

$$\rho_t(r) = \gamma_t(r, r)$$

► Product of occupied and virtual orbitals

¹FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

Excitation energy

CIS excitation energy

$$\Delta E = \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - \langle \gamma_t | \gamma_t \rangle$$

$$\approx \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - (\rho_h | \rho_e)$$

	$(\rho_t \rho_t)$	$\langle \gamma_t \gamma_t \rangle$
Hartree-Fock	Coulomb/Hartree	Exchange
Electron/hole	Exchange repulsion	Coulomb attraction Exciton binding
Applicability	Only for singlets	Singlets and triplets
Type	Static interaction	Dynamic two-body term
TDDFT	Included	Non-local X
GW		W

Excitation energy

CIS excitation energy

$$\begin{aligned}\Delta E &= \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - \langle \gamma_t | \gamma_t \rangle \\ &\approx \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - (\rho_h | \rho_e)\end{aligned}$$

► $(\rho_t | \rho_t)$

- **Exchange splitting** between singlets and triplets
- Energetic penalty for **bright states**
- Basis for **Förster coupling**
- Repulsive term for **plasmons**¹

¹S. Bernadotte, F. Evers, C. R. Jacob, *JPCC* **2013**, 117, 1863–1878.

Excitation energy

CIS excitation energy

$$\begin{aligned}\Delta E &= \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - \langle \gamma_t | \gamma_t \rangle \\ &\approx \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - (\rho_h | \rho_e)\end{aligned}$$

► $(\rho_h | \rho_e)$

→ Energetic penalty for **charge-transfer states**

► $\langle \gamma_t | \gamma_t \rangle$

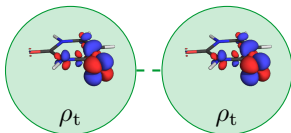
→ Dynamic **exciton** binding in large molecules¹

¹S. A. Mewes, FP, A. Dreuw, *JPCL* **2017**, 8, 1205–1210.

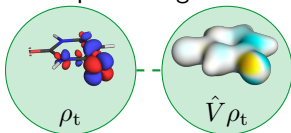
Visualisation

$$\begin{aligned}
 (\rho_t | \rho_t) &= \iint \frac{\rho_t(r_1) \rho_t(r_2)}{r_{12}} dr_1 dr_2 = \int \rho_t(r_1) \left(\int \frac{\rho_t(r_2)}{r_{12}} dr_2 \right) dr_1 \\
 &= \int \rho_t(r_1) \hat{V} \rho_t(r_1) dr_1
 \end{aligned}$$

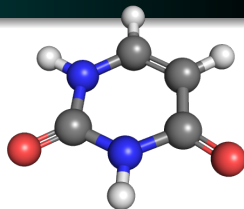
- Electrostatic interaction between two charge distributions



- Overlap of charge distribution with electrostatic potential

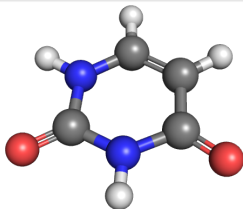


Uracil



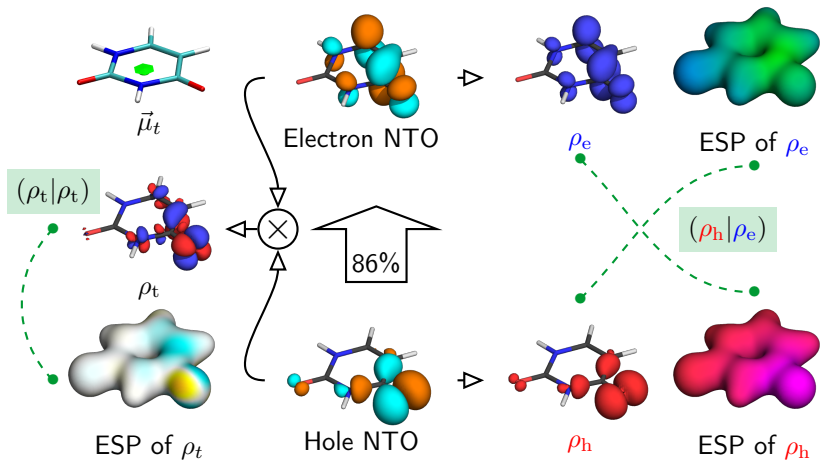
- Uracil
 - Computation of singlet and triplet states
 - ADC(2)/def2-SV(P)

Uracil

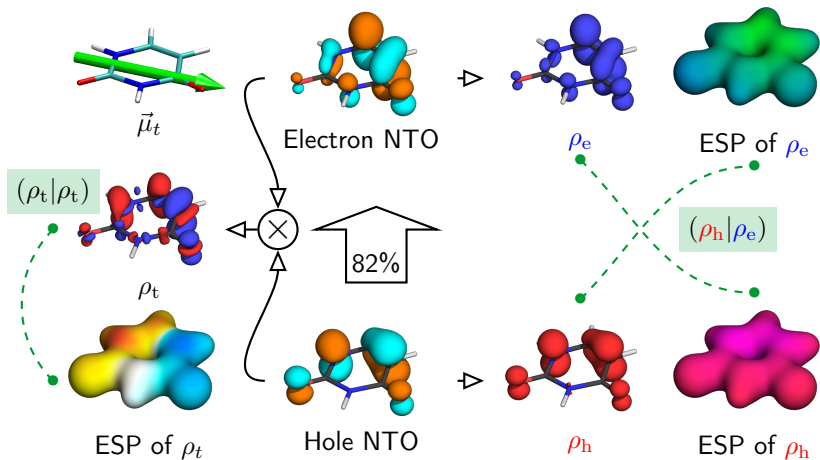


State	ΔE	f	Configurations
$1^3\pi\pi^*$	4.07	-	$0.95hl$
$1^3n\pi^*$	4.70	-	$0.85h_2l + 0.27h_2l_1 + 0.23h_3l$
$1^1n\pi^*$	4.95	0.00	$0.87h_2l + 0.23h_2l_1 + 0.14h_3l$
$2^3\pi\pi^*$	5.68	-	$0.79h_1l - 0.41hl_1 - 0.23h_2l_2$
$1^1\pi\pi^*$	5.76	0.23	$0.91hl$

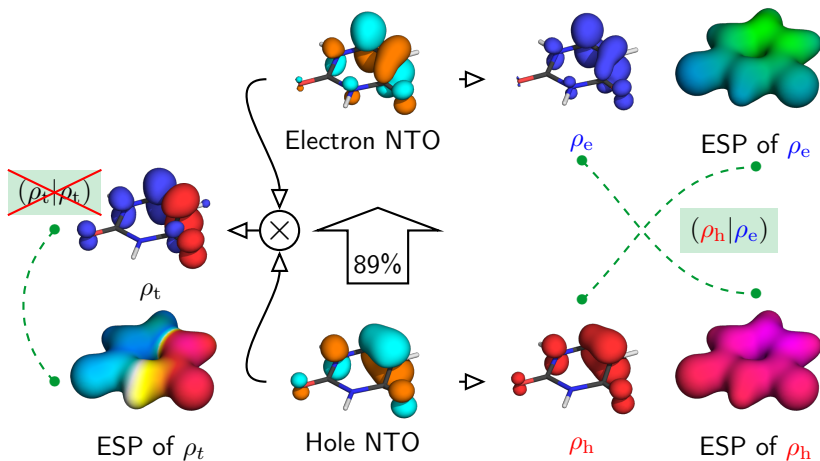
- ⑦ Why is the **HOMO-LUMO transition** the lowest triplet but not the lowest singlet
- ⑦ Why is the **exchange splitting** between the $n\pi^*$ lower than between the $\pi\pi^*$ states

Uracil $1^1n\pi^*$ state

- ▶ Weak $(\rho_t|\rho_t)$ term $\rightarrow$ weak **exchange splitting**
- ▶ ESPs of ρ_h and ρ_e are very uniform $\rightarrow$ small effect

Uracil $1^1\pi\pi^*$ state

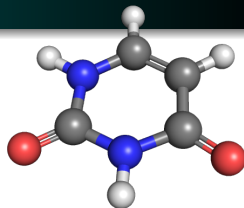
- Stronger $(\rho_t|\rho_t)$ term $\rightarrow$ stronger **exchange splitting**
 - Enhanced transition dipole moment $\vec{\mu}_t$
 - Small adjustment of ρ_e

Uracil $1^3\pi\pi^*$ state

► “Cleaner” transition spin-density

❗ $(\rho_t|\rho_t)$ term would be even stronger

Uracil



State	ΔE	f	Configurations	$(\rho_t \rho_t)$
$1^3\pi\pi^*$	4.07	-	$0.95hl$	6.42
$1^3n\pi^*$	4.70	-	$0.85h_2l + 0.27h_2l_1 + 0.23h_3l$	0.60
$1^1n\pi^*$	4.95	0.00	$0.87h_2l + 0.23h_2l_1 + 0.14h_3l$	0.41
$2^3\pi\pi^*$	5.68	-	$0.79h_1l - 0.41hl_1 - 0.23h_2l_2$	
$1^1\pi\pi^*$	5.76	0.23	$0.91hl$	0.85

❗ Even HOMO-LUMO transitions can be complicated

- Strong difference between singlet and triplet
- The singlet is the *ionic* L_a state

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

❓ Relation to transition density

☹ 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.

Ionic and covalent states

- ▶ Excited states in **polyenes** and **polyacenes** come in two flavours¹
 - **+** **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
 - ▶ Important methodological implications (see above)

¹R. Pariser, *J. Chem. Phys* **1956**, 24, 250.

²K. Schulten, I. Ohmine, and M. Karplus, *J. Chem. Phys* **1976**, 64, 4422.

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 VBSCF³
 - Specific and involved computational methods
- ⑦ Can we **reconstruct** ionic and covalent character from the **wavefunctions**
 - Application of **standard quantum chemistry** methods

¹K. Hirao, H. Nakano, and K. Nakayama. J., *Chem. Phys.* **1997**, 107, 9966.

²C. Angeli, R. Cimiraglia and J. P. Malrieu, *Mol. Phys.* **2013**, 111, 1069.

³J. Gu, W. Wu, D. Danovich, R. Hoffmann, Y. Tsuji, and S. Shaik., *JACS* **2017**, 139, 9302.

Naphthalene

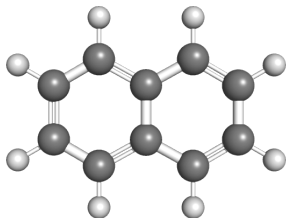
- ▶ Naphthalene molecule
- ▶ Vertical excitations
 - ADC(2)/def-SV(P) level

- ▶ **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

Naphthalene 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**

B_{3u} 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

Naphthalene B_{3u} states

B_{3u} states

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

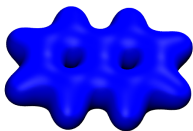
$$^3B_{3u}^{\pm} = \frac{1}{2} \left(\left(\Phi_{H1,\alpha}^{L,\alpha} - \Phi_{H1,\beta}^{L,\beta} \right) \pm \left(\Phi_{H,\alpha}^{L1,\alpha} - \Phi_{H,\beta}^{L1,\beta} \right) \right)$$

- ▶ 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**

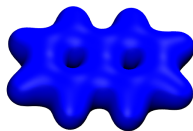
❗ Only difference: **signs**

Naphthalene B_{3u} states

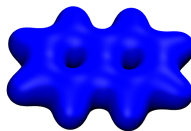
► ADC(2) densities



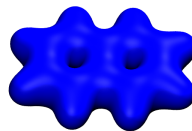
${}^3B_{3u}^+$



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



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

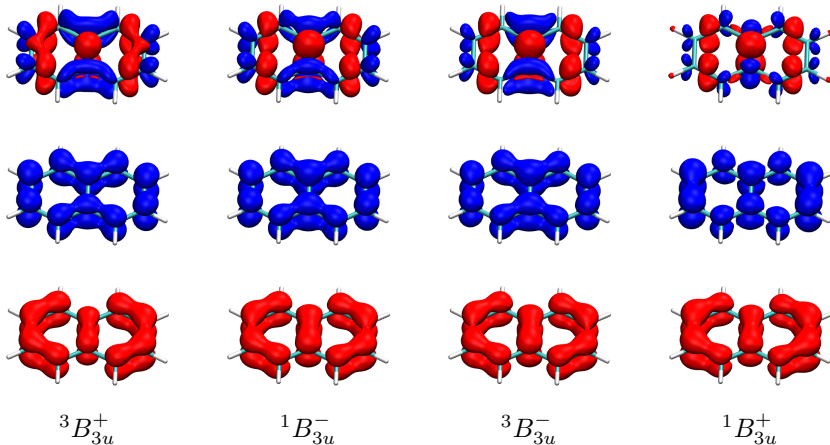


${}^1B_{3u}^+$

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

Naphthalene B_{3u} states

► ADC(2) difference, **attachment**, **detachment**¹ densities



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

The major analysis methods fail!

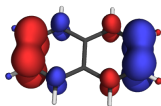
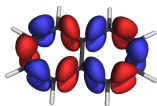
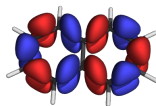
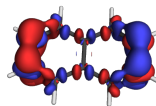


What do we do?

Naphthalene B_{3u} states

► ADC(2) transition densities

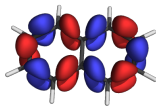
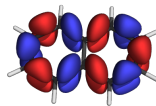
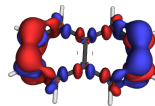
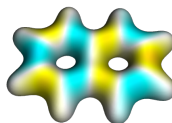
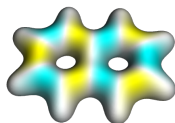
- *For triplets*: Spin-difference transition densities


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

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

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

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

☺ +/- assignment clear → + on atoms, - on bonds

Naphthalene B_{3u} states

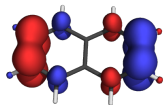
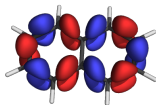
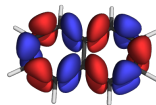
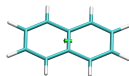
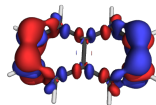
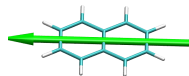
► ADC(2) transition density ESPs


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

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

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

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


- Enhanced ESP for + states
 - Triplet stronger than singlet
 - Triplet again “cleaner”

Naphthalene B_{3u} states

► ADC(2) transition moments


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

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

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

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


► Strong transition moment for singlet + state

CIS excitation energy

$$\Delta E = \sum_{ia} |C_{ia}|^2 (\epsilon_a - \epsilon_i) + (\rho_t | \rho_t) - \langle \gamma_t | \gamma_t \rangle$$

State	ADC(1)	ADC(2)	ADC(3)	$(\rho_t \rho_t)$
$^3B_{3u}^+$	4.24	4.39	3.91	4.57
$^1B_{3u}^-$	5.27	4.49	4.16	0.22
$^3B_{3u}^-$	4.91	5.14	4.88	0.41
$^1B_{3u}^+$	7.23	6.37	6.41	1.36

- ▶ Highest energy for $^1B_{3u}^+$ – exchange repulsion
- ▶ What about the other states
- ⑦ How to analyse $\gamma_{0I}(r_h, r_e)$

Conditional densities

Conditional density for the excited electron

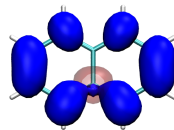
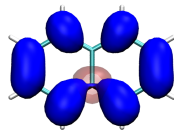
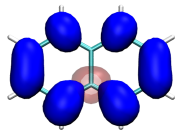
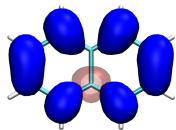
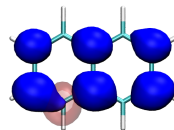
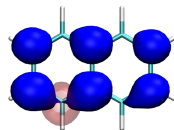
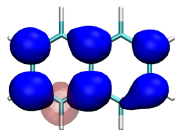
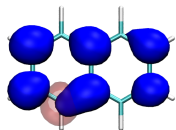
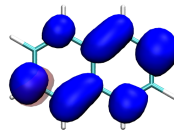
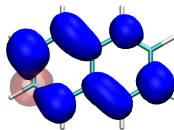
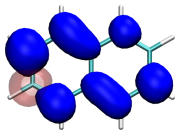
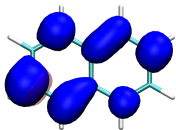
$$\rho_e^{h:A}(r_e) = \int_A |\gamma_t(r_h, r_e)|^2 dr_h$$

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

- ▶ Evaluation after Löwdin orthogonalisation
- Straightforward matrix operations
- ▶ Let's move the **hole** over individual carbon atoms

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

Conditional densities


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

Energetics

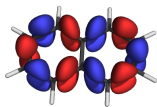
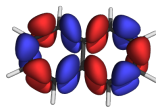
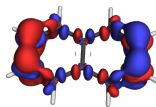
- ▶ **Ionic + states:** Enhanced electron-hole overlap
 - **More** exchange repulsion and Coulomb attraction
- ▶ **Covalent – states:** Reduced electron-hole overlap
 - **Less** exchange repulsion and Coulomb attraction

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

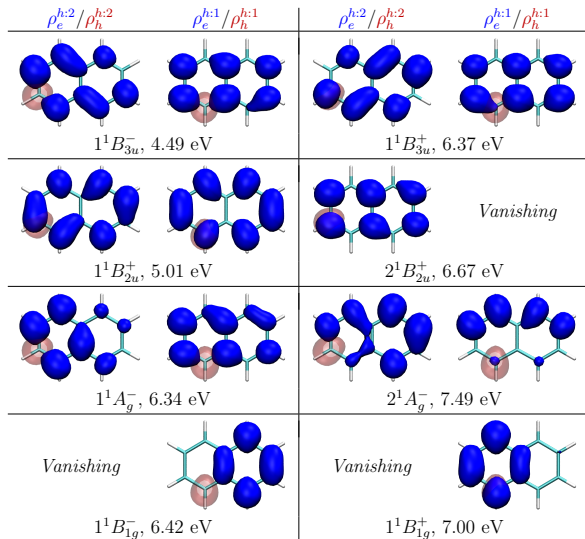
Naphthalene B_{3u} states

► Transition densities

- Only “*differential overlap*” terms for **covalent** – states


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

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

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

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

Naphthalene - Singlet States



¹FP, *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 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

¹FP, H. Lischka, *JCTC* **2012**, 8, 2777.

²FP, *ChemPhotoChem* **2019**, 3, 702.

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 **excited-state density** does **not** tell us anything at all about the **absorption strengths** and **relative energies**
- ② Is the transition density matrix **physically observable**?

Summary

- ▶ Excited state energies **beyond the MO picture**
- ▶ Main physics
 - **Exchange repulsion** of the transition density → bright states
 - Dynamic **Coulomb attraction** (transition density matrix)
- ▶ Uracil
 - Relative order of singlet and triplet $\pi\pi^*$ and $n\pi^*$ states→ Different strength of exchange repulsion
- ▶ Naphthalene
 - Differentiation between ionic and covalent states→ Correlation effects decisive

Outlook

- ▶ Tuning **singlet-triplet gaps**
 - Singlet fission
 - Thermally activated delayed fluorescence
- ▶ **Transition metal complexes**
 - Relative energies of singlet and triplet locally excited and CT states

Software

Extended *wavefunction analysis toolbox*.

TheoDORE - **Theo**retical **D**ensity, **O**rbital **R**elaxation and **E**xciton analysis¹

- ▶ 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 library²

- ▶ **Q-Chem**: Single-reference methods
- ▶ **MOLCAS**: Multireference methods

¹<http://theodore-qc.sourceforge.net>

²<https://github.com/libwfa/libwfa>

Acknowledgements

Vienna

S. Mai
L. González

Heidelberg

S. A. Mewes
M. Wormit
A. Dreuw

Vienna/Lubbock/Tianjin

H. Lischka



**Loughborough
University**

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