

Understanding ionic and covalent wavefunction character without valence bond theory

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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, ...

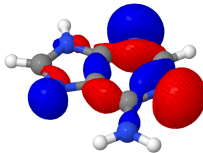
😊 *Algorithmic efforts:* Linear scaling, density fitting, parallelization, GPUs, ...

- Comparison to experiment

😊 *Linear and non-linear optical properties*

- Chemical insight

😞 **Look at the HOMO and LUMO**



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 theory²
 - **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 **independent of the molecular orbital picture**

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

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

Methodological implications

☹ Ionic states cause **problems for CASSCF**

→ Energies overestimated by > 1 eV

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

→ **Dynamic σ polarisation** effects

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

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

→ Energies too low

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

State of the art

- ▶ How do we characterise ionic and covalent states?
- ▶ VB wavefunctions **constructed** using **dedicated valence-bond protocols**
 - CASVB,¹ orthogonal VB,² VBSCF³
 - Specific and involved computational methods
- ⑦ Can we **reconstruct** ionic and covalent character from the **wavefunctions**
 - Application of **standard quantum chemistry** methods

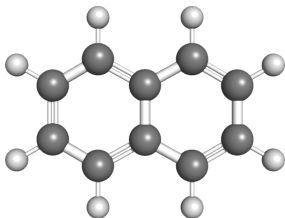
¹K. Hirao, H. Nakano, and K. Nakayama. J., *Chem. Phys.* **1997**, 107, 9966.

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

► Detailed energetics

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

- ① Why are the singlet and triplet – **states** similar in energy
- ① Why is there a large gap between the singlet and triplet + **states**

Naphthalene B_{3u} states

B_{3u} states

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

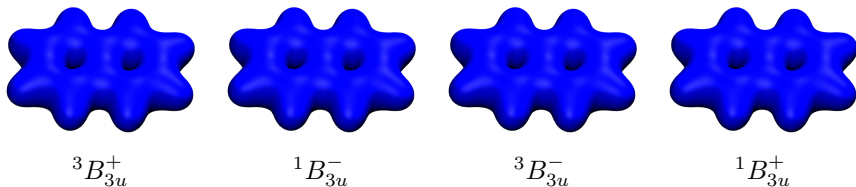
$$^3B_{3u}^{\pm} = \frac{1}{2} \left(\left(\Phi_{H1,\alpha}^{L,\alpha} - \Phi_{H1,\beta}^{L,\beta} \right) \pm \left(\Phi_{H,\alpha}^{L1,\alpha} - \Phi_{H,\beta}^{L1,\beta} \right) \right)$$

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

❗ Only difference: **signs**

Naphthalene B_{3u} states

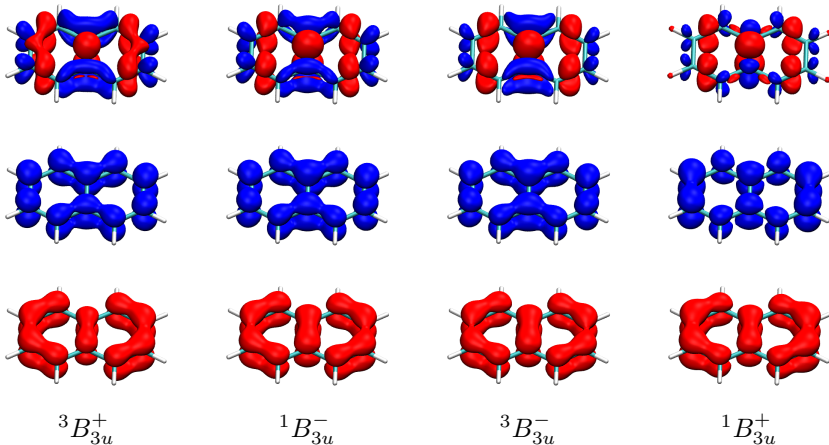
► ADC(2) densities



❗ The **ground state** density contains all physically relevant information
about the ground state 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?

Transition density matrix

Transition density matrix (1TDM)

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

Ψ_0, Ψ_I Ground and excited state wavefunctions

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

ϕ_p Molecular orbital

$\mathbf{r}_h, \mathbf{r}_e$ Coordinates of the **hole** and **electron**

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

Transition density

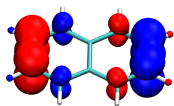
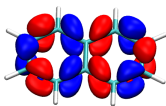
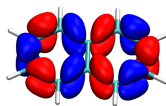
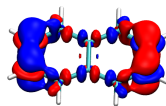
$$\rho_{0I}(\mathbf{r}) = \gamma_{0I}(\mathbf{r}, \mathbf{r})$$

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

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

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

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

❓ What about the energies

CIS excitation energy

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

C_{ia} CI coefficient

ϵ_i Orbital energy

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

CIS excitation energy

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

► Excitation involving only two orbitals o, v

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

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

CIS excitation energy - two orbitals

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

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

¹FP, *JCP* **2016**, 144, 194107.

CIS excitation energy

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

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

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

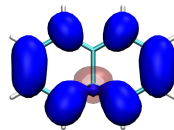
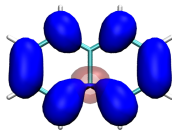
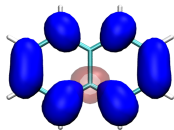
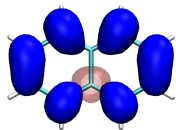
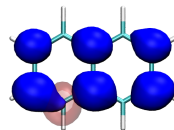
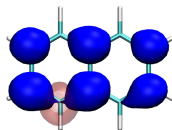
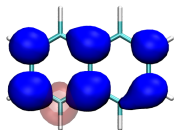
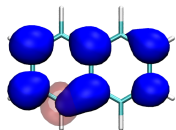
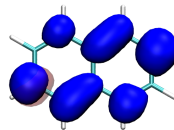
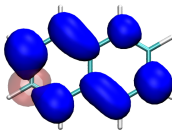
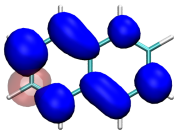
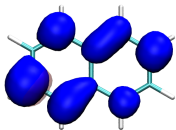
Conditional density for the excited electron

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

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

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

Conditional densities

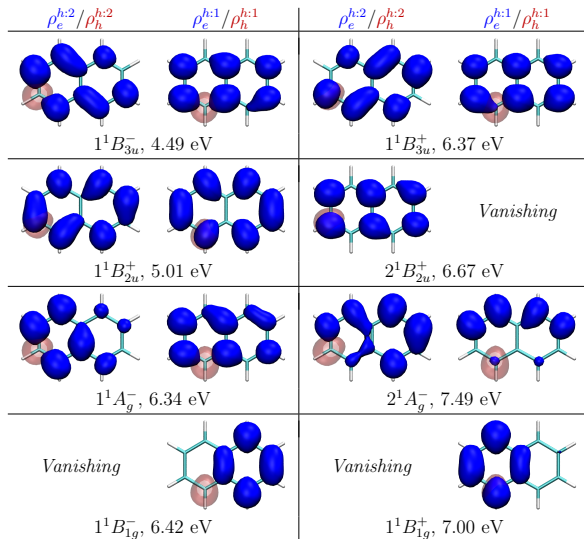

 ${}^3B_{3u}^{+}$
 ${}^1B_{3u}^{-}$
 ${}^3B_{3u}^{-}$
 ${}^1B_{3u}^{+}$

Energetics

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

State	ADC(1)	ADC(2)	ADC(3)
${}^3B_{3u}^+$	4.24	4.39	3.91
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${}^1B_{3u}^+$	7.23	6.37	6.41

Naphthalene - Singlet States



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

- ▶ Alternative
- ▶ Use **CT measure**¹
 - Weight of all the charge-transfer contributions between atoms
- Automatised analysis possible
- ▶ **CT=0.9** for simple delocalised transition over 10 atoms
 - **CT<0.9** for **ionic + states**
 - **CT>0.9** for **covalent – states**

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**, DOI: 10.1002/cptc.201900014.

Physical Observability

- ▶ Knowledge of the **transition density** allows us to make testable predictions about the **absorption strengths**
 - ▶ Knowledge of the **transition density matrix** allows us to make testable predictions about the **absorption strengths** and **relative energies**
 - ▶ The **density** does **not** tell us anything at all about the **absorption strengths** and **relative energies**
- ① Is the transition density matrix **physically observable**?

Conclusions

- ▶ Valence-bond picture reconstructed from general quantum chemistry computations
 - **Visualisation of correlation effects**
 - **Quantification of dynamic charge transfer**

Further examples

- ▶ How can we analyse **thousands of excited states** in DNA in a completely automatised fashion¹
- ▶ How can we automatically assign excite-state character to **transition metal complexes**²
- ▶ How can we visualise and quantify **excitonic correlation effects** in conjugated polymers³

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

²M. Fumanal, F. Plasser, S. Mai, C. Daniel, E. Gindensperger, *JCP* **2018**, 148, 124119.

³S. A. Mewes, J.-M. Mewes, A. Dreuw, FP, *PCCP* **2016**, 18,2548.

Implementation

Extended *wavefunction analysis toolbox*.

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

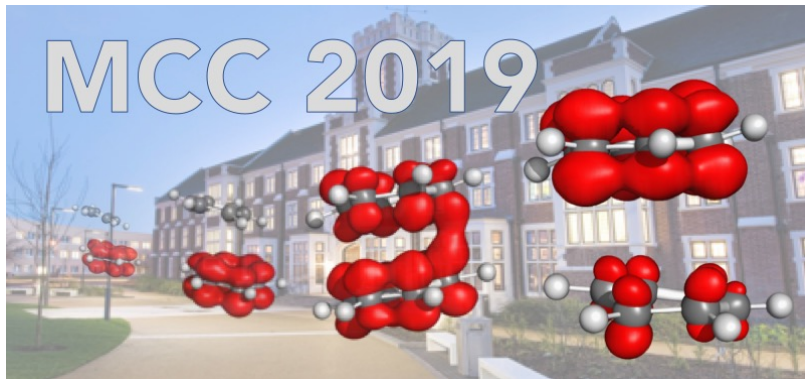
- ▶ Program package for wavefunction analysis
- ▶ Interfaces to various quantum chemistry programs:
Columbus, Turbomole, Orca, GAMESS, Gaussian, ADF, Terachem,
...
- ▶ Open-source

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>



► Midlands Computational Chemistry Meeting 2019

- 15th April 2019, Loughborough
 - **No registration fee** thanks to the Centre for the Science of Materials (Loughborough), CCP9, and CCP5
 - Registration closes 31st March
- <https://www.lboro.ac.uk/departments/chemistry/news-events/computational-chemistry-meeting-19/>

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Loughborough
University



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