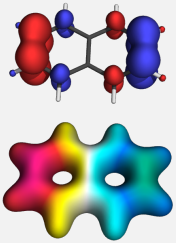
New analysis tools for excited-state quantum chemistry: Turning numbers into chemical insight



Felix Plasser

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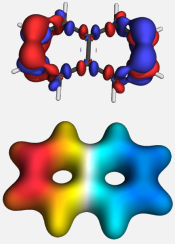
Faraday Joint Interest Group Conference
29 March 2021

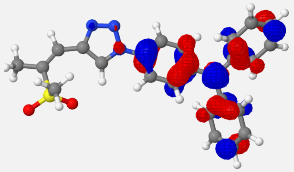


Loughborough University

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 **approximate theories**



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

→ **Excited-state aromaticity**

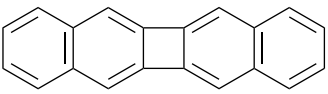
Triplet energies

- Two isomeric polycyclic hydrocarbons
  - Built around cyclobutadiene
- (?) Which one has higher singlet and triplet **excitation energies**

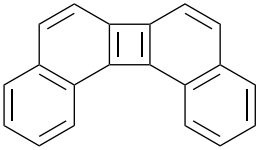
Vertical excitation energy (eV) – TDDFT/CAM-B3LYP

	1	**2**
T_1	2.74	1.56
S_1	3.71	2.63

(!) Energies shifted by **more than 1 eV**



Dibenzo[b,h]biphenylene (**1**)



Dibenzo[a,i]biphenylene (**2**)

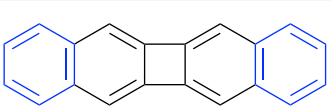
[1] FP, *submitted* **2021**, DOI: 10.26434/chemrxiv.14143730.

Excited-state aromaticity

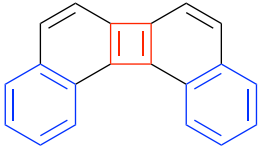
- **Baird aromaticity**
  - Antiaromatic molecules become aromatic in their excited triplet state[1]
- **Resonance structures**
  - **1** cannot have quartet and sextets at the same time
  - **2** has quartet + two sextets

→ *Hypothesis*: **2** is more antiaromatic in its ground state and more aromatic in its excited states (see Ref. 2)

(?) How do we quantify/visualise aromaticity



Dibenzo[b,h]biphenylene (**1**)



Dibenzo[a,i]biphenylene (**2**)

[1] N. C. Baird, *JACS* **1972**, 94, 4941–4948.
[2] R. Ayub, O. El Bakouri, K. Jorner, M. Sola, H. Ottosson, *J. Org. Chem* **2017**, 82, 6327–6340.

Nucleus independent chemical shift

- Perform **virtual NMR experiment**
  - Nucleus independent chemical shift[1]

→ **Shielding** for **aromatic** systems

→ **Deshielding** for **antiaromatic** systems

? How do we visualise a tensor
  - 3×3 matrix at every point in 3D space

Chemical shielding tensor

$$\mathbf{B}_{\mathrm{ind}}(\mathbf{R}) = -\underline{\sigma}(\mathbf{R})\mathbf{B}_{\mathrm{ext}}$$

$\mathbf{B}_{\mathrm{ext}}$ External magnetic field

$\mathbf{B}_{\mathrm{ind}}$ Induced magnetic field

$\underline{\sigma}$ Shielding tensor

[1] P. von R. Schleyer, et al., *J. Am. Chem. Soc.* **1996**, 118, 6317–6318.

Visualisation of chemical shielding tensors (VIST)

Eigenvalue decomposition

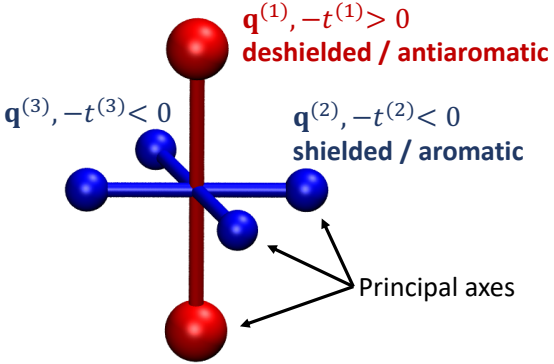
$$\underline{\sigma}\mathbf{q}^{(i)} = t^{(i)}\mathbf{q}^{(i)}$$

- $\mathbf{q}^{(i)}$ Eigenvectors – principal axes
- $t^{(i)}$ Eigenvalues

☺ Full information from local shielding tensor encoded graphically

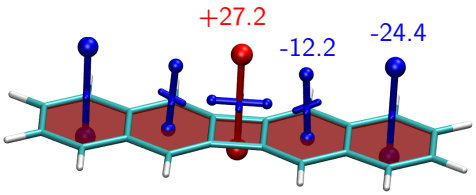
→ Suitable even for non-planar systems[1]

Visualisation of chemical shielding tensors (VIST)

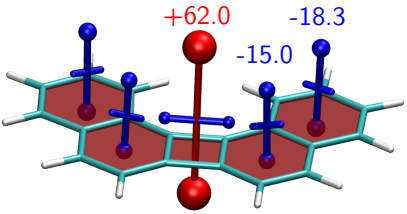


[1] FP, F. Glöcklhofer, *submitted* **2021**, DOI: 10.26434/chemrxiv.13580885.

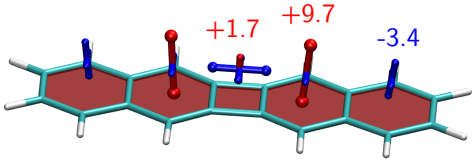
Molecule 1 – S_0 – RKS/TPSSh



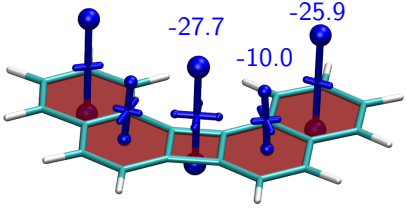
Molecule 2 – S_0 – RKS/TPSSh



Molecule 1 – T_1 – UKS/TPSSh

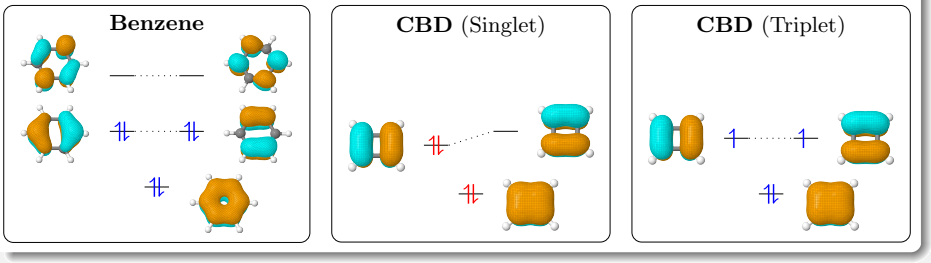


Molecule 2 – T_1 – UKS/TPSSh



Molecular orbital picture

Cyclic π-systems



- Lowest π-orbital non-degenerate, higher π-orbitals come in degenerate pairs

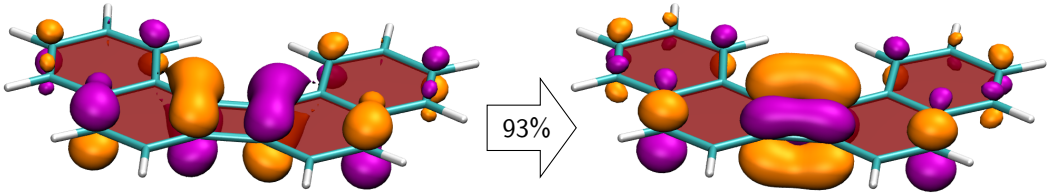
$\rightarrow$ **Filled shells** for **odd** number of electron pairs ($4n + 2$ electrons)

- **Low HOMO/LUMO gap** for **even** number of electron pairs ($4n$ electrons)
- Triplet: **Filled shells** with $4n$ electrons
- Singlet excited states: also stabilised due to low HOMO/LUMO gap
  - More complicated because of possible *double excitations*
  - Significant **exchange repulsion** $\rightarrow$ higher energy

Excitation process

- ? Rigorous representation of the excitation process
- Natural transition orbitals[1]
  - Singular value decomposition of the *transition density matrix*[2]

Molecule 2 – Natural transition orbitals ($S_0 \rightarrow T_1$)



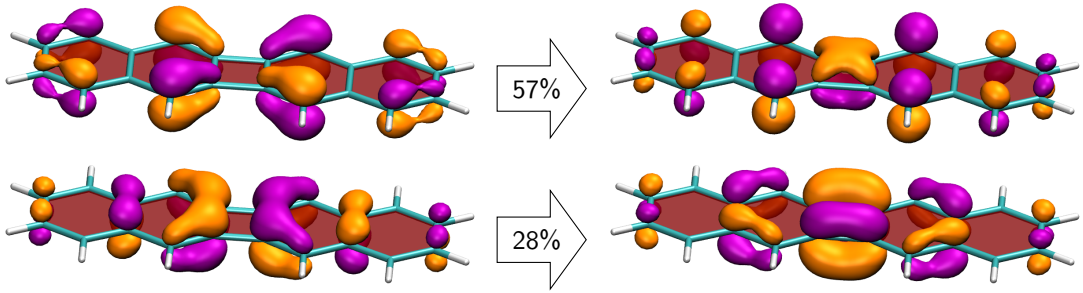
- Dominant transition around cyclobutadiene

→ Fits with previous discussion on **Baird aromaticity**

[1] R. L. Martin, *JCP* **2003**, 118, 4775–4777.
[2] FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

Natural transition orbitals

Molecule 2 – Natural transition orbitals ($S_0 \rightarrow T_1$)



- Two interacting configurations
  - Only second one around cyclobutadiene

→ **Reduced Baird aromaticity**

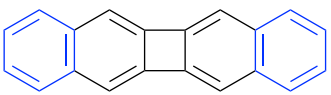
Summary

- **Consistent picture**

→ **Baird aromaticity** enhanced for **2**

- Quartets/sextets
- Excitation energies
- Chemical shielding tensors
- Natural transition orbitals

- Interpretation in MO picture
- *Low* HOMO/LUMO gap with *large* spatial overlap



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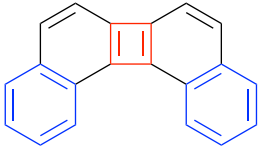

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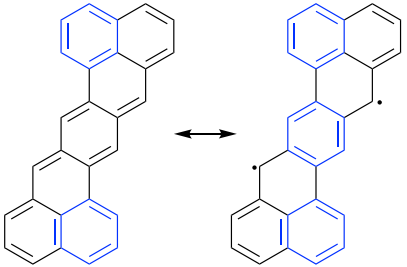
[1] FP, F. Glöcklhofer, *submitted* **2021**, DOI: 10.26434/chemrxiv.13580885.
[2] FP, *submitted* **2021**, DOI: 10.26434/chemrxiv.14143730.

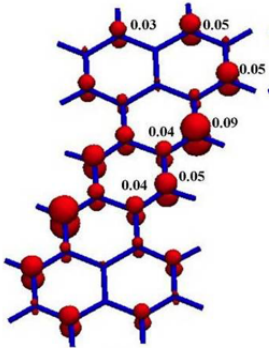
Related chemistry

- Fused benzene rings
  - Maximal number of sextets only with **biradical formation**

Zethrenes[1]



Unpaired electrons

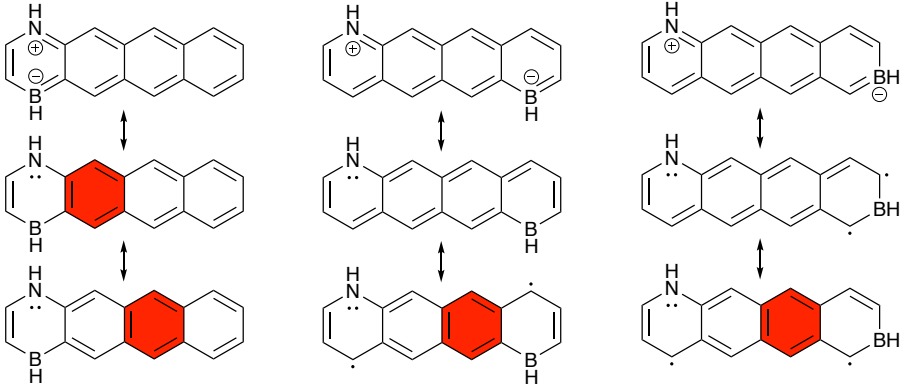


[1] A. Das, T. Müller, FP, H. Lischka, *JPCA* **2016**, 120, 1625–1636.

Related chemistry

- Doping with heteroatoms
  - *Ionic* / *biradical* resonance structures vs sextets

Heteroatoms – BN-doped tetracenes



[1] M. Pinheiro, F. B. C. Machado, FP, A. J. A. Aquino, H. Lischka, *JMCC* **2020**, 8, 7793–7804.

Conclusions

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

- Deep **physical insight**[1]
  - Excited-state **aromaticity**
  - **Unpaired electrons**
  - **Valence-bond** picture: Ionic/covalent (+/-) states
  - **Excitons** in conjugated polymers

- **Automated assignment** of excited-state character[2]
  - Push-pull systems
  - Transition metal complexes
  - Multichromophoric systems
  - Rydberg *vs* valence states
  - Single *vs* double excitations

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

Acknowledgements

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