Understanding excited states of functional molecules beyond the molecular orbital picture

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Design of functional molecules

- Synthesis
- Ever more intricate structures
- Spectroscopy
- Time-resolved, high-resolution, ...
- Computation
- More accurate methods + faster computers

How do we put it all together

Look at some blobs of colour
How can we understand excited states beyond the MO picture

- Detailed insight
  - Structure-property relationships → rational design

- Singlet/triplet gaps
  - Cannot be understood from orbital energies

- Electron correlation in large systems
Push-pull systems

- Synthesis of push-pull chromophores
  - Different isomers
  - Different oxidation states of sulphur

Optical spectra

Strongly different emission for **sulfoxides**

- **EMSO₂M-14TPA** < **ZMSO₂M-14TPA** < **ZMSO₂M-15TPA**
- Ab initio computations
  - ADC(2)
- Emission energies
  $\rightarrow$ Trends reproduced
Frontier orbitals

First excited state ($S_1$)

Frontier orbitals do not tell the whole story

How do we move beyond?
Electron-hole densities

- Summation over all the **occupied** and **virtual** orbitals involved in the transition
- Density of the excitation **hole**
- Density of the excited **electron**
- Densities of the **excited electron**
  - **Hole** always on triphenyl amine

- **Solvent**
  - **Wavefunction altered** by solvent

  → Acetonitrile pulls stronger than cyclohexane

- **E vs Z**
  - Curved structure for Z

  → Larger **dipole moment** for E

- **1,4 vs 1,5**
  - **Conjugation** break
Electron-hole densities

- Electron-hole densities
- 😊 Compact graphical representation
- 😞 Still looking at blobs of colour
Charge-transfer numbers

- Excited state interpreted as a correlated **electron-hole** pair
  - Molecule divided into **fragments**

- Analysis of the **mutual** probability distribution of **electron** and **hole**
  - **Charge-transfer numbers** $\Omega_{AB}$
    - $\Omega_{AB}$ – probability of $A \rightarrow B$ charge transfer
    - $\Omega_{AA}$ – probability of local excitation on fragment $A$

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- **Automatic assignment** of state character
  - Localisation and charge transfer

- **Brightest state**: $S_1$
  - Some CT character

- **Next band**
  - TPA centred

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Dicynoanthracene

- **Dicynoanthracene** with electron donating substituents
  - Symmetric and asymmetric substitution
  - **Two-photon absorption**
- Correlated ab initio computations
  - ADC(2)

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Dicyanoanthracene

- High two-photon absorption strength for Q2 and Q3
  - Good agreement with computation
- Three states involved: $S_1$ (bright), $S_2$ (dark), $S_3$ (2P-active)
Orbitals involved

- $S_1$ (bright)
  - HOMO\(\rightarrow\)LUMO ($L_\alpha$)
- $S_2$ (dark)
  - HOMO\(-1\rightarrow\)LUMO ($L_b$)
- $S_3$ (2P-active)
  - HOMO\(-2\rightarrow\)LUMO

Selection rules
Overall comparison experiment vs theory

All observed states can be uniquely assigned

State character: strong R→Ant **charge-transfer** for 2P-active states

Importance of **CN group** (*not directly involved*)

- No strong 2P absorption for **anthraquinone analogues**
Dicyanoanthracene

1P-Wavelength (nm)

2P-Wavelength (nm)

1P-Absorption

2P-Absorption

Strong donor 😊
Asymmetric 😞

Strong donor 😊
Symmetric 😊

Weak donor 😞
Symmetric 😊


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Benzodithiophene-dione

- Synthesis of new Benzodithiophene-dione derivative (1)\(^1\)
  - D-\(\pi\)-A-\(\pi\)-D
- Target application: delayed fluorescence
- Does it work as efficiently as 2?\(^2\)

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Benzodithiophene-dione

😊 HOMO and LUMO spatially separated
→ Low singlet-triplet gap?

😢 Low photoluminescence quantum yield
First **triplet** 0.5 eV below first **singlet**

Reverse intersystem crossing unlikely

Low-energy region

→ **Local** states on BDT

→ $S_2$ - bright

→ HOMO-LUMO transition

Why

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1S. Montanaro et al., *PCCP* 2019, 21, 10580–10586.
Motivation

▸ **Singlet/triplet gaps**

→ Delayed fluorescence $\rightarrow \Delta E_{ST} \approx 0$

→ Singlet fission $\rightarrow \Delta E_{ST} \approx E_{S1}/2$

→ Spintronics $\rightarrow \Delta E_{ST} \approx E_{S1}$

⚠ Cannot be understood from orbital energies
  - HOMO/LUMO overlap
  - Anti-aromaticity
  - Unpaired electrons$^1$

❓ Can we create a unified theory

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Uracil

- Small organic molecule with different heteroatoms
  - $n\pi^*$ and $\pi\pi^*$ states

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

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### Uracil

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E$</th>
<th>$f$</th>
<th>Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^3\pi\pi^*$</td>
<td>4.07</td>
<td>-</td>
<td>0.95hl</td>
</tr>
<tr>
<td>$1^3n\pi^*$</td>
<td>4.70</td>
<td>-</td>
<td>0.85$h_2l + 0.27h_2l_1 + 0.23h_3l$</td>
</tr>
<tr>
<td>$1^1n\pi^*$</td>
<td>4.95</td>
<td>0.00</td>
<td>0.87$h_2l + 0.23h_2l_1 + 0.14h_3l$</td>
</tr>
<tr>
<td>$2^3\pi\pi^*$</td>
<td>5.68</td>
<td>-</td>
<td>0.79$h_1l - 0.41hl_1 - 0.23h_2l_2$</td>
</tr>
<tr>
<td>$1^1\pi\pi^*$</td>
<td>5.76</td>
<td>0.23</td>
<td>0.91hl</td>
</tr>
</tbody>
</table>

- Why is the HOMO-LUMO transition the lowest triplet but not the lowest singlet?
- Why is the exchange splitting between the $n\pi^*$ states lower than between the $\pi\pi^*$ states?
Uracil $1^1n\pi^*$ state

- Weak $\langle \rho_t | \hat{V} | \rho_t \rangle$ term $\rightarrow$ weak exchange splitting
- ESPs of $\rho_h$ and $\rho_e$ are very uniform $\rightarrow$ small effect
Uracil $1^1\pi\pi^*$ state

- Stronger $\langle\rho_t|\hat{V}|\rho_t\rangle$ term $\rightarrow$ stronger exchange splitting
  - Enhanced transition dipole moment $\vec{\mu}_t$
  - Small adjustment of $\rho_e$
Uracil $1^3\pi\pi^*$ state

- Electron NTO
- Hole NTO
- ESP of $\rho_t$
- ESP of $\rho_e$
- ESP of $\rho_h$

- “Cleaner” transition spin-density
- $\langle \rho_t | \hat{V} | \rho_t \rangle$ term and transition moment would be even stronger
### Uracil

| State     | $\Delta E$ | f  | Configurations                                      | $\langle \rho_t | \hat{V} | \rho_t \rangle$ |
|-----------|------------|----|-----------------------------------------------------|---------------------|
| $1^3\pi\pi^*$ | 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 $L_\alpha$ state
Anthracene

- Anthracene
- HOMO/LUMO picture vs full description
- $\sigma$-polarisation
  - Reduced transition moment and ESP

⚠️ Only full description consistent with experiment

\[\text{Transition density} \quad \text{ESP} \]

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<thead>
<tr>
<th>HOMO/LUMO</th>
<th>ESP</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="HOMO/LUMO" /></td>
<td><img src="image2.png" alt="ESP" /></td>
</tr>
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<thead>
<tr>
<th>Full - ADC(2)</th>
<th>Experimental</th>
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<tbody>
<tr>
<td><img src="image3.png" alt="Full - ADC(2)" /></td>
<td><img src="image4.png" alt="Experimental" /></td>
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</table>

\[1\] P. Kimber, F. Plasser, *PCCP* 2020, DOI: 10.1039/D0CP00369G.
Methodological implications

⚠ Ionic states cause problems for CASSCF

→ Energies overestimated by $> 1$ eV
  - M. Boggio-Pasqua, M. J. Bearpark et al., *JCP* 2004, 120, 7849.

→ Dynamic $\sigma$ polarisation effects

⚠ Relation to transition density

⚠ Ionic states behave like hidden charge-transfer states with TDDFT

→ Energies too low
Conjugated Polymers

- Excited states of conjugated polymers
  - Many electronic configurations

? Can we **visualise** the ensuing **electron correlation** effects

→ Conditional electron densities

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\(^1\)FP, *ChemPhotoChem* 2019, 3, 702.
Conditional densities

Conditional density for the excited electron

\[ \rho_e^{h:A}(r_e) = \int_A \gamma^{0I}(r_h, r_e)^2 dr_h \]

\( \gamma^{0I}(r_h, r_e) \)  Transition density matrix in real space
\( \rho_e^{h:A}(r_e) \)  Conditional electron density for the hole localized on fragment \( A \)

- Real-space version of charge-transfer numbers
- Evaluated through multiplication of matrix blocks

\[ 1 \text{FP, ChemPhotoChem 2019, 3, 702.} \]

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Oligothiophene

- Prototypical conjugated polymer

CAM-B3LYP computations
Oligothiophene

- $S_1$ state
- Overall hole and electron densities
Oligothiophene

- $S_1$ state
- Conditional densities
Oligothiophene

- $S_2$ state
- Overall hole and electron densities
Oligothiophene

- $S_2$ state
  - Conditional densities
Oligothiophene

- $S_3$ state
- Overall hole and electron densities
Oligothiophene

▶ $S_3$ state
- Conditional densities
Oligothiophene

- $S_4$ state
- Overall hole and electron densities
Oligothiophene

- $S_4$ state
- Conditional densities
Oligothiophene

- $S_5$ state
  - Overall hole and electron densities
Oligothiophene

- $S_5$ state
- Conditional densities
Conclusions

- Push-pull systems
  → Detailed insight into experimentally observed properties

- Singlet/triplet gaps

- New design principles

- Conjugated polymers
  → Visualisation of electron correlation
Extended *wavefunction analysis toolbox*.

**TheoDORE** - *Theoretical Density, Orbital Relaxation and Exciton 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 library²

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

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