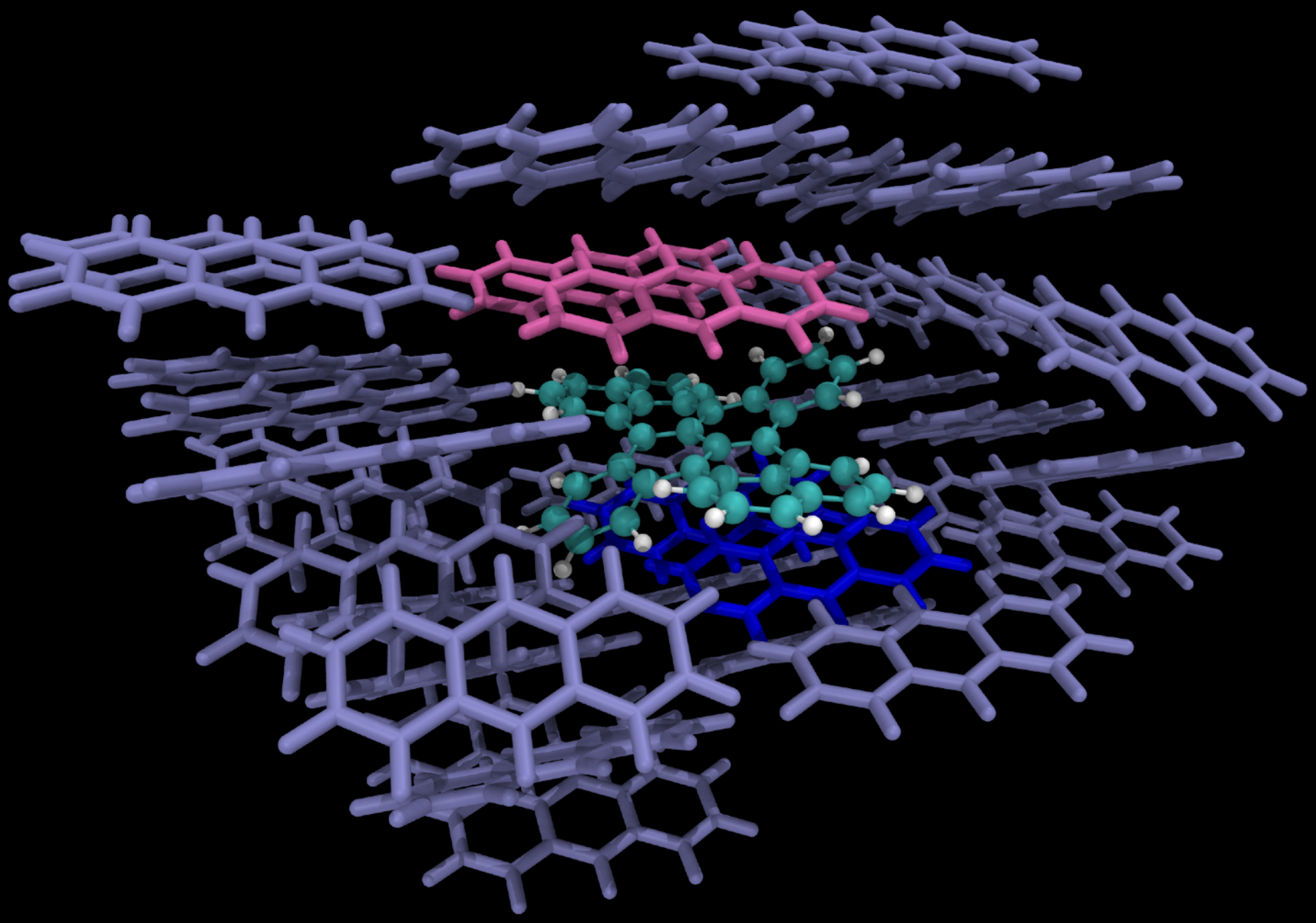
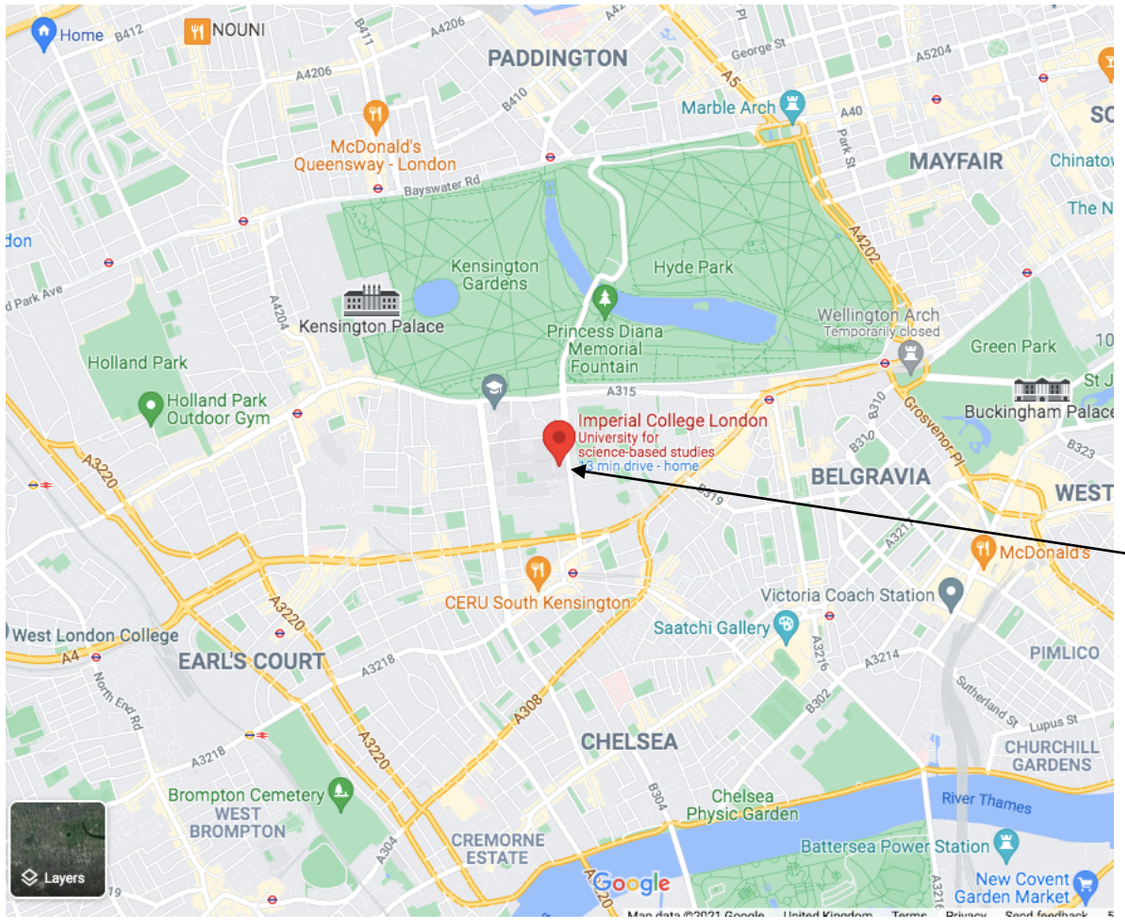
Towards the robust treatment of excitations in supramolecular systems



exciting NEWS 2021

Martina Stella, 21/06/2021



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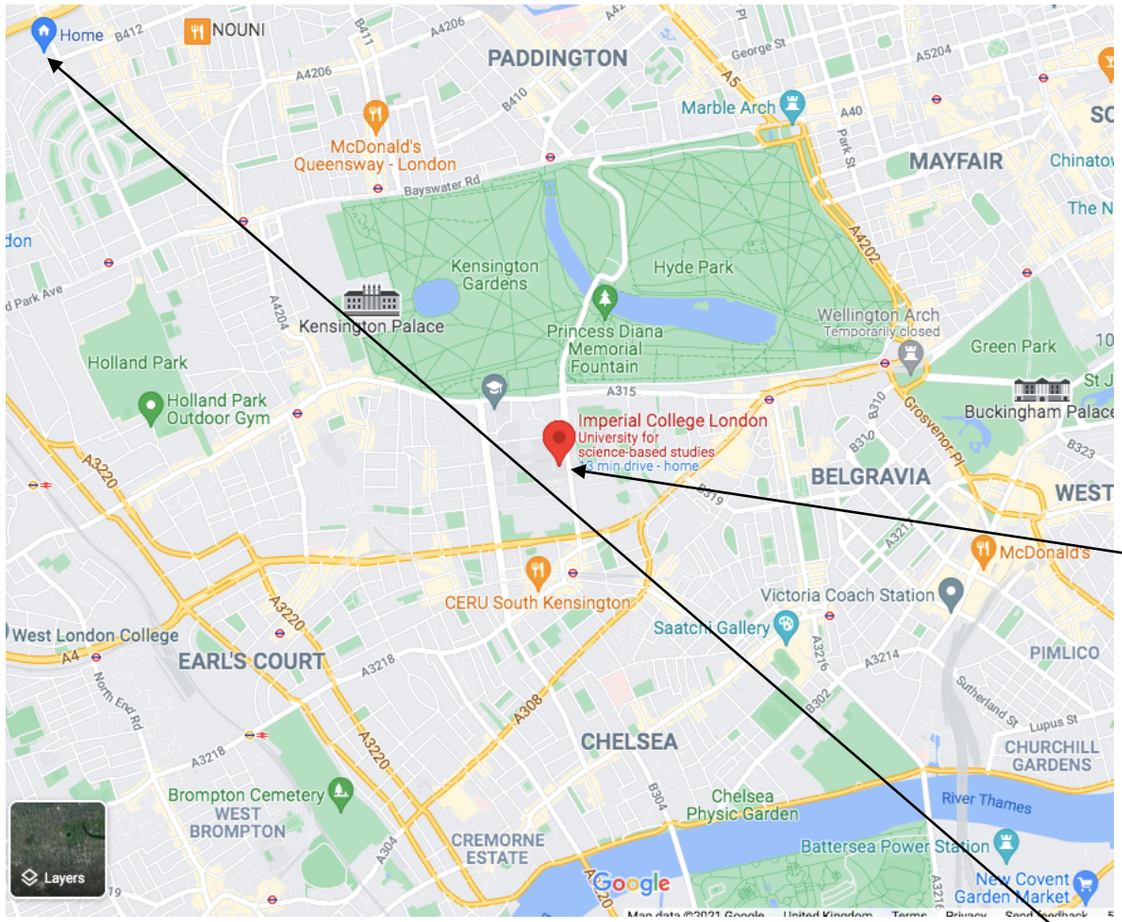
Where I formally work



Royal School of Mines
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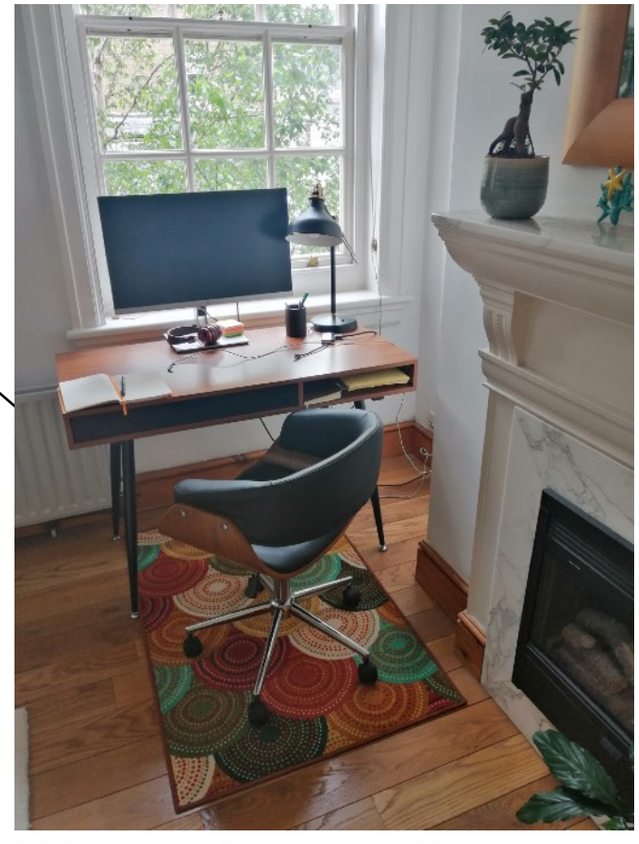

Where I actually work

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Outline

Introduction:

- Classification of excitations in molecular systems (CT vs Local)
- DFT-based methods for modelling excitations

Main Body:

- Principles of linear scaling DFT
- Transition constrained DFT (T-CDFT) in the BigDFT code:
- OLEDs and acene molecules: method comparison

Future work:

- Fragment calculations in the BigDFT code
- Towards the robust simulation of supramolecular systems with T-CDFT

Excited states in molecular systems

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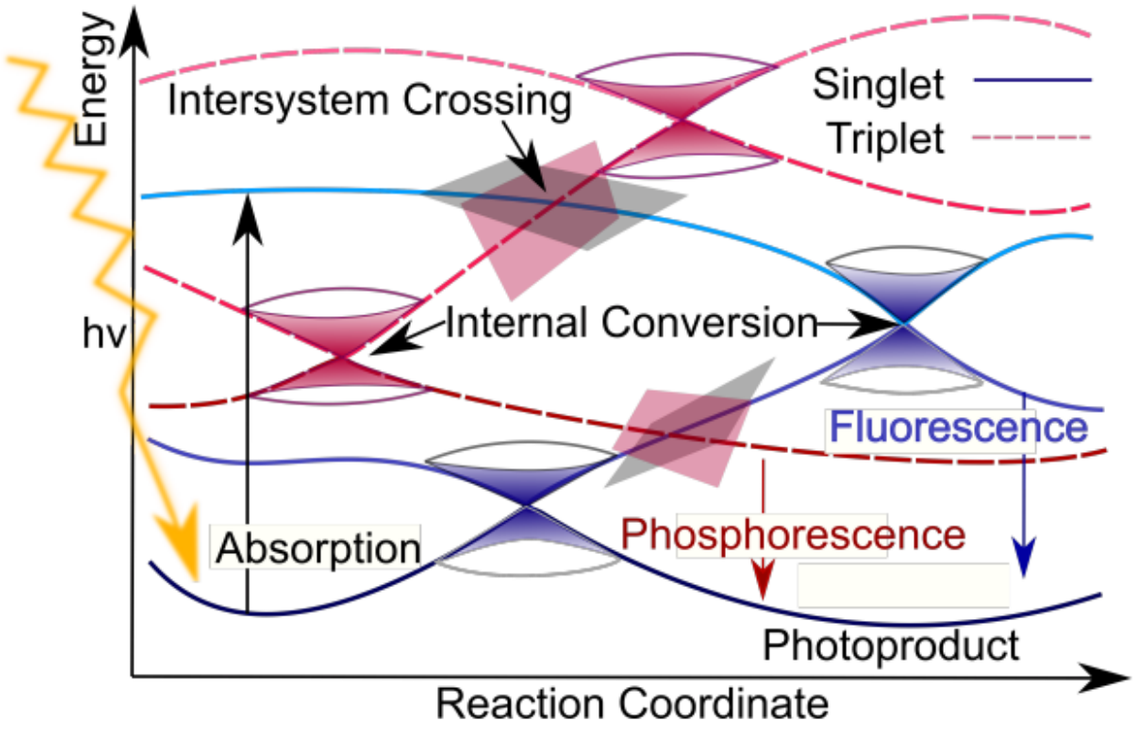
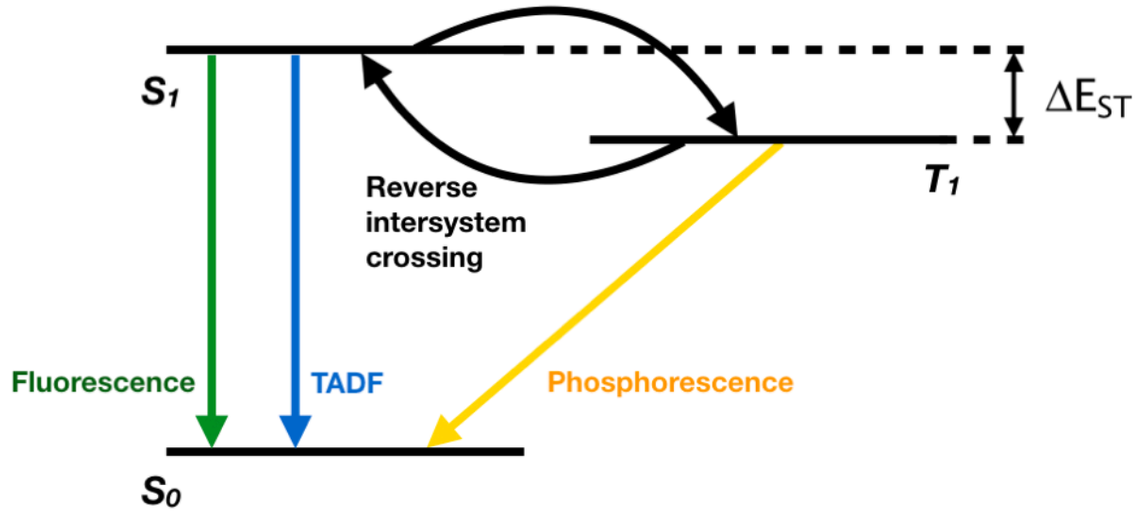
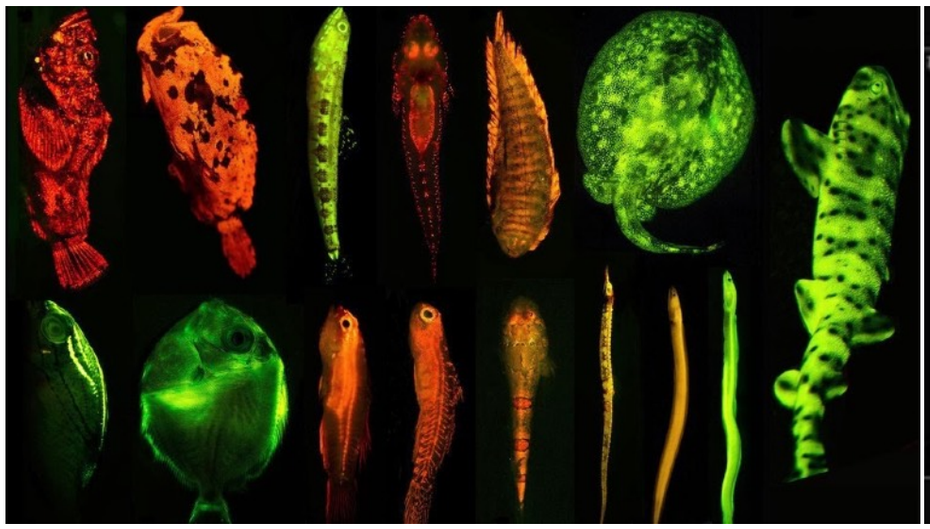
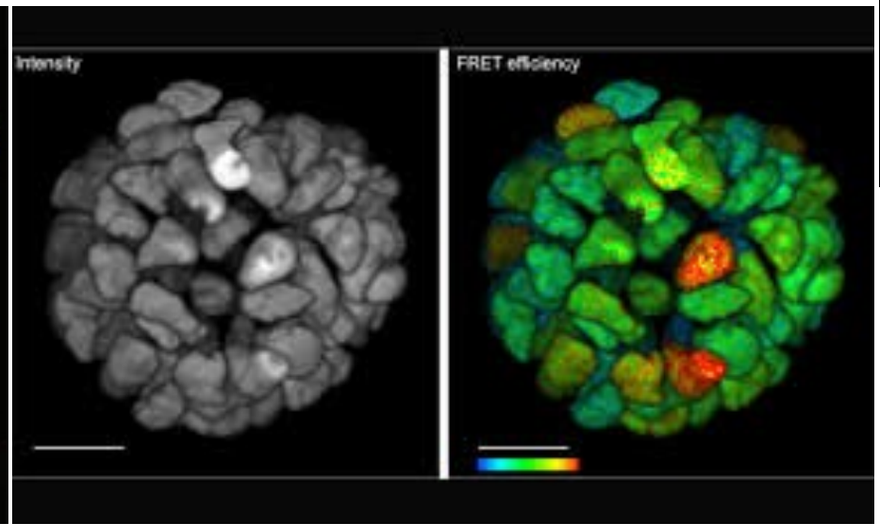




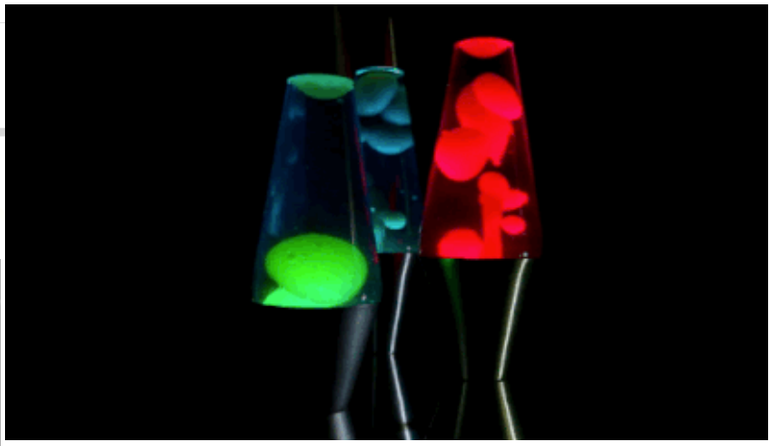


Bioluminescent fish

Julia Westermayr et al. 2020



Bio applications



Design

Excited states in molecular systems

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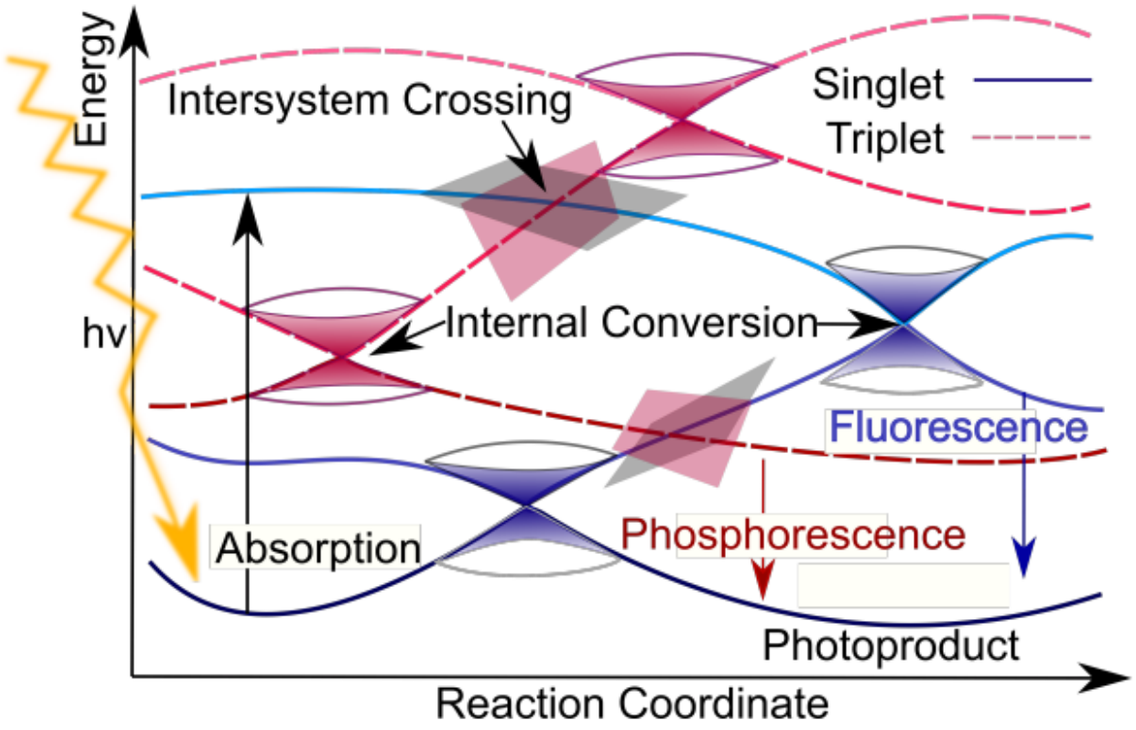
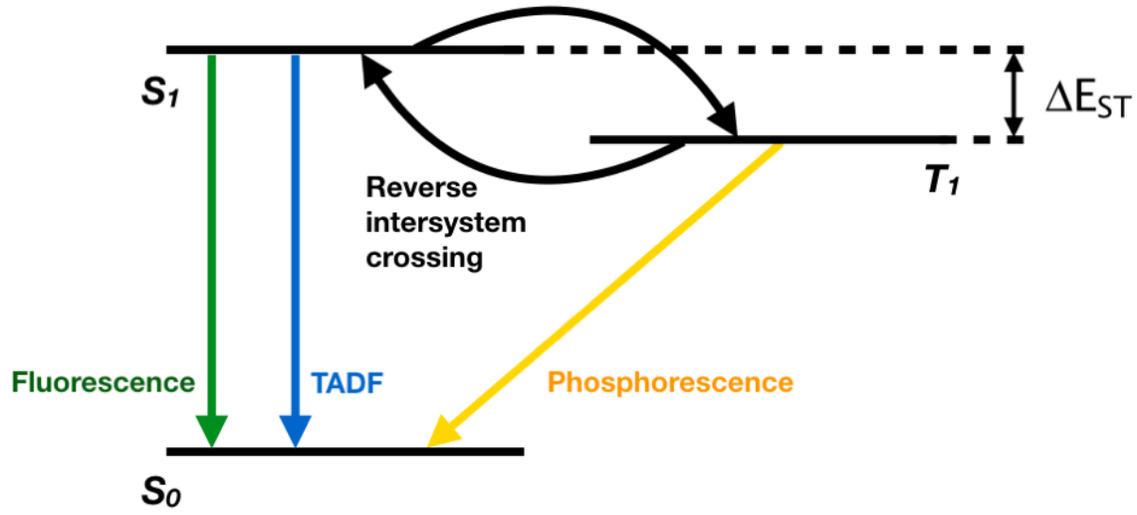
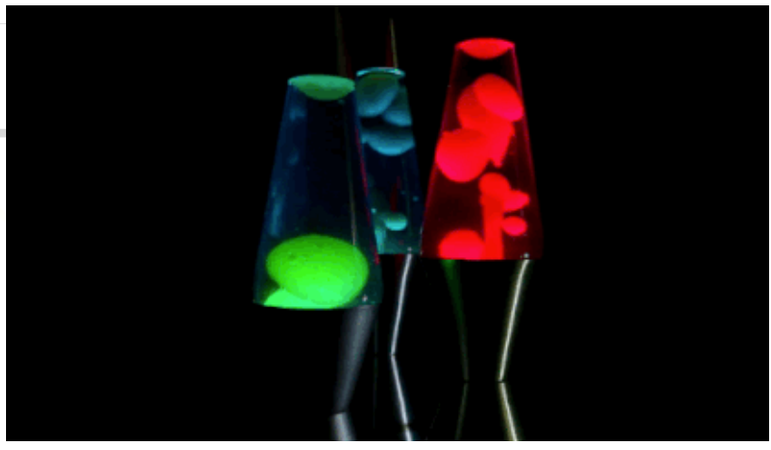




OLED

Technological applications



Design

Julia Westermayr et al. 2020 , Image: Samsung Display, https://www.oled-info.com/flexible-oled

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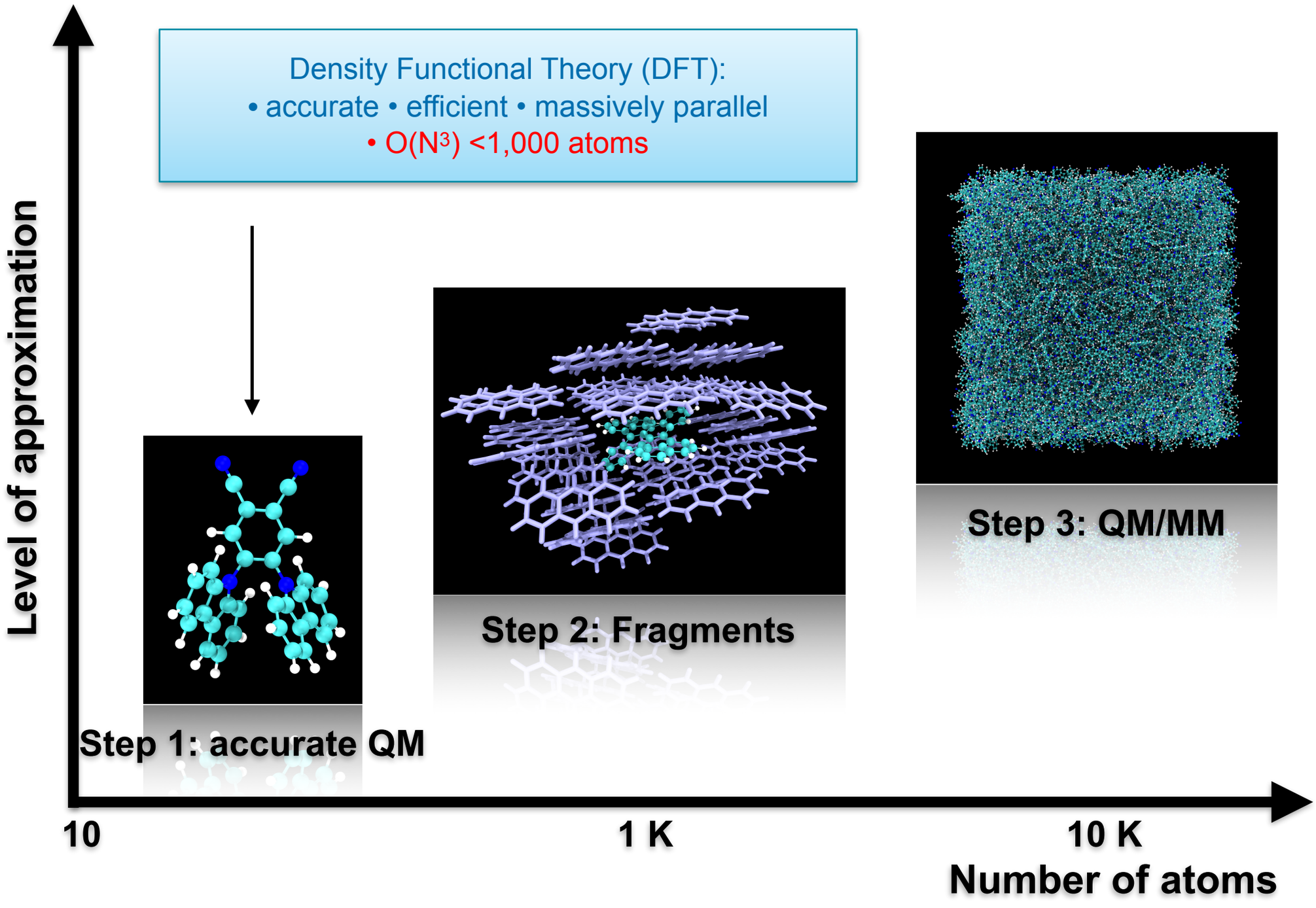
The challenge - First principle simulation of systems of realistic sizes (e.g Organic Light Emitting Diode -OLED- materials): large, complex and disordered; **while -** developing computational tools for performing an analysis of excitations as a workflow



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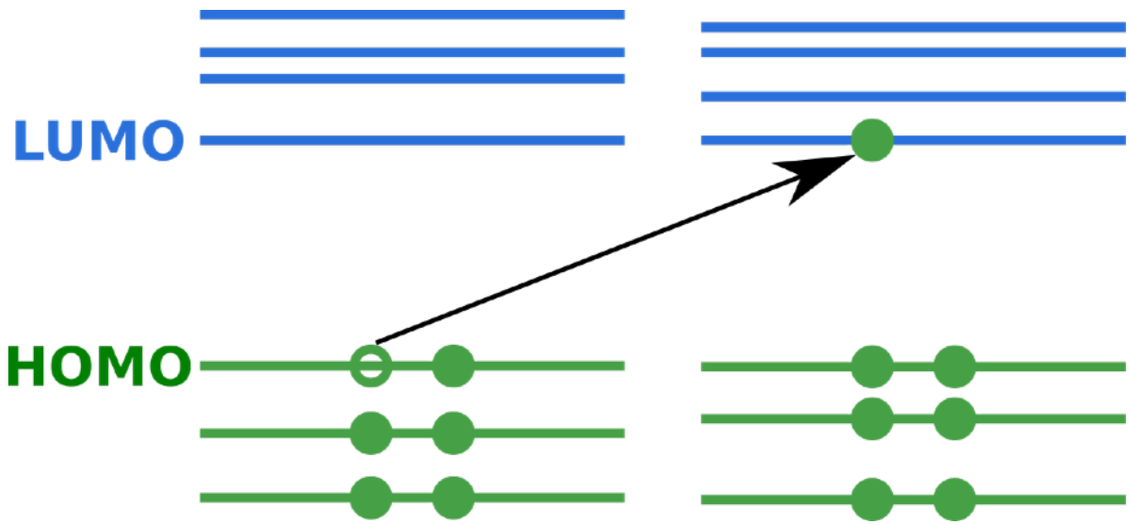
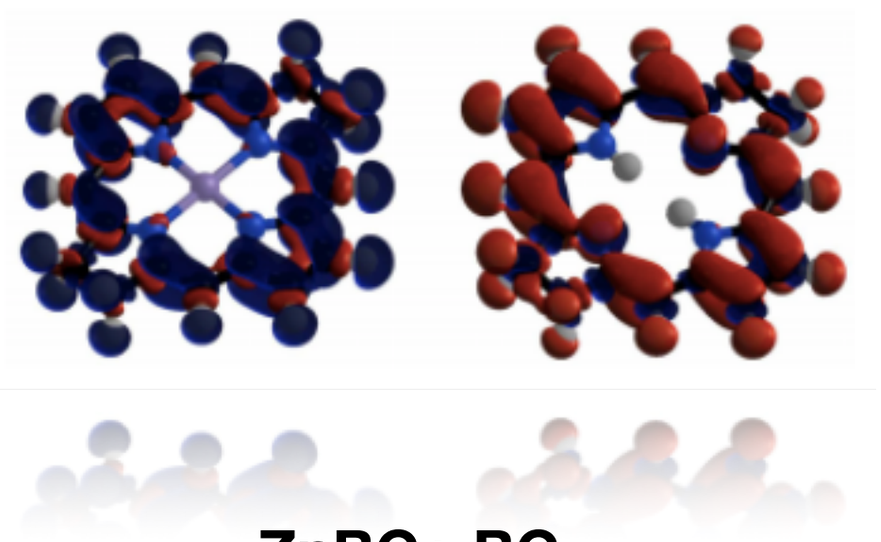
Excitations classification:
Charge Transfer vs Local Excitations

CT excitation

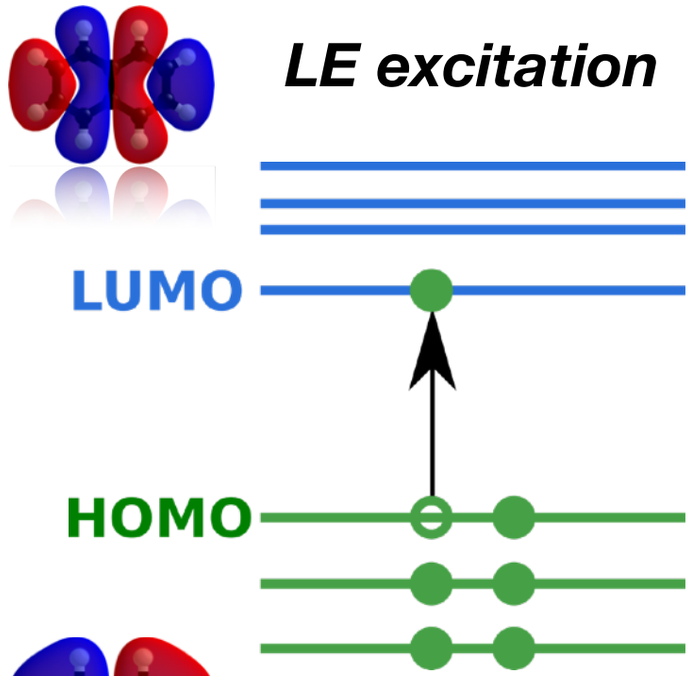


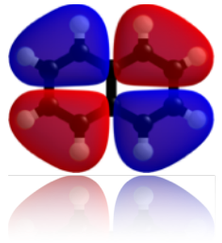
A **B**



ZnBC+ BC-

LE excitation





Napth.

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Methods for modelling excited states:

- **Δ-SCF**
- **TD-DFT (Linear-response theory approach)**
- **CDFT (Constrained DFT)**

Δ-SCF

Excitation energy is given by : $\Delta E_{SCF} = E_n - E_0$

Simplest formalism
Imposition of KS occupancy while self-consistency is reached
Affordable computational costs
Versatile formalism: RKS, UKS, RHF, UHF, ROKS

Geared towards energy minimisation
Possible spin contamination
Occasional convergence instabilities

Methods for modelling excited states:

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- Δ-SCF
- **TD-DFT (Linear-response theory approach)**
- CDFT (Constrained DFT)

TD-DFT

DFT	TD-DFT
Ground state	Excited state
Hohenberg-Kohn theorem	*Runge-Gross* theorem
Minimal of total energy	Stationary point of the action
Stationary orbitals	Time-dependent orbitals
Stationary density	Time-dependent density

HK 1: There is a one-to-one correspondence between any external potential on the system and the resulting electron density (up to a constant).

RG 1: There is a one-to-one correspondence between any time-dependent external potential on the system and the resulting time-dependent density (up to a time-dependent constant).

Methods for modelling excited states:

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- Δ-SCF
- **TD-DFT (Linear-response theory approach)**
- CDFT (Constrained DFT)

TD-DFT

DFT	TD-DFT
Ground state	Excited state
Hohenberg-Kohn theorem	*Runge-Gross* theorem
Minimal of total energy	Stationary point of the action
Stationary orbitals	Time-dependent orbitals
Stationary density	Time-dependent density

Excitation energies can be extracted within the Linear-Response TDDFT where a small td-perturbation is added to the system Hamiltonian

Methods for modelling excited states:

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- Δ-SCF
- **TD-DFT (Linear-response theory approach)**
- CDFT (Constrained DFT)

TD-DFT

It includes dynamic screening
Good agreement with experimental values
Correctly model local excitations in molecules
Cheaper than sophisticated post-Hartree-Fock methods

Unknown exchange-correlation functional
Problems with modelling charge-transfer states
Still too expansive for large systems in standard cubic scaling formalism
...

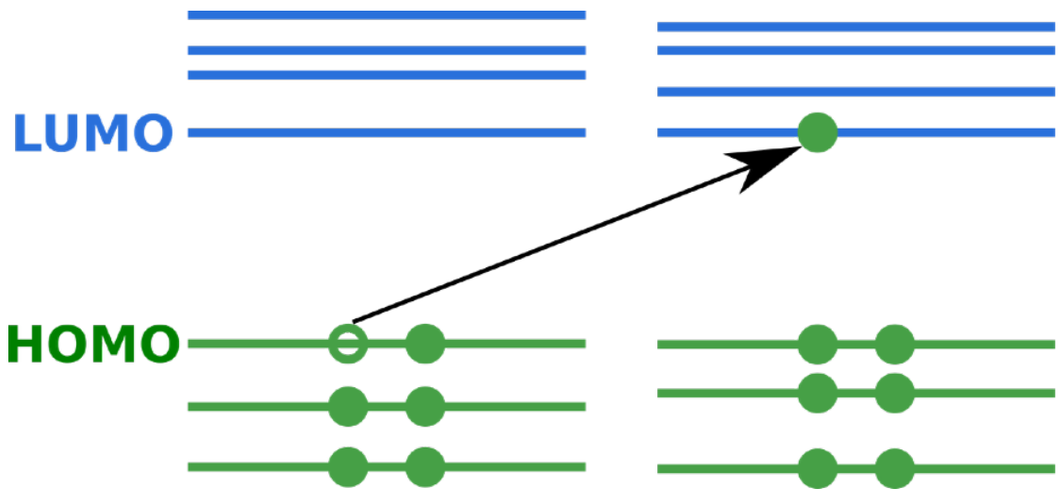
Methods for modelling excited states:

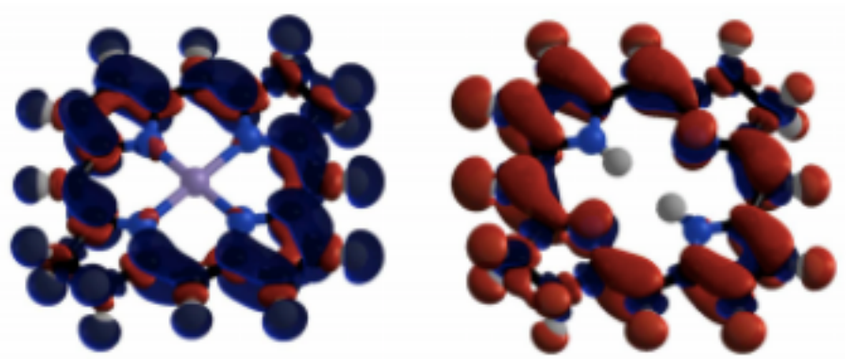
- **Δ-SCF**
- **TD-DFT (Linear-response theory approach)**
- **CDFT (Constrained DFT)**

CDFT

In **CDFT** we find the **lowest energy state** satisfying a given (charge) constraint on the density

- One associates a charge with a particular **fragment** (in space)





ZnBC+ BC-

Methods for modelling excited states:

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- Δ-SCF
- TD-DFT (Linear-response theory approach)
- **CDFT (Constrained DFT)**

CDFT

It can accurately model charge transfer excitations
Formalism is straightforward
Computational cost is comparable to cubic scaling DFT

In its standard implementation fails to model local excitations

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Outline

Introduction:

- Excitations in molecules
- DFT-based methods for modelling excitations

Take-home:
excit. type: CT vs LE
TDDFT: good for LE, not so good for CT, expensive
CDFT: good for CT, not so good for LE, cheap

Main Body:

- Principles of linear scaling DFT
- Transition constrained DFT (T-CDFT) in the BigDFT code:
- OLEDs and acene molecules: method comparison

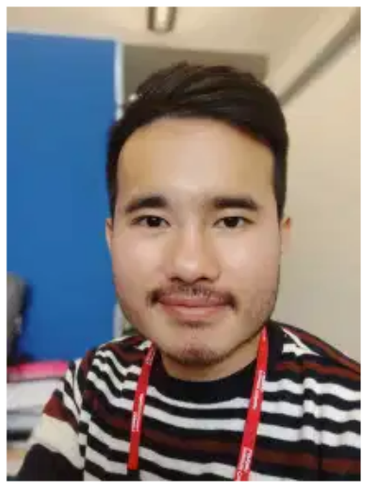
Future work:

- Fragment calculations in the BigDFT code
- Towards the robust simulation of supramolecular systems with T-CDFT

Acknowledgments

Dr. Laura Ratcliff

Mr. Kritam Thapa



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London, UK

Dr. Luigi Genovese

Grenoble, France

Materials and Molecular Modelling Hub

archer

EPSRC Pioneering research and skills

The Thomas Young Centre

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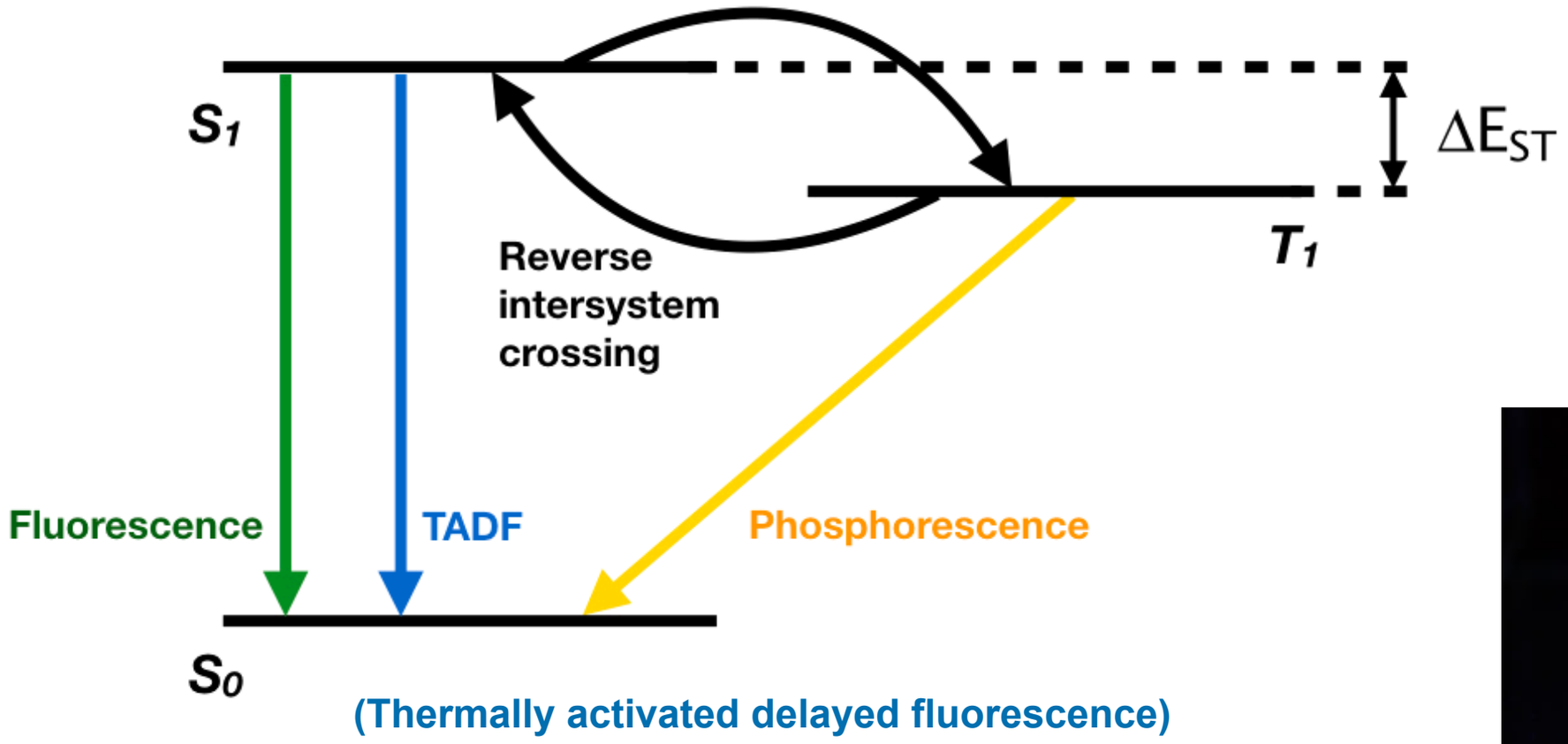
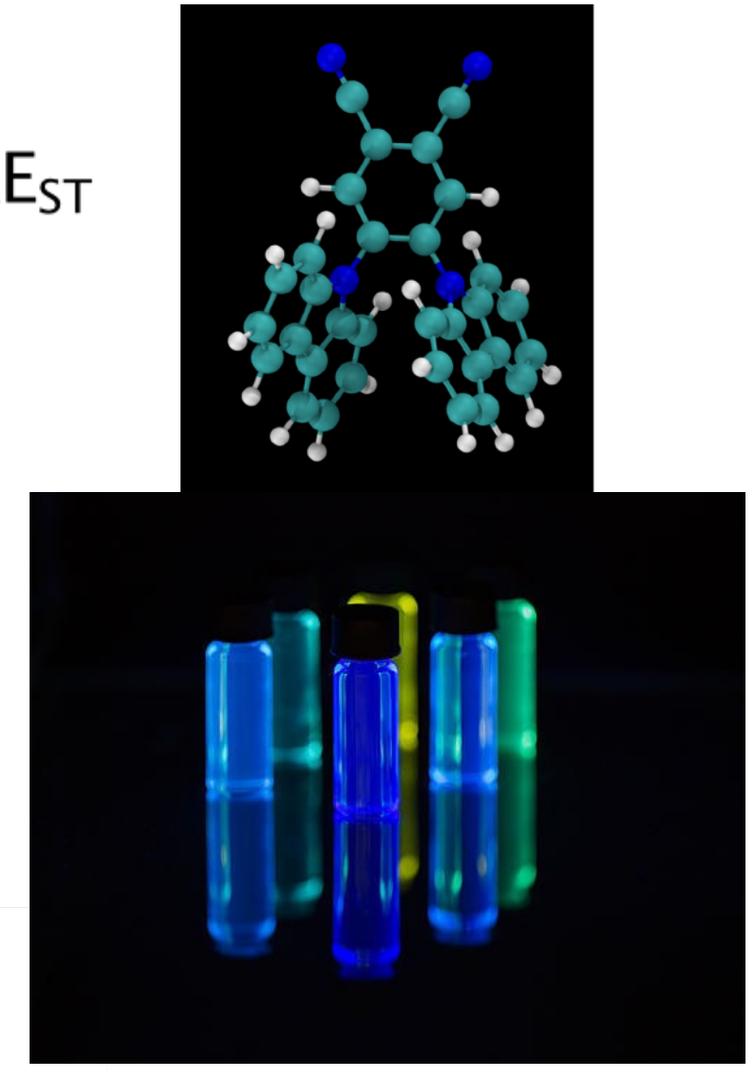
Case study: TADF

2CzPN





Thermally activated delayed fluorescence (TADF) represents a promising mechanism for the design of the next generation of OLEDs: **cheaper** and **environmentally less harmful** than previous generation

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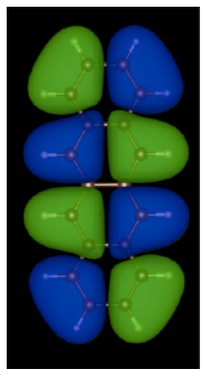
Excitations classification:
A simple descriptor, Λ_T

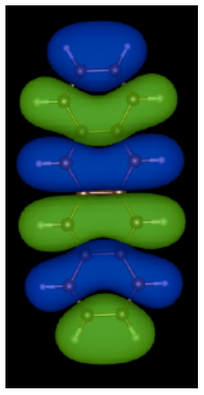
Spatial overlap between HOMO and LUMO: $\Lambda_{\mathrm{T}} = \int |\psi_H(\mathbf{r})|\,|\psi_L(\mathbf{r})|\ \mathrm{d}\mathbf{r}$

Tetracene

HOMO



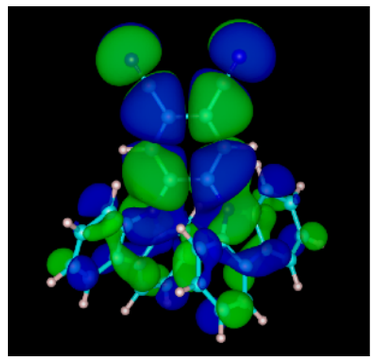
LUMO



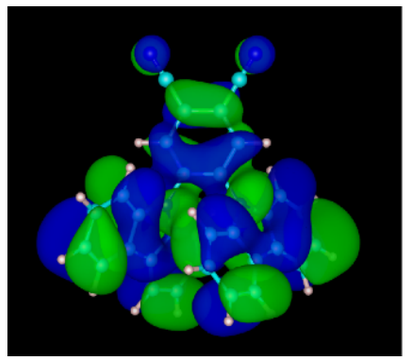
Λ_T = ~ 1.00

2CzPN

HOMO



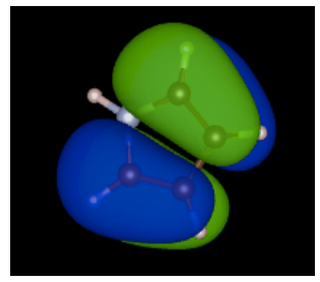
LUMO



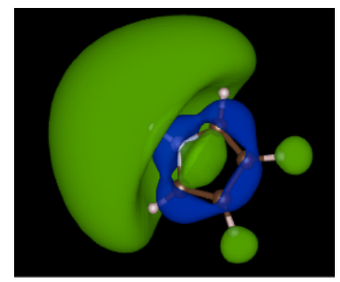
Λ_T = ~ 0.5

Pyrrole

HOMO



LUMO



Λ_T = ~ 0.2

mix of LE and CT

large overlap between hole-elec = LE

small overlap between hole-elec = CT

Transition-based Constrained DFT (T-DFT)

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In T-CDFT, instead of imposing a spatial constrain, we impose a specific orbital transition, e.g. HOMO — LUMO

Transition operator:

$$\hat{T}_a \equiv \frac{1}{2}\left(\hat{E}_a + \hat{E}_a^t\right) = \sum_p \frac{1}{2}\left(|w_p^a\rangle\langle\psi_p| + |\psi_p\rangle\langle w_p^a|\right)$$

unocc occ

Excitation energy:

$$E^{(a)}_{\mathrm{T-CDFT}} \equiv E[\rho]\Big|_{\mathrm{tr}\left(\hat{\rho}\hat{T}_a\right)=1} - E[\rho_0]$$

- The density matrix operator is constrained such as to include the transitions
- This may involve only one occupied orbital, e.g. the HOMO, or it may involve a mixture of several orbitals (pure or mixed)

(1) M Stella, K Thapa, L Genovese, LE Ratcliff, JCTC, submitted, 2021.

The BigDFT suite: DFT with *wavelets*

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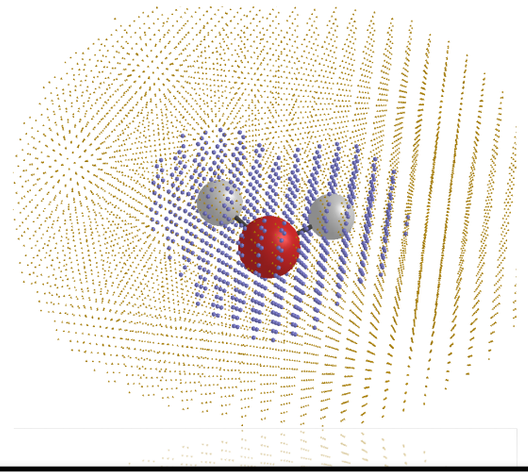
Daubechies wavelets basis set:

- systematic • orthogonal • localised • adaptive
- analytic operators

BigDFT:

• real space based • flexible • many functionalities (*O*(*N*) calculations,LR-TDDFT) • open source • efficient Poisson solver • free, wire, surface and periodic b.c.'s • hybrid MPI/OpenMP • GPU ported



adaptivity: the grid is divided into low and high resolution points

BigDFT

The BigDFT suite: DFT with *wavelets*

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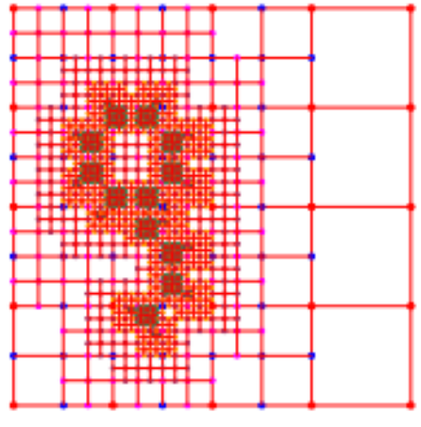
BigDFT

Wavelets

A basis with optimal properties for expanding localised information



- Localised in real space
- Smooth (localised in Fourier space)
- Orthogonal basis
- Multi-resolution basis
- Adaptive
- Systematic

From early 80's

Applied in several domains

Interesting properties for DFT

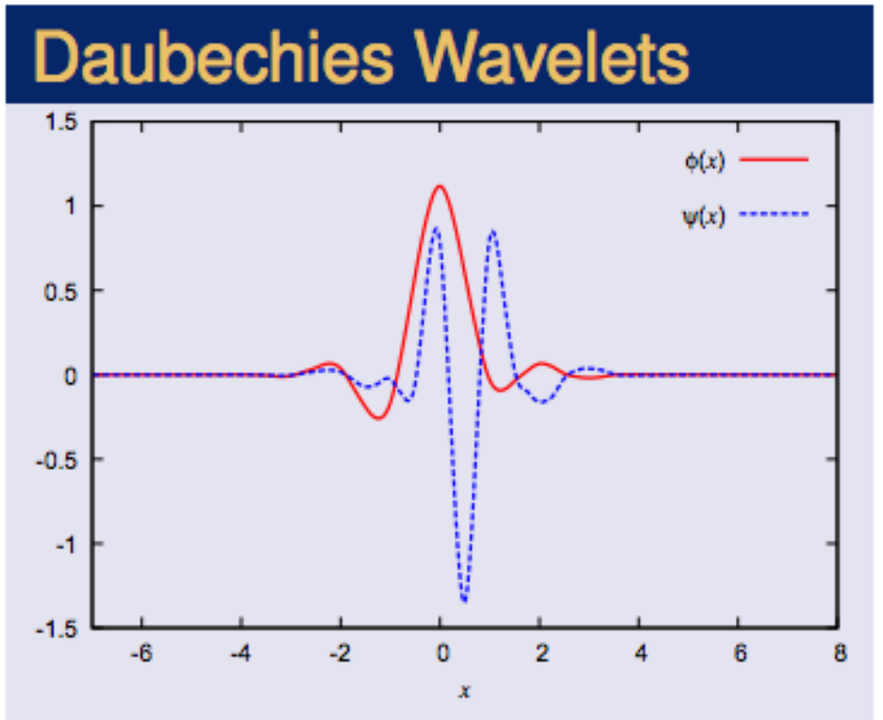


Image from: Motivations for BigDFT formalism: overview of Daubechies wavelets in DFT - *Thierry Deutsch*

The BigDFT suite: DFT with *wavelets*

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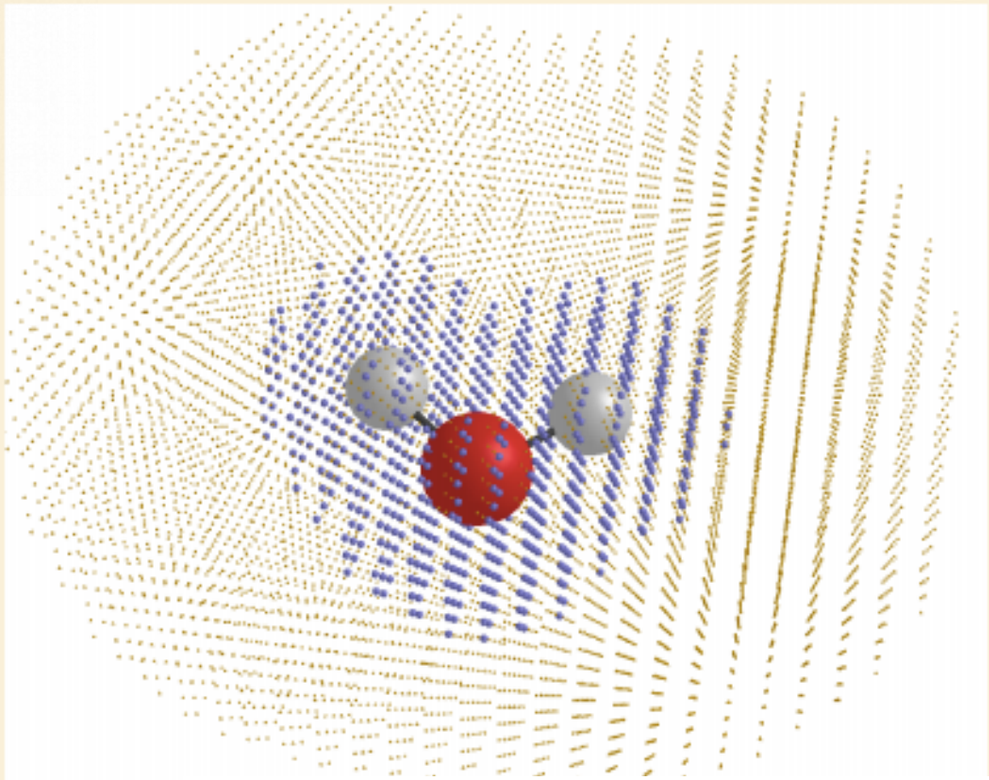
BigDFT

Adaptivity

Resolution can be refined following the grid point.



The grid is divided in Low (1 DoF) and High (8 DoF) resolution points.
Points of different resolution belong to the same grid.
Empty regions must not be "filled" with basis functions.

Nearsightedness

- the behaviour of large systems is short-ranged (nearsighted)
- the density matrix, $\rho(\mathbf{r}, \mathbf{r}')$, decays exponentially in systems with a gap

$\rightarrow$ how can we exploit nearsightedness to treat large systems?

Image from: Motivations for BigDFT formalism: overview of Daubechies wavelets in DFT - *Thierry Deutsch*

The BigDFT suite: linear-scaling formalism (1)

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BigDFT

Support Functions (SFs)

write KS orbitals as linear combinations of SFs $\phi_\alpha(\mathbf{r})$:

$$\Psi_i(\mathbf{r}) = \sum_\alpha c_i^\alpha \phi_\alpha(\mathbf{r})$$

- localized ($\sim 6-8$ a_0 radius)
- atom-centred
- minimal – 1 SF per H, 4 per C/N/O…
- numerical functions – expanded in wavelets
- quasi-orthogonal
- Γ-point only – real

Density Kernel (K)

define the density matrix ρ:

$$\rho(\mathbf{r},\mathbf{r}') = \sum_i f_i \left|\Psi_i(\mathbf{r})\right\rangle\left\langle\Psi_i(\mathbf{r}')\right| = \sum_{\alpha,\beta} \left|\phi_\alpha(\mathbf{r})\right\rangle K^{\alpha\beta}\left\langle\phi_\beta(\mathbf{r}')\right|$$

$$H_{\alpha\beta} = \langle\phi_\alpha|\hat{H}|\phi_\beta\rangle; \qquad S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$$

$$E = \mathrm{Tr}(\mathbf{KH}); \qquad N = \mathrm{Tr}(\mathbf{KS})$$

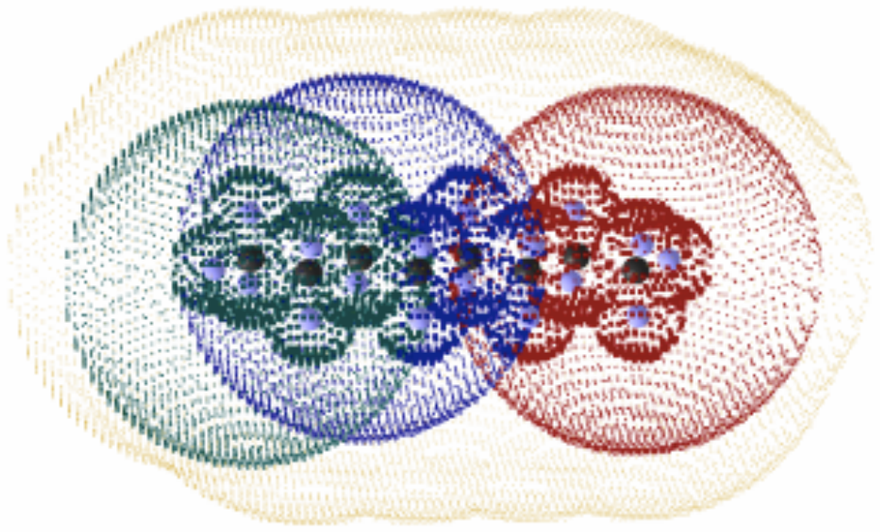

Image from: Approach to Large Scale Systems with BigDFT: from Ground State to electronic excitations - *Laura Ratcliff*

The BigDFT suite: linear-scaling formalism (2): The algorithm

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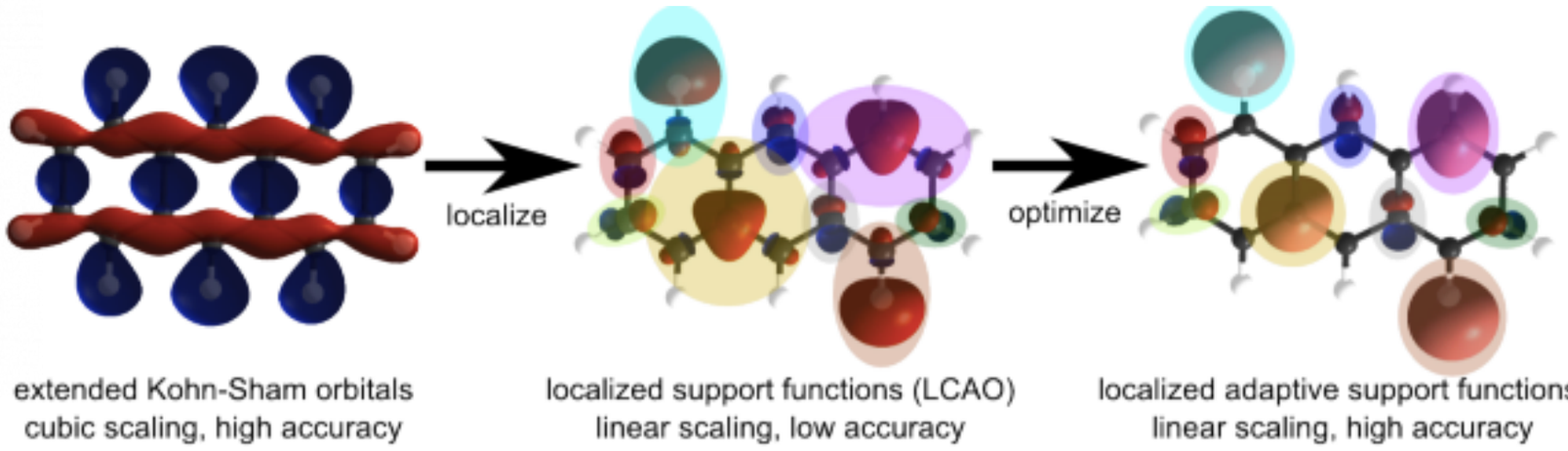
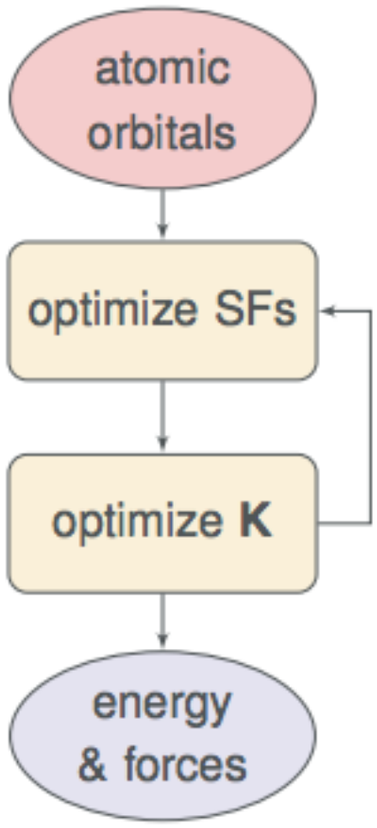
BigDFT





Accurate Minimal Basis:

- Minimize energy wrt both SFs and kernel (subject to constraints)
- SFs adapt to the environment – minimal, localized basis with wavelet accuracy
- 3 methods for K – Fermi Operator Expansion for O (N), direct minimization (virtual states), diagonalization
- Forces – geometry optimizations, MD

Image from: Approach to Large Scale Systems with BigDFT: from Ground State to electronic excitations - *Laura Ratcliff*

Gas Phase benchmark: OLEDs and acenes

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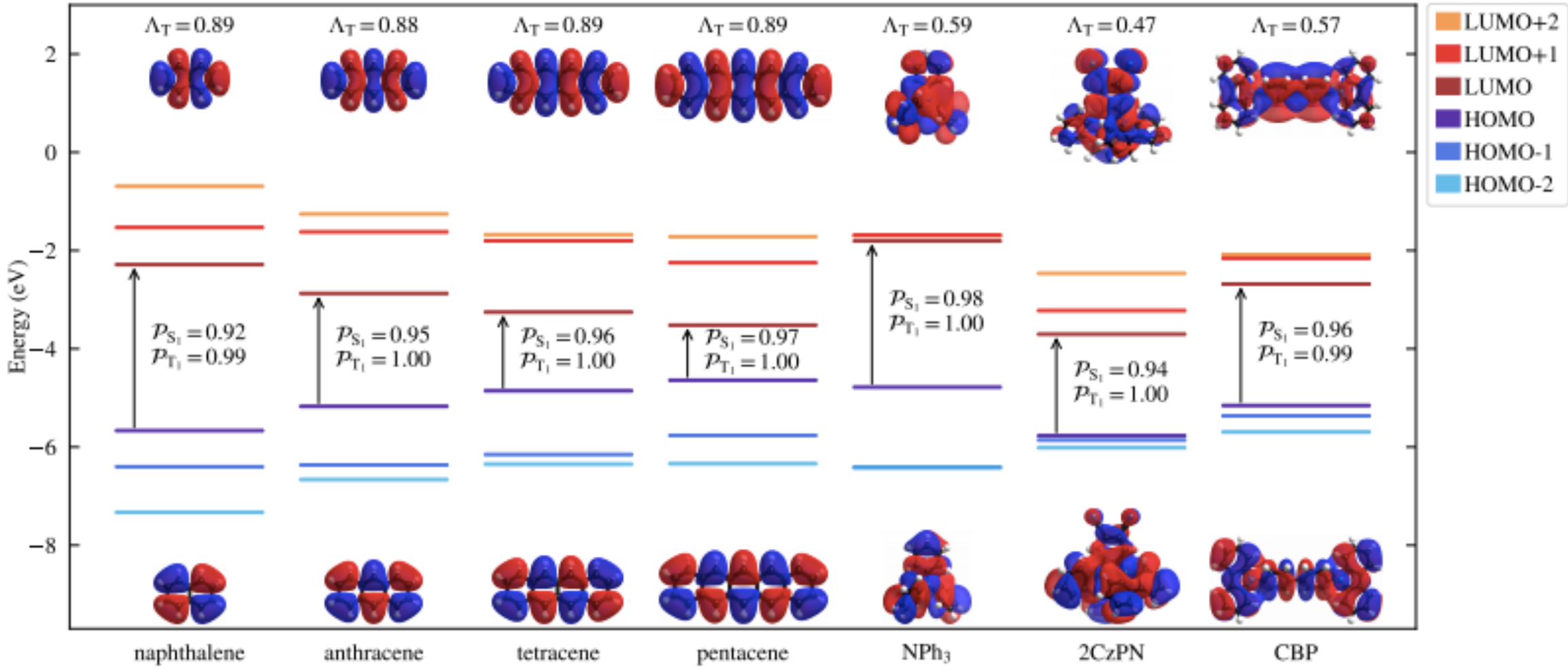
Homo-Lumo orbitals and excitation character



LDA, cc-pVTZ with NWCHEM

(1) image from M Stella, K Thapa, L Genovese, LE Ratcliff, JCTC, submitted, 2021.

Gas Phase benchmark: OLEDs and acenes

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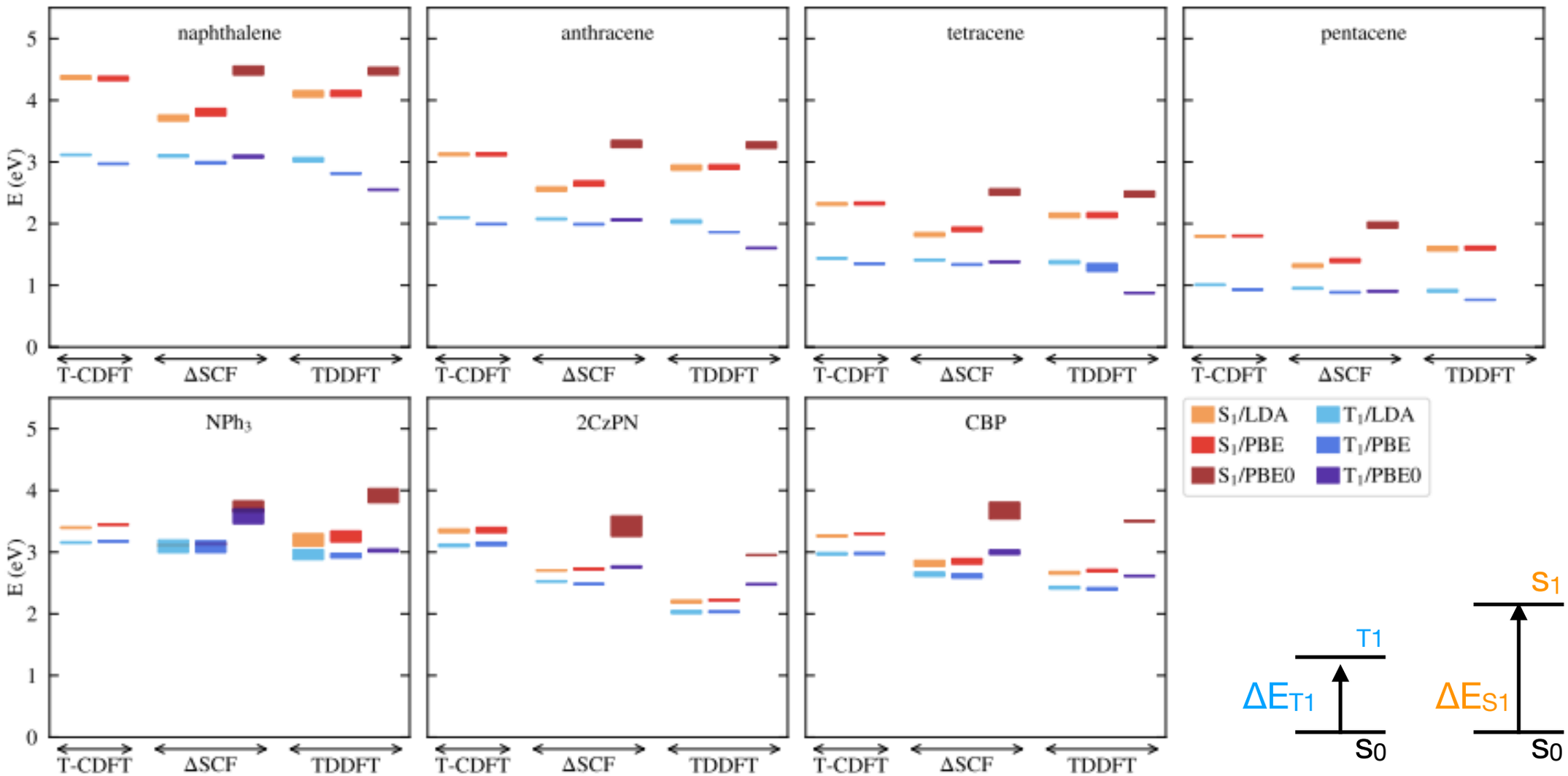
Energy splittings



Vertical S1 and T1 energies computed using different methods (T-CDFT, ΔSCF, TDDFT), basis sets (6-31G*, cc-pVTZ, wavelets) and functionals (LDA, PBE, PBE0) using BigDFT and NWChem. The T-CDFT results are those for the largest considered basis, for the SF case with 4/9/9 SFs per H/C/N atom and Rloc = 4.76 Å

(1) image from M Stella, K Thapa, L Genovese, LE Ratcliff, JCTC, submitted, 2021.

Gas Phase benchmark: OLEDs and acenes

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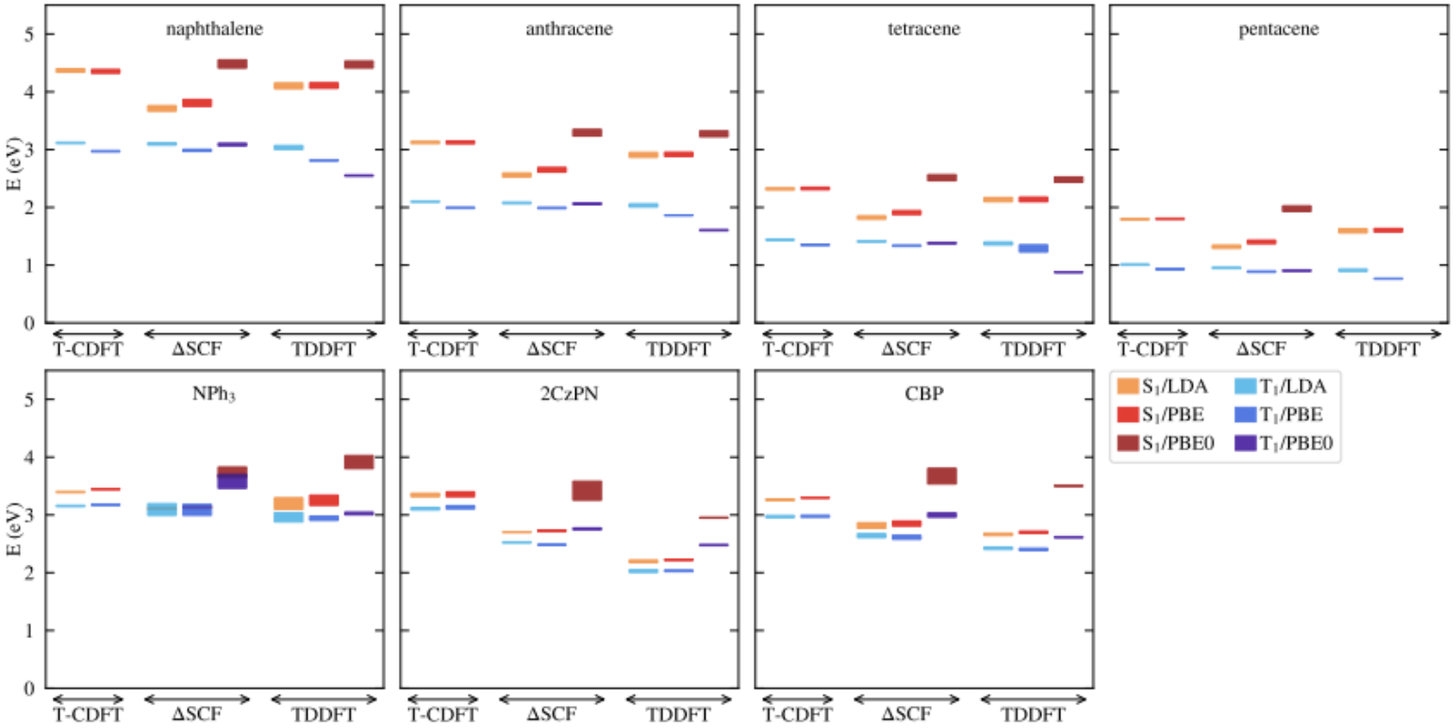

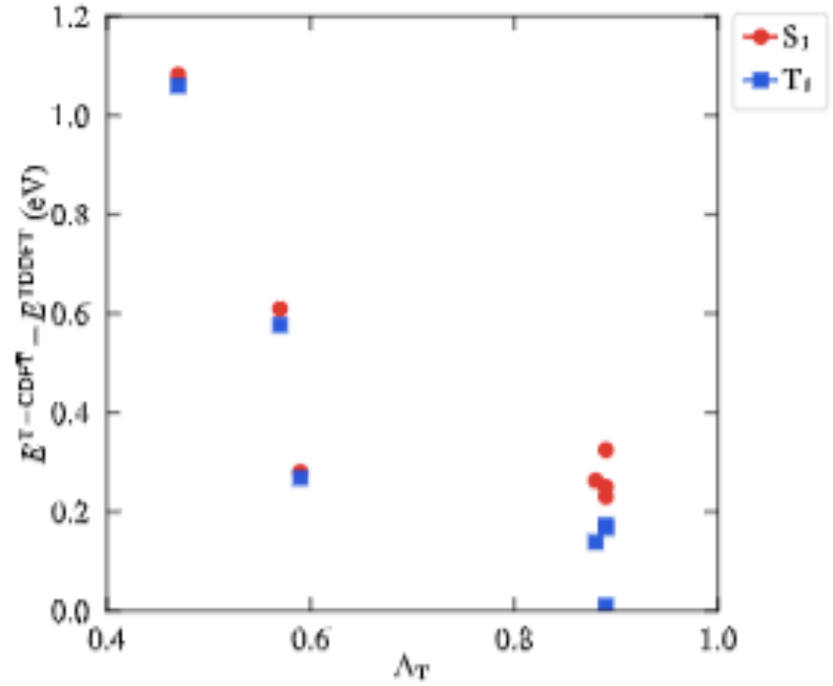

Take home messages are:

- T-CDFT performs well with predominately local excitations (acenes)
- **T-CDFT results from semi-local functionals are comparable to hybrid functional ones with TDDFT and Delta SCF.**
- For OLEDs results are a little more fluctuating
- In OLEDs TDDFT underestimates triplet in highly CT states
- **T-CDFT is found to be robust with respect to the nature of the excitations**

What about ΔE_{ST}?

(1) images from M Stella, K Thapa, L Genovese, LE Ratcliff, JCTC, submitted, 2021.

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Outline

Introduction:

- Excitations in molecules
- DFT-based methods for modelling excitations

Take-home:
excit. type: CT vs LE
TDDFT: good for LE, not so good for CT, expensive
CDFT: good for CT, not so good for LE, cheap

Main Body:

- Principles of linear scaling DFT
- Transition constrained DFT (T-CDFT) in the BigDFT code:
- OLEDs and acene molecules: method comparison

Future work:

- Fragment calculations in the BigDFT code
- Towards the robust simulation of supramolecular systems with T-CDFT

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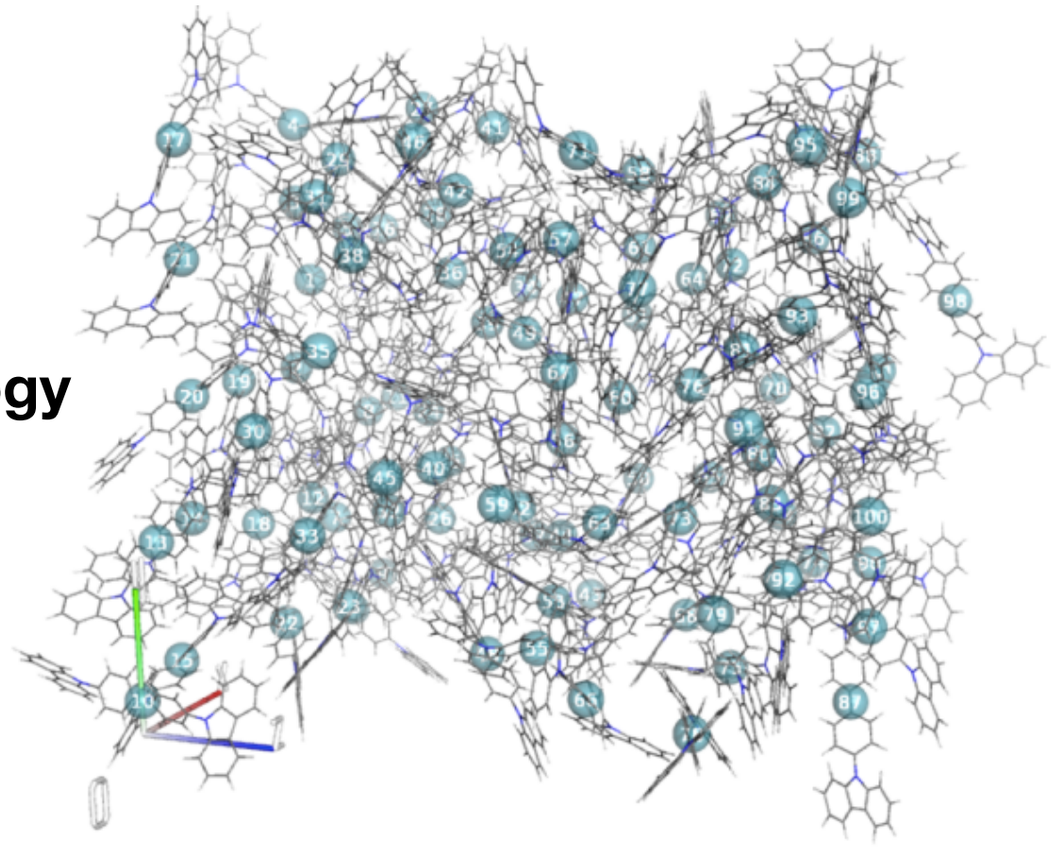
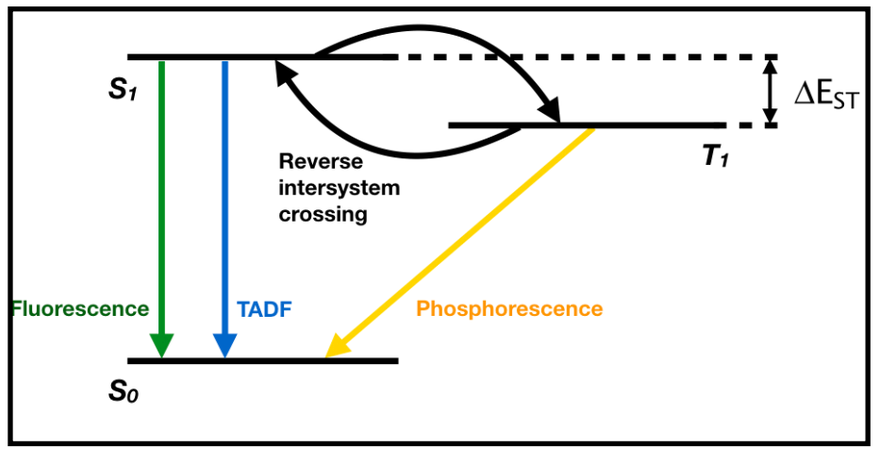
Disorder and environment effects in OLEDs

OLEDs' morphology is disordered



ΔE_{ST} with T-CDFT is slightly worse than the one we get from TDDFT with hybrid.
Can we make it better?



Environment effects

Environment and morphology can affect excitations - need for ***LARGE SYSTEMS***

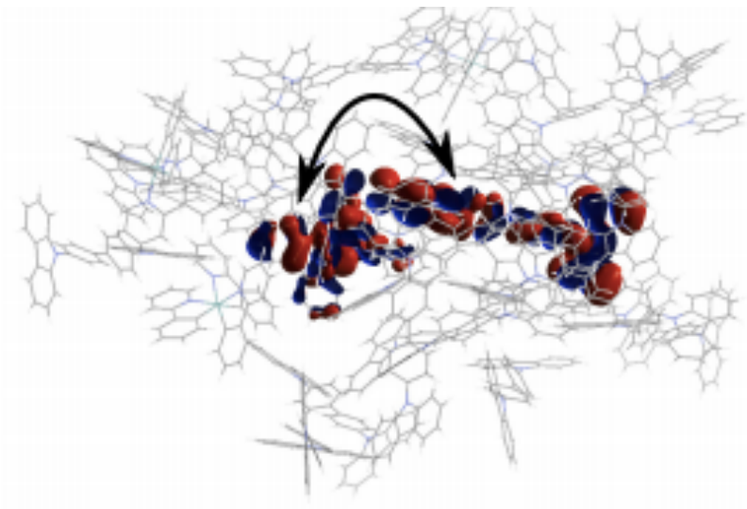


Image from: Approach to Large Scale Systems with BigDFT: from Ground State to electronic excitations - *Laura Ratcliff*

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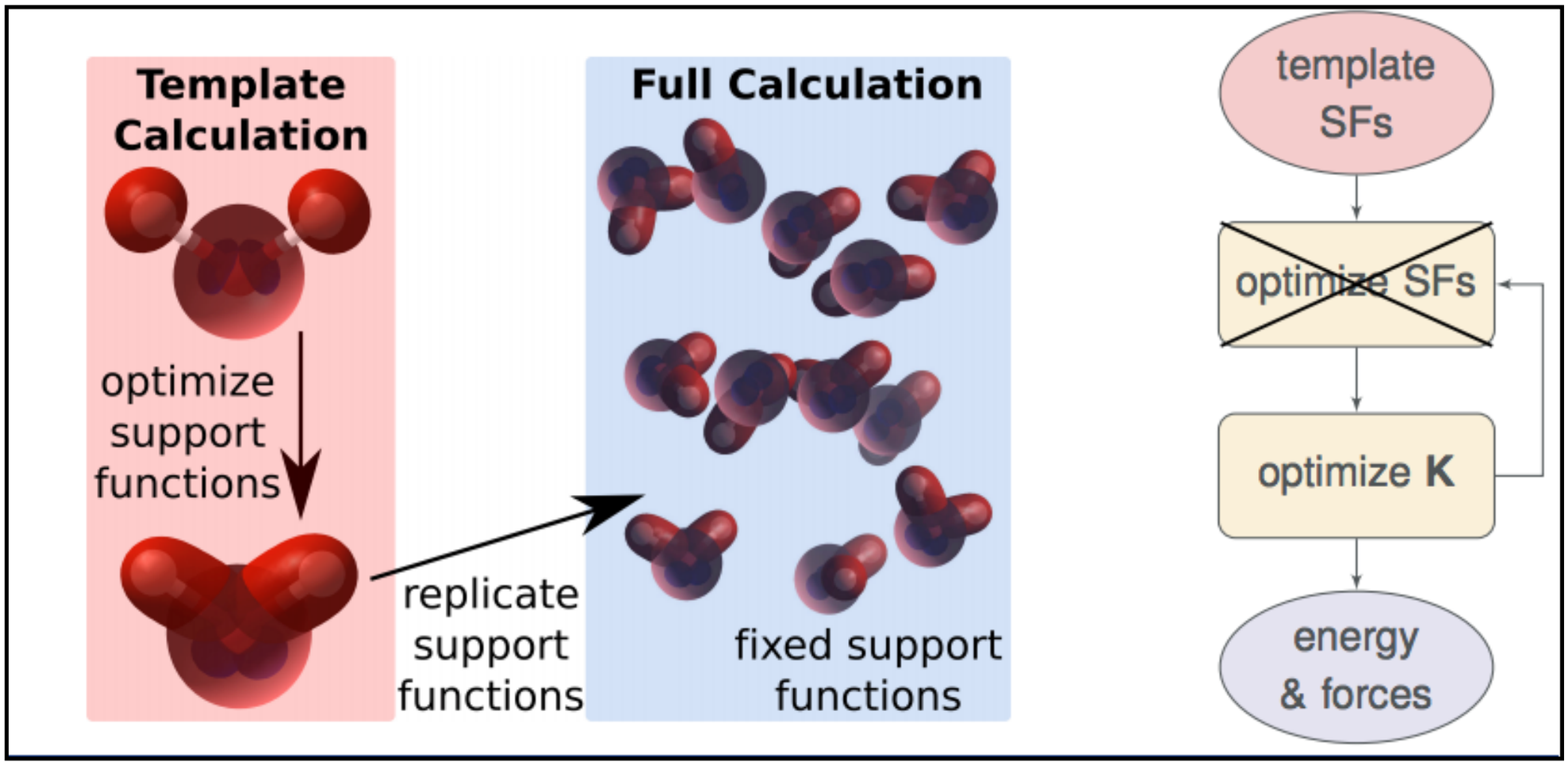
How do we go to supramolecular level?

Exploiting similarities

- SF optimization dominates prefactor
- similar chemical environments → similar SFs
- can we reuse SFs?

The molecular fragment approach



Ratcliff, Genovese, Mohr and Deutsch, J. Chem. Phys. 142, 234105 (2015) Image from: Approach to Large Scale Systems with BigDFT: from Ground State to electronic excitations - *Laura Ratcliff*

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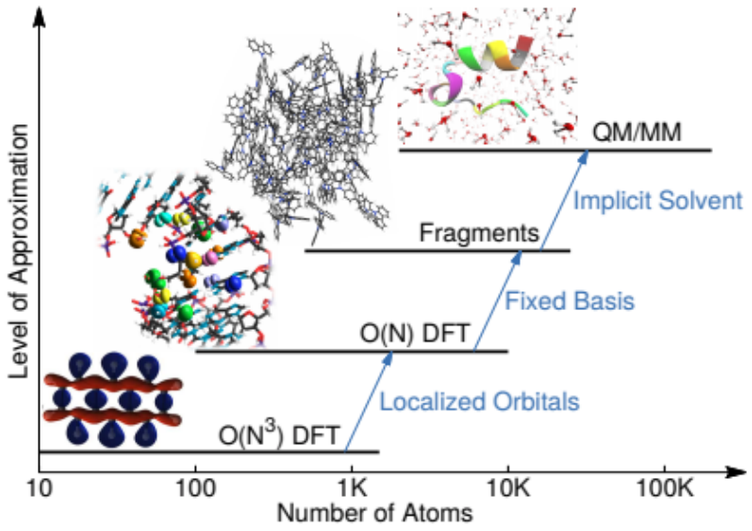
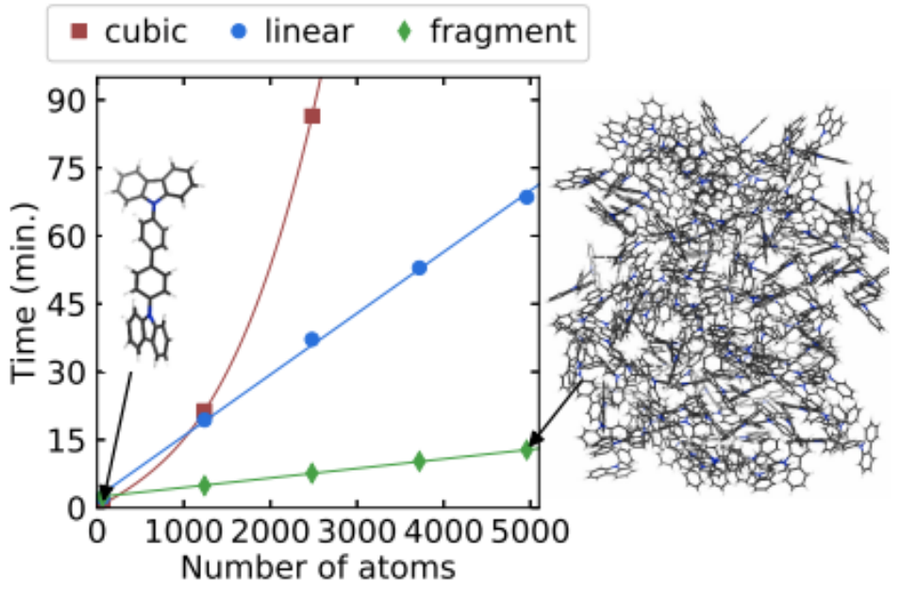
How do we go to supramolecular level?





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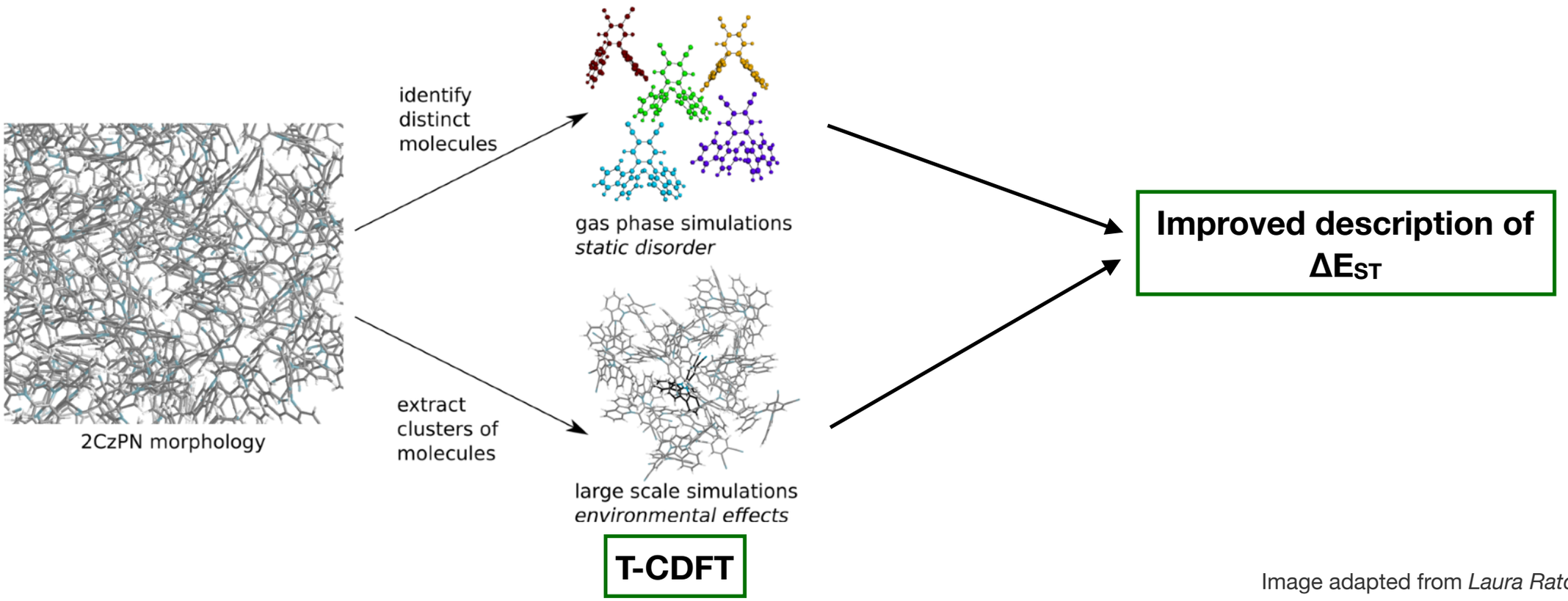

Image adapted from *Laura Ratcliff.*

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Final remarks

- **T-CDFT** gives a comparable accuracy to both **ΔSCF** and **TDDFT** with hybrid functionals, with lower computational cost and robust convergence

- **T-CDFT** does not suffer from the problems encountered when applying **TDDFT** to CT states, and can model both LE and CT states

- This conclusion is further supported through comparisons with higher-level theory calculations from the literature, based on CCSD(T) for the acenes and tuned range-separated functional **TDDFT** calculations for the OLED emitters

- The SF-based implementation, which is designed for large systems, is ideally suited to exploring the effects of an explicit environment on ΔEST

We foresee that the combination of **T-CDFT** with the fragmentation approaches which are already available within the BigDFT code, will represent a powerful tool for the study of excitations in realistic supramolecular morphologies

Thank you!