

# Fragments and Transition-Based Constrained DFT in BigDFT

Laura Ratcliff<sup>1,2</sup>  
and Martina Stella<sup>3</sup>

<sup>1</sup>School of Chemistry, University of Bristol

<sup>2</sup>UiT The Arctic University of Norway

<sup>3</sup>ICTP, Italy

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# Outline

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The Fragment  
Approach

Molecular Fragments  
Embedded Fragments

Beyond the  
Ground State

Constrained DFT  
Transition-Based  
CDFT

Tutorials and  
Outlook

## ① The Fragment Approach

Molecular Fragments  
Embedded Fragments

## ② Beyond the Ground State

Constrained DFT  
Transition-Based CDFT

## ③ Tutorials and Outlook

# Exploiting Similarity Between Fragments

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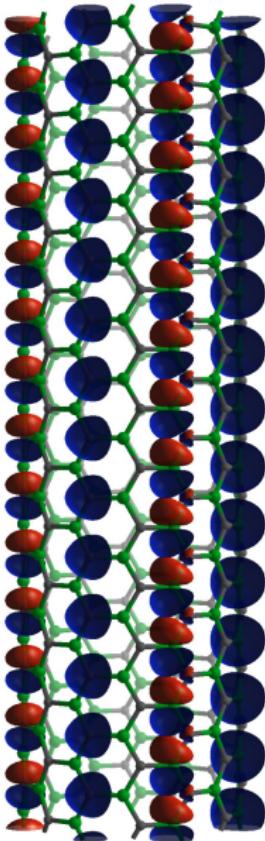
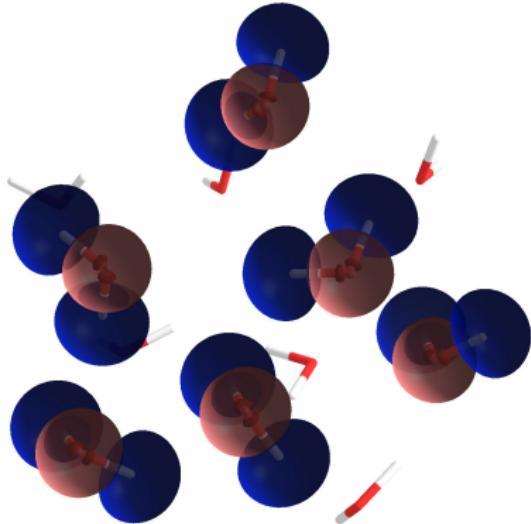
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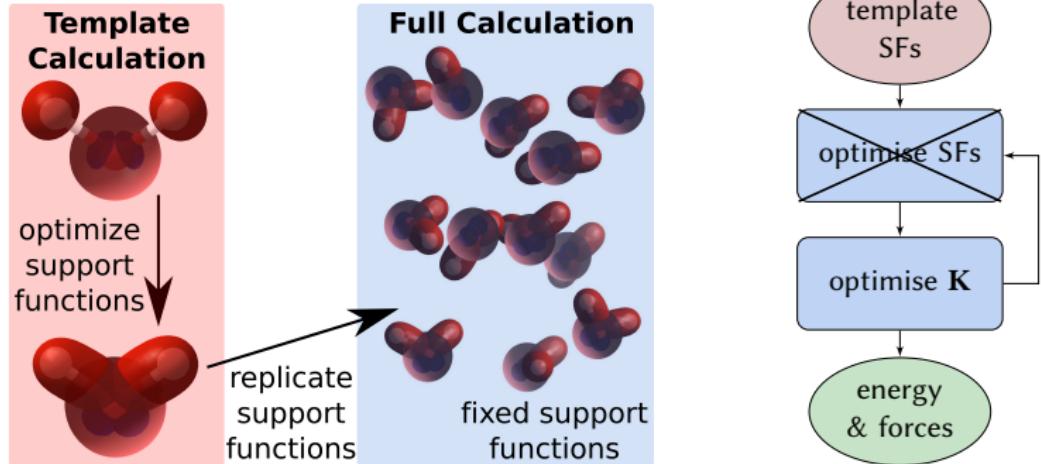
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## SF Similarity

- SF optimisation takes a lot of compute time
- what happens in similar chemical environments?
- can we reuse SFs?

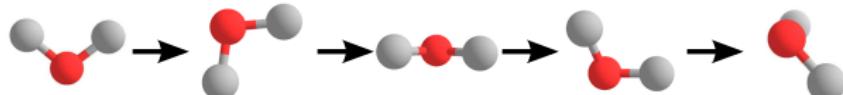


# Molecular Fragment Approach I



## Accounting for Varying Orientations and Positions

- minimise cost function to find **rotation** from template:
- $$\mathcal{J}(\mathcal{R}) = \frac{1}{N} \sum_{a=1}^N \left\| \mathbf{R}_a^S - \sum_{b=1}^N \mathcal{R}_{ab} \mathbf{R}_a^T \right\|^2$$
- reformat SFs using **wavelet interpolation** (eggbox effect)

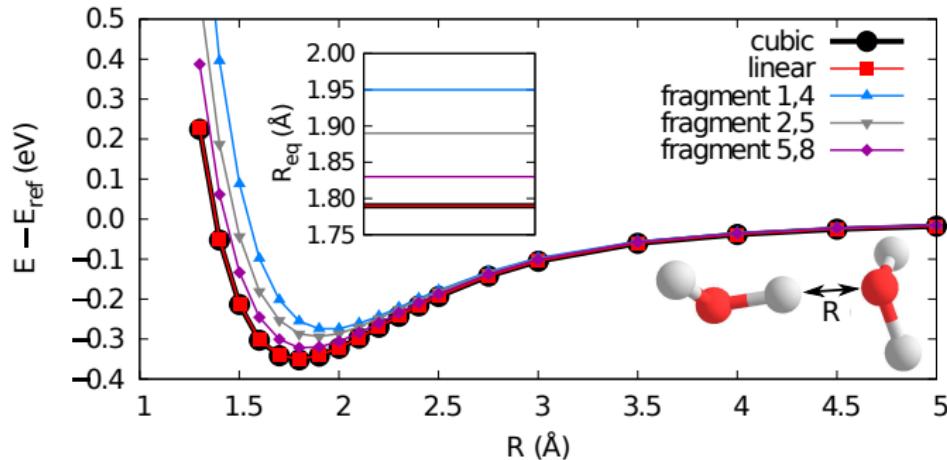


# Molecular Fragment Approach II

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## Suitability of the Fragment Approach

- suitable for weakly interacting fragments:
  - water dimer – basis set superposition error at short distances
- want fragments which are **not too distorted**:
  - use cost function – larger  $\tilde{\beta} \rightarrow$  larger error
- can use fragments to generate an **input guess** for LS-BigDFT



# Fragments in Periodic SiC Nanotube

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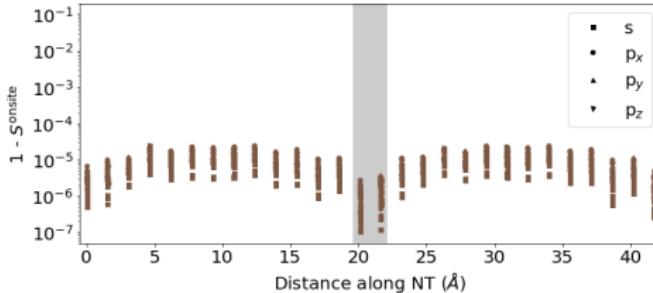
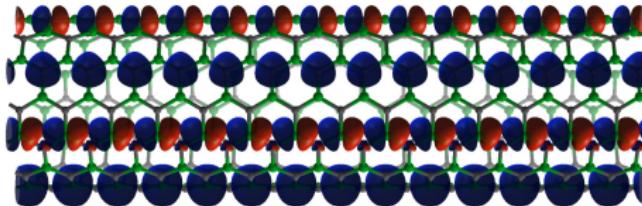
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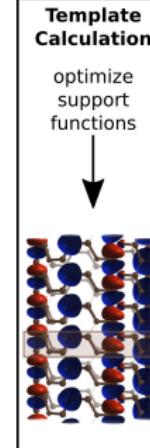
## SF Repetition in Extended Systems

- how can we adapt to extended systems?
- quantitative measure of SF similarity (onsite overlap matrix)
- generate SFs using an **embedded pseudo-fragment template**
- → can cut covalent bonds between fragments



Template  
Calculation

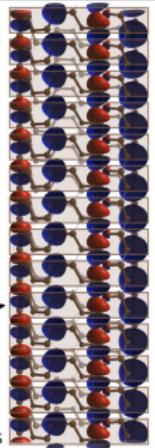
optimize  
support  
functions



Fragment  
Calculation

replicate  
support  
functions

fixed  
support  
functions



# Finite SiC Nanotube

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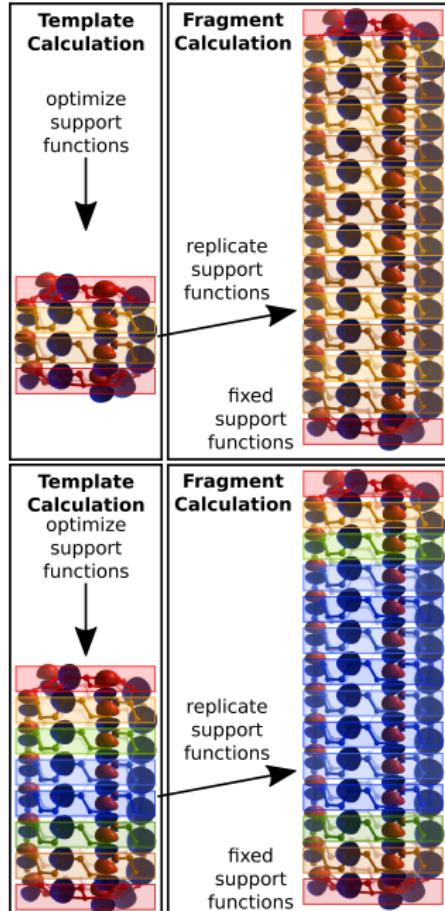
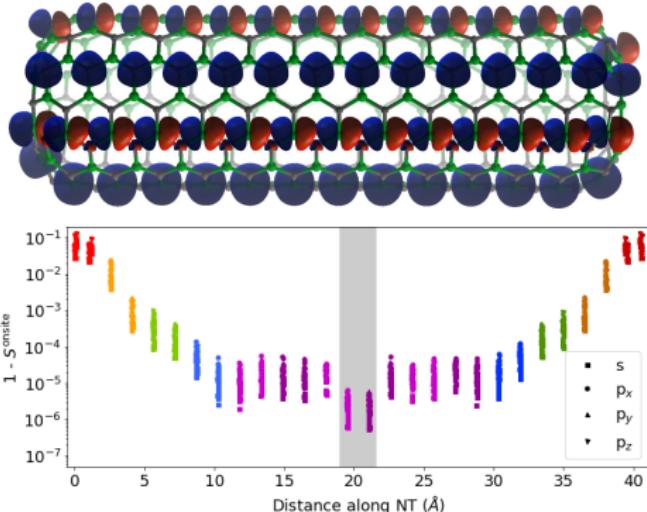
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## Edge Effects

- SFs feel the effects of the edges
- multiple fragment types needed
- use onsite overlap and  $\beta$  to assess setup



# Molecular vs. Embedded Fragments

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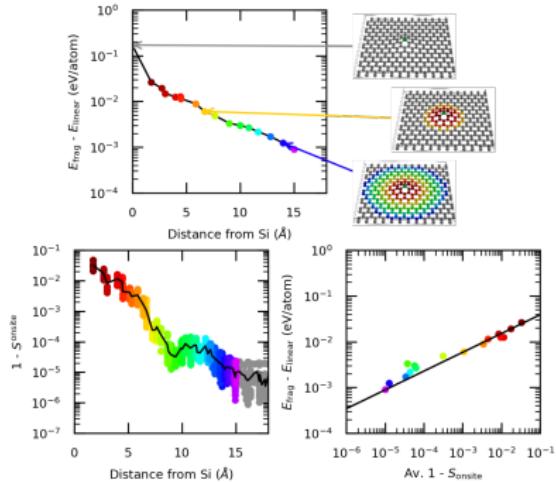
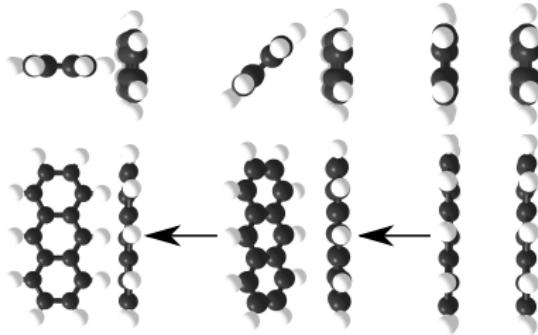
Molecular Fragments

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## Molecular Fragments

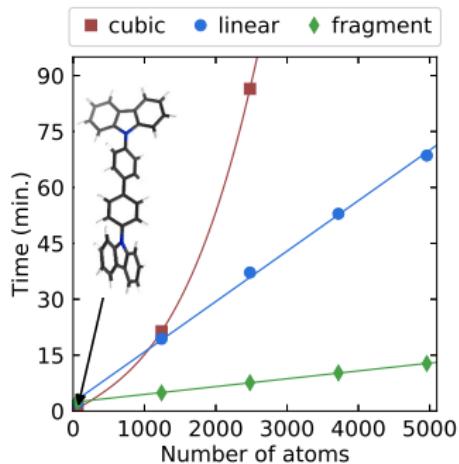
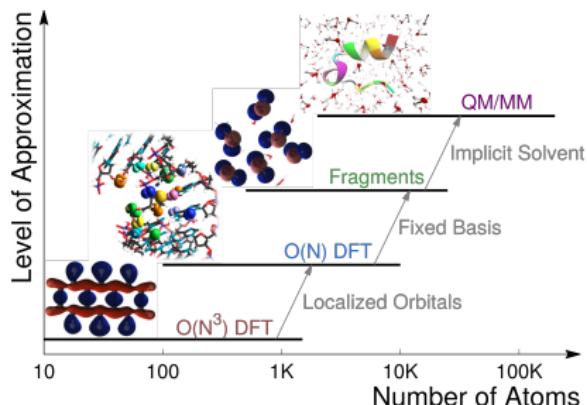
- weak interactions between fragments
- smaller template calculation (isolated or implicit solvent)
- use  $\beta$

## Embedded Fragments

- stronger interactions between fragments
- larger template calculation (not just the fragment)
- use  $\beta$  and onsite overlap

## BigDFT: From Small to Large Systems

- system size limited to  $\sim 1000$  atoms by **cubic scaling**
- exploit locality with optimized local orbitals  $\rightarrow$  **linear scaling**
- exploit repetition  $\rightarrow$  **fragment approach** with lower prefactor
- **implicit solvent**



# Constrained DFT with Fragments

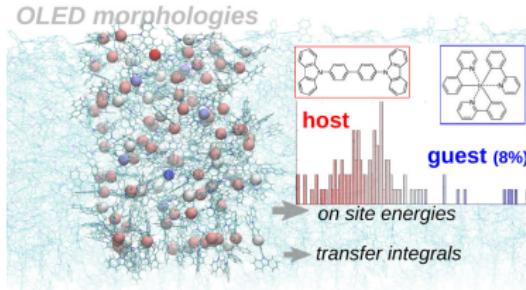
## Constrained DFT (CDFT)

- find the **lowest energy state** satisfying a given (charge) **constraint** on the density
- ideal for treating charge transfer (CT) excitations
- cost **similar to ground state**

## CDFT with Fragments

- add an extra constraint term to the KS functional
$$W[n, V_c] = E_{\text{KS}}[n] + V_c (2\text{Tr}[\mathbf{Kw}_c] - N_c)$$
- find Lagrange multiplier  $V_c$  which gives the required charge  $N_c$
- SF basis lends itself to a Löwdin like approach
$$\mathbf{w}_c = \mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}}$$
- → can associate the weight function with a given fragment
- accuracy depends on validity of fragment approach and suitability of SFs for charged fragments (need virtual states)

# OLED Charge Transport Parameters



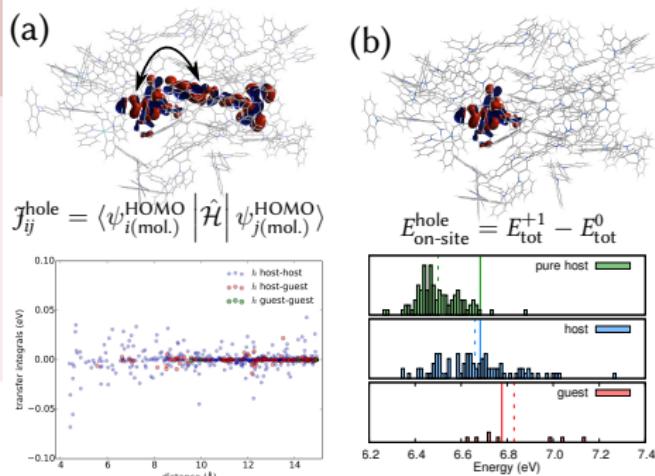
## Fragment Setup

- isolated template calculations for each molecule
- calculate transfer integrals (a)
- calculate on-site energies using constrained DFT (b)

## Environmental and Statistical Effects

- disorder  $\rightarrow$  dispersion in  $E_{\text{on-site}}$  and  $J_{ij}$
- environment  $\rightarrow$  shift in average  $E_{\text{on-site}}$  (- -) vs. isolated molecules (-)

**Host-Guest Application:** LER, Grisanti, Genovese *et al.*, J. Chem. Theory Comput. **11**, 2077 (2015)



# Beyond Charge Transfer Excitations

## Challenge for Excited States

- CDFT – cheap, but spatial constraint → CT excitations only
- TDDFT – expensive, issues with long range CT states and semi-local functionals
- $\Delta$ SCF – cheap, but problems with local minima and spin contamination
- want to treat CT *and* local excitations (LE) in large systems

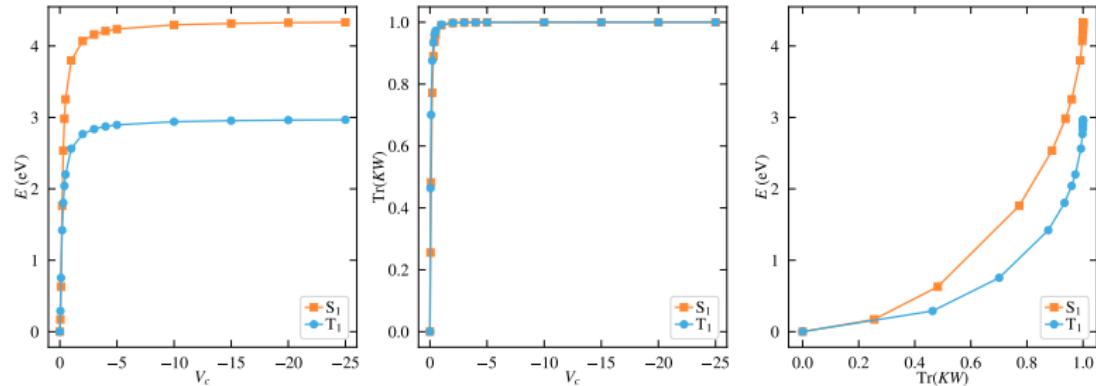
## Transition-Based Constrained DFT

- replace spatial constraint with an (off-diagonal) transition-based constraint
- includes self-consistency (beyond linear response)
- allows treatment of LE and CT states
- compatible with fragment approach (using ground state SF basis) → large systems

# Pure Excitations

## Lagrange Multiplier

- first approximation: assume pure HOMO $\rightarrow$ LUMO transition
- can only transfer  $1e^-$ , i.e.  $\text{Tr}(KW) \rightarrow 1$  as  $V_c \rightarrow -\infty$
- $\rightarrow$  can use arbitrarily large  $V_c$  (naphthalene PBE example)
- no need to optimise  $V_c \rightarrow$  cost similar to ground state



# Beyond Pure Excitations

## Transition-Based Constrained DFT

- not all excitations can be treated as pure
- mixed excitations – impose each transition separately, and **combine density kernels** (use TDDFT to inform weights)
- cost proportional to number of transitions, but can still fix  $V_c$

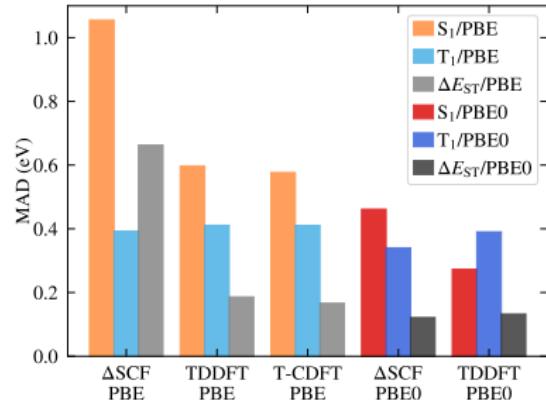
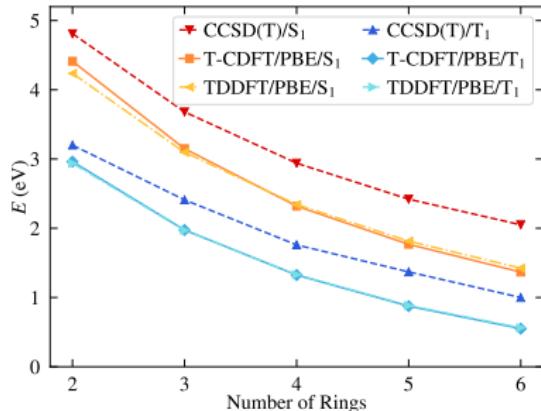
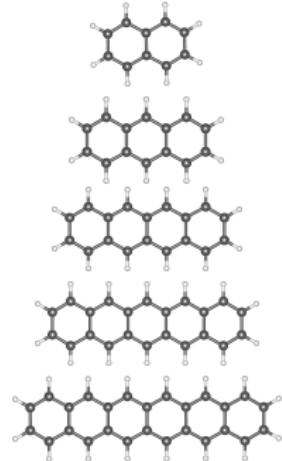
### Mixed Excitations in Acenes ( $S_1$ )

	HOMO→ LUMO	HOMO-1→ LUMO+1	HOMO-2→ LUMO+2	Energy
<b>naphthalene</b>				
pure	1.000	-	-	4.33
mixed	0.935	0.027	0.038	4.41
<b>anthracene</b>				
pure	1.000	-	-	3.09
mixed	0.975	0.010	0.015	3.15
<b>tetracene</b>				
pure	1.000	-	-	2.29
mixed	0.988	0.012	-	2.32

# Acenes

## Benchmarking T-CDFT/PBE

- captures trend of CCSD(T) reference
- LE – TDDFT/PBE performs well
- similar cost to  $\Delta\text{SCF}/\text{PBE}$ , but more accurate
- similar accuracy to TDDFT/PBE, but cheaper



CCSD Values: Rangel, Hamed, Bruneval & Neaton, J. Chem. Phys. 146, 194108 (2017)

# OLEDs

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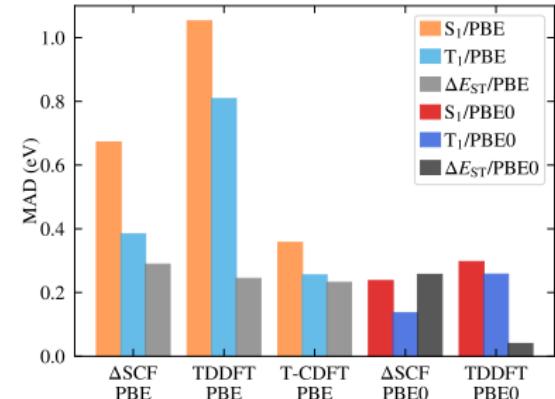
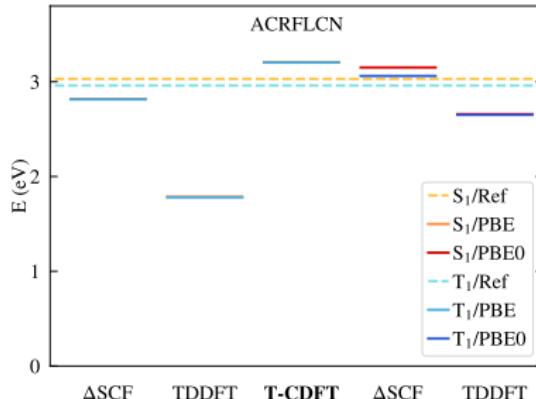
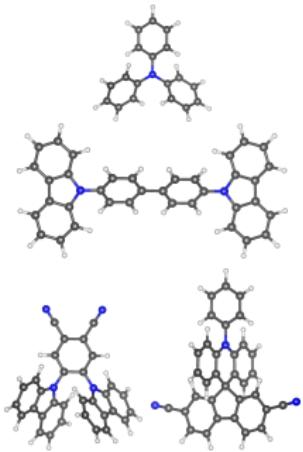
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## Benchmarking T-CDFT/PBE

- reference – TDDFT with tuned range-separated functional
- CT-like excitations – TDDFT/PBE **underestimation** (e.g. ACRFLCN)
- T-CDFT **outperforms** PBE results for both  $\Delta\text{SCF}$  and TDDFT



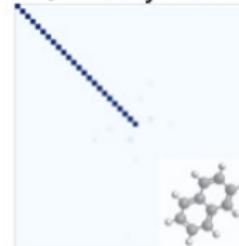
# T-CDFT Summary

## Excited States in Molecules

- T-CDFT → effective for both LE and CT states

### Transition-Based Constrained DFT (T-CDFT)

$S_0$  density matrix

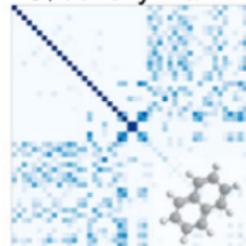


optical excitation

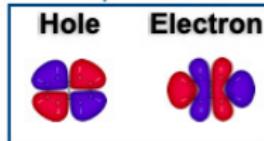
$$\hbar v$$

$\rho^{ij} = \langle \psi_0^i | \hat{F} | \psi_0^j \rangle$

$S_1$  density matrix



Naphthalene



Local Excitation

TDDFT/PBE

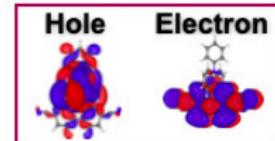
T-CDFT/PBE

Charge Transfer

TDDFT/PBE

T-CDFT/PBE

ACRFLCN



large

small

Hole-Electron overlap

# T-CDFT and Workflows

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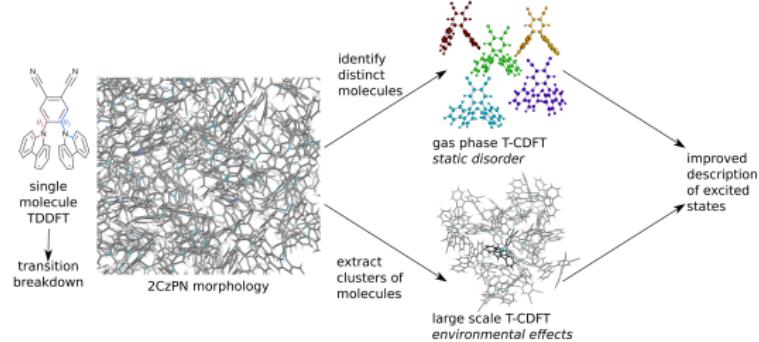
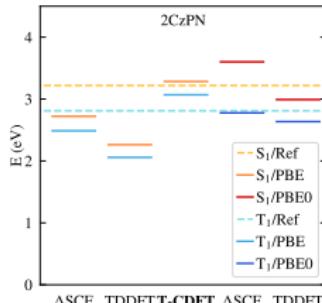
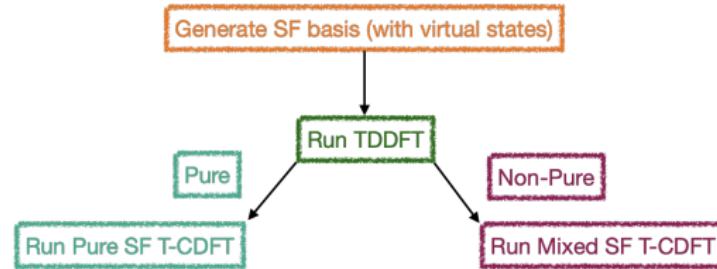
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## T-CDFT in Practice

- workflow combines TDDFT (cubic scaling, LDA only) with T-CDFT (linear scaling, LDA and GGA)
- T-CDFT uses the fragment approach → can treat large systems



# Tutorials and Perspective

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## Tutorials

- molecular fragments: anthracene dimer (4A)
- embedded fragments: carbon chain (4B)
- T-CDFT: naphthalene (4C)

## What About Biology? Some Ideas

- may not work out of the box –  
but could use (embedded) **fragment  
guess**, especially if many snapshots  
or related systems
- example: combine T-CDFT with (ex-  
plicit and/or implicit) **solvent effects  
on organic fluorophores**

