Max Webinar

BigDFT

Approach to Large Scale Systems with BigDFT; from Ground State to Electronic Excitations

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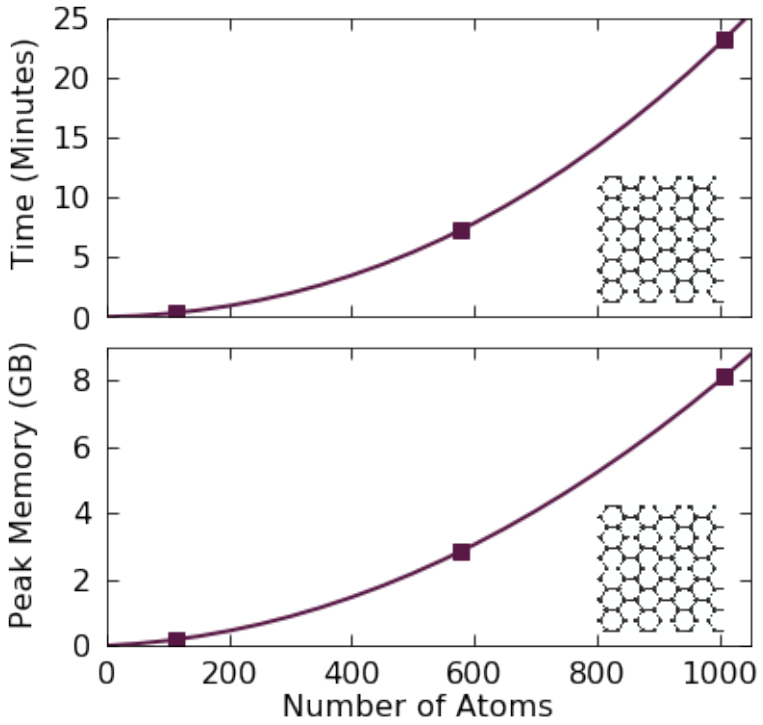
Virtual Room

The Cubic Scaling Limit

Size Limitations

- $\sim$ 1000 atoms thanks to wavelet properties and efficient parallelization
- for bigger systems $O(N^3)$ dominates in time and memory
- $\rightarrow$ need new approach



Nearsightedness

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

Key Quantities for Linear Scaling

Support Functions (SFs)

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

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

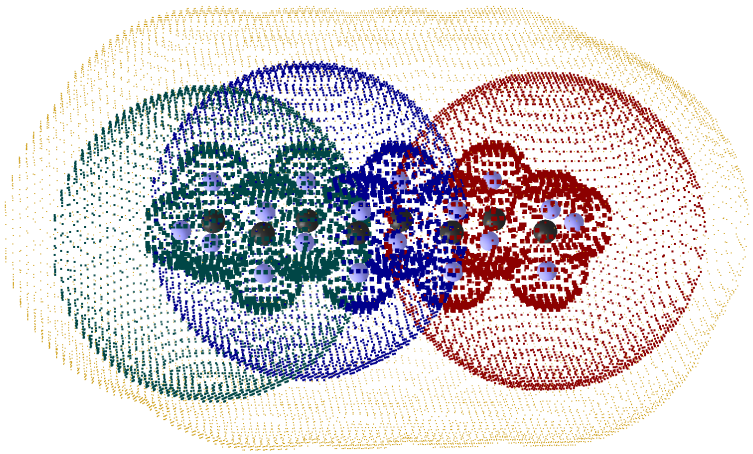
- localized ($\sim 6-8$ a_0 radius)
- atom-centred
- minimal – 1 SF per H, 4 per C/N/O...
- numerical functions – expanded in wavelets
- quasi-orthogonal
- Γ-point only – real

Density Kernel (**K**)

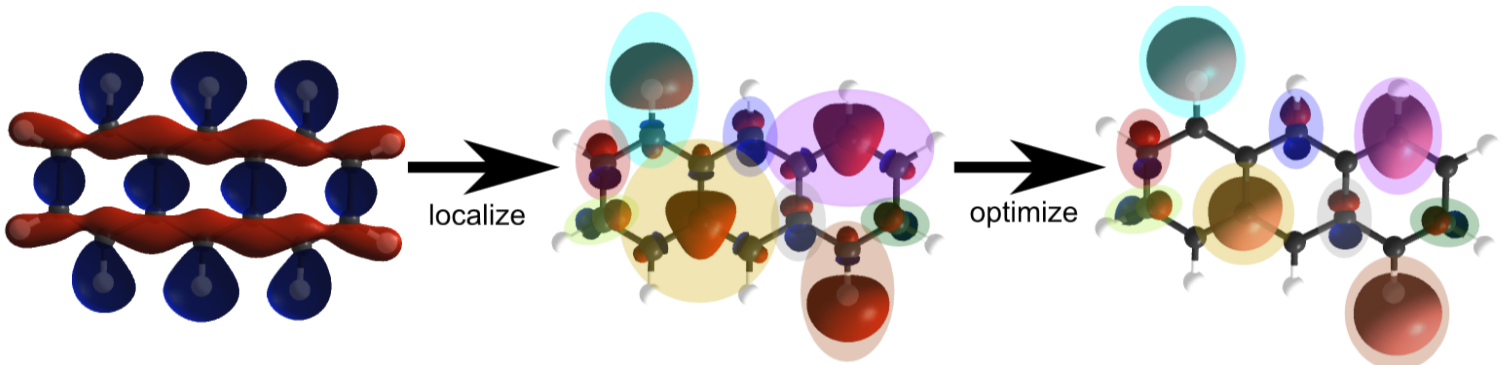
define the density matrix ρ:

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

$$H_{\alpha\beta} = \langle\phi_\alpha|\hat{H}|\phi_\beta\rangle; \qquad S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$$
$$E = \mathrm{Tr}(\mathbf{KH}); \qquad N = \mathrm{Tr}(\mathbf{KS})$$



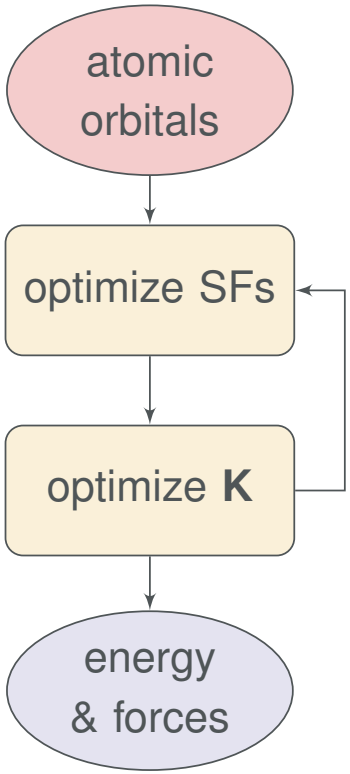
The Algorithm



extended Kohn-Sham orbitals
cubic scaling, high accuracy

localized support functions (LCAO)
linear scaling, low accuracy

localized adaptive support functions
linear scaling, high accuracy



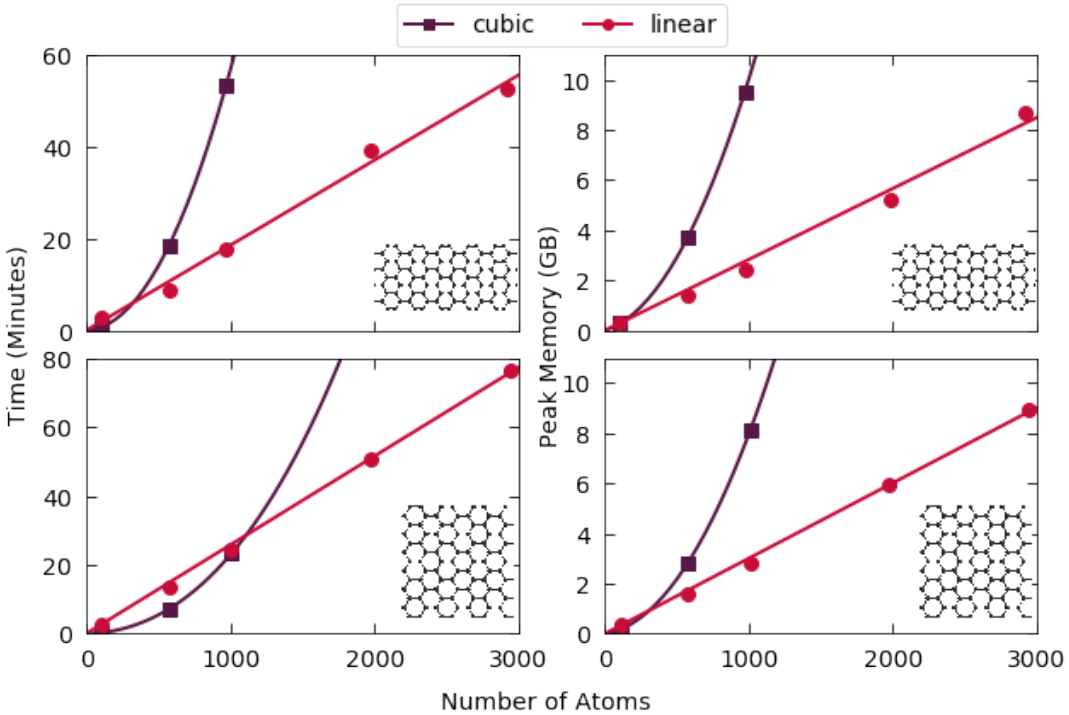
Accurate Minimal Basis

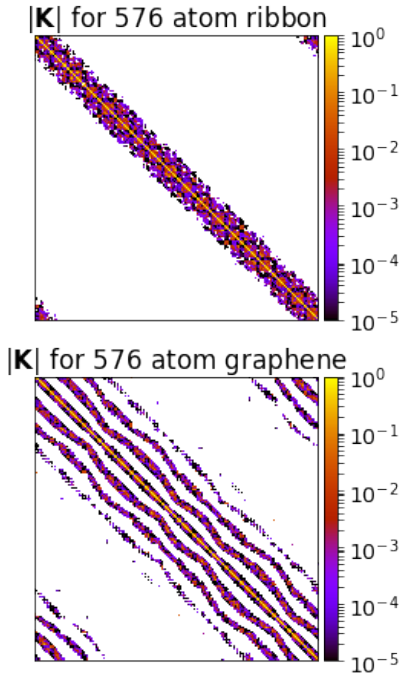
- minimize energy wrt both SFs and kernel (subject to constraints)
- SFs adapt to the environment – minimal, localized basis with wavelet accuracy
- 3 methods for **K** – Fermi Operator Expansion for $\mathcal{O}(\mathcal{N})$, direct minimization (virtual states), diagonalization
- forces – geometry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

From Sparsity to Linear Scaling

Sparse Matrices

- strict localization leads to sparse matrices (**K** truncation)
- crossover depends on size, dimensionality, SF radii...
- speed also depends on band gap (can treat metals)



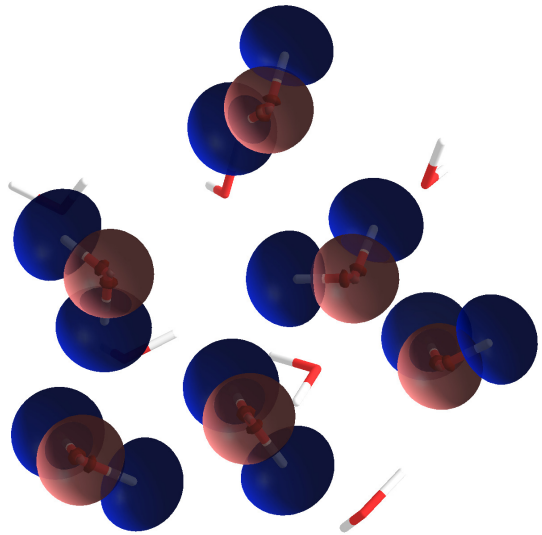


LS-BigDFT: Mohr *et al.*, J. Chem. Phys. **140**, 204110 (2014); Mohr *et al.*, Phys. Chem. Chem. Phys. **17**, 31360 (2015)
Metals: Mohr *et al.*, J. Nucl. Mater. Energy **15**, 64 (2018)

Exploiting Similarity Between Fragments

Calculation Bottleneck

- SF optimization dominates prefactor
- similar chemical environments $\rightarrow$ similar SFs
- can we reuse SFs?

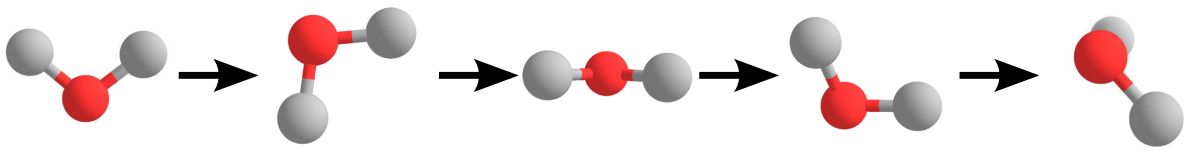


Acccounting for Varying Orientations and Positions

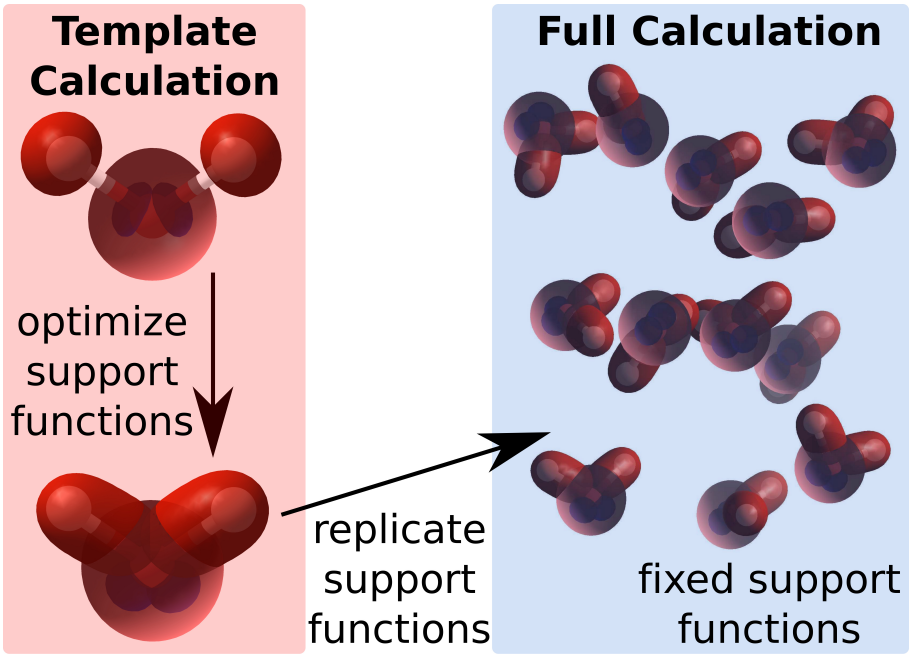
- minimize cost function to find rotation from template:

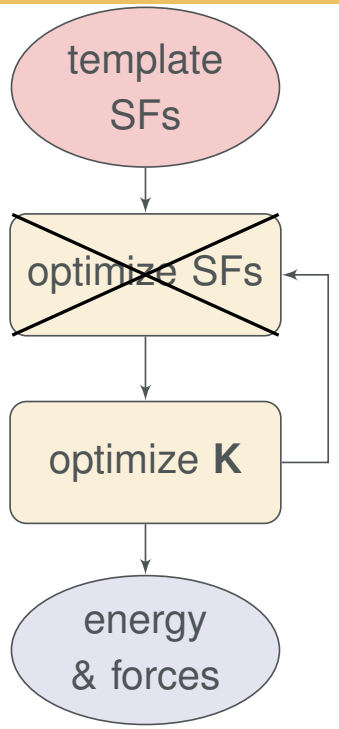
$$J(\mathcal{R}) = \frac{1}{N}\sum_{a=1}^{N} ||\mathbf{R}_a^S - \sum_{b=1}^{N} \mathcal{R}_{ab}\mathbf{R}_a^T||^2$$

- apply accurate and efficient wavelet interpolation scheme



Molecular Fragment Approach





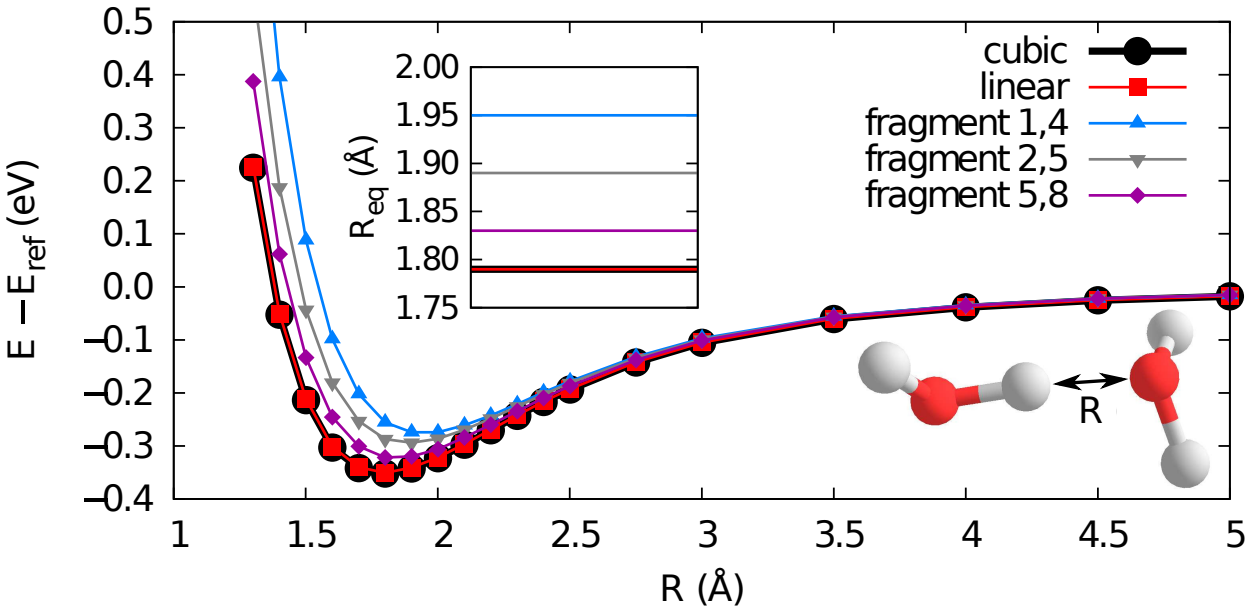
Calculation Steps

- template calculation: optimize SFs for isolated fragment
- reformatting: replicate and rototranslate template SFs for each fragment instance
- full calculation: use fragment SFs as a fixed basis, optimizing density kernel only

Applicability of the Fragment Approach I

Effect of Fragment Interactions – Water Dimer

- basis set superposition error at small distances
- increase basis to improve accuracy
- applicability depends on quantity of interest
- $\rightarrow$ suited to weakly interacting fragments

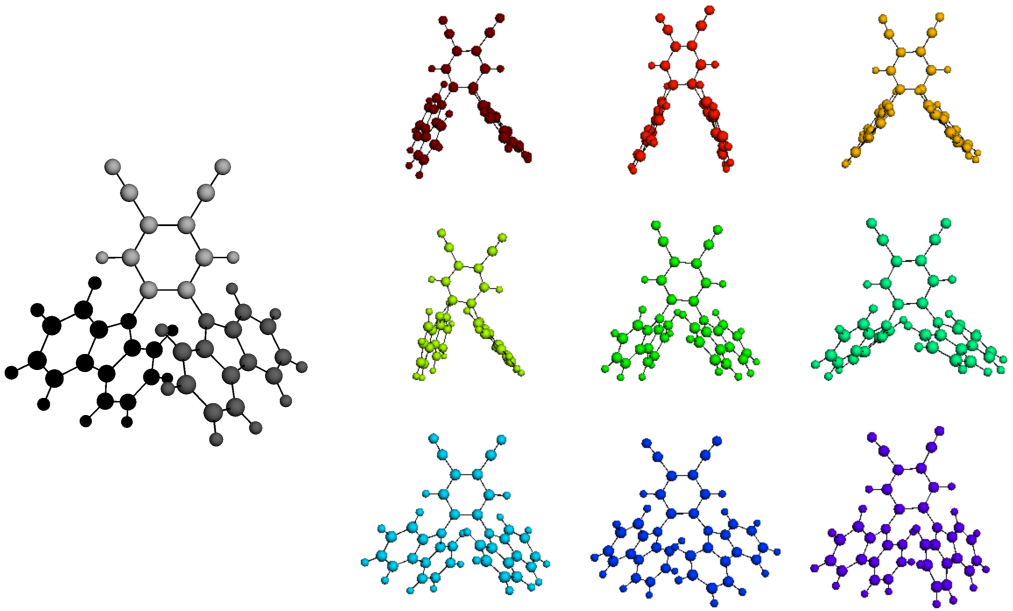


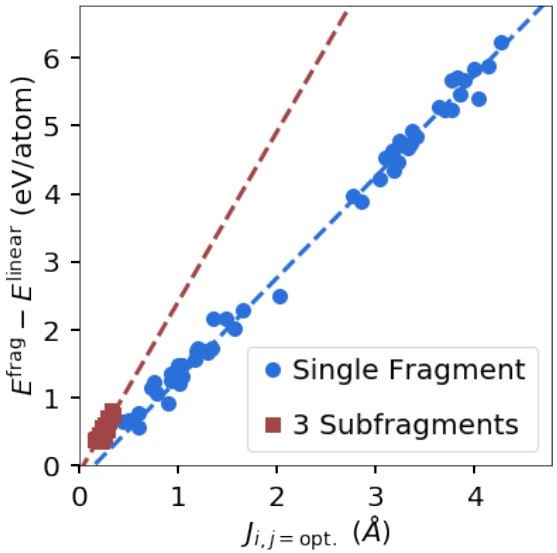
Ratcliff, Genovese, Mohr and Deutsch, J. Chem. Phys. **142**, 234105 (2015)

Applicability of the Fragment Approach II

Effect of Distortions – 2CzPN

- use optimized molecule as template
- more distorted fragments $\rightarrow$ larger error
- cost function J used to predict accuracy
- $\rightarrow$ suited to fragments which are not too distorted

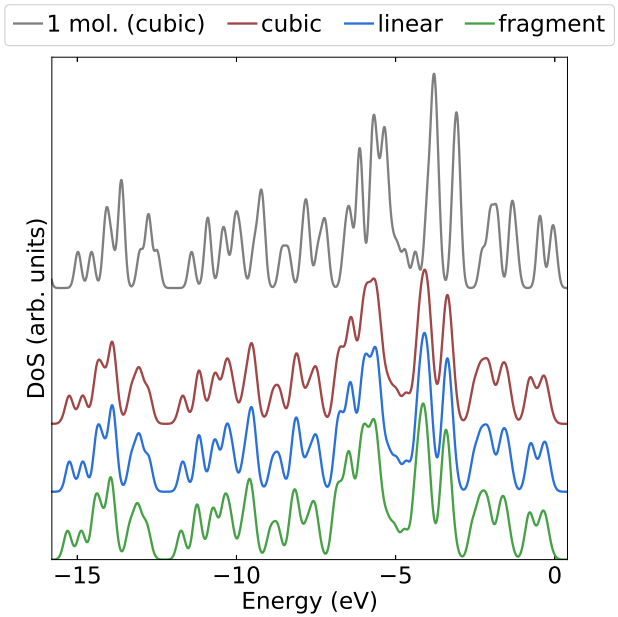


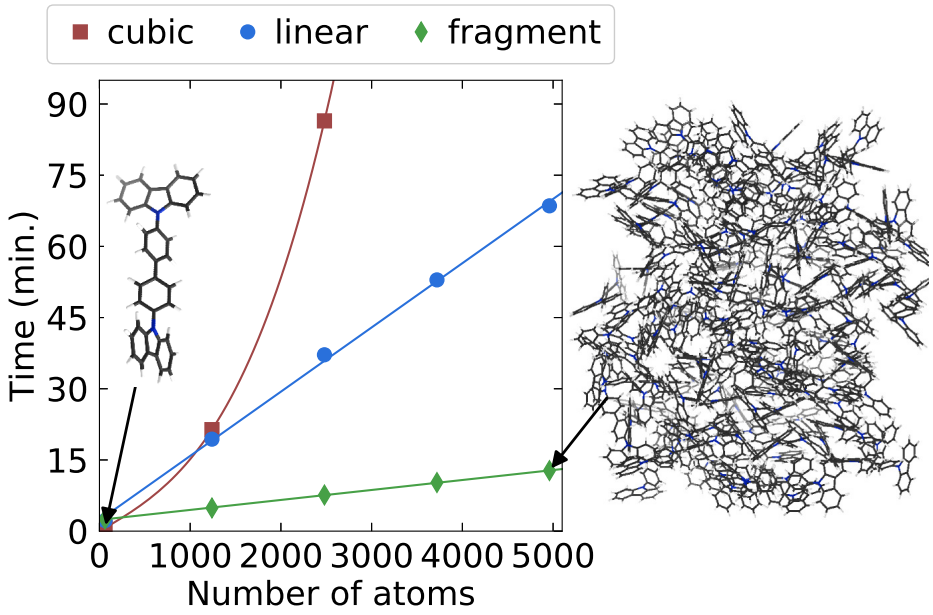


Applicability of the Fragment Approach III

Cluster of Rigid CBP Molecules

- $E_{\text{frag}} - E_{\text{cubic}} \simeq 30$ meV/atom
- fragment approach reproduces (occupied) DoS
- $\sim$5000 atom single point calculation (48 nodes on Archer) – fragment approach $\sim 7\times$ cheaper than full linear scaling

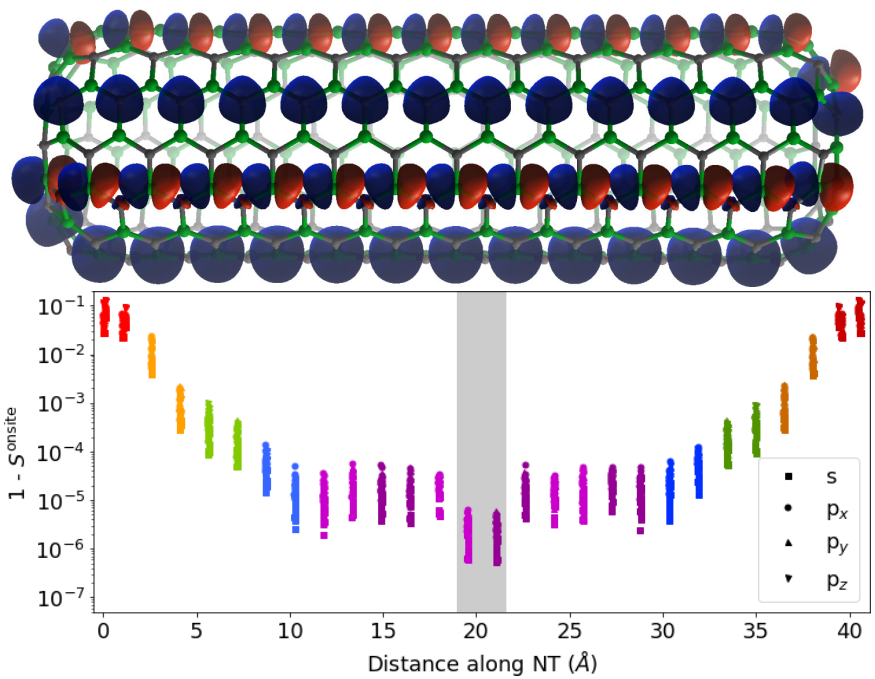


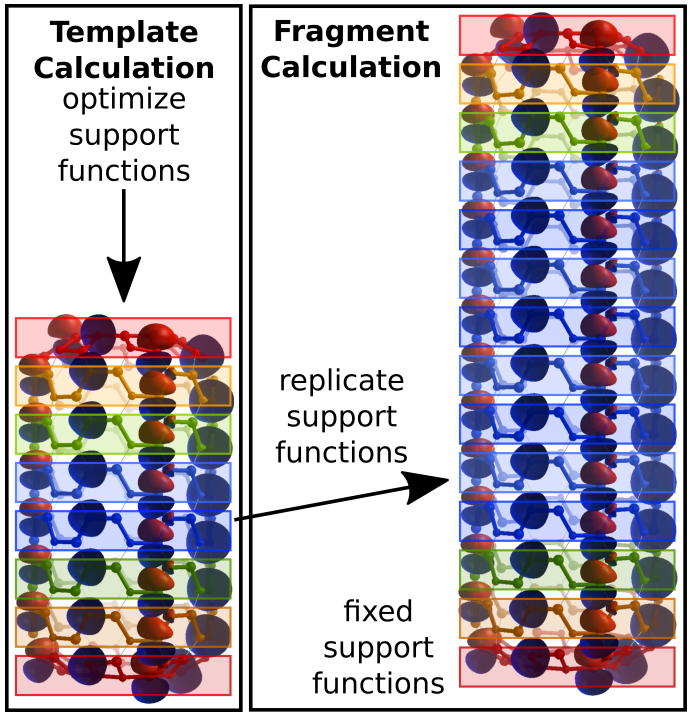


Fragment Approach: Beyond Molecules

Finite SiC Nanotube

- use J and onsite overlap matrix to inform setup
- optimize SFs in embedded pseudo-fragments
- also applied to defective graphene





Ratcliff and Genovese, J. Phys.: Condens. Matter **31**, 285901 (2019)
Ratcliff and Genovese, In: E. Levchenko, Y. Dappe, G. Ori. (Eds), Springer Series in Materials Science, vol. 296 (2020)

OLED Simulation Challenge

Simulating Charge Transport

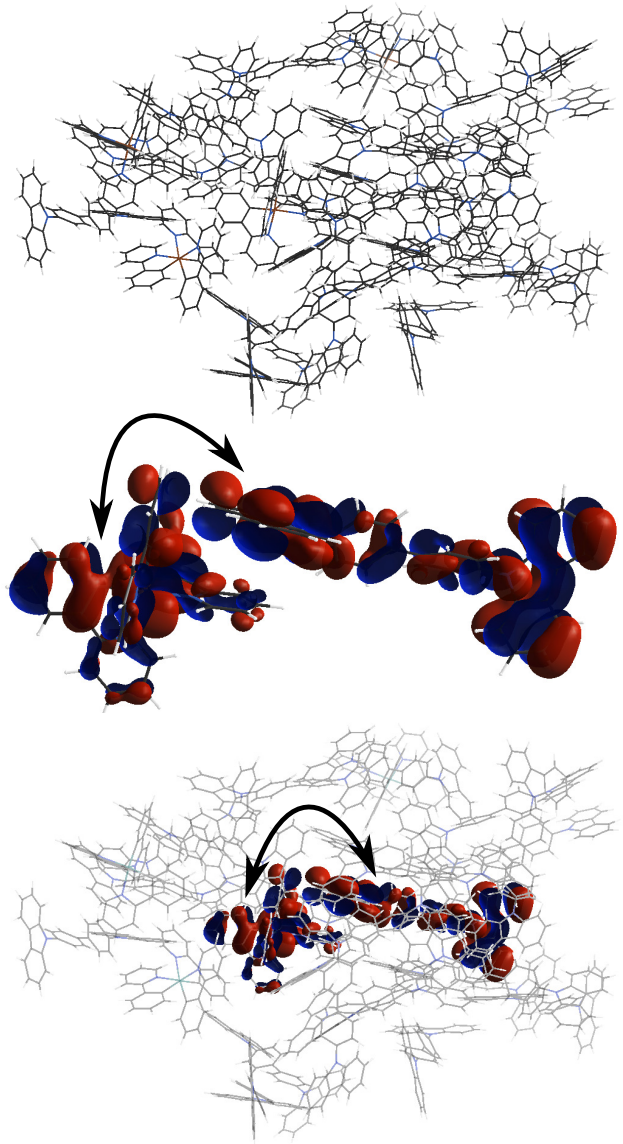
need to calculate parameters like transfer integrals in a disordered host-guest material

Typical Procedure

extract pairs of molecules from morphology and calculate transfer integrals for each pair

Environmental Effects

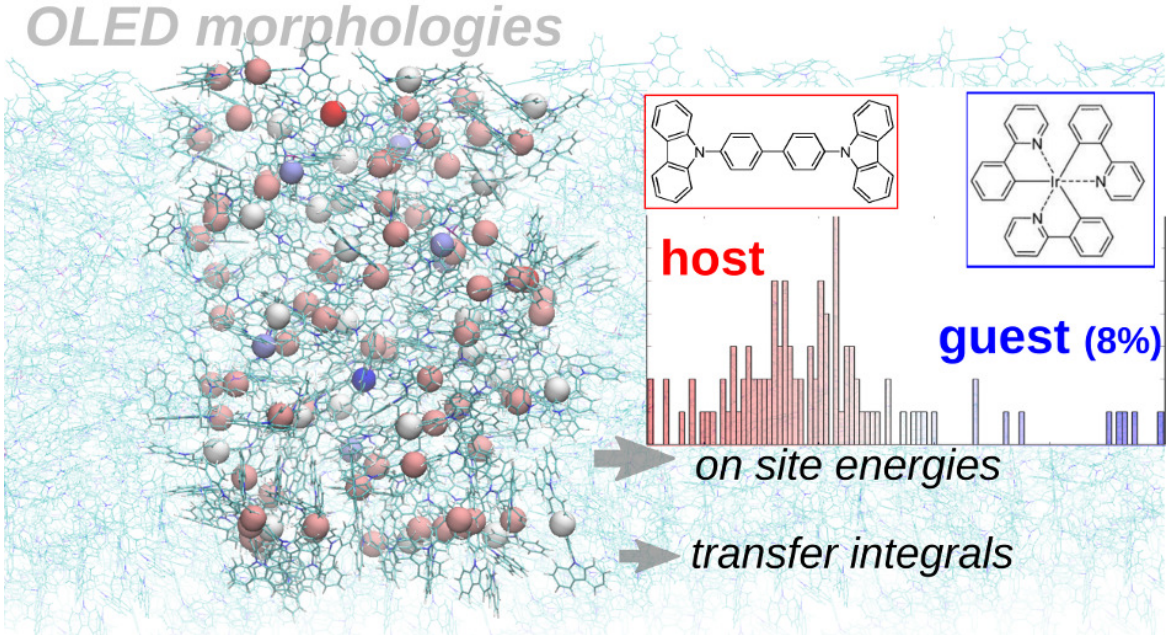
BUT the environment can affect parameters – need large systems



Host-Guest OLED

Host-Guest OLED Morphology

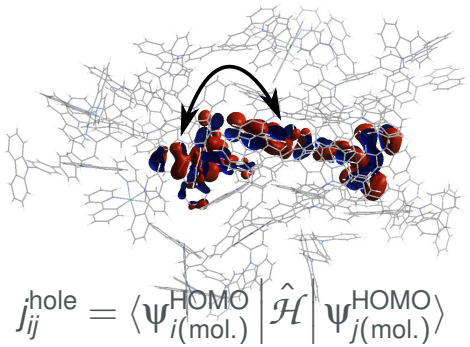
- CBP doped with $Ir(ppy)_3$ ($\sim$ 6200 atoms)
- Metropolis Monte Carlo with simulated annealing of rigid molecules (mimic physical vapor deposition)
- use constrained DFT to introduce net confined charge $\rightarrow$ polarization effects for on-site energies



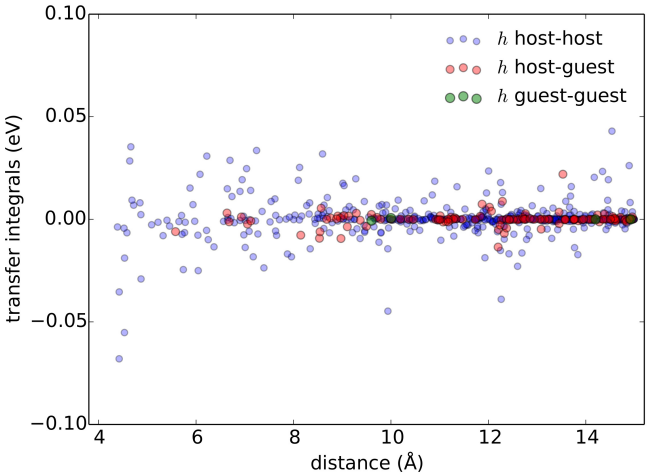
OLED Charge Transport Parameters

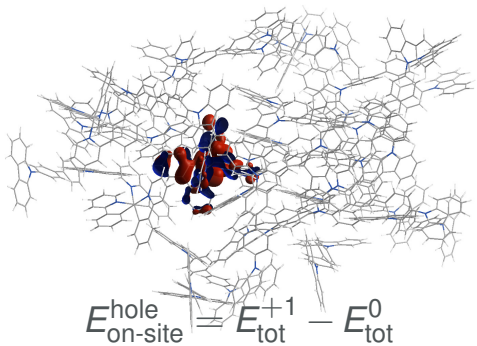
Environmental and Statistical Effects

- disorder $\rightarrow$ dispersion in $E_{\text{on-site}}$ and j_{ij}
- environment $\rightarrow$ shift in $E_{\text{on-site}}$ (- -) cf. isolated molecule (—)

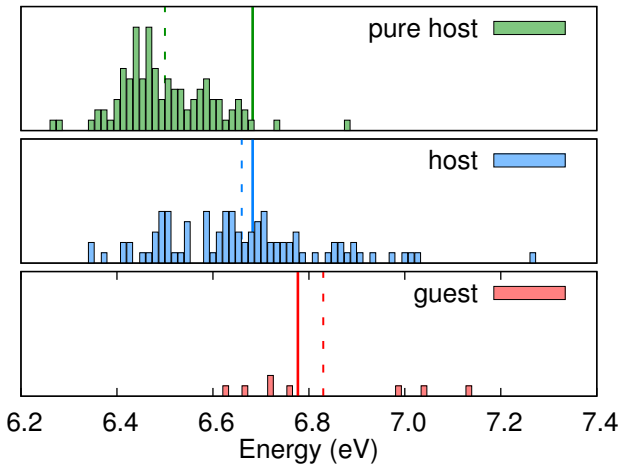


$$j_{ij}^{\text{hole}} = \langle \psi_{i(\text{mol.})}^{\text{HOMO}} | \hat{\mathcal{H}} | \psi_{j(\text{mol.})}^{\text{HOMO}} \rangle$$





$$E_{\text{on-site}}^{\text{hole}} = E_{\text{tot}}^{+1} - E_{\text{tot}}^{0}$$

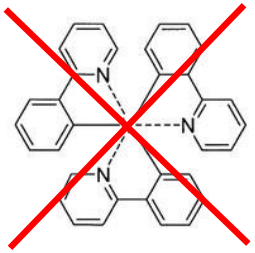


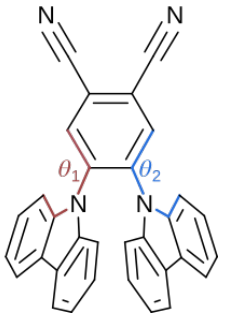
Ratcliff *et al.*, J. Chem. Theory Comput. **11**, 2077 (2015)

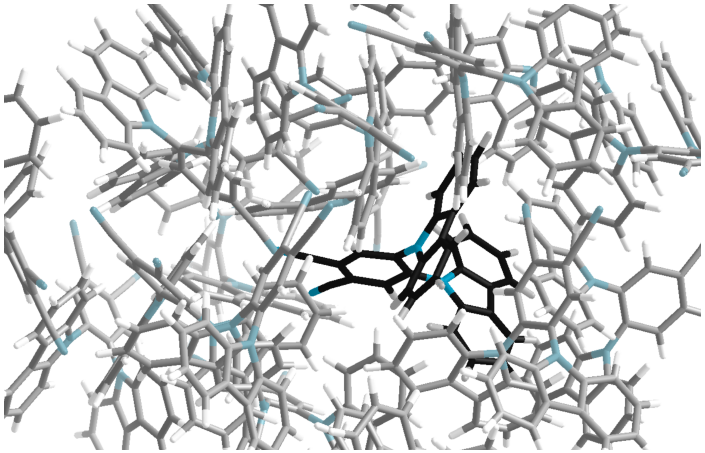
Towards More Sustainable OLEDs

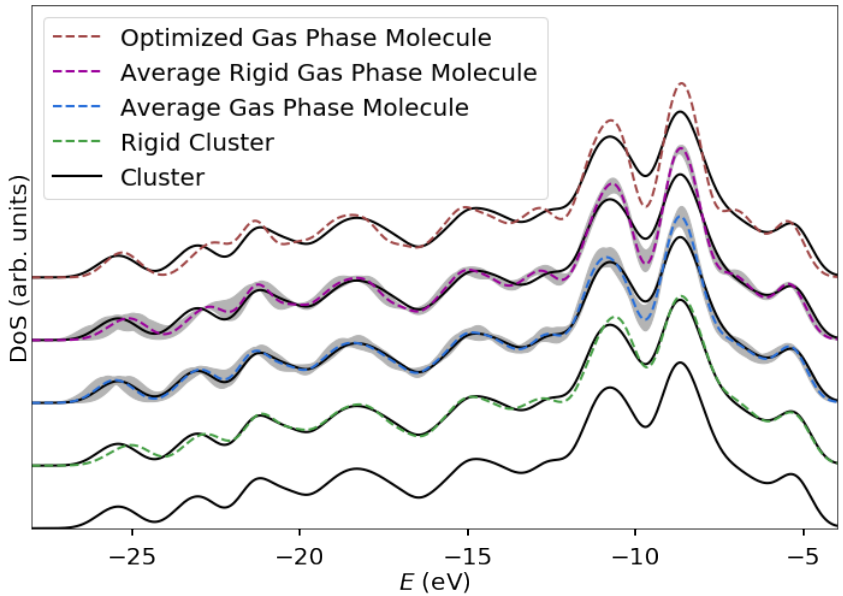
Ground State of 2CzPN

- current OLEDs rely on Ir, Pt $\rightarrow$ unsustainable
- thermally activated delayed fluorescence – efficient and purely organic, e.g. 2CzPN
- 50 molecule cluster extracted from MD run







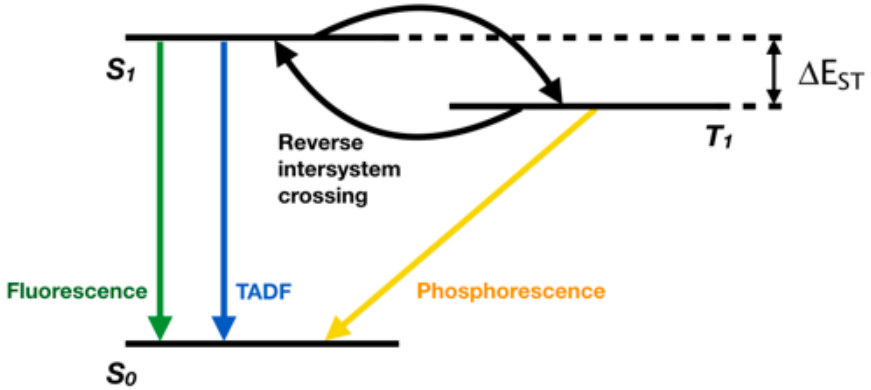


MD snapshot: Olivier *et al.*, Phys. Rev. Mater. **1**, 075602 (2017)

TADF and Excited States I

Beyond the Ground State

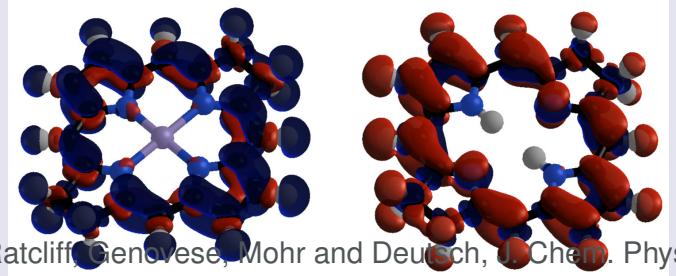
- need small ΔE_{ST}
- mix of charge transfer and local excitations



CDFT and CT Excitations

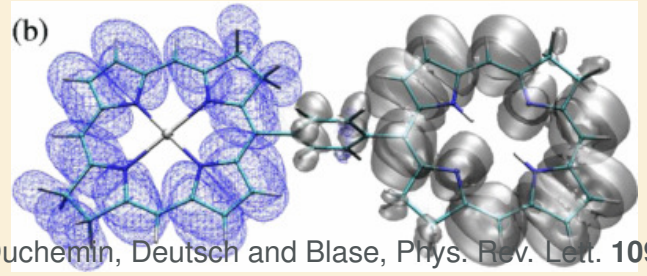
- TDDFT – expensive, issues with long range CT
- CDFT – cheap, can treat long range CT excitations

CDFT



Ratcliff, Genovese, Mohr and Deutsch, J. Chem. Phys. **142**, 234105 (2015)

MBPT



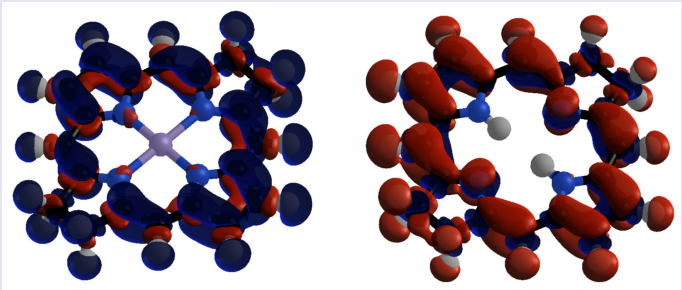
Duchemin, Deutsch and Blase, Phys. Rev. Lett. **109**, 167801 (2012)

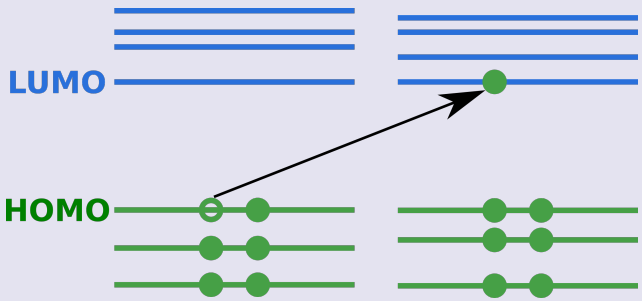
TADF and Excited States II

Charge Transfer vs. Localized Excitations

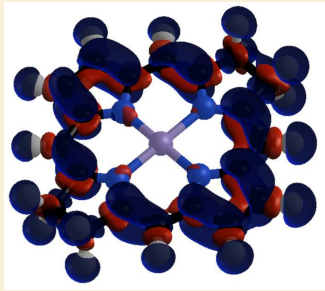
- CT states – can use (fragment based) spatial constraint
- LE states – impose a constraint between orbitals

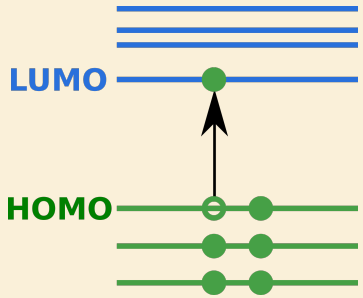
CT – Spatial Constraint





LE – Orbital Constraint

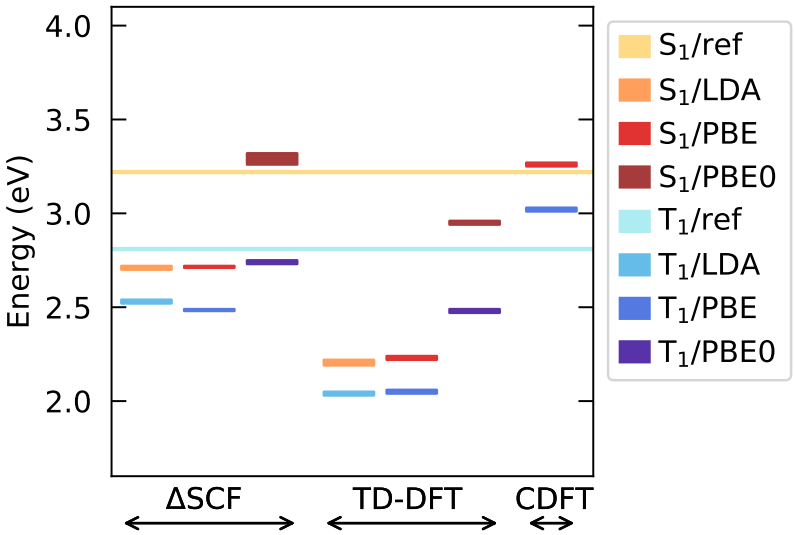




Gas Phase CDFT Benchmarks: 2CzPN

Vertical Excitations

- assume pure transition (HOMO→LUMO only)
- use cubic scaling wvfns as basis
- compare excited state approaches with CDFT/PBE
- reference – TDA with tuned range separated functional



	vertical		adiabatic
	S_1	ΔE_{ST}	ΔE_{ST}
2CzPN			
CDFT/PBE	3.26	0.24	-
TDDFT/PBE	2.23	0.18	-
TDA/RS[1]	3.22	0.41	0.24
exp.[2]	3.19	-	0.31

1. Sun, Zhong and Brédas, J. Chem. Theory Comput. **11** 3851 (2013)
2. Huang *et al.*, J. Chem. Theory Comput. **9** 3872 (2013)

Stella, Thapa, Genovese and Ratcliff, in preparation (2020)

From Cubic Scaling to Multiscale

Across Lengthscales

- extended orbitals $\rightarrow O\left(N^3\right)$
- exploit locality $\rightarrow O(N)$
- exploit repetition $\rightarrow \downarrow$ cost $O(N)$
- larger systems $\rightarrow$ increasing complexity
- $\rightarrow$ how to treat complex systems?