Imperial College London

THE THOMAS YOUNG CENTRE TYC

Upscaling DFT Capabilities for the Many Thousand Atoms Regime

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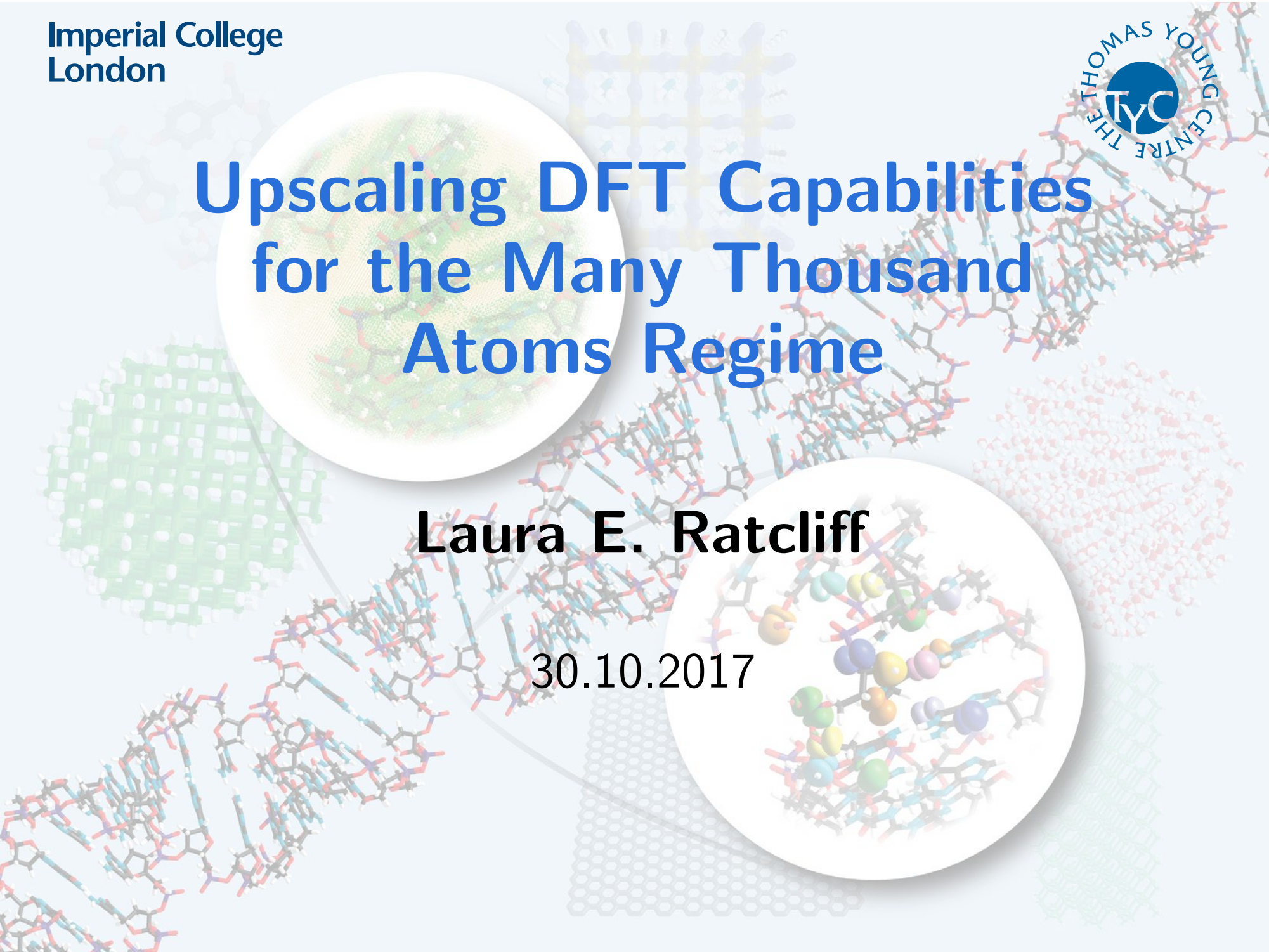
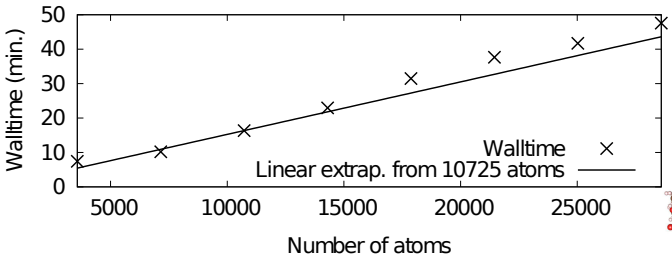
30.10.2017

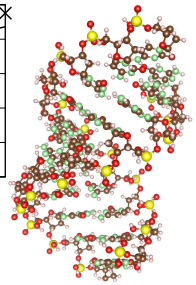


Outline

Linear-Scaling DFT

QM of large systems





BigDFT

www.bigdft.org

ONETEP

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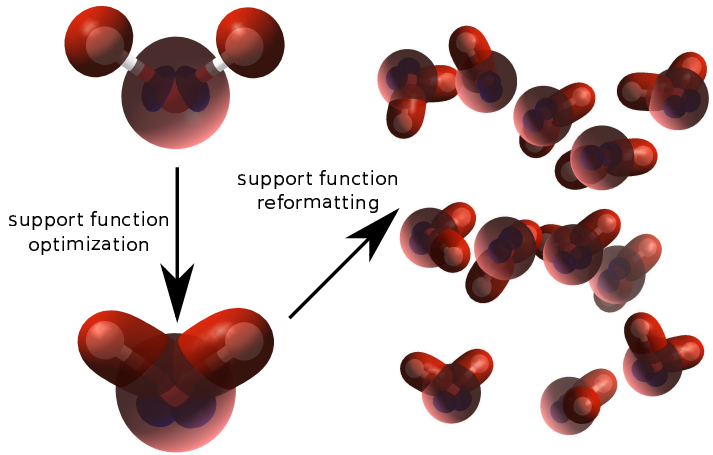
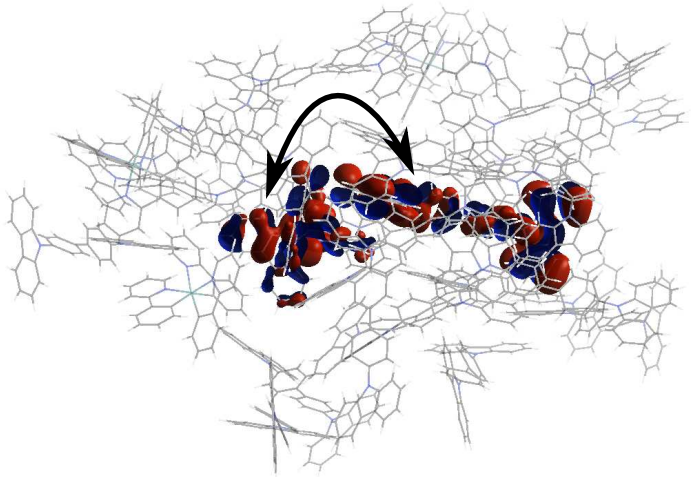
Fragment Approach

exploiting repetition



Simulating OLEDs

excitations in an environment

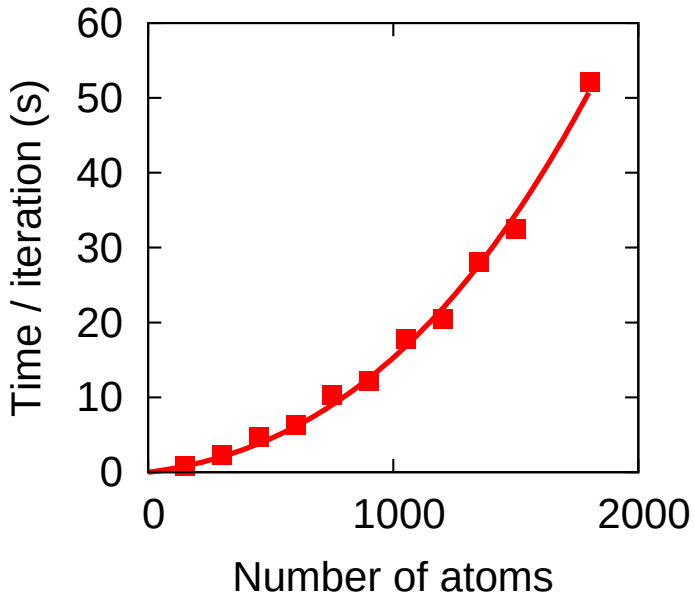


Outline

Beyond the Cubic-Scaling Limit

Size Limits

thanks to supercomputers we can treat up ~ 1000 atoms with DFT, but $\mathcal{O}(\mathcal{N}^3)$ scaling limits system sizes



Nearsightedness

- the behaviour of large systems is short-ranged, or "nearsighted"
- the density matrix decays exponentially in systems with a gap

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

Key Quantities

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 (user-defined radius)
- atom-centred
- expanded in systematic basis

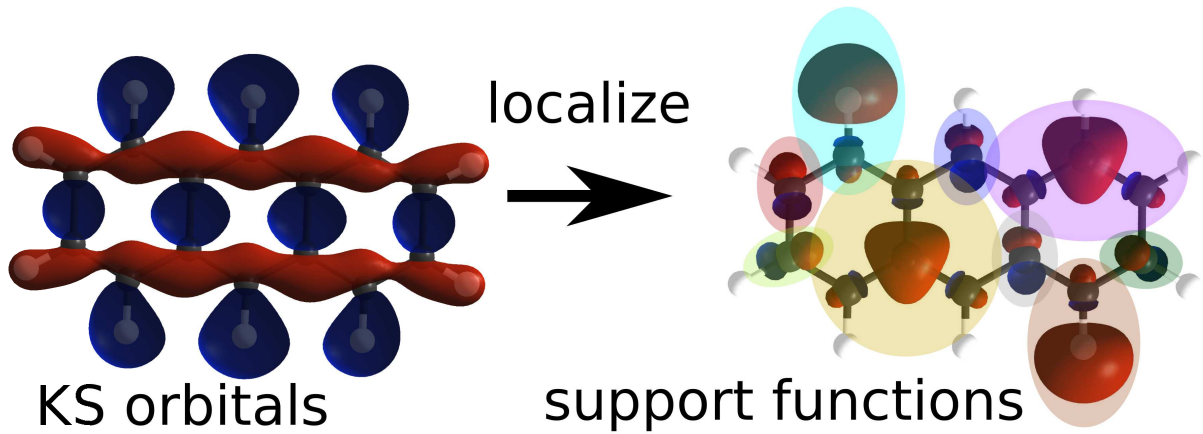
Density Kernel

define the density matrix $\rho(\mathbf{r}, \mathbf{r}')$ and kernel $K^{\alpha\beta}$:

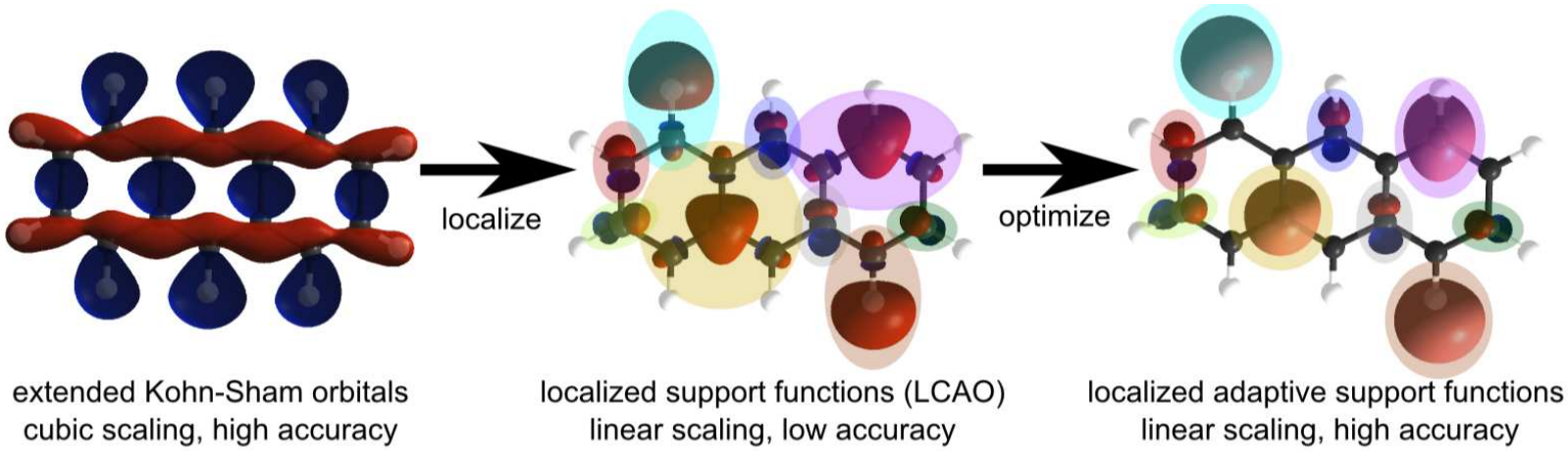
$$\begin{aligned}\rho(\mathbf{r}, \mathbf{r}') &= \sum_i f_i \left|\Psi_i(\mathbf{r})\right\rangle\left\langle\Psi_i(\mathbf{r}')\right| \\ &= \sum_{\alpha,\beta} \left|\phi_\alpha(\mathbf{r})\right\rangle K^{\alpha\beta}\left\langle\phi_\beta(\mathbf{r}')\right|\end{aligned}$$

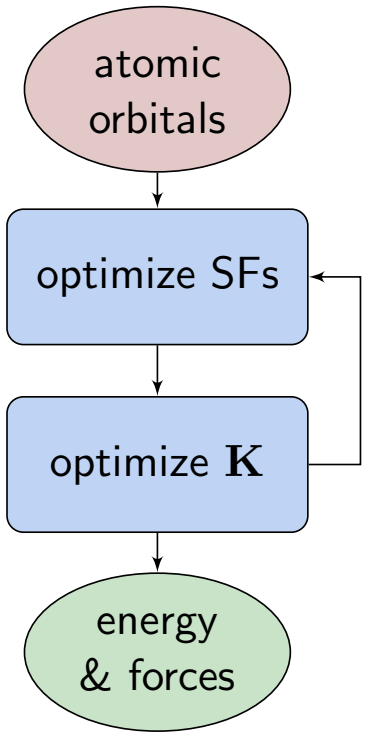
Total Energy

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



The Algorithm





Accurate Minimal Basis

- energy is minimized with respect to both SFs and kernel
- SFs adapt to the environment
- different options for kernel optimization: Fermi Operator Expansion (FOE), penalty functional, purification, LNV...

$\Rightarrow$ minimal, localized basis with the same high accuracy as underlying systematic basis

Basis Sets – Psincs and Wavelets

Common Features

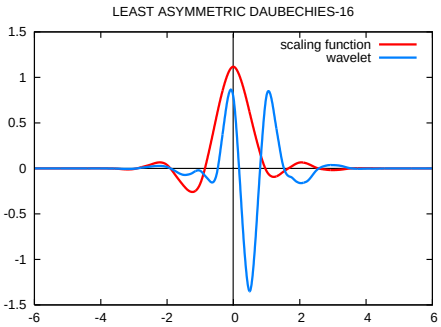
- localized
- orthogonal
- systematic
- use of PSPs

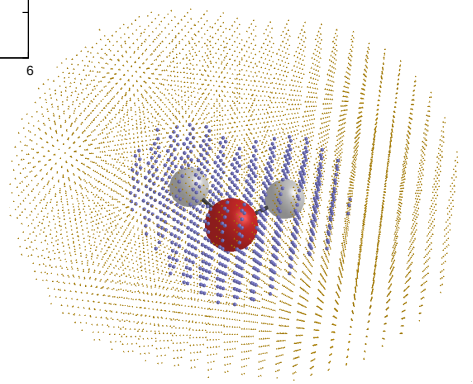
Wavelet Features

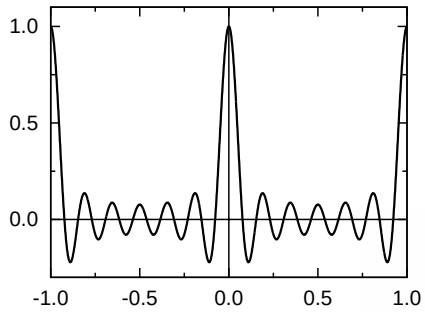
- flexible boundary conditions
- analytic operators
- multiresolution grid: 1 grid, 2 resolution levels

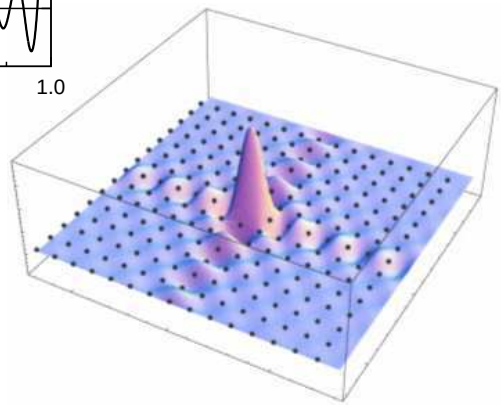
Psinc Features

- periodic boundary conditions
- equivalence with plane waves
- regular grid: 1 psinc function centred at each grid point









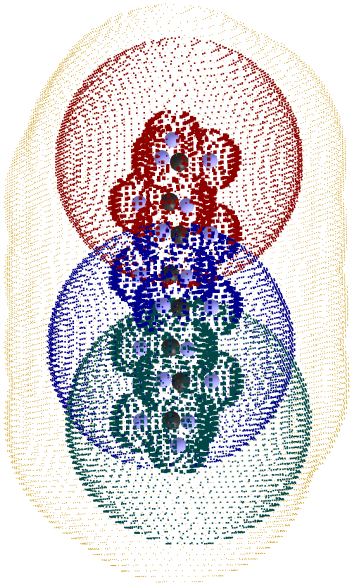
Support Functions

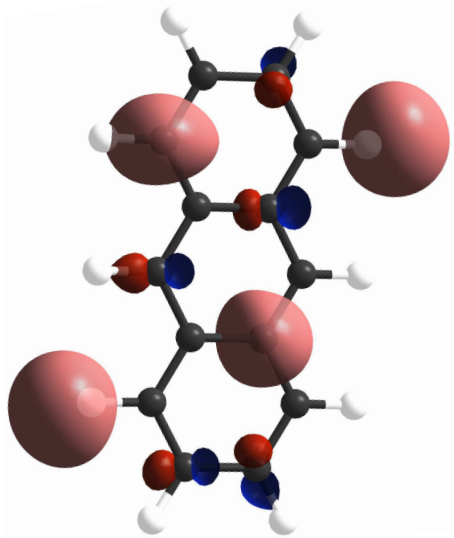
Common Features

- strict localization ($\sim 6 - 8$ bohr)
- minimal number: e.g. 1 SF per H, 4 per C/N/O etc.

BigDFT

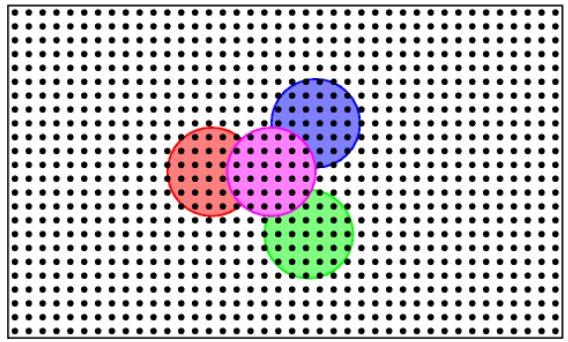
- quasi-orthogonal SFs
- use of a confining potential

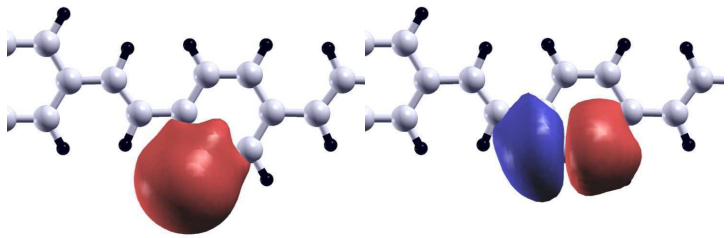




ONETEP

- Non-orthogonal Generalized Wannier Functions (NGWFs)

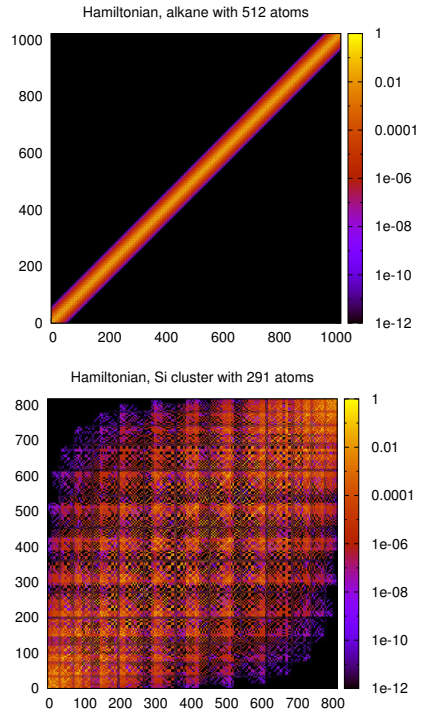


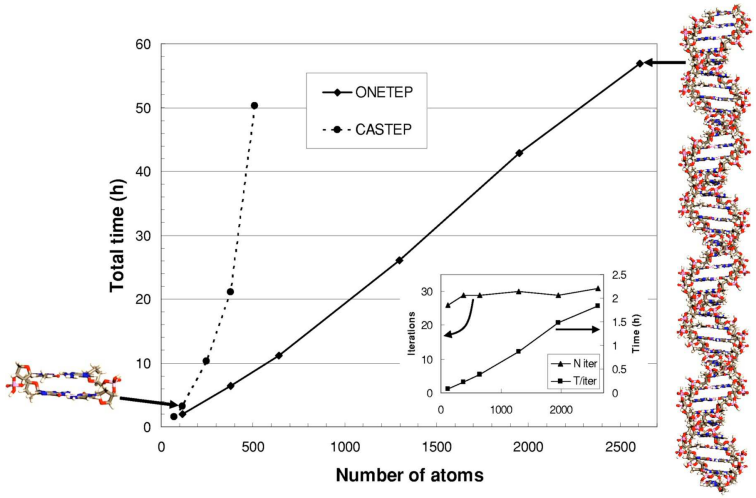


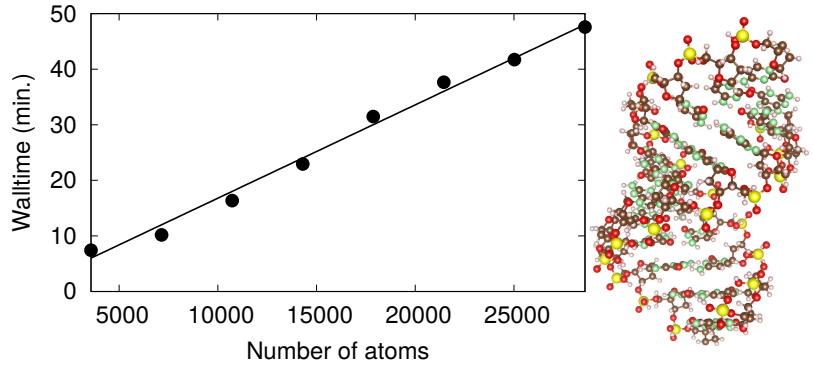
From Sparsity to Linear Scaling

Sparse Matrices

- strict localization leads to sparse matrices
- sparsity depends on size and dimensionality
- make use of sparse matrix algebra
- sparsity impacts crossover point







$\mathcal{O}(\mathcal{N})$ DFT

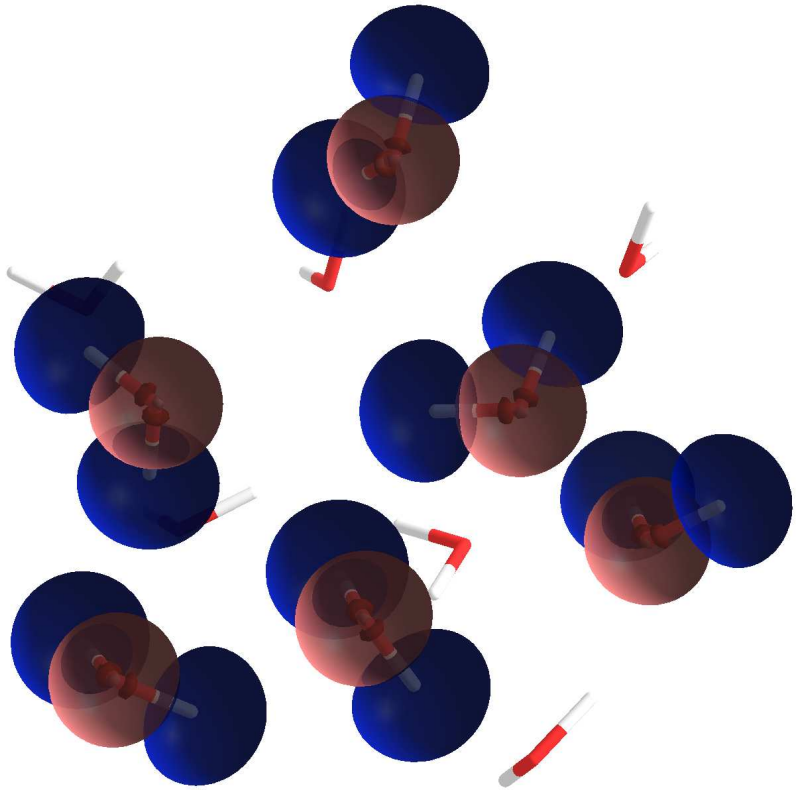
- can treat 1000s of atoms using DFT at a high accuracy
- many functionalities and features available

Outline

Exploiting Repetition

Calculation Bottleneck

- SF optimization takes the majority of compute time
- what happens in similar chemical environments?



Water Droplet

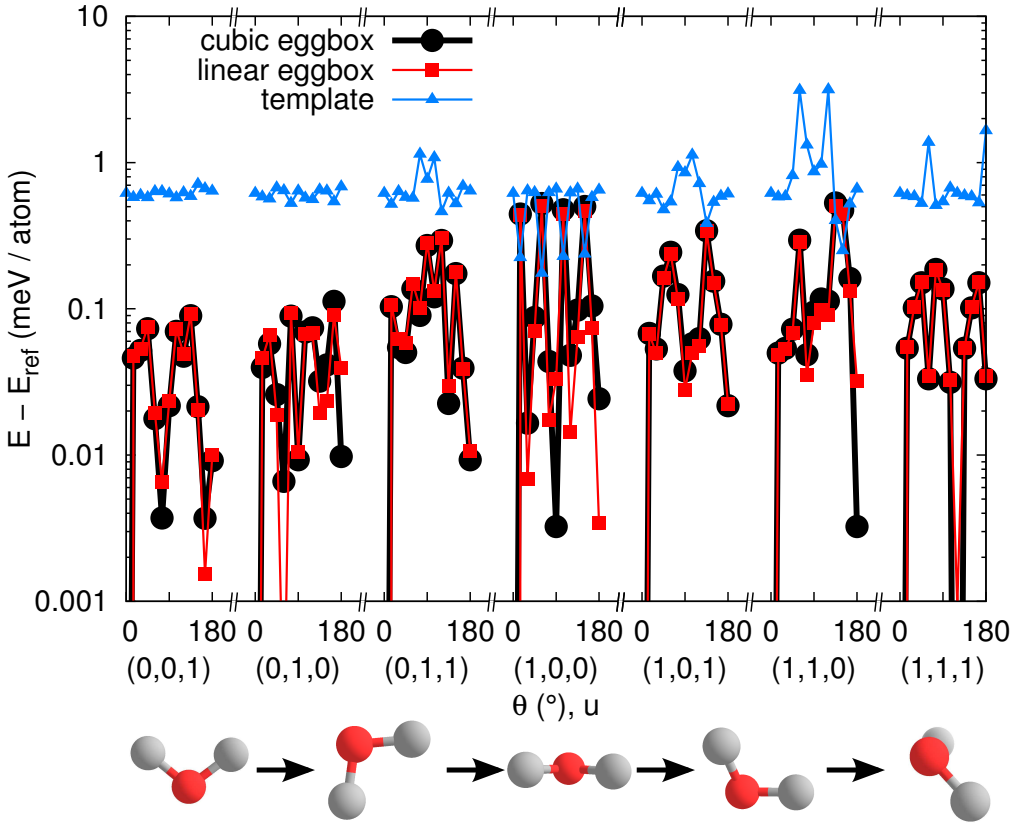
- internal molecular environment dominates
- differences between water molecules are small
- can we use the same SFs for each molecule?

Reformatting

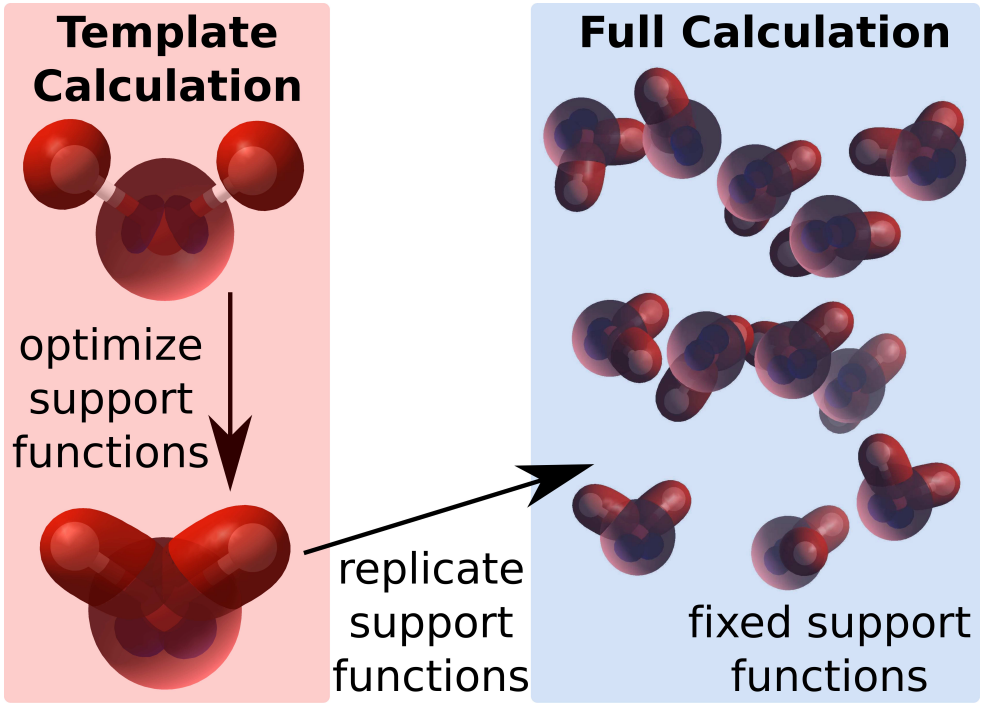
Rototranslations

how do we account for varying orientations and positions?

- scheme to detect rototranslations with respect to reference ("template") coordinates
- accurate and efficient wavelet interpolation scheme



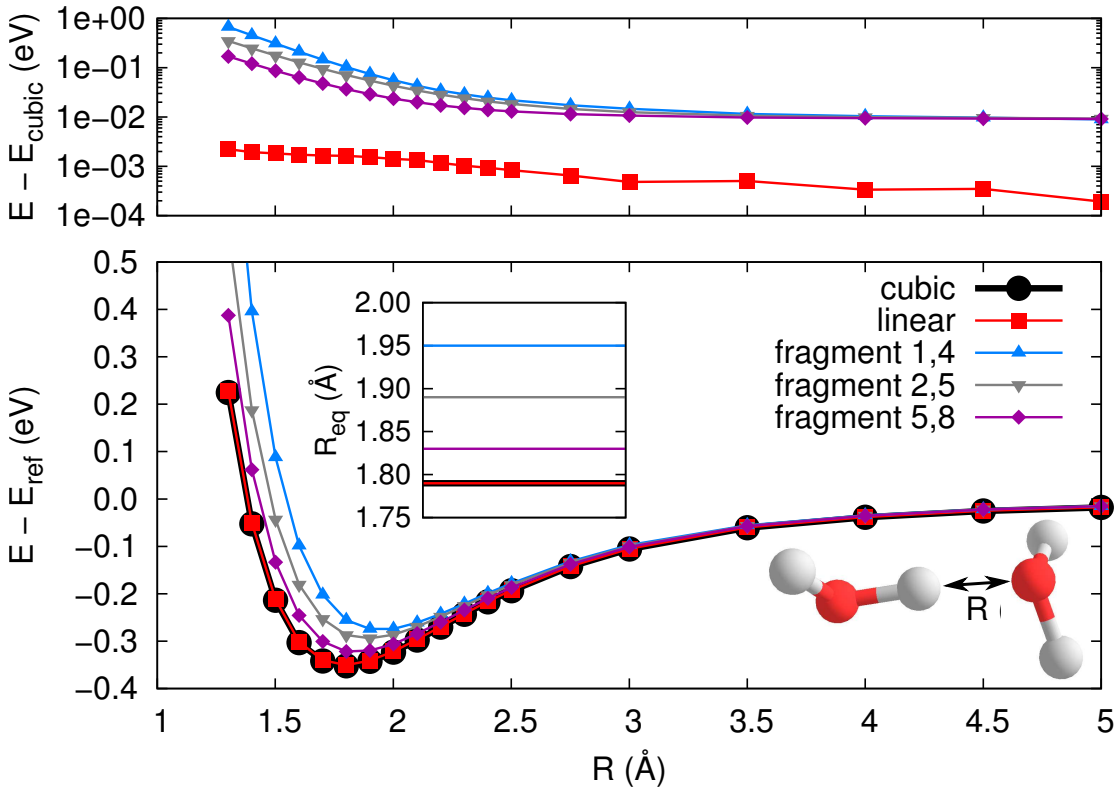
Fragment Approach



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

Fragments in Action



H_2O Dimer

- energies affected by basis set superposition error
- but equilibrium bond length less affected
- can increase basis to improve accuracy
- approach is suited to weakly interacting fragments

Constrained DFT I

Constrained DFT (CDFT)

- wavelet basis is ideal for adding a (constrained) charge
- in CDFT we find the lowest energy state satisfying a given (charge) constraint on the density
- we want to associate a given charge with a particular fragment
- can be used to reduce the self-interaction problem and include environmental effects on site energies

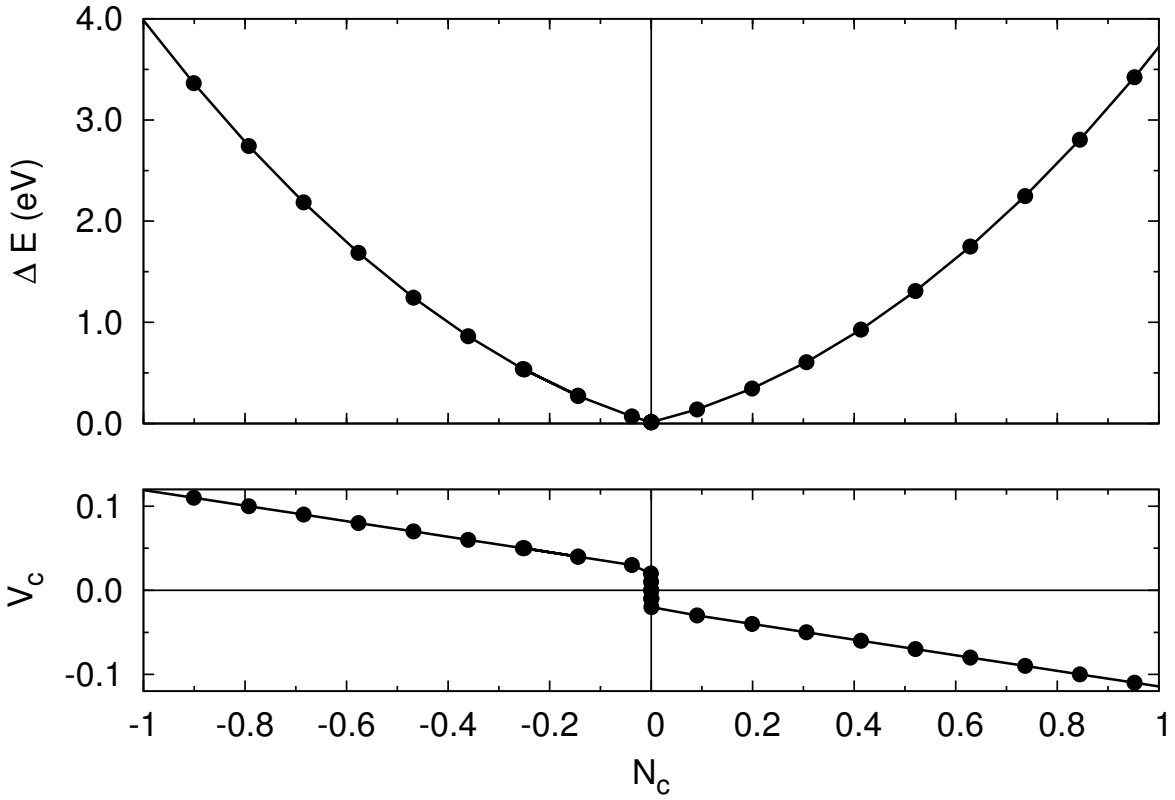
CDFT with SFs

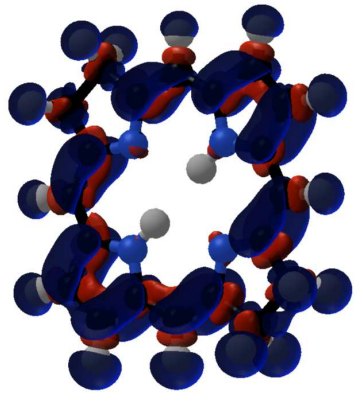
$$W\left[n, V_c\right] = E_{\mathsf{KS}}\left[n\right] + V_c\left(2\mathrm{Tr}\left[\mathbf{K}\mathbf{w_c}\right] - N_c\right)$$

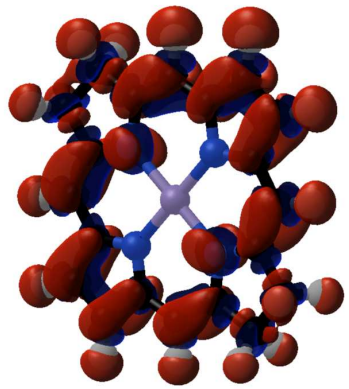
The SF basis lends itself to a Löwdin like approach for the weight function:

$$\mathbf{w_c} = \mathbf{S}^{\frac{1}{2}}\mathbf{P}\mathbf{S}^{\frac{1}{2}}$$

Constrained DFT II





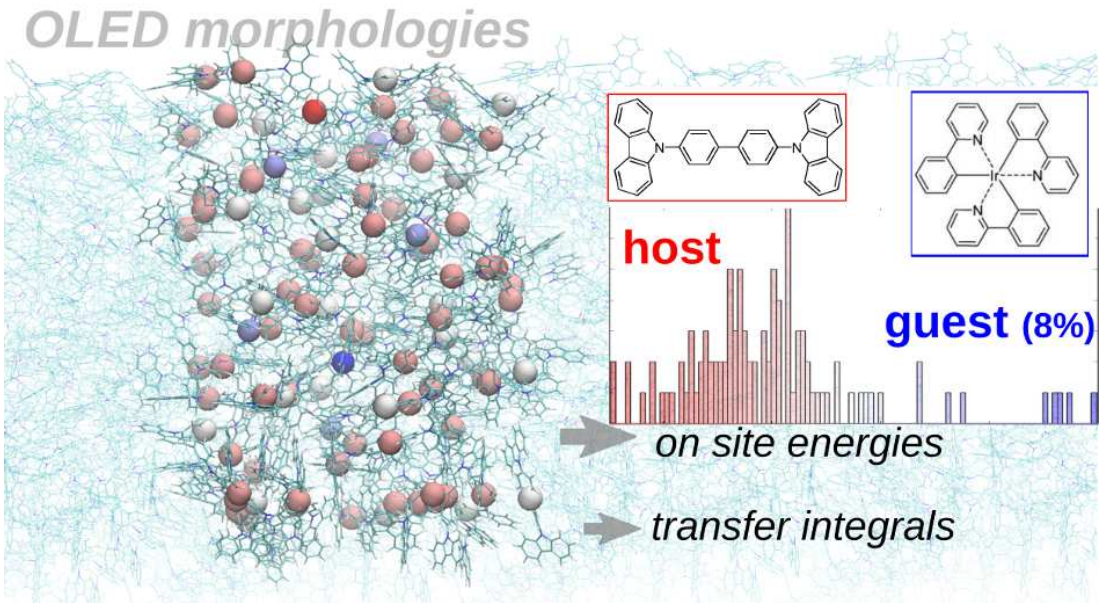


ZnBC-BC complex

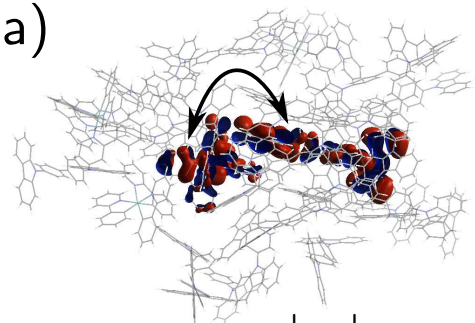
- varying charge separation between two molecules
- can find charge transfer states

Outline

OLED Transport Parameters

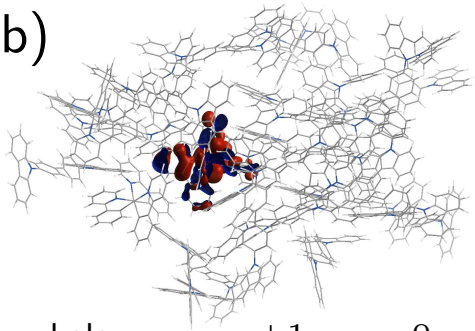


(a)



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

(b)

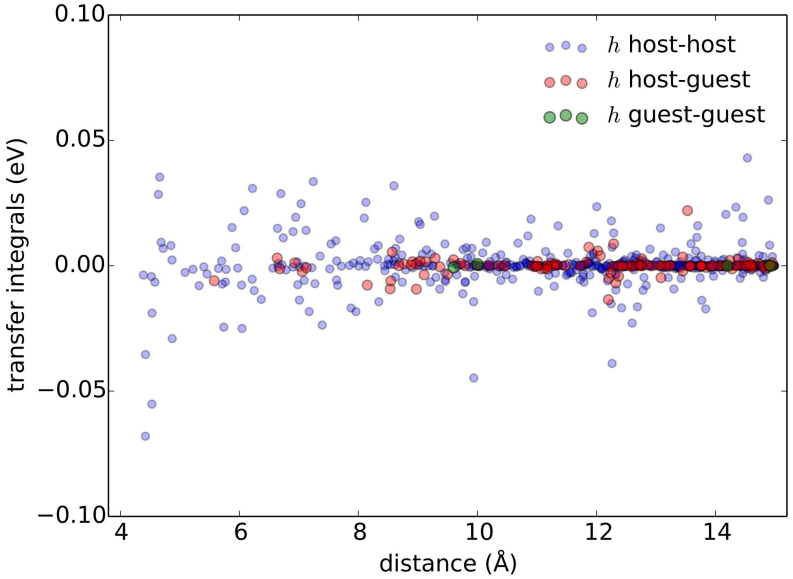


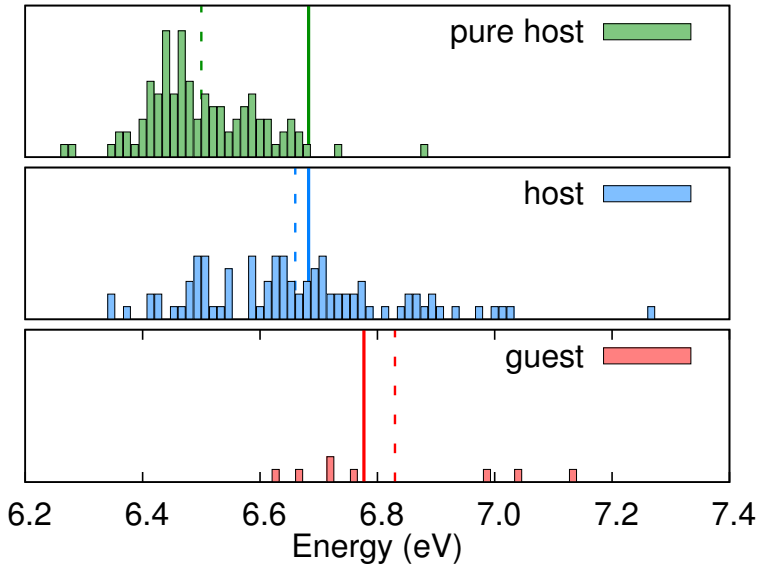
$$E_{\text{on-site}}^{\text{hole}} = E_{\text{tot}}^{+1} - E_{\text{tot}}^{0}$$

Fragments in Disordered Host-Guest Material

- extract cluster of nearest neighbours for each molecule
- template calculations for isolated host and guest molecules
- use fragment basis to calculate transfer integrals in clusters (a)
- use CDFT to add charge to central molecule in each cluster
- calculate on site energies using CDFT results (b)

OLED Transport Parameters





Statistics

- disorder $\Rightarrow$ dispersion of values for $E_{\text{on-site}}$ and J_{ij}

Environmental Effects

- shift in average $E_{\text{on-site}}$ (- - -) vs. isolated molecules (—)
- differences between pure host and host guest materials

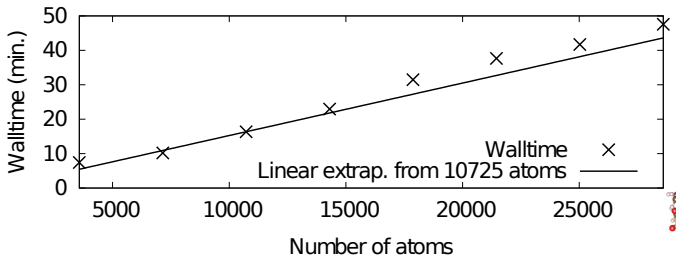
Future Challenge for Simulating OLEDs

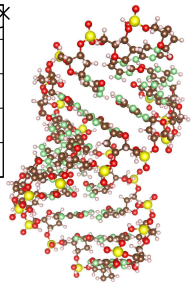
improve the description of excitations in realistic morphologies

Summary

Linear-Scaling DFT

QM of large systems





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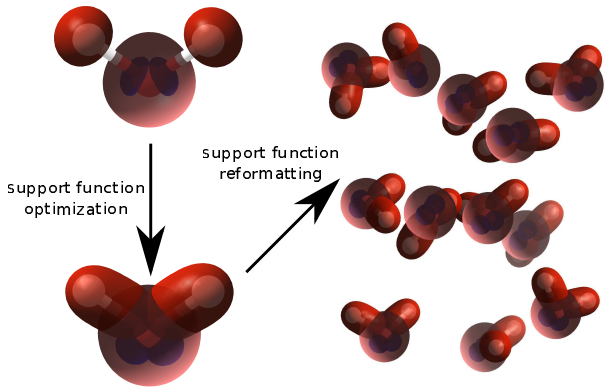

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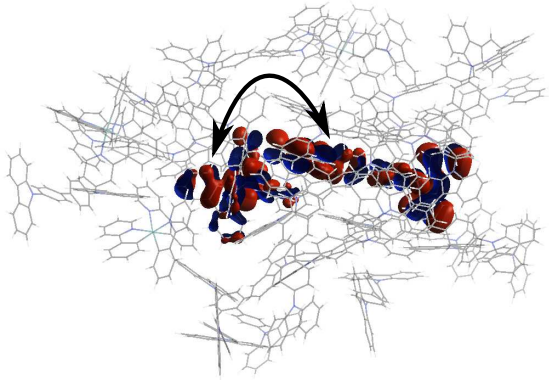

PhD and postdoc position available

Thank you for your attention!