

Quantum embedding in ONETEP

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ONETEP Masterclass

23rd August 2023



Quantum embedding

EMFT in ONETEP

Time-dependent EMFT in ONETEP

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- ▶ Meta-GGAs (rSCAN, ...) – somewhere between above choices, but less developed

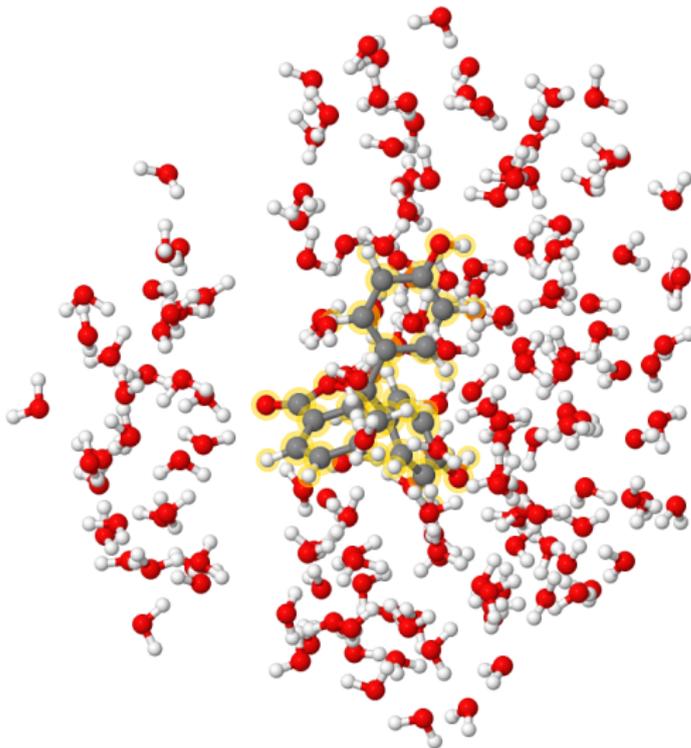
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 - ▶ For example, hybrid DFT for quantitatively correct band gaps for several thousand atoms?
- ▶ **Solution:** If interesting physics/chemistry is localised on an 'active region', but is influenced by the environment, we can use embedding:
 - ▶ Treat environment at a low level of theory, and active region at a high level, within a single calculation
 - ▶ Reduces cost for minimal reduction in accuracy
 - ▶ Self-consistent

Schematic embedding system



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- ▶ But quantum effects often important – need to describe environment quantum mechanically
- ▶ \therefore *quantum* embedding schemes
- ▶ Extend the size of system accessible quantum mechanically whilst maintaining accuracy
- ▶ Quantum embedding combined with linear-scaling DFT would allow very large systems to be studied very accurately

Embedded mean-field theory

Scheme used here is embedded mean-field theory (EMFT)¹

- ▶ Partition basis functions (NGWFs) into active region (A) and environment (B)
- ▶ Similarly block partition density kernel K

$$\{\phi\} = \{\phi^A, \phi^B\}$$

$$K = \begin{pmatrix} K_{AA} & K_{AB} \\ K_{BA} & K_{BB} \end{pmatrix}$$

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- ▶ Write total energy as sum of one- and two-electron parts
- ▶ Assume levels of theory are only different in $E_{2\text{-el}}$

$$E[K, \{\phi\}] = E_{1\text{-el}}[K, \{\phi\}] + E_{2\text{-el}}[K, \{\phi\}]$$

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- ▶ EMFT total energy is then given as shown

$$E^{\text{EMFT}} [K, \{\phi\}] = E_{1\text{-el}} [K, \{\phi\}] + E_{2\text{-el}}^{\text{low}} [K, \{\phi\}] + \left(E_{2\text{-el}}^{\text{high}} [K_{AA}, \{\phi^A\}] - E_{2\text{-el}}^{\text{low}} [K_{AA}, \{\phi^A\}] \right)$$

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Advantages

- ▶ In principle, very simple and very general
- ▶ Partitions naturally along atomic basis functions
- ▶ No need for *a priori* information: bonding, charges of subregions
- ▶ No chemical termination of subregions required
- ▶ Interaction and entanglement between regions naturally included
- ▶ Previous successes²
- ▶ Easy to extend to obtain response theories, e.g. TDDFT³

²J Chem Theory Comput: 11, 568 (2015); 12, 5811 (2016); 13, 4216 (2017)

³J Chem Theory Comput 13, 4216 (2017)

Block orthogonalisation

- ▶ Normalisation is maintained as long as $\text{Tr}[KS] = N_e$
- ▶ However, upon partitioning, charge spillover can occur
- ▶ Diagonal terms in this trace become unphysically large, being balanced by large negative values for off-diagonal terms
- ▶ This can be avoided by block orthogonalisation – forcing the environment orbitals to be orthogonal to the active region's

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ONETEP implementation

- ▶ ONETEP is a DFT code – hence only DFT-in-DFT embedding
- ▶ Intended mode of use is hybrid-in-semi-local (e.g. B3LYP-in-PBE)
- ▶ Previous EMFT implementations used Gaussian basis sets – unoptimised
- ▶ Block orthogonalisation interferes with NGWF optimisation
- ▶ Instead, can converge NGWFs at lower level of theory, and optimise only kernel with EMFT

Theory

- ▶ We partition the Hamiltonian, using different levels of theory for different blocks
- ▶ Total energy is obtained by minimising $\text{Tr} [KH^{\text{EMFT}}]$

$$H^{\text{EMFT}} = \begin{pmatrix} H_{AA}^{\text{high}} & H_{AB}^{\text{low}} \\ H_{BA}^{\text{low}} & H_{BB}^{\text{low}} \end{pmatrix}$$

$$\hat{H}^{\text{high}} = \hat{T} + \hat{V}_{\text{local}} + \hat{V}_{\text{Hartree}} + \hat{V}_{\text{XC}}^{\text{high}}$$

$$\hat{H}^{\text{low}} = \hat{T} + \hat{V}_{\text{local}} + \hat{V}_{\text{Hartree}} + \hat{V}_{\text{XC}}^{\text{low}}$$

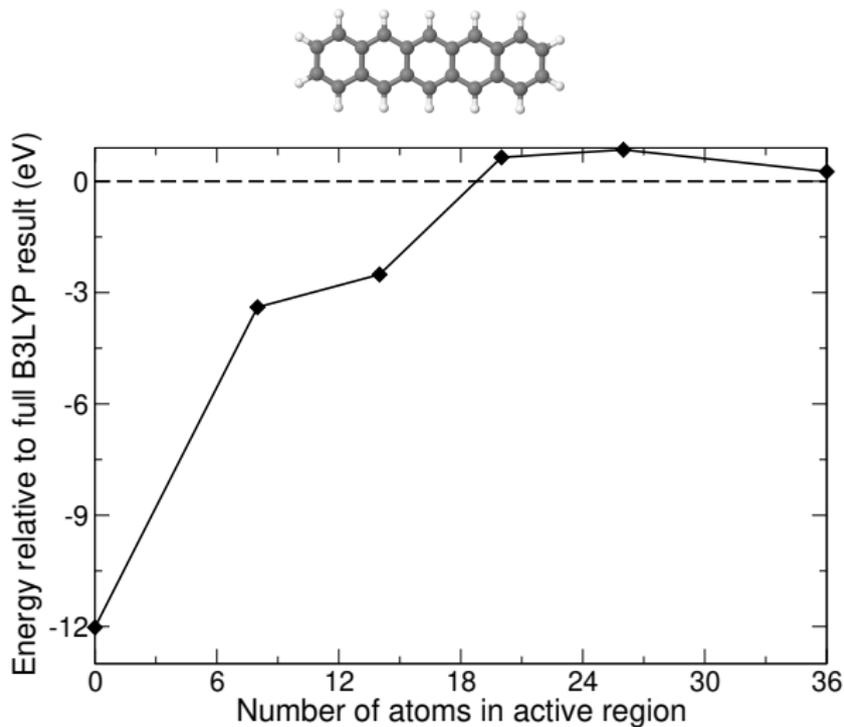
Theory

- ▶ V_{XC}^{low} is calculated from the total electron density (i.e. the full system NGWFs and kernel)
- ▶ $V_{XC}^{low,A}$ and $V_{XC}^{high,A}$ is calculated from the active region density (i.e. K_{AA} and the active region NGWFs), using the appropriate levels of theory
- ▶ Finally, $V_{XC}^{high} = V_{XC}^{low} + \left(V_{XC}^{high,A} - V_{XC}^{low,A} \right)$

Exact exchange with EMFT

- ▶ Exact exchange isn't calculated from partitioned electronic density, so how do we include it?
 - ▶ EX0: Only exchange *within* the active region is included
 - ▶ EX1: Inter-region exchange is symmetrically averaged
 - ▶ EX2: Full exchange interaction between regions
- ▶ EX0 comparable in accuracy or better than others, at a much lower cost – this is what is implemented
- ▶ This means calculating inter-region exact exchange is not implemented – hybrid-in-hybrid calculations will give a different result to a single-region calculation

Results



Example input file

```
%block species
H H 1 1 9.0
C C 6 4 9.0
H1 H 1 1 9.0
C1 C 6 4 9.0
%endblock species
%block species_ngwf_regions
C1 H1
C H
%endblock species_ngwf_regions
%block species_swri-for_hfx
C1
H1
%endblock species_swri-for_hfx
```


Example input file

```
task : singlepoint
cutoff_energy : 750 eV
xc_functional : PBE
active_xc_functional : B3LYP
use_emft : T
use_emft_follow : T
use_emft_lnv_only : T
block_orthogonalise : T
parallel_scheme : HOUSE
active_region : 1
```

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TD-EMFT in ONETEP

- ▶ As noted before, linear-response theories are easy to add onto EMFT framework
- ▶ For LR-TDDFT, need second derivative of E_{xc}

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- ▶ Easy to calculate using EMFT:

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}^{\text{low}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} + \frac{\delta^2 E_{xc}^{\text{high}}[\rho_{AA}]}{\delta\rho_{AA}(\mathbf{r})\delta\rho_{AA}(\mathbf{r}')} - \frac{\delta^2 E_{xc}^{\text{low}}[\rho_{AA}]}{\delta\rho_{AA}(\mathbf{r})\delta\rho_{AA}(\mathbf{r}')}$$

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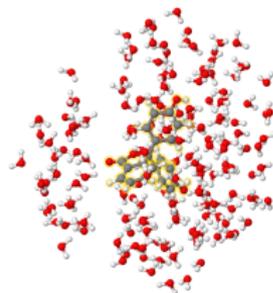
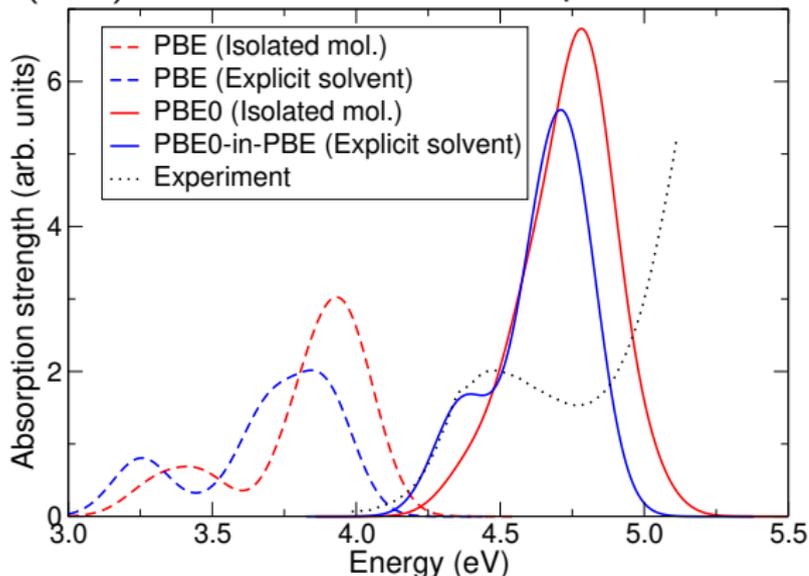
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- ▶ Input file same as normal (plus previously shown EMFT additions) – but advisable to restrict TDDFT kernel to active region (or smaller):
 - ▶

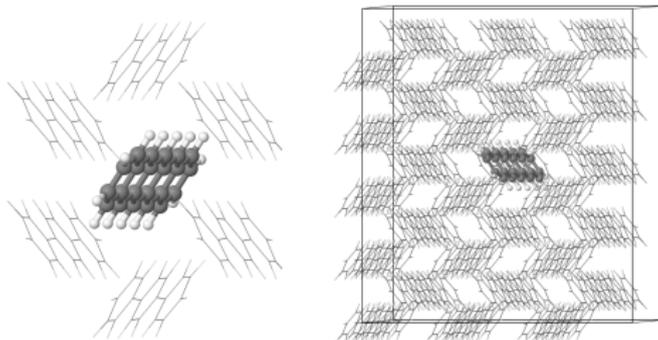
```
%block species_tddft_kernel  
C1 H1  
%endblock species_tddft_kernel
```

TD-EMFT results – phenolphthalein in water

(TD-)EMFT combined with implicit solvent = multi-level model!



Exp data from J Am Chem Soc 48, 1994 (1926)

TD-EMFT results – pentacene-doped *p*-terphenyl

Configuration	$\Delta E_{S_0 \rightarrow S_1}$ (eV)		
	PBE	B3LYP-in-PBE	Exp.
Vacuum	1.880	2.198	2.31
Cluster	1.792	2.069	2.09
Crystal	1.810	2.089	

Exp data from Chem Phys Lett 250, 137 (1996) & JCP 109, 906 (1998)

References

Ground state EMFT: J C A Prentice, R J Charlton, A A Mostofi & P D Haynes, J Chem Theory Comput 16, 354 (2020)

TD-EMFT: J C A Prentice, J Chem Theory Comput 18, 1542 (2022)

Any questions?

Funded by:



Computational Electronic Structure of Condensed Matter



**Engineering and
Physical Sciences
Research Council**

Thank you for your attention!