

# Embedded mean field theory in ONETEP

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## Quantum embedding

Embedded mean-field theory

EMFT in ONETEP

Hartree-Fock exchange with EMFT

# Why embedding?

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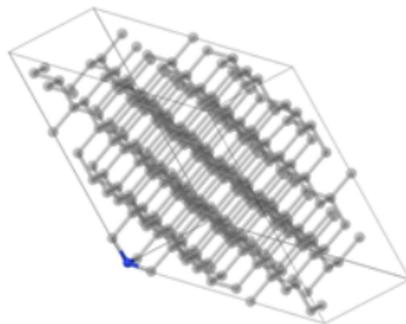


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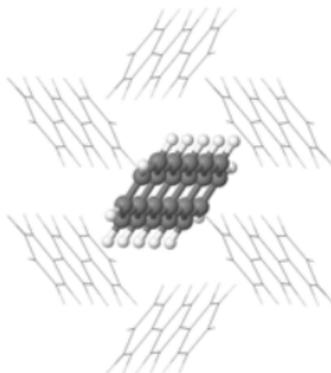


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- ▶ ∴ quantum embedding schemes

# Quantum embedding schemes

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THE JOURNAL OF CHEMICAL PHYSICS    VOLUME 55, NUMBER 12    15 DECEMBER 1971

## Theory of Separability of Many-Electron Systems

S. HUZINAGA AND A. A. CANTU

*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada*

(Received 10 May 1971)

Atomic and molecular systems are often intuitively separated into almost independent subsystems as, for example, the core and valence parts of an atom. Consequently, if this separation provides a good approximation, one can obtain the states of the system from the states of the subsystems which best represent the entire system. In the light of the work of McWeeny, in which one assumes strong orthogonality among subsystem wavefunctions, we determine an effective Hamiltonian for a given subsystem which should properly describe the states of that subsystem. Previous work is shown to have dealt with an improper effective Hamiltonian.

# Quantum embedding schemes

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THE JOURNAL OF CHEMICAL PHYSICS **133**, 084103 (2010)

## Exact nonadditive kinetic potentials for embedded density functional theory

Jason D. Goodpaster,<sup>1</sup> Nandini Ananth,<sup>1</sup> Frederick R. Manby,<sup>2</sup> and Thomas F. Miller III<sup>1,a)</sup>

<sup>1</sup>*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

<sup>2</sup>*Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol BS8 ITS, United Kingdom*

(Received 26 April 2010; accepted 12 July 2010; published online 23 August 2010)

# Quantum embedding schemes

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**JCTC**

Journal of Chemical Theory and Computation

Letter

pubs.acs.org/JCTC

## A Simple, Exact Density-Functional-Theory Embedding Scheme

Frederick R. Manby,<sup>\*,†</sup> Martina Stella,<sup>†</sup> Jason D. Goodpaster,<sup>‡</sup> and Thomas F. Miller, III<sup>‡</sup>

<sup>†</sup>Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol B88 1TS, United Kingdom

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Article

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## Embedded Mean-Field Theory

Mark E. Fornace,<sup>†,¶</sup> Joonho Lee,<sup>†,¶</sup> Kaito Miyamoto,<sup>‡,¶</sup> Frederick R. Manby,<sup>\*,‡</sup>  
and Thomas F. Miller, III<sup>\*,†</sup>

<sup>†</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

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Difficulty lies in making sure active region's orbitals remain  
orthogonal to environment's

Scheme we have chosen to implement is embedded mean-field  
theory (EMFT)

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# Theory

- ▶ Begin by partitioning density matrix by basis function

$$\rho = \begin{pmatrix} \rho_{AA} & \rho_{AB} \\ \rho_{BA} & \rho_{BB} \end{pmatrix}$$

# Theory

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- ▶ Separate total energy into one- and two-electron parts

$$E[\rho] = \text{tr}[\rho H_0] + G[\rho]$$

# Theory

- ▶ Begin by partitioning density matrix by basis function
- ▶ Separate total energy into one- and two-electron parts
- ▶ EMFT total energy is then given as shown
- ▶ Ground state found by minimising this as usual

$$E^{\text{EMFT}}[\rho] = \text{tr}[\rho H_0] + G^{\text{low}}[\rho] + \left( G^{\text{high}}[\rho_{AA}] - G^{\text{low}}[\rho_{AA}] \right)$$

## 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
- ▶ Simple to extend to obtain response theories, e.g. TDDFT<sup>1</sup>
- ▶ Previous successes<sup>2</sup>

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<sup>1</sup>JCTC 13, 4216 (2017)

<sup>2</sup>JCTC: 11, 568 (2015); 12, 5811 (2016); 13, 4216 (2017)

## Block orthogonalisation

- ▶ Normalisation is maintained as long as  $\text{Tr}[\rho S] = N_e$
- ▶ 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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## Considerations

- ▶ 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 implementations used Gaussian basis sets – unoptimised
- ▶ Block orthogonalisation makes NGWF optimisation much more difficult – see similar charge spilling problems
- ▶ 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  $\text{Tr} [\mathbf{K}\mathbf{H}^{\text{EMFT}}]$

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

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

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

# Theory

- ▶  $V_{XC}^{\text{low}}$  is calculated from the total electron density (i.e. the full system NGWFs and kernel)

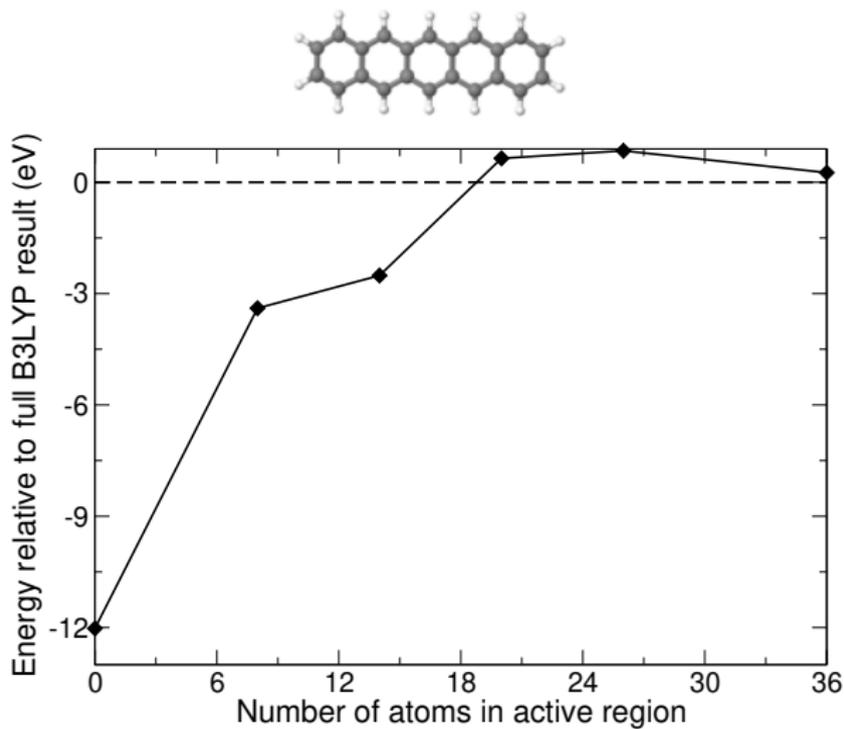
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- ▶  $V_{XC}^{low}$  is calculated from the total electron density (i.e. the full system NGWFs and kernel)
- ▶  $V_{XC}^{low,A}$  and  $V_{XC}^{high,A}$  is calculated from the active region density (i.e.  $K_{AA}$  and the active region NGWFs), using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

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- ▶  $V_{XC}^{low}$  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,  $V_{XC}^{high} = V_{XC}^{low} + \left( V_{XC}^{high,A} - V_{XC}^{low,A} \right)$

# 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
do_fandt : F
freeze_switch_steps : -1
use_emft : T
use_emft_follow : T
use_emft_lnv_only : T
block_orthogonalise : T
parallel_scheme : HOUSE
active_region : 1
read_sub_denskern : F
```

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## Exact exchange with EMFT

- ▶ So far haven't really discussed exact exchange – this isn't calculated from the partitioned electronic density
- ▶ Several ways that exact exchange can be included in EMFT:
  - ▶ 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

Now over to James to described a bit more about HFX in general  
in ONETEP...