

Interactive DEMO – Perform DFT based embedding in the cloud

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References

1. [T. Wesolowski, A. Warshel, *J. Phys. Chem.* 97, 8050 \(1993\).](#)
2. [C. Müller, M. Sharma, M. Sierka, *J. Comput. Chem.* 41, 2573 \(2020\)](#)
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5. [R. Łazarski, A.M. Burow, M. Sierka, *J. Chem. Theory Comput.* 11, 3029 \(2015\).](#)
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Poster

Density Functional Embedding Scheme for Molecular and Periodic Systems using Gaussian Basis Functions

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SCAN ME



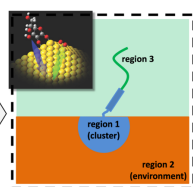
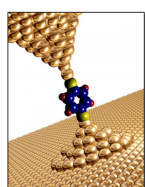
INTRODUCTION

An implementation of density functional embedding theory (DFET), within the frozen density embedding (FDE) formalism^[1], using Gaussian basis functions is presented.

The implementation is coupled with real-time time-dependent DFT (RT-TDDFT)^[2] and wavefunction theory (WFT) methods to perform RT-TDDFT-in-DFT and WFT-in-DFT, respectively.

Highlights: Molecule-in-molecule, molecule-in-periodic and periodic-in-periodic embedding within the TURBOMOLE program package^[3-5].

DENSITY FUNCTIONAL EMBEDDING THEORY (DFET)



The central idea of DFET with a molecule attached to the surface of a nanostructure.

Region 1 (cluster) is the region of interest embedded in region 2 (environment).

Density Functional Embedding Theory
 $E[\rho^{\text{tot}}] = E[\rho^{\text{clu}}] + E[\rho^{\text{env}}] + E^{\text{int}}[\rho^{\text{clu}}, \rho^{\text{env}}]$

Density partition:

$$\rho^{\text{tot}} = \rho^{\text{clu}} + \rho^{\text{env}}$$

Total Energy

$$E[\rho^{\text{tot}}] = E[\rho^{\text{clu}}] + E[\rho^{\text{env}}] + E^{\text{int}}[\rho^{\text{clu}}, \rho^{\text{env}}]$$

The key quantity in DFET is a DFT based embedding potential v_{emb} which can be defined in an approximate or exact manner as

Embedding potential (Approximate)

$$v_{\text{emb}}[\rho^{\text{act}}, \rho^{\text{env}}, v_{\text{nuc}}^{\text{env}}](\mathbf{r}) = v_{\text{nuc}}^{\text{env}}(\mathbf{r}) + \int \frac{\rho^{\text{env}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}^{\text{nadd}}[\rho^{\text{act}}, \rho^{\text{env}}]}{\delta \rho^{\text{act}}(\mathbf{r})} + v_T[\rho^{\text{act}}, \rho^{\text{env}}](\mathbf{r})$$

with non-additive kinetic potential

$$v_T[\rho^{\text{act}}, \rho^{\text{env}}](\mathbf{r}) = \frac{\delta T_s^{\text{nadd}}[\rho^{\text{act}}, \rho^{\text{env}}]}{\delta \rho^{\text{act}}(\mathbf{r})} = \frac{\delta T_s[\rho^{\text{tot}}]}{\delta \rho^{\text{tot}}(\mathbf{r})} - \frac{\delta T_s[\rho^{\text{act}}]}{\delta \rho^{\text{act}}(\mathbf{r})}$$

where T_s is evaluated using approximate kinetic energy density functional (KEDF)

Embedding potential (Exact)

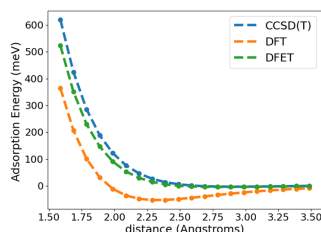
In matrix form

$$\mathbf{V}_{\text{emb}} = \mathbf{V}_{\text{nuc}}^{\text{env}} + \mathbf{J}_{\text{elec}}^{\text{env}} + \mathbf{X}_{\text{nadd}} + \mathbf{P}_B$$

with Projection operator:

$$\mathbf{P}_B = \mu \mathbf{S}^{\text{AB}} \mathbf{D}^{\text{B}} \mathbf{S}^{\text{BA}} \quad \text{with } \mu = 10^6$$

MOLECULE-in-PERIODIC EMBEDDING



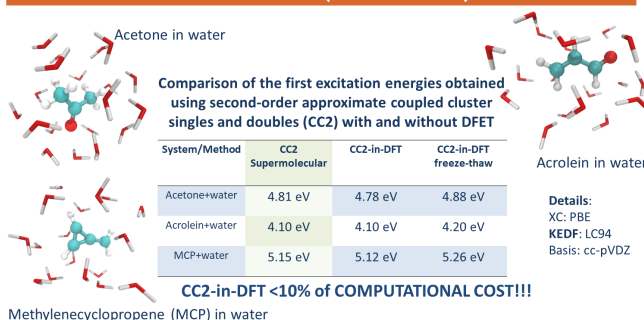
CCSD(T)-DFET much closer to regular CCSD(T) at just 10% of COMPUTATIONAL COST!!!

H₂ (molecule)

Colored atoms are treated as cluster

H₁₀ (1D periodic chain)

MOLECULE-in-MOLECULE (WFT-in-DFT) EMBEDDING



Methylenecyclopropane (MCP) in water

PERIODIC-in-PERIODIC EMBEDDING

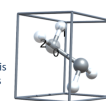
Total energies (Hartrees) obtained using periodic KS-DFT and DFET

System/Method	DFT	DFET
Polyethylene (gamma)	-78.3875751502	-78.3875735082
Polyethylene (32 k-points)	-78.4571146741	-78.4571160584
Neoprene (gamma)	-614.9728903786	-614.9728912891

Details:

- 1D Periodicity
- Basis: def2-SVP
- PBE-in-PBE DFET
- with Projection operator and supermolecular basis
- 5 freeze-thaw cycles

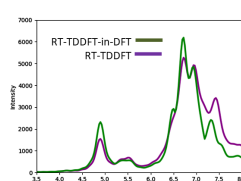
Neoprene 1D periodic chain. Labelled atoms treated as cluster.



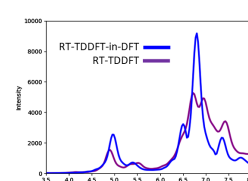
Polyethylene 1D periodic chain. Labelled atoms treated as cluster.

The embedding procedure is similar to the implementation of Chulhai *et al.* using PySCF^[6]. However, in contrast to their implementation, the KS matrices here are calculated in real space. Furthermore, the Coulomb contributions are calculated using highly efficient density fitting and the continuous fast multipole methods^[5].

RT-TDDFT-in-DFT



Benzene-Fulvene Dimer at 4 Angs. separation



- using Projection Operator (5 freeze-thaw cycles), supermolecular basis and updating embedding potential

The environment density was kept frozen to the ground state density while the cluster was evolved in time.

- using nadd KEDF (5 freeze-thaw cycles), supermolecular basis and updating embedding potential

CONCLUSION & OUTLOOK

- DFET (KEDF), coupled with WFT methods (WFT-in-DFT), offers reasonable accuracy for adsorption energy and excitation energies of weakly interacting systems with a significant reduction in computational cost.
- Supermolecular DFET (Projection) coupled with RT-TDDFT () offers great accuracy, even for strongly interacting systems, and can play a crucial role in studying excitation energy transfer^[7].
- Periodic-in-periodic embedding paves the way for exact cluster-in-periodic RT-TDDFT/WFT calculations.

References:

1. T. Wesolowski, A. Warshel, *J. Phys. Chem.* **97**, 8050 (1993).
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Video Presentation



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I'm a physicist specializing in computational material science with a PhD in Physics from Friedrich-Schiller University Jena, Germany. I write efficient codes for simulating light-matter interactions at atomic scales. I like to develop Physics, DFT, and Machine Learning related apps and software from time to time. Can code in most of the popular languages. I like to share my knowledge in Physics and applications using this Blog and a YouTube channel.

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