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)
3. TURBOMOLE, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com. (development version)
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Poster

Density Functional Theory Based Embedding Scheme for Molecular and Periodic Systems

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SCAN ME

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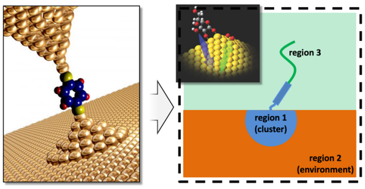
INTRODUCTION

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 partition:

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

Total Energy

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

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)

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

with non-additive kinetic potential

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

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

Embedding potential (Exact)

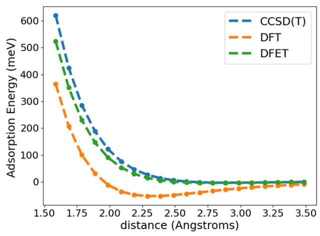
In matrix form

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

with Projection operator :

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

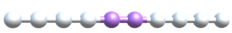
MOLECULE-in-PERIODIC EMBEDDING



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

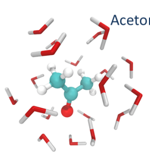
H_2 (molecule)

Colored atoms are treated as cluster

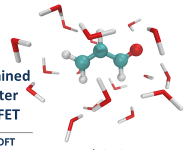


H_{10} (1D periodic chain)

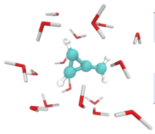
MOLECULE-in-MOLECULE (WFT-in-DFT) EMBEDDING



Acetone in water



Acrolein in water



Methylenecyclopropene (MCP) in water

Comparison of the first excitation energies obtained using second-order approximate coupled cluster singles and doubles (CC2) with and without DFET

System/Method	CC2 Supermolecular	CC2-in-DFT	CC2-in-DFT freeze-thaw
Acetone+water	4.81 eV	4.78 eV	4.88 eV
Acrolein+water	4.10 eV	4.10 eV	4.20 eV
MCP+water	5.15 eV	5.12 eV	5.26 eV

Details:
XC: PBE
KEDF: LC94
Basis: cc-pVDZ

CC2-in-DFT <10% of COMPUTATIONAL COST!!!

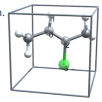
PERIODIC-in-PERIODIC EMBEDDING

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

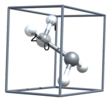
System/Method	DFT	DFET
Polyethylene (gamma)	-78.3875751502	-78.3875735082
Polyethylene (32 k-points)	-78.4571146741	-78.4571160584
Neoprene (gamma)	-614.9728903786	-614.9728912891

Details:

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



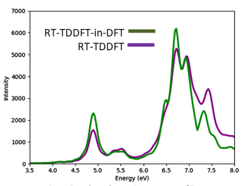
Neoprene 1D periodic chain. Labelled atoms treated as cluster.



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

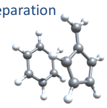
The embedding procedure is similar to the implementation of Chulhai *et al.* using PySCF[6]. However, in contrast to their implementation, the KS matrices here are calculated in real space. Furthermore, the Coulomb contributions are calculated using highly efficient density fitting and the continuous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

RT-TDDFT-in-DFT

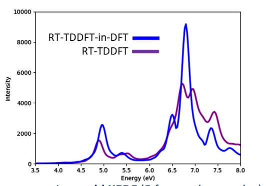


- using **Projection Operator** (5 freeze-thaw cycles), supermolecular basis and updating embedding potential

Benzene-Fulvene Dimer at 4 Angs. separation



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).
2. C. Müller, M. Sharma, M. Sierka, *J. Comput. Chem.* **41**, 2573 (2020)
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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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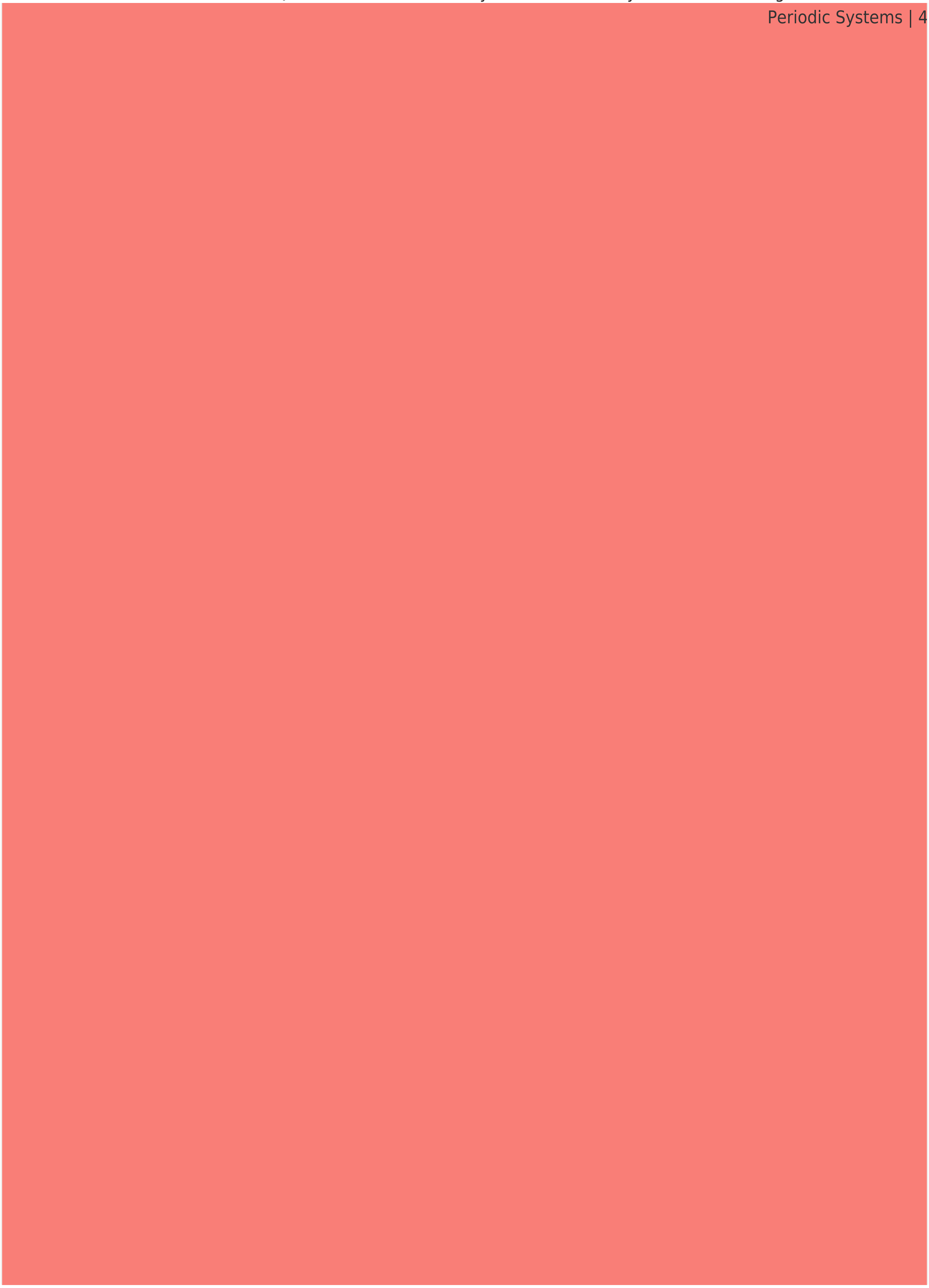

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