Density Functional Embedding Scheme for Molecules and Periodic Systems

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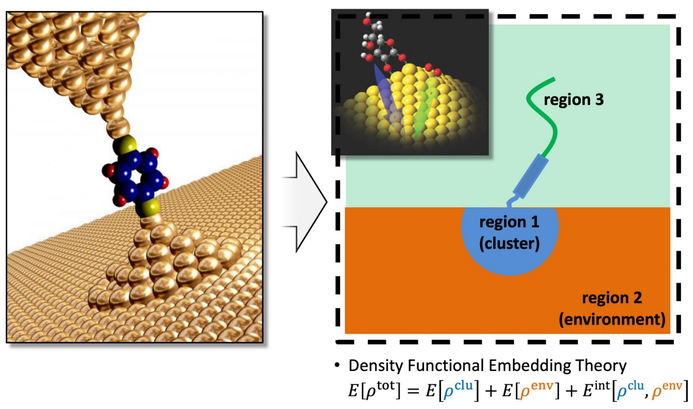
INTRODUCTION

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)



- Density Functional Embedding Theory

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

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:

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

Total Energy

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

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)

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

with non-additive kinetic potential $v_T\left[\rho^{\mathrm{act}}, \rho^{\mathrm{env}}\right](\boldsymbol{r}) = \frac{\delta T_s^{\mathrm{nadd}}[\rho^{\mathrm{act}}, \rho^{\mathrm{env}}]}{\delta \rho^{\mathrm{act}}(\boldsymbol{r})} = \frac{\delta T_s[\rho^{\mathrm{tot}}]}{\delta \rho^{\mathrm{tot}}(\boldsymbol{r})} - \frac{\delta T_s[\rho^{\mathrm{act}}]}{\delta \rho^{\mathrm{act}}(\boldsymbol{r})}$

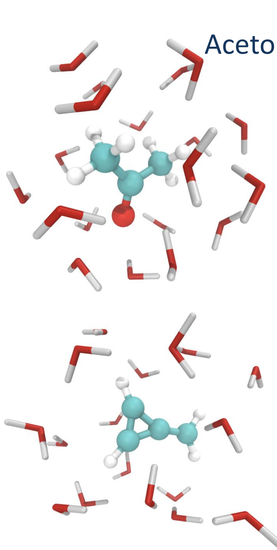
where T_s is evaluated using approximate kinetic energy density functional (KEDF)

Embedding potential (Exact)

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

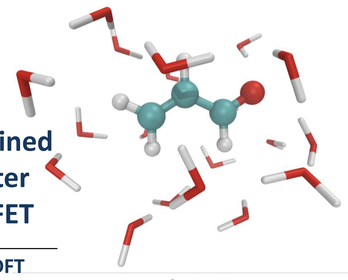
with Projection operator : $\mathbf{P}_{\mathrm{B}} = \mu \mathbf{S}^{\mathrm{AB}} \mathbf{D}^{\mathrm{B}} \mathbf{S}^{\mathrm{BA}}$ with $\mu = 10^6$

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



Acetone in water

Methylenecyclopropene (MCP) in water



Acrolein 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

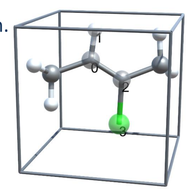
Total energies (Hartrees) obtained using periodic KS-DFT and DFET

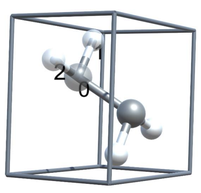
System/Method	DFT	DFET
Polyethylene (gamma)	-78.3875751502	-78.3875735082
Polyethylene (32 k-points)	-78.4571146741	-78.4571160584
Neoprene (gamma)	-614.9728903786	-614.9728912891

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.

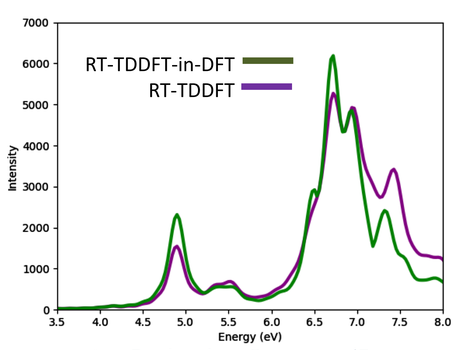




Polyethylene 1D periodic chain. Labelled atoms treated as cluster.

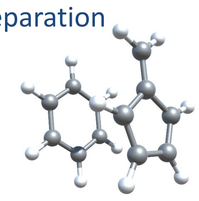
The embedding procedure is similar to the implementation of Chulhai *et al*. using PySCF[6]. However, in contrast to their implementation, the KS matrices here are calculated in real space. Furthermore, the Coulomb contributions are calculated using highly efficient density fitting and the continuous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

RT-TDDFT-in-DFT

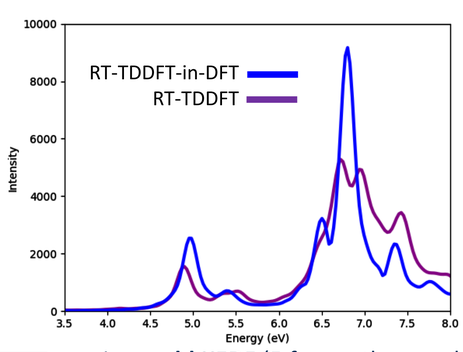


- using **Projection Operator** (5 freeze-thaw cycles), supermolecular basis and updating embedding potential

Benzene-Fulvene Dimer at 4 Angs. separation

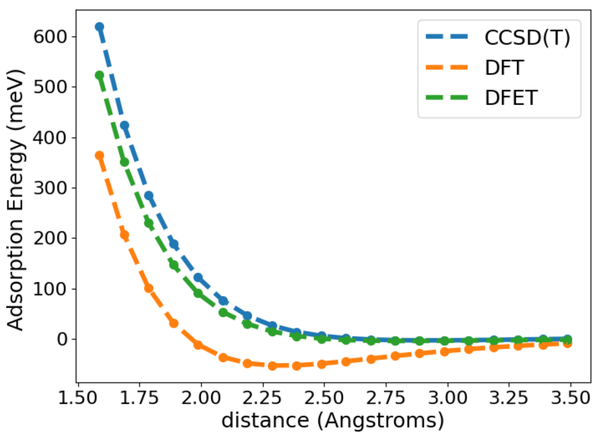


The environment density was kept frozen to the ground state density while the cluster was evolved in time.



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

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)

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)
3. TURBOMOLE 7.5, 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)
4. F. Furche, R. Ahlrichs, C. Hattig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput.Mol. Sci.* **4**, 91 (2014).
5. R. Łazarski, A.M. Burow, M. Sierka, *J. Chem. Theory Comput.* **11**, 3029 (2015).
6. D. Chulhai, J. Goodpaster, *J. Chem. Theory Comput.* **14**, 1928–1942 (2018).
7. A. Krishtal, D. Ceresoli, M. Pavanello, *J. Chem. Phys*. **142**, 154116 (2015).

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