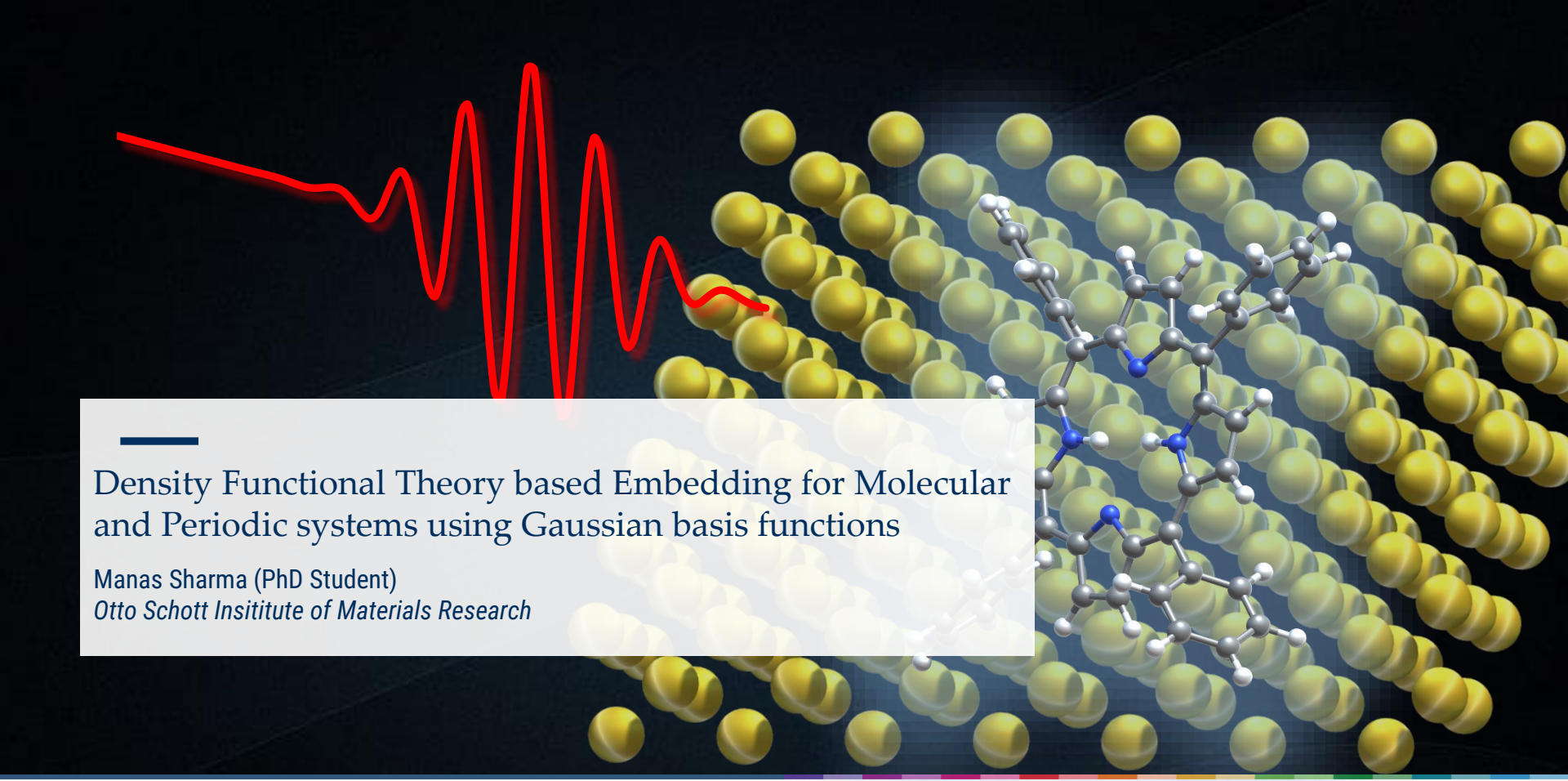
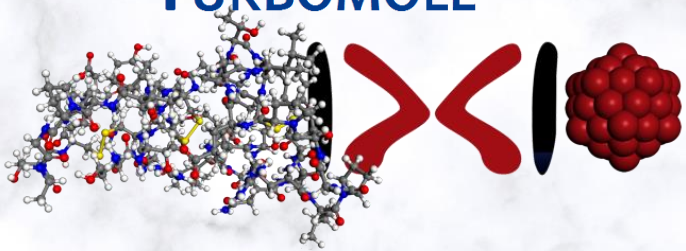


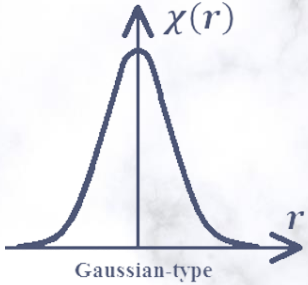
Density Functional Theory based Embedding for Molecular and Periodic systems using Gaussian basis functions

Manas Sharma (PhD Student)
Otto Schott Insititute of Materials Research

Density Functional Embedding Theory (DFET)

TURBOMOLE

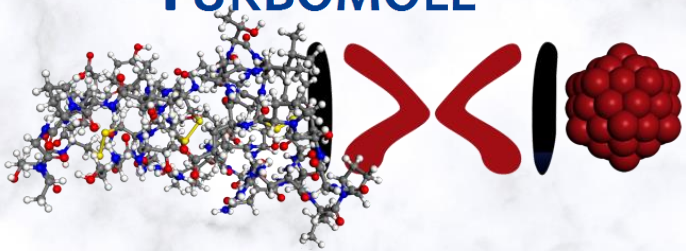




$$\chi(r) \propto e^{-\alpha r^2}$$

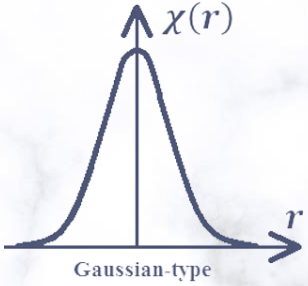
Density Functional Embedding Theory (DFET)

TURBOMOLE

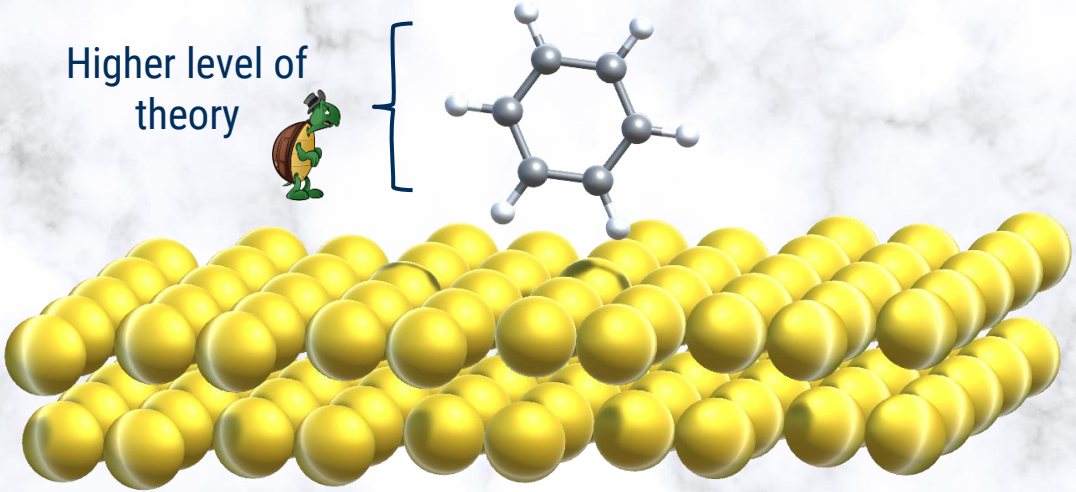


DFET coupled with

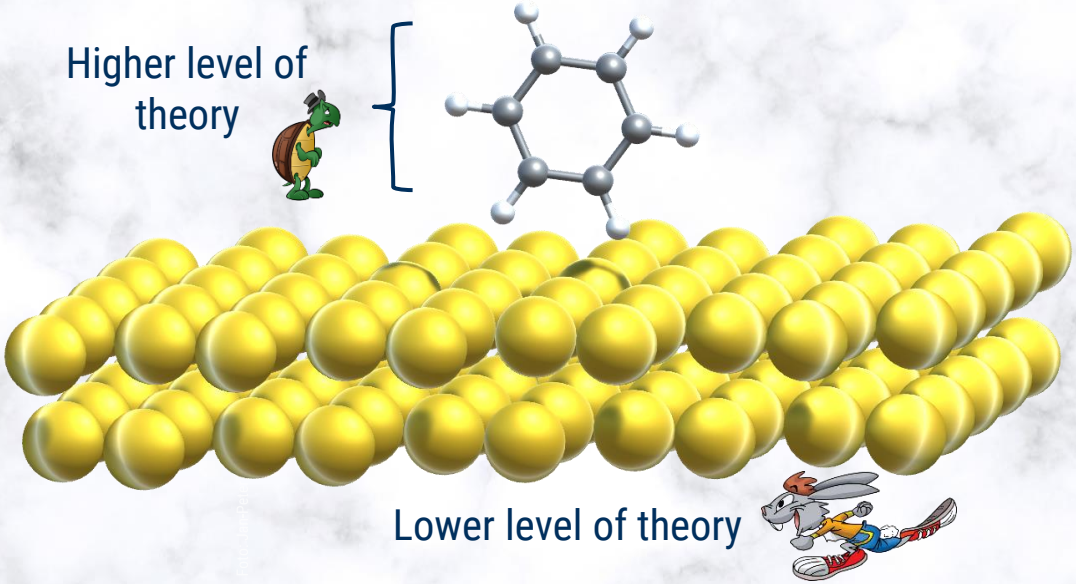
- Wave Function Theory methods like MP2, CCSD(T), etc.
- Real Time – Time Dependent Density Functional Theory (RT-TDDFT)



DFET in a nutshell

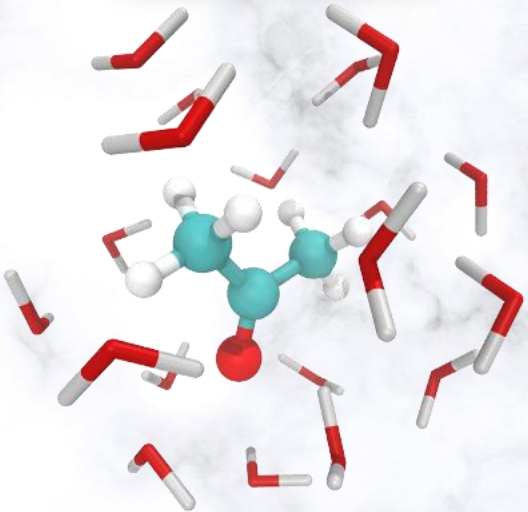


DFET in a nutshell

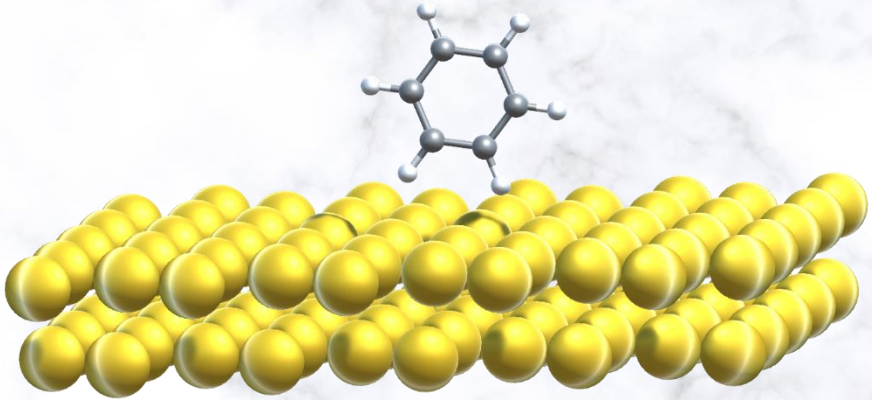


DFET is well suited for the study of …

Solvated Molecules

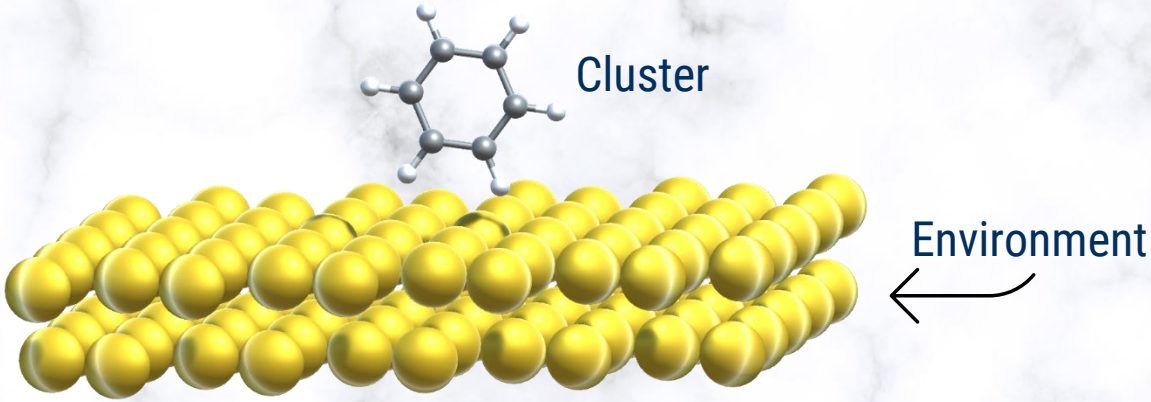


Molecule adsorbed on a surface



DFET Motivation

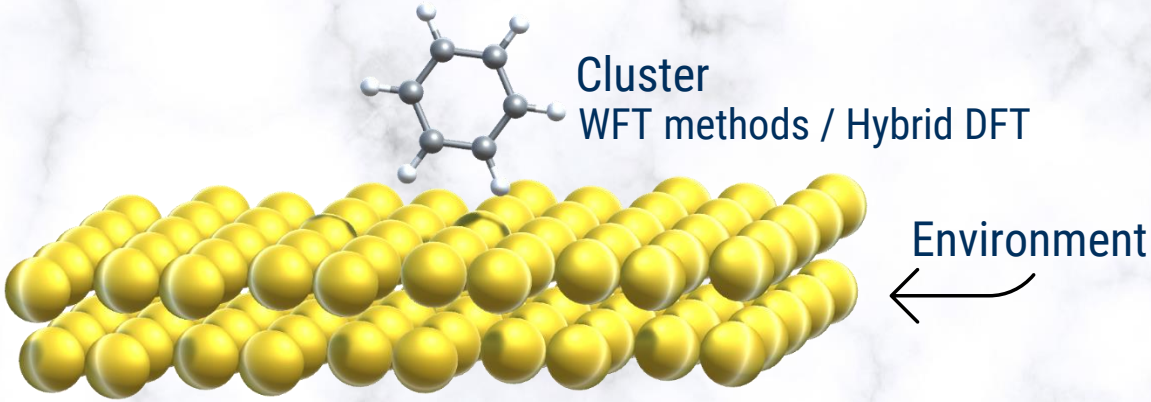
The region of interest is usually small



Lower level of theory: LDA/GGA - DFT

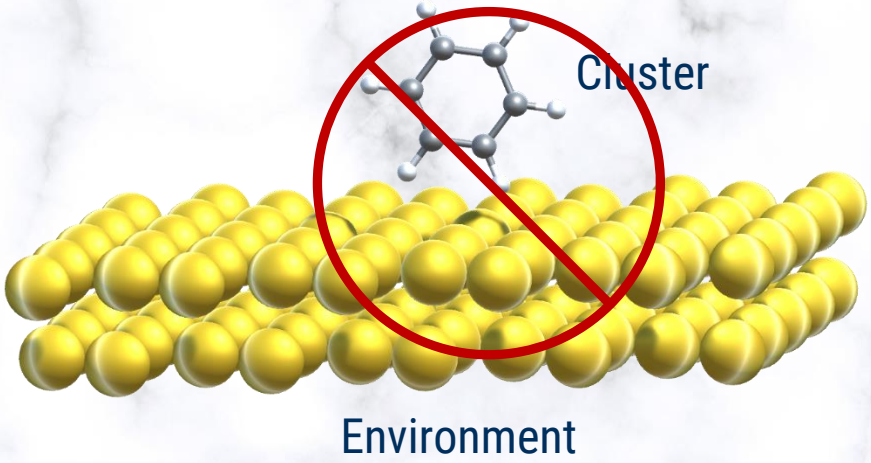
DFET Motivation

The region of interest is usually small



DFET Motivation

The region of interest is usually small

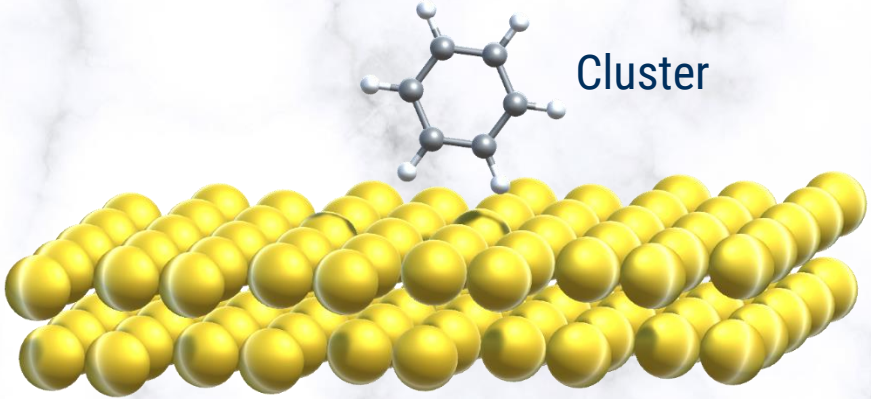


GGA-DFT

Leads to large errors

DFET Motivation

The region of interest is usually small



Cluster

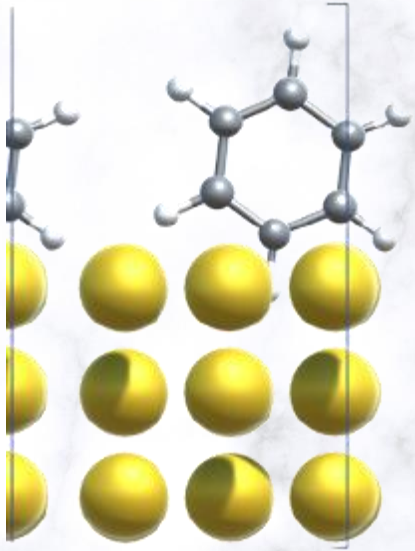
Environment

CCSD(T)

Costly and impractical

DFET Motivation

Periodic Boundary Conditions

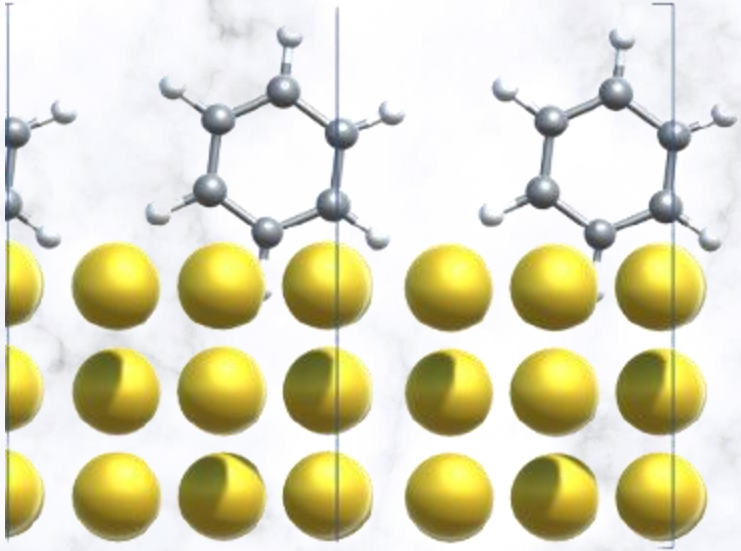


cluster

environment

DFET Motivation

Periodic Boundary Conditions → unrealistic surface coverages

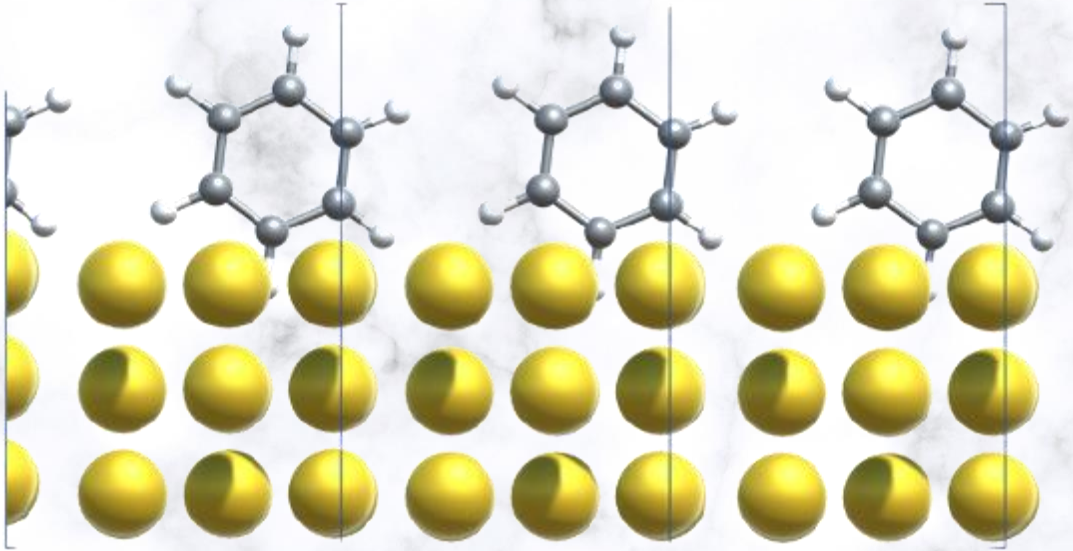


cluster

environment

DFET Motivation

Periodic Boundary Conditions → unrealistic surface coverages

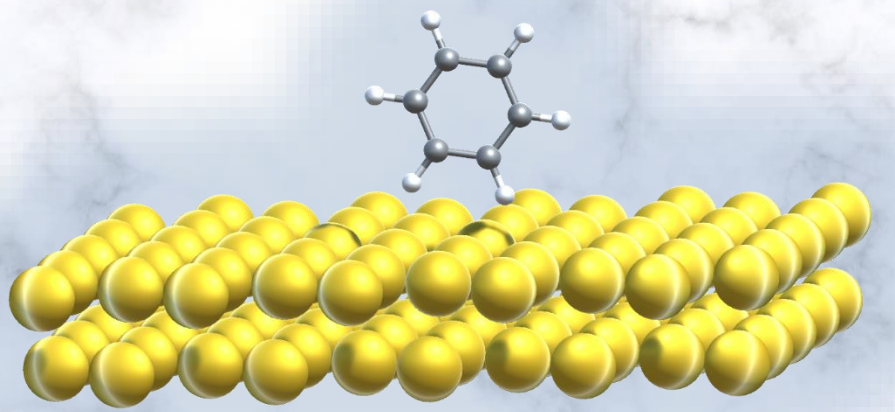


cluster

environment

Density Functional Embedding Theory

$$E_{DFT}[\rho(\mathbf{r})] = E_{gs}$$



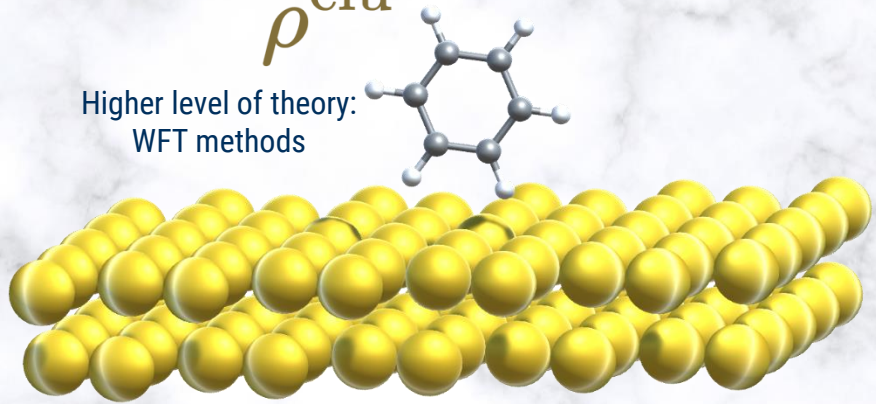
Density Functional Embedding Theory

Density partition:

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

ρ^{clu}

Higher level of theory:
WFT methods



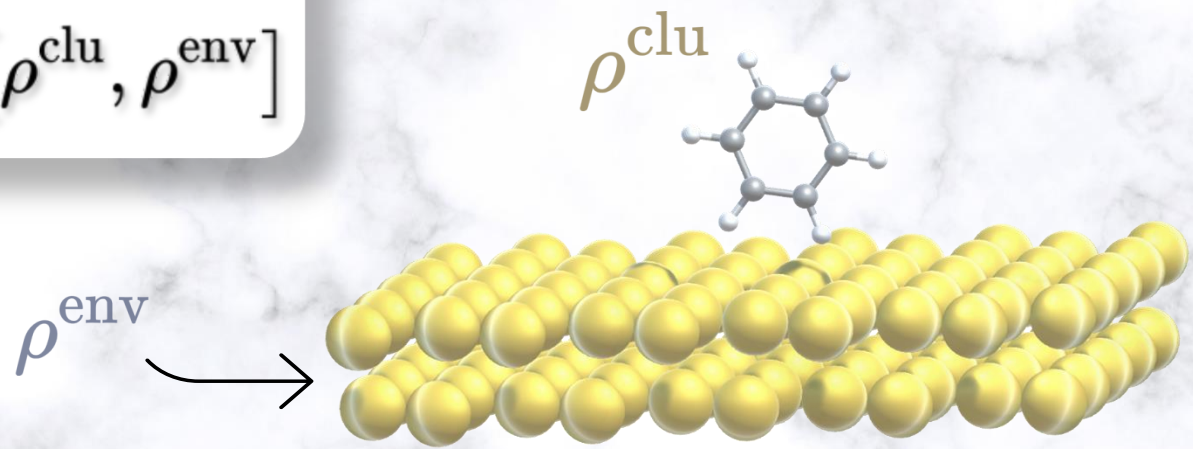
ρ^{env}

Lower level of theory: DFT

Density Functional Embedding Theory

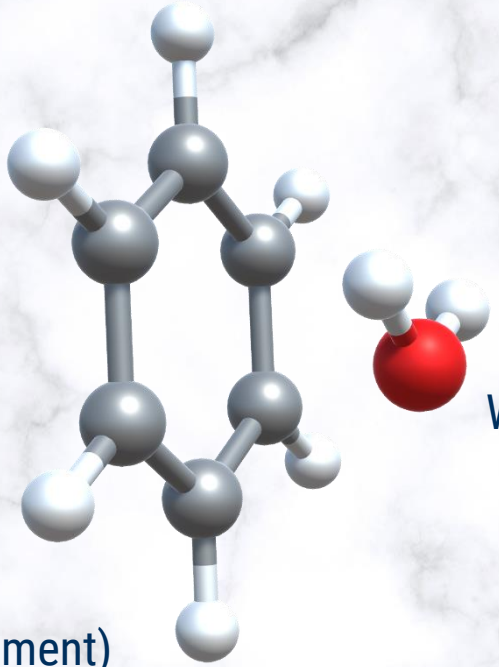
Central Quantity

$$V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$$



Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Model System

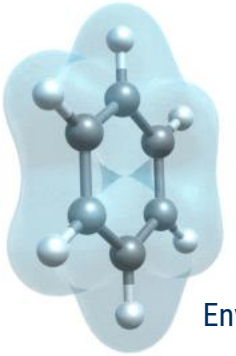


Water (Cluster)

Benzene (Environment)

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Method 1
(approximate)

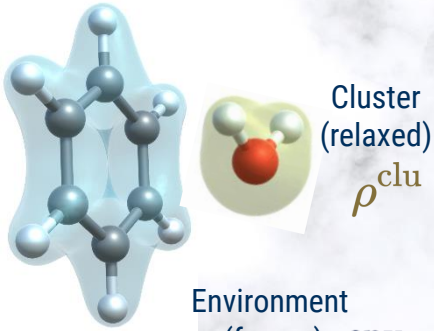


Environment
$\rho_{\mathrm{iso}}^{\mathrm{env}}$

J. Phys. Chem. **1993**, 97, 30, 8050–8053

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Method 1
(approximate)



Cluster
(relaxed)
ρ^{clu}

Environment
(frozen) $\rho^{\mathrm{env}}_{\mathrm{iso}}$

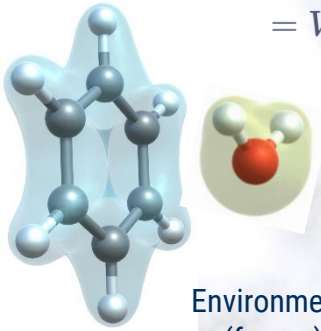
J. Phys. Chem. **1993**, 97, 30, 8050–8053

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Method 1
(approximate)

$$V_{\mathrm{emb}}^{\mathrm{clu}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right](\mathbf{r}) = \frac{\delta E^{\mathrm{int}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]}{\delta \rho^{\mathrm{clu}}}$$

$$= V_{\mathrm{ne}}^{\mathrm{env}}(\mathbf{r}) + \int \frac{\rho^{\mathrm{env}}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' + V_{\mathrm{xc}}^{\mathrm{tot}}(\mathbf{r}) - V_{\mathrm{xc}}^{\mathrm{clu}}(\mathbf{r}) + \frac{\delta T_{\mathrm{s}}^{\mathrm{nadd}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]}{\delta \rho^{\mathrm{clu}}}$$

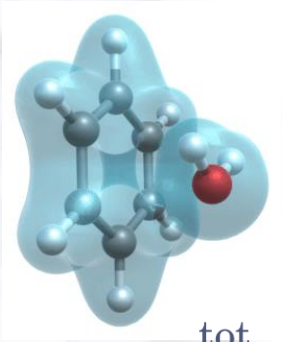


Cluster
(relaxed)
ρ^{clu}

Environment
(frozen) $\rho_{\mathrm{iso}}^{\mathrm{env}}$

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

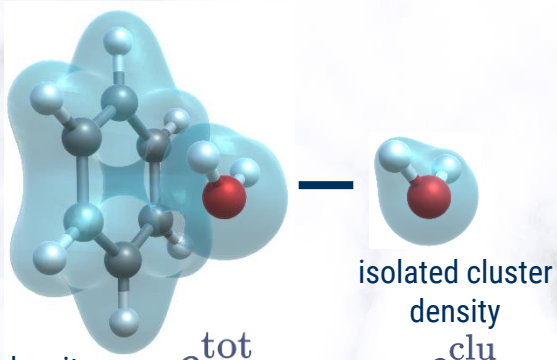
Method 2
(approximate)



total density (relax) ρ^{tot}

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Method 2
(approximate)

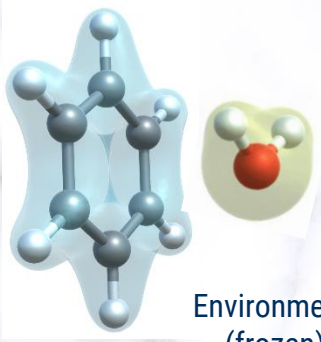


total density ρ^{tot}

isolated cluster density $\rho^{\mathrm{clu}}_{\mathrm{iso}}$

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Method 2
(approximate)



Cluster
(relaxed)
ρ^{clu}

Environment
(frozen)

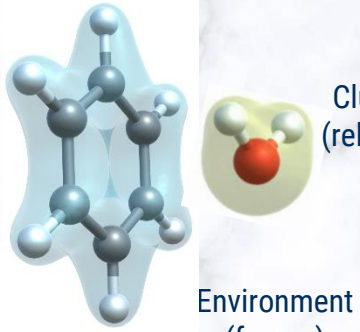
$$\rho^{\mathrm{env}} = \rho^{\mathrm{tot}} - \rho^{\mathrm{clu}}_{\mathrm{iso}}$$

Phys. Rev. Lett. **2001**, 86, 5954

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

Method 3
(exact)

Projection Operator based Embedding



Cluster
(relaxed)

Environment
(frozen)

J. Chem. Theory Comput. **2012**, 8, 8, 2564–2568

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$

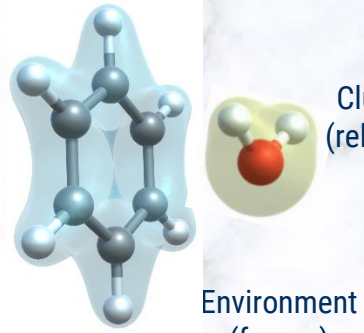
Method 3
(exact)

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

Projection Operator based Embedding

Projection Operator

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

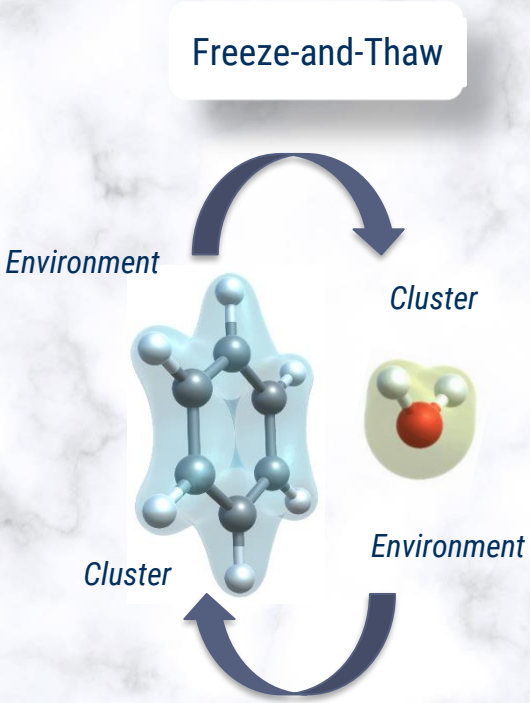


Cluster
(relaxed)

Environment
(frozen)

J. Chem. Theory Comput. **2012**, 8, 8, 2564–2568

Strategies for Embedding Potential Construction $V_{\mathrm{emb}}\left[\rho^{\mathrm{clu}}, \rho^{\mathrm{env}}\right]$



Chem. Phys Lett., **1996**, 248, 71-76

Results

Ground state properties with DFET

Molecule-in-molecule DFET

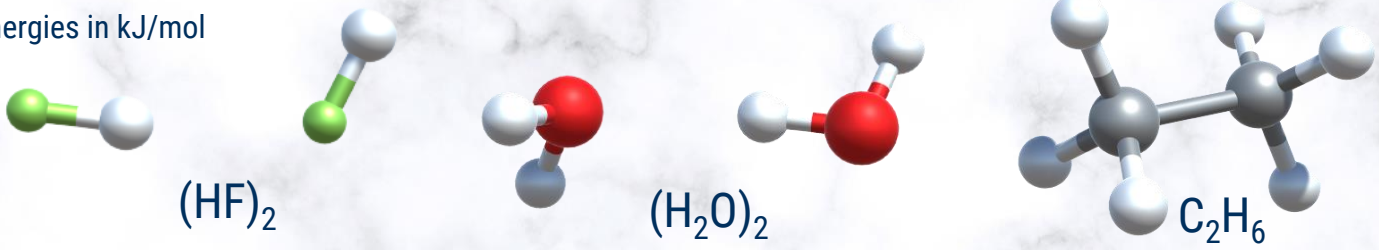
Molecular Binding Energies

Binding Energy:

$$E_b = E_{tot} - E_A - E_B$$

System/Method	E_b (DFET) Method 1	E_b (DFET) Method 1 + F&T Supermolecular Basis	E_b (DFET) Method 3 + F&T Supermolecular Basis	E_b (DFT) Reference
H_2O - H_2O	-24.87	-22.39	-20.57	-20.57
HF - HF	-17.28	-18.59	-19.09	-19.09
CH^+_3 - CH^-_3	-619.32	-2412.84	-1521.84	-1521.84

Energies in kJ/mol



$(HF)_2$ $(H_2O)_2$ C_2H_6

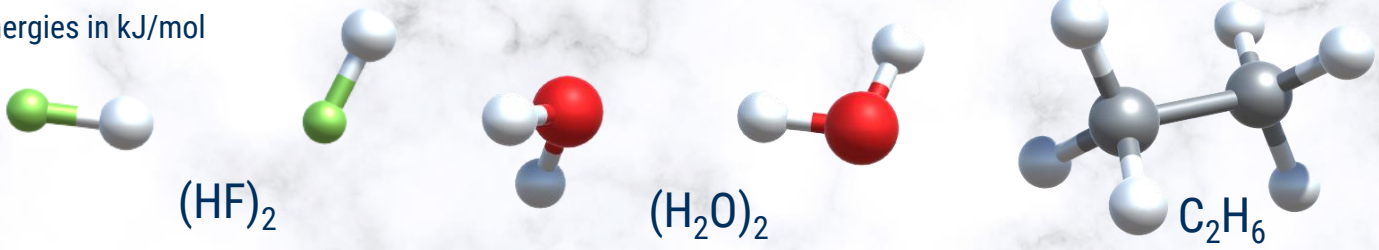
Molecular Binding Energies

Binding Energy:

$$E_b = E_{tot} - E_A - E_B$$

System/Method	E_b (DFET) Method 1	E_b (DFET) Method 1 + F&T Supermolecular Basis	E_b (DFET) Method 3 + F&T Supermolecular Basis	E_b (DFT) Reference
H_2O - H_2O	-24.87	-22.39	-20.57	-20.57
HF - HF	-17.28	-18.59	-19.09	-19.09
CH^+_3 - CH^-_3	-619.32	-2412.84	-1521.84	-1521.84

Energies in kJ/mol



$(HF)_2$ $(H_2O)_2$ C_2H_6

Molecular Binding Energies

Binding Energy:

$$E_b = E_{tot} - E_A - E_B$$

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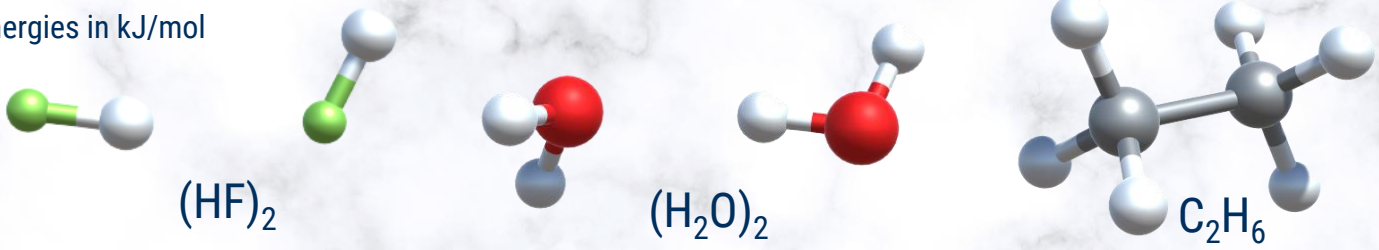
H_2O - H_2O	-24.87	-22.39	-20.57	-20.57
HF - HF	-17.28	-18.59	-19.09	-19.09
CH^+_3 - CH^-_3	-619.32	-2412.84	-1521.84	-1521.84

Energies in kJ/mol



$(HF)_2$ $(H_2O)_2$ C_2H_6

Molecular Binding Energies

Binding Energy:

$$E_b = E_{tot} - E_A - E_B$$

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H_2O - H_2O	-24.87	-22.39	-20.57	-20.57
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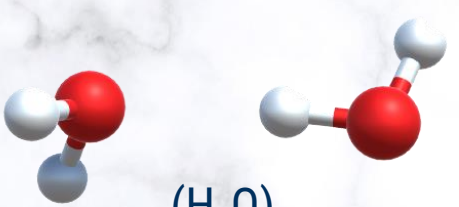
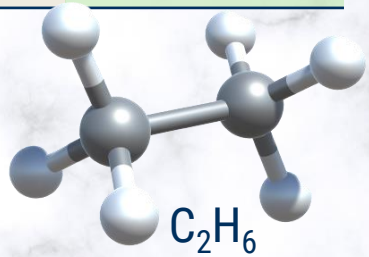
Energies in kJ/mol

$(HF)_2$



$(H_2O)_2$



C_2H_6

Results

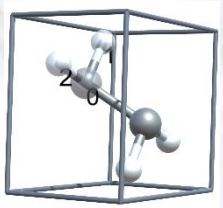
Ground state properties with DFET

Periodic-in-periodic DFET

Periodic-in-periodic DFET

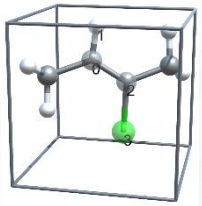
Ground state total energies (a.u.)

System/Method	DFT	$\Delta E = E_{DFET} - E_{DFT}$
Polyethylene 1D (32 x 1 x 1 *k*-mesh)	-78.457114	2×10^{-6}
Neoprene 1D (10 x 1 x 1 *k*-mesh)	-614.9723856	1.2×10^{-6}
Diamond 3D (10 x 10 x 10 *k*-mesh)	-304.3591154	2.1×10^{-6}



- Polyethylene 1D periodic chain
- Labelled atoms treated as one subsystem

- Neoprene 1D periodic chain
- Labelled atoms treated as one subsystem



Details:

- Basis: def2-SVP
- PBE-in-PBE FDE
- with Projection operator and supermolecular basis
- 5 freeze-thaw cycles

Results

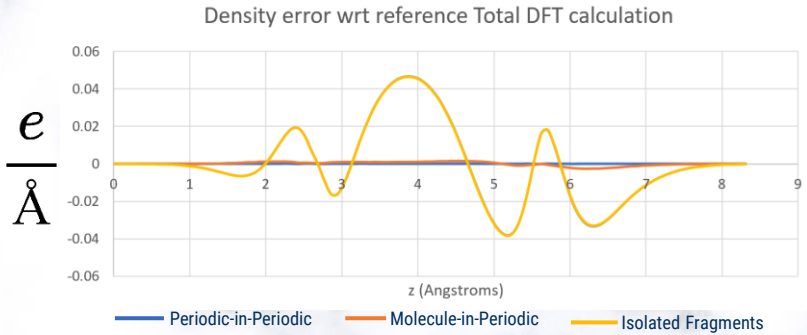
Ground state properties with DFET

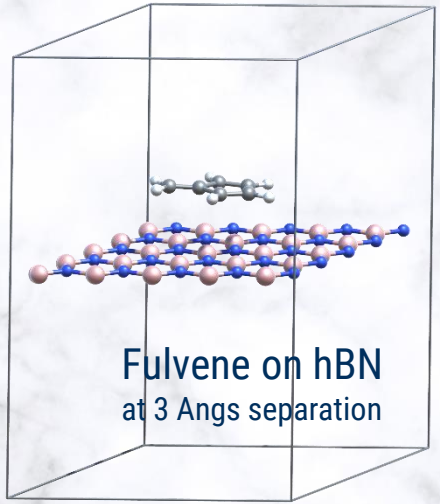
Molecule-in-periodic DFET

Molecule-in-periodic DFET

Error in density wrt reference total DFT density e/A^3 using Method 3

	Periodic-in-Periodic	Molecule-in-Periodic	Isolated Fragments
Max Abs. Error	0.0002	0.0026	0.0464
Mean Abs. Error	1.3E-05	0.000775	0.014105





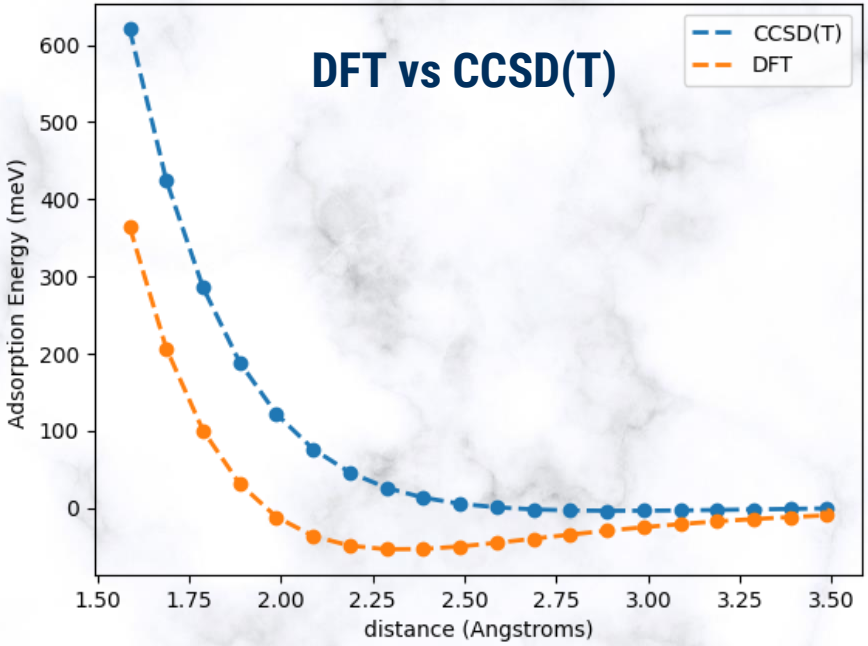
Results

Ground state properties with DFET

Molecule-in-periodic DFET

coupled with CCSD(T)

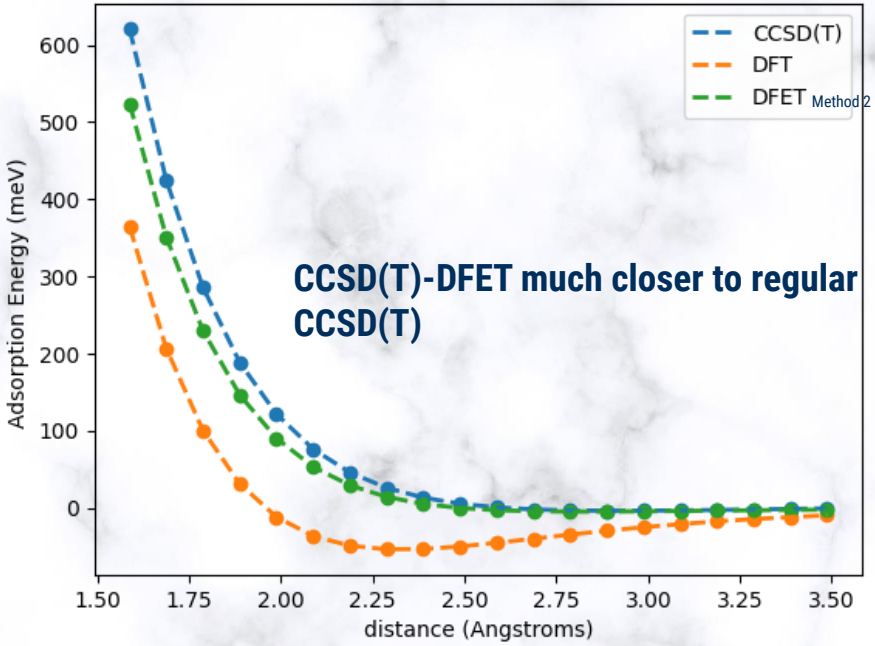
Adsorption Energy : H_2 (molecule) on H_{10} (periodic)



H_2 (molecule)

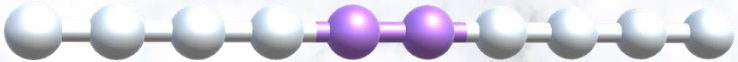
H_{10} (1D periodic chain)

Adsorption Energy : H_2 (molecule) on H_{10} (periodic)



H_2 (molecule)

H_{10} (1D periodic chain)



Colored atoms are treated as cluster

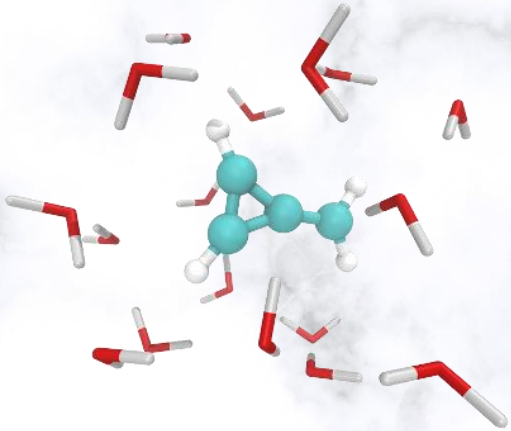
Results

Excited state properties with DFET

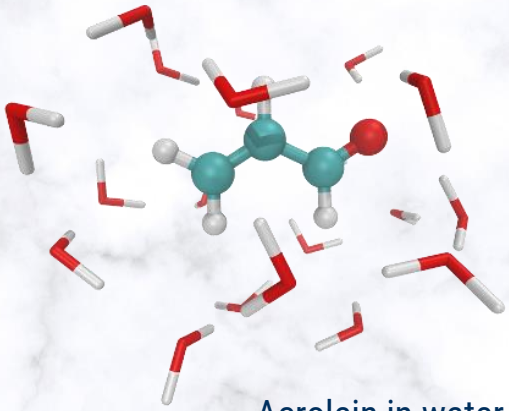
Molecule-in-molecule DFET

coupled with CC2

CC2-DFET Excitation Energies



Methylenecyclopropene (MCP) in water



Acrolein in water

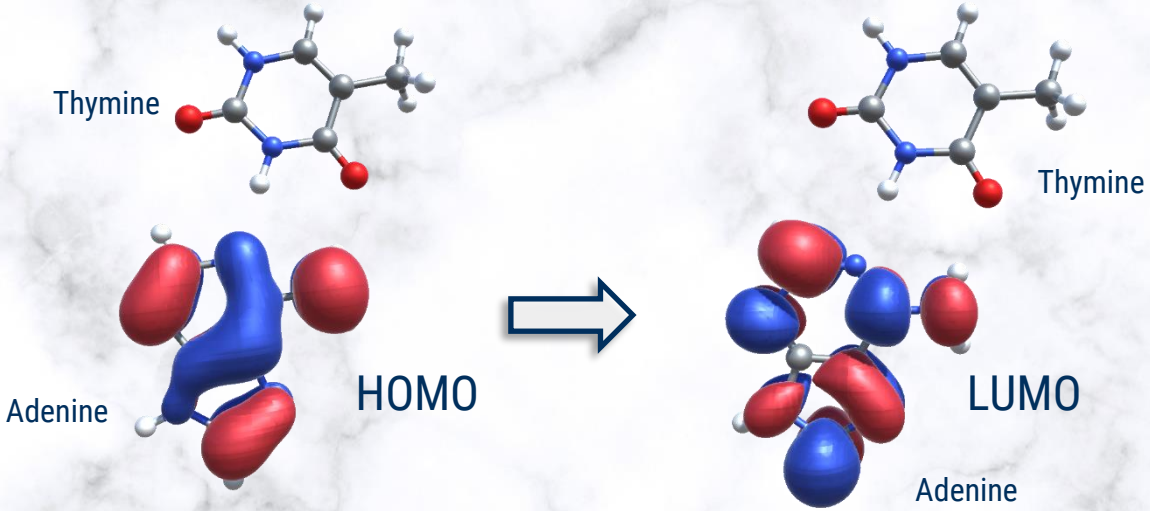
Solvated Molecules

CC2-DFET Excitation Energies

First excitation energies (eV) from supermolecular second-order approximate coupled cluster singles and doubles (CC2) and the CC2-DFET errors

System/Method	CC2 Isolated	CC2 Supermolecular	CC2-DFET Method 1 ΔE	CC2-DFET Method 1 F&T ΔE	CC2-DFET Method 2 ΔE
Acrolein + water $n \rightarrow \pi^*$	3.71	4.10	0.00	-0.10	-0.62
MCP + water $\pi \rightarrow \pi^*$	4.61	5.15	0.03	-0.11	-0.03

CC2-DFET Excitation Energies



Adenine-Thymine base pair

CC2-DFET Excitation Energies

Lowest excitation energies (eV) for thymine-adenine pair and the CC2-DFET errors

Transition/Method	CC2 Isolated	CC2 Supermolecular	CC2-DFET Method 1 ΔE	CC2-DFET Method 1 F&T ΔE	CC2-DFET Method 2 ΔE
Thymine $n \rightarrow \pi^*$	5.20	5.34	0.00	-0.03	-0.16
Adenine $\pi \rightarrow \pi^*$	5.56	5.52	0.00	-0.03	-0.04
Adenine $n \rightarrow \pi^*$	5.38	5.58	0.02	-0.03	-0.02
Thymine $\pi \rightarrow \pi^*$	5.74	5.65	-0.05	-0.04	-0.08
Adenine $\pi \rightarrow \pi^*$	5.79	5.74	-0.03	-0.02	-0.04
Adenine $n \rightarrow \pi^*$	6.01	6.13	-0.01	-0.04	-0.11

Results

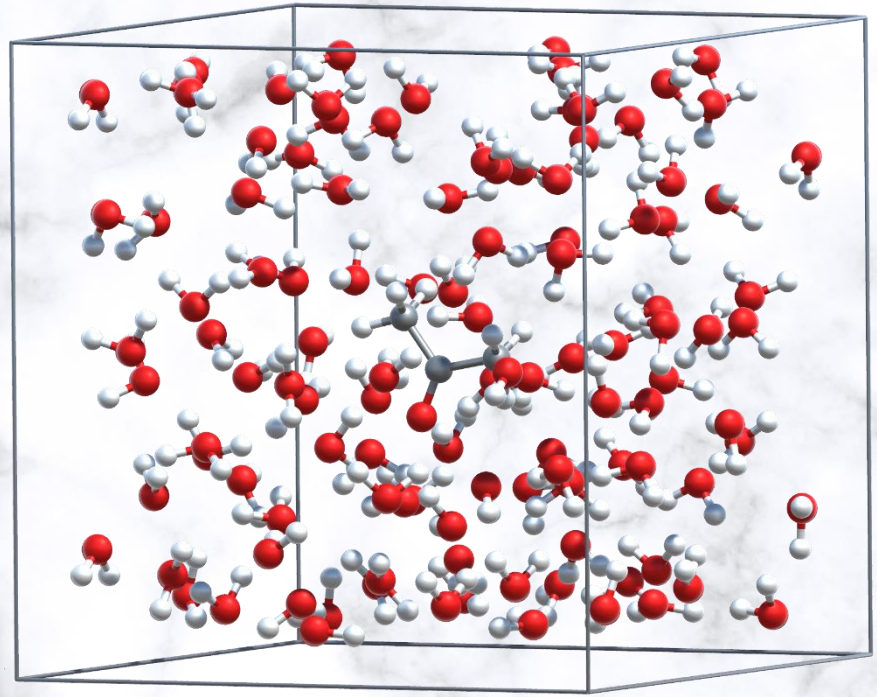
Excited state properties with DFET

Molecule-in-periodic DFET

coupled with CC2

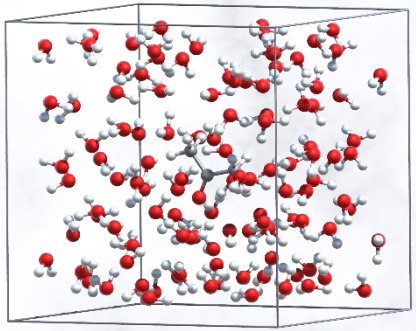
CC2-DFET Excitation Energies

Acetone-in-Water



3D Periodicity, 113 water molecules

CC2-DFET Excitation Energies



First excitation energy (eV)

CC2 Isolated	CC2 Acetone+$(H_2O)_{20}$	CC2 Acetone+$(H_2O)_{35}$	CC2 Acetone+$(H_2O)_{48}$	CC2-DFET Method 3 Supermolecular basis	CC2-DFET Method 3 Supermolecular basis F&T
4.29	4.47	4.46	4.50	4.49	4.59

Results

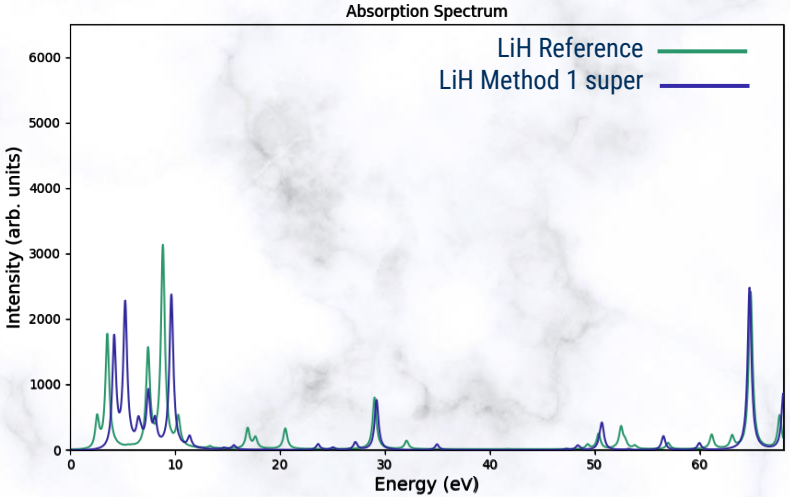
Excited state properties with DFET

Molecule-in-molecule DFET

coupled with RT-TDDFT

RT-TDDFT - DFET Absorption Spectra

Test case: LiH (Excitations of H- uncoupled with Li+)



Method 1 (5 freeze-thaw cycles) and supermolecular basis

Parameters

XC: PBE; KEDF: LC94; Basis set: def2-TZVPPD Evolution Time: 700 au,
Time step size: $\Delta t = 0.1$ au,
Damping: $\gamma = 0.008$ au,
PC scheme for time integration,
Electric field parameters: $E_0 = 2 \cdot 10^{-5}$ au , $t_0 = 3$ au, $w = 0.2$ au

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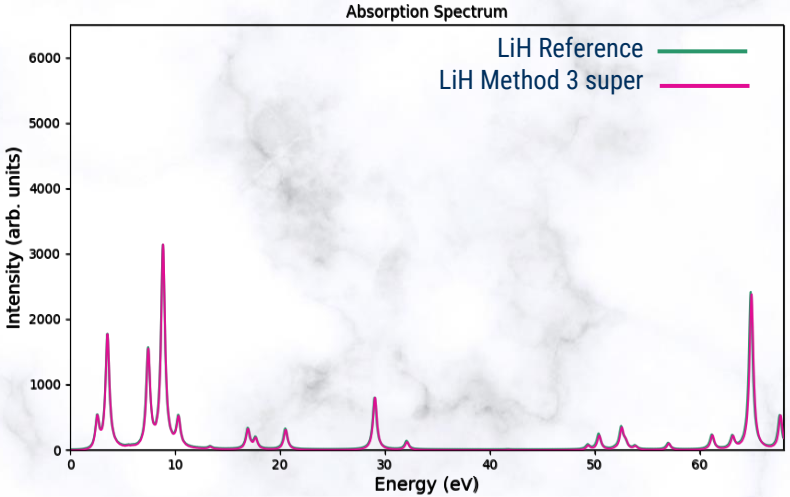
RT-TDDFT - DFET Absorption Spectra

Test case: LiH (Excitations of H- uncoupled with Li+)



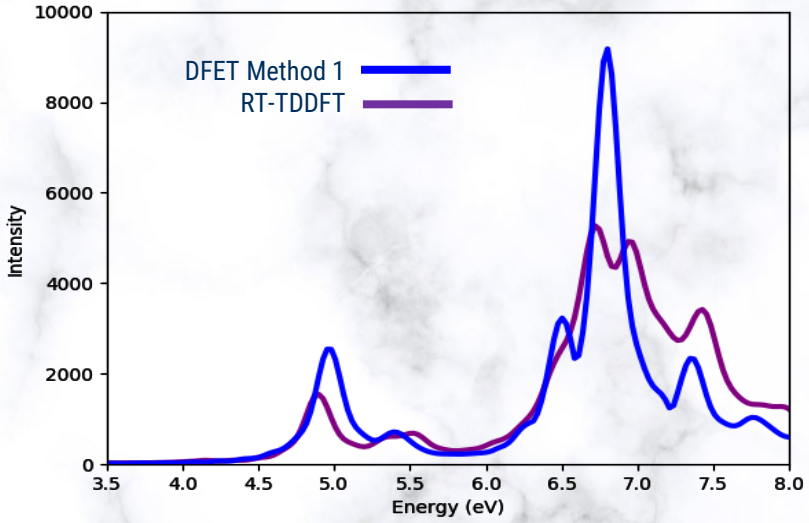
Method 3 (5 freeze-thaw cycles) and supermolecular basis

Parameters

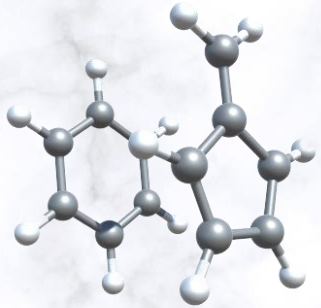
XC: PBE; KEDF: LC94; Basis set: def2-TZVPPD Evolution Time: 700 au,
Time step size: $\Delta t = 0.1$ au,
Damping: $\gamma = 0.008$ au,
PC scheme for time integration,
Electric field parameters: $E_0 = 2 \cdot 10^{-5}$ au , $t_0 = 3$ au, $w = 0.2$ au

J. Chem. Theory Comput. **2022**, 18, 11, 6892–6904

RT-TDDFT - DFET Absorption Spectra



KEDF (5 freeze-thaw cycles) and supermolecular basis

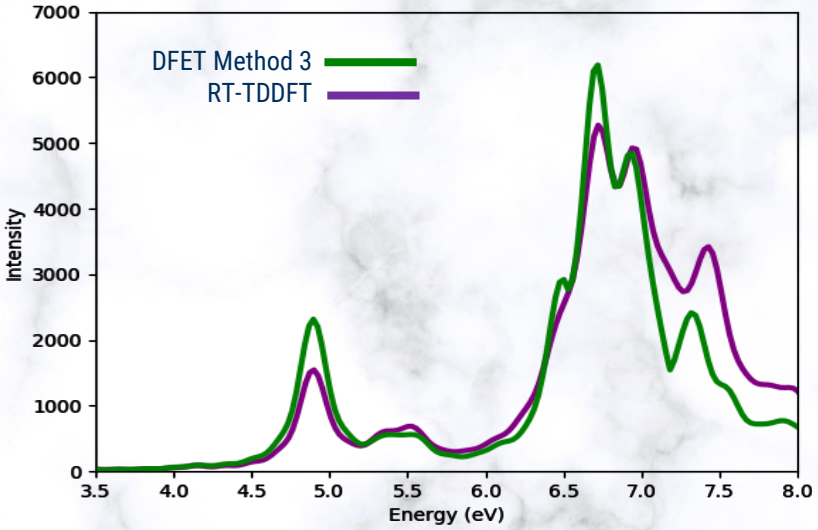


Benzene-Fulvene Dimer
at 4 Angs. separation

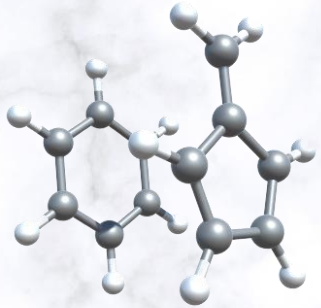
Parameters

XC: PBE; KEDF: LC94; Basis set: def2-TZVPPD Evolution Time: 1000 au,
Time step size: $\Delta t = 0.1$ au,
Damping: $\gamma = 0.004$ au,
PC scheme for time integration,
Electric field parameters: $E_0 = 2 \cdot 10^{-5}$ au ,
$t_0 = 3$ au, $w = 0.2$ au

RT-TDDFT - DFET Absorption Spectra



Projection Operator (5 freeze-thaw cycles) and supermolecular basis



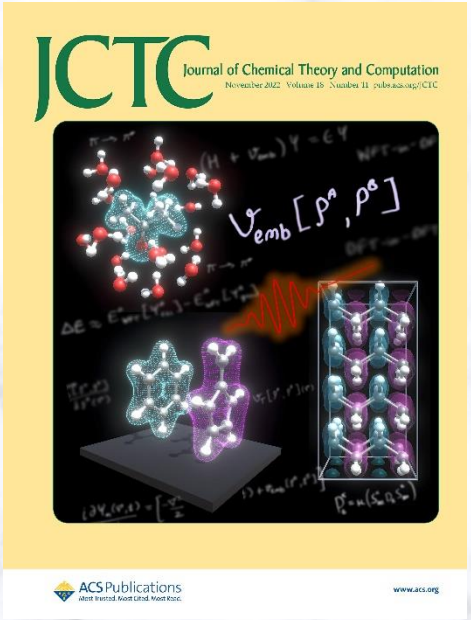
Benzene-Fulvene Dimer
at 4 Angs. separation

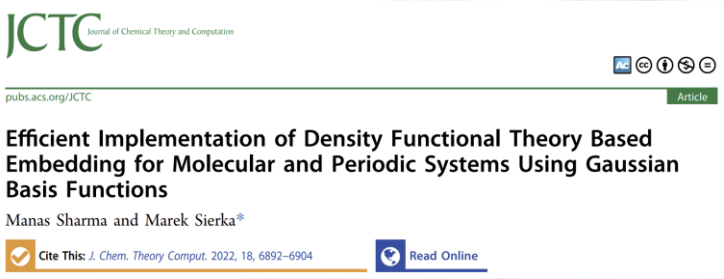
Parameters

XC: PBE; KEDF: LC94; Basis set: def2-TZVPPD Evolution Time: 1000 au,
Time step size: $\Delta t = 0.1$ au,
Damping: $\gamma = 0.004$ au,
PC scheme for time integration,
Electric field parameters: $E_0 = 2 \cdot 10^{-5}$ au ,
$t_0 = 3$ au, $w = 0.2$ au

Summary

- DFET using Gaussian basis functions: **useful to study Complex systems.**
- **Molecule-in-molecule, molecule-in-periodic** and **periodic-in-periodic DFET** have been implemented using efficient techniques.
- **DFET coupled with WFT** methods offers a reasonably improved description of **ground and excited state properties.**
- **DFET coupled with RT-TDDFT** provides reasonably accurate absorption spectra.




JCTC Journal of Chemical Theory and Computation

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Efficient Implementation of Density Functional Theory Based Embedding for Molecular and Periodic Systems Using Gaussian Basis Functions

Manas Sharma and Marek Sierka*

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Outlook

- Molecule-in-periodic DFET using **Projection operator** (Method 3) for strongly interacting systems.
- Couple **DFET with HHG** to investigate light-matter interactions of **functionalized surfaces**.
- Explore ways to circumvent the use of supermolecular basis.

Acknowledgement

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Otto Schott Institute of Materials Research
FSU Jena

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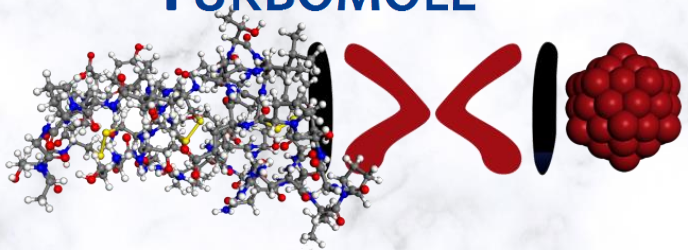

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Thank you very much for your attention!