Ab-initio electronic structure methods for large-scale simulations

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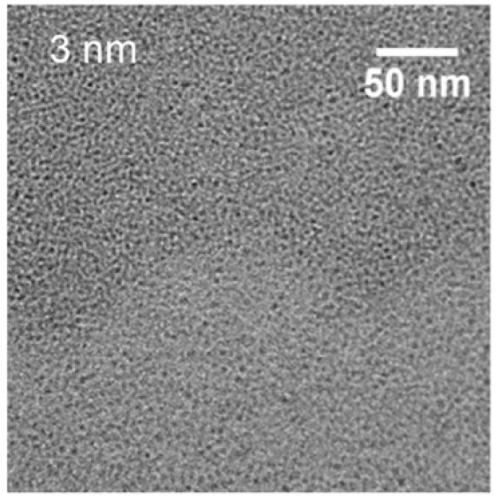
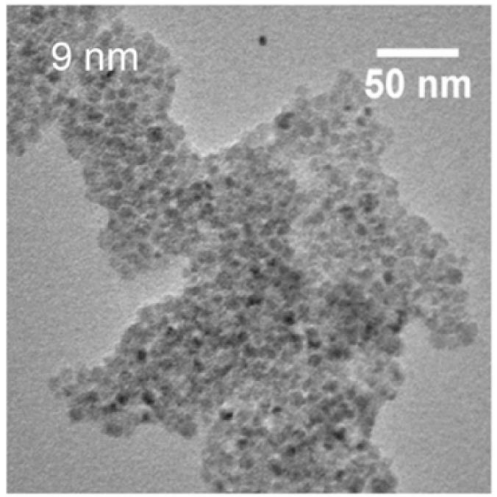
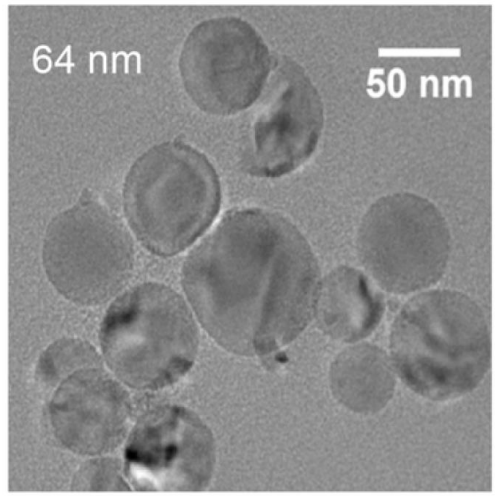
Mesoscopic systems

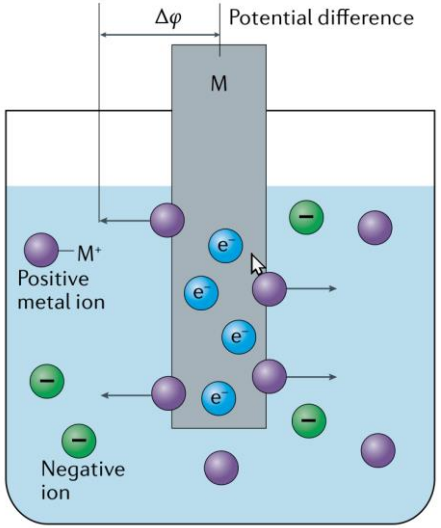




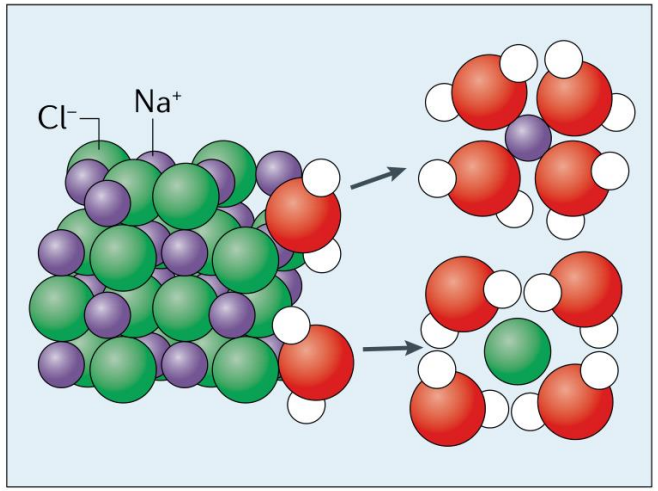
silicon nanoparticles



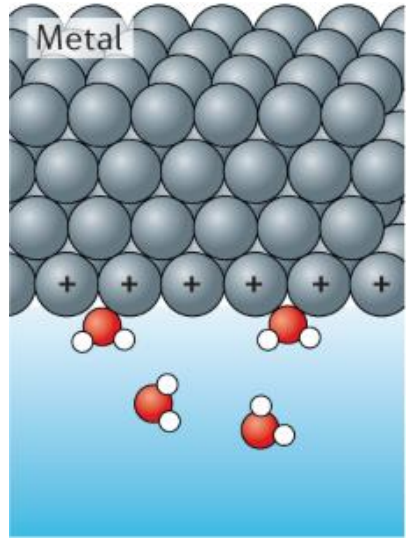
† *Thiessen & Michaelis, Chem. Mater. 31, 678 (2019)*



electrolysis



ion dissolution

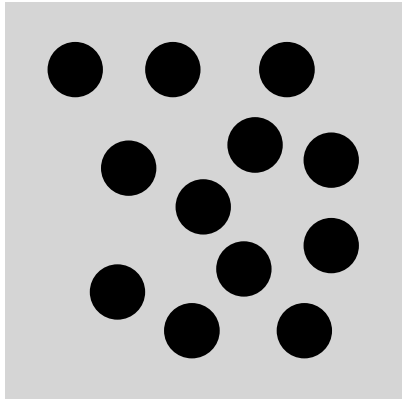


liquid on a metal surface

† *Gonella & Bonn Nat. Rev. Chem. 5, 466 (2021)*

Density Functional Theory (DFT)

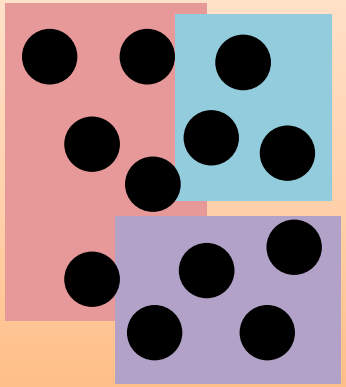
Kohn-Sham DFT



$$\rho(\mathbf{r}) = \sum_i^N \psi_i(\mathbf{r})$$

$$E_{\mathrm{KS-DFT}} = T_s[\{\psi_i\}] + E_{eff}$$

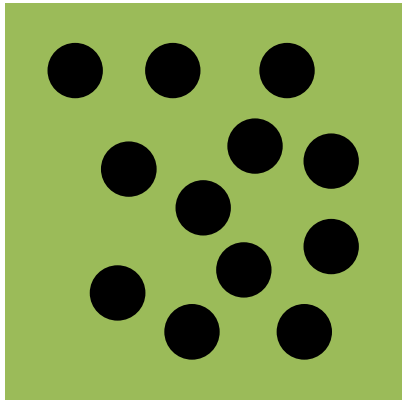
Subsystem DFT



$$\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r}) = \sum_I \sum_i^{N_I} \psi_{I,i}(\mathbf{r})$$

$$E_{\mathrm{SDFT}} = \sum_I T_s[\{\phi_{I,i}\}] + T_s[\rho] - \sum_I T_s[\rho_I] + E_{eff}$$

Orbital-Free DFT



$$\rho(\mathbf{r})$$

$$E_{\mathrm{OF-DFT}} = T_s[\rho] + E_{eff}$$

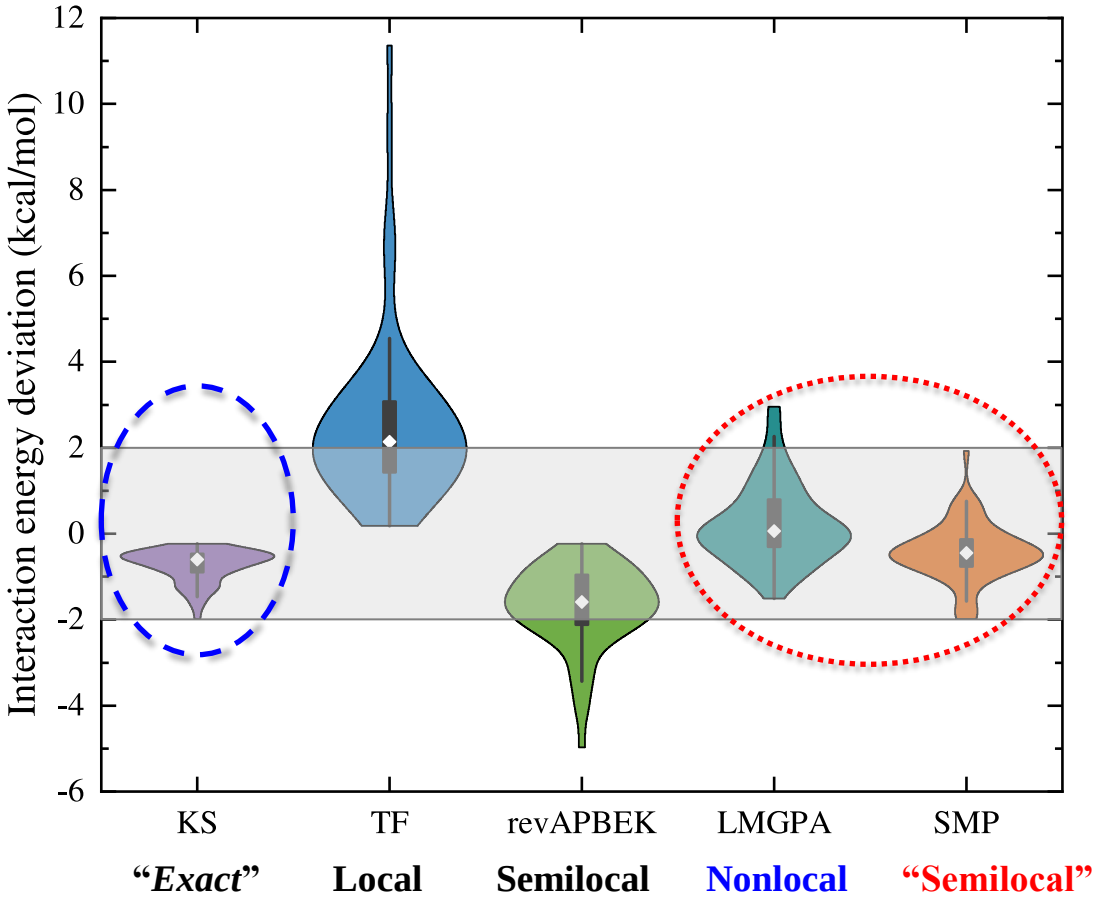
$$T_s^{\mathrm{nad}} \approx T_s[\rho] - \sum_I T_s[\rho_I]$$

Efficiency

Accuracy

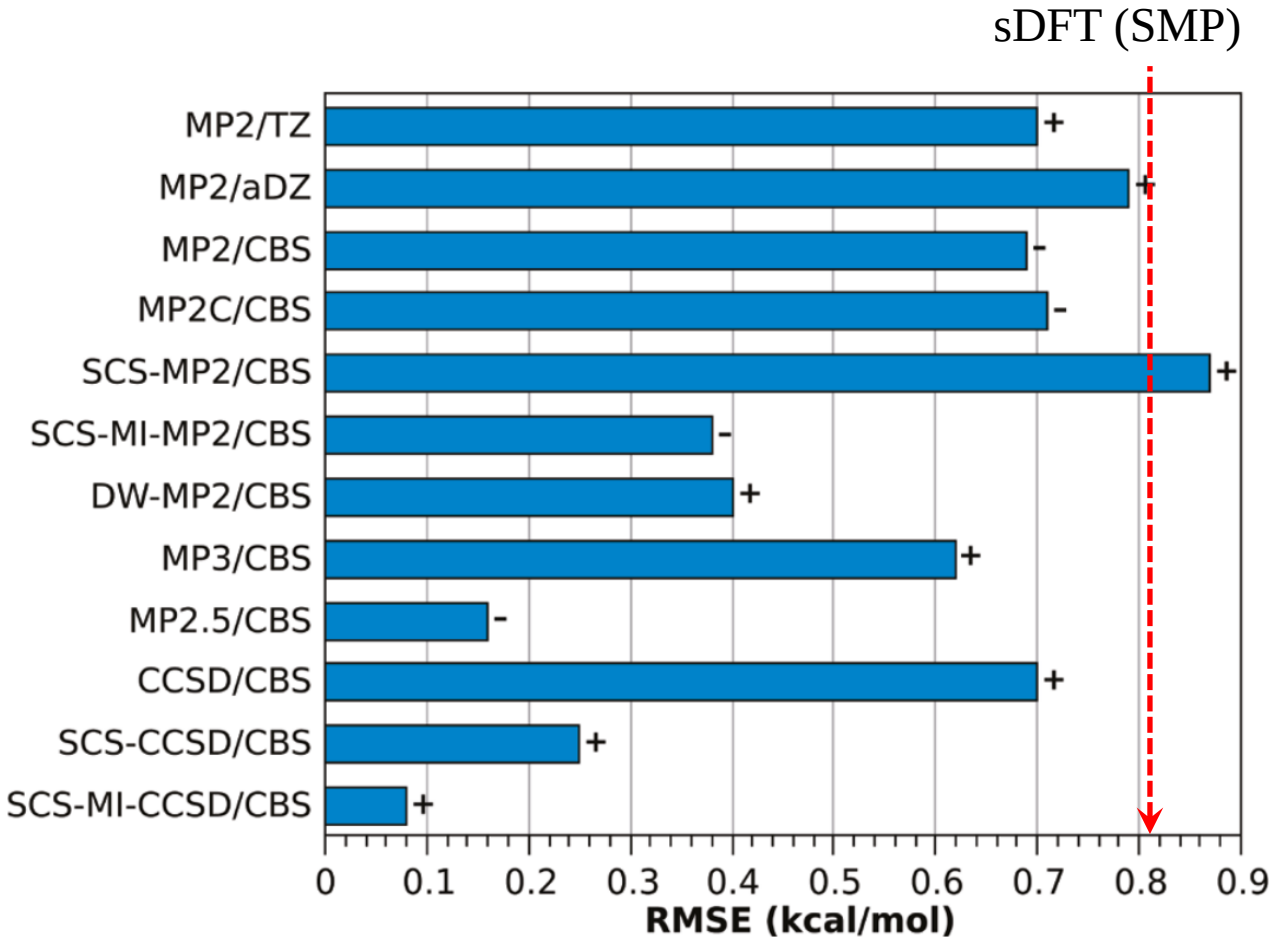
How accurate is sDFT?

Deviation against CCSD(T)/CBS for the S66 test set



$$T_s^{\mathrm{nad}} \approx T_s[\rho] - \sum_I T_s[\rho_I]$$

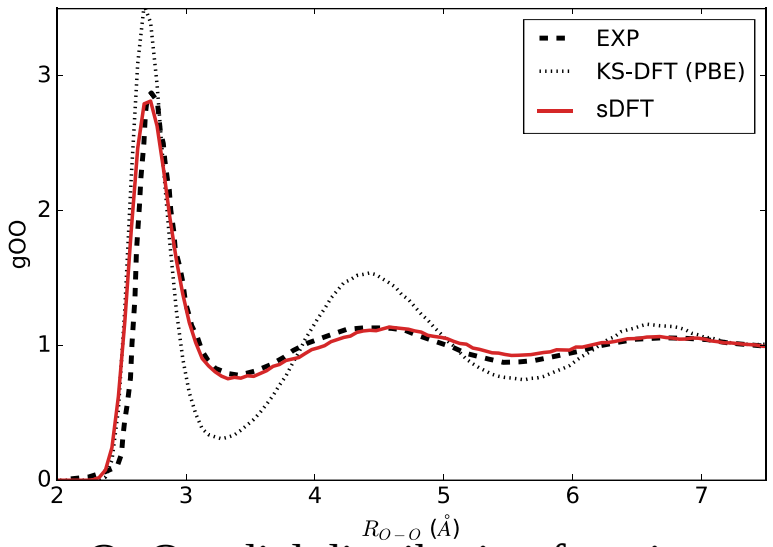
† X. Shao, W. Mi, and M. Pavanello, J. Chem. Theory Comput. 17, 3455 (2021)



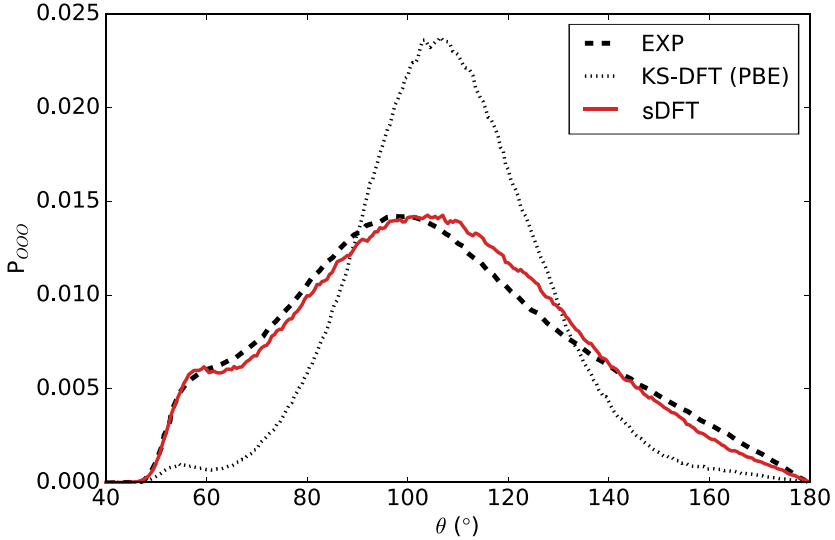
† *J. Chem. Theory Comput. 7, 2427 (2011)*

Success stories of sDFT

Liquid water



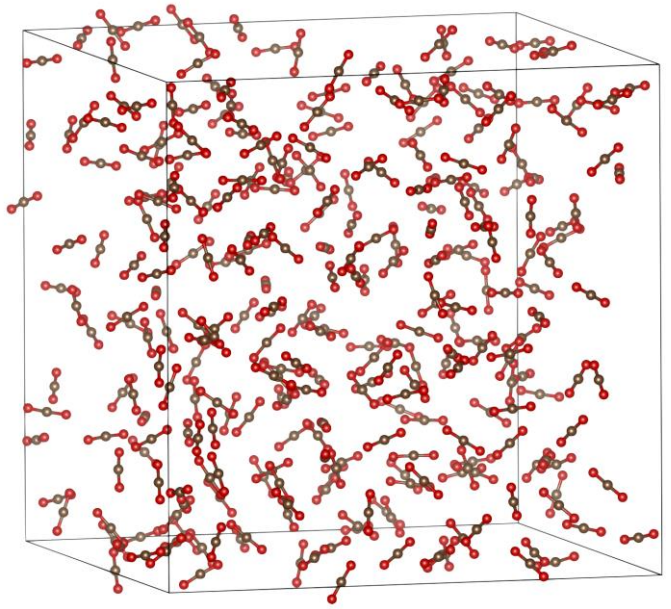
O−O radial distribution functions

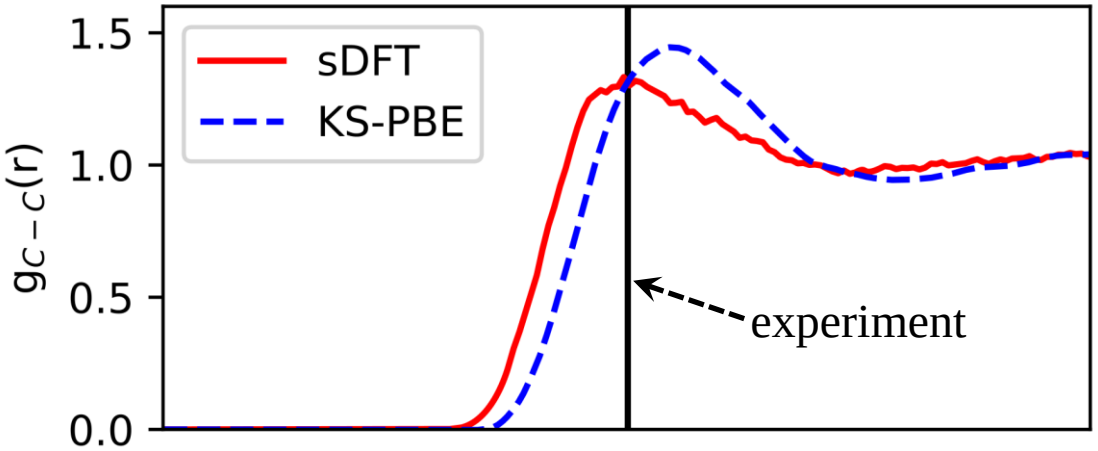


O−O−O angular distribution functions

† *Genova, Ceresoli & Pavanello J. Chem. Phys. 144, 234105 (2016)*

Liquid CO_2

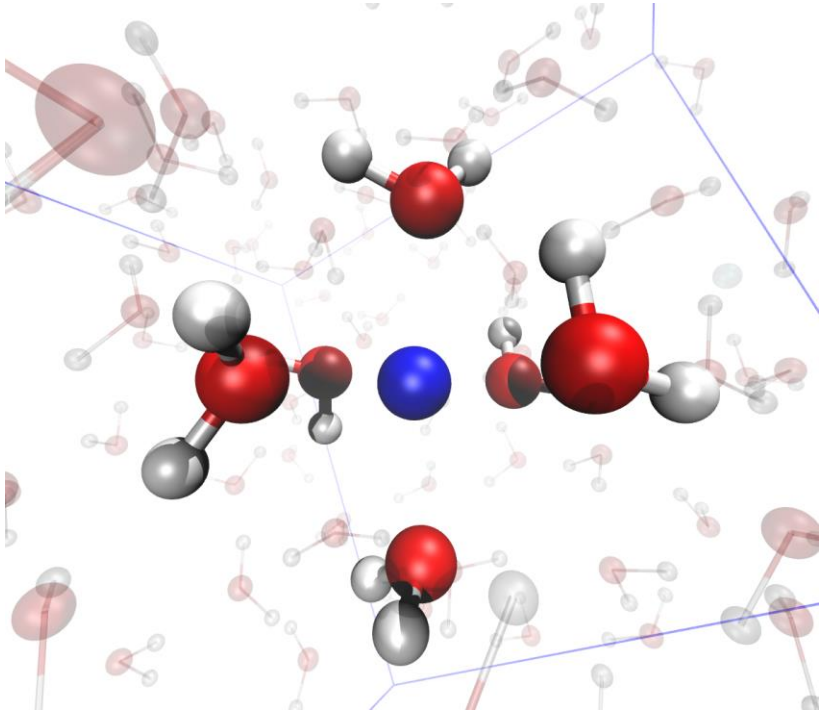


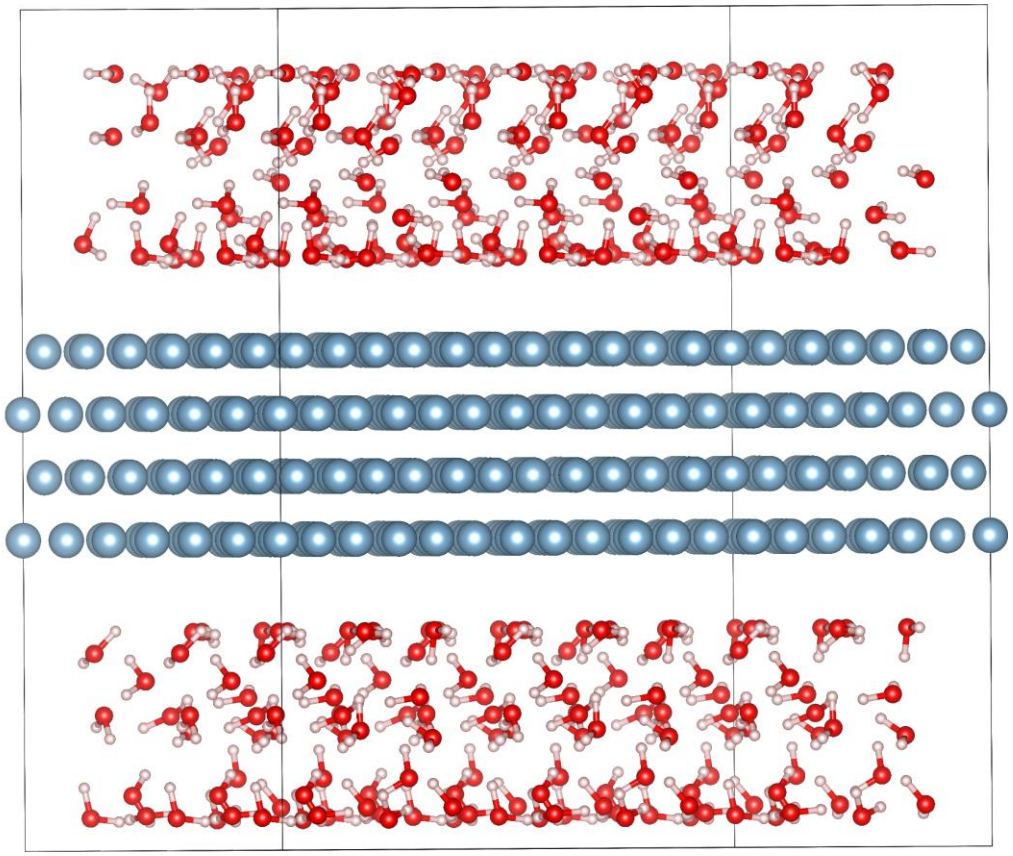


C−C radial distribution functions

† *Mi, Ramos, Maranhao & Pavanello, J. Phys. Chem. Lett. 10, 7554 (2019)*

Limitation of current sDFT





Problem

strongly interacting subsystems

a single large subsystem

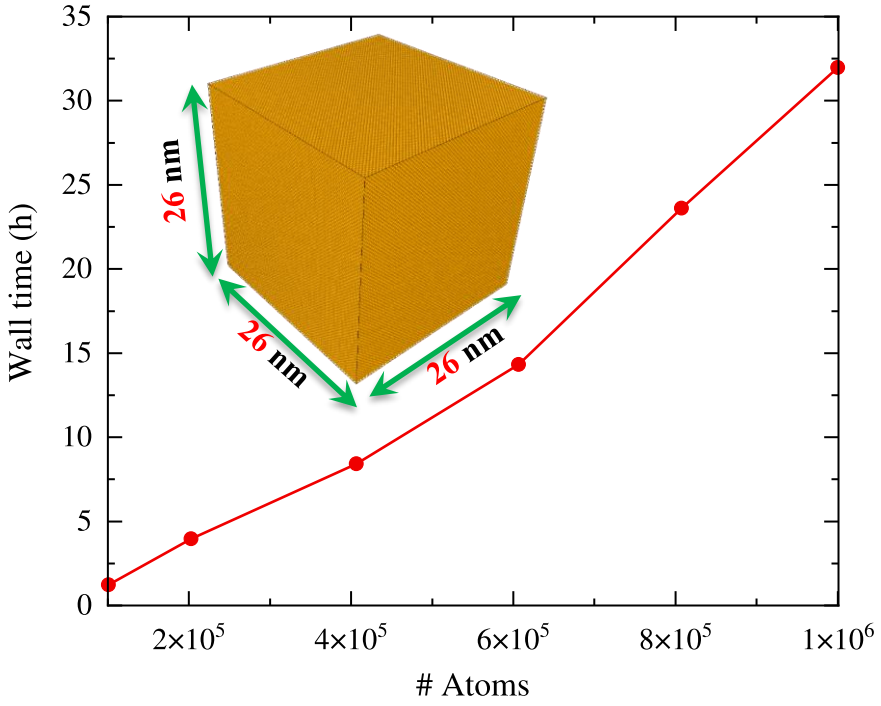
Solution

Merge the strongly interacting subsystems

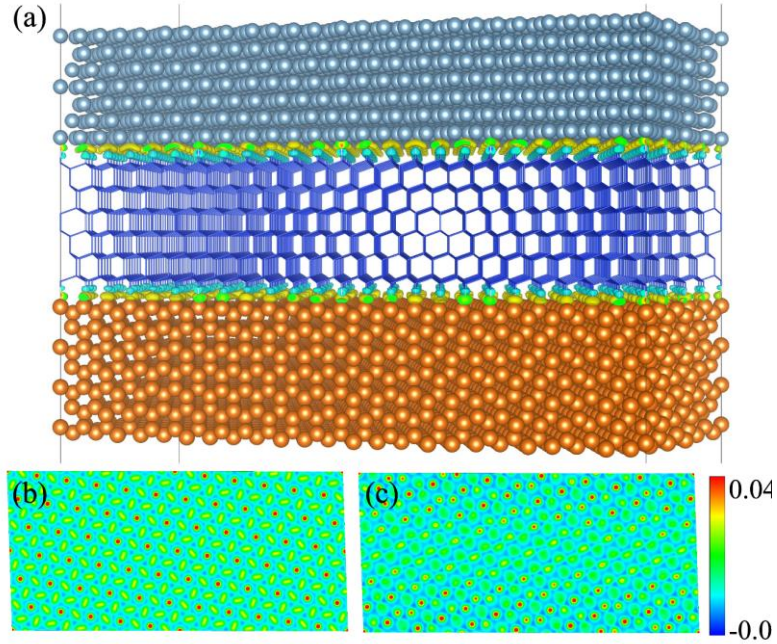
OF-DFT for the larger metallic subsystem

Just OF-DFT (1 CPU)

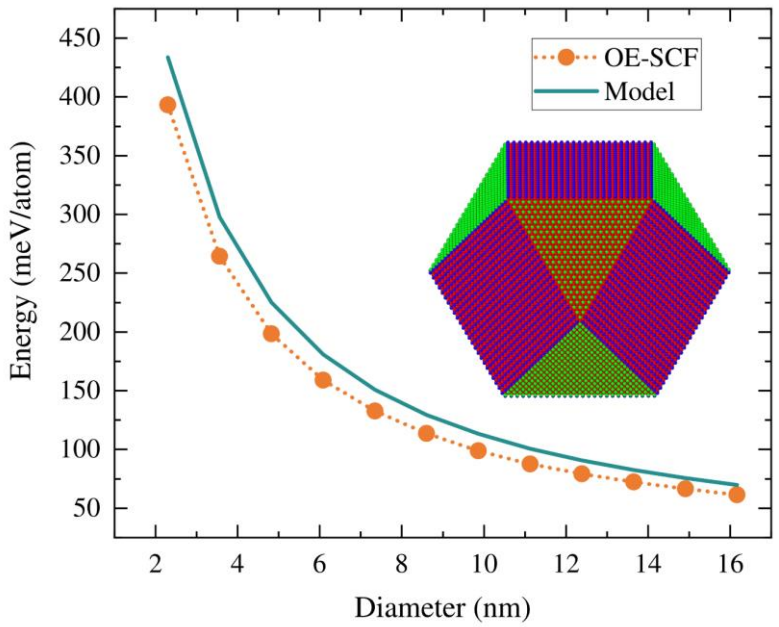
OF-DFT timing: bulk Al



Interface polarization



Nanoparticles



OF-DFT can be used for some metals and some semiconductors

† X. Shao, K. Jiang, W. Mi, A. Genova, and M. Pavanello, WIREs Comput Mol Sci 11, (2020)
† X. Shao, W. Mi, and M. Pavanello, J. Phys. Chem. Lett. 12, 4134 (2021)

sDFT implementation

http://edftpy.rutgers.edu

Python+drivers

http://dftpy.rutgers.edu

- OF-DFT calculation
- All kinds of density functionals

http://qepy.rutgers.edu

- KS-DFT calculation
- Design different workflows

• • •

- Other drivers
- QM-MM

DFTpy and QEpy

http://dftpy.rutgers.edu

http://qepy.rutgers.edu

Installation

$ pip install dftpy

$ pip install qepy

Script

```
....
funcDict = {'KE':KE, 'XC':XC, 'HARTREE':HARTREE, 'PSEUDO':PSEUDO}
EnergyEvaluator = TotalFunctional(**funcDict)
opt = Optimization(EnergyEvaluator=EnergyEvaluator)
rho_new = opt.optimize_rho(guess_rho=rho)
```

```
from qepy.driver import Driver
driver = Driver('qe.in', comm = None)
driver.scf()
energy = driver.get_energy()
wf  = driver.get_wave_function()
```

Command

$ python -m dftpy config.ini

$ python -m qepy --pw.x -i qe.in

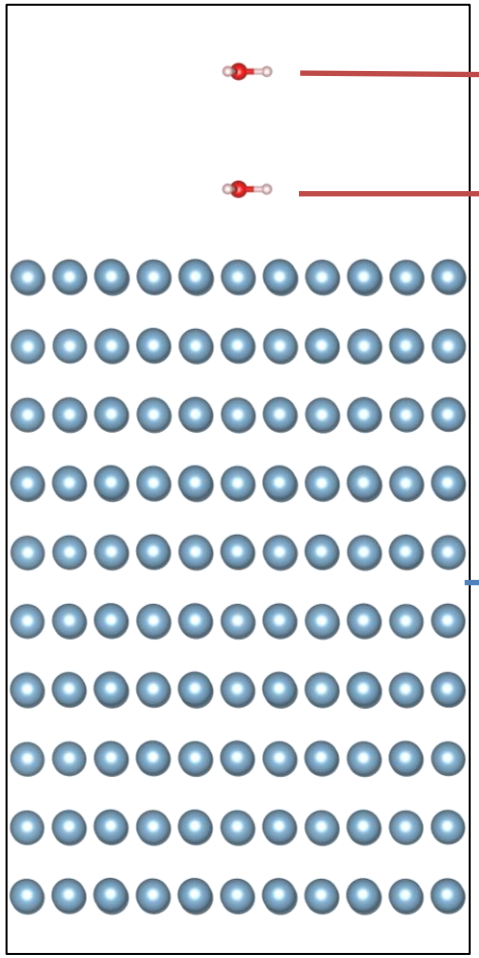
With mpi4py-fft:

$ mpirun -n 4 python -m dftpy config.ini

Same as QE:

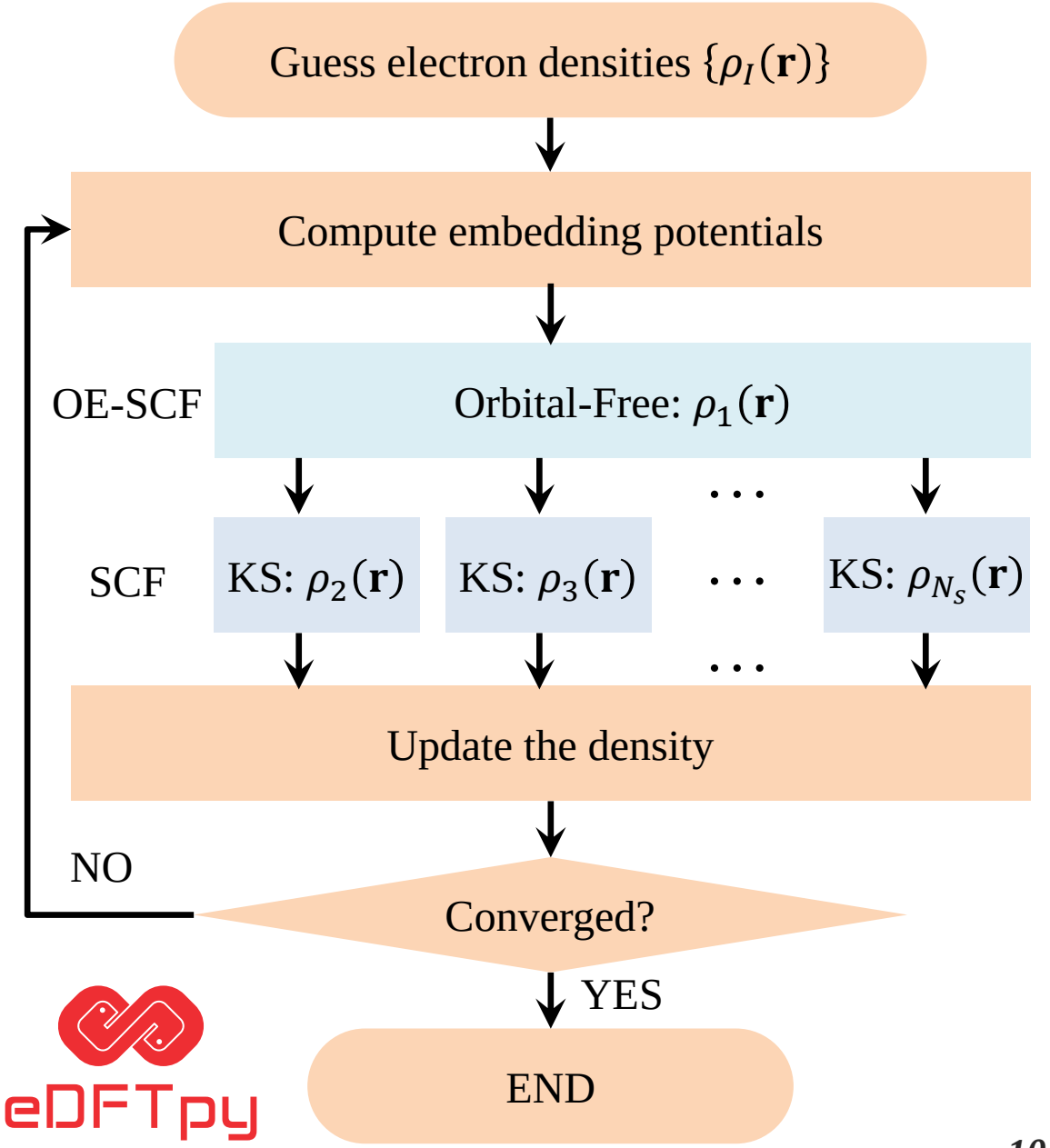
$ pw.x -i qe.in

Embedding KS-DFT with OF-DFT



QEpy

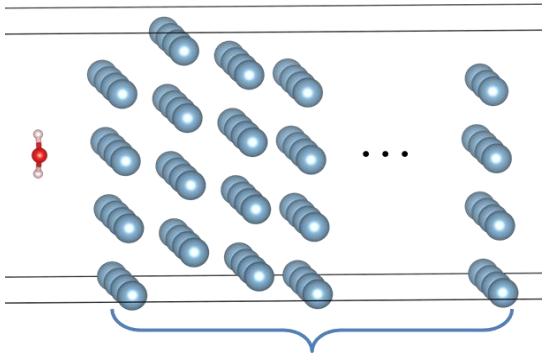
DFTpy



eDFTpy

† X. Shao, W. Mi, and M. Pavanello, J. Phys. Chem. Lett. 12, 4134 (2021)
† X. Shao, W. Mi, and M. Pavanello, J. Phys. Chem. Lett. 13, 7147 (2022).

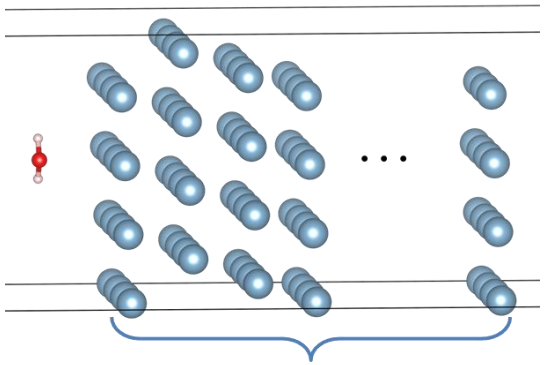
Binding energies of molecules on the Al(111) surfaces

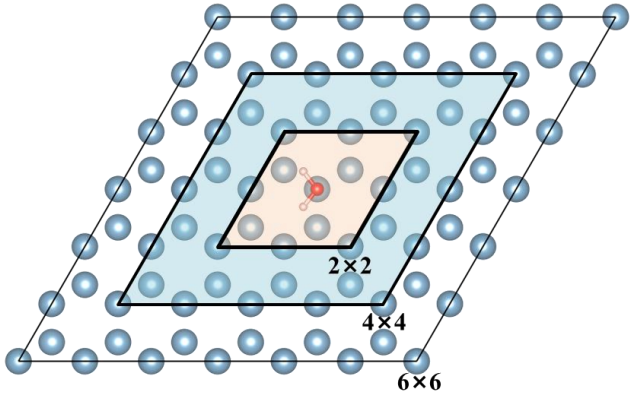


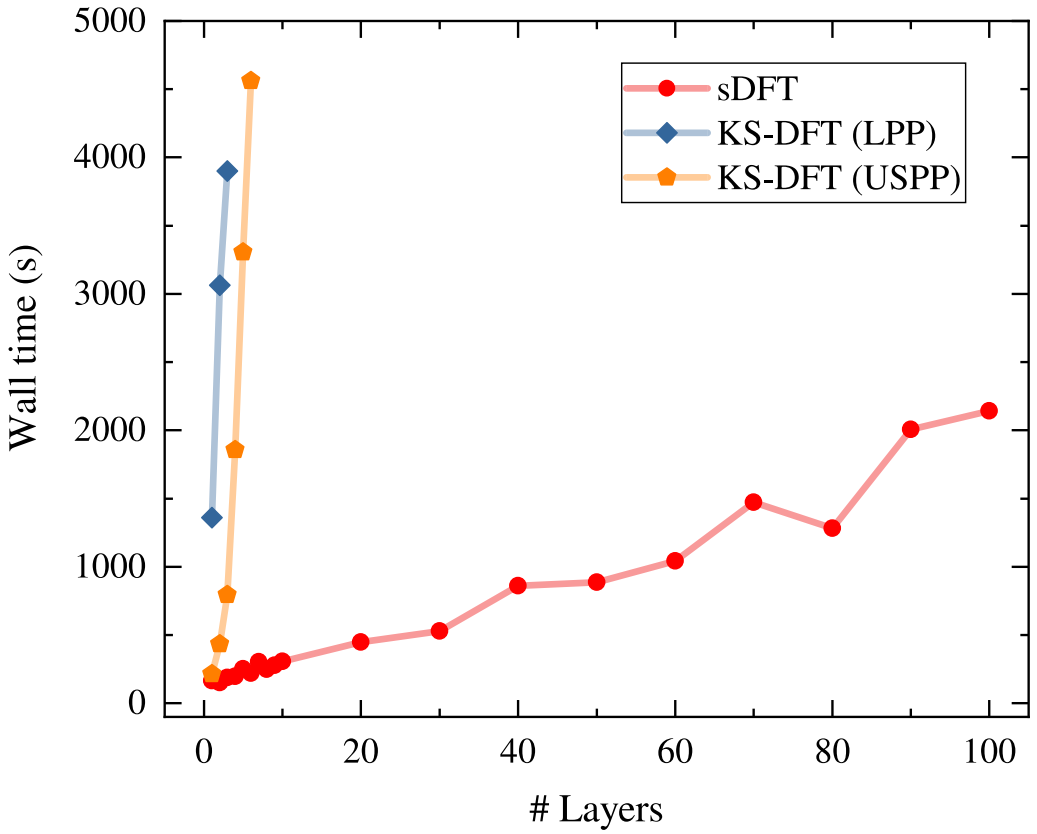
system	Method	E_B^{top} (meV)					$E_B^{top} - E_B^{hollow}$ (meV)				
		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 40$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 40$
H_2O	**sDFT (OF+KS)**	**40**	**34**	**33**	**30**	**30**	**52**	**48**	**49**	**49**	**45**
	sDFT (KS+KS)	75	52	33	45		63	50	46	52	
CO_2	**sDFT (OF+KS)**	**-181**	**-181**	**-180**	**-181**	**-181**	**-44**	**-42**	**-43**	**-45**	**-44**
	sDFT (KS+KS)	-134	-154	-165	-145		-32	-31	-40	-13	

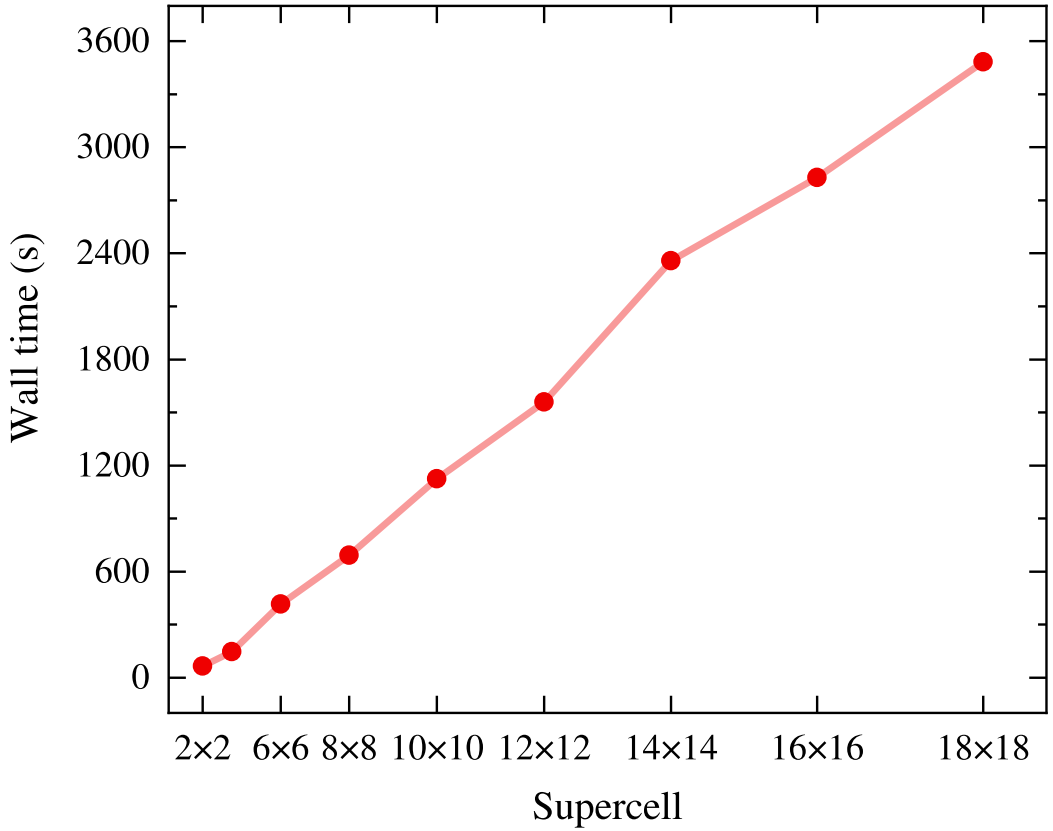
† X. Shao, W. Mi, and M. Pavanello, J. Phys. Chem. Lett. 13, 7147 (2022)

Efficiency

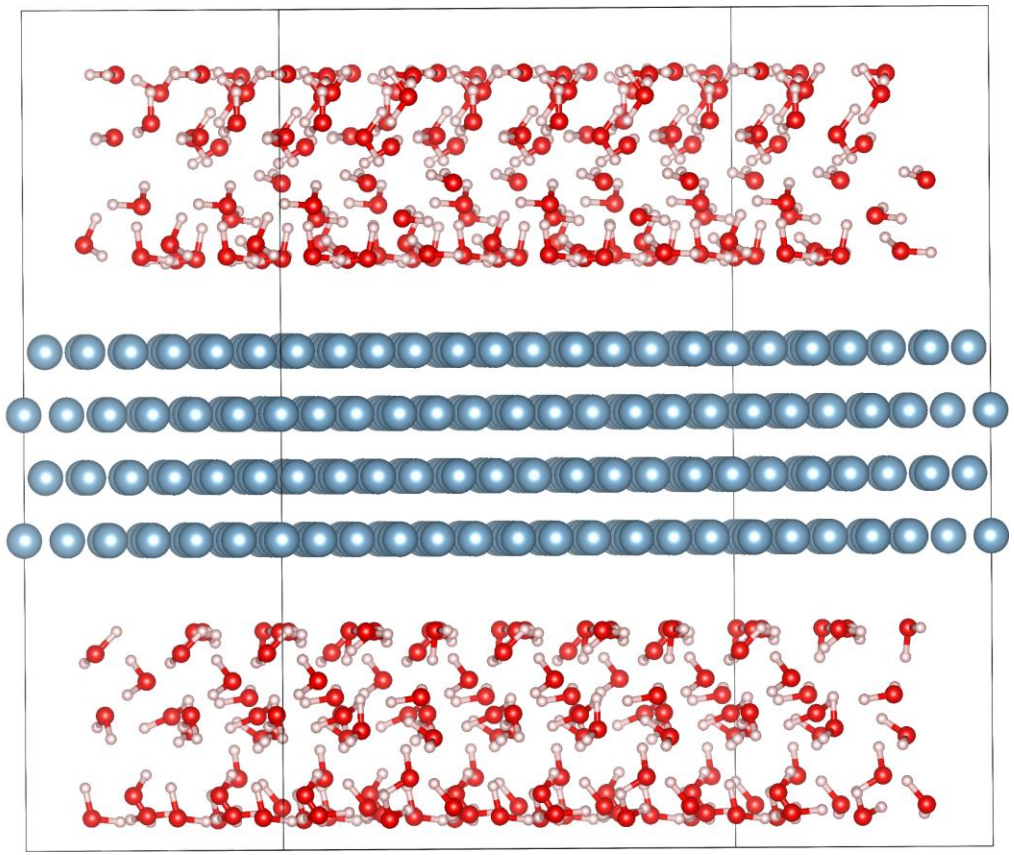

n layers

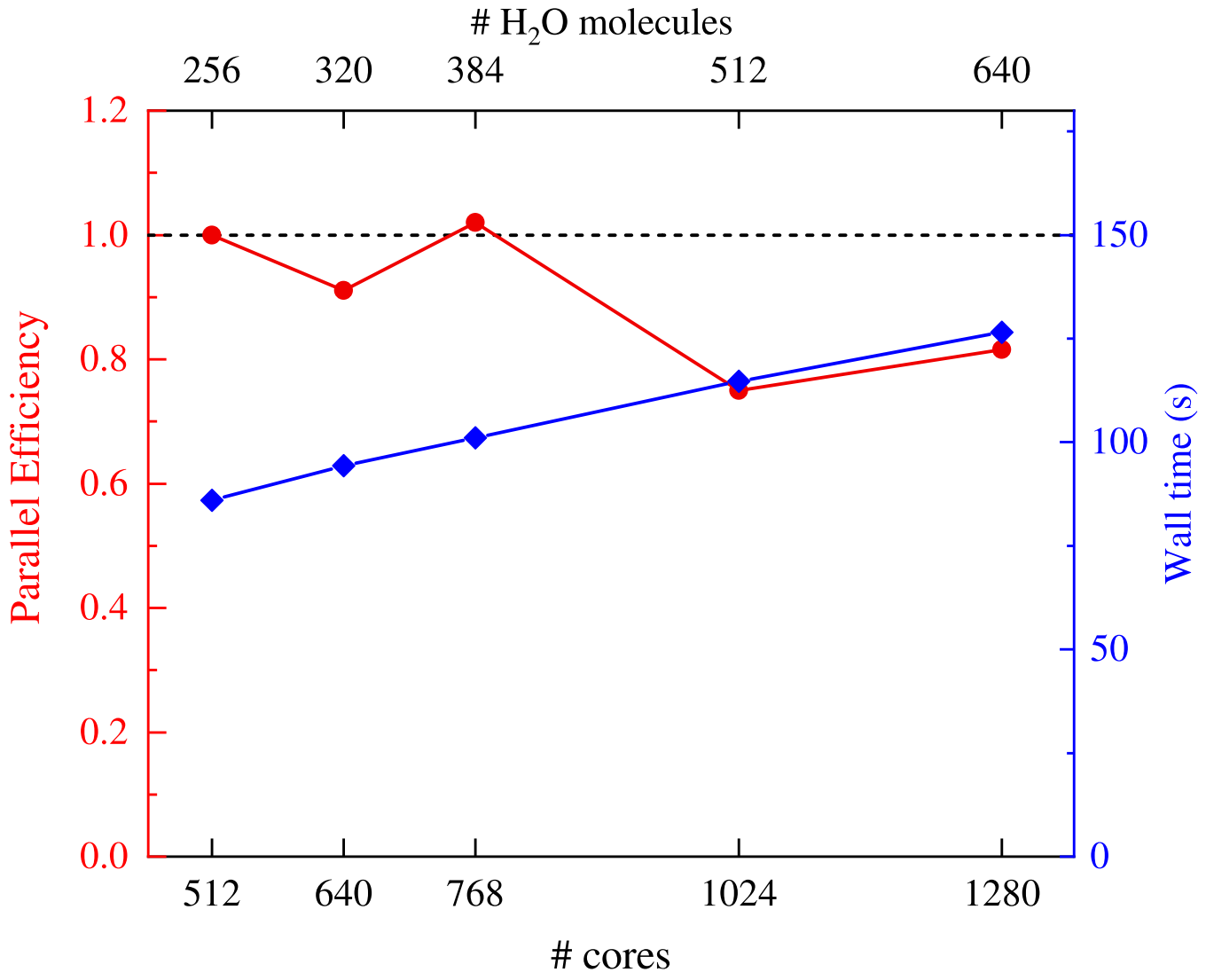

2×2
4×4
6×6


sDFT
KS-DFT (LPP)
KS-DFT (USPP)
Wall time (s)
Layers
0
1000
2000
3000
4000
5000
0
20
40
60
80
100


Wall time (s)
Supercell
0
600
1200
1800
2400
3000
3600
2×2
6×6
8×8
10×10
12×12
14×14
16×16
18×18

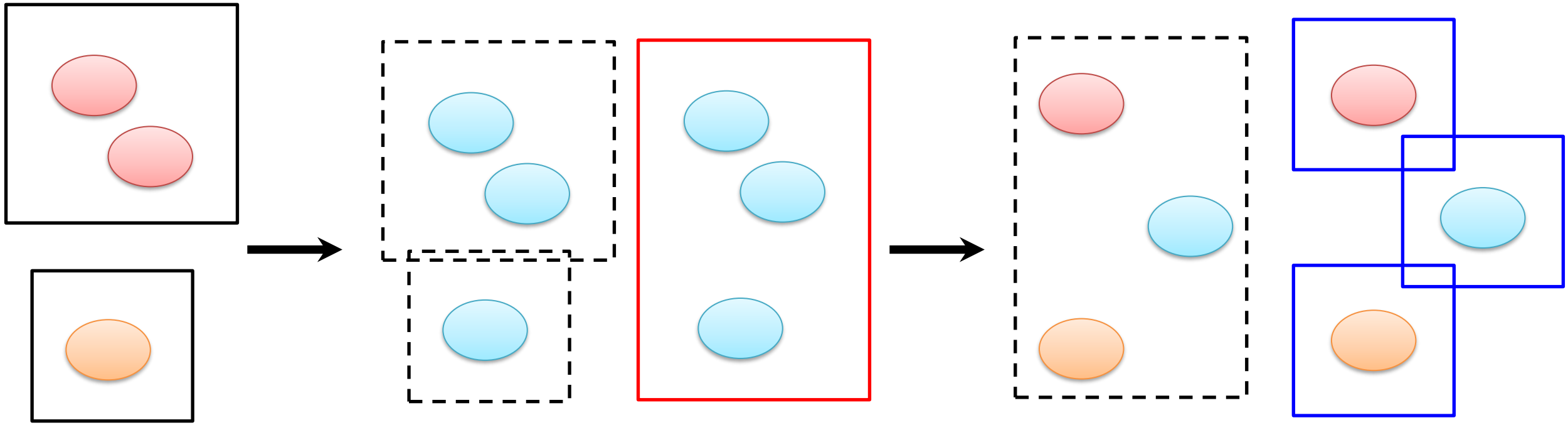
Water on Al slab





† X. Shao, W. Mi, and M. Pavanello, J. Phys. Chem. Lett. 13, 7147 (2022)

Adaptive sDFT : merge and split



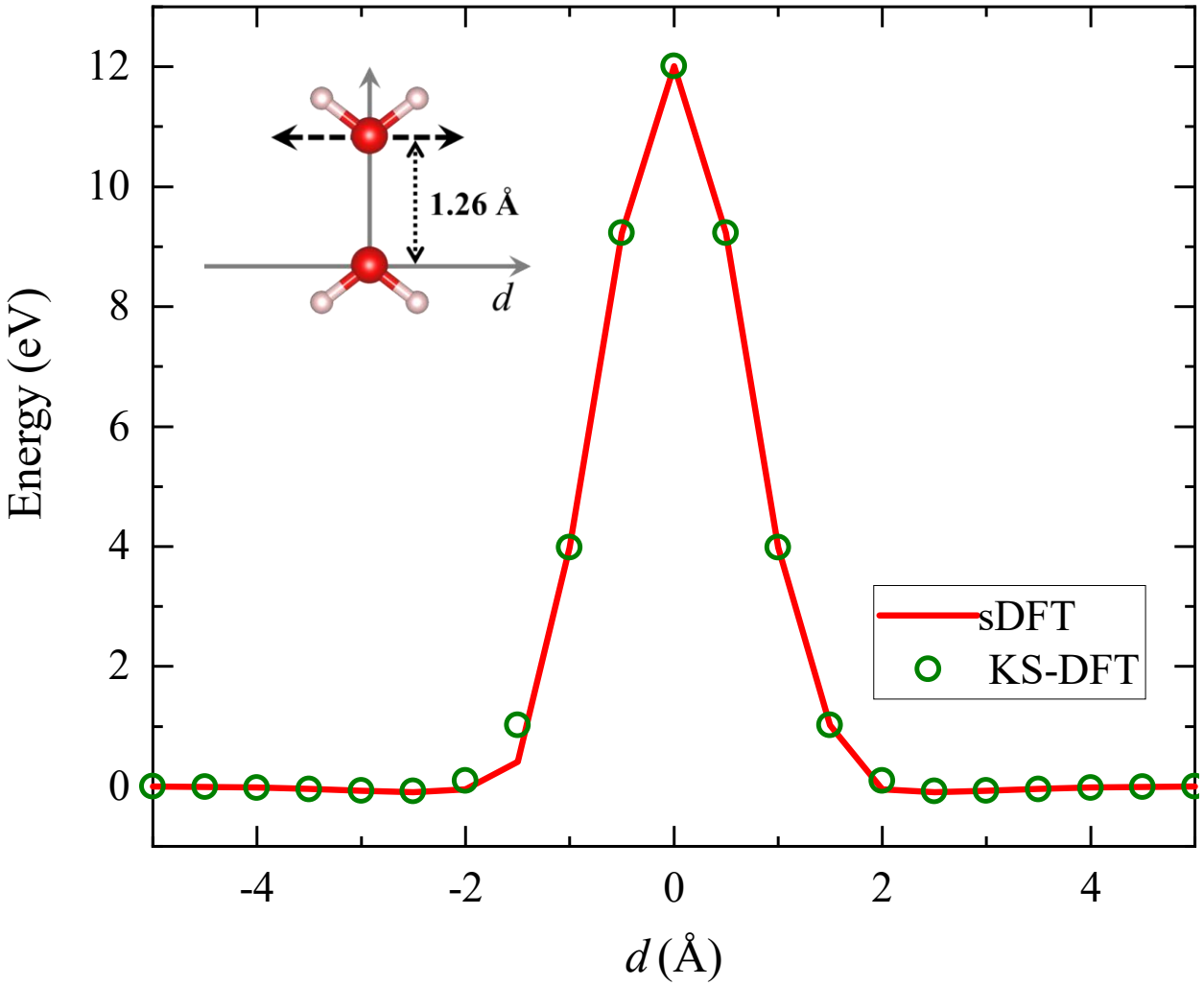
- Automatically “**Merge**” and “**Split**" subsystems
- Update computational settings
- Redefine parallelization on-the-fly

} **Adaptive** sDFT

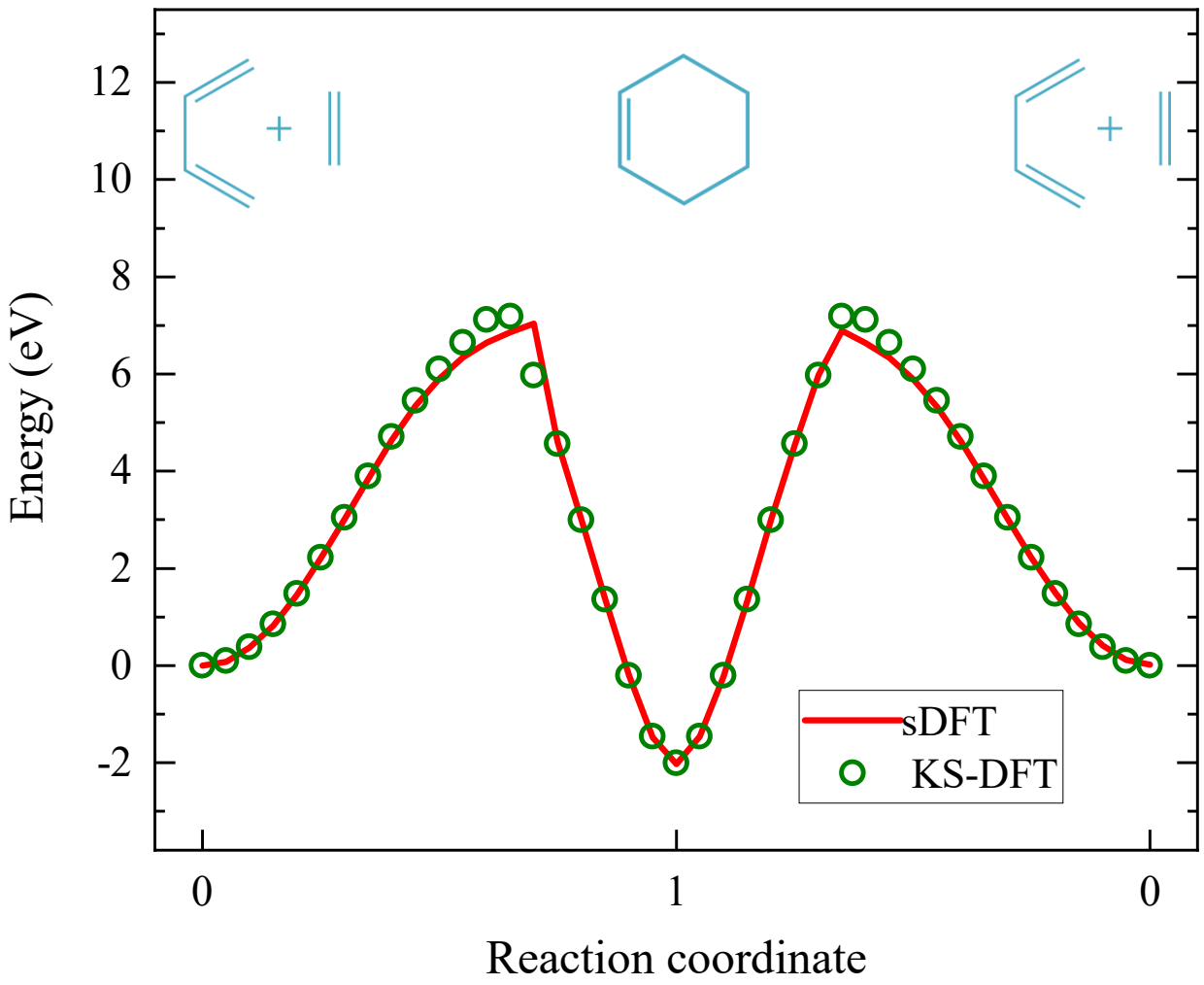
† Shao, Lopez, Musa, Nouri, and Pavanello, J. Chem. Theory Comput. 18, 6646 (2022)

Accuracy

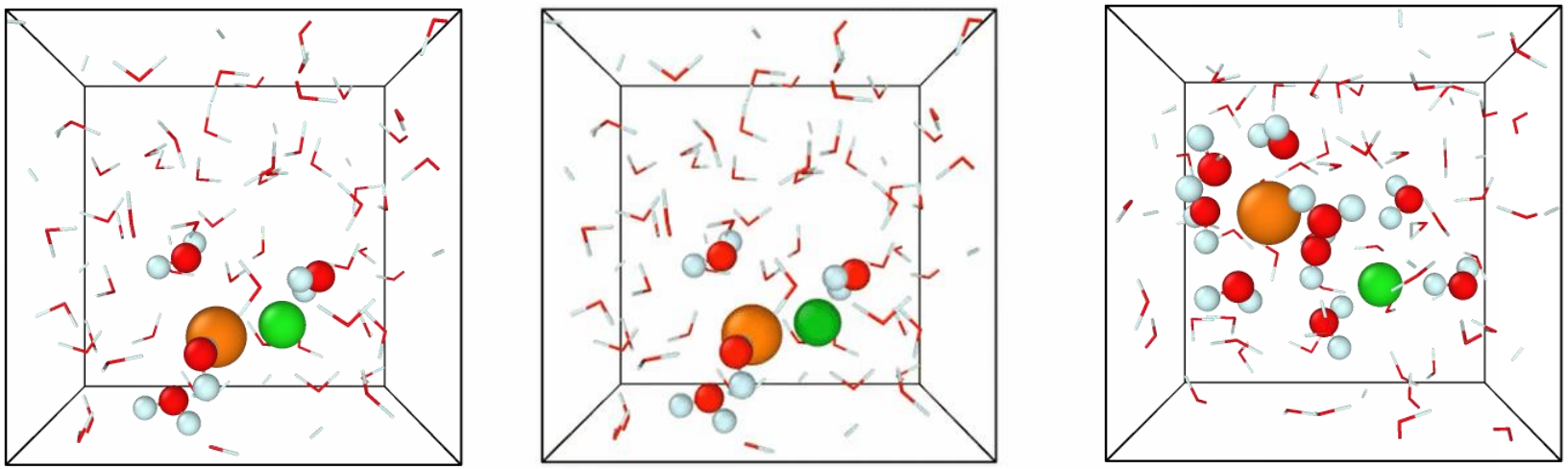
water dimer

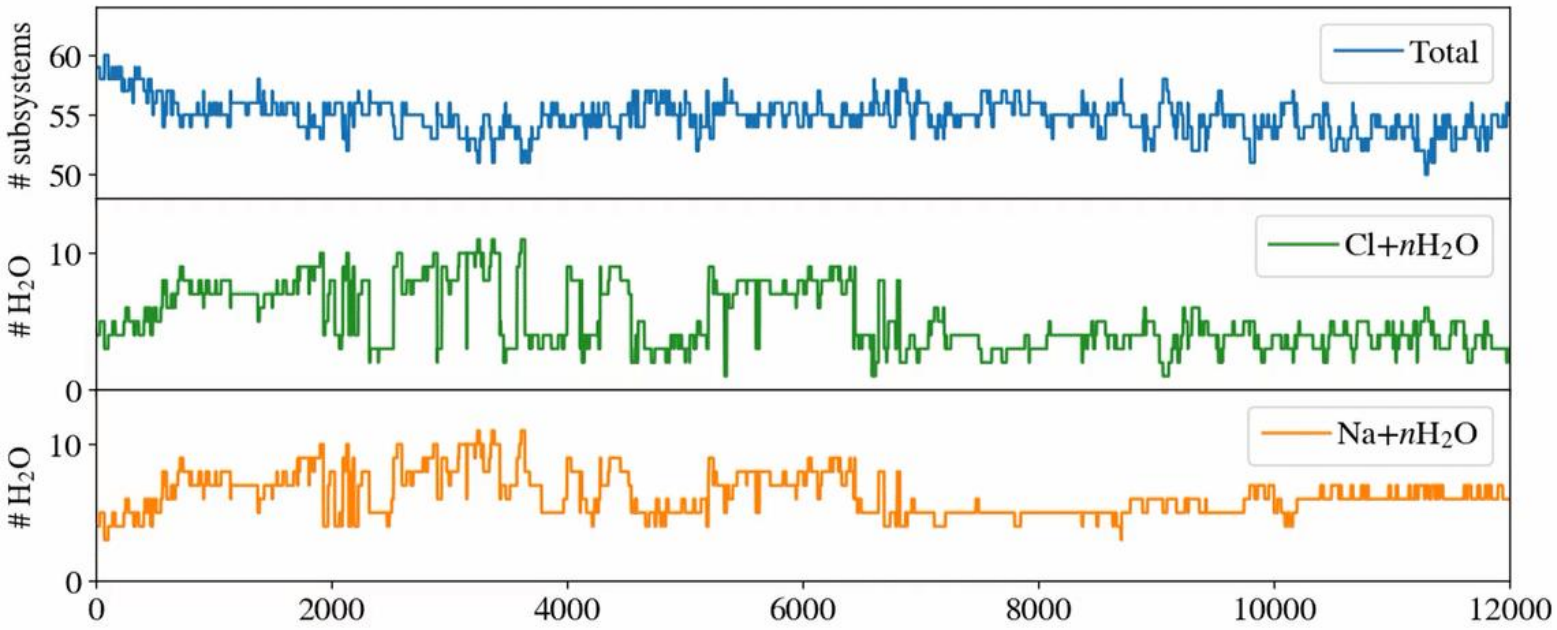


Diels-Alder reaction



Dissolution of NaCl in Water





- NVT ab-initio dynamics for 12 ps
- NaCl in water -> Na^+_{aq} + Cl^-_{aq}

† Shao, Lopez, Musa, Nouri, and Pavanello, J. Chem. Theory Comput. 18, 6646 (2022)

Acknowledgements

- **Prof. Michele Pavanello**
  - Dr. Wenhui Mi
  - Dr. Kaili Jiang
  - Dr. Alessandro Genova
  - Dr. Rajib Khan
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  - Jessica Martinez
  - Andres Camilo Cifuentes

Thank you