

Subsystem DFT: A quantum embedding method

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Q-MS school on Quantum ESPRESSO - October 10-13, 2021

Acknowledgements



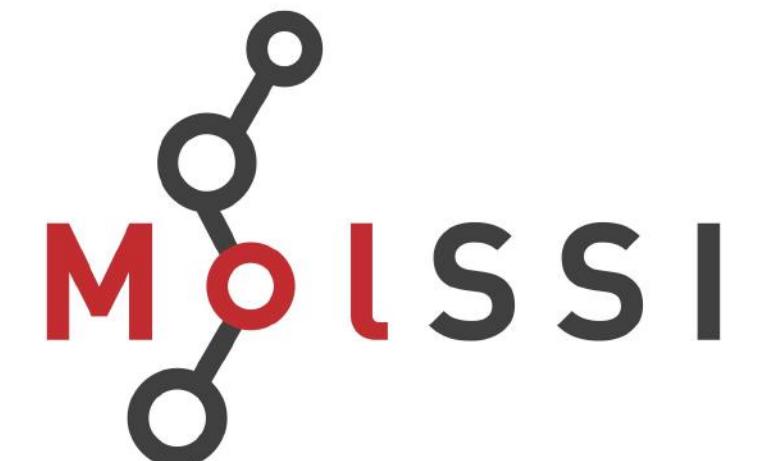
...and the workshop organizers!

- **Students**

- Alina Umerbekova
- Jessica Martinez
- Andres Cifuentes

- **Postdocs**

- Dr Xuecheng Shao
- Dr Wenhui Mi → Jilin U
- Dr Pablo Ramos → Suggy Jang
- Dr Kaili Jiang

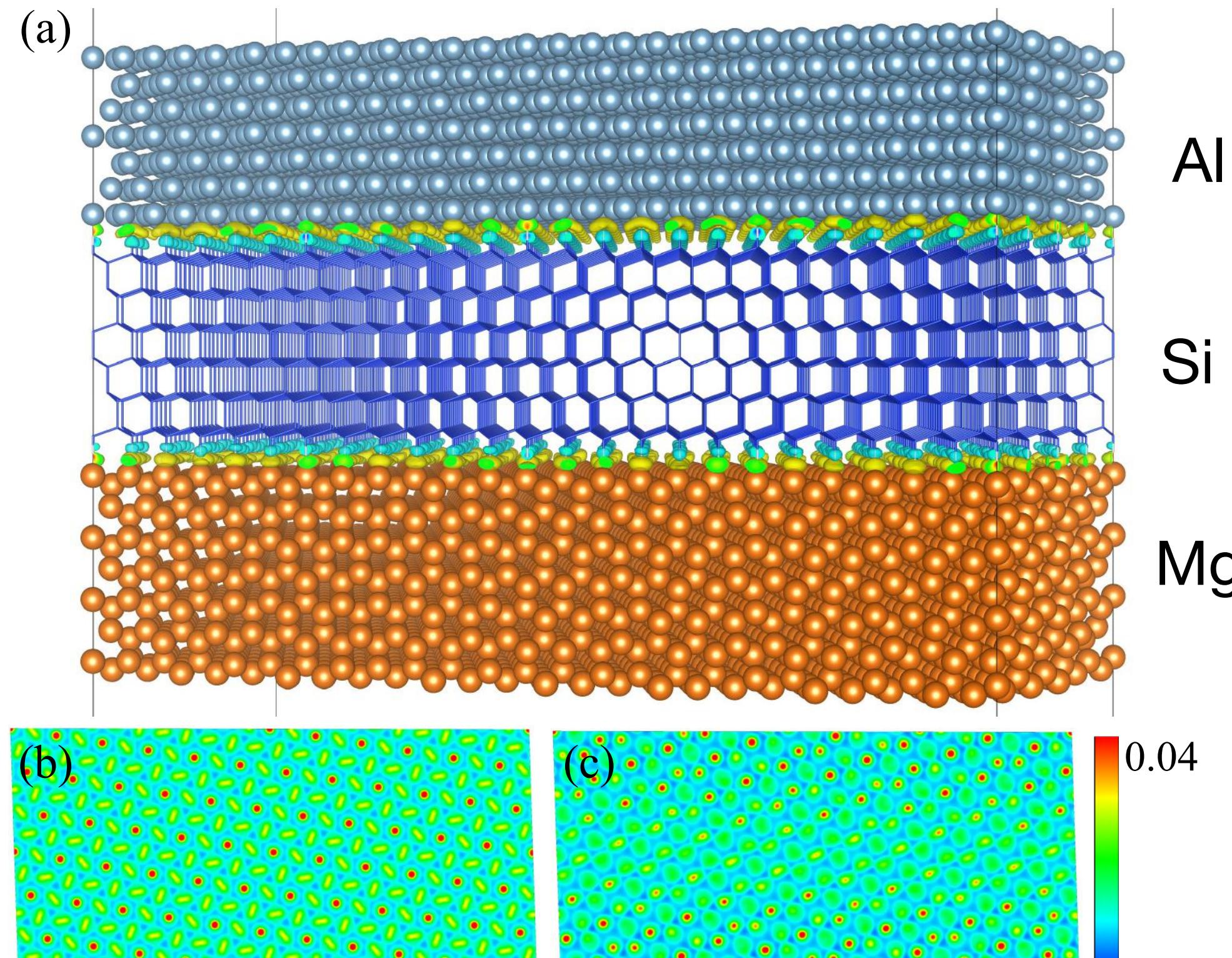


U.S. DEPARTMENT OF
ENERGY

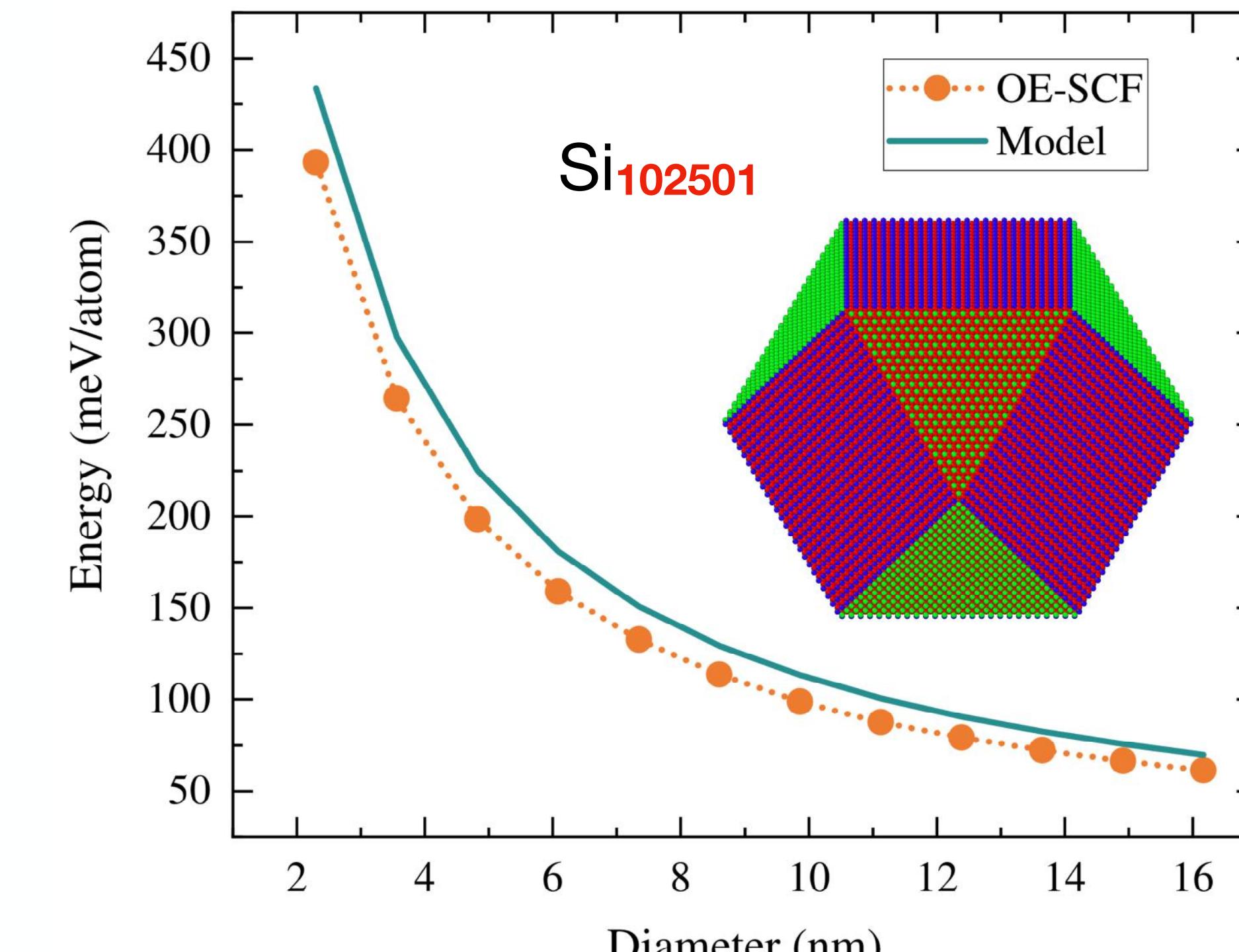
Outline

- What are large systems? Why most methods/software are ill-equipped?
- Simplification, fragmentation, approximation: subsystem DFT
- AIMD of liquids: water, fluid carbon dioxide
- Electron dynamics with subsystem TDDFT: molecule-surface and liquid water
- Tackle truly large systems with OFDFT and TD-OFDFT
- Nonstandard embedding workflows “OFDFT in DFT” (**science fiction?**)

What are large systems?



Realistic interface

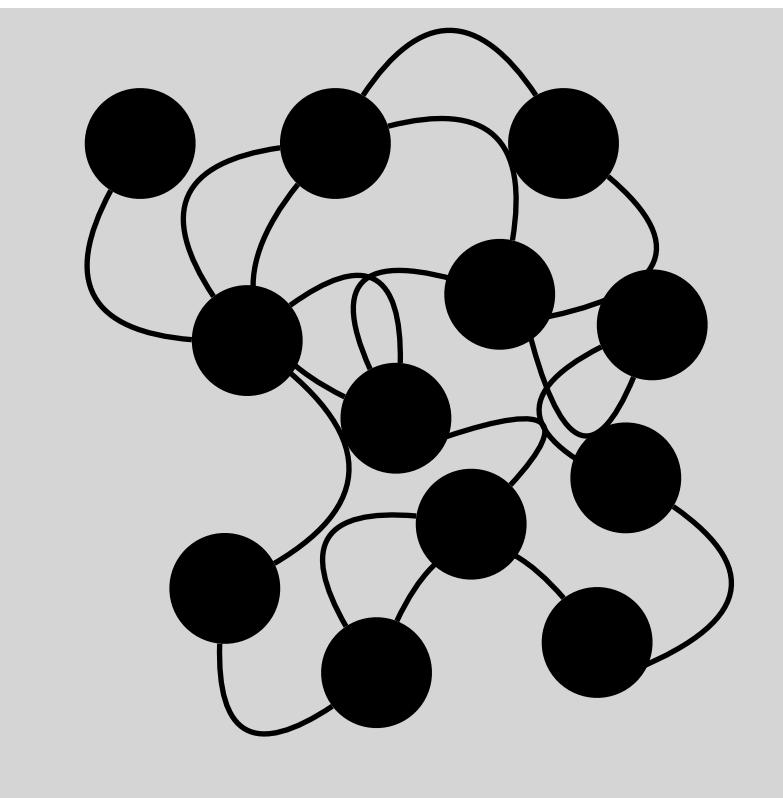


Realistic nanoparticle

A system is “large” when anything that scales quadratically or worse cannot be computed

Fragmentation, approximation, ...

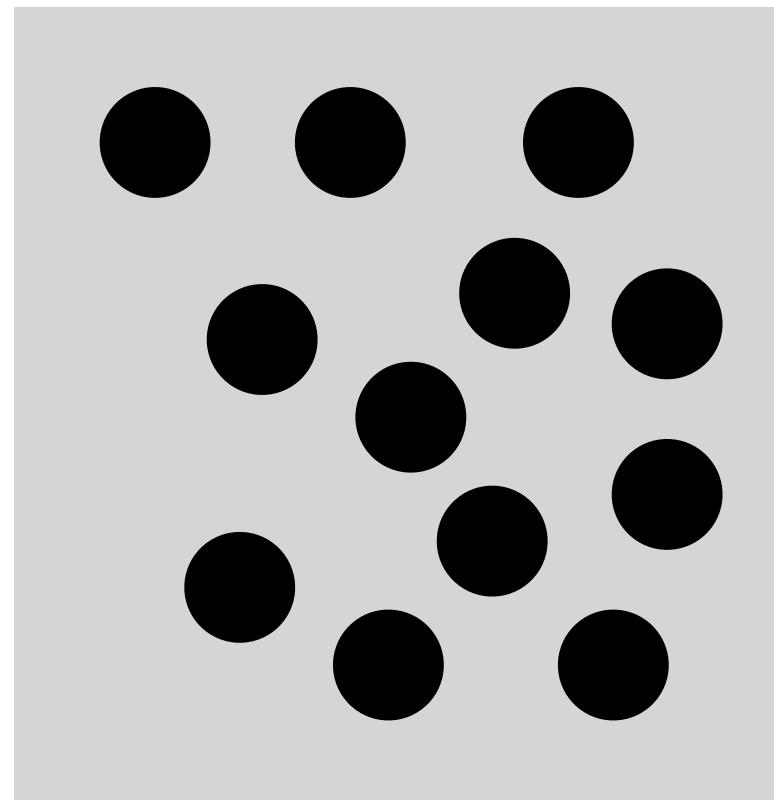
Quantum Chemistry



$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N$$

$$E[\Psi] = T[\Psi] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} + E_{ee}[\Psi]$$

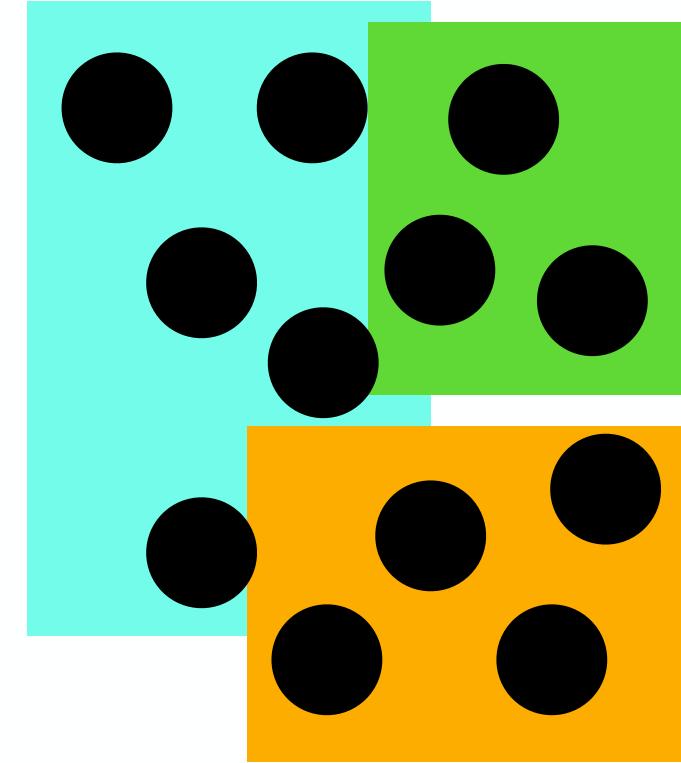
Kohn-Sham DFT



$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$$

$$E[\rho] = T_s[\{\phi_i\}] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} + E_{Hxc}[\rho]$$

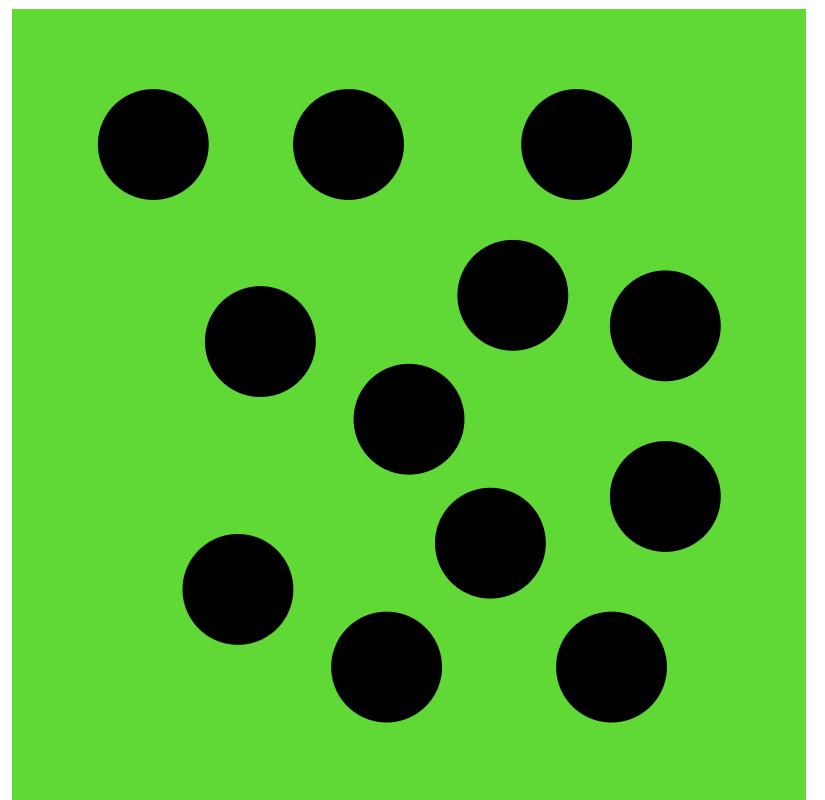
Subsystem DFT



$$\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$$

$$E_{sDFT}[\rho] = ??$$

Orbital-free DFT



$$\rho(\mathbf{r}) = |\psi_1(\mathbf{r})|^2$$

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} + E_{Hxc}[\rho]$$

Rearrange of the energy functional to introduce approximations, lower comp. cost, exploit error cancellation, ...



Subsystem DFT: “Divide et impera”

Total density

$$\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$$

Subsystem density

$$\rho_I(\mathbf{r}) = \sum_{(i)_I}^{occ} |\phi_{(i)_I}(\mathbf{r})|^2$$

Energy functional

$$E[\rho] = \sum_I E[\rho_I] + E^{nadd}[\{\rho_I\}]$$

Subsystem energy

$$E[\rho_I] = T_s[\rho_I] + E_{Hxc}[\rho_I] + \int v_{ext}(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r}$$

Nonadditive energy

$$E^{nadd}[\{\rho_I\}] = E[\rho] - \sum_I E[\rho_I] \rightarrow \tilde{T}_s^{nadd}[\{\rho_I\}] + E_{Hxc}^{nadd}[\{\rho_I\}]$$

Most studies involve **semilocal NAKE**: cheap and qualitatively OK

$$T_s^{nadd}[\{\rho_I(r)\}]$$

We developed the first **nonlocal NAKE** with much improved performance

$$T_s^{nadd}[\{\rho_I(r), \rho_I(r')\}]$$

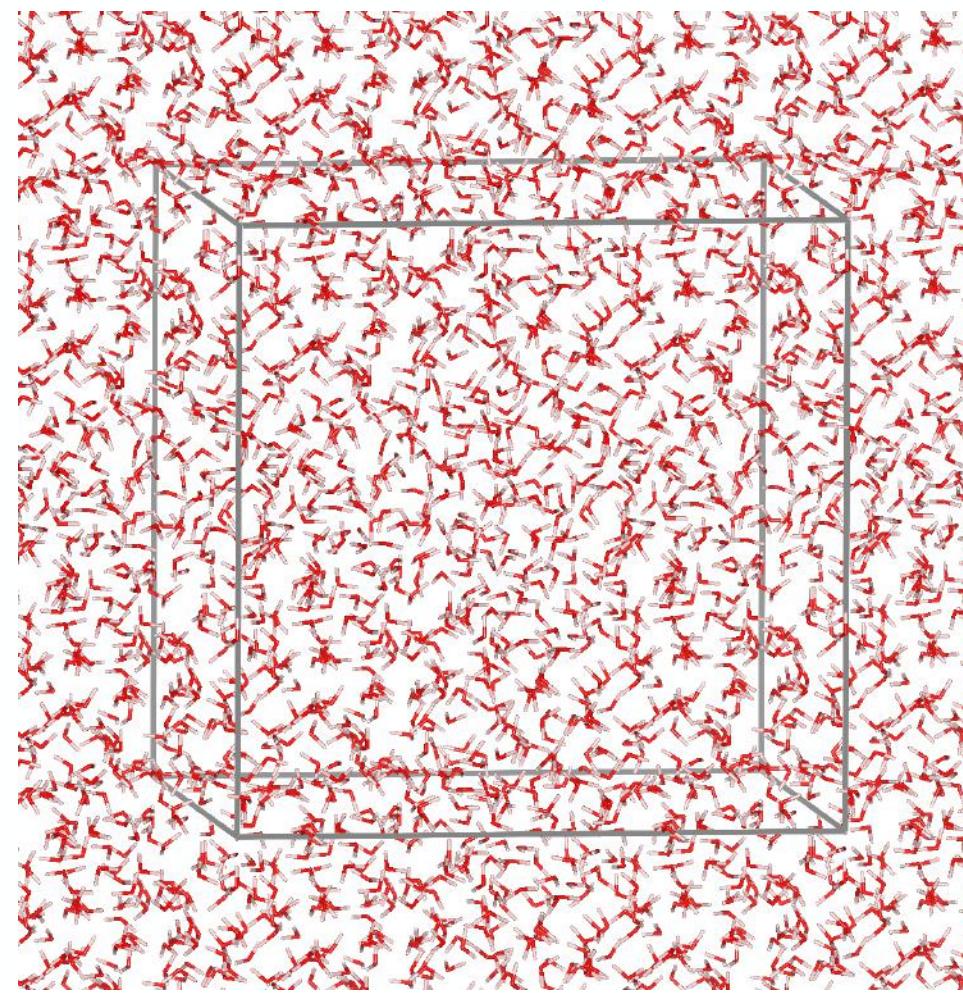


Embedded Quantum ESPRESSO
eqe.rutgers.edu

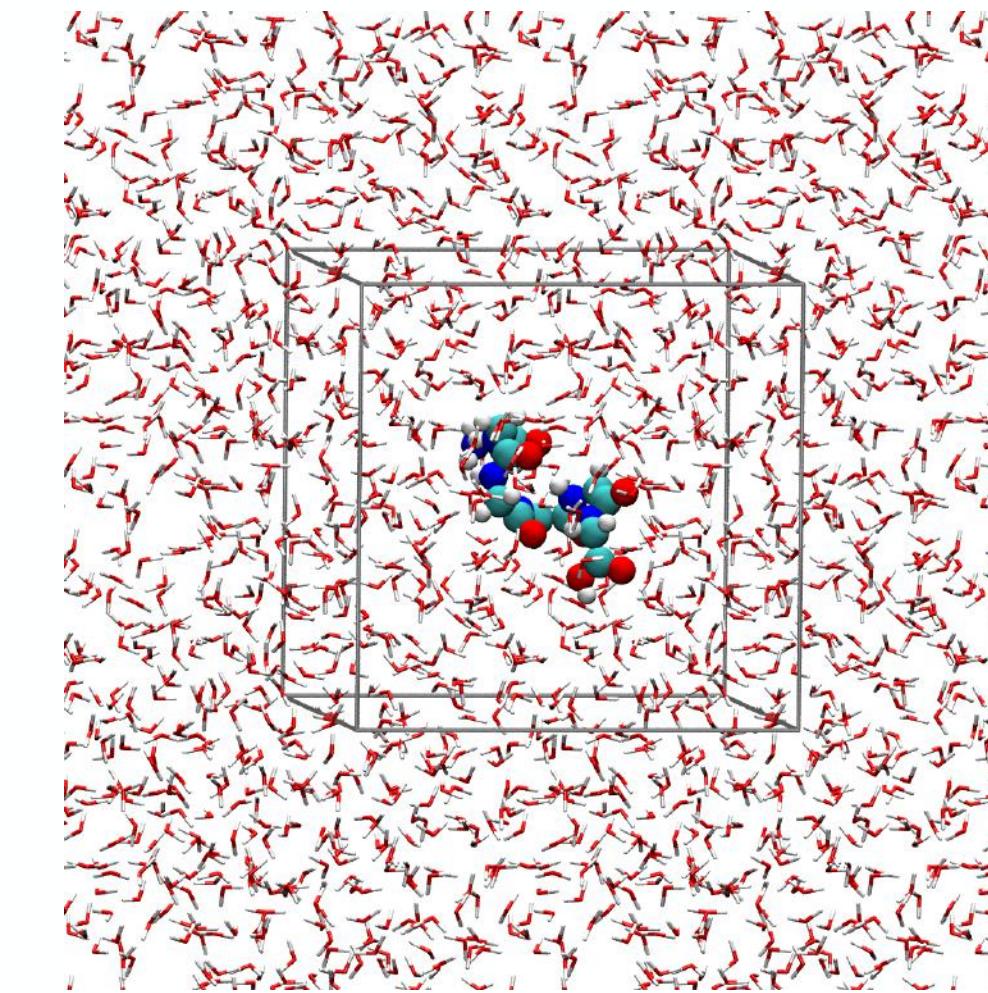
Embedded DFTpy
edftpy.rutgers.edu

sDFT with semilocal NAKEs: timings

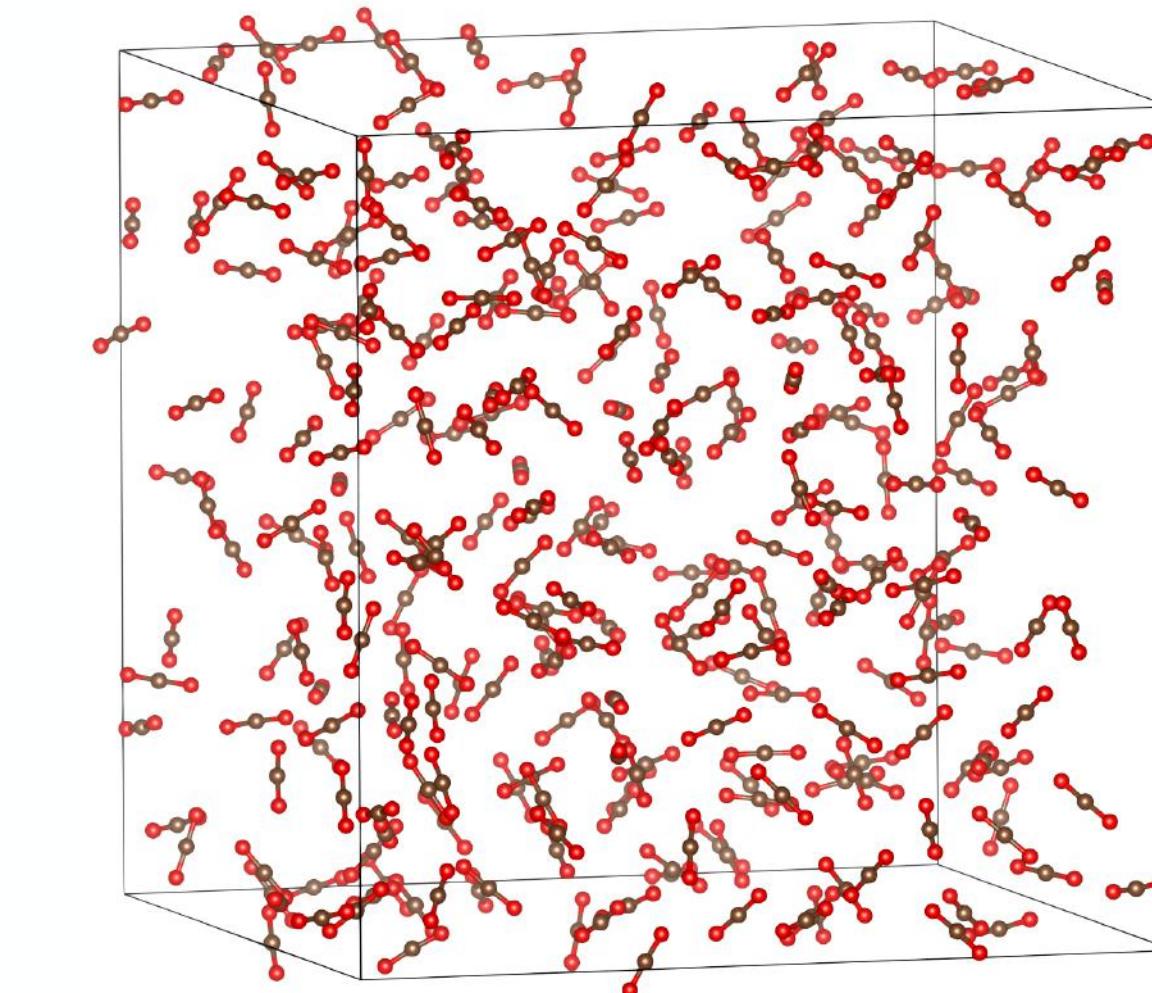
1024 H₂O



(GLY)₆(H₂O)₃₉₅



256 CO₂



Volume

30726 Å

12656 Å

27000 Å

Time
sDFT / DFT

25 ×

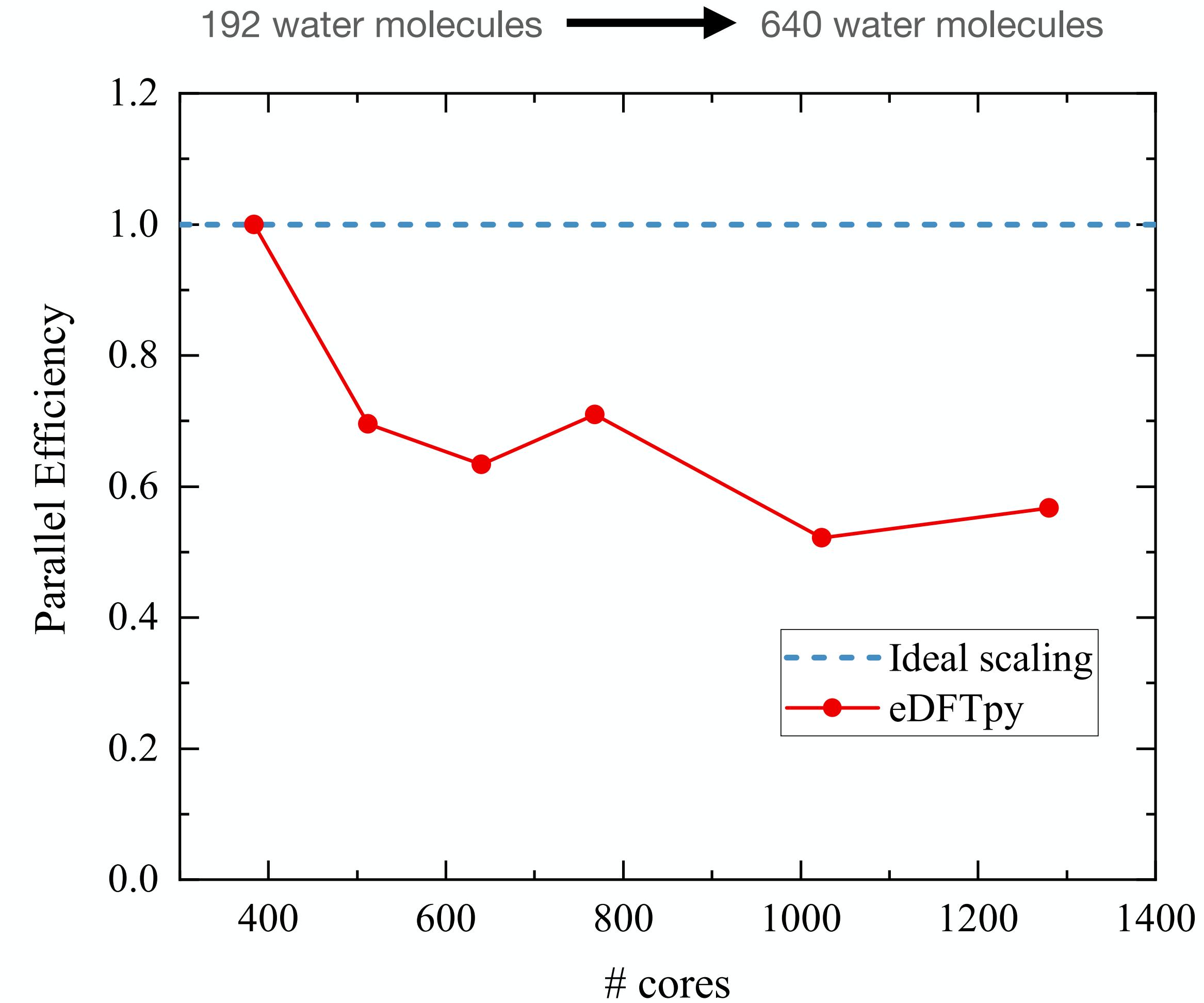
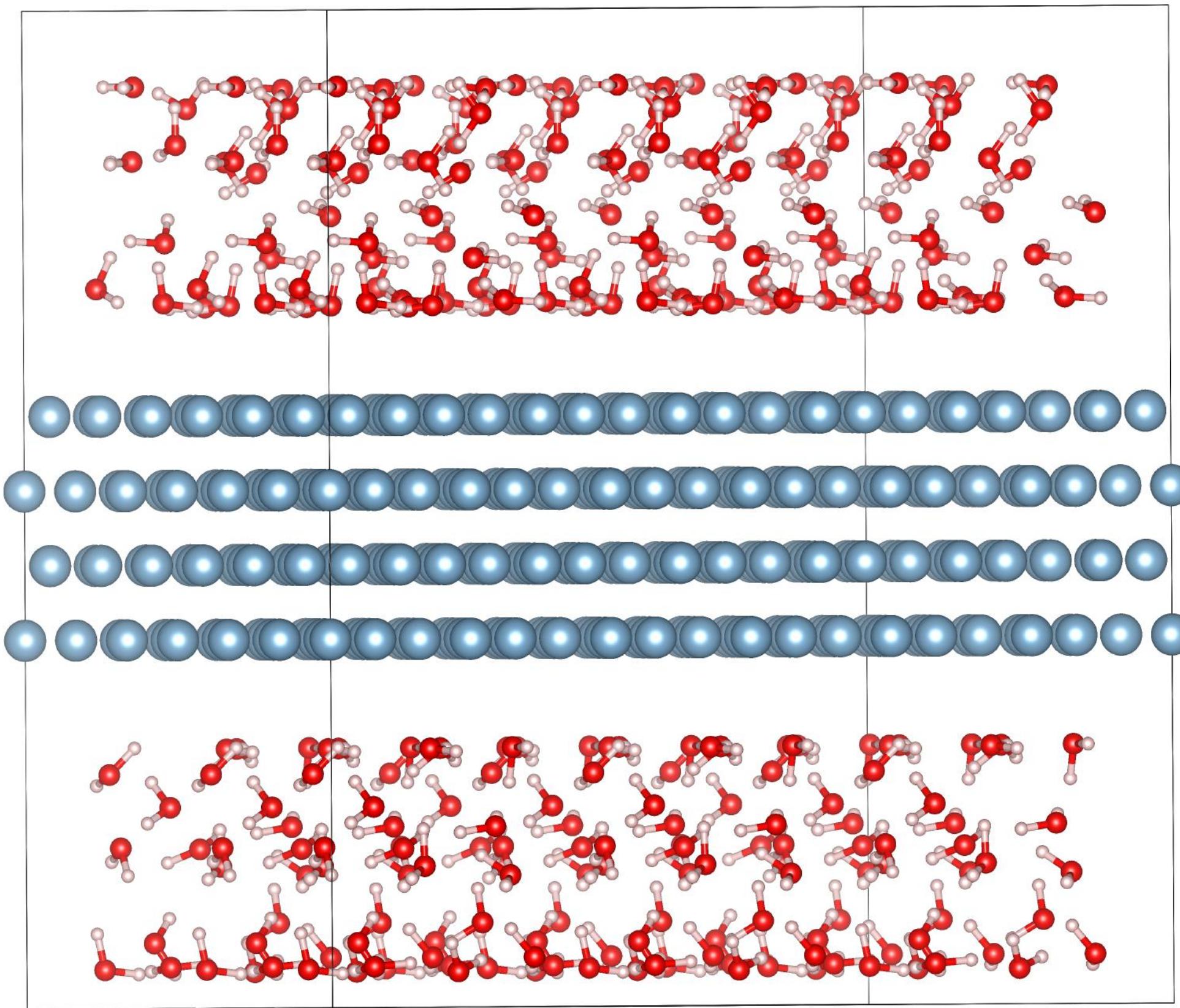
37 ×

150 ×

Mi, Shao, Ceresoli, Genova, Pavanello, CPC 269, 108122 (2021)

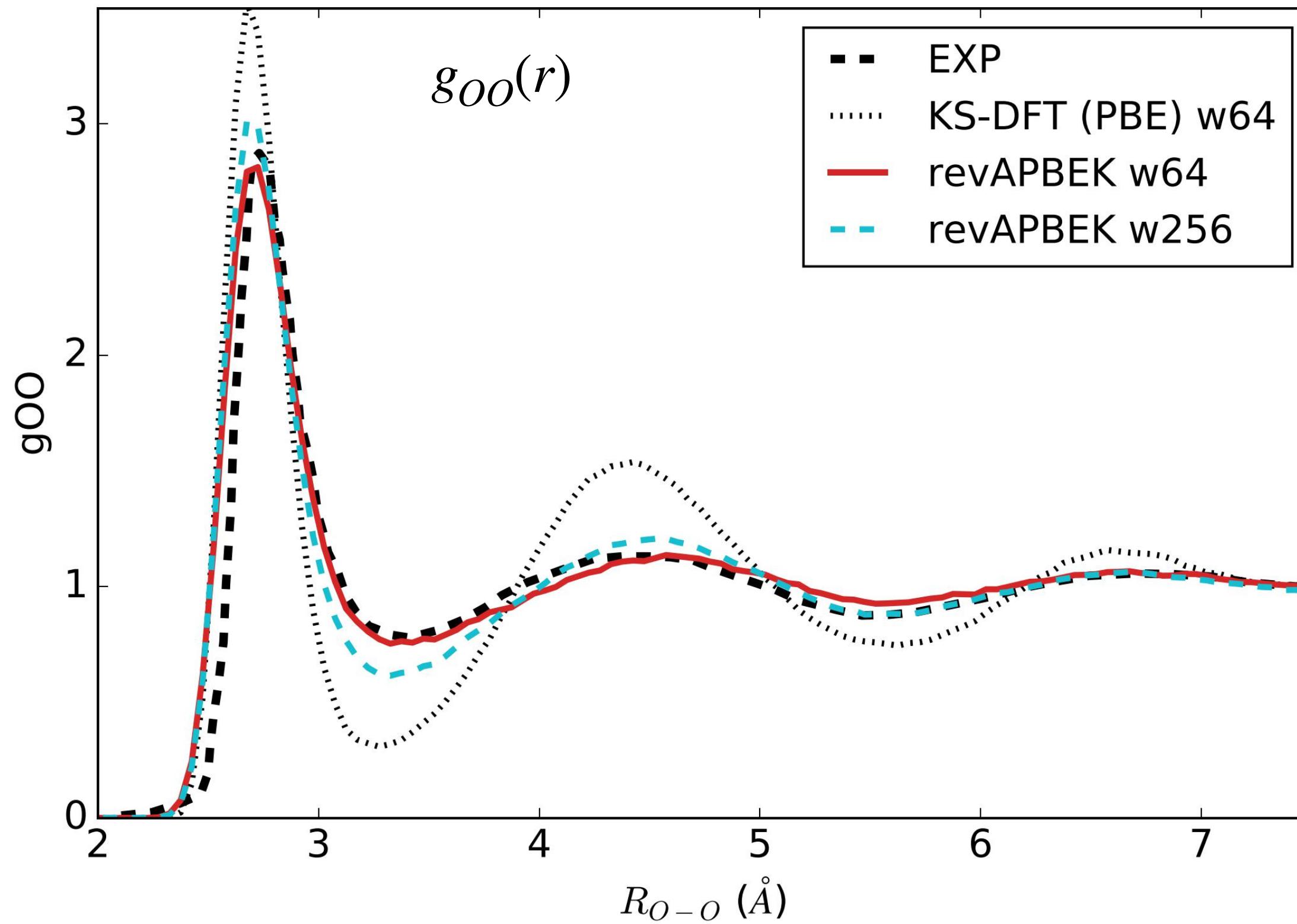
Genova, Ceresoli, Krishtal, Andreussi, DiStasio, Pavanello, IJQC (2017) Mi, Ramos, Maranhao, Pavanello JPC Lett (2019)

Parallel efficiency



sDFT: AIMD of molecular fluids

Liquid water

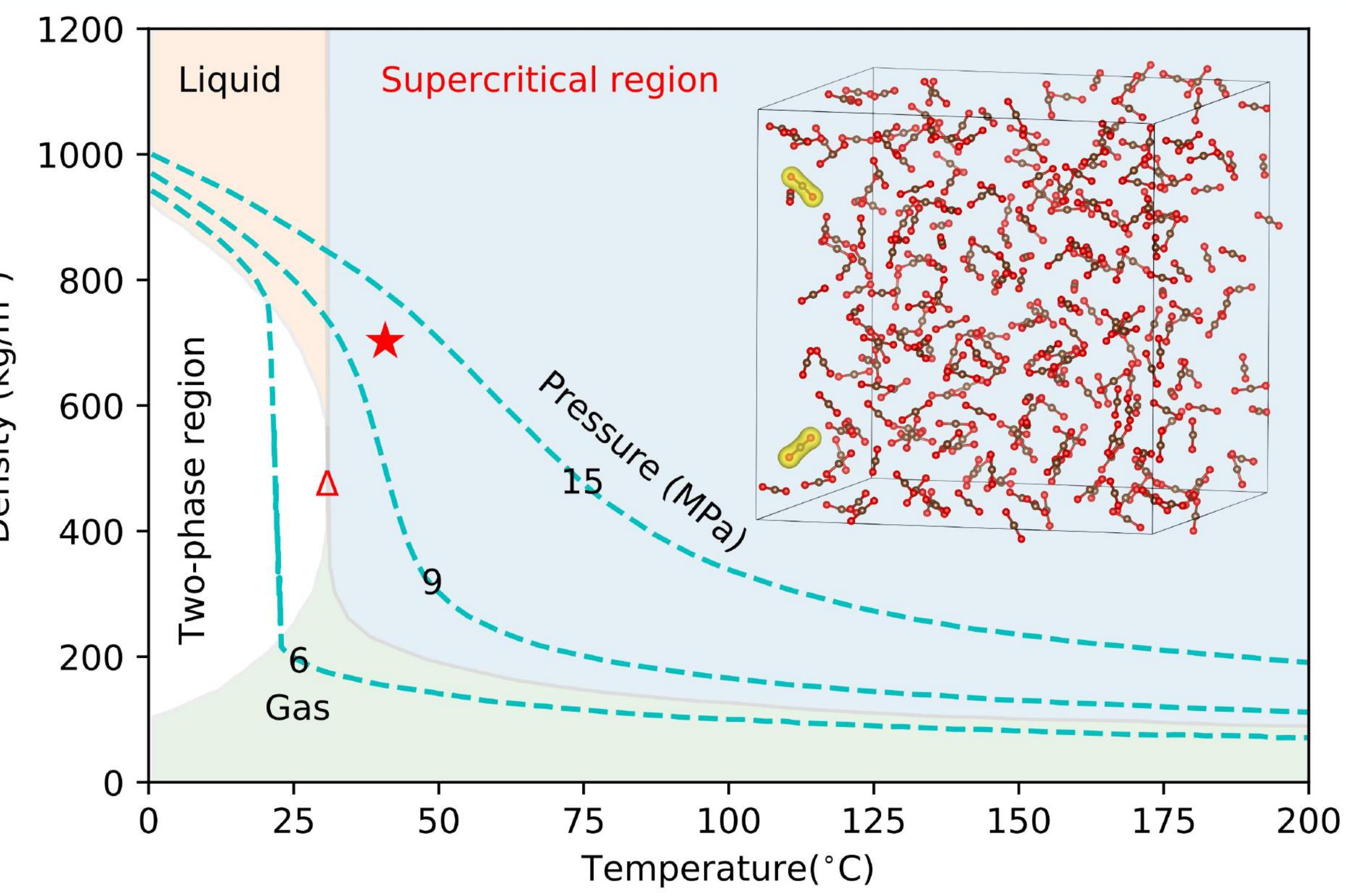


Genova, Ceresoli & MP, JCP (2016)

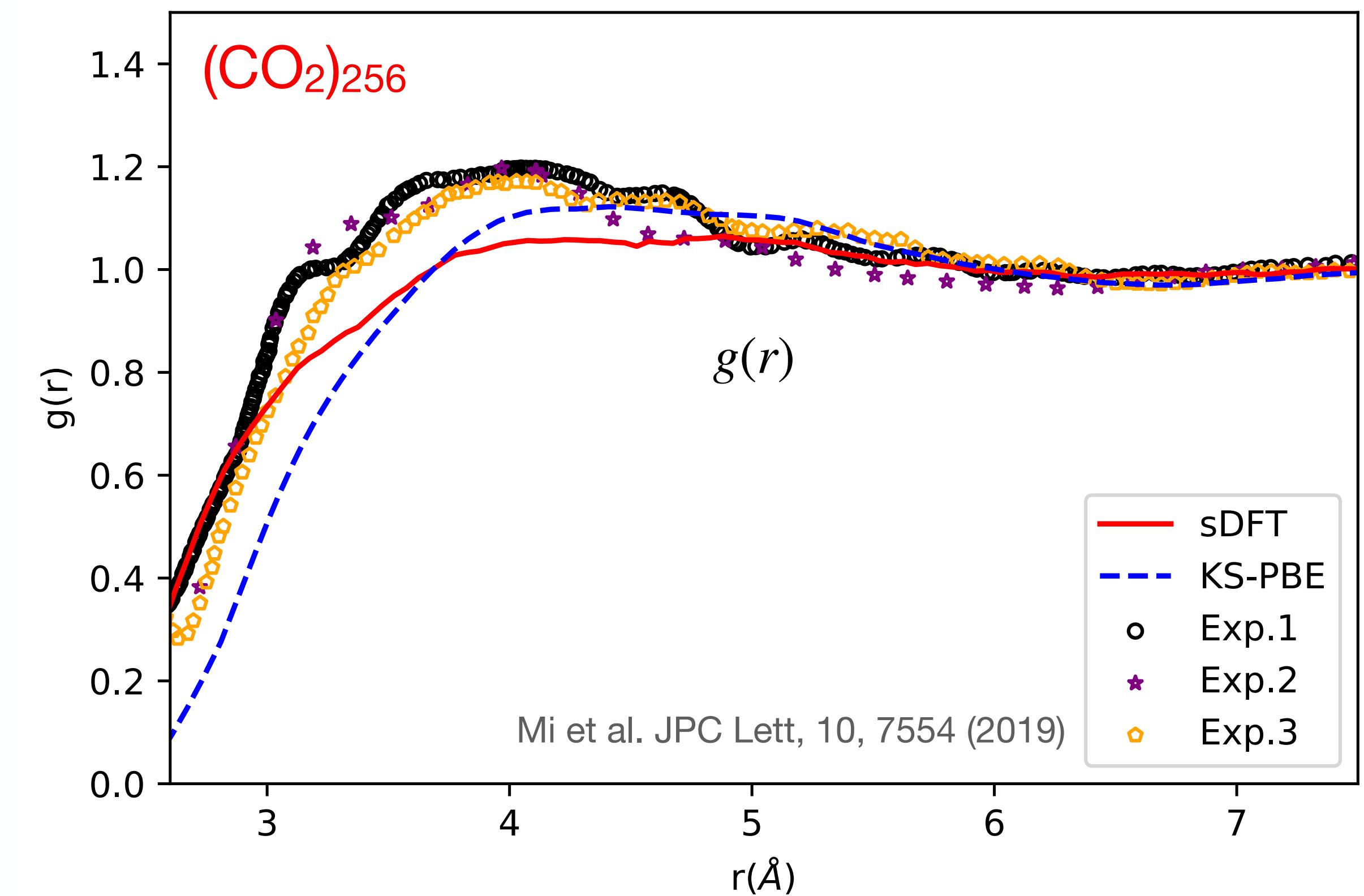
- 1) sDFT reproduces O-O RDF correctly
- 2) Tackles finite-size effects (assuming you have a supercomputer)

All calculations done with PBE xc and GGA NAKE (revAPBEK)

sDFT: AIMD of molecular fluids



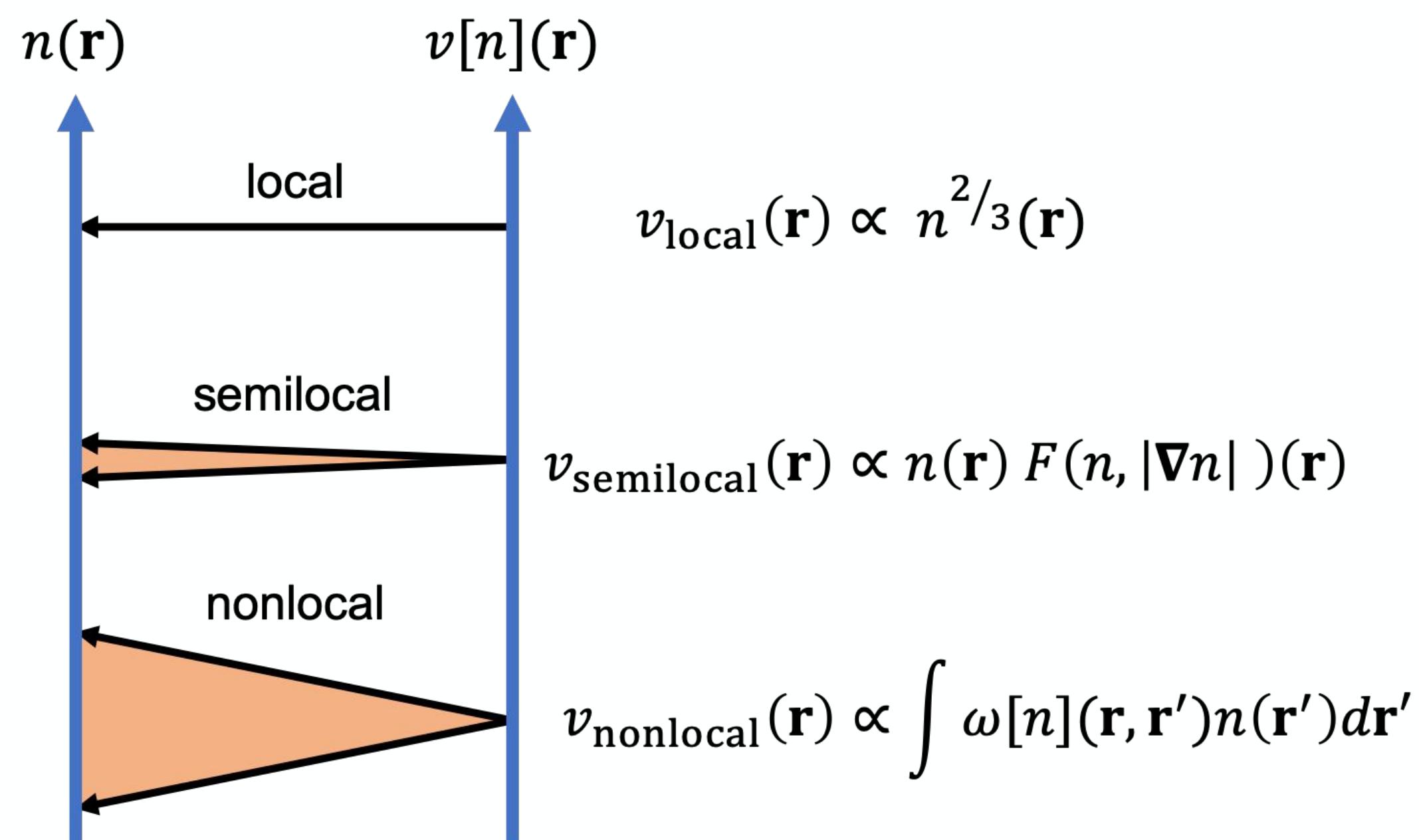
Supercritical CO_2



All calculations done with PBE xc and GGA NAKE (revAPBEK)

Mi et al. JPC Lett, 10, 7554 (2019)

sDFT NAKEs: semilocal and nonlocal



Nonlocal with density **independent** kernel

$$T_{NL}[n] = \left\langle n(\mathbf{r})^\alpha \left| \omega(\mathbf{r}, \mathbf{r}') \right| n(\mathbf{r}')^\beta \right\rangle$$

Wang & Teter, PRB (1992)

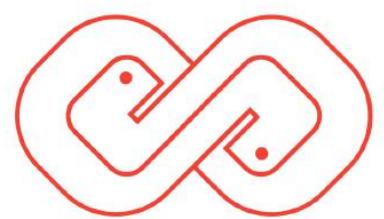
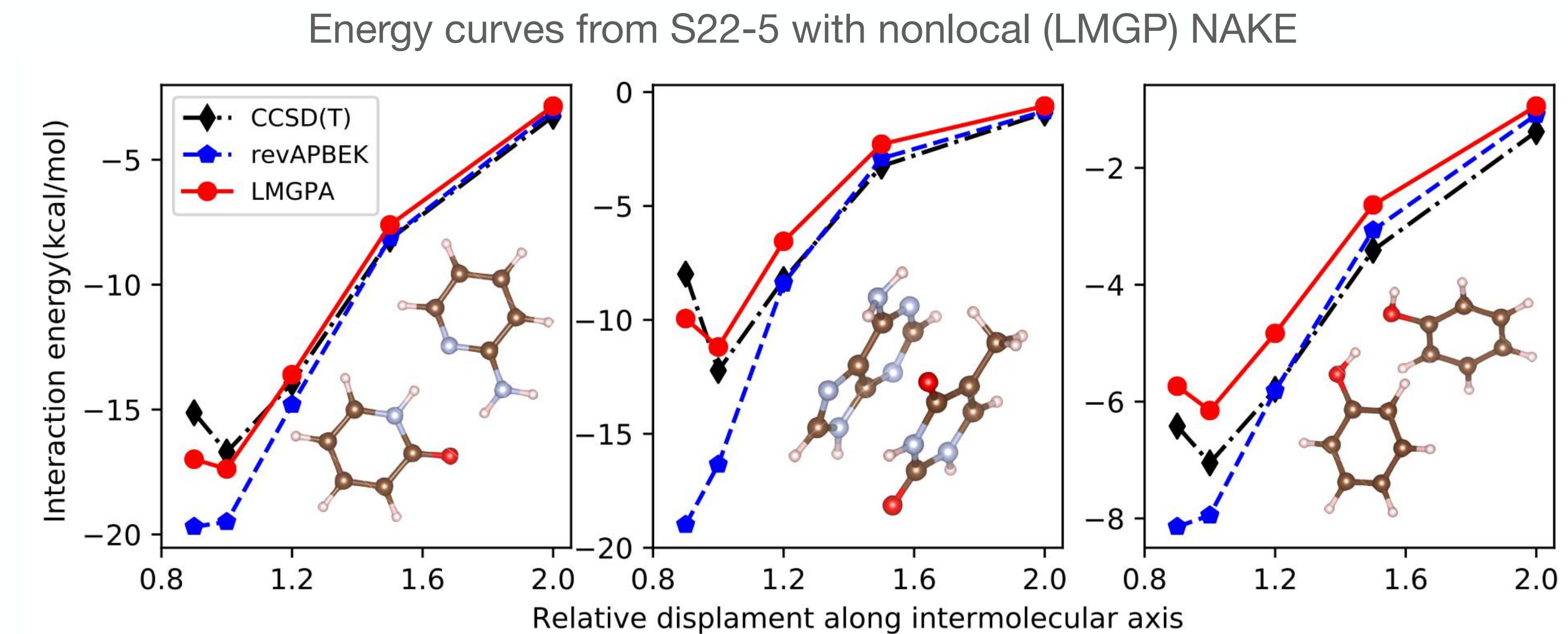
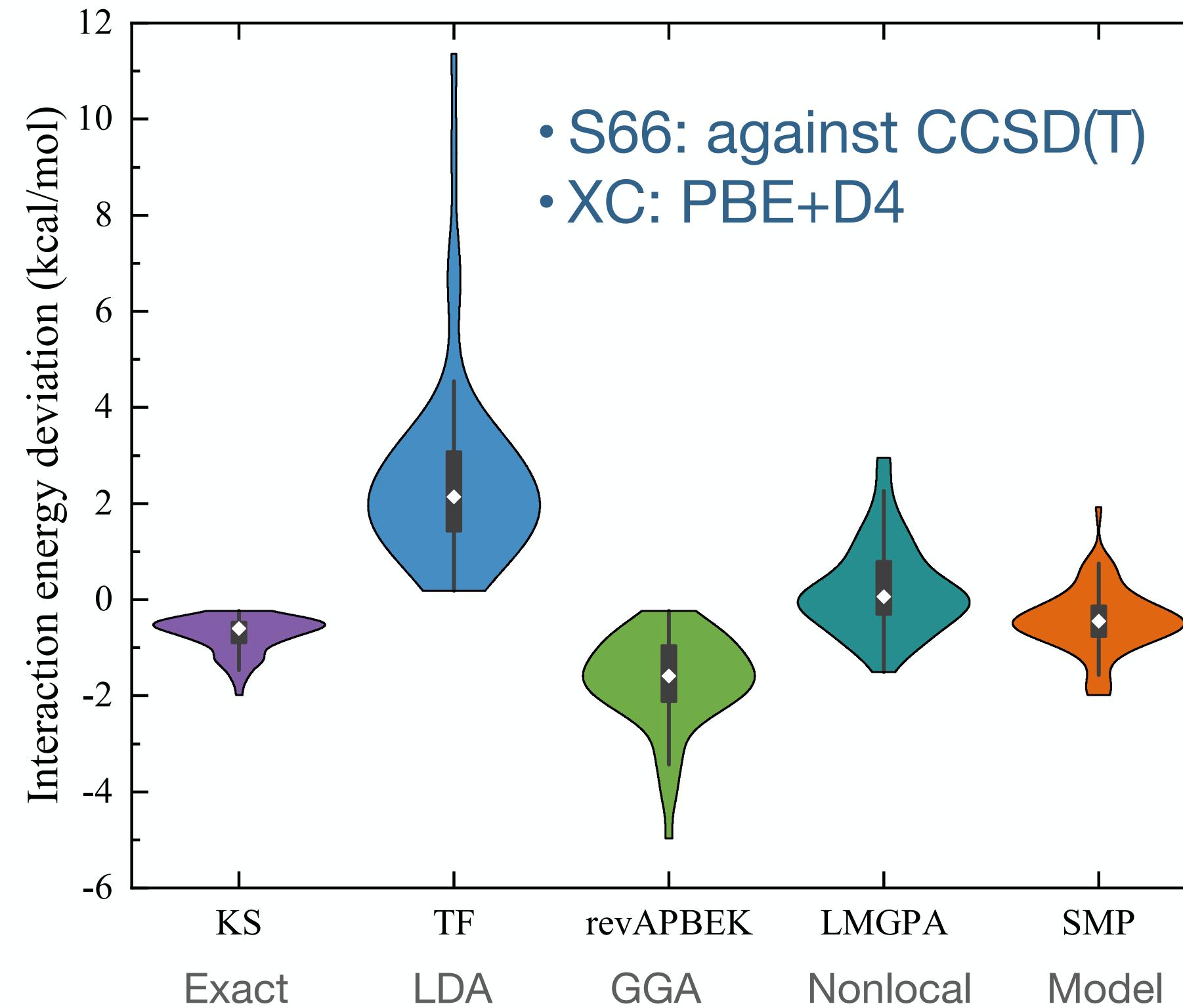
Nonlocal with density **dependent** kernel

$$T_{NL}[n] = \left\langle n(\mathbf{r})^\alpha \left| \omega[n](\mathbf{r}, \mathbf{r}') \right| n(\mathbf{r}')^\beta \right\rangle$$

Huang & Carter, PRB (2010)

Mi & Pavanello, PRB (2019)

Weak interactions with subsystem DFT



eDFTpy

edftpy.rutgers.edu

Mi & MP JPCL (2020) • Shao, Mi & MP JCTC (2021)

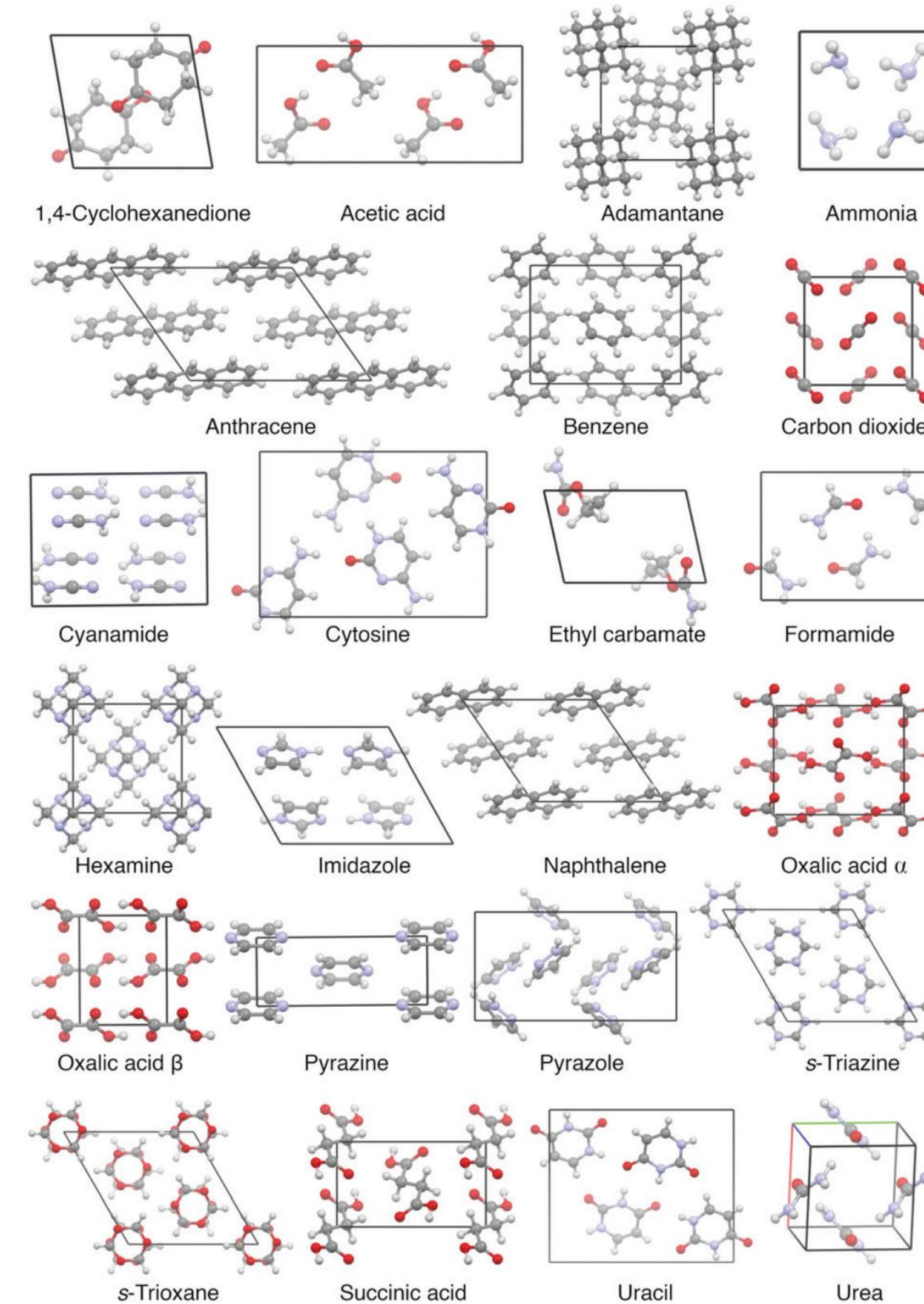
Wesolowski (1993-) • Götz, Beyhan, Visscher JCTC (2009) • Klahr, Schlüns, Neugebauer JCTC (2018) • Schlüns *et al.* PCCP (2015)

sDFT: Nonlocal NAKE improve the results

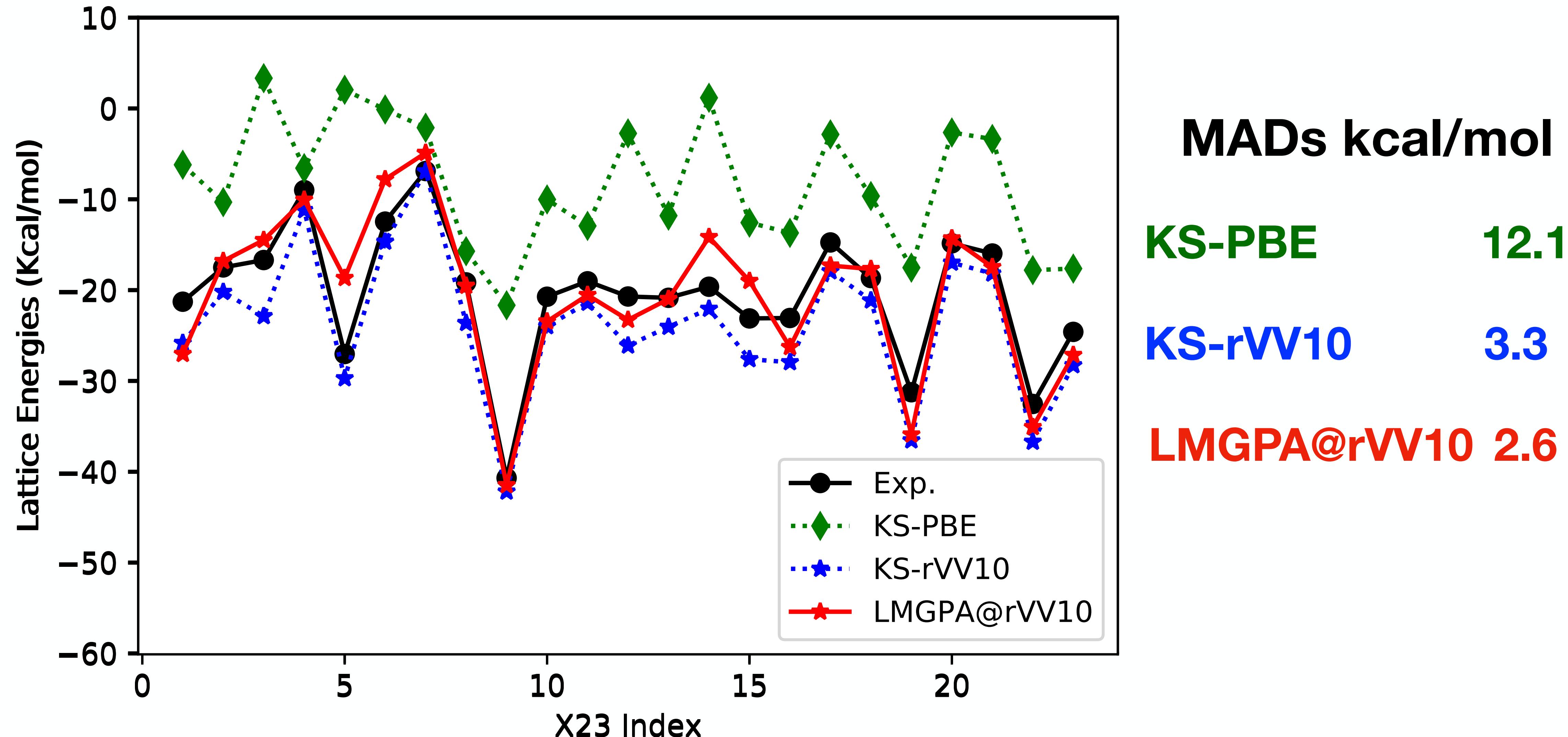
The X23 test set

Dolgonos et al. Phys. Chem. Chem. Phys., 2019, 21, 24333-24344

Reilly and Tkatchenko, J. Chem. Phys., 2013, 139, 024705



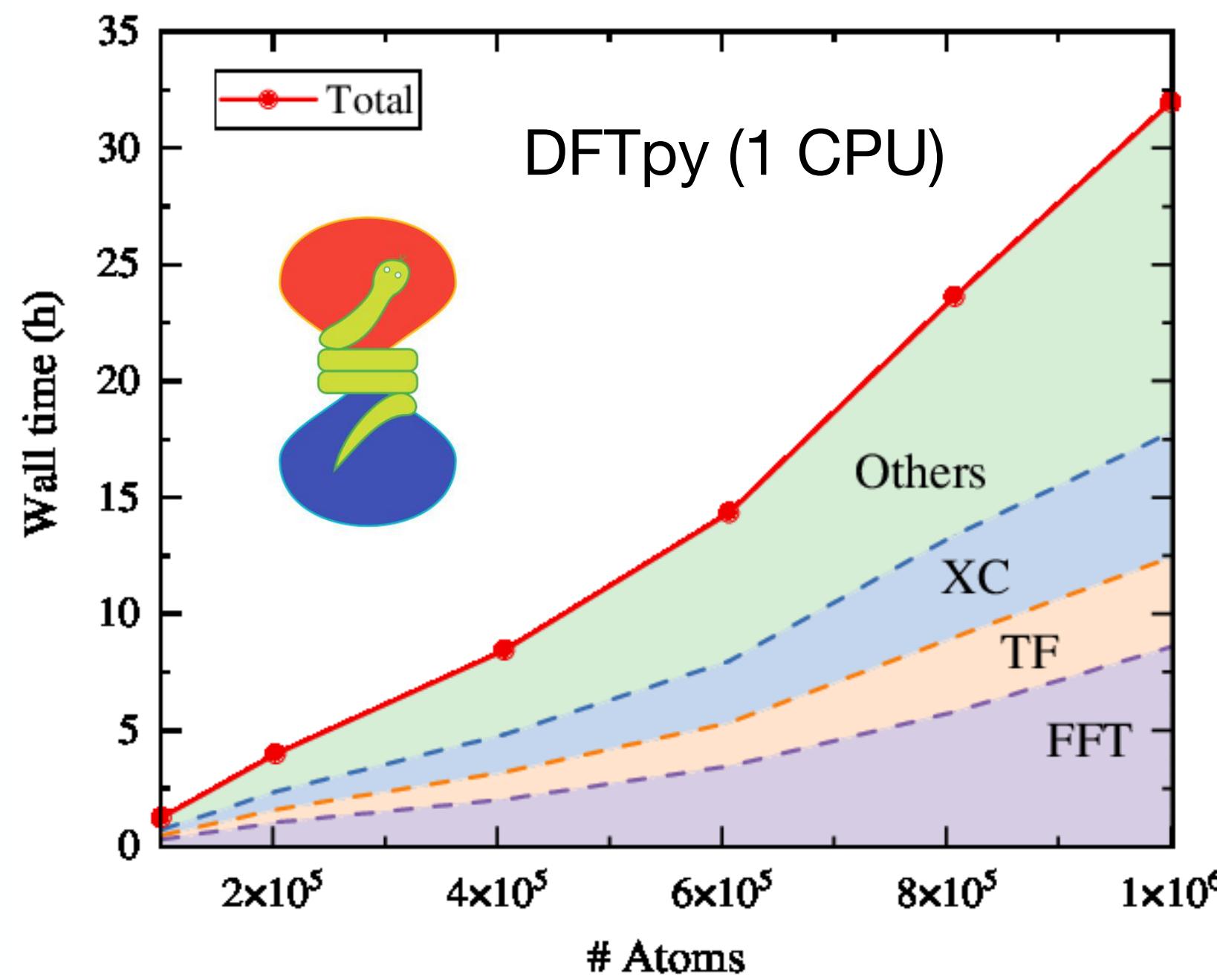
sDFT: Nonlocal NAKE improve the results



Combining OF-DFT with embedding

New ways to use orbital-free DFT

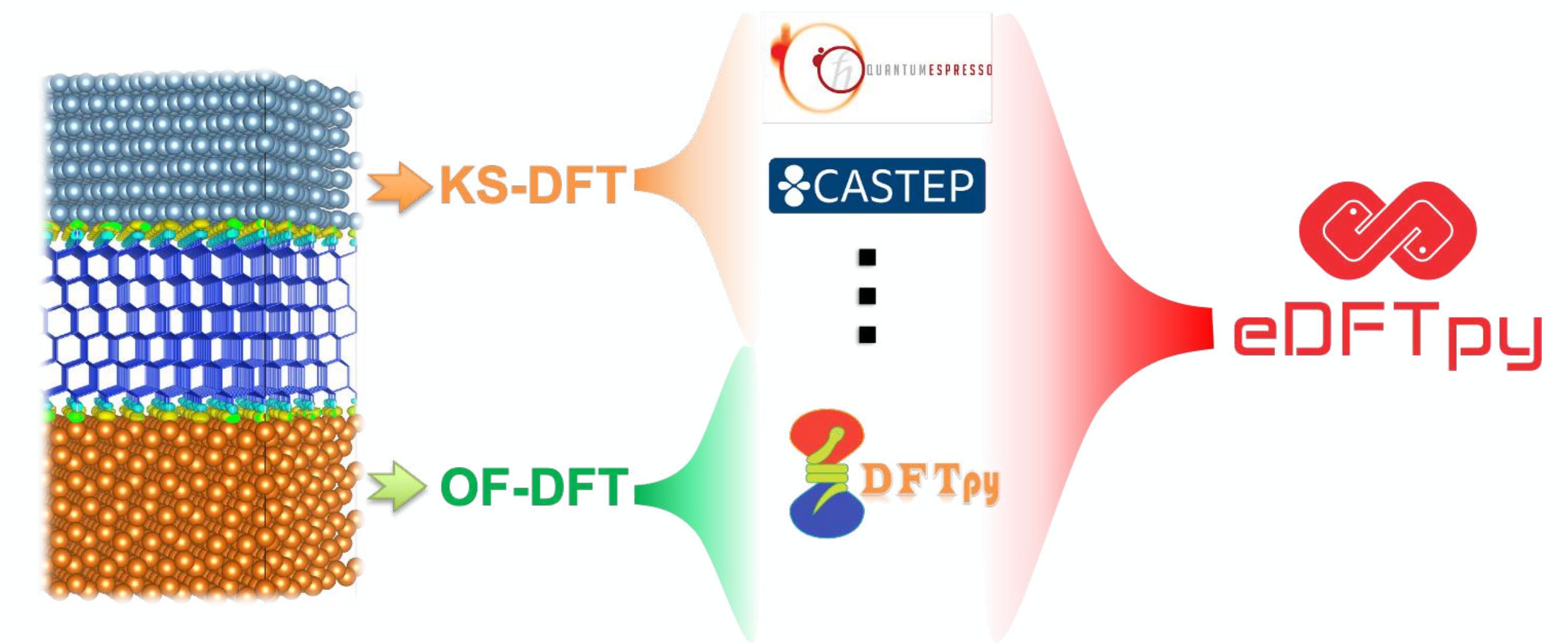
1. Combine OFDFT and KSDFT with embedding!
2. Extend to non equilibrium systems
3. Use Python



dftpy.rutgers.edu

Shao, Mi, Pavanello, in preparation

Shao, Jiang, Mi, Genova & MP, WIREs Comp. Mol. Sci. (2021)

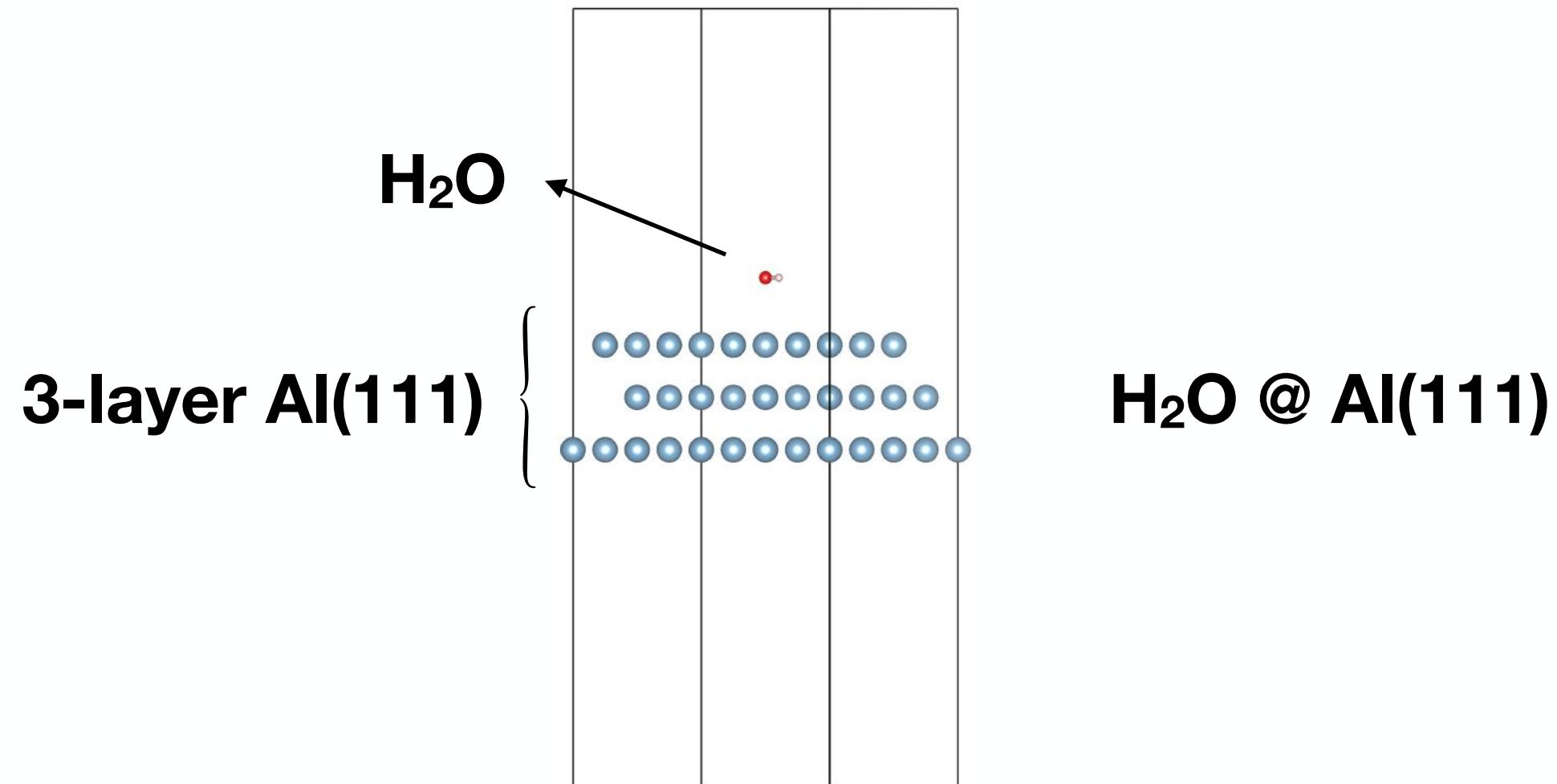
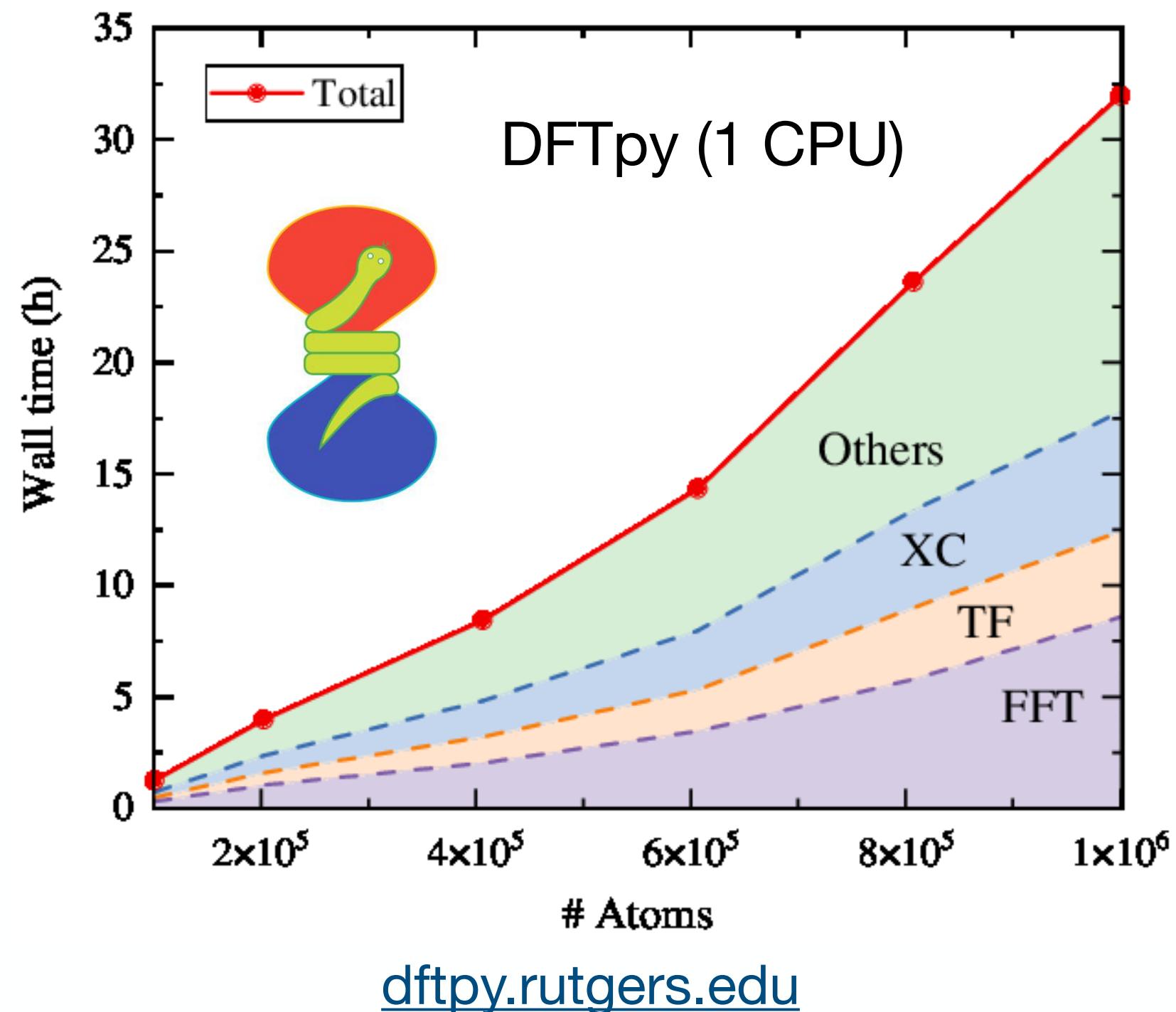


Is this science fiction?

Combining OF-DFT with embedding

New ways to use orbital-free DFT

1. Combine OFDFT and KSDFT with embedding!
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3. Use Python



Binding Energy in meV

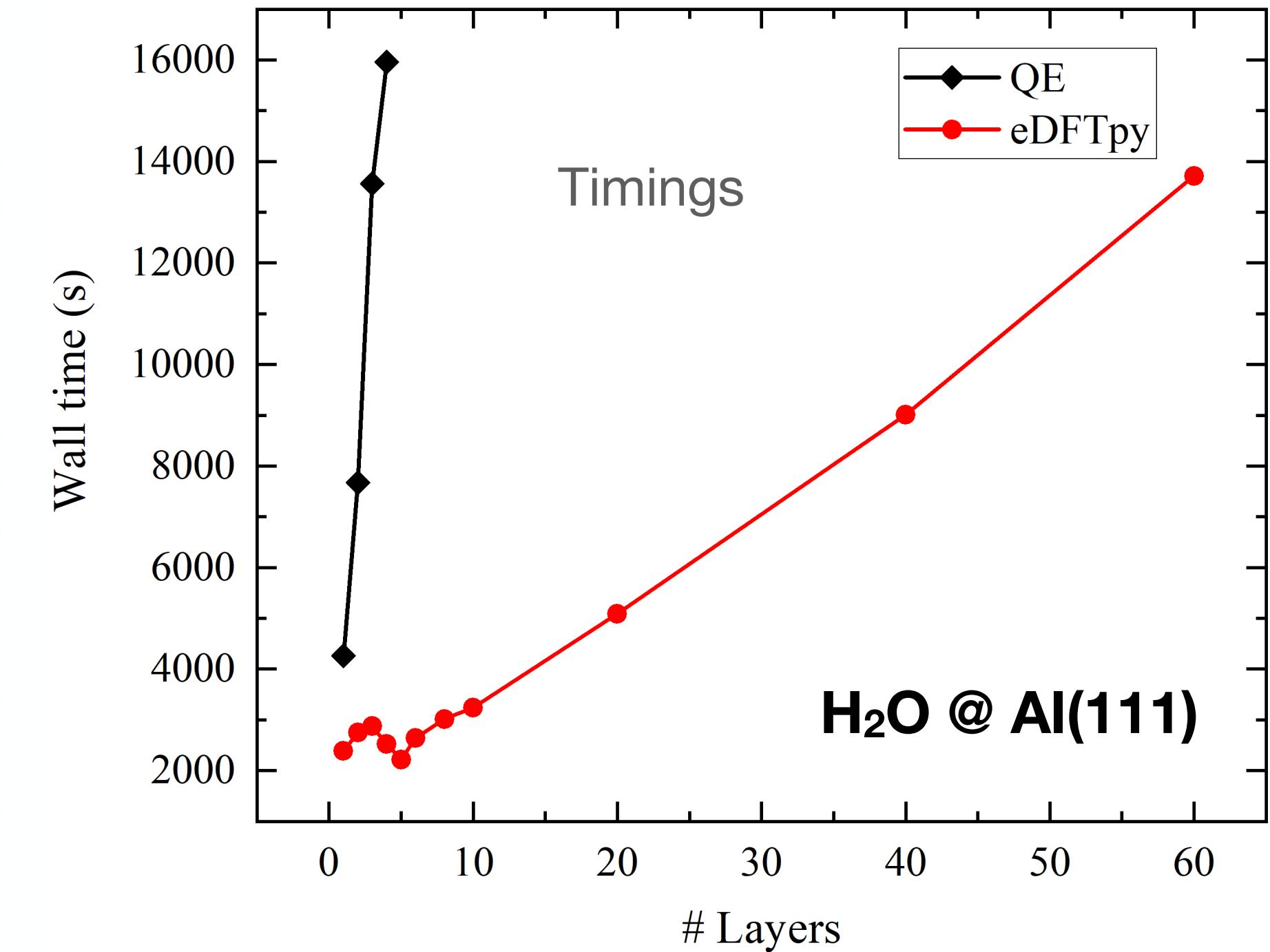
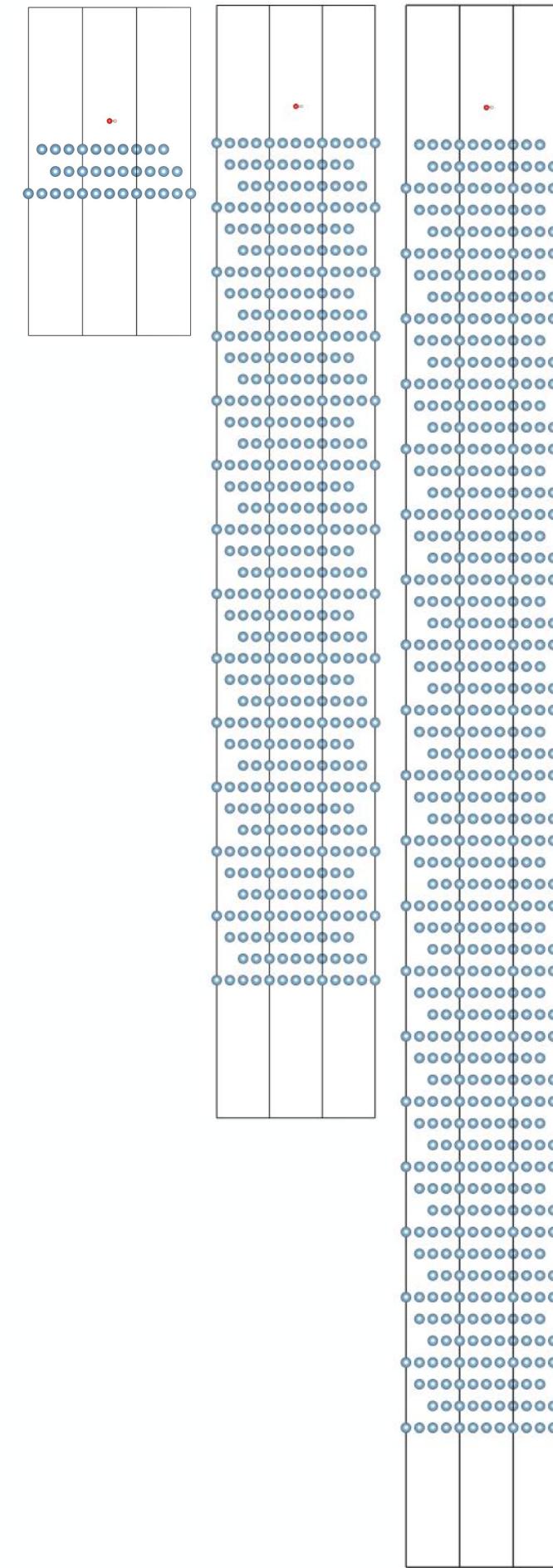
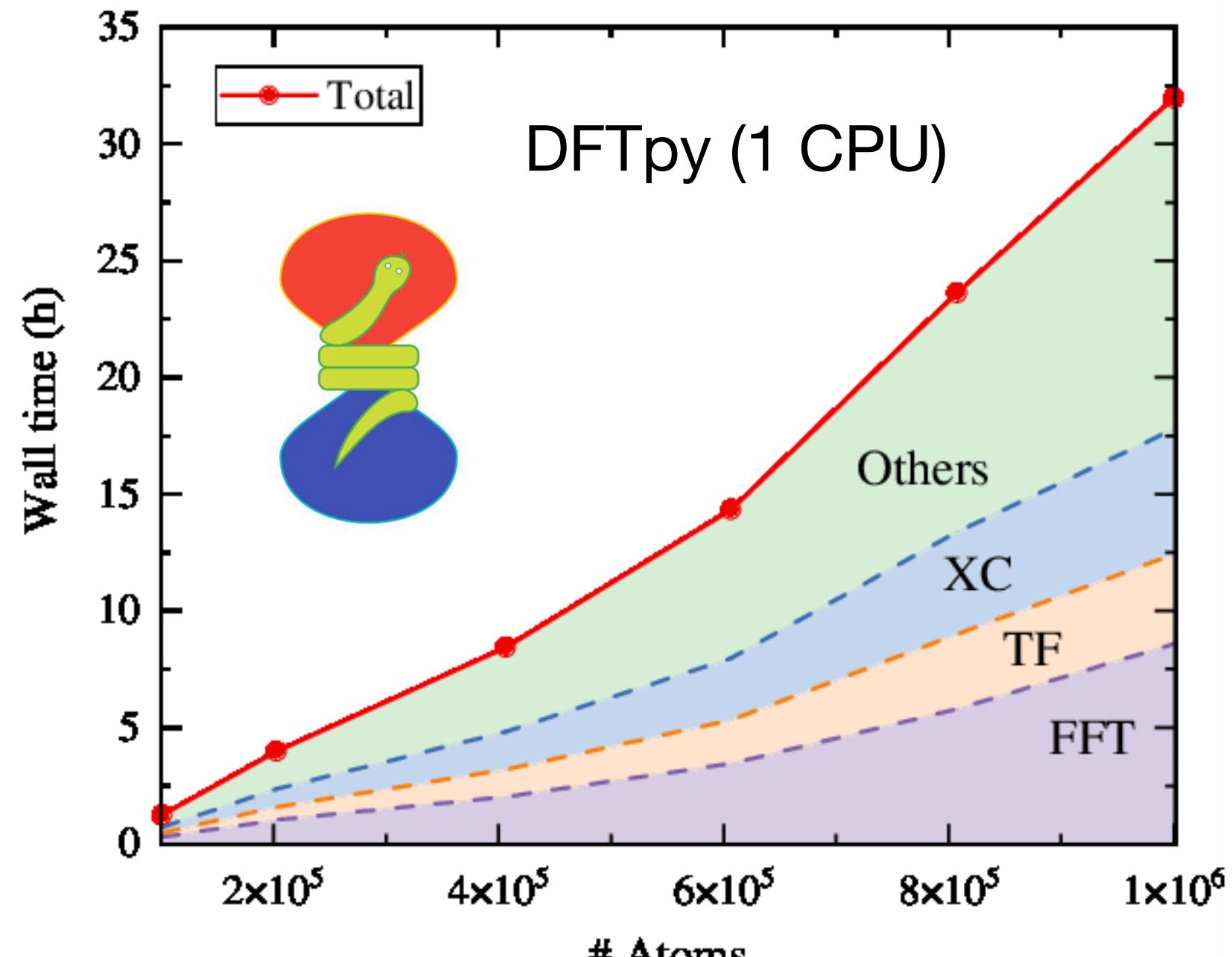
H ₂ O @ Al(111)	1 layer	2 layers	3 layers
QE	192	100	103
eQE	220	191	184
eDFTpy (QE)	176	123	128

revPBE+D3

Combining OF-DFT with embedding

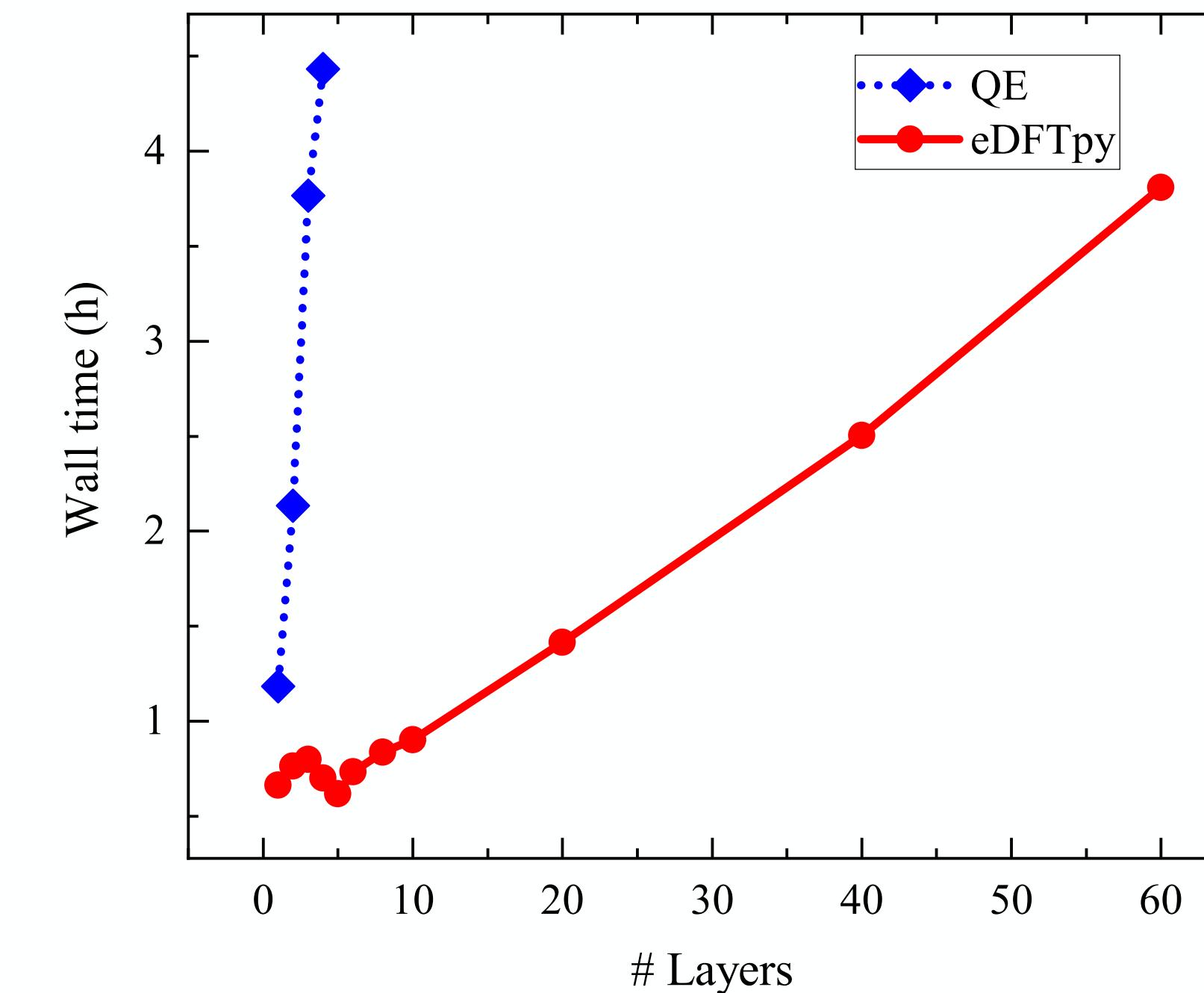
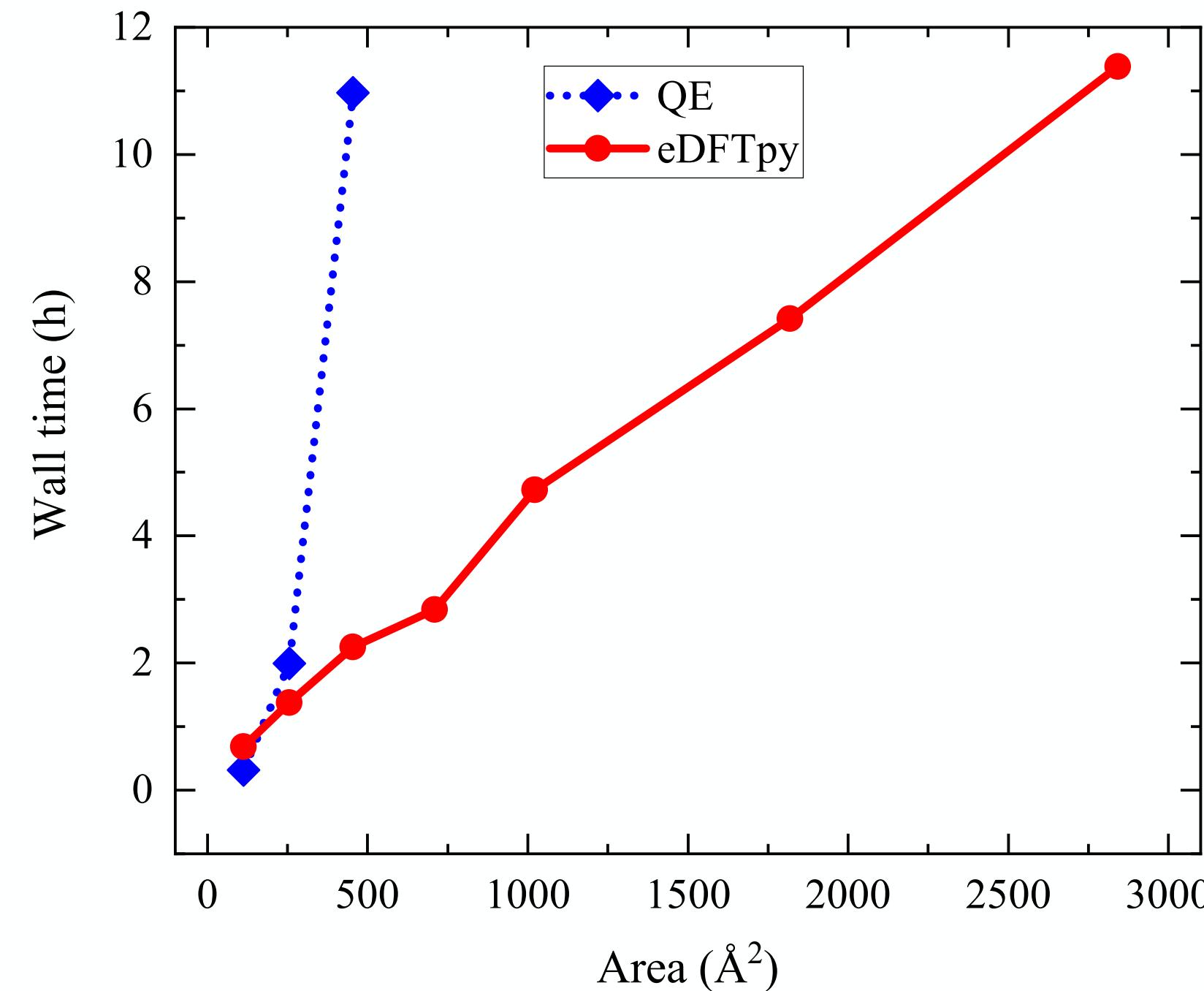
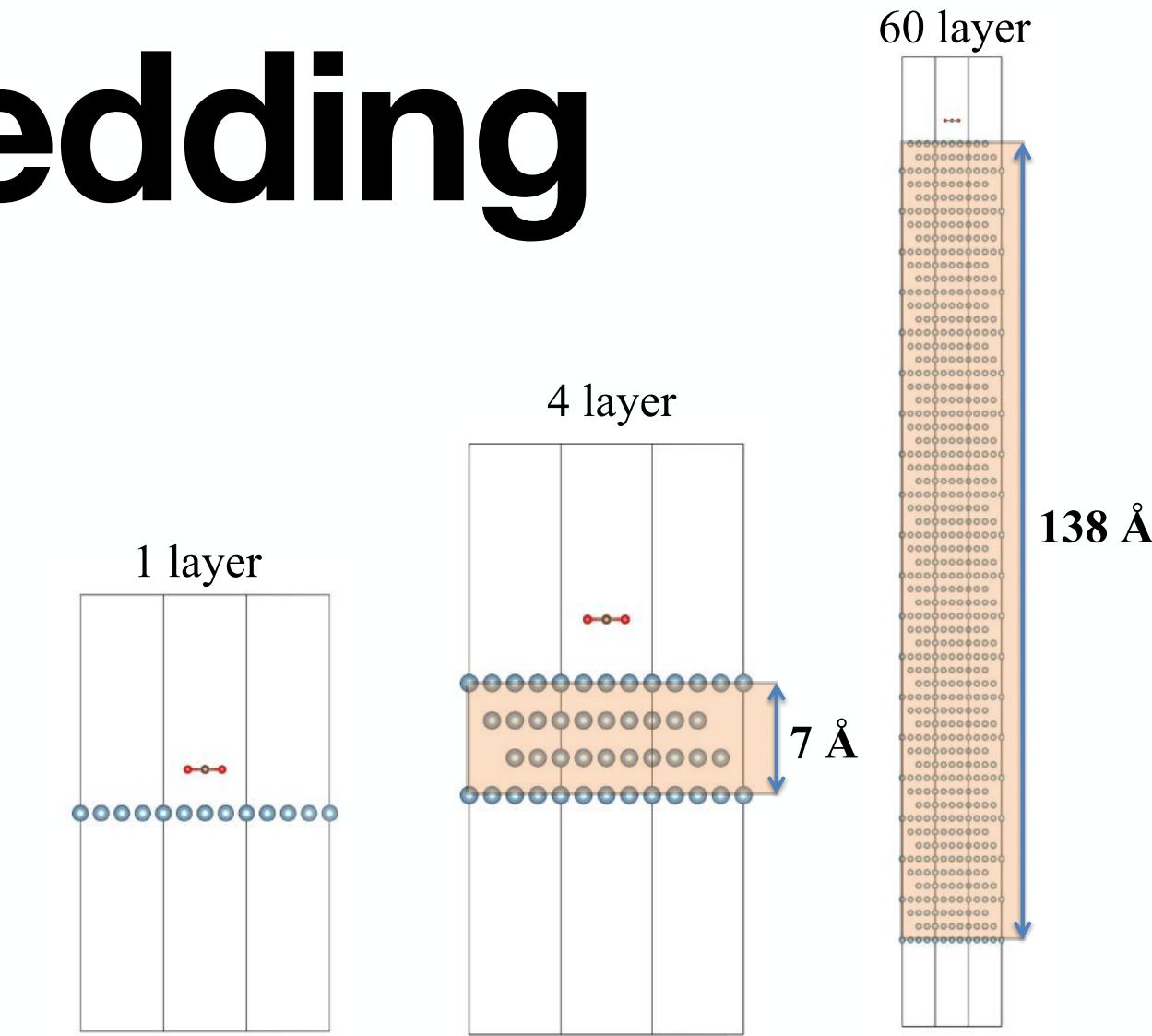
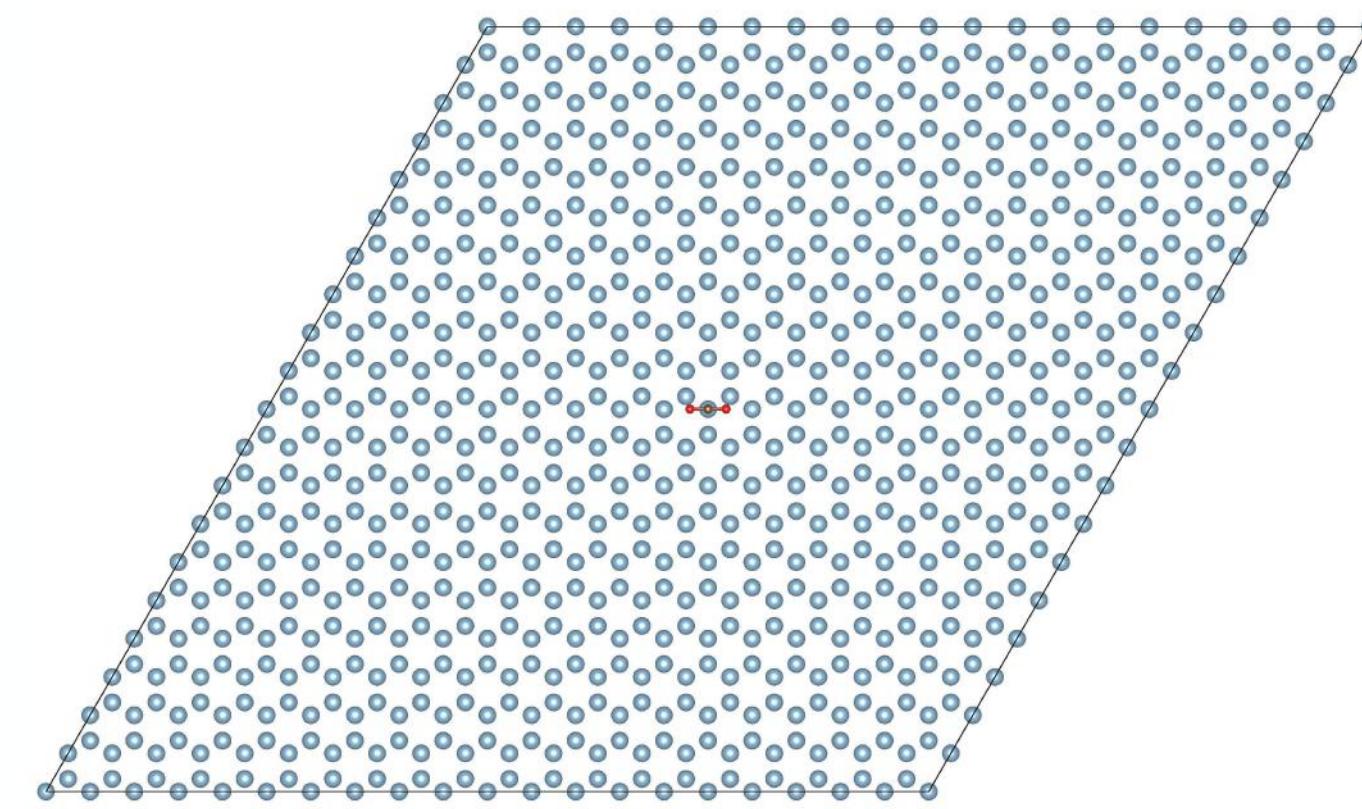
New ways to use orbital-free DFT

1. Combine OFDFT and KSDFT with embedding!
2. Extend to non equilibrium systems
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For excited states, we need to generalize
OF-DFT to the time-domain
...it may be science fiction after all!

Combine OF-DFT with embedding



Going beyond the ground state...

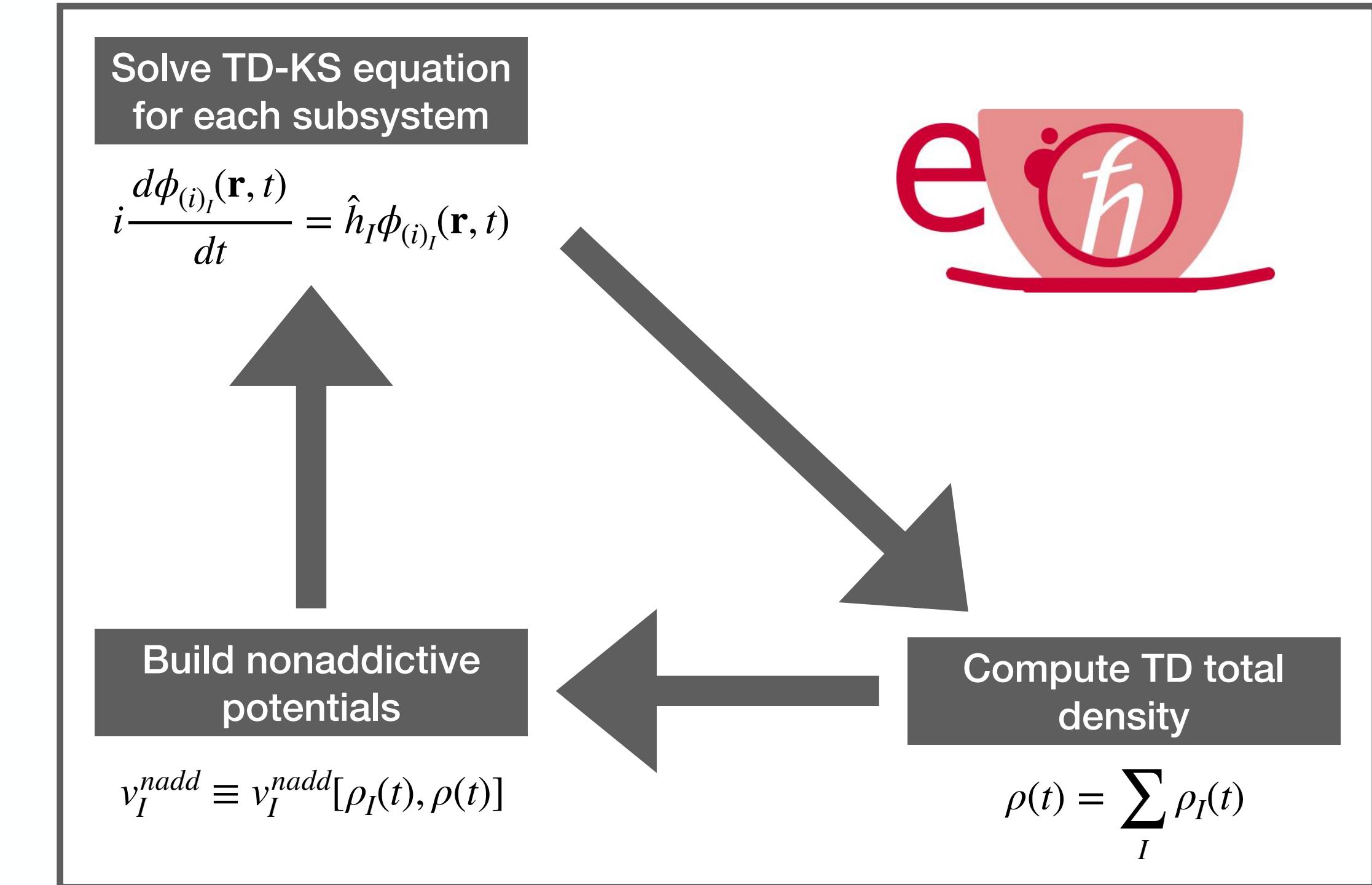
Subsystem TDDFT & many-body expansion

Real time $i\frac{d\phi_{(i)_I}(\mathbf{r}, t)}{dt} = \hat{h}_I \phi_{(i)_I}(\mathbf{r}, t)$

Density response $\chi = \sum_I \chi_I$

Dyson “uncoupled” $\chi_I^u = \chi_I^0 + \chi_I^0 K_{II} \chi_I^u$

Dyson “coupled” $\chi_I = \chi_I^u + \sum_{J \neq I} \chi_J^u K_{IJ} \chi_J$



Krishtal *et al.* JCP (2015) and (2016) • SKP, Genova & MP JPCL (2017) • Umerbekova and Pavanello EPJ-B (2018), IJQC (2020)

Casida & Wesolowski, IJQC (2004) • Neugebauer, Phys Rep (2010) • Neugebauer, JCP (2007,2009)

Optical spectrum of liquid water

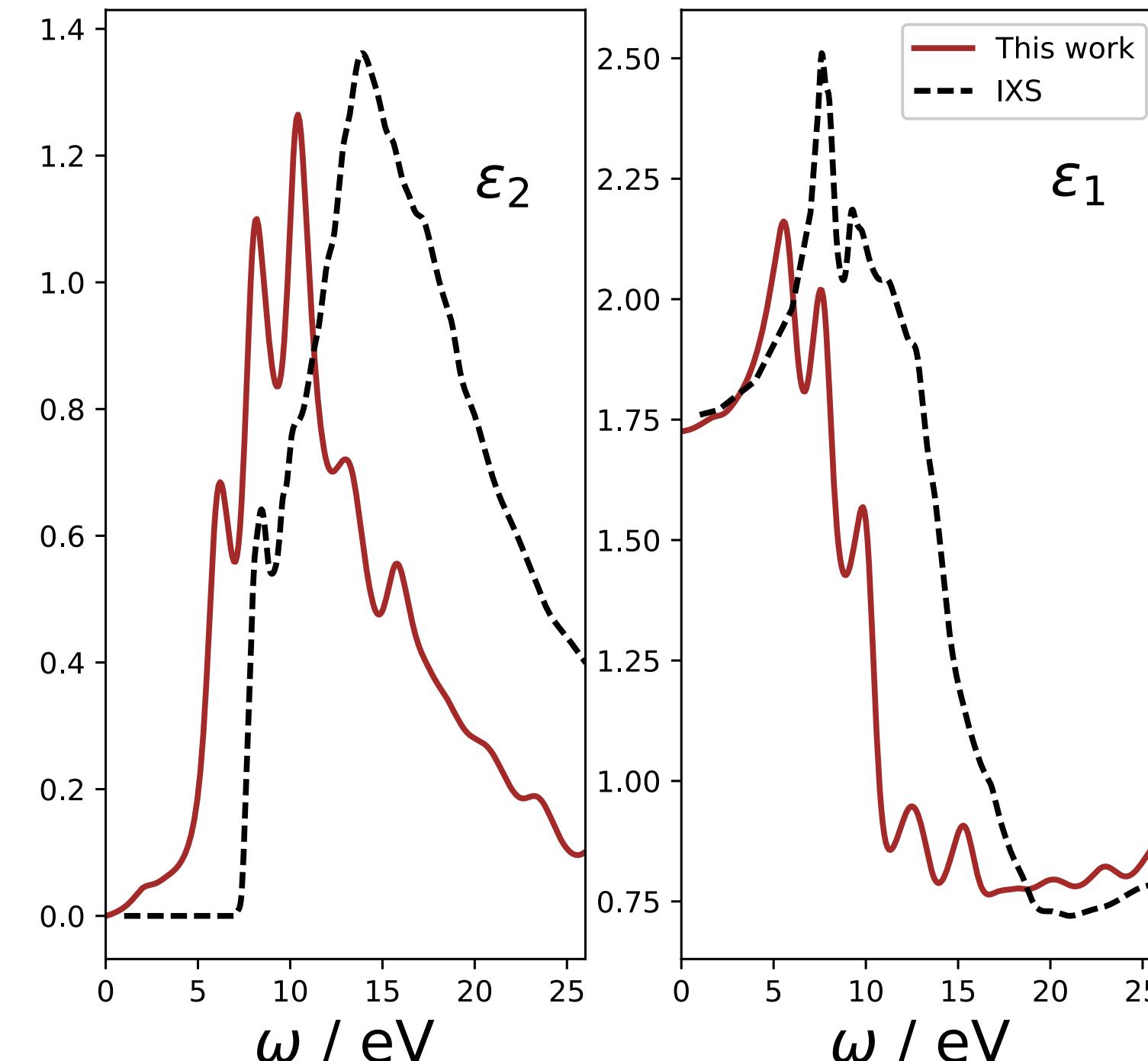
$$\chi = \sum_I \chi_I$$

$$\chi_I = \underbrace{\chi_I^u}_{One} + \underbrace{\sum_{J \neq I} \chi_I^u K_{IJ} \chi_J}_{Many}$$

- 64 water molecules in a box
- MD with eQE
- sTDDFT with eQE
- PBE xc and PW basis set

Comparison with the experiment

1. Compare against IXS



Optical spectrum of liquid water

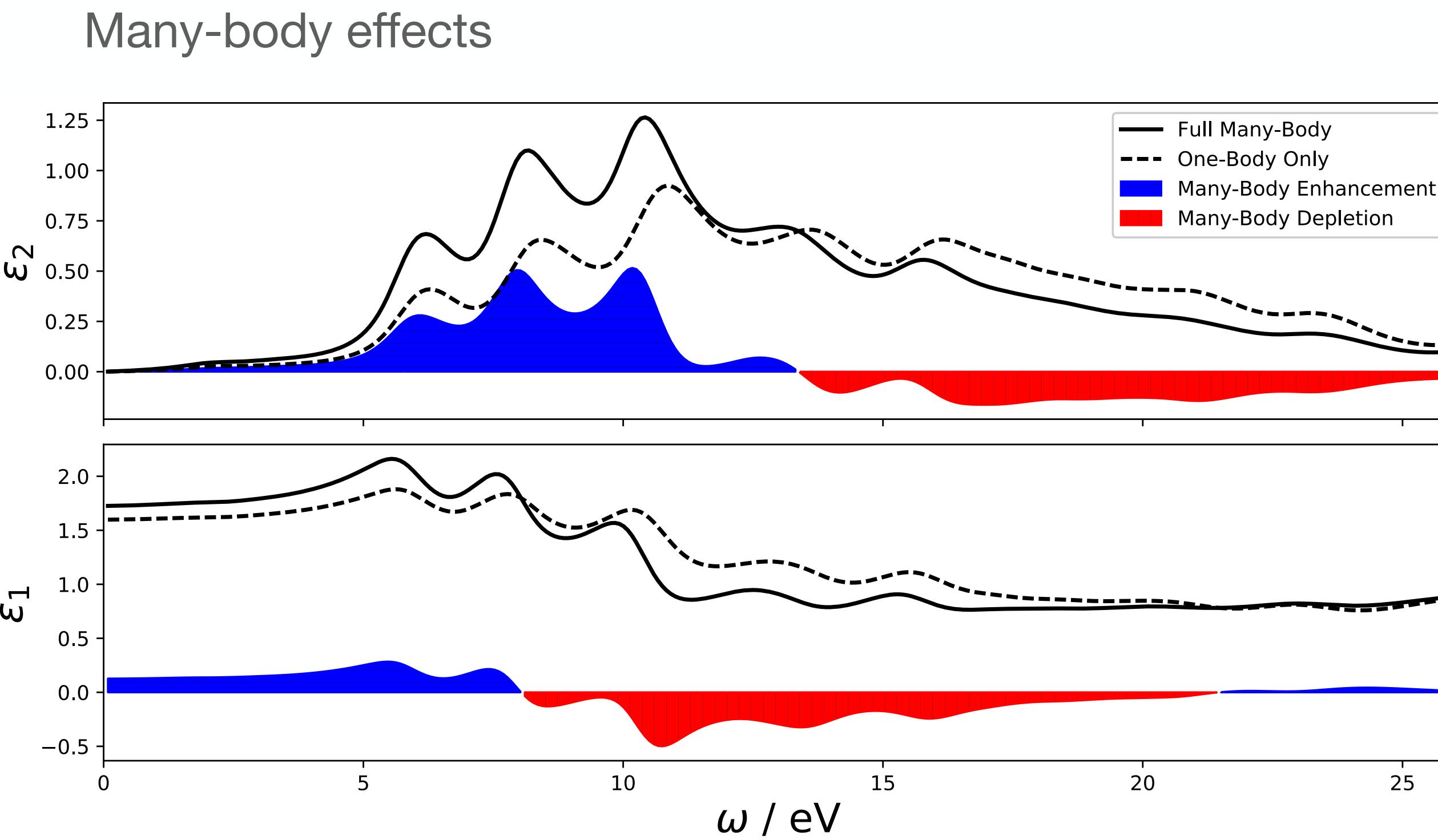
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Optical spectrum of liquid water

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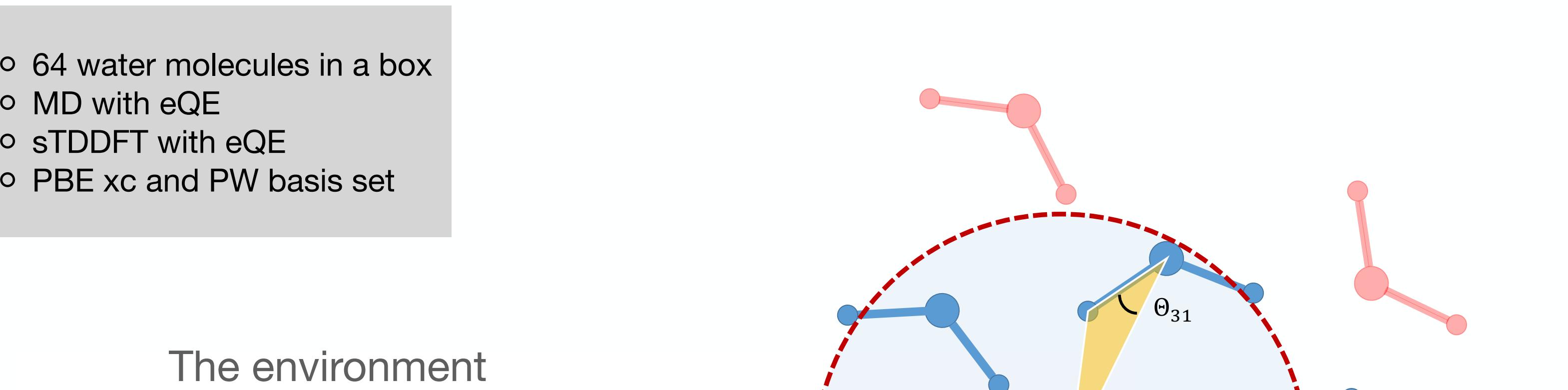
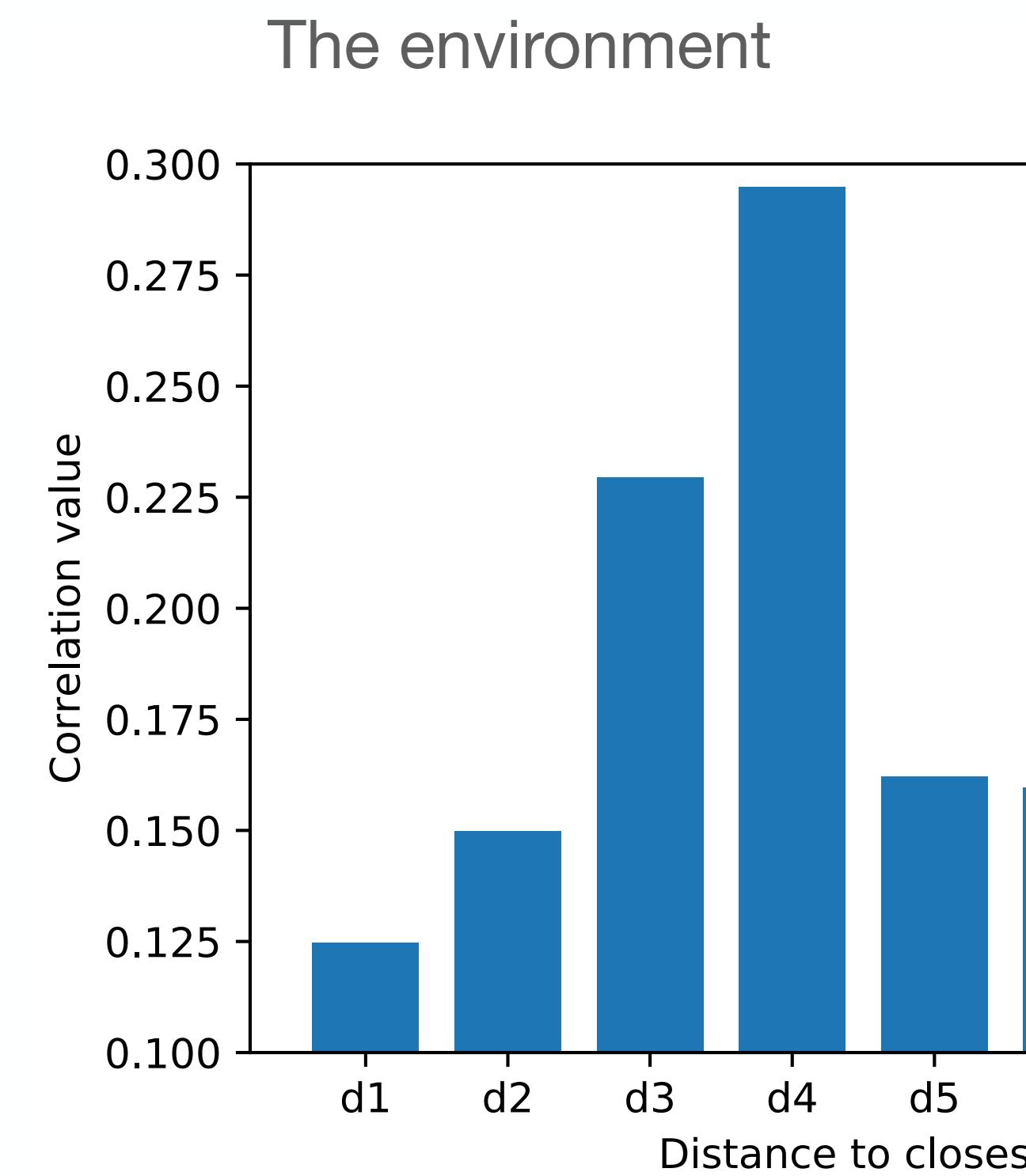
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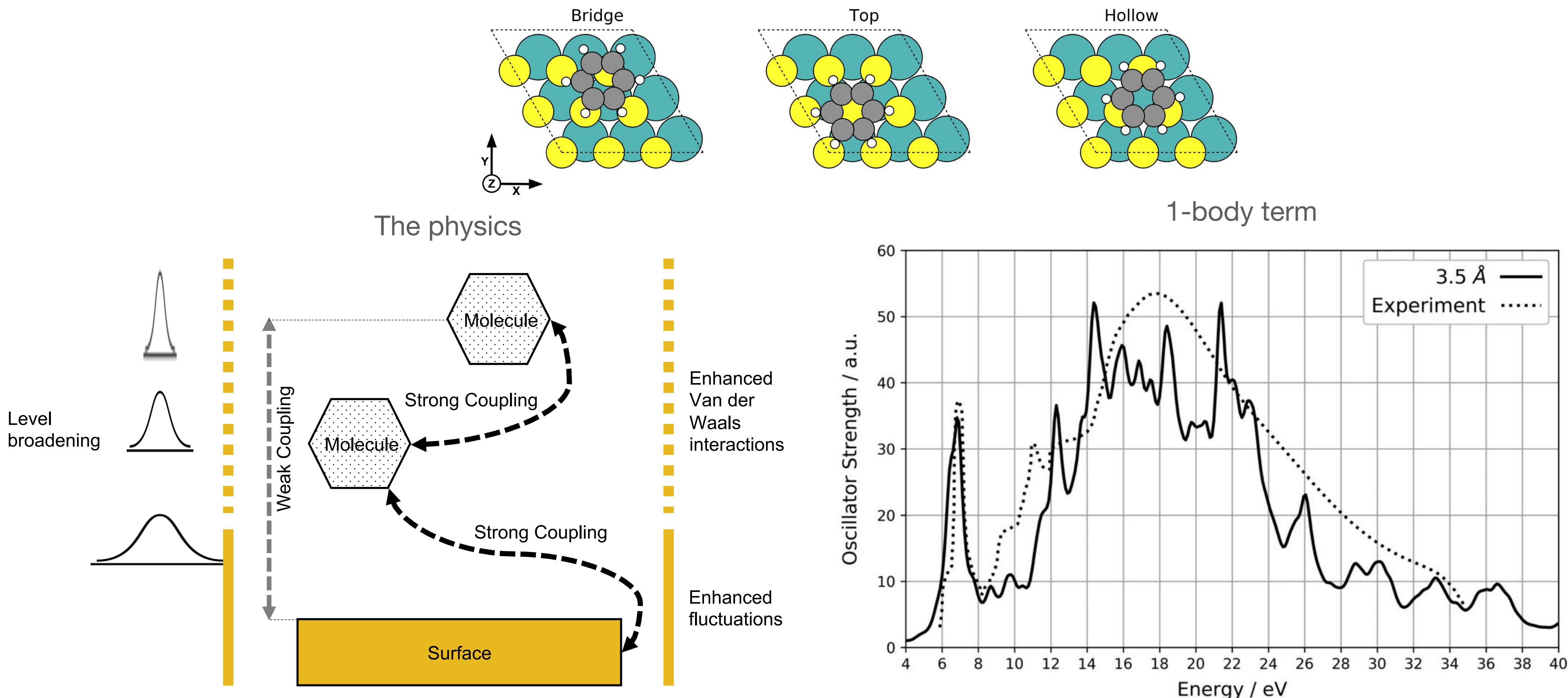
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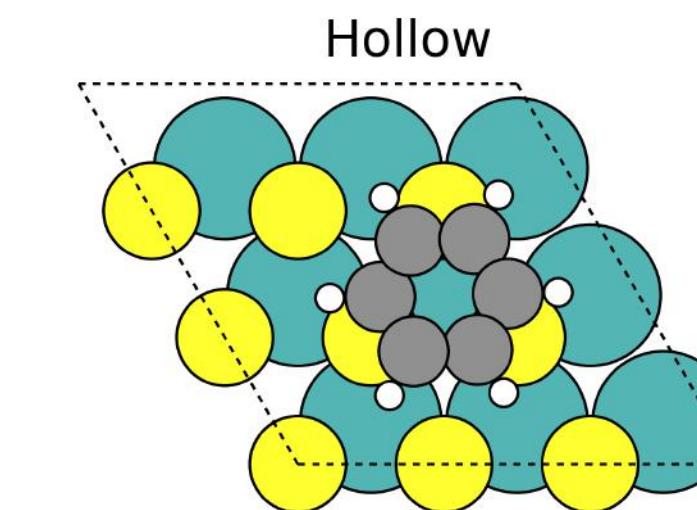
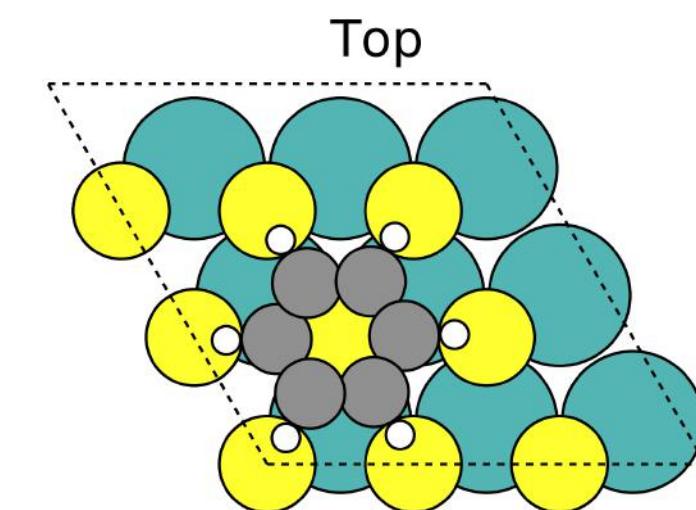
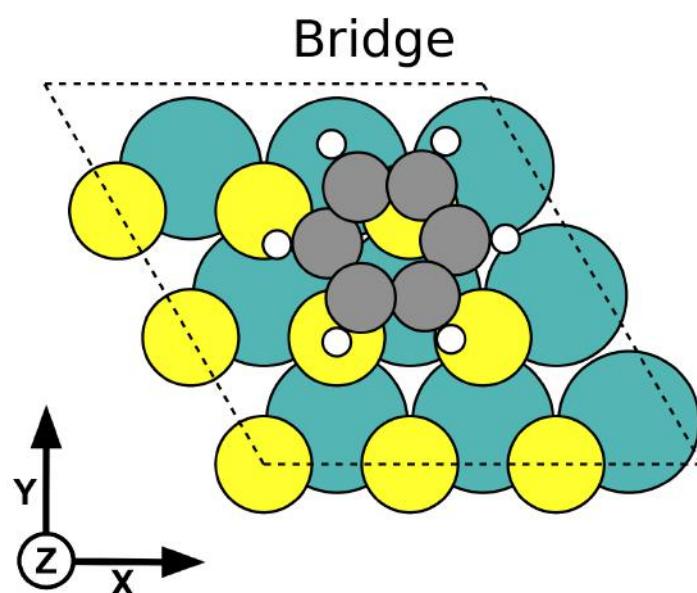
3. Correlate to liquid's structure



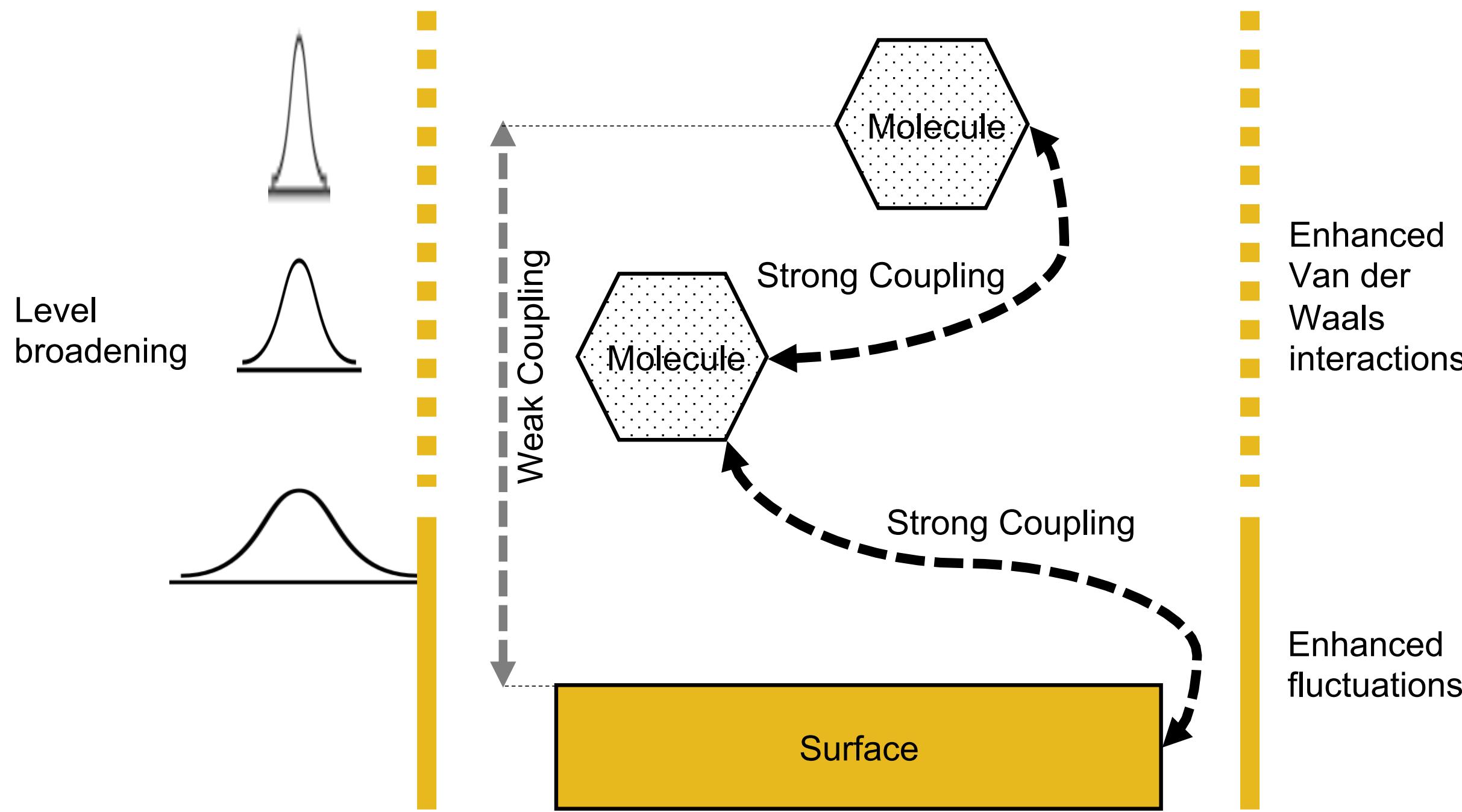
Electron dynamics of molecules at surfaces



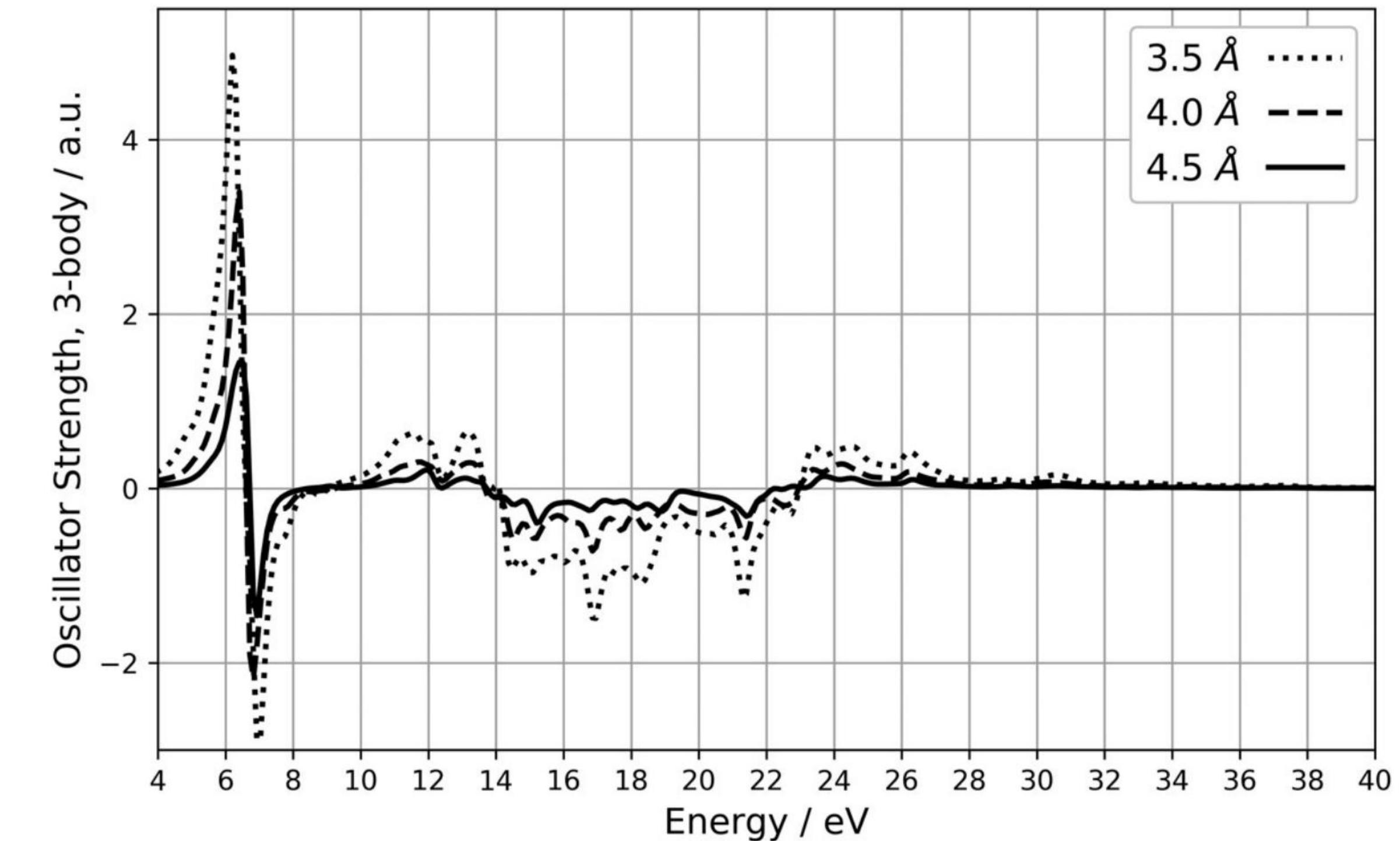
Electron dynamics of molecules at surfaces



The physics



3-body terms



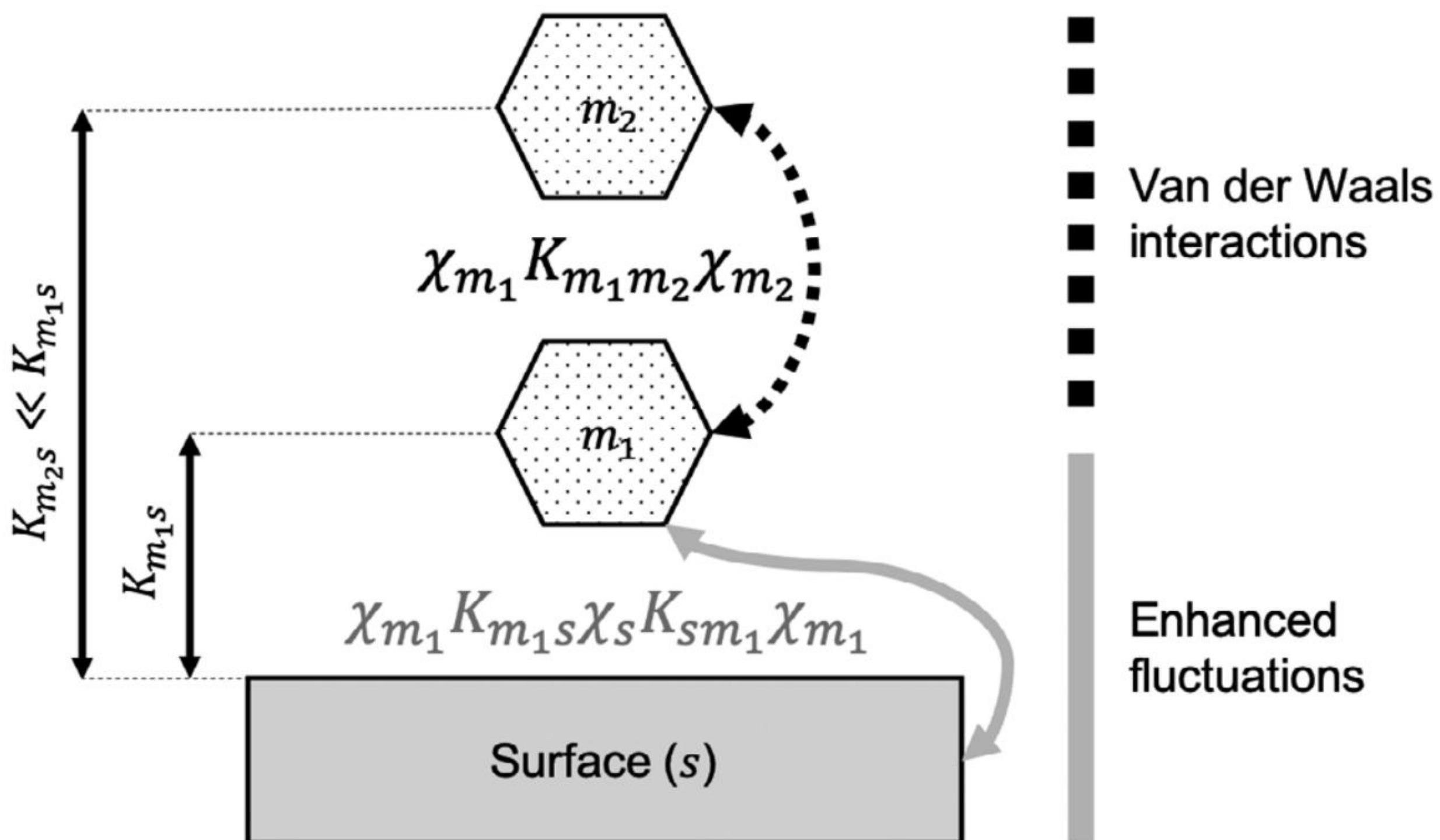
Electron dynamics of molecules at surfaces

Benzene's C₆ coefficients

$$\Delta C_6 \propto \int d\omega \text{Im} \left[\chi_m^u K_{ms} \chi_s^u K_{sm} \chi_m \right]$$

Spectra and response properties

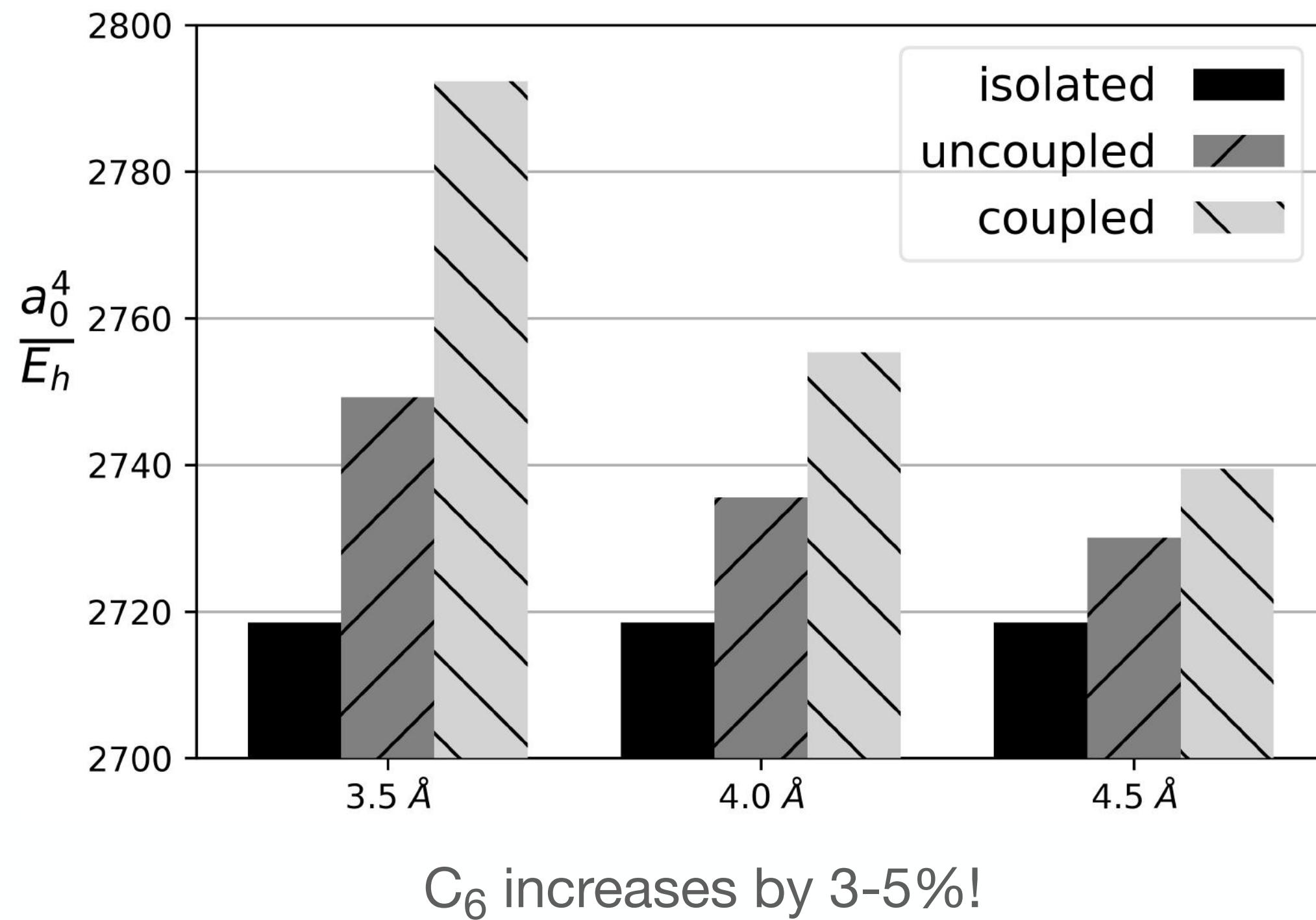
$$\Gamma = \text{Im} \left[\chi_m^u K_{ms} \chi_s^u K_{sm} \chi_m \right]$$



Electron dynamics of molecules at surfaces

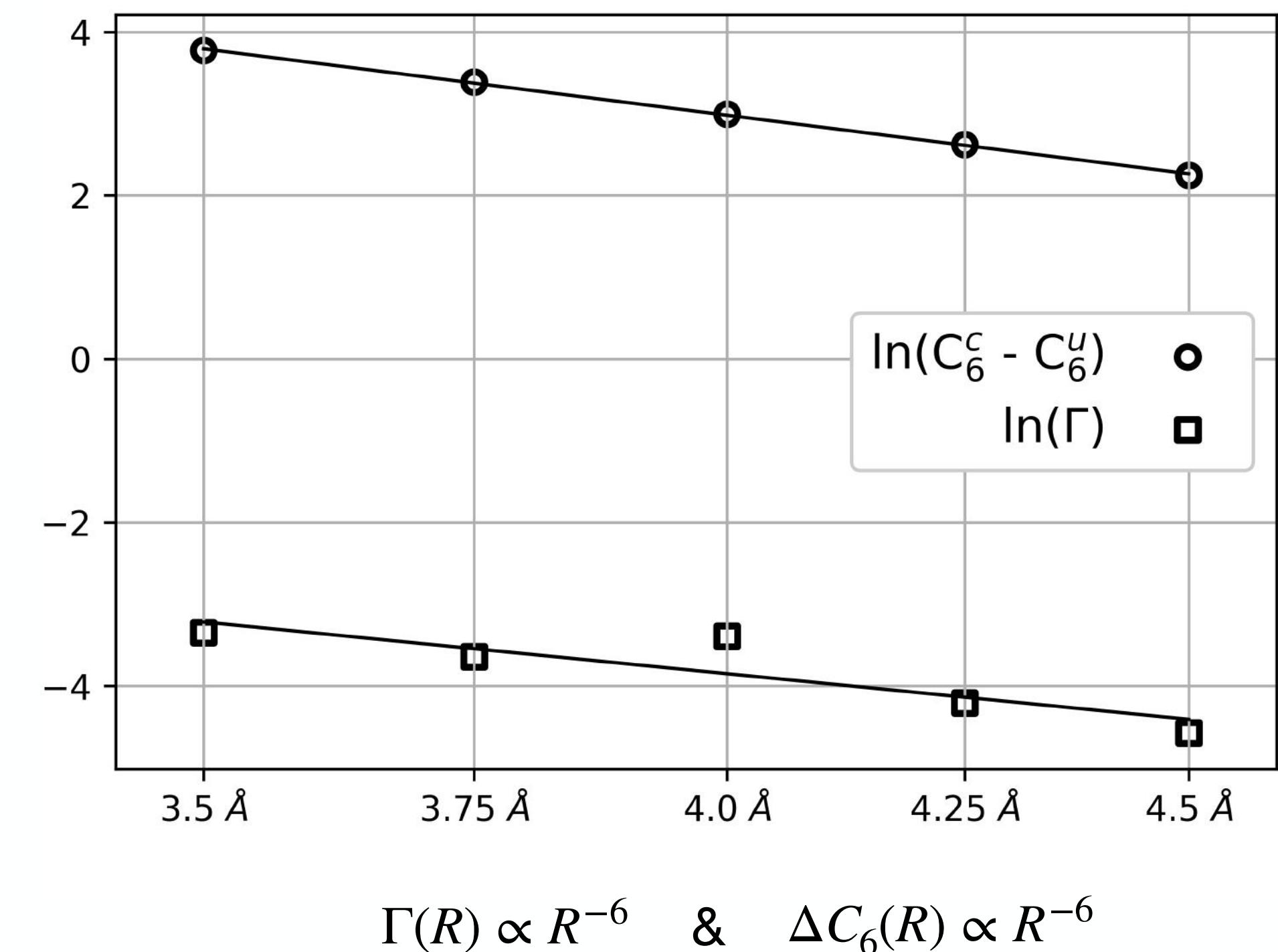
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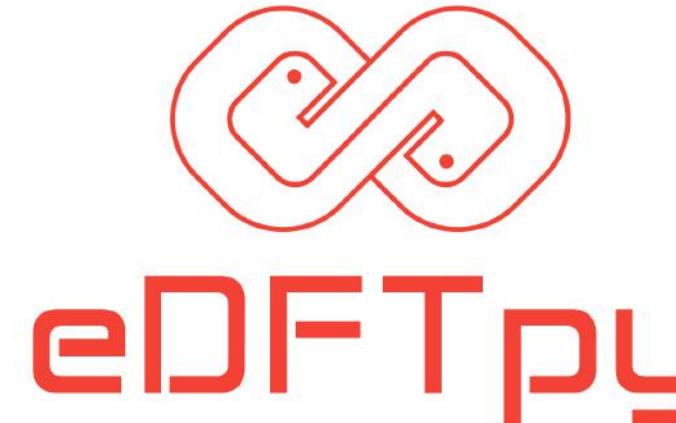
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Multiscale modeling

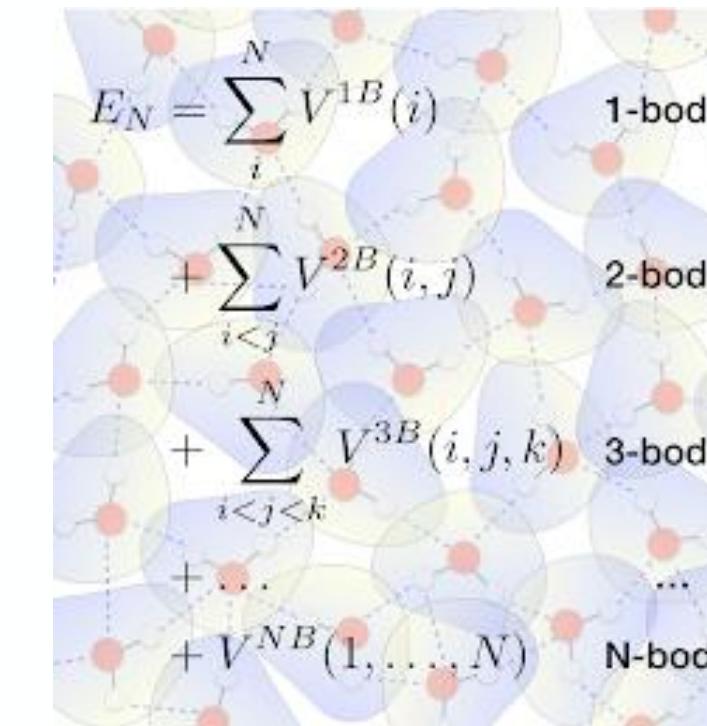
Object-oriented DFT, embedding, and QM/MM

Software development

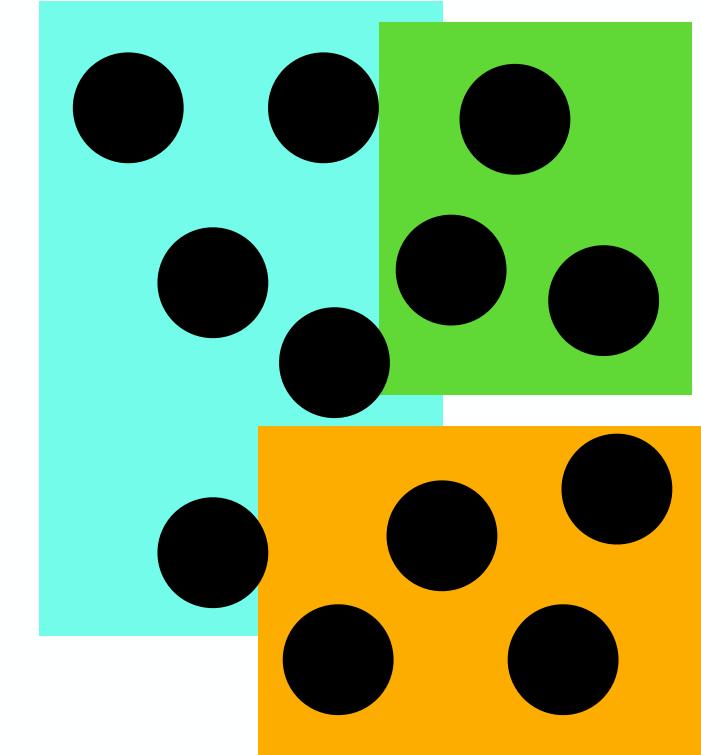


Methods

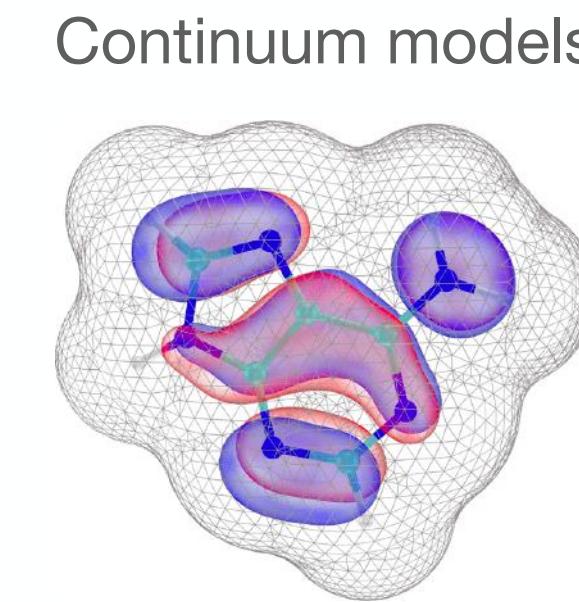
Many body



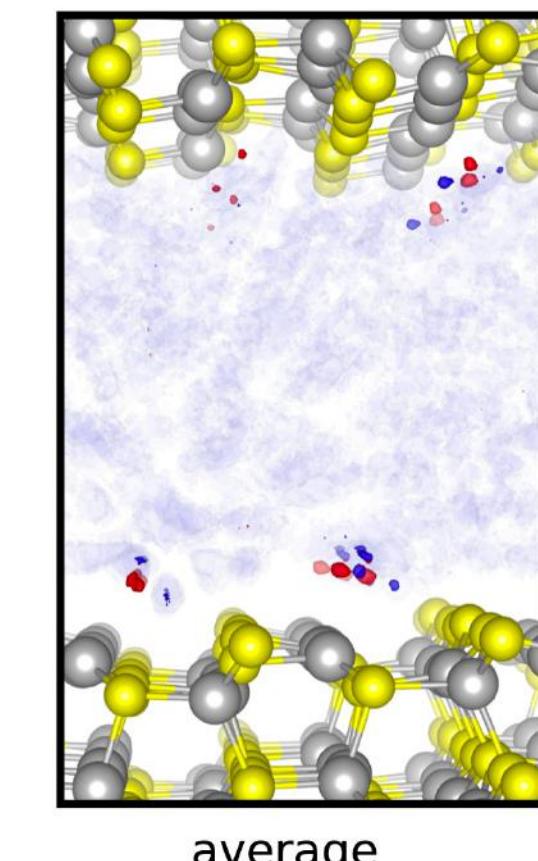
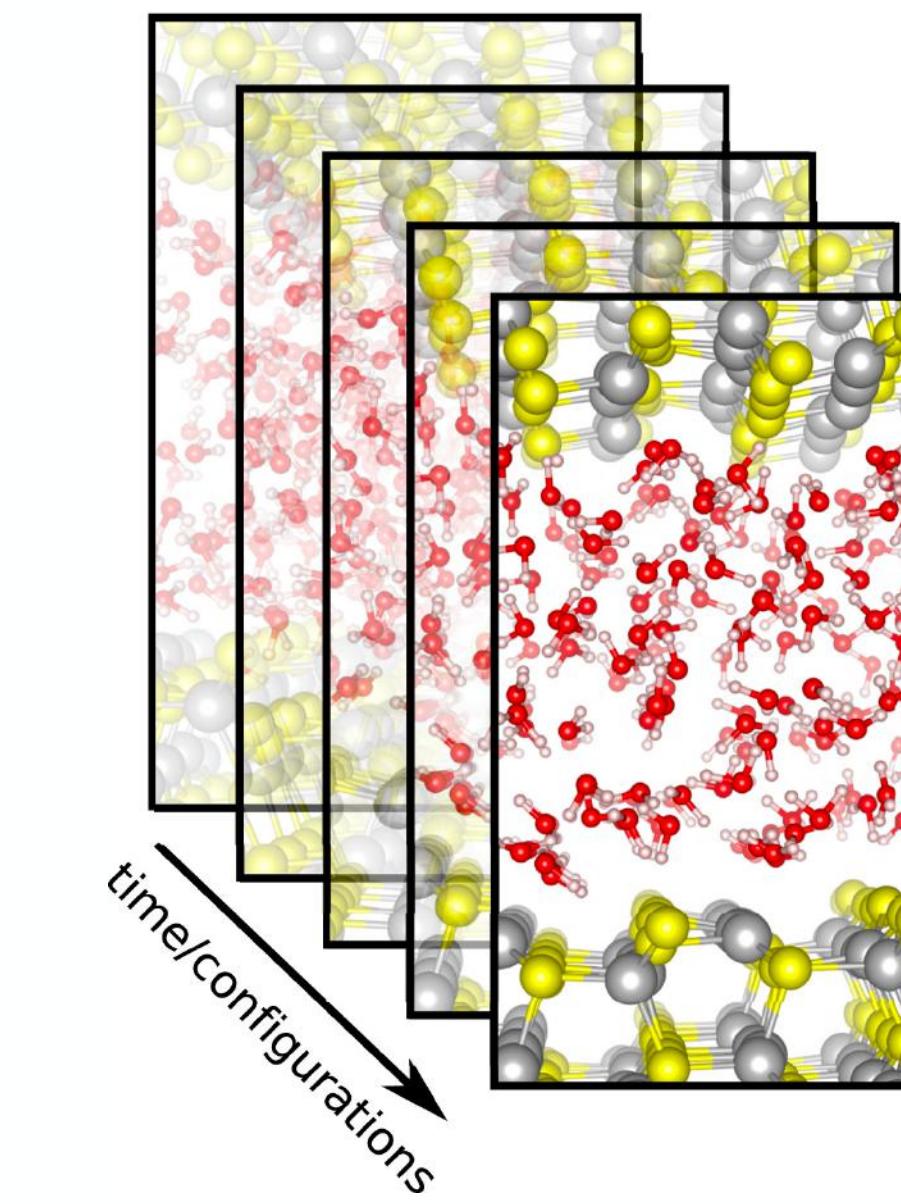
Subsystem DFT



$$\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$$



Applications



To conclude:

1. Subsystem DFT/TDDFT is accurate for weak inter-subsystem interactions
 - Nonlocality in the nonadditive functionals (NAKE) is important
 - Excited states of complex (condensed phase) systems **are** accessible
2. To tackle large systems:
 - Smarter parallelization schemes
 - Nonstandard embedding schemes (mix of KS-DFT and OF-DFT)
3. Implementations available in open-source software:
 - (a) eQE: sDFT in Fortran based on QE 5.1
 - (b) DFTpy: orbital-free DFT in Python
 - (c) eDFTpy: sDFT in Python based on QE 6.5



Thank you!