Towards sustainable electronic structure predictions

Lessons from embedding and machine learning

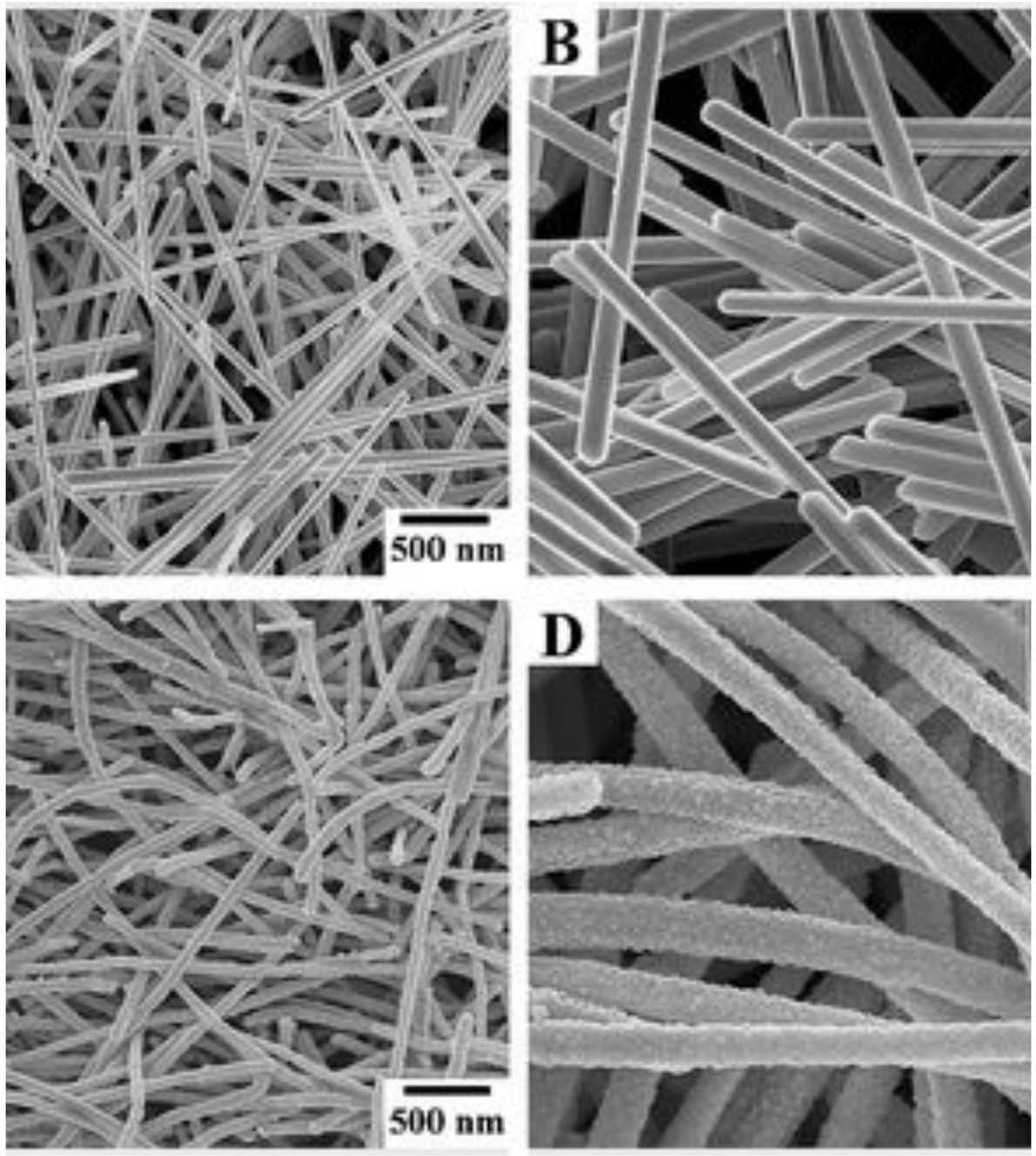
Part 1	Part 2
Embedding and ML Developments and some applications	***The code***

Michele Pavanello August 15, 2024 MolSSI Workshop @ University at Buffalo

Mesoscopic

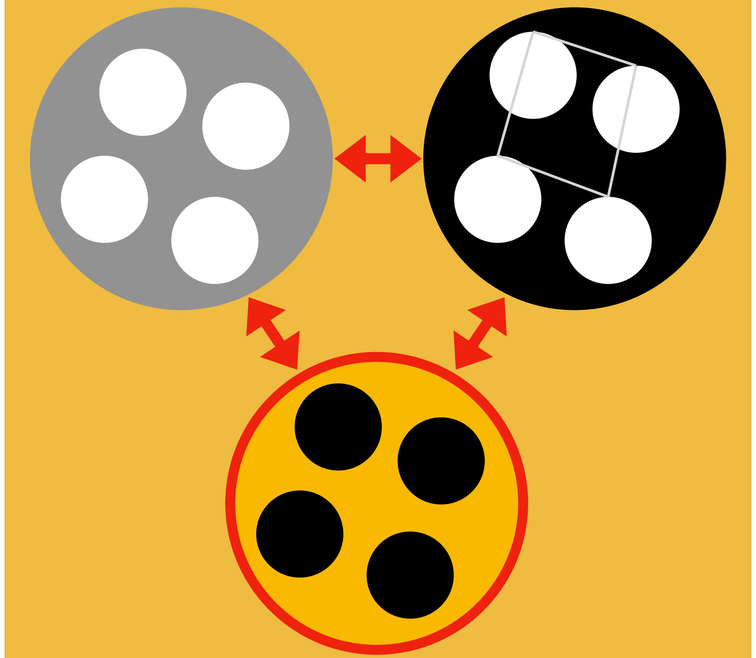
A synonym for reality

- Characteristic length scales of realistic chemical systems **> 100 nm**
- Electronic structure is #1 priority
- DFT scales like
- We focus on alternatives
  - Orbital-free DFT
  - Density Embedding / sDFT
  - Machine learning
- Other valid alternatives



Alternatives to Kohn-Sham DFT

Orbital-free DFT



Fermions

Boson s

Density Embedding

KS KS KS KS

Machine learning

Learn what?

- Electronic energy?
- Dipole moment?
- Solvation energy?
- Electronic structure

Orbital-free DFT

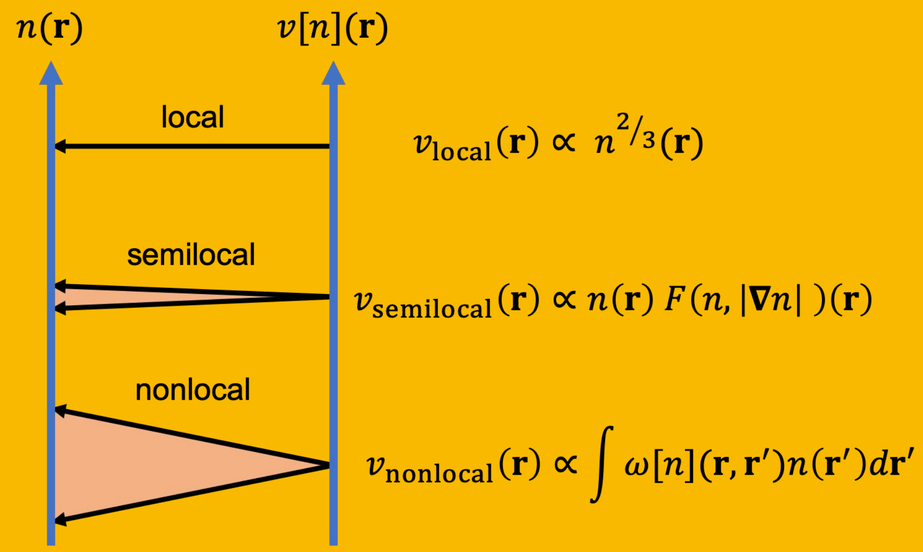
What can(t) be done

- ✓ Very large (mesoscopic) systems
- ✓ Some semiconductors
- ✓ TD-OFDFT for light-matter interaction

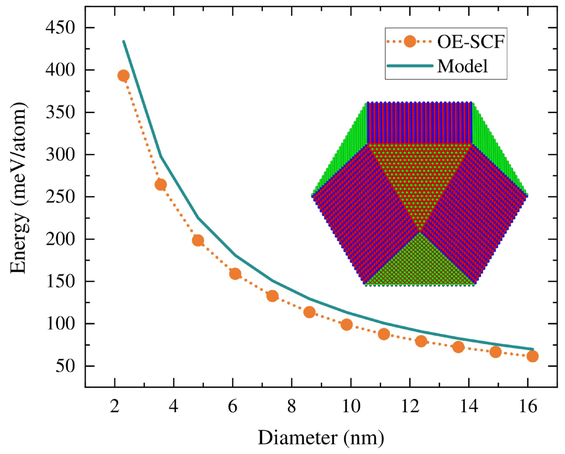
- ⊙ 2nd row
- ⊙ It's approximate…

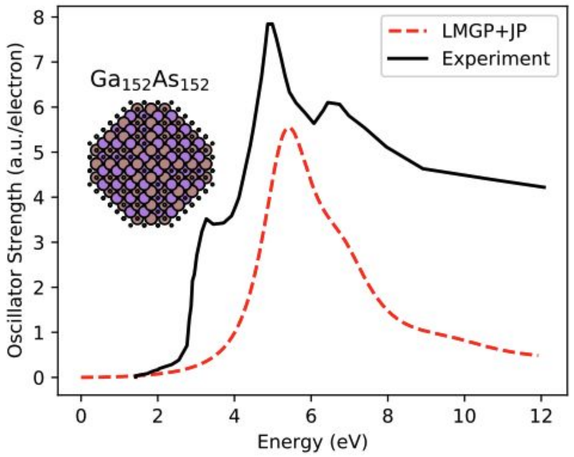
Functional development

Mi, Luo, Trickey & MP, **Chem Rev.** (2023)



Applications





TD-OFDFT: Jiang & MP, **PRB** (2021) Jiang, Shao & MP, **PRB** (2021,2022)

Density Embedding

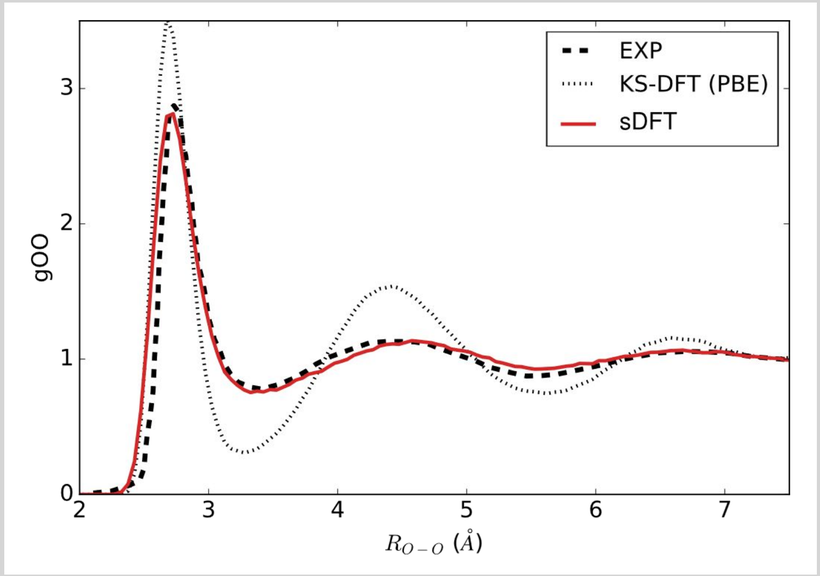
sDFT — Universally useful

- ✓ Very large (mesoscopic) molecular condensed phases
- ✓ Liquids, solvated systems
- ⊙ Only weakly interacting subsystems

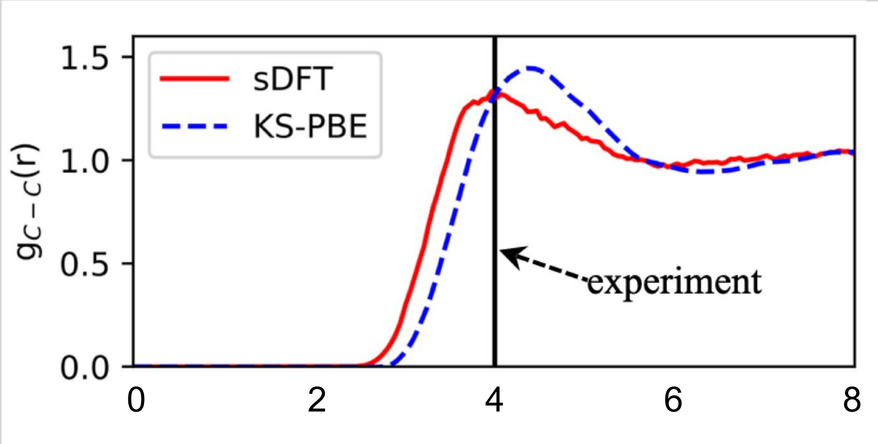
➡ **Liquid water**: Genova, Ceresoli and MP, **J. Chem. Phys.** (2016)
➡ **Liquid CO_2**: Mi, Ramos, Maranhao and MP, **J. Phys. Chem. Lett.** (2019)
➡ **Optical spectrum of water**: Kumar, Genova and MP, **J. Phys. Chem. Lett.** (2017)
➡ Neugebauer, Jacob **WIREs Comput. Mol. Sci.** (2014 and 2024)

Early success stories

➡ **Liquid water**: Genova, Ceresoli and MP, **J. Chem. Phys.** (2016)



➡ **Liquid CO_2**: Mi, Ramos, Maranhao and MP, **J. Phys. Chem. Lett.** (2019)



Functional development:

✓ Non-additive kinetic energy borrowed from OF-DFT
✓ Special-purpose “non-decomposable” non-additive functionals
⊙ Strong inter-subsystem interactions

➡ Mi and MP, **J. Phys. Chem. Lett.** (2019)
➡ Shao, Mi and MP **J. Chem. Theory Comput.** (2022)

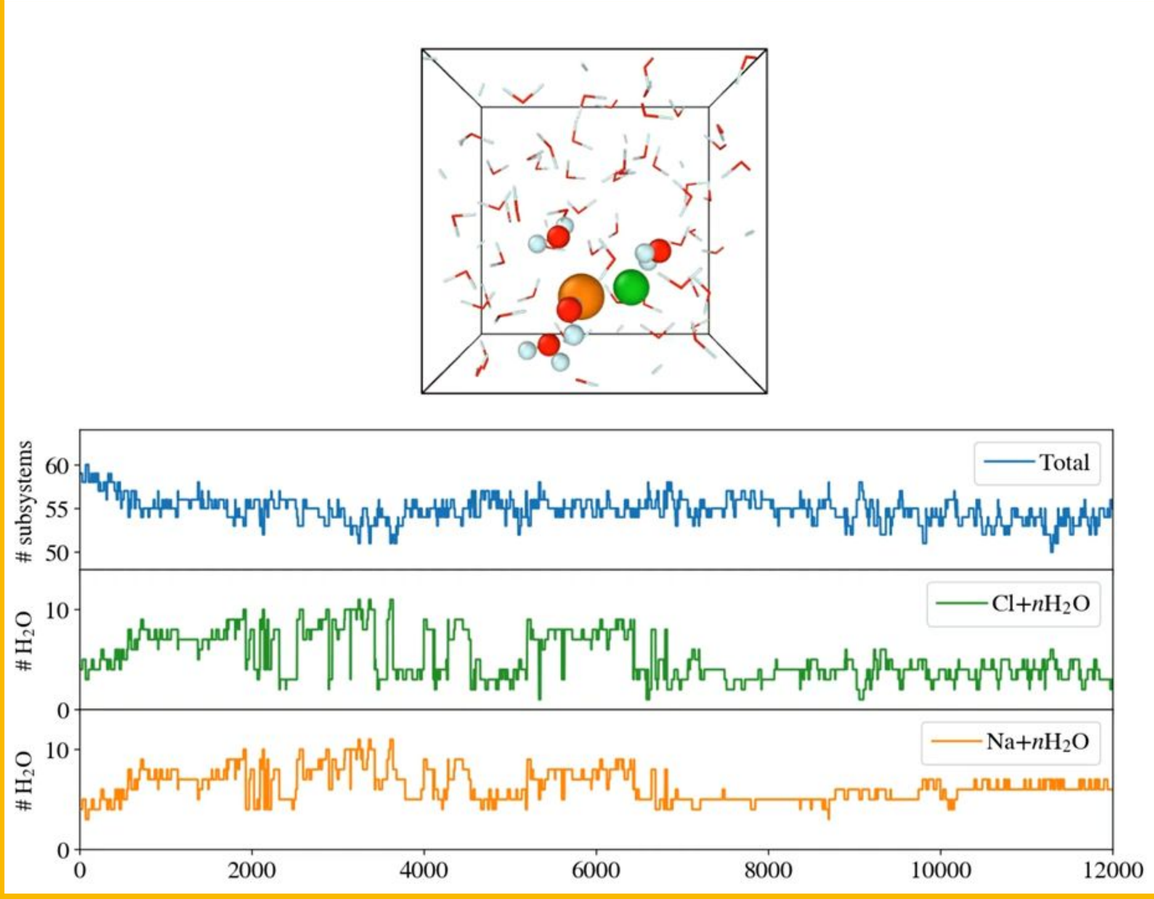
Method development: subsystem TD-DFT

✓ Real-time subsystem TD-DFT for complex systems
✓ Van der Waals interactions between subsystems from first principles

➡ Kevorkyants, Eshuis and MP, **J. Chem. Phys.** (2014)
➡ Sinha and MP, **J. Chem. Phys.** (2015)
➡ Krishtal and MP, **J. Chem. Phys.** (2015, 2016)
➡ Umerbekova and MP, **Eur. J. Phys. B** (2018)
➡ SKP, Genova and MP, **J. Phys. Chem. Lett.** (2019)
➡ Umerbekova and MP, **Int. J. Quantum Chem.** (2020)
➡ Shao, Umerbekova and MP, **Electronic Structure** (2022)

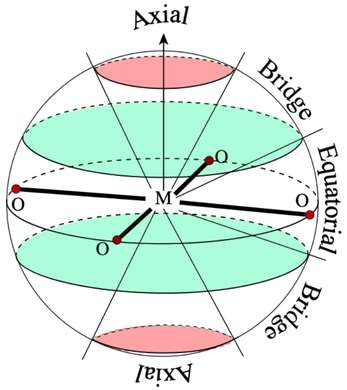
Workflow development

✓ Stong inter-subsystem interaction: adaptive sDFT dynamics



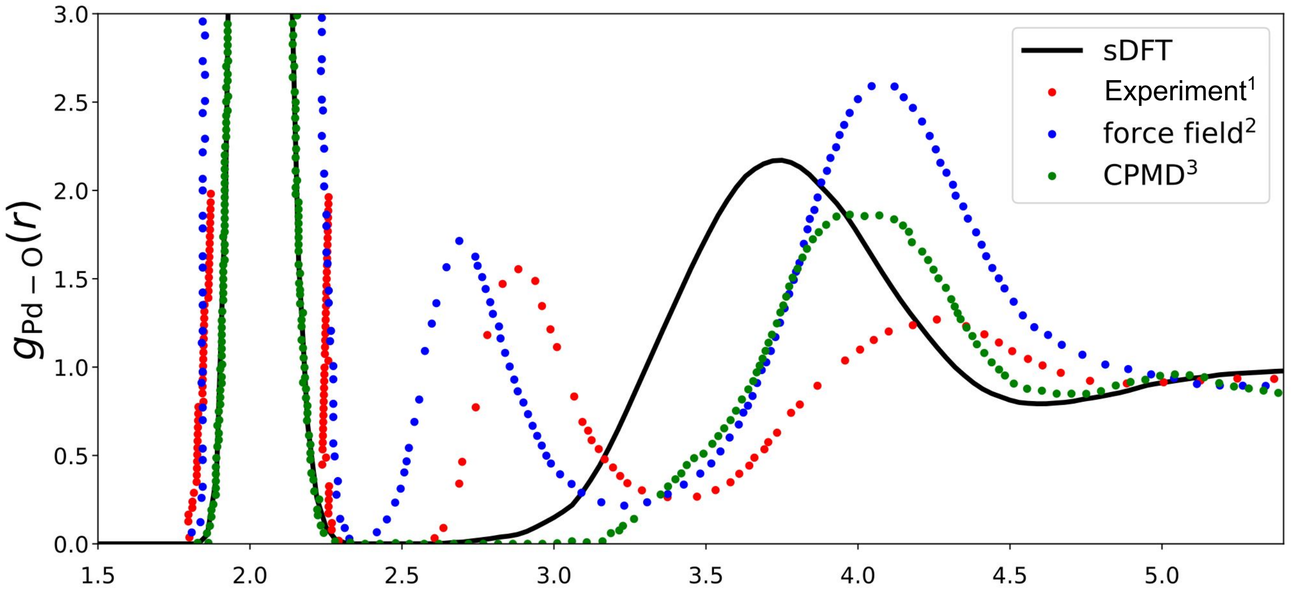
Shao, Cifuentes, Nouri Musa and MP, **J. Chem. Theory Comput.** (2022)

Hydration of aqua ions



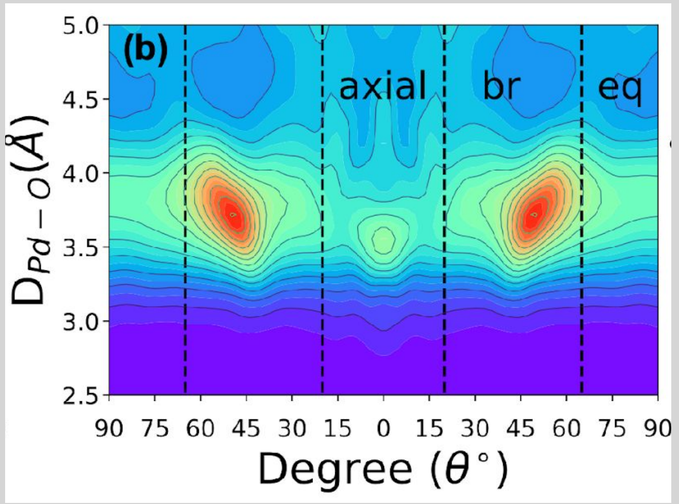
✓ 4 water molecules in the first solvation shell
✓ Axial hydration is crucial for chemistry

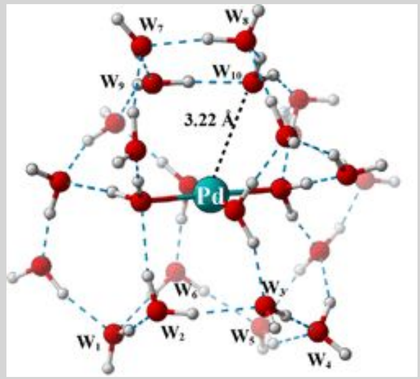
[1]Bowron et al. **JACS** 134, 962 (2012)
[2]Martinez et al. **J. Phys. Chem. B** 108, 15851 (2004)
[3]Beret et al. **J. Chem. Theory Comput.** 4, 2108 (2008)

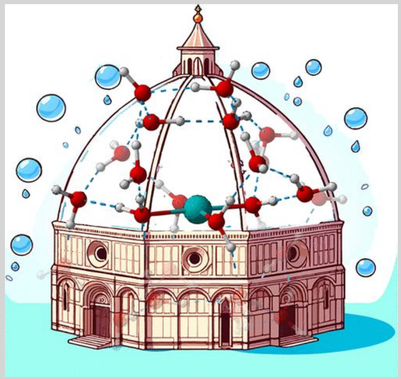


Pd aqua ion $Pd^{2+}(H_2O)_?$

- Experiments do not give direct access to partial structure factors
- Calculations are either too approximate or only reproduce a selected set of experiments
- We don't have definitive information on the axial hydration structure and dynamics







➡ **Fresh out of the press!** **J. Phys. Chem. Lett.** 15, 20, 5517–5528 (2024)

Software from PRG

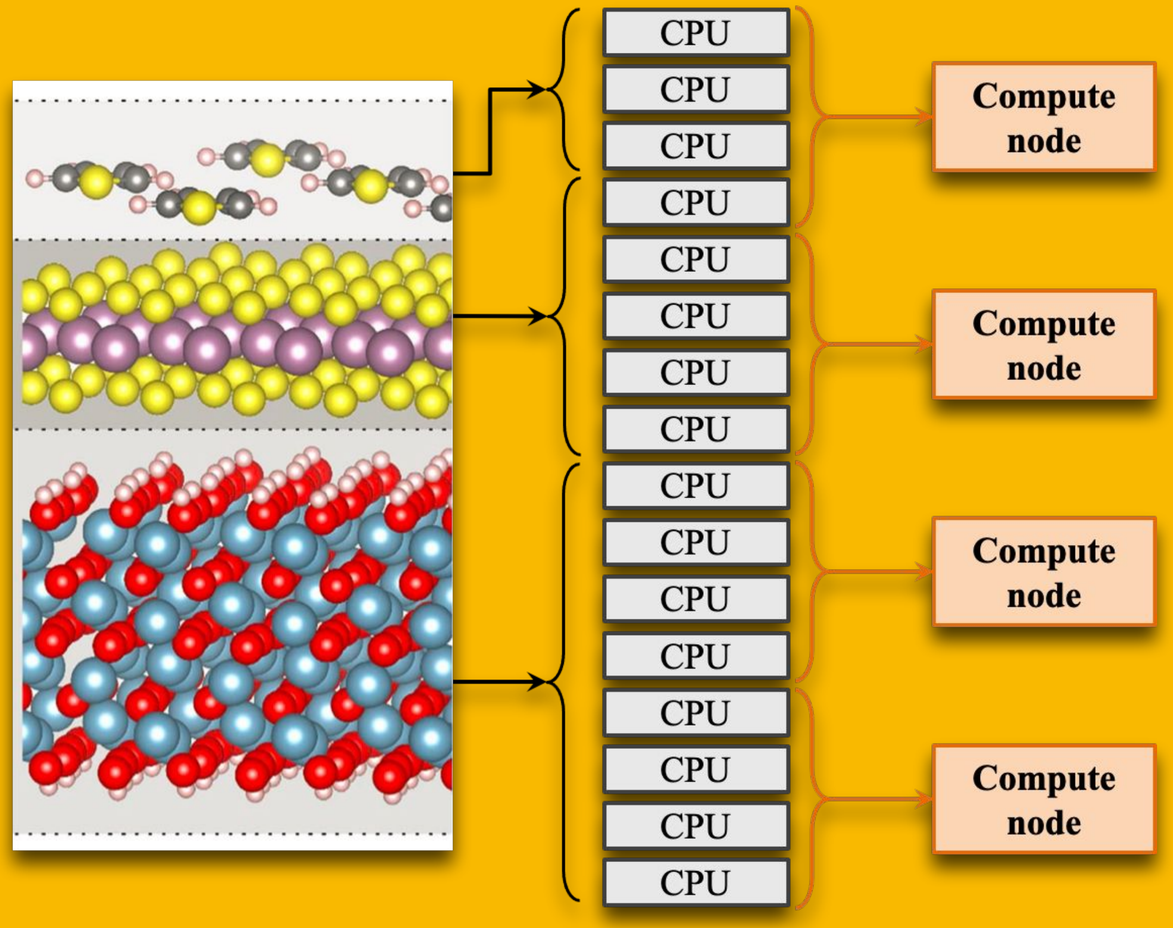
	Embedded Quantum ESPRESSO eqe.rutgers.edu	s(TD)DFT	2016-2021
	DFTpy dftpy.rutgers.edu	(TD)OF-DFT	2019-present
	QEpy https://gitlab.com/shaoxc/qepy	KS-DFT	2020-present
	Embedded DFTpy edftpy.rutgers.edu	s(TD)DFT	2020-present

Density Embedding

Has an Achille's heel

- Requires self-consistency across all subsystems
- Requires at least
  #CPUs #subsystems
- Requires exascale computers to tackle the mesoscale

sDFT vs computer architecture



Machine Learning
The Electronic Structure

✓ Learn quantities rich in information

- ⊙ Wavefunction?
- ⊙ Electron density?
- ✓ 1-rdm and/or 2-rdm

✓ Rest on rigorous grounds

➡ Short and insightful: von Lilienfeld & Burke, **Nat. Commun.** 11, 4895 (2020)

Maps

➡ Carleo, Noé, **Nat. Rev. Chem.** 7, 692 (2023)

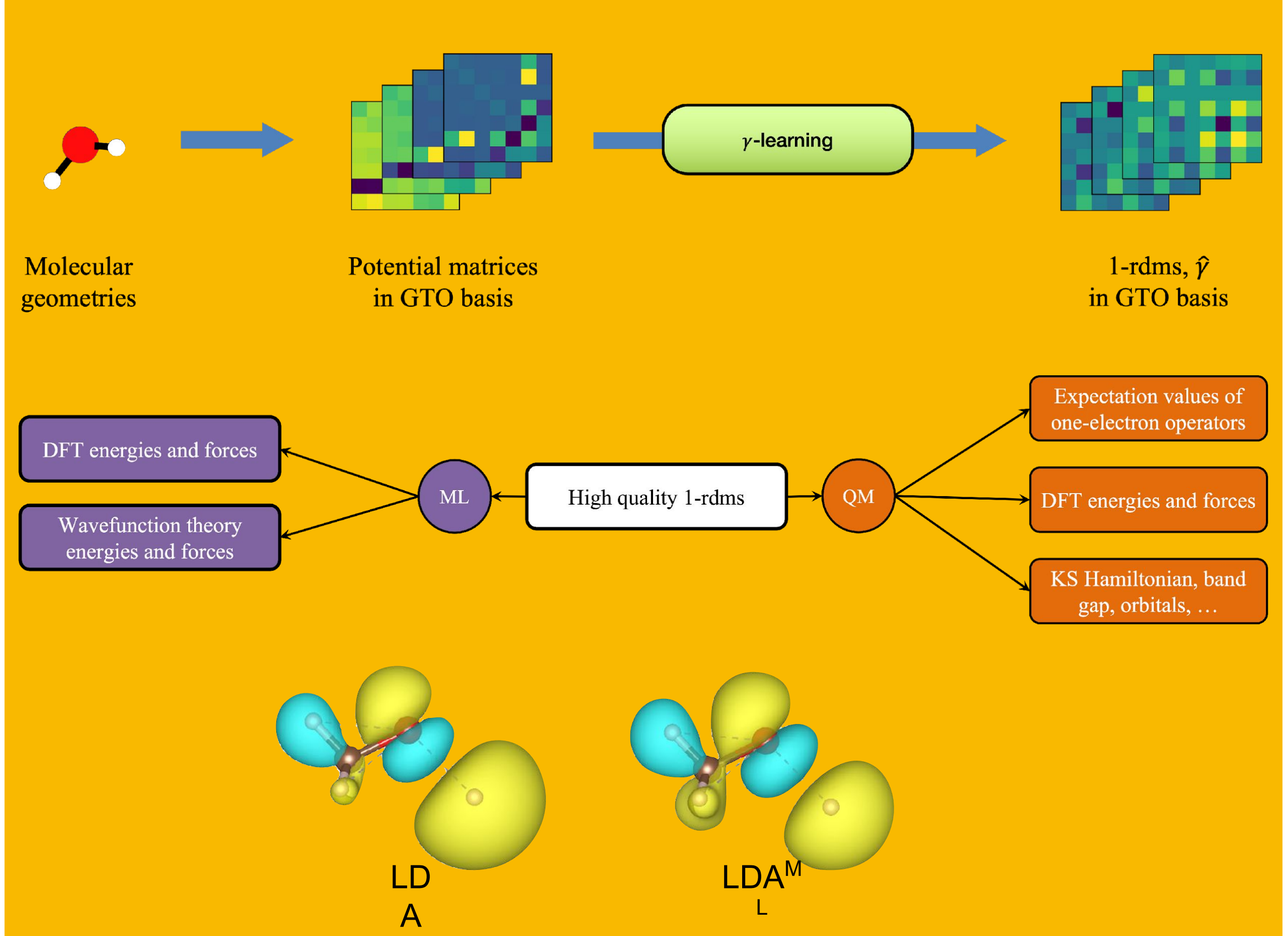
➡ Shao, Paetow, Tuckerman & Pavanello **Nat. Commun.** 14, 6281 (2023)

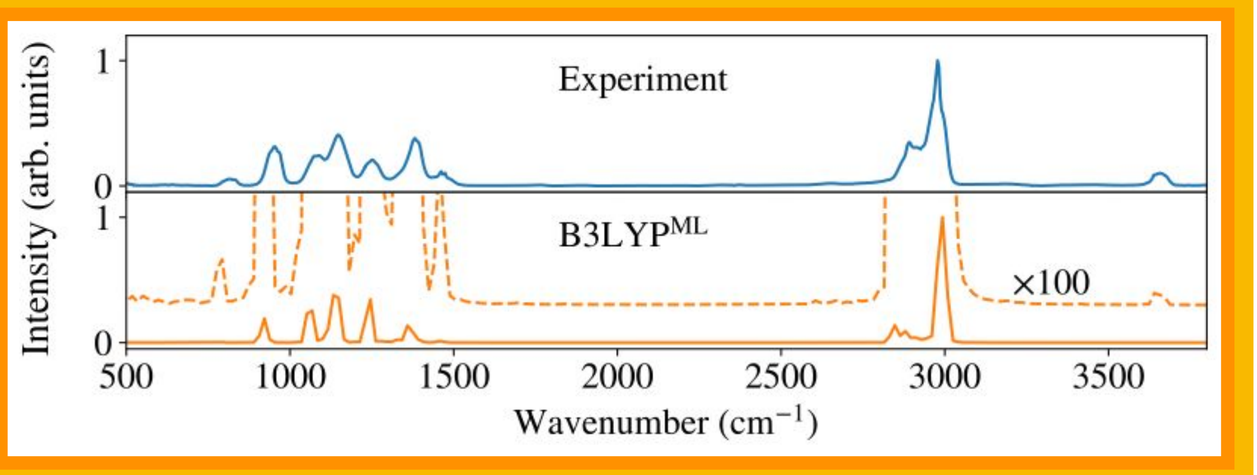
➡ Sager-Smith & Mazziotti, **JACS** 144, 18959 (2022)

➡ Tuckerman, Burke, Müller et al. in **Nat. Commun.** (2017, 2020)
➡ Glover, Tuckerman et al. **Nat. Commun.** 13, 7044 (2022)
➡ Ceriotti et al. in **J. Chem. Phys.** (2019, 2021), **JCTC** (2021, 2023), **PRB** (2020)…

Learning 1-rdms

1. Xuecheng Shao & Nick Viot
2. Learn the map
3. Use QM machinery to
   - ✓ Calculate any , gaps …
   - ✓ Calculate



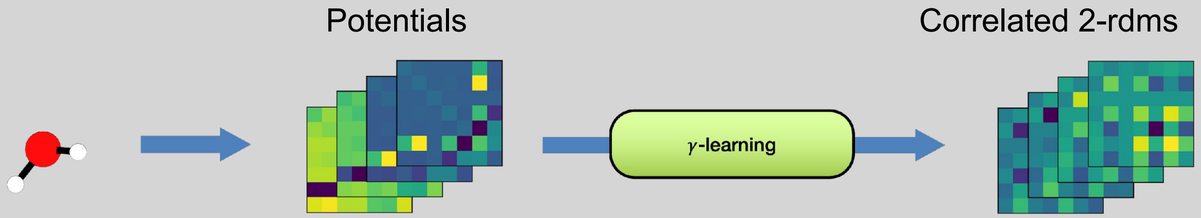


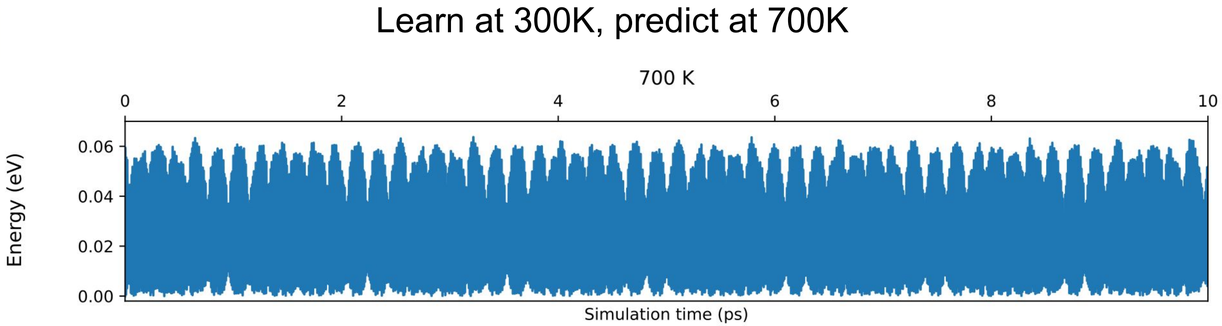
Shao, Paetow, Tuckerman & Pavanello **Nat. Commun.** 14, 6281 (2023)

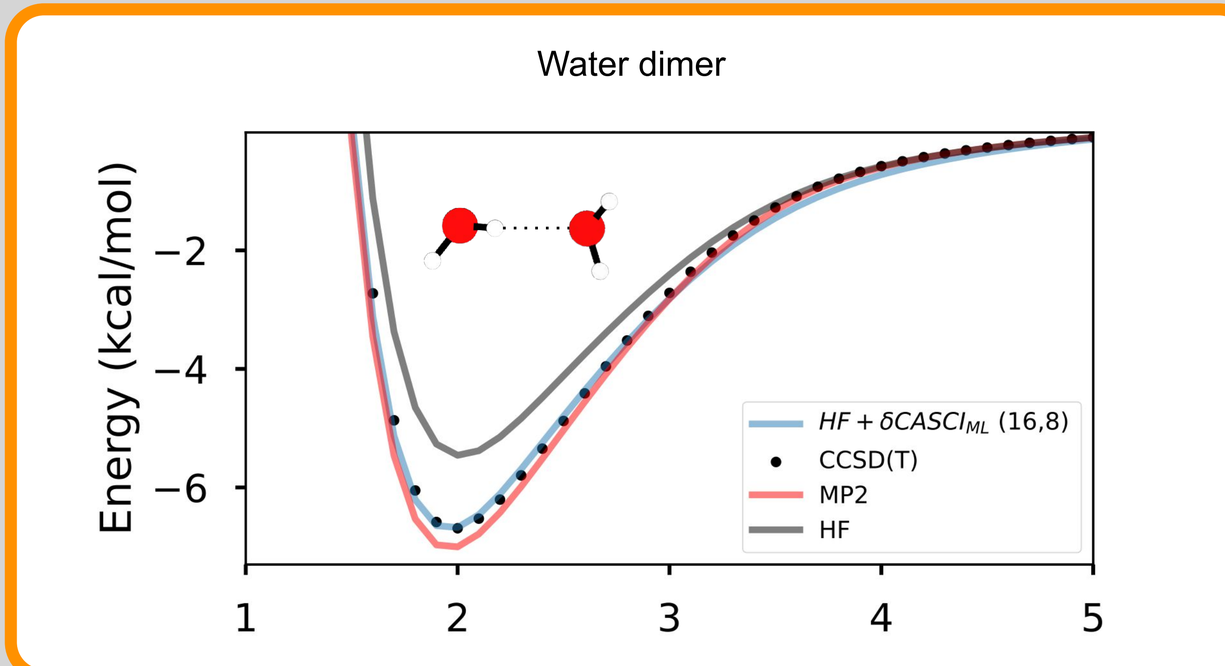
Learning 2-rdms

1. Jessica Martinez & Xuecheng Shao
2. Start from HF
3. Learn the map
4. readily available
5. Stable AIMDs
6. MB expansion for the 2-rdm

✓ Tackle condensed phases



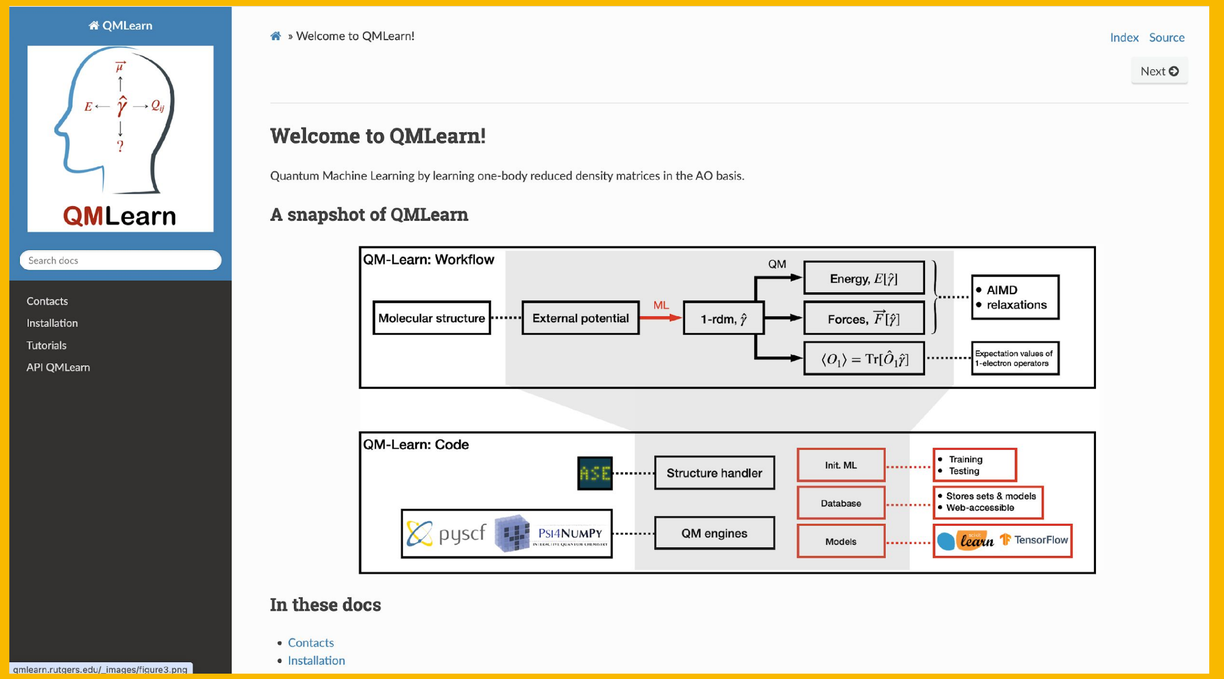




QMLearn

- ✓ Xuecheng Shao, Jessica Martinez, Nick Viot
- ✓ Learn 1- and 2-rdms
- ✓ Builds training set
- ✓ Handles databases
- ✓ Surrogate QM calculations

http://qmlearn.rutgers.edu/



Shao, Paetow, Tuckerman & Pavanello **Nat. Commun.** 14, 6281 (2023)

THANK YOU

Funding

NEWARK

U.S. DEPARTMENT OF ENERGY