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Combining DFT and Machine Learning

Towards faster and more accurate ab-initio calculations

Sebastian Dick, Department of Physics and Astronomy, Stony Brook University
Fernandez-Serra Group
Jr. Researcher Award, 08/16/2018

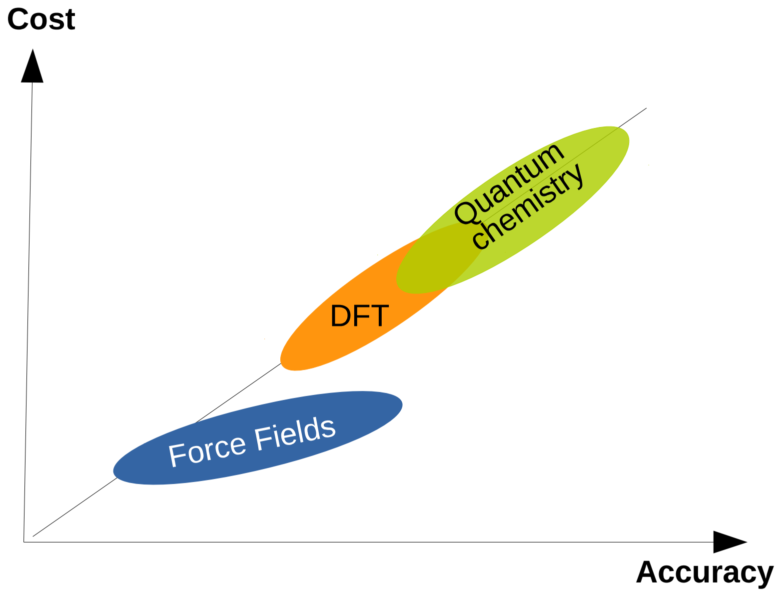
Introduction

Simulations in Molecular Sciences

Atomic coordinates

- **Force Fields**
- **Density Functional Theory (DFT)**
- **Quantum Chemistry**

Energies, **Forces**, Stress, Electron density, Spectra, ...

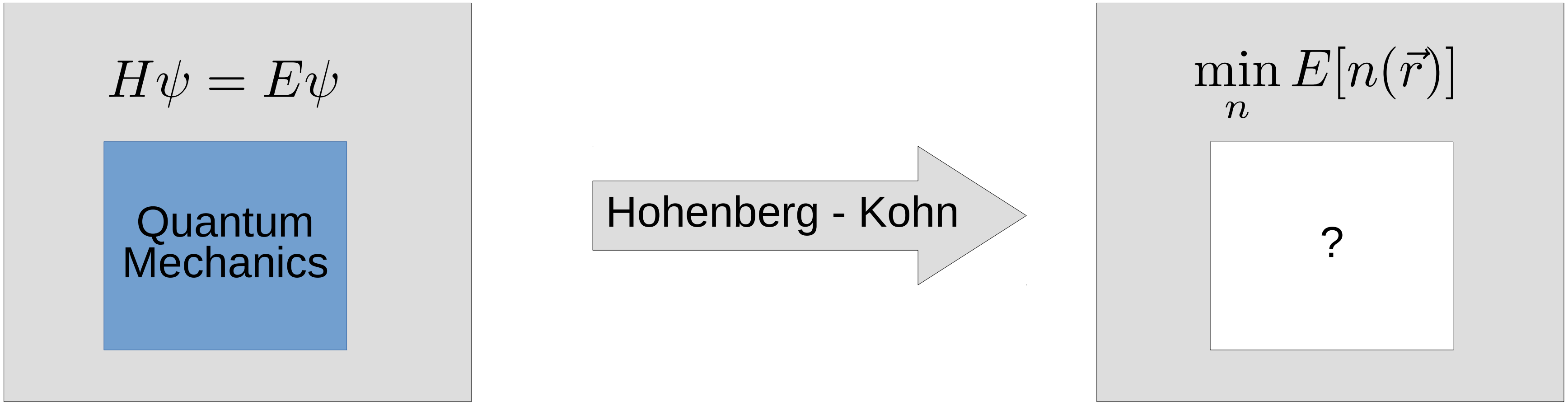


We use DFT because:

- Can scale to large systems sizes (100s to 1000s of atoms) + Periodic boundary conditions

  → Condensed systems
- Non-empirical, hence unbiased
- Fully reactive

How does DFT work ?



$$H\psi = E\psi$$

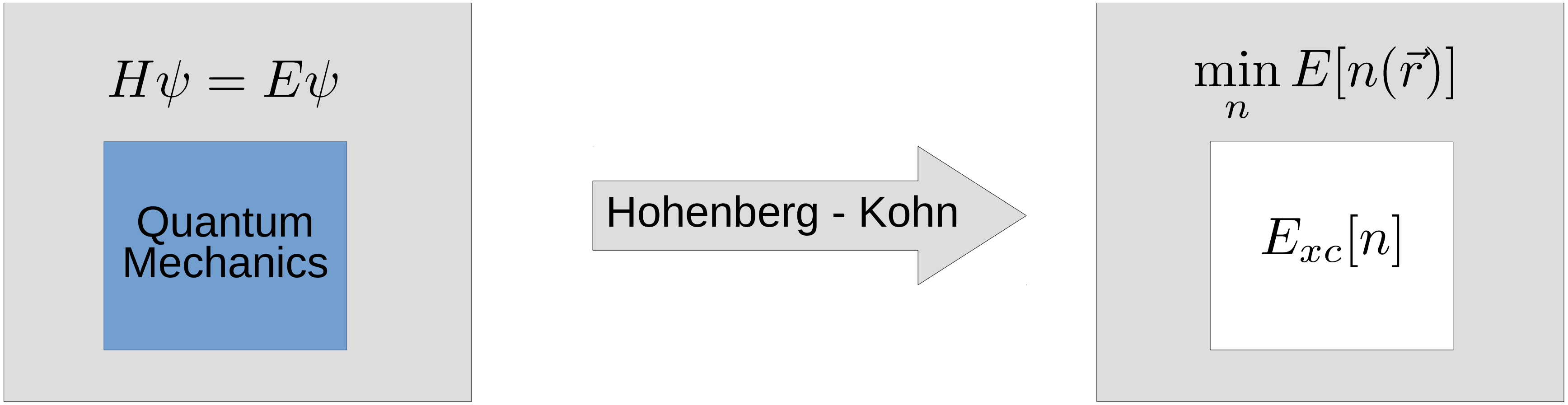
Quantum Mechanics

Hohenberg - Kohn

$$\min_{n} E[n(\vec{r})]$$

?

How does DFT work ?



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Quantum Mechanics

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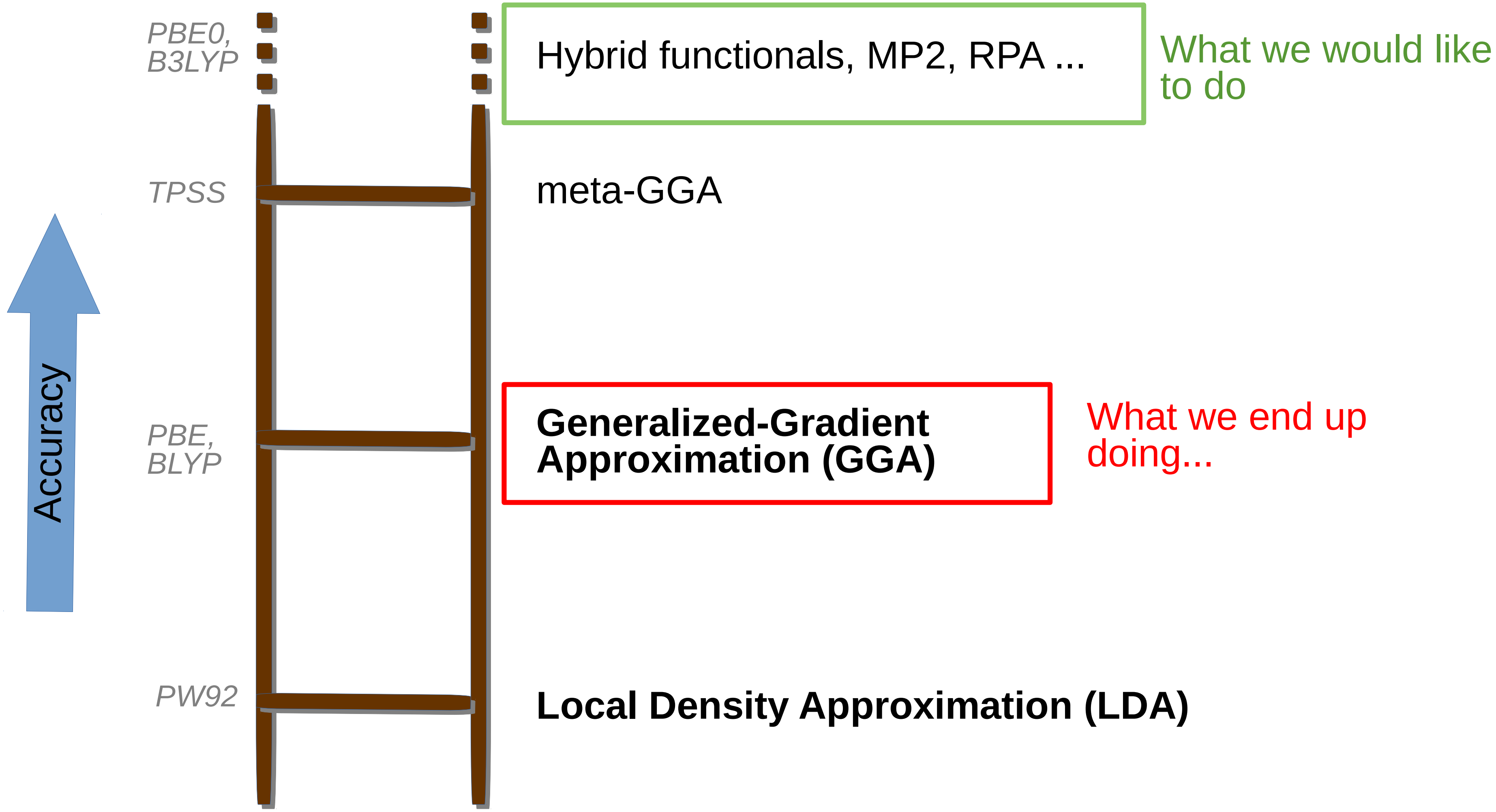
$\min_{n} E[n(\vec{r})]$

$E_{xc}[n]$

$$E[n] = T[n] + E_{xc}[n] + \int d\vec{r}\, V_{ext}(\vec{r}) n(\vec{r}) + E_{Hartree}[n] + E_{II}$$

Jacob's ladder

- A density functional approximation is uniquely defined by choosing $E_{xc}[n]$
- Accuracy, Cost ↔ Locality



PBE0,
B3LYP

Hybrid functionals, MP2, RPA ...

What we would like to do

TPSS

meta-GGA

PBE,
BLYP

Generalized-Gradient Approximation (GGA)

What we end up doing...

PW92

Local Density Approximation (LDA)

Accuracy

Machine learning in Molecular Sciences

Force Fields

Towards Exact Molecular Dynamics Simulations
with Machine-Learned Force Fields
Chmiela et al, arXiv:1802.09238 (2018)

SchNet – A deep learning architecture
for molecules and materials
JCP 148 (2018), Schutt et al

Generalized Neural-Network Representation of
High-Dimensional Potential-Energy Surfaces
PRL 98 (2007), Behler, Parrinello

Electronic Structure

By-passing the Kohn-Sham equations
with machine learning
Brockerde et al., Nature Comm. 8 (2017)

Finding density functionals with machine learning
Snyder et al, Phys. Rev. Lett. 108 (2012)

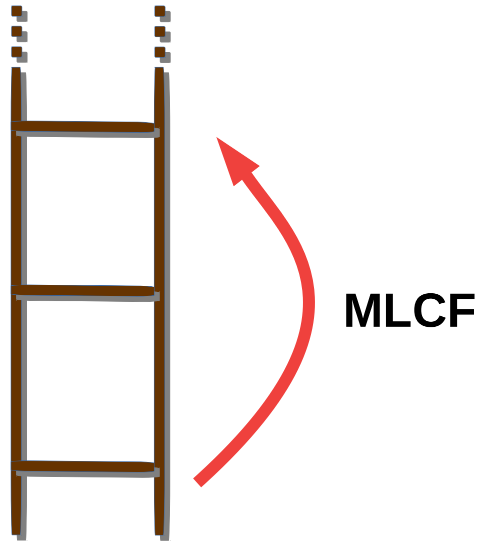
Semi-local machine-learned kinetic
energy density functional
with third-order gradients of electron density
Seino et al, JCP 148 (2018)

Machine learning in Molecular Sciences

Our idea: **Machine Learned Correcting Functionals (MLCFs)**

Train a neural network on the difference in predictions of physical observables (E, F, ...) of a lower accuracy **baseline** method (GGA) and a higher level **reference** method (Hybrid DFT, Coupled Cluster, …)

→ get a higher accuracy at the cost of the baseline method



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Machine learned correcting functionals (MLCFs)

Informed Machine Learning for Maximal Extrapolation

Rather than provide all available (raw) data in an unbiased way, **knowledge about the physical mechanisms** involved is used to pre-process and select relevant data.

Trained on a small representative dataset the model should **generalize to unseen data**. In particular, the model has to be valid for **arbitrary system sizes**.

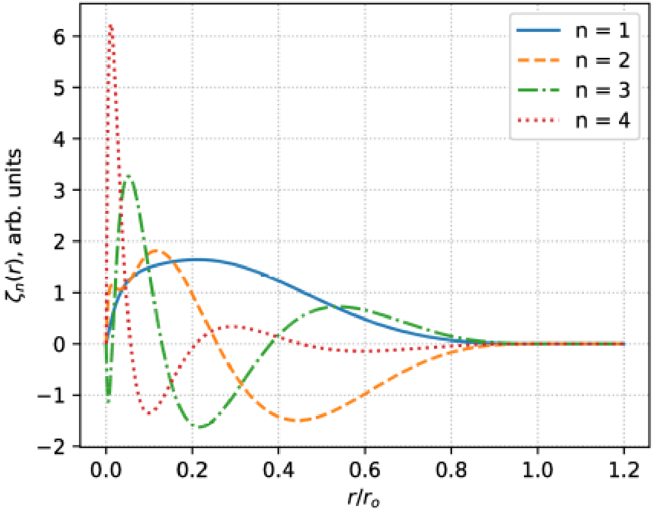
Data

- **Dataset: Water**
  - *Training:* 640 Monomers, 1600 Dimers, 1200 Trimers
  - *Testing:* 160 Monomers, 400 Dimers, 300 Trimers, 50 Tetramers, 50 Pentamers, …

- **Input:** Expansion of electron density around each atom into basis functions:

$$\psi_{nlm}(\vec{r}) = Y_l^m(\theta,\phi)\zeta_n(r)$$

$$\int_{\vec{r}} \psi^*_{nlm}(\vec{r})\psi_{n'l'm'}(\vec{r}) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$



Electronic descriptors:

$$\boxed{c^{\alpha,I}_{nlm} = \int_{\vec{r}} \rho(\vec{r} - \vec{r}_{\alpha,I})\psi^{*\alpha}_{nlm}(\vec{r})}$$

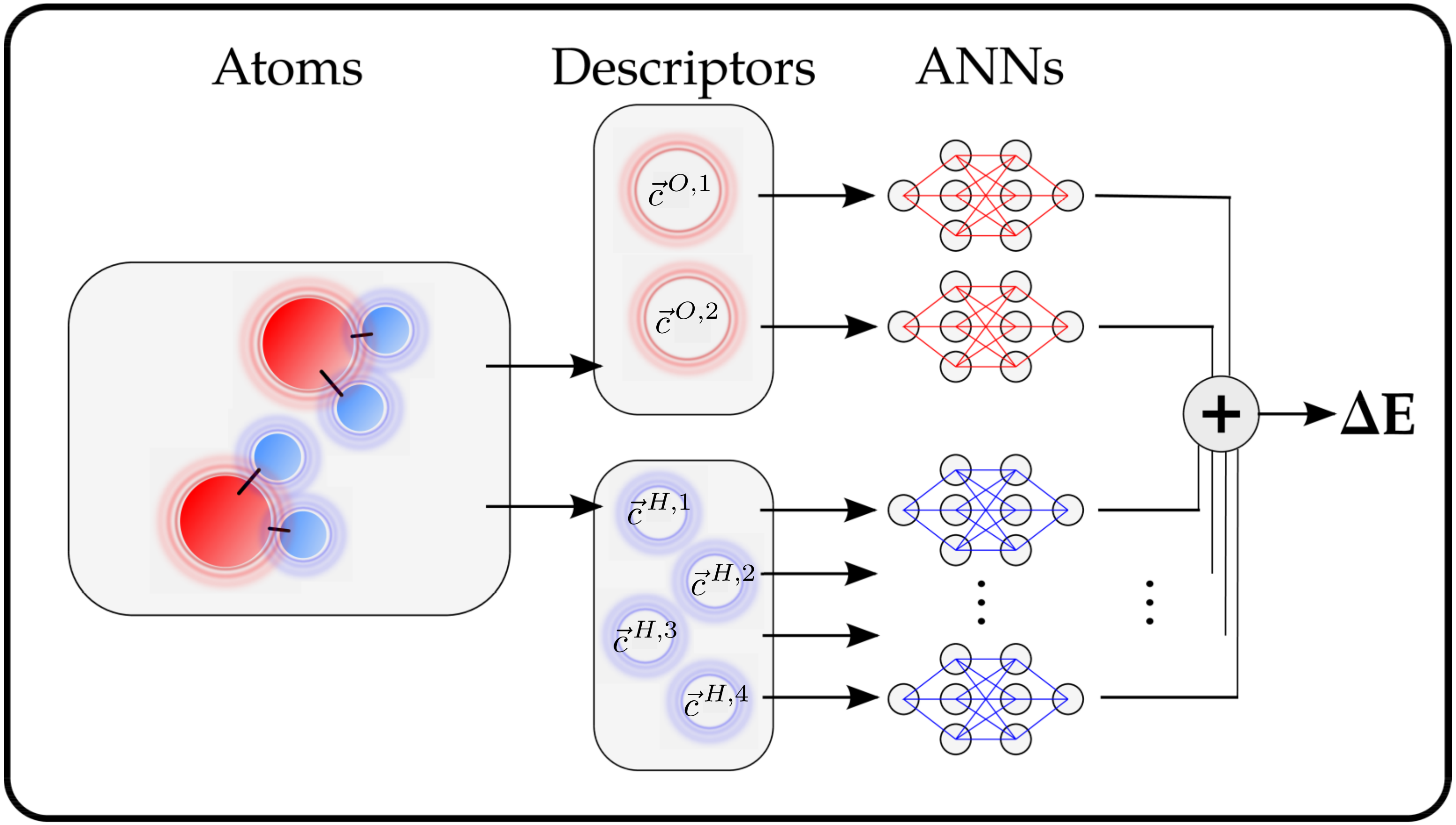
Atomic species Atom index

- **Targets:** Difference between reference (MB-pol) and baseline (GGA + vdW) energies(/forces)

$$\Delta E = E_{reference} - E_{baseline}$$

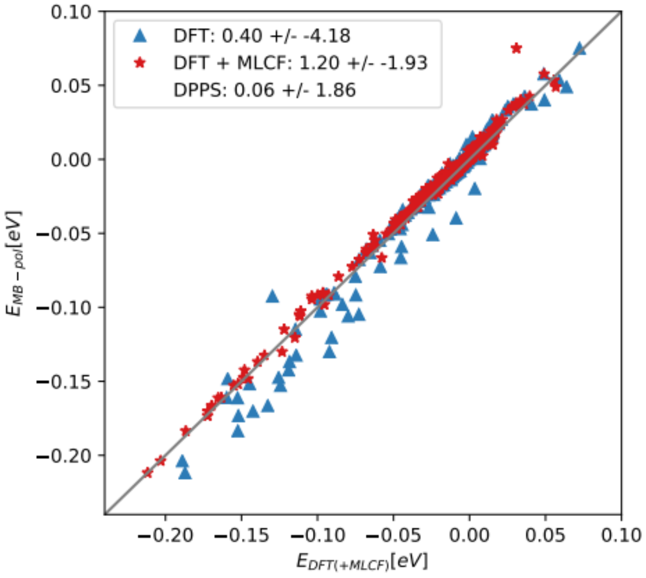
Architecture

$$n \rightarrow \Delta E_{MLCF}[n]$$



Performance on water clusters

2-body energy

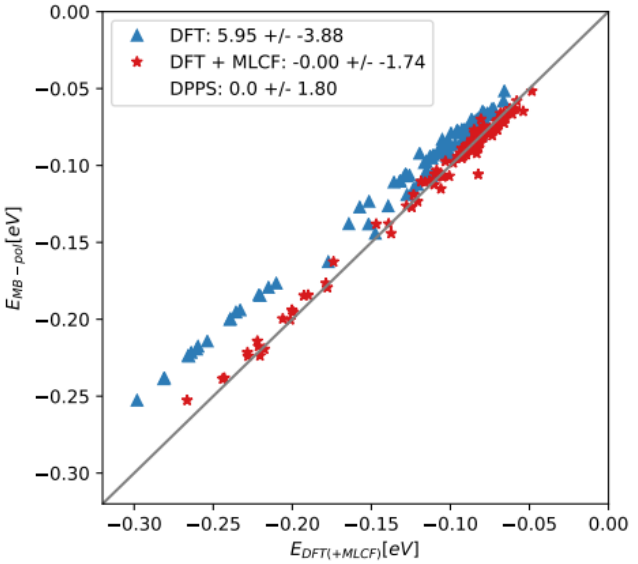


$$\delta E = E_{ref} - E_{pred}$$

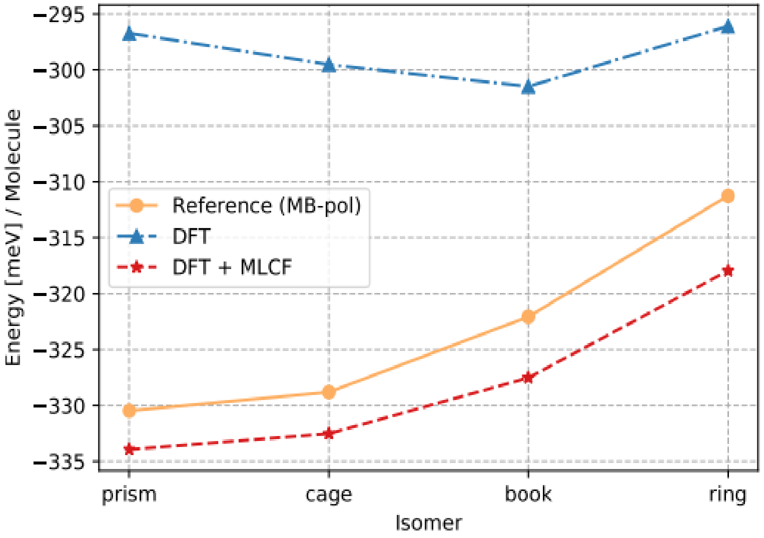
Molecules	$\langle \delta E \rangle$		$\sqrt{\langle (\delta E)^2 \rangle - \langle \delta E \rangle^2}$	
	DFT	**DFT+MLCF**	**DFT**	**DFT+MLCF**
1	-4.2	-1.4	64.3	**2.0**
2	-5.8	-1.3	42.5	**3.4**
3	-14.8	0.6	31.9	**2.3**
4	-31.2	-1.0	9.4	**2.7**
5	-31.9	0.0	12.3	**3.0**
8	-28.9	2.3	9.3	**3.1**
16	-26.1	6.6	6.2	**2.5**

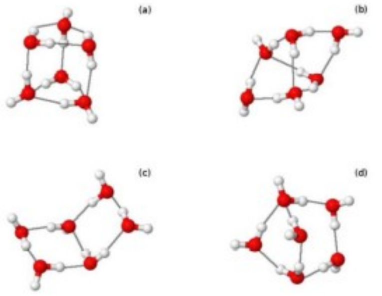
Energies in meV/molecule

3-body energy



Hexamers



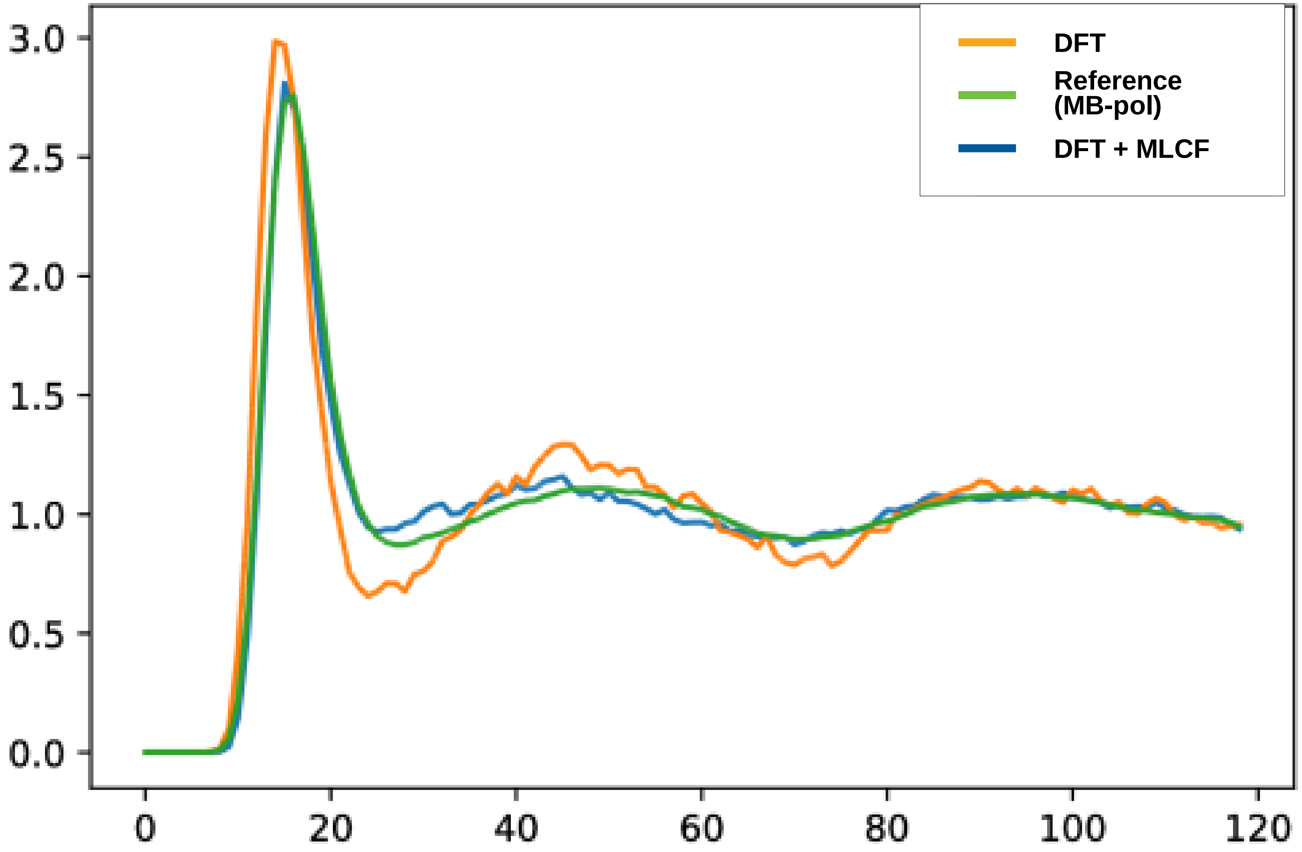


Fritz, Fernandez-Serra, Soler, J. Chem. Phys. 144, 224101 (2016), Supplementary Information

Correcting molecular dynamics simulations

- **Ab initio molecular dynamics:** Integrate the equations of motion with forces obtained from ab-intio calculations.
- GGA (DFT) is known to over-structure liquid water (peaks too high)
- Even though simulations not well converged yet (simulation time too short), MLCFs seem to correct this over-structuring

Simulation of a box with periodic boundary conditions containing 128 water molecules, with Nose-Hoover Thermostat at 300 K



Using MLCFs to speed up MD calculations

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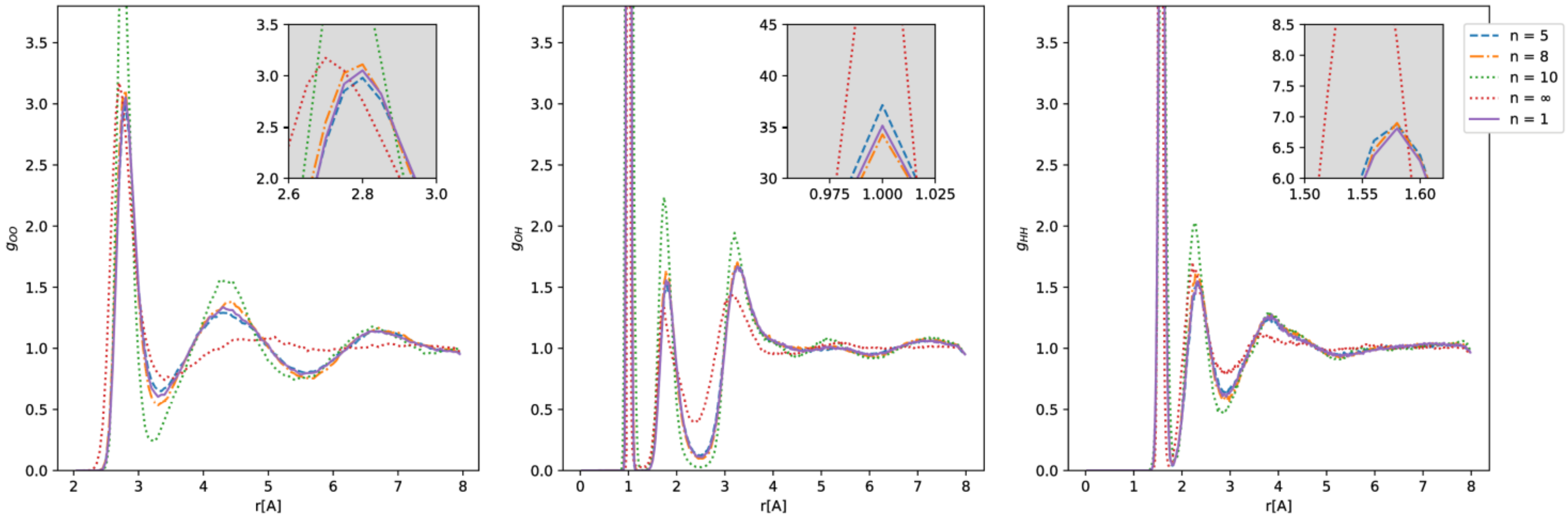
- Start from very fast DFT calculation with very low accuracy (GGA, minimal basis set, coarse grid, relaxed convergence criteria)
- Large difference between baseline and reference → only approximate correction
- Solution: Every n-th MD step use reference method to calculate correction
- **Speed-ups of up to a factor of 8 for water**
- But: possible speed-up system dependent, careful validation necessary



Outlook

Python toolkit

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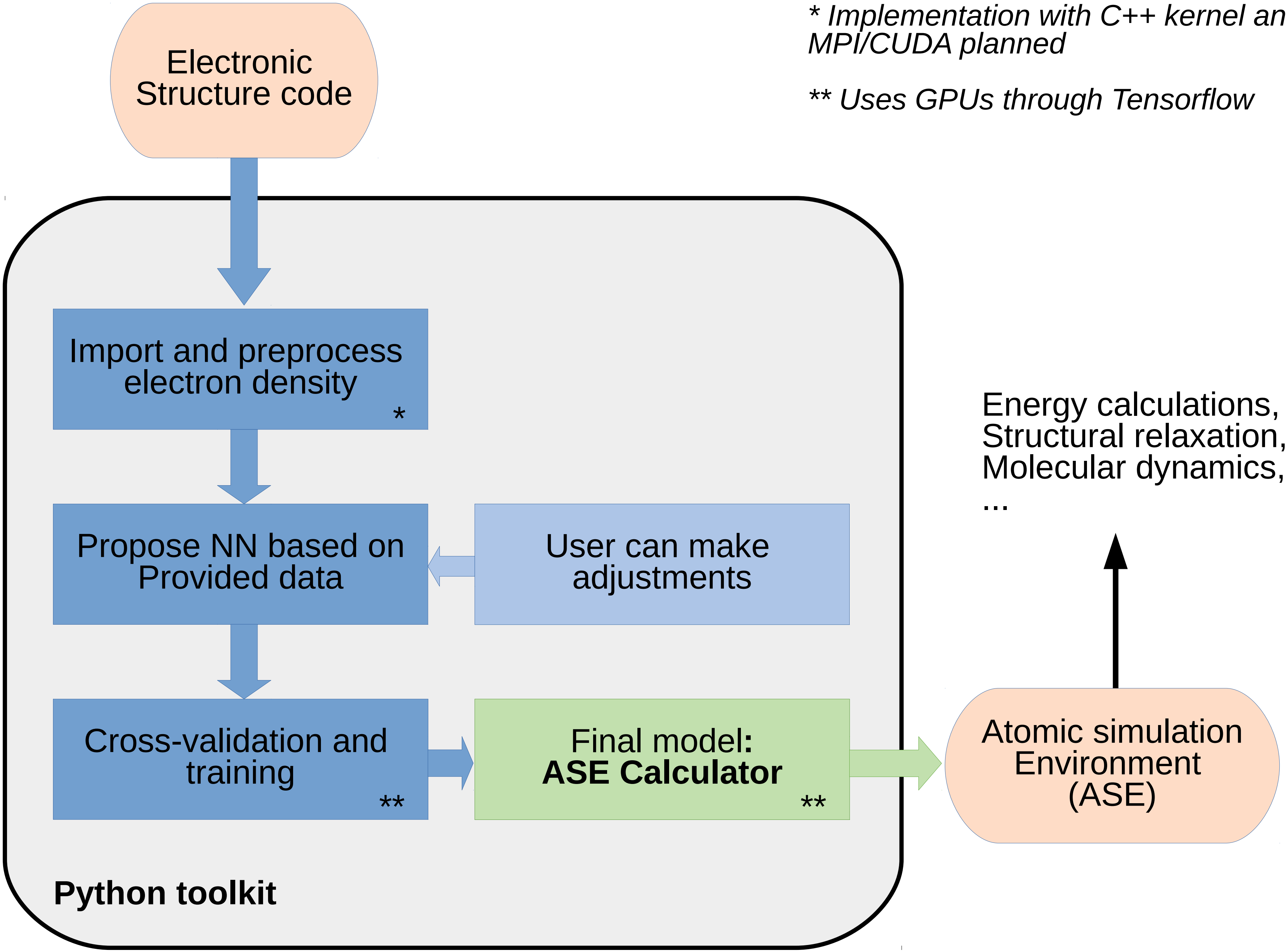

** Implementation with C++ kernel and MPI/CUDA planned*

*** Uses GPUs through Tensorflow*

Electronic Structure code

Import and preprocess electron density *

Propose NN based on Provided data

User can make adjustments

Cross-validation and training **

Final model: **ASE Calculator** **

Atomic simulation Environment (ASE)

Energy calculations,
Structural relaxation,
Molecular dynamics,
...

Python toolkit

Timeline

Timeline for 2018/2019:

- Sep – Dec:
  - Implementation of basic Python toolkit, v0.1 on Github
  - First publication on MLCFs
  - Using MLCFs to study the solvation of NaCl in water (together with Alec Wills)
- Jan – Apr:
  - Performance optimization (C++ and MPI/CUDA), v1.0 on Github
  - MLCF accelerated simulations of water-metal interfaces
- May – Aug:
  - MLCF accelerated simulations of water-metal interfaces
  - MLCFs as an alternative to QM/MM? Implementation of QM/QM-MLCF algorithms.

Plans for 2019/2020:

- Can ML be used to correct the self consistent electron density? (Possible collaboration with Alan Aspuru Guzik @ Toronto)
- Machine learned density functional kernels?
- Other semi-empirical methods for faster electronic sturcture calculations (Electron ‘force-field’, Collaboration with Jose Solers group @ Madrid)

Thank you!

Using MLCFs to speed up MD calculations

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Replace QM/MM with QM/QM-MLCF: