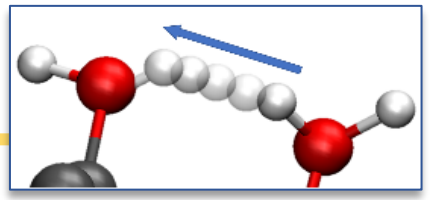
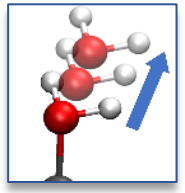
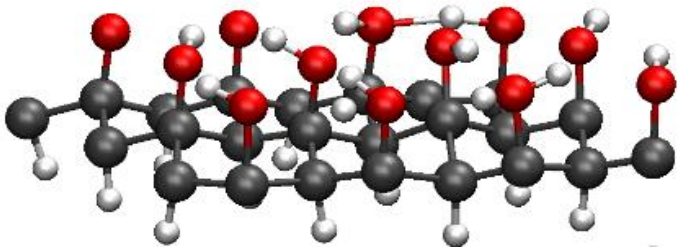
2021 AIChE ANNUAL MEETING

Studying Anhydrous Proton Transport on Graphene-based Materials using Deep Learning Methods







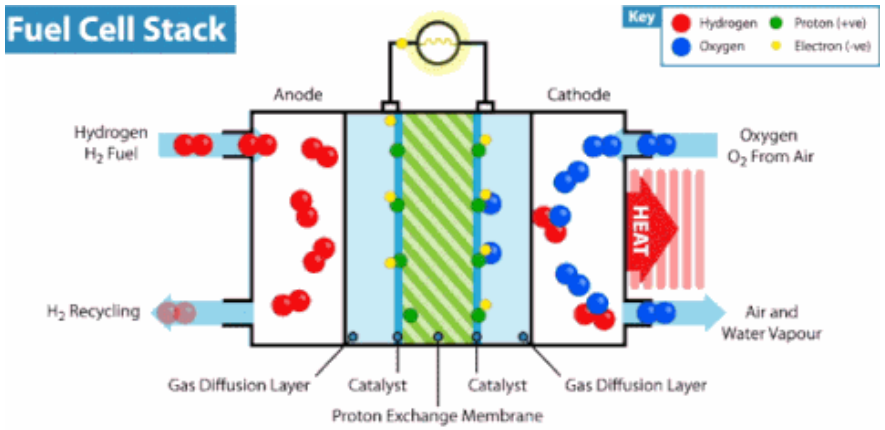
Siddarth Achar
Leonardo Bernasconi, Linfeng Zhang, J Karl Johnson

Session: Data-Driven Design and Modeling II
8th November 2021
4:45-5:00 PM

University of Pittsburgh

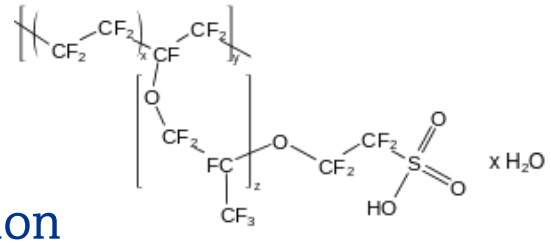
Why anhydrous proton transport?

Fuel cells membranes

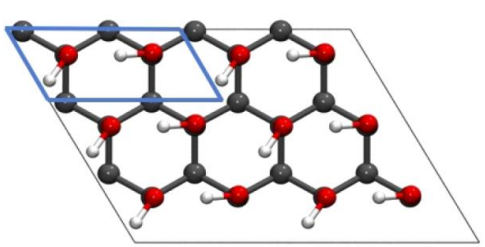


Nafion

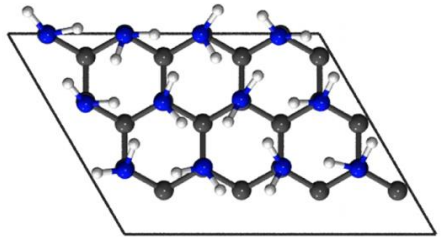
- Commonly used
- Requires hydration
- Operation at max 80°C
- Decrease in the rate of conduction
- Water flooding issues



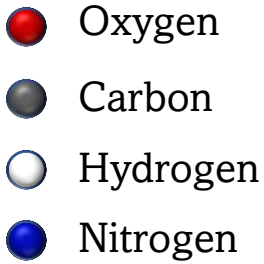
Chemical structure of Nafion



Graphanol



Graphamine



Graphane-based membranes

- Novel material
- Conducts protons at elevated temperatures (without hydration)
- Increased reaction rates
- Decreased CO poisoning of anode
- Targeted operating temperature 200°C

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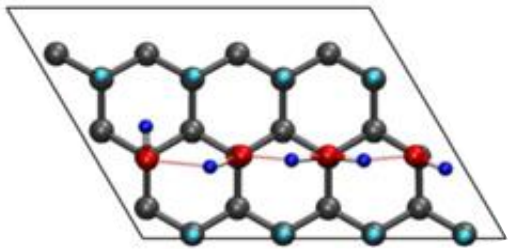
https://giphy.com/gifs/cell-13HsQGjr68hH3y, https://www.fuelcellstore.com/nafion-117

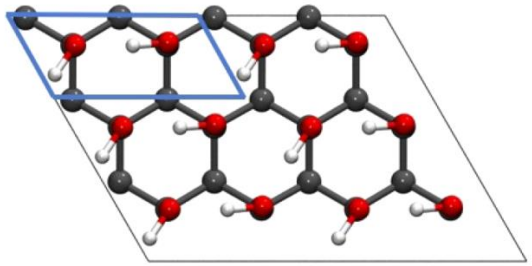
DFT used previously, but restrictive

1D-Graphanol



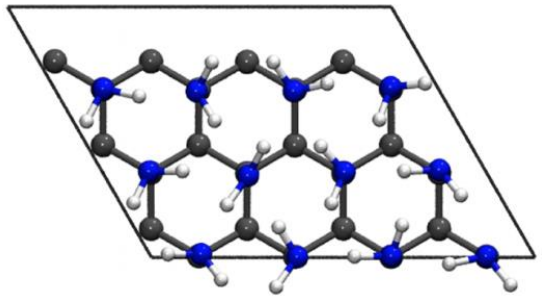
Bagusetty et al. PRL 2017

2D-Graphanol

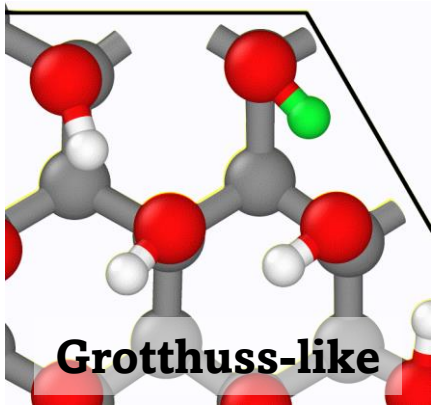


Bagusetty et al. JPCC 2019

Graphamine

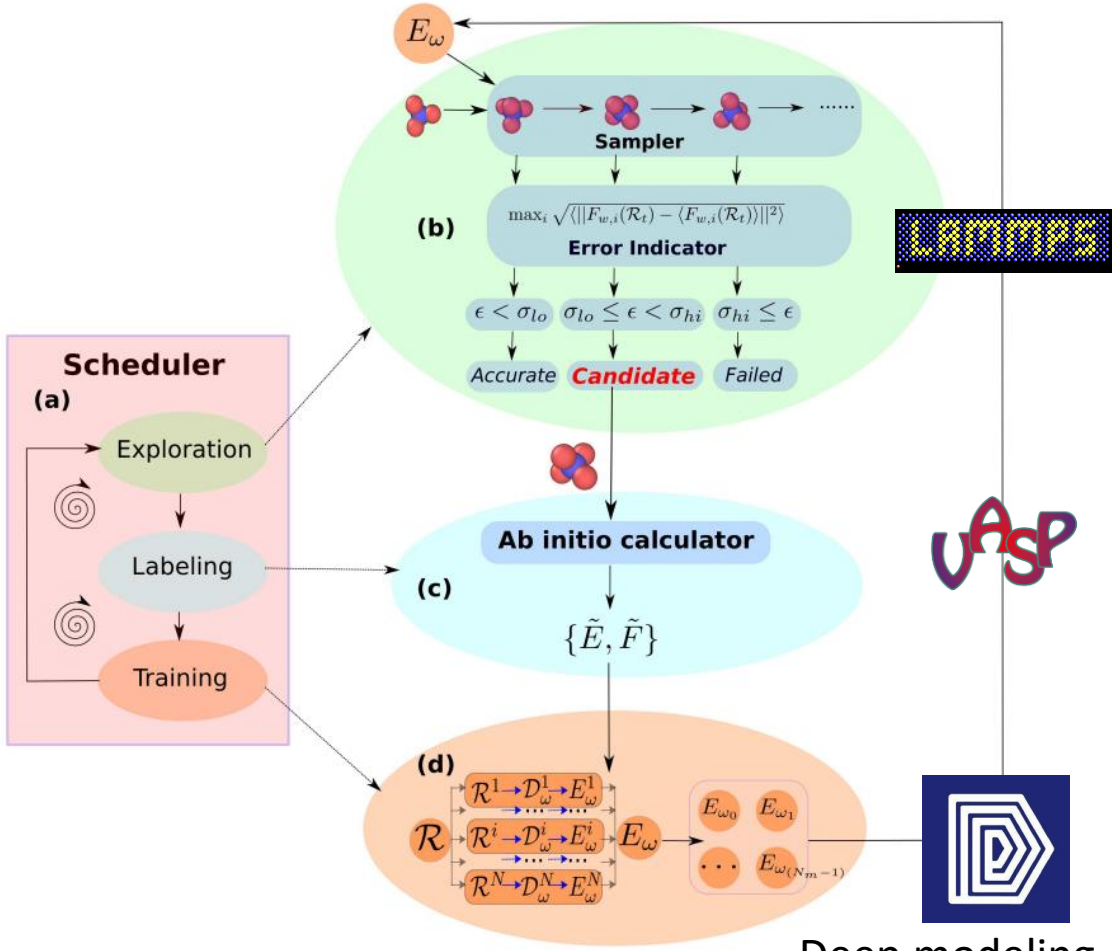


Bagusetty et al. JPCL 2019



- DFT results show **proton hopping**
- Fickian diffusion in 1D graphanol
- **Grotthuss-like mechanism** in higher functionalized graphane
- Restrictive to run for larger structures and longer time

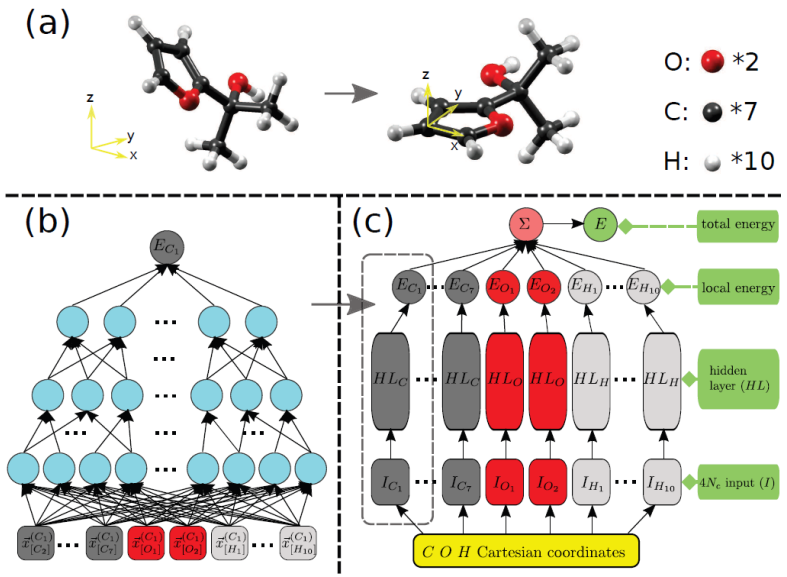
Active learning (AL) using Deep modeling (DPGEN)



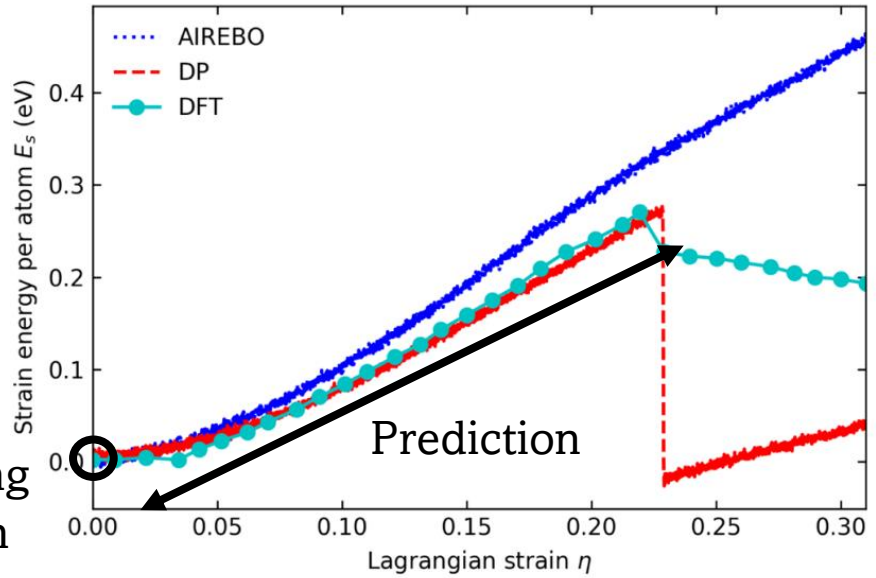
Zhang et al. CPC 2020

Deep modeling

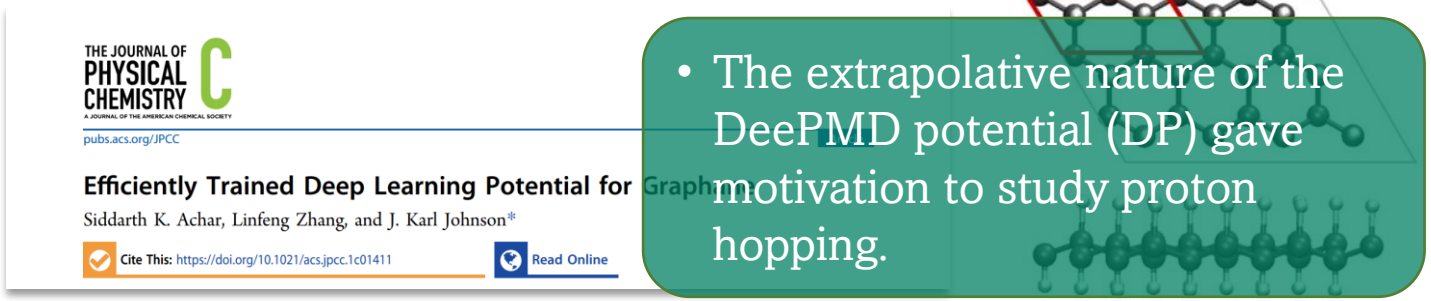
Initial success with DeePMD for graphane



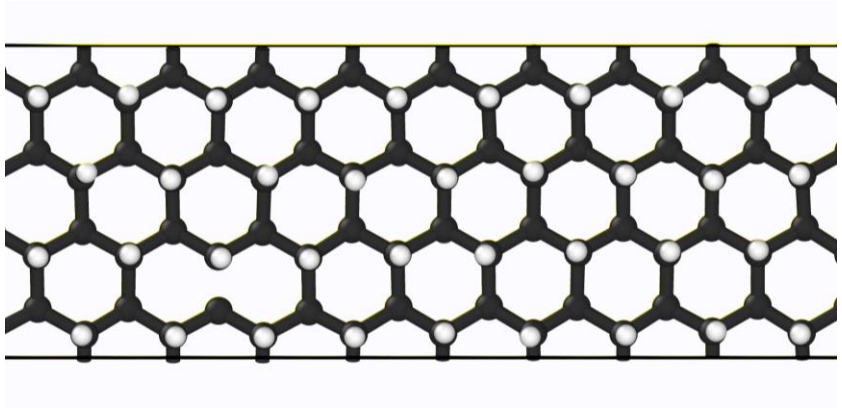
$$L(p_\epsilon, p_f) = \frac{p_\epsilon}{N}\Delta E^2 + \frac{p_f}{3N}|\Delta F_i|^2$$



(a) Transformation from global to local reference frame for a Carbon atom
(b) Sub-network structure for atom C1.
(c) Complete structure of the deep potential network

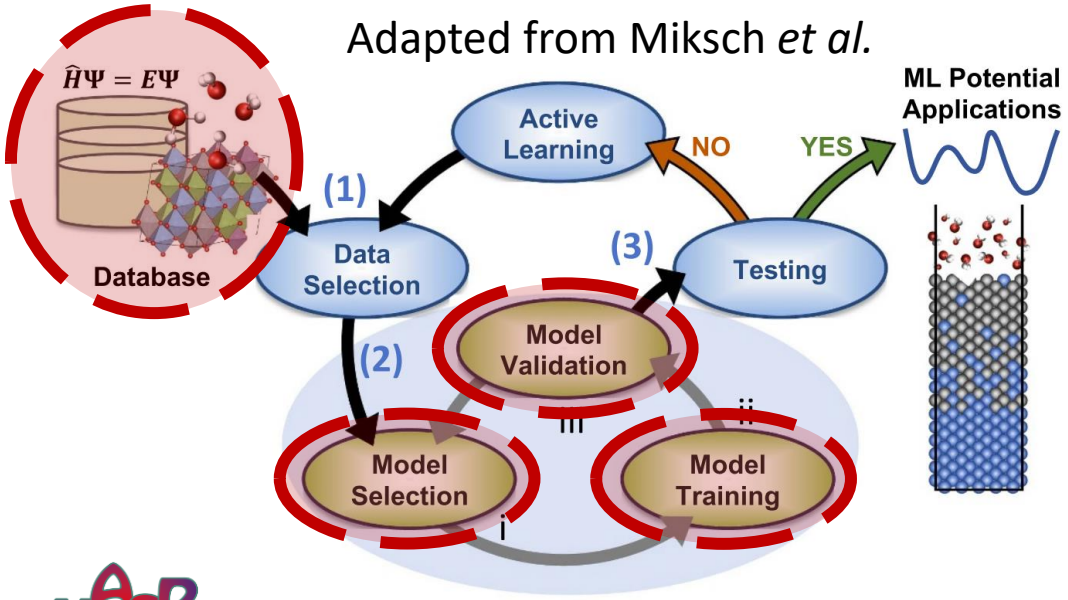


- The extrapolative nature of the DeePMD potential (DP) gave motivation to study proton hopping.



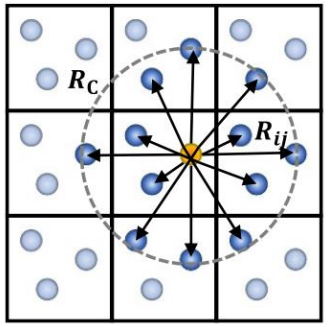
Preliminary DP generation and validation

Adapted from Miksch *et al.*

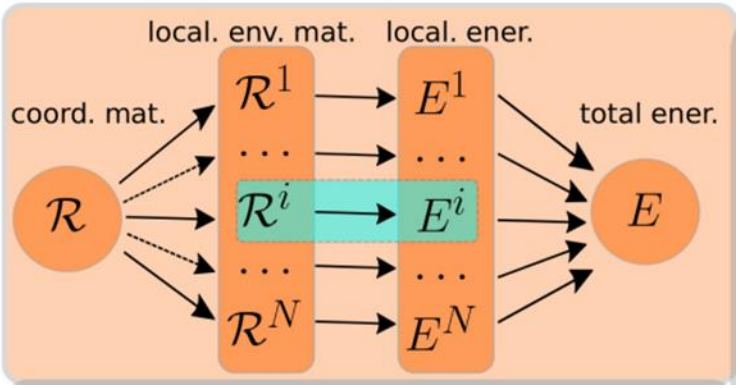


R_c = 6 Å

$R_{c(s)}$ = 1 Å



Fitting net: 240, 240, 240

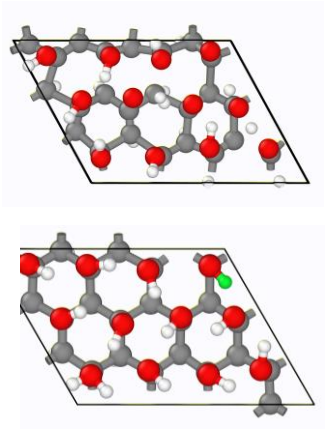


GGA-PBE, PP:PAW

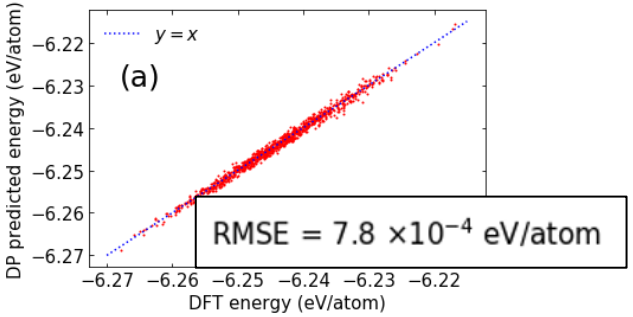
Uncharged
NVT-MD (Nose-Hoover thermostat)
20 ps simulation at 1000 K

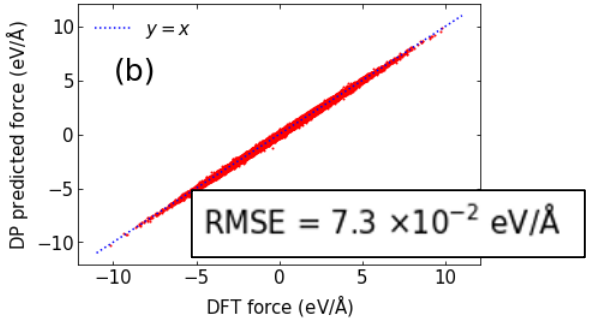
Charged
NVT-MD (Nose-Hoover thermostat)
20 ps simulation at 800 K and 1000 K

24C graphanol



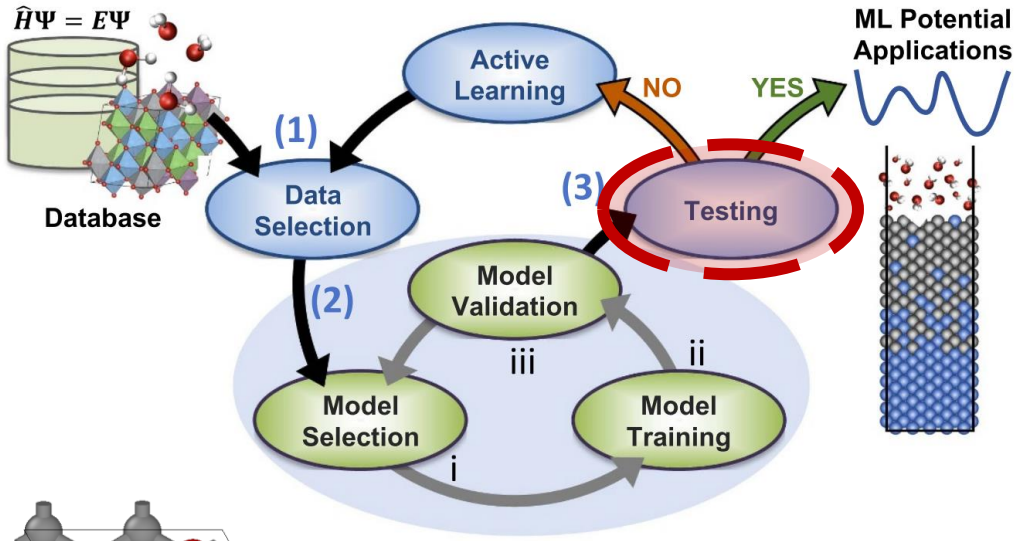
9995 images

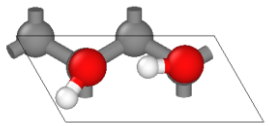




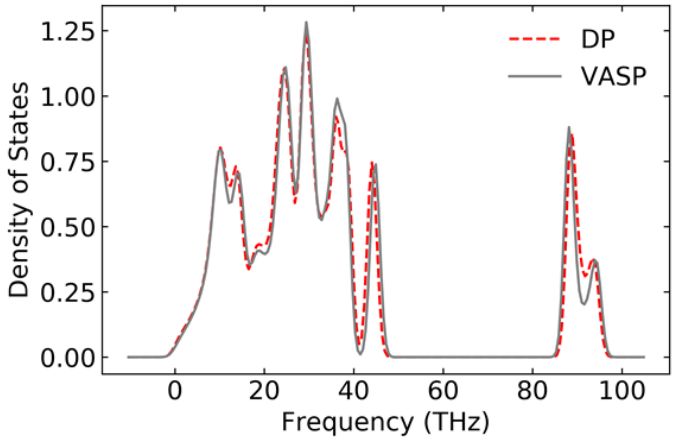
Miksch *et al.* "Strategies for the construction of machine-learning potentials for accurate and efficient atomic-scale simulations"

DP could achieve a few things



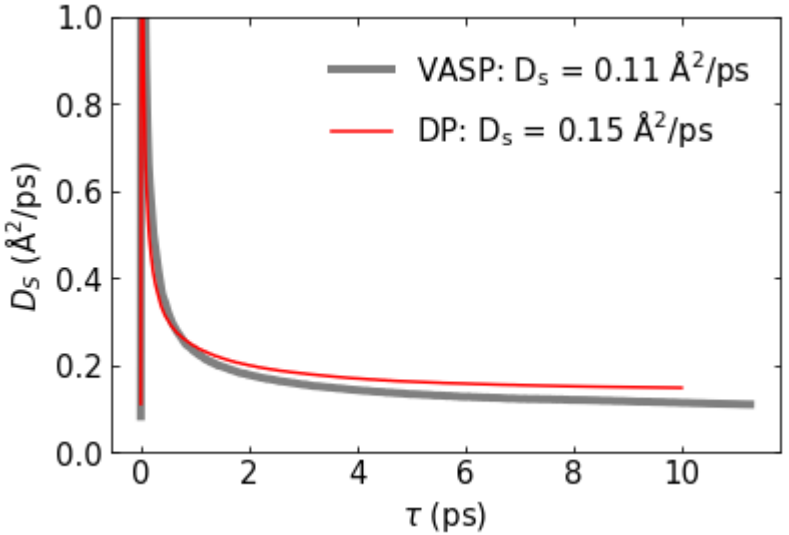


Accurate phonon densities of states

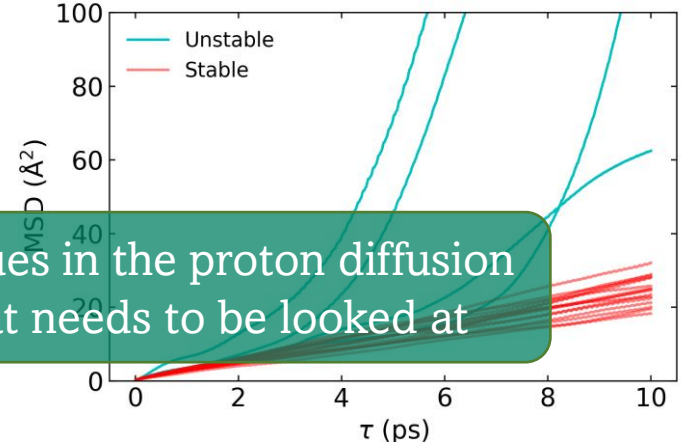


Mean squared Displacement $MSD(t) = \langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle$

Diffusion coefficient $D_s = \frac{MSD(t)}{2dt}$



Good approximation of proton diffusion at T=800K
(For simulations that were stable)

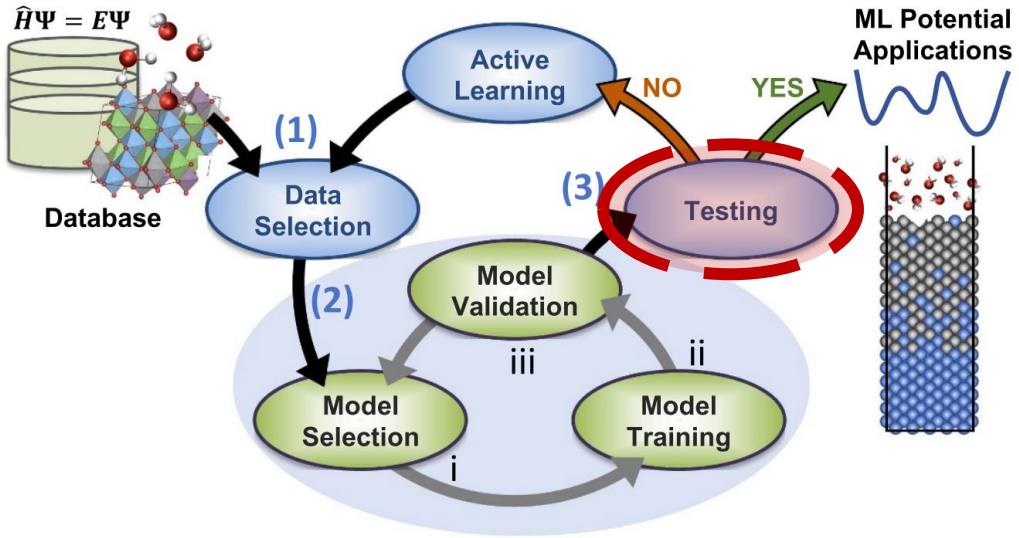


Unexpected behavior in MSDs for few independent runs at T=800 K
Also, this behavior was frequent at T=1000 K

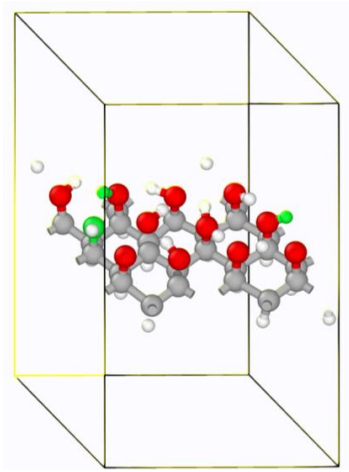
Major issues in the proton diffusion aspect that needs to be looked at

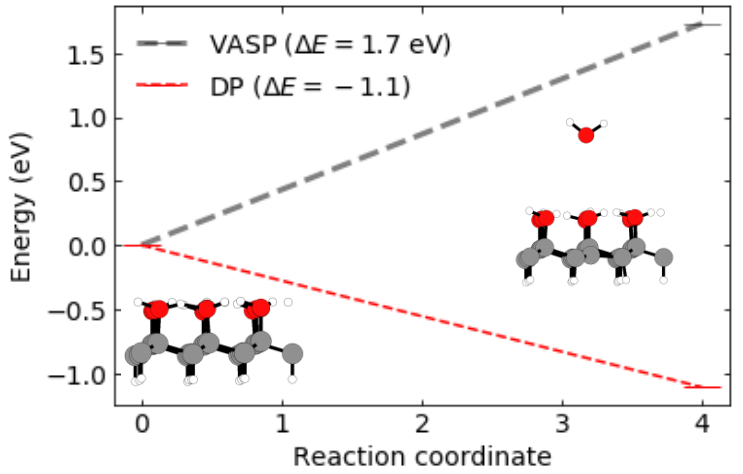
University of Pittsburgh

DP had three major shortcomings

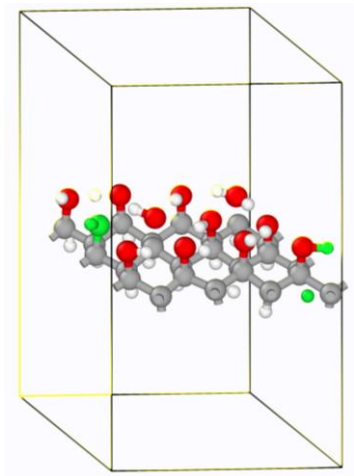


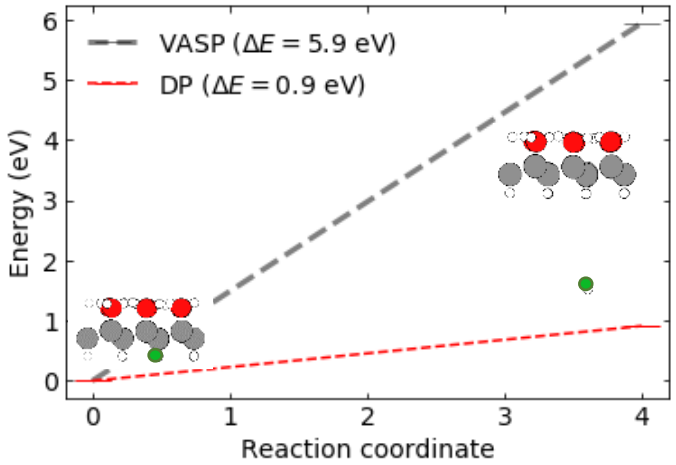
Wrong energetics: **formation** of **water**





Wrong energetics: **formation** of **protons**

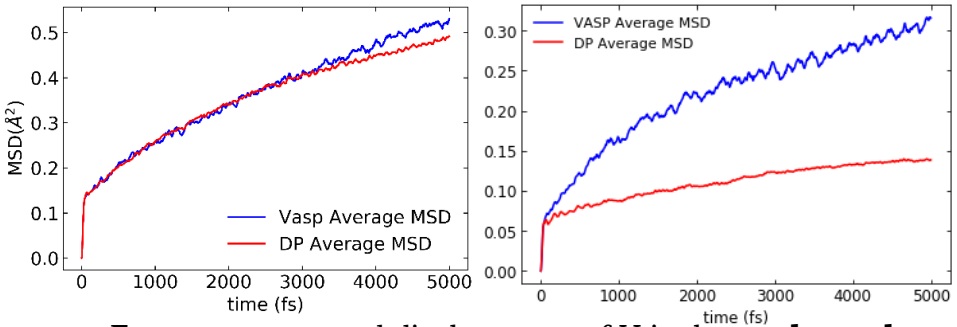




"**Overestimation**" of **OH rotation barrier**

T=700 K

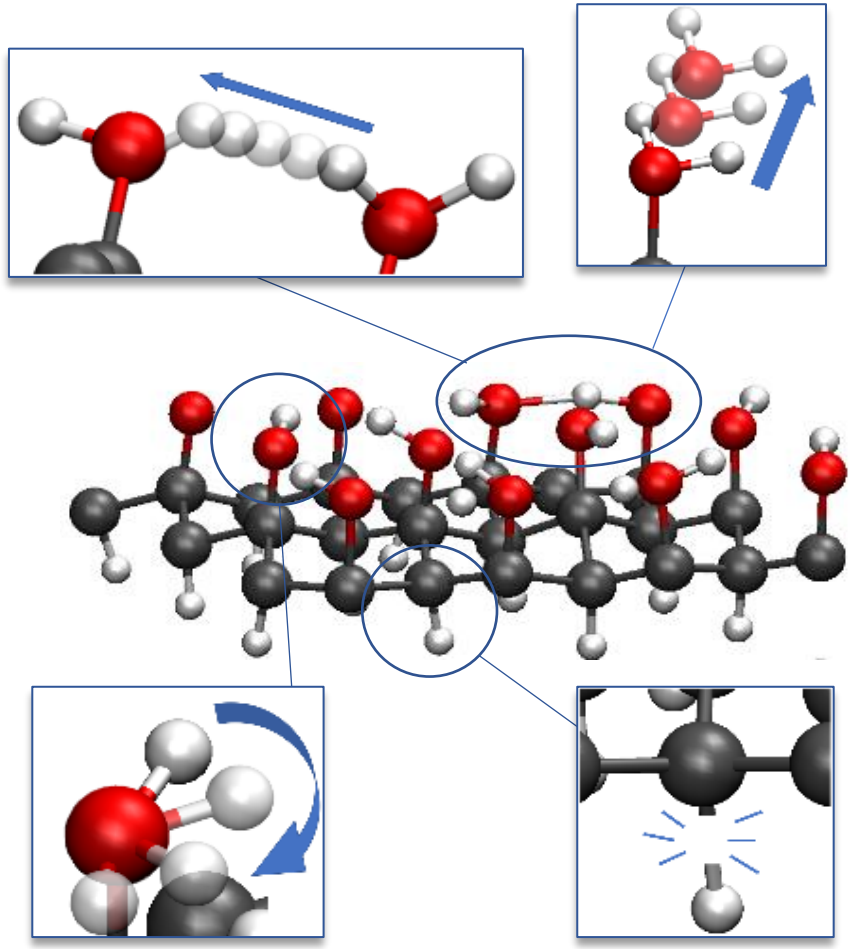
T=400 K



From mean squared displacement of H in the **uncharged** system

Critical aspects to be tuned from active learning

Finally, accurate description of proton transfer



Accurate description of water bond breaking

Accurate description of OH rotation barrier

Accurate description of proton bond breaking

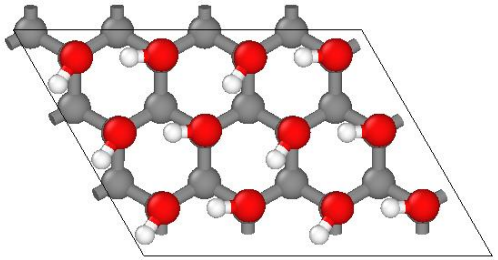
Building various starting configurations for updated DP

Atom and cell **soft perturbation**

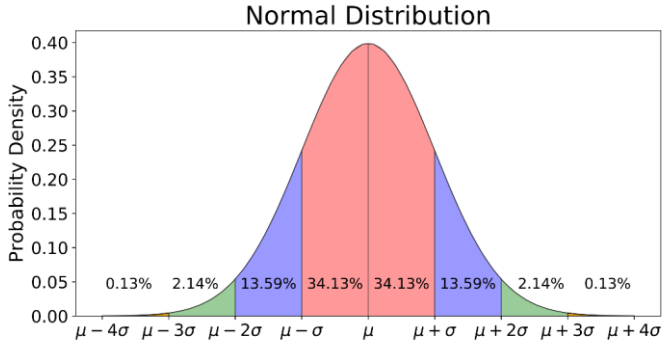
- Cell perturbation fraction: 5%
- Atom perturbation distance: 0.3 Å

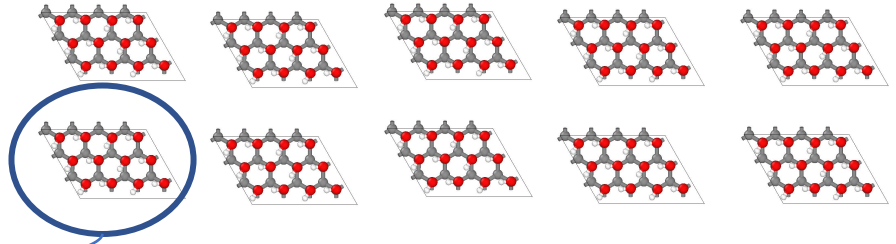
$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

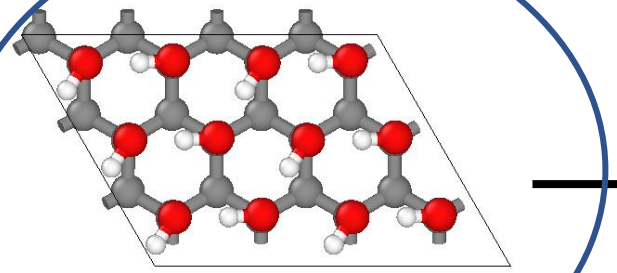
10 initial structures were obtained



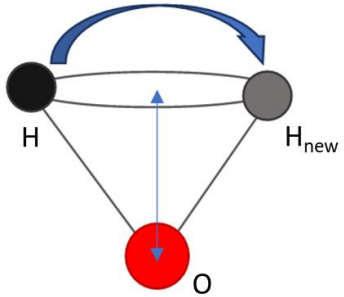
Equilibrium structure



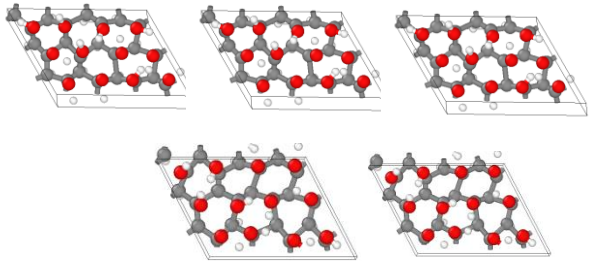




Perturbed structures



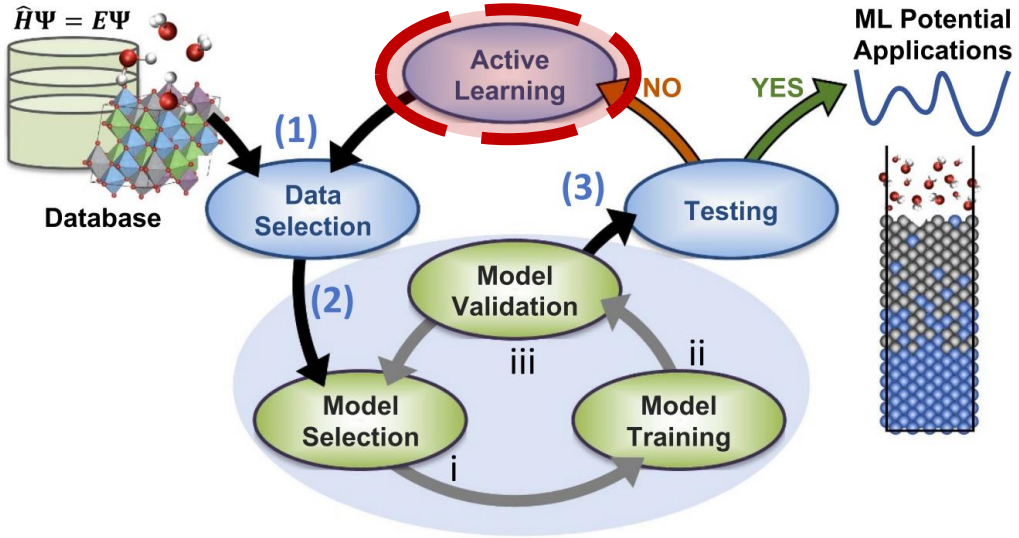
Random rotation function

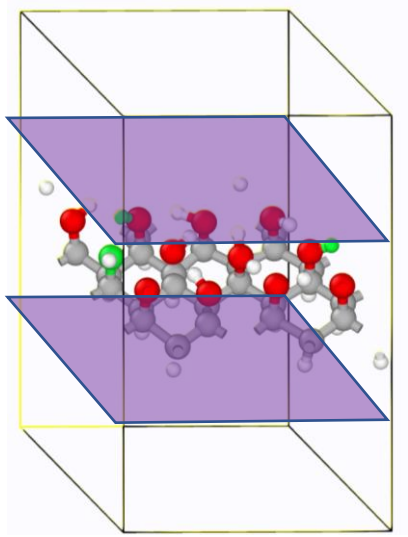


5 initial structures generated with random OH rotation

These random perturbations are useful for OH rotation sampling

Modifications to the error indicator (the intelligence)

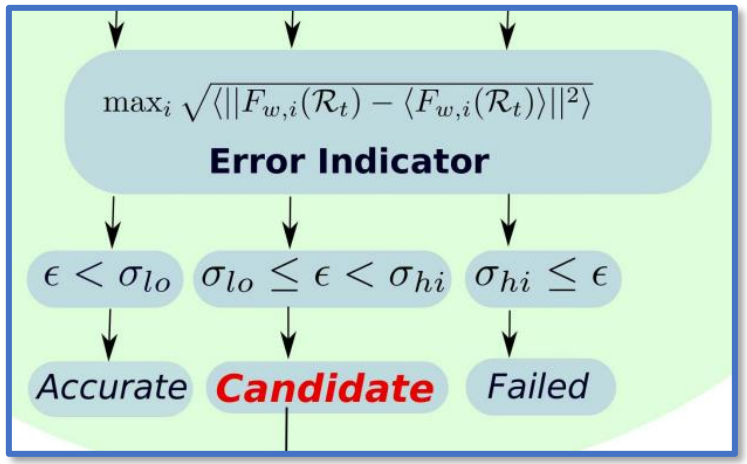




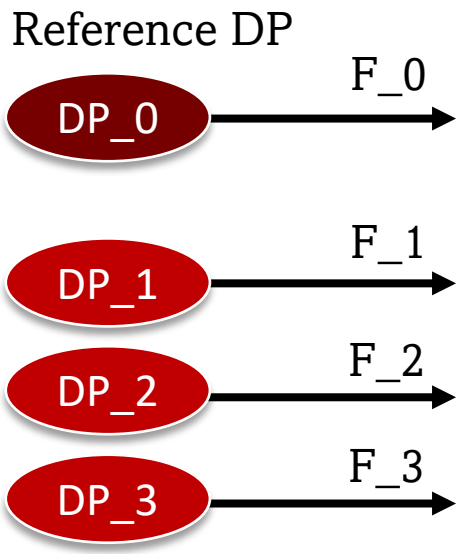
Unphysical H_2O and proton travel due to P.B.C.

Applied a **z-axis constraint** on selecting configs. for relabeling

May have many configurations with low force deviation, especially when away from 2D sheet.



As per the DP-GEN workflow

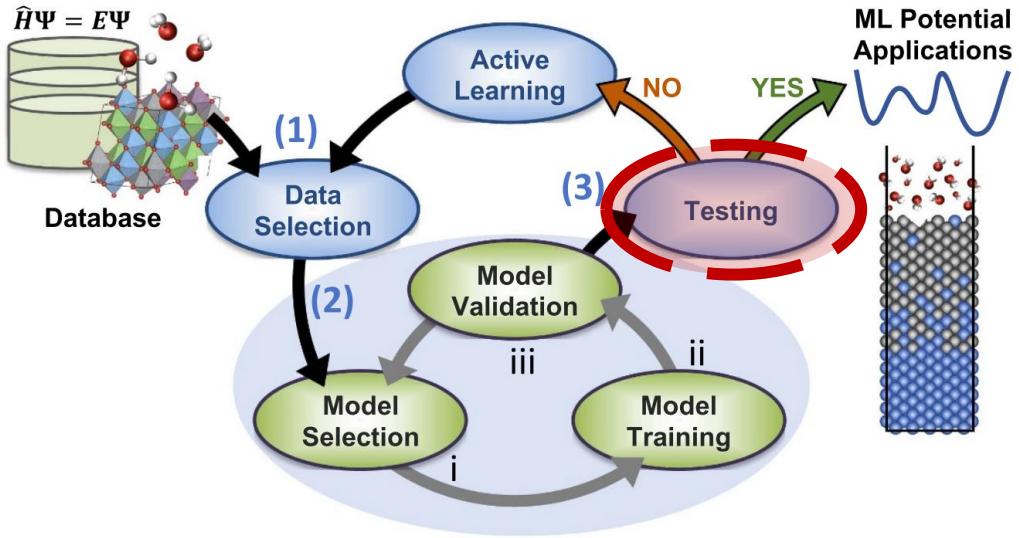


3 iterations of AL for uncharged GOH
+
3 iterations of AL for charged GOH

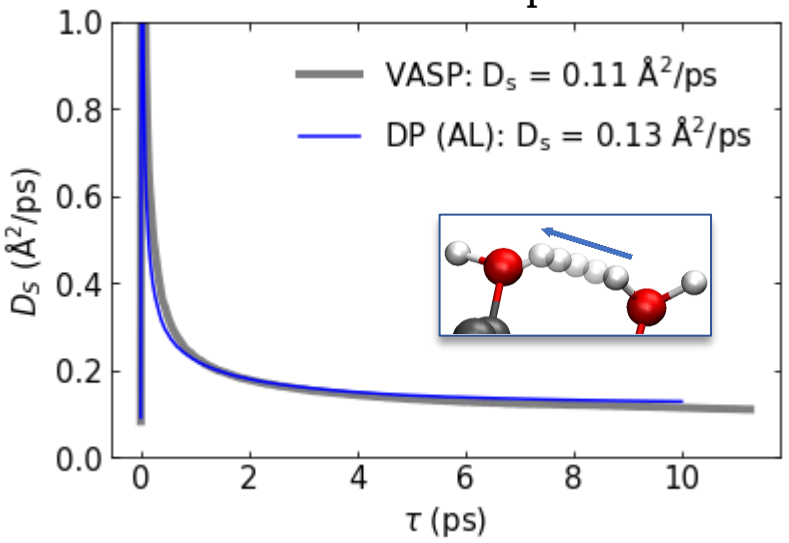
- LAMMPS NVT at both high and low temperatures.
- 6000 configurations used out of 1 million generated

Calc. Max. Force deviation w.r.t 1, 2, 3

Significant improvement on all tests



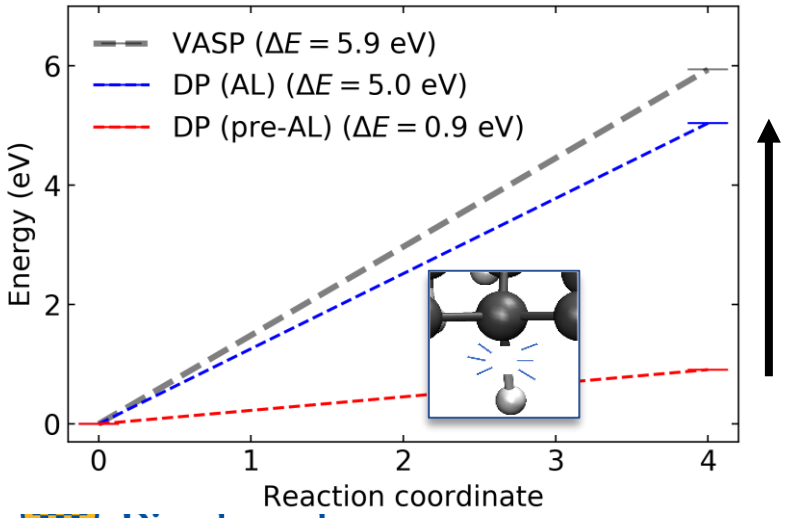
Proton transport



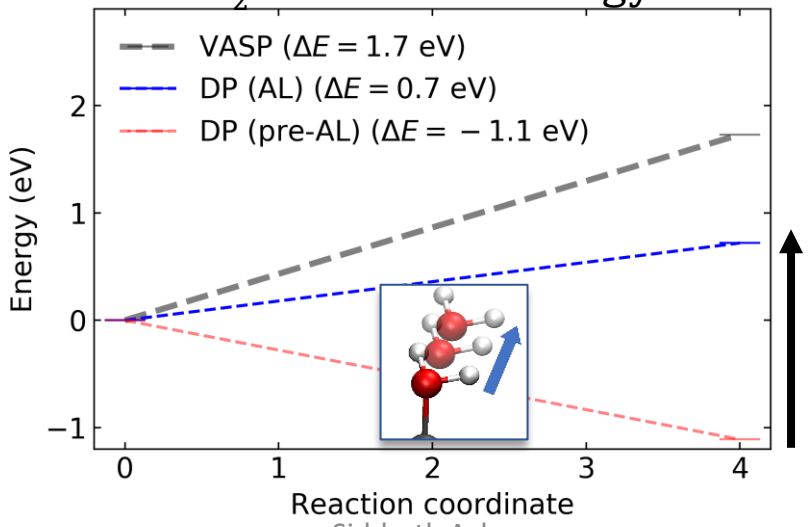
VASP results from Bagusetty *et al.* for 96 C graphanol

All MSDs were stable

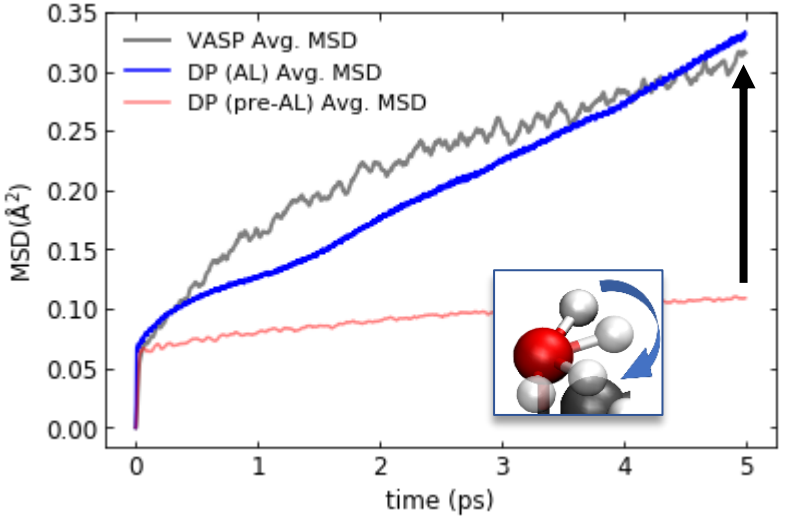
Proton formation energy



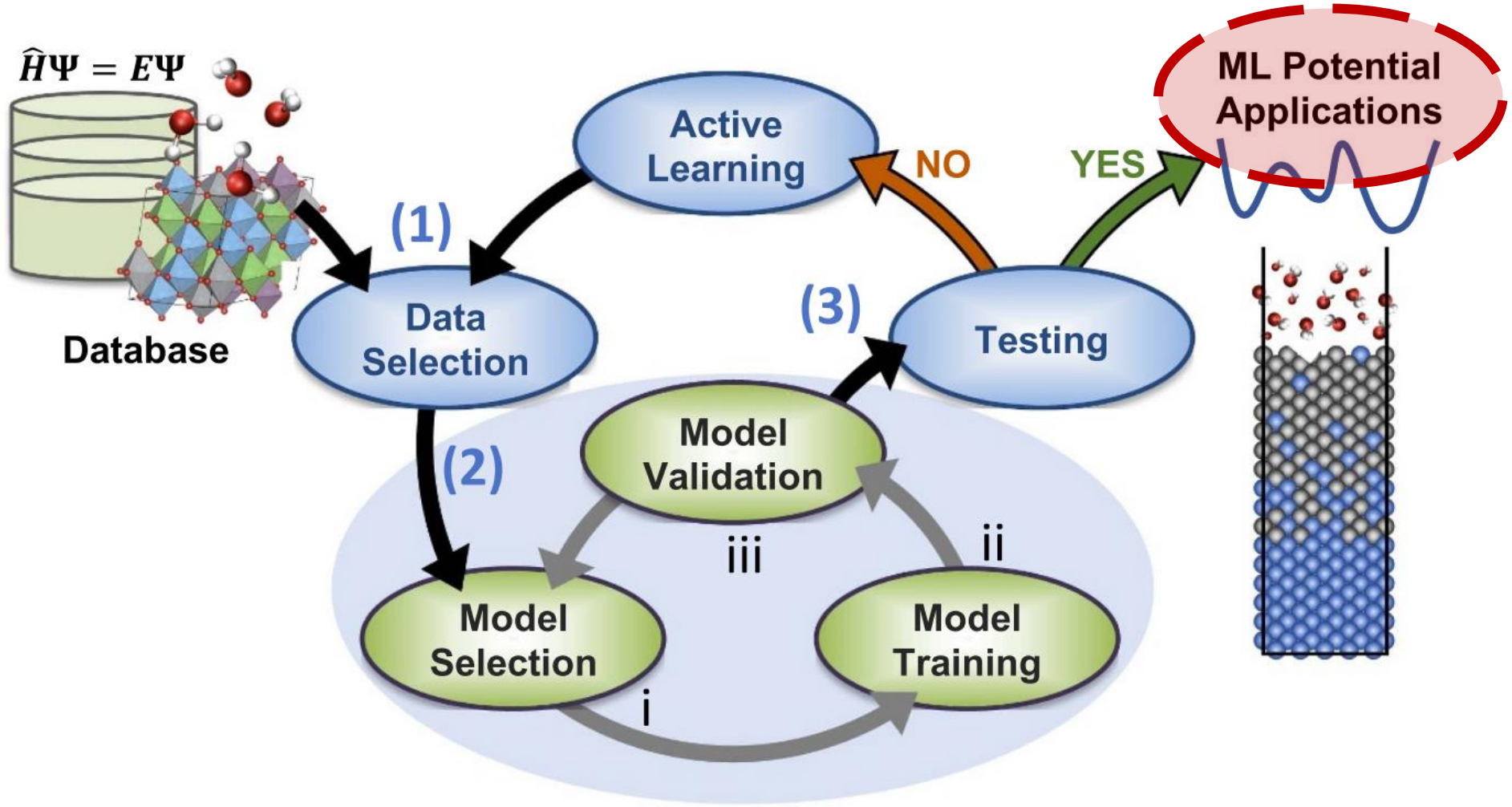
H_2O formation energy



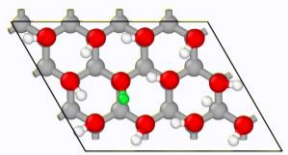
-OH rotation at 400 K



Analyzing size effects for proton diffusion

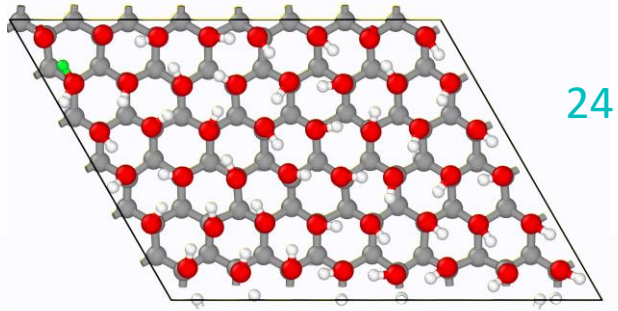


There are size effects for proton transport

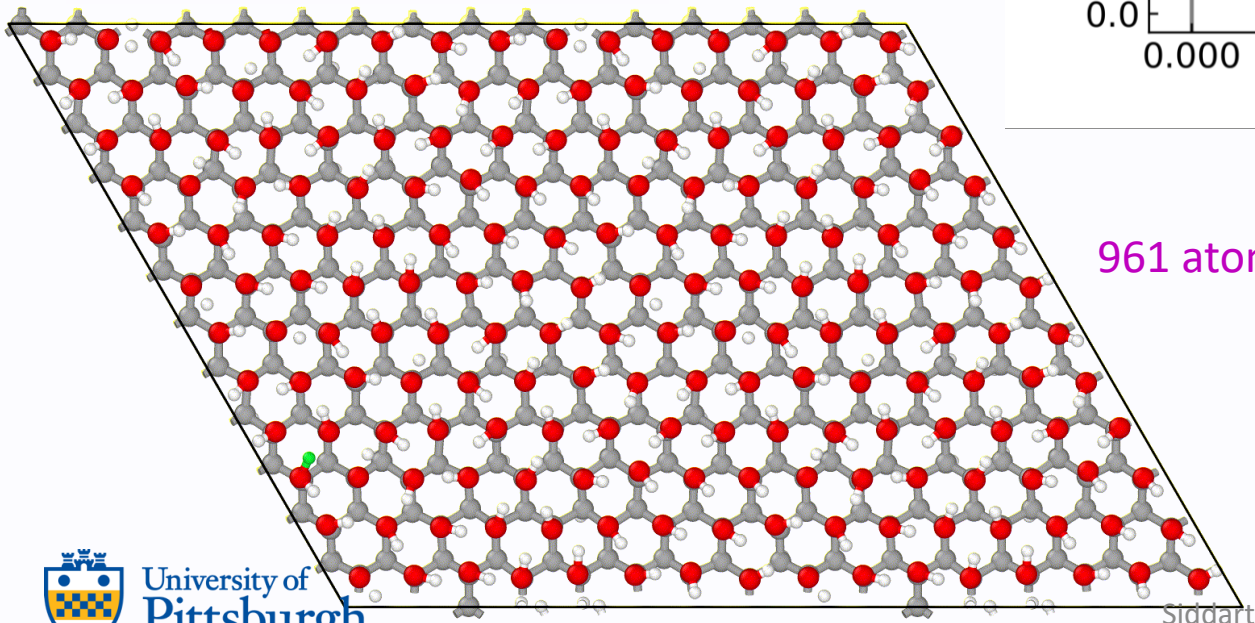


61 atoms

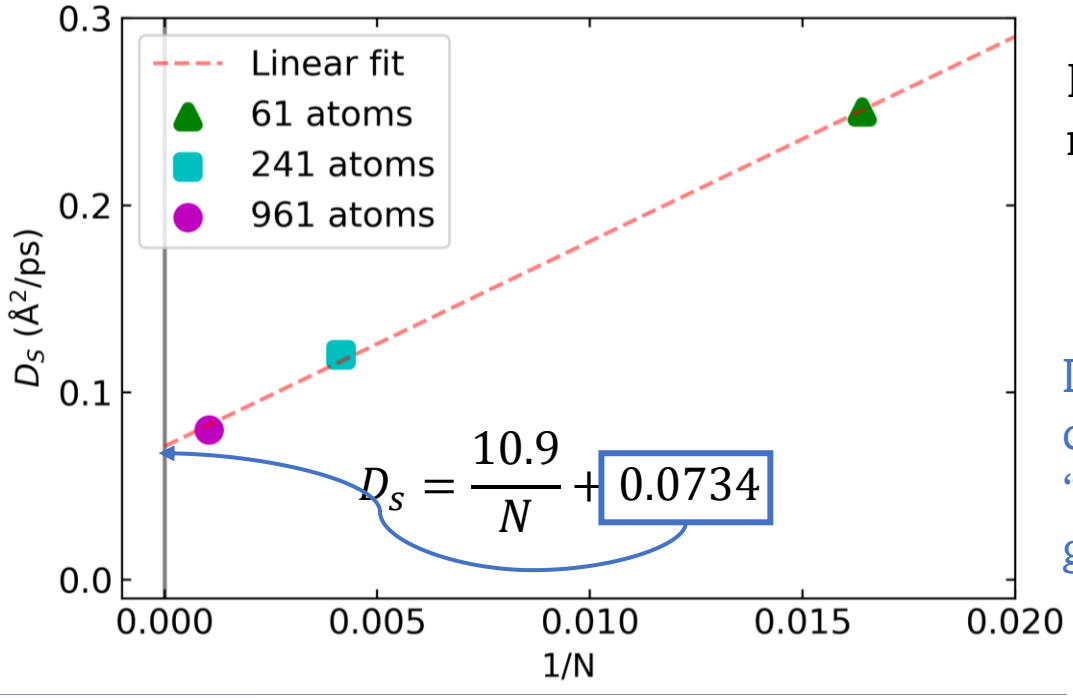
T=800 K



241 atoms



961 atoms



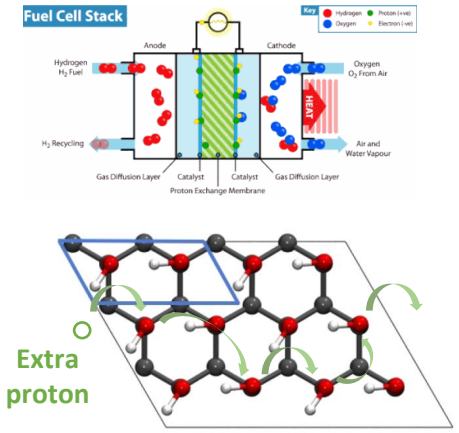
N = Total number of atoms

Diffusion coefficient of an "infinitely" large graphanol cell

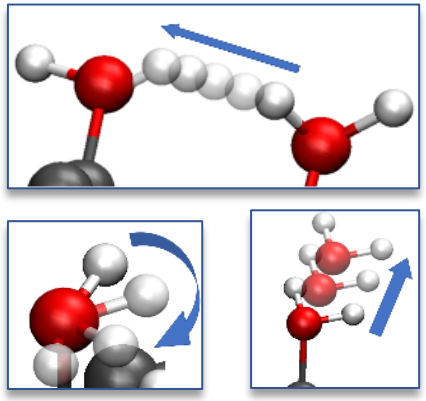
Displays a **concerted rotation** of OH groups with increase in system size and thus a **reduction in proton diffusion**.

Summary and Future work

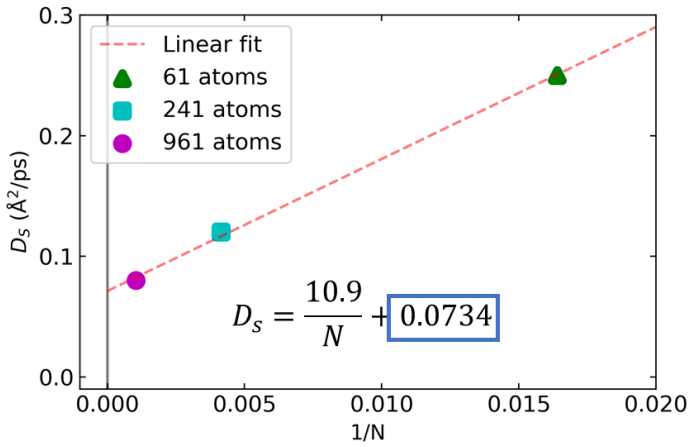
Anhydrous proton conduction is promising for a fuel cell membrane



Active learning helps in fine-tuning essential aspects of proton transport



Found **size effects** for **proton transport** in graphanol using DP



- Studying **multi-protonated** systems
- Building an empirical model to **link** the **electron densities** to **functional groups** for proton transport

Acknowledgement

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