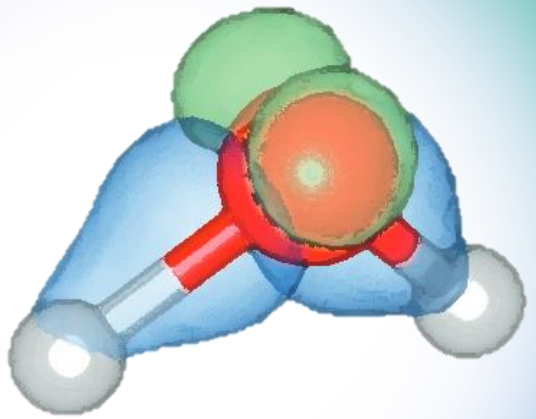
2023 Chemistry in Solution and at Interfaces (CSI)
Workshop: Deep Modeling for Molecular Simulation



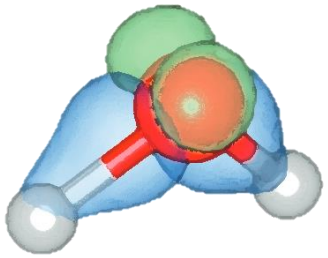
Tutorial Session: Deep Dipole

SPEAKER: PINCHEN XIE

PACM, PRINCETON

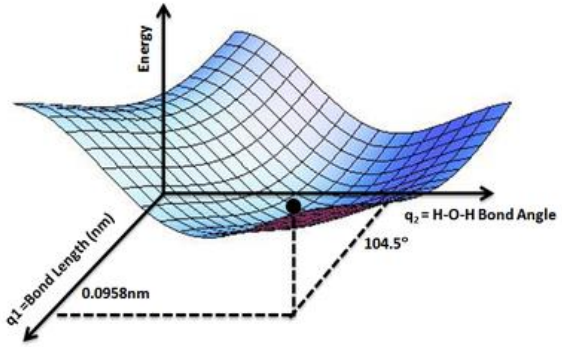
JULY, 2023

Beyond potential energy surface



First-Principles theory (e.g., DFT/MBPT/…)

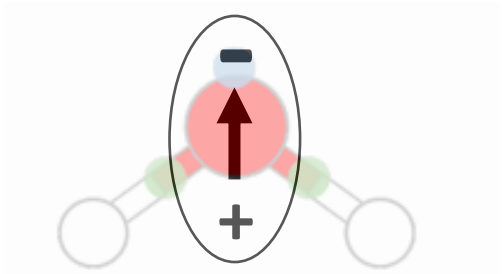
Atom



Potential Energy Surface

Deep Potential Model

Electron



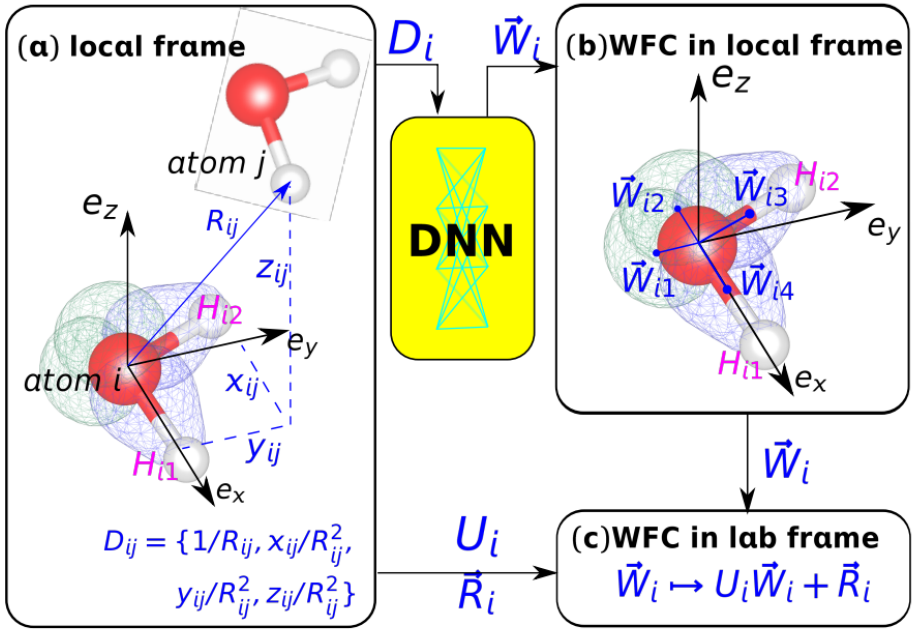
Atomic/Molecular Dipole

Deep Dipole model

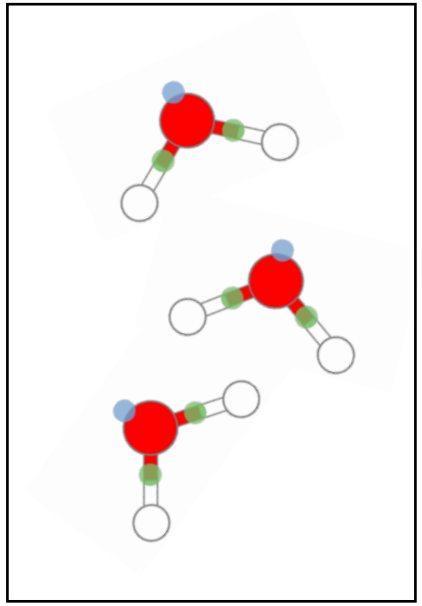
Sketch of water molecule adapted from Fig.2 of *PNAS* 114.41 (2017): 10846-10851.

A very short introduction to Deep Dipole

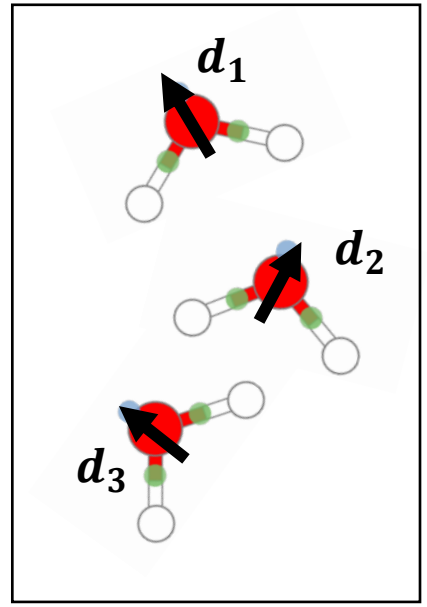
The open box



The black box



Deep Dipole



Atomic coordinates $\{r_i\}$

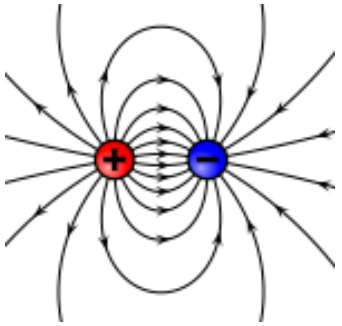
The dipole moment $\{d_j\}$

Zhang, Linfeng, et al. "Deep neural network for Wannier function centers." *arXiv preprint arXiv:1906.11434* (2019).

Zhang, Linfeng, et al. "Deep neural network for the dielectric response of insulators." Physical Review B 102.4 (2020): 041121.

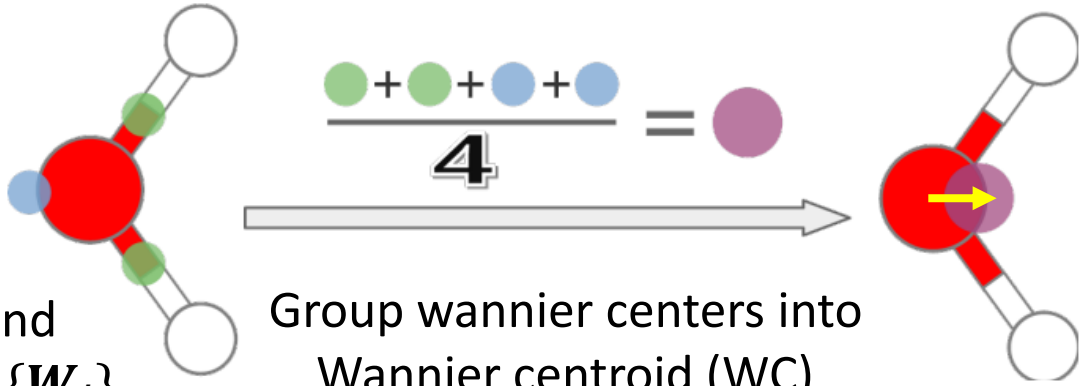
A very short introduction to Deep Dipole

Example: the water molecule



Classical picture

Valence Electron: 8
Wannier centers: 4



Atomic coordinates $\{\boldsymbol{r}_i\}$ and assigned wannier centers $\{\boldsymbol{W}_j\}$

Group wannier centers into Wannier centroid (WC)

The training label

Position vector of WC w.r.t. central atom (e.g. Oxygen)

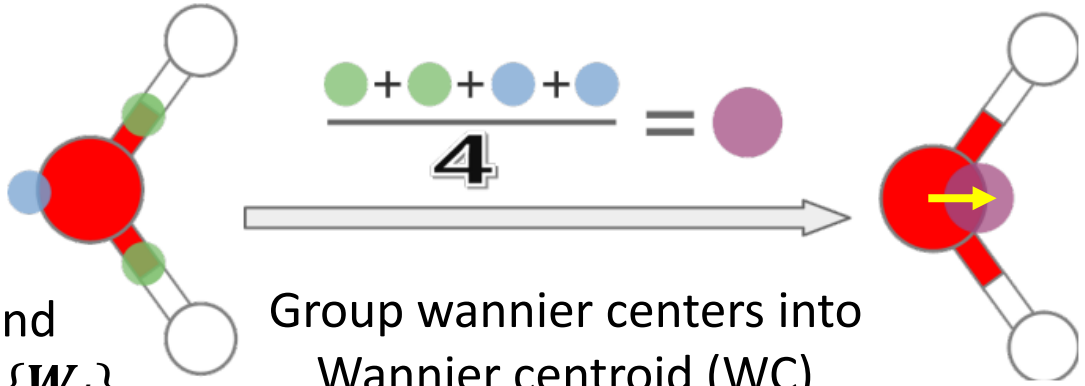
Zhang, Linfeng, et al. "A deep potential model with long-range electrostatic interactions." *The Journal of Chemical Physics* 156.12 (2022): 124107.

A very short introduction to Deep Dipole

Example: the water molecule

Issue: wannier centers not unique (U(1) Gauge)

Valence Electron: 8
Wannier centers: 4



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A very short introduction to Deep Dipole

Implemented in Wannier90

Maximally localized Wannier functions (MLWF)

The General wannier function:

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^{J} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}\rangle$$

Bloch orbitals

Arbitrary Unitary Rotation

The MLWF:

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^{J} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}\rangle$$

The optimal rotation minimizing the total spreading of wannier functions

Total spreading

$$\Omega = \sum_n \left[\langle \mathbf{0}n | r^2 | \mathbf{0}n\rangle - \langle \mathbf{0}n | \mathbf{r} | \mathbf{0}n\rangle^2\right]$$
$$= \sum_n \left[\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2\right]$$

wannier centers $\bar{r}_n$

Marzari, Nicola, et al. "Maximally localized Wannier functions: Theory and applications." Reviews of Modern Physics 84.4 (2012): 1419.

Hands-on Exercise 1 -- 30 minutes

Goal:

(1) Compute maximally localized wannier centers of given water configuration with Quantum-Espresso and Wannier90

Folder: hands-on-sessions/day-3/7-deep-wannier/1-wannier90_example/ice_mlwf_exercise

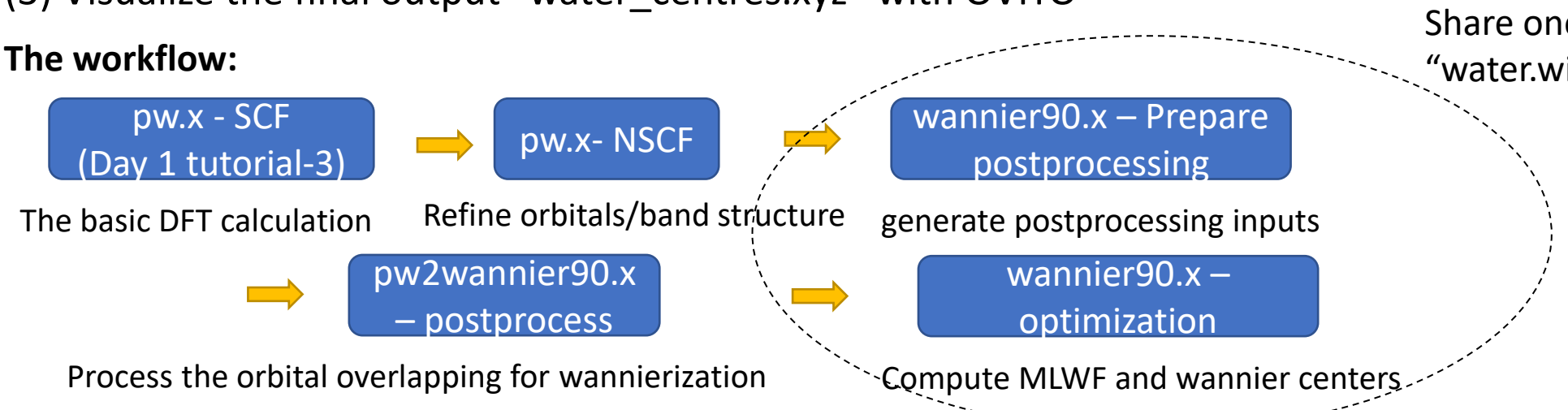
How:

(1) Read and execute “run.sh” (better line by line so you can see the succession of outputs) ~ 10mins

(2) Meanwhile, get familiar with the inputs&outputs

(3) Visualize the final output “water_centres.xyz” with OVITO

The workflow:



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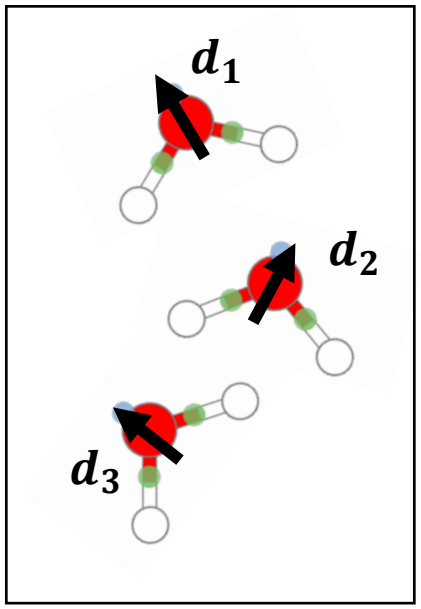
Basic setup of the wannier90 input

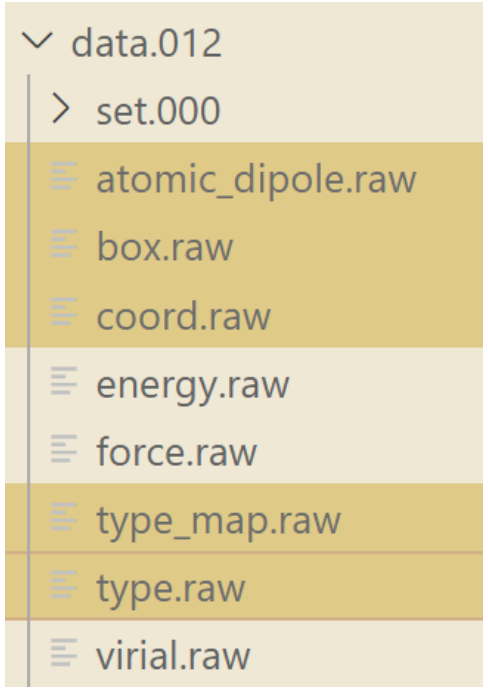
```
num_wann  = 64     ← Number of wannier centers = #Occupied orbitals
num_iter  = 100    ← Iterations for MLWF optimization. 100 is default. If not converging in
100 steps, probably k-grid is too sparse.
write_xyz          = True

guiding_centres = .true. ← Provide an initial guess for the optimization problem
begin projections ← specify the atomic orbital as initial guess
  O: sp3
end projections
```

https://github.com/wannier-developers/wannier90/raw/v3.1.0/doc/compiled_docs/user_guide.pdf

Training Deep Dipole: Dataset



- Required data



Optional: dipole.raw

- Format

Reference atoms for dipole moments, e.g. oxygen for H2O

atomic_dipole.raw:(#frames, #sel_atom× 3)

Vector concatenated in the same order as its reference atom appearing in coord.raw

dipole.raw: (#frames, 3) <- the sum of atomic dipole

atomic_dipole.npy&dipole.npy:

Same thing but in numpy format.

Training Deep Dipole: parameters

Difference between training Deep Potential & Deep Dipole

	fitting_net	loss
Energy model	"fitting_net": { "type": "ener", "neuron": [240, 240, 240], },	"loss": { "start_pref_e": 0.01, "limit_pref_e": 1, "start_pref_f": 100, "limit_pref_f": 1, "start_pref_v": 0, "limit_pref_v": 0, },
Dipole model	"fitting_net": { "type": "dipole", "sel_type": [0], "neuron": [100, 100, 100], },	"loss": { "type": "tensor", "pref": 1.0, "pref_atomic": 1.0, },

0.0 if there is no dipole.npy

Types of atom that carries a dipole.

Hands-on Exercise 2 -- 10 minutes

Goal:

(1) Train a deep dipole with the dataset hands-on-sessions/day-2/4-deep-wannier/data

Folder: hands-on-sessions/day-3/7-deep-wannier/2-train_dipole_model

How:

(1) Check “input.json”

(2) Before training, examine dataset and verify that the number of columns in “atomic_dipole.raw” is compatible with "sel_type” and the number of water molecules.

(3) Run “train.sh”. Check logs.

(4) Terminate the training due to the lack of time. We provide the trained model in

hands-on-sessions/day-3/7-deep-wannier/dipole_model

Application of Deep Dipole

- Postprocessing (Today)

  After a regular DPMD simulation. Process the dumped trajectory with deep dipole model. You can compute dipole distribution / polarization/ dielectric response …..

- Enhanced sampling / Electric field-driven MD

  Pair Lammps up with PLUMED and use deep dipole model as a collective variable.

Hands-on Exercise 3 -- 20 minutes

Goal:

(1) Run a DPMD for liquid water with provided Deep Potential model. Then analyzed the dumped trajectory with Deep Dipole model.

Folder: hands-on-sessions/day-3/7-deep-wannier/3-MD_exercise

How:

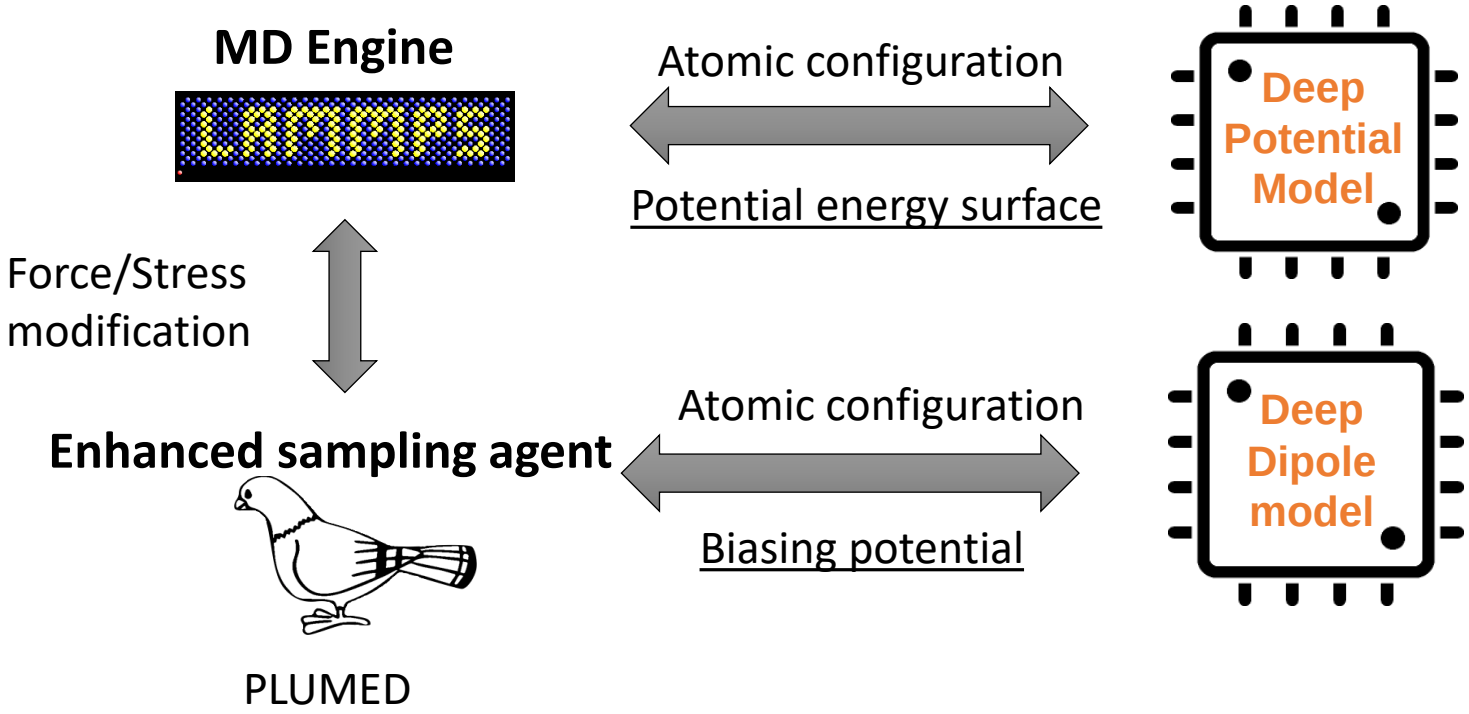
(1) Follow “run.sh”

(2) Compute and plot the molecule dipole moments distribution with Python. Example script:

hands-on-sessions/day-3/7-deep-wannier/dipole_distribution.py

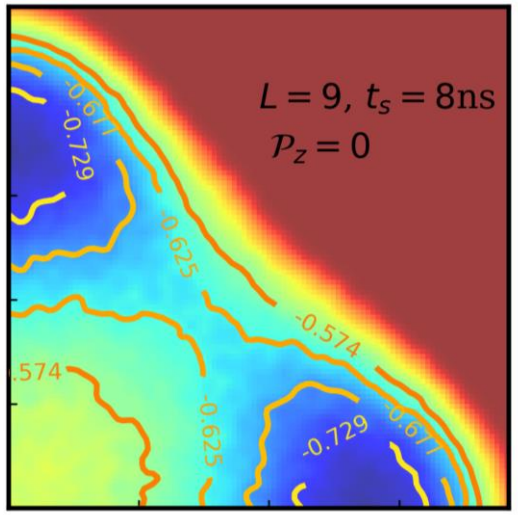
(3) Experiment with “`dipole_model.eval`”!

Enhanced sampling



Global polarization from Deep Dipole

$\mathcal{G}(T = 600K, \boldsymbol{\mathcal{P}})$



A cross section of the 3D free energy surface for the polarization of PbTiO3. Computed by metadynamics.

Reference: Xie, P., Chen, Y. E, W. and Car, R., 2022. Ab initio multi-scale modeling of ferroelectrics: The case of PbTiO3. arXiv preprint arXiv:2205.11839.

PLUMED plugin: https://github.com/y1xiaoc/deepmd-plumed (not MPI-ready yet)