Constructing and evaluating machine-learned interatomic potentials for Li-based disordered rocksalts

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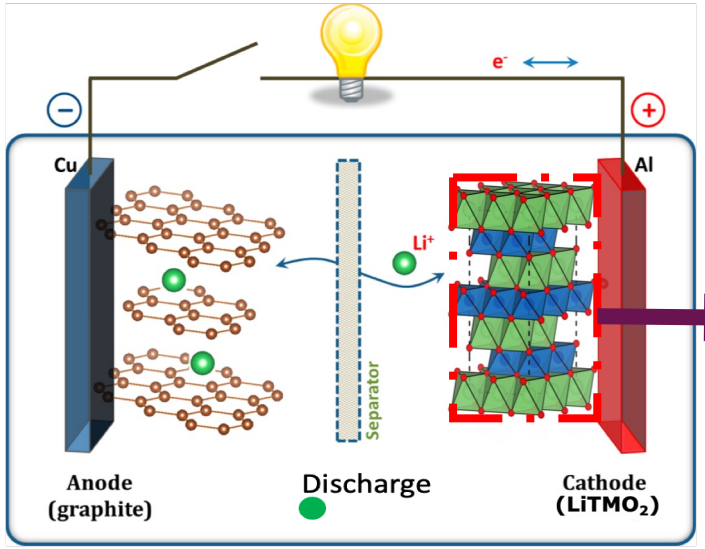
Introduction

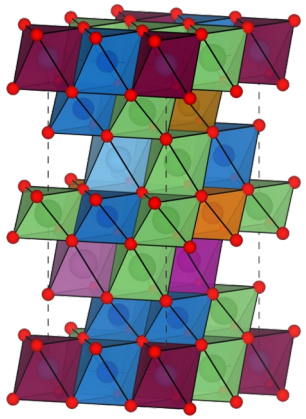
- Growing demands for electric power: need high energy and power density energy storage devices[1]
- Increasing the performance of cathode materials of Lithium ion batteries (LIBs) : ongoing and active area of research[2]



increase the energy density of LIB cathodes is to utilize anionic redox (i.e., oxygen redox), which can be reversibly access in cathode materials with a Li-excess composition[3]

$(Li_{1+x}TM_{1-y}O_2)$ **Disordered Rocksalts (DRX) cathodes**

Cathode



Advantages of using DRX compared to layered rocksalts

- Better structural stability upon Li removal
- Anionic redox: Higher voltage
- Operate at low rates and for low cycles

Difficulties modelling DRX using density functional theory (DFT)

- Many possible configurations
- High computational costs for large supercells

Need a computational technique which can provide 'quick' and 'accurate' estimates of energies and atomic forces

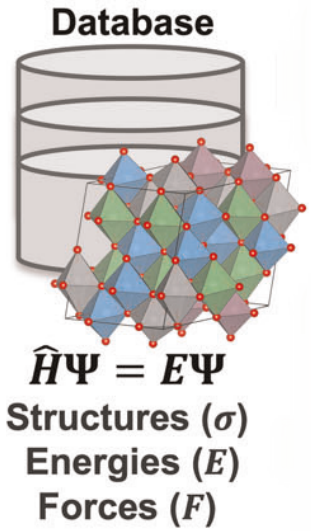
Machine-learned interatomic potentials (MLIPs)

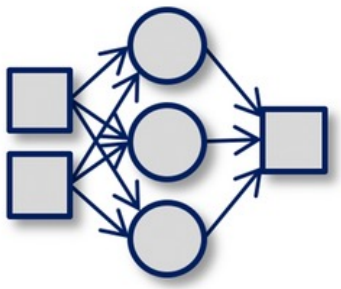
1. Kang et al., Science, 2006, 311, 977–980, 2. Goodenough et al., J Am Chem Soc. 2013, 135, 1167–1176, 3. Clément et al., Energy Environ Sci, 2020, 13, 345–373

Machine-learned interatomic potentials (MLIPs)

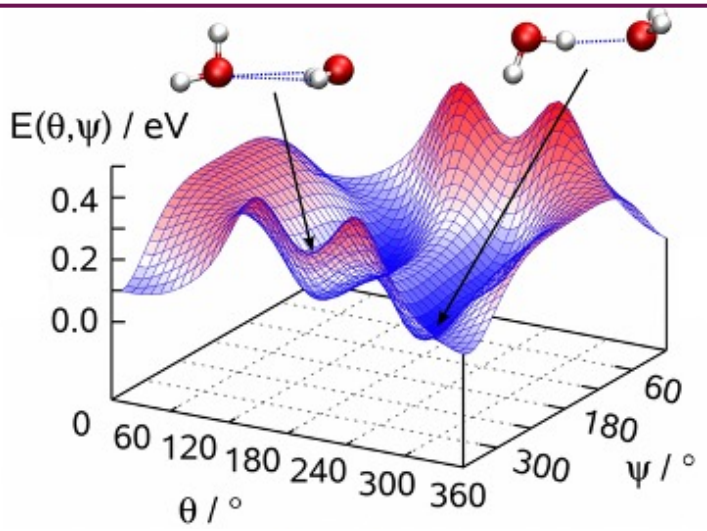
Represent **potential energy surface (PES)**[1]

Map the atomic configuration of a structure to its total energy (by minimizing the **loss function**)





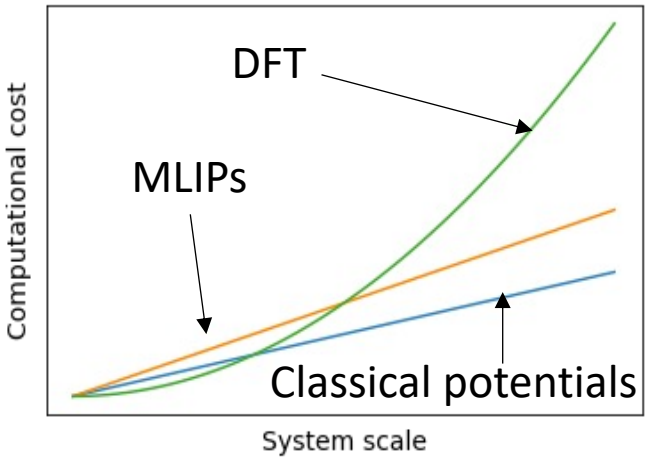
ML models



MLIPs

Applications: Large scale/long time simulation: molecular dynamics (MD) and Monte Carlo (MC)

- **MTP (moment tensor potential)**
- **SNAP (spectral neighbor analysis potential)**
- **GAP (Gaussian approximation potential)**
- **AENET (atomic energy network)**

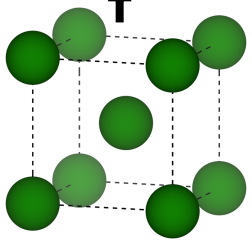


1.Artrith et al. J Comput Aided Mol Des, 2021, 35, 557-586

Constructing MLIPs

- $LiTMO_2$ + $Li_{1+x}TM_{1-y}O_2$ + TMO_2 compositions = **Total Structures = 10842**
- TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and/or Cu **(11-components)**

Literature



Pymatgen[1]

Ordered $LiTMO_2$
Ordered TMO_2
Disordered $LiTMO_2$
Disordered TMO_2
Multi-species disordered $LiTMO_2$
Multi-species disordered TMO_2

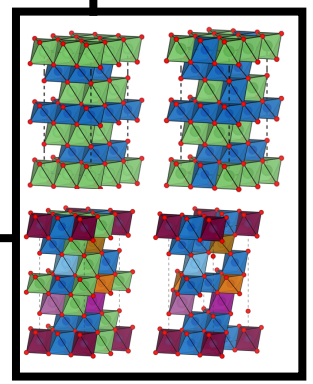
DFT

Dataset

- DFT+ *U* calculations
- PBE[2] with PAW[3,4] potentials, as implemented in the Vienna ab initio simulation package (VASP)[5]

DFT properties

Y (Energies, Forces)



Crystal structures

Machine learning
$Y = f(X; w)$

AENET | GAP | SNAP | MTP

Check error (Energy, Force)

Feedback

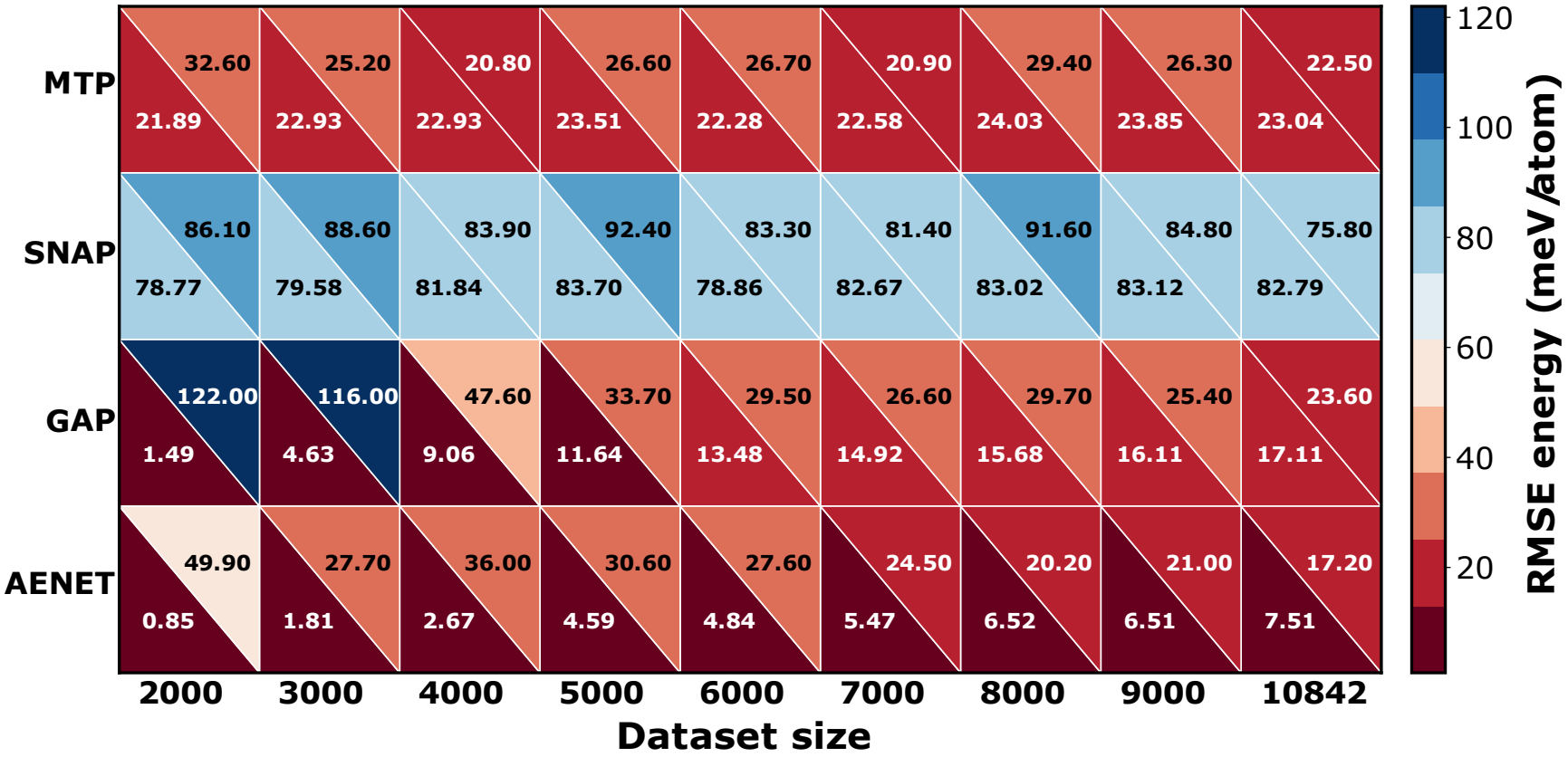
Best Model

DFT voltages
vs.
Model voltages

1. Ong et al., Comput Mater Sci, 2013, 68, 314–319, 2.Perdew et al., Phys Rev Lett, 1996, 77, 3865, 3. Blöchl, Phys Rev B, 1994, 50, 17953–17979,
4. Kresse and Joubert, Phys Rev B, 1999, 59, 1758–1775, 5. Kresse and Hafner, Phys Rev B, 1993,48, 13115

AENET : best potential for predicting total energies

Upper triangle: Test errors *Lower triangle: Training errors*



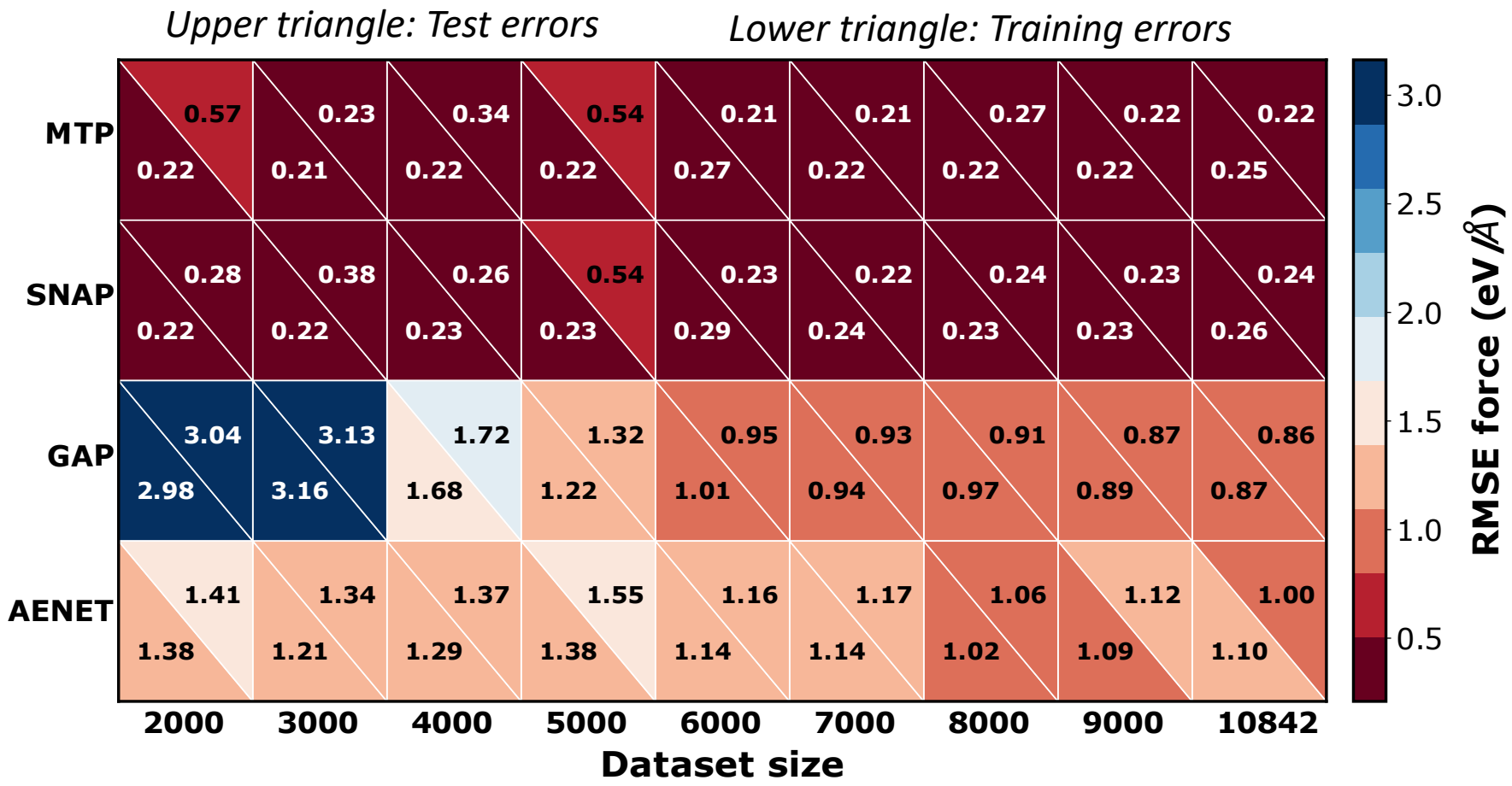
Train (90%): Test (10%)

- AENET's **root mean squared errors (RMSE)** ~7.5 meV/atom on energies: similar to DFT (~1 meV/atom)
- SNAP: **largest errors** on energies
- AENET and GAP display **similar energy** RMSEs in training and testing for all large datasets: **improvement in transferability**

- Lower training errors: Better accuracy (AENET)
- Lower test errors: Better transferability (AENET)

AENET performs best when dataset size is good enough, MTP reasonable at small datasets

MTP: best potential for predicting total forces



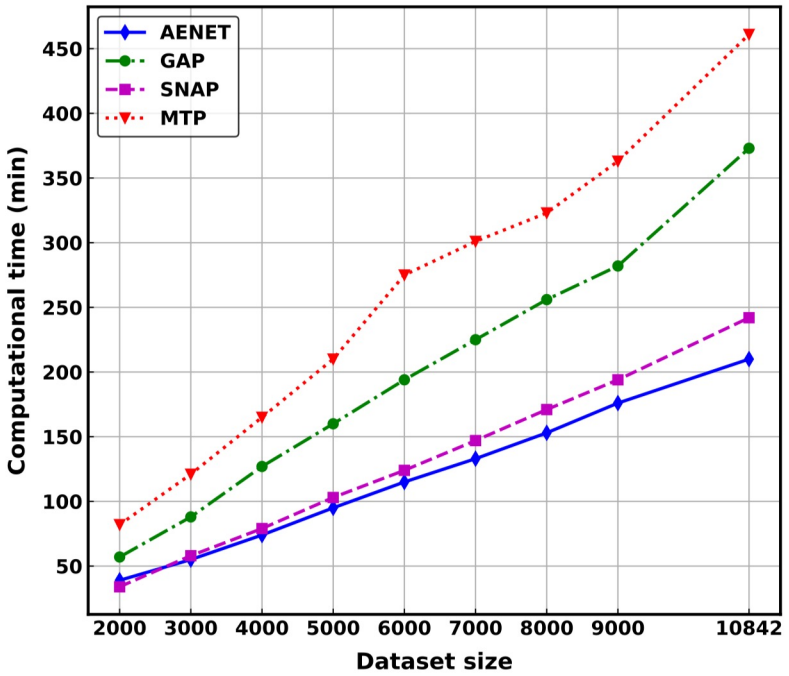
Train (90%): Test (10%)

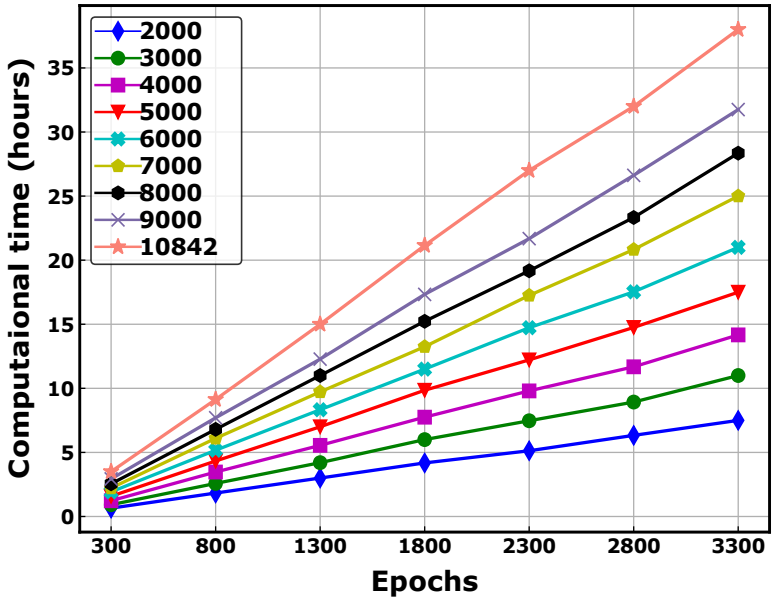
- Lower training errors: Better accuracy (MTP): above 7000 dataset size
- Lower test errors: Better transferability (MTP)

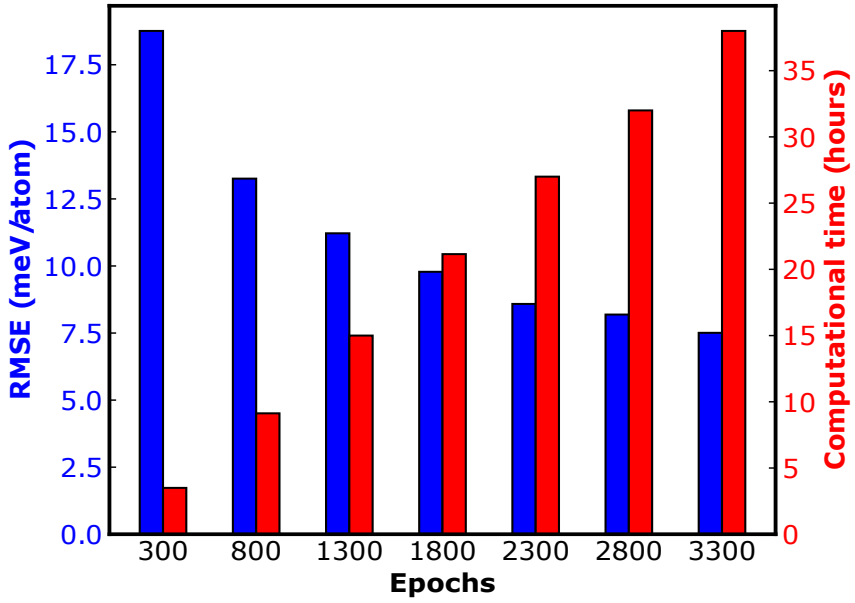
- AENET and GAP show significantly high training errors on atomic forces
- MTP and SNAP: good **accuracy** and **transferability** on **force** predictions

MTP to be the best performer for any dynamics simulations among the MLIP

Ease of training: AENET train fast at low epochs







- MTP train time ~ 2 X (AENET train time at 300 epochs)
- MTP is the **slowest** to train for all dataset sizes, followed by GAP

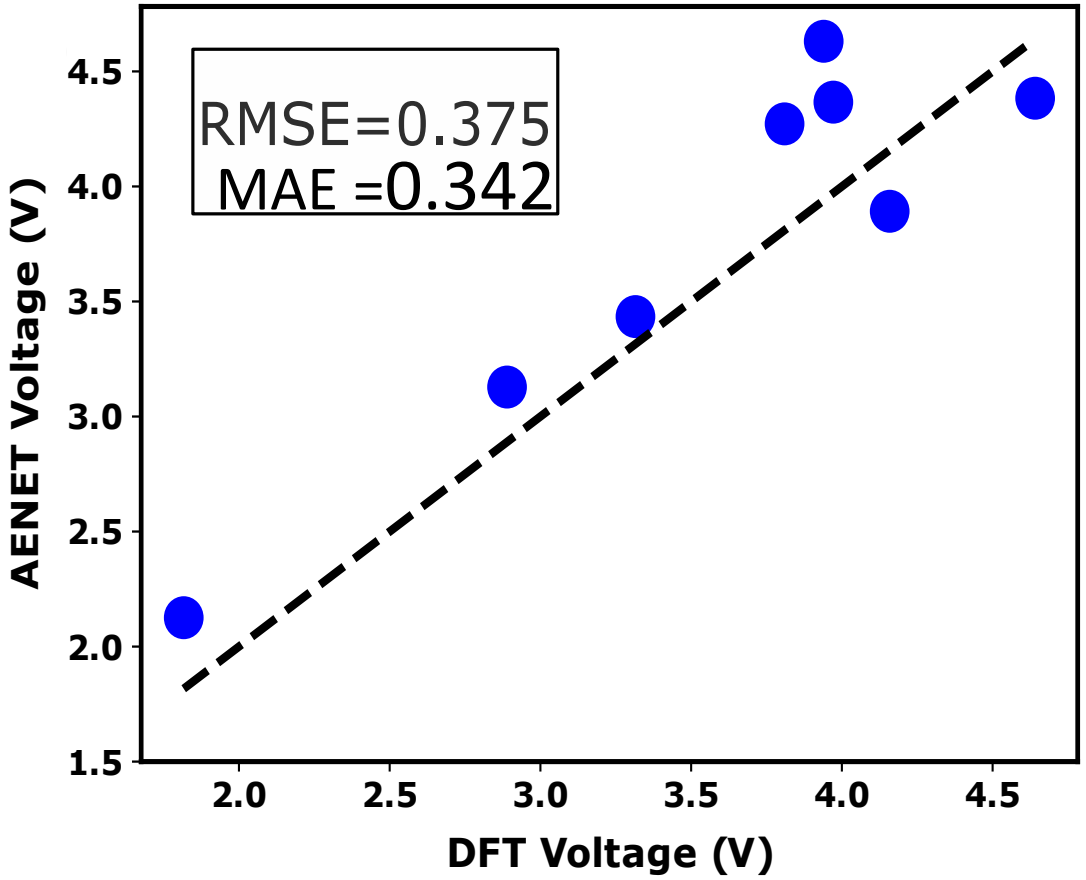
Increase in training **time** is more rapid with increasing **epochs** for larger datasets

Rapid increase in computational time for the full **10842 dataset** may not be worth the marginal gain in accuracy, after **2300 epochs**

AENET(2300 epochs) is the best potential to predict energies in terms of accuracy and computational time

Single core of a Intel® Xeon® Gold 6271 CPU, with a maximum random access memory of 128 Gigabytes, without any hyperthreading

Voltage predictions: AENET is reasonable



Prediction of average intercalation voltages, in ordered, layered, single-TM $LiTMO_2$ as a test of accuracy, versus DFT calculations using AENET (2300 epochs)

- Voltage errors: 10.05% against DFT
- largest voltage errors: $LiFeO_2$ and $LiTiO_2$
- AENET potential to be useful for obtaining 'quick' voltage predictions for several DRX

- High-throughput screening may be feasible with AENET potentials to identify high-voltage DRX cathode compositions

This MLIPs can be used to model highly disordered ceramic and/or metallic systems

Conclusions

- Difficult to model disorder rocksalts (DRX) using DFT
- Quantified the **accuracy, transferability**, and **ease of training** of atom-centered MLIPs **(MTP, SNAP, GAP, and AENET)**, in their ability to model the **PES** of DRX
- **AENET :** best potential for predicting total **energies.** **MTP:** the best performer for atomic **forces**; **AENET (MTP)** exhibit the **smallest (largest)** computational training time

Acknowledgment

Vijay Choyal, Nidhish Sagar and Gopalakrishnan Sai Gautam, *Constructing and evaluating machine-learned interatomic potentials for Li-based disordered rocksalts*, arXiv:2304.01650 [cond-mat.mtrl-sci], 2023

Draft

Data and Code

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