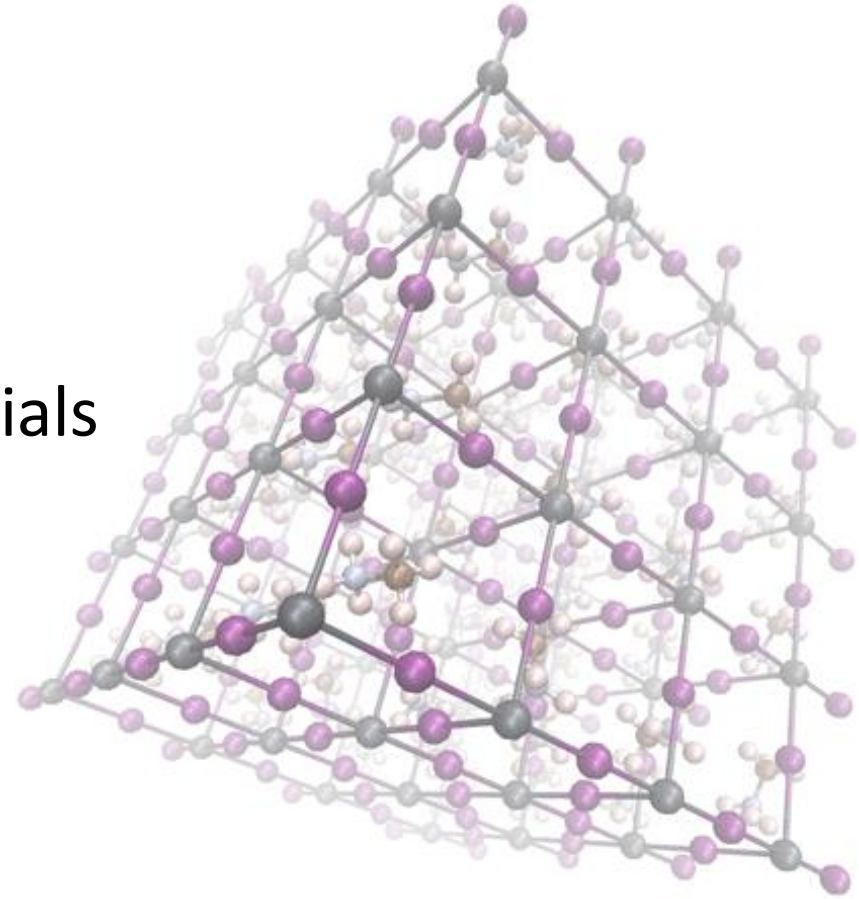
On-the-fly machine-learning force fields with near first-principles precision: Predicting phase transitions in complex solids

Joint 4TU.HTM & M2i
Workshop on AI in materials
June 23 2021



Menno Bokdam

UNIVERSITY OF TWENTE. | MESA+ INSTITUTE

Nano Electronic Materials cluster

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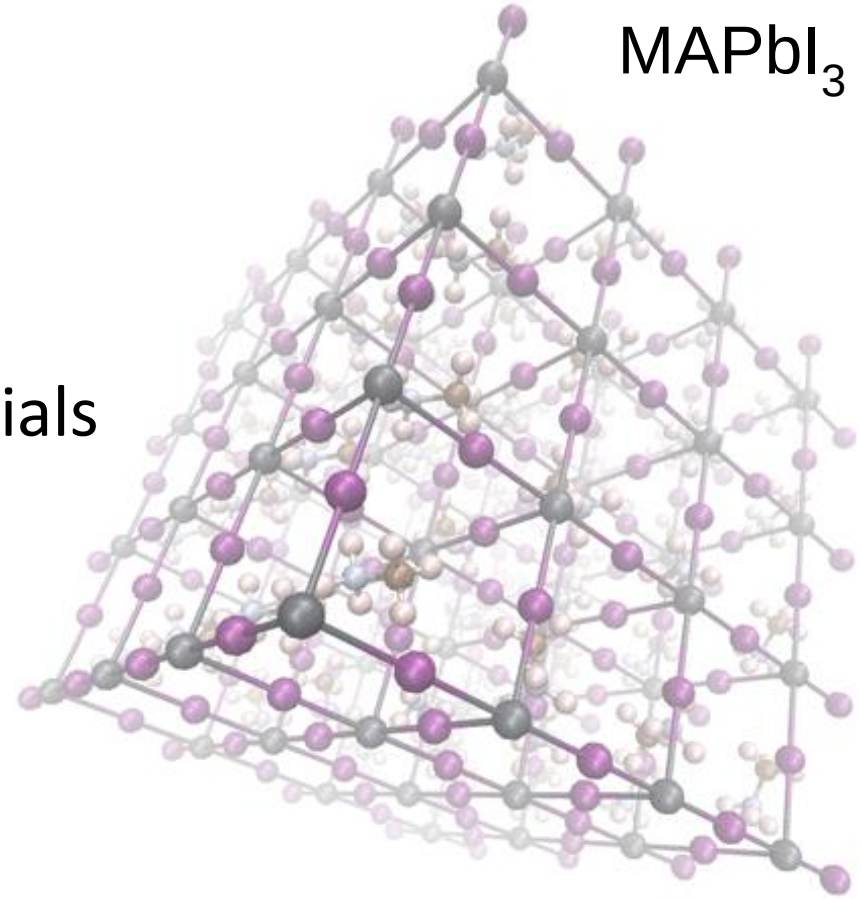

$MAPbI_3$

- Good Absorption (UV-Vis)
  - 25% solar cell efficiency
- High dielectric constant
  - $\varepsilon_0 = 100$
  - $\varepsilon_{infty} = 7$
- Excitons and Polarons
- Ultra-low thermal conductivity
  - $\kappa = 0.4$ W/(mK)
- High thermal electric figure of merit
  - (ZT=~1-2)
- Bad material stability

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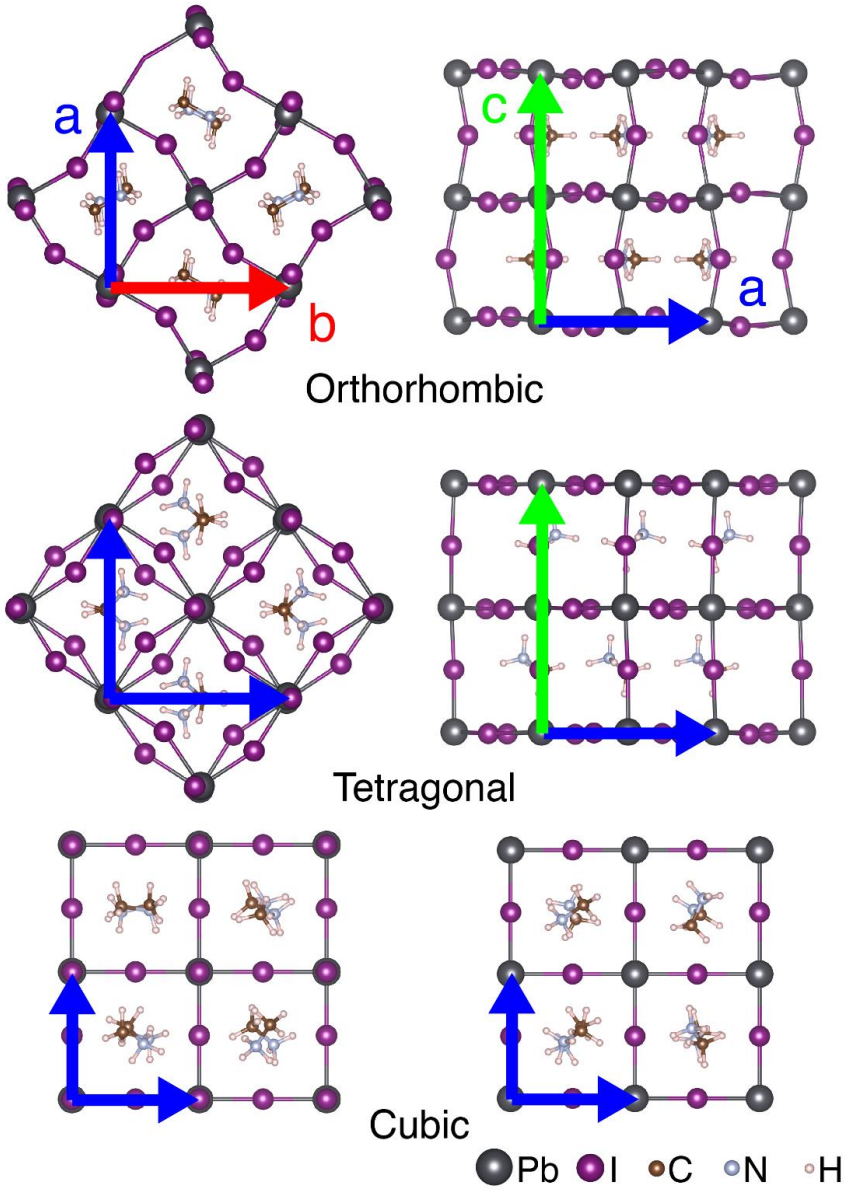
Phase transitions in $MAPbI_3$



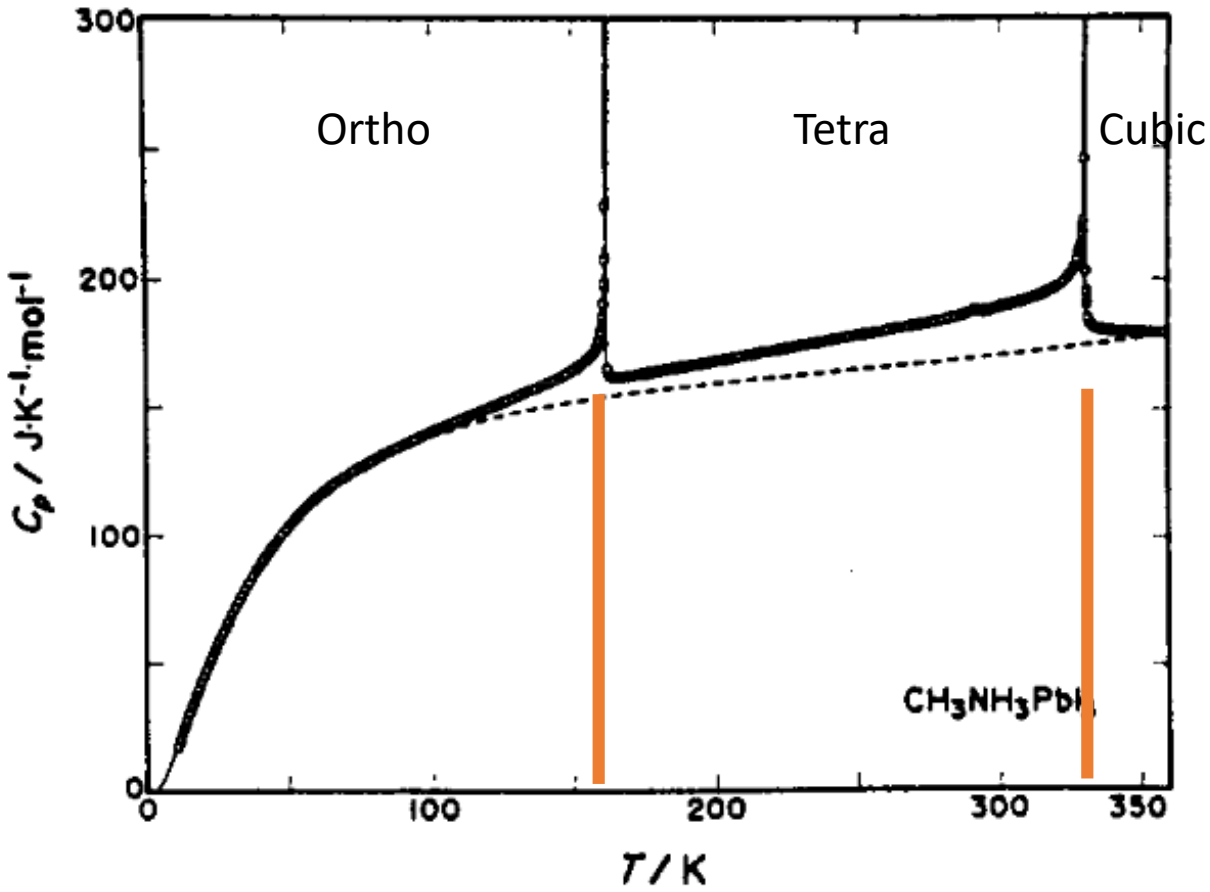
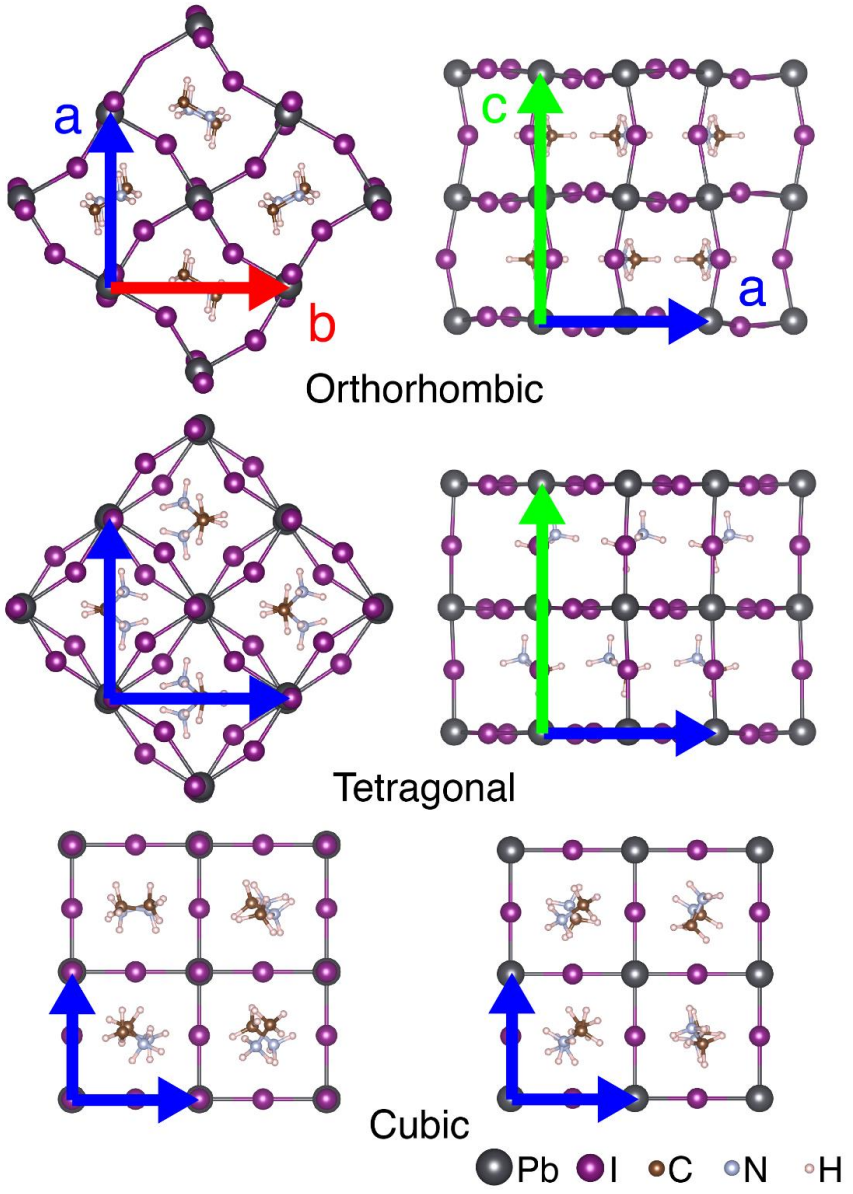
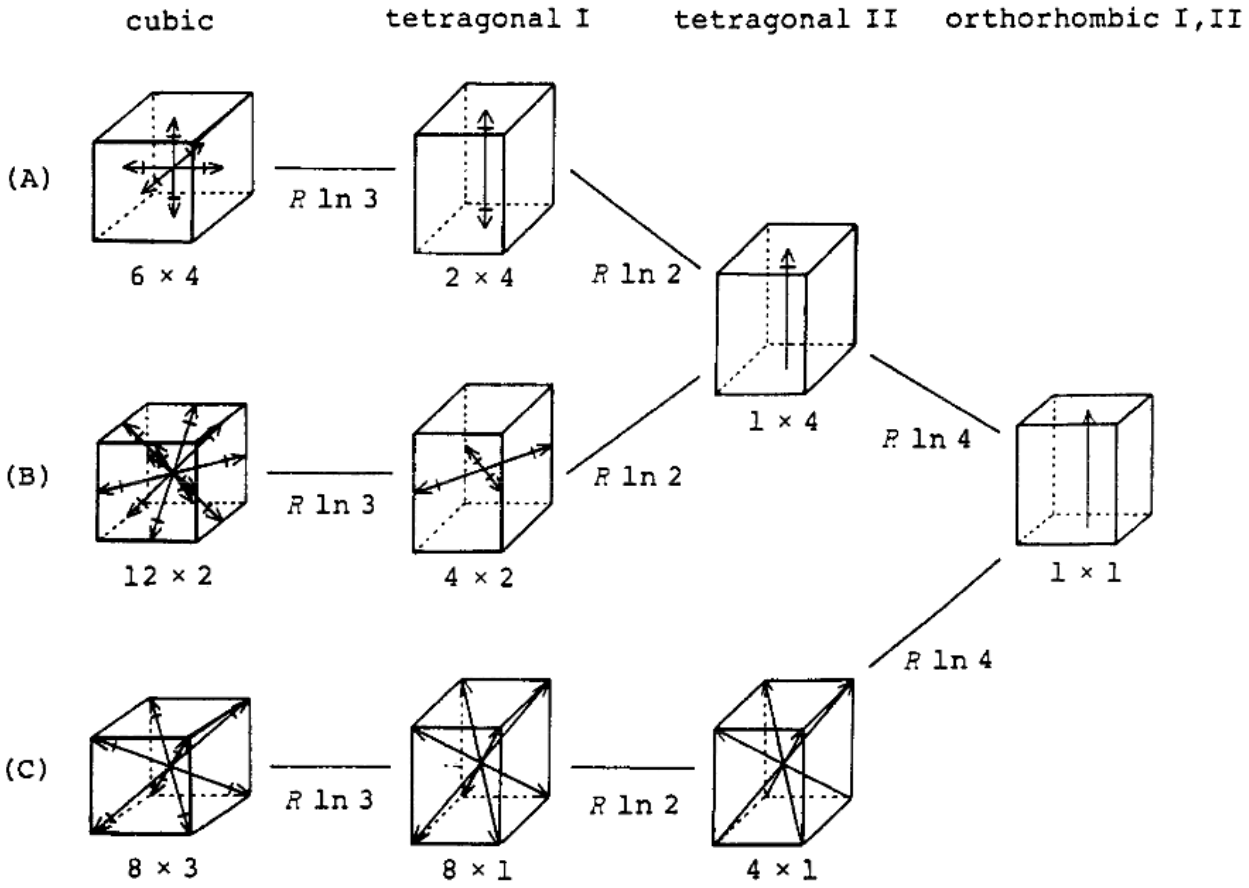


Fig. 6. Molar heat capacity of $MAPbI_3$.

N. Onoda-Yamamuro, T. Matsuo, and H. Suga, Calorimetric and ir spectroscopic studies of phase transitions in methylammonium trihalogenoplumbates (ii), J. Phys. Chem. Sol. **51**, 1383 (1990).

Phase transitions in $MAPbI_3$





N. Onoda-Yamamuro, T. Matsuo, and H. Suga, Calorimetric and ir spectroscopic studies of phase transitions in methylammonium trihalogenoplumbates (ii), J. Phys. Chem. Sol. **51**, 1383 (1990).

Entropy-driven phase transitions

intuitive definition of order always coincides with the one based on Eqn. 1. In fact, the aim of this paper is to show that many "ordering"-transitions that are usually considered to be energy-driven may, in fact, be entropy driven. I stress that the idea of entropy-driven phase transitions is an old one. However, it has only become clear during the past few years that such phase transformations may not be interesting exceptions, but the rule!

D. Frenkel / Physica A 263 (1999) 26–38

We want to do **Isothermal-Isobaric** simulations

$$G(p,T) = U + pV - TS$$

and allow the system to minimize its free energy under constant p,T.

U Internal Energy

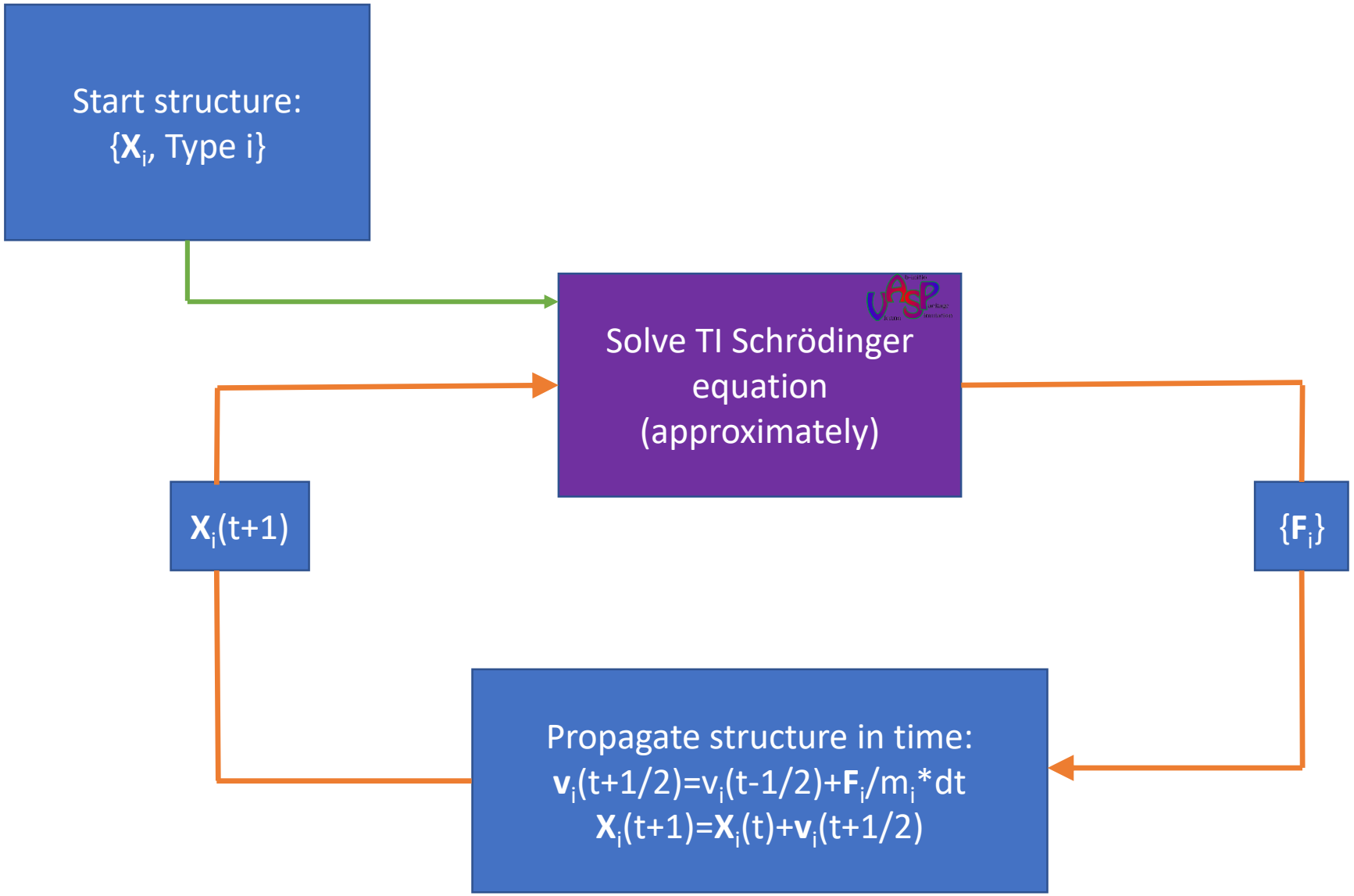
p Pressure

T Temperature

V Volume

S Entropy

Ok, so let's do first principles Molecular Dynamics

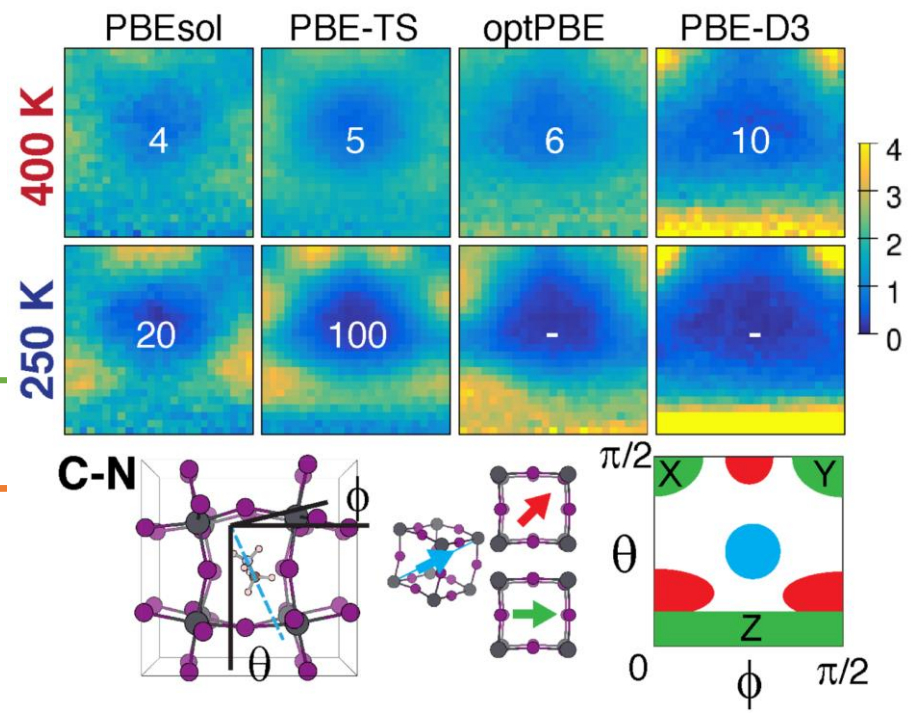


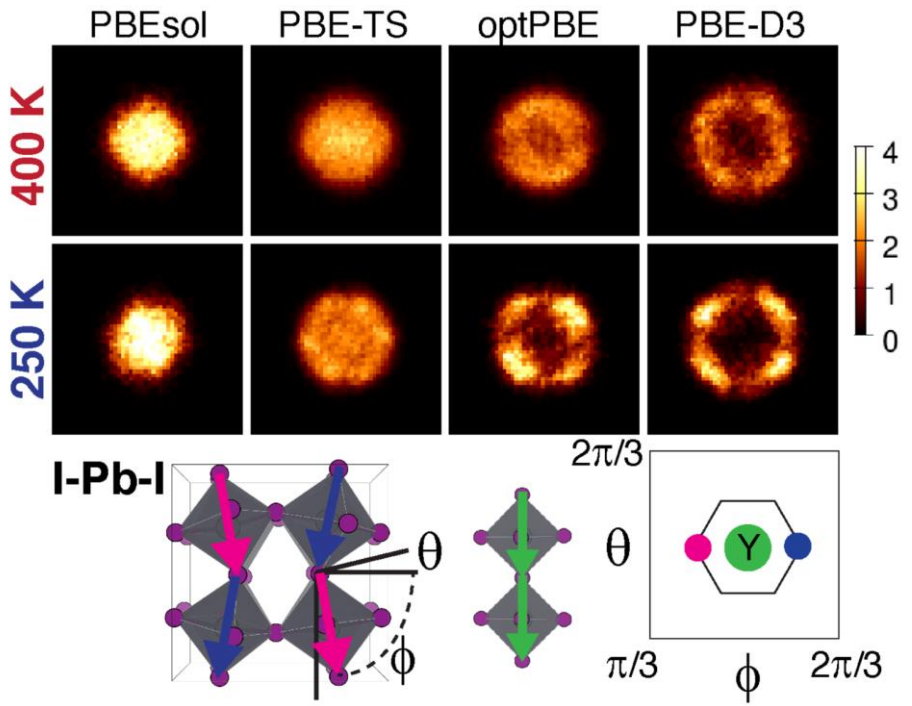
Advantage:

- High Accuracy
- Predictive value
- Flexiblity

Ok, so let's do first principles Molecular Dynamics

Start structure:
{$\mathbf{X}_i$, Type i}





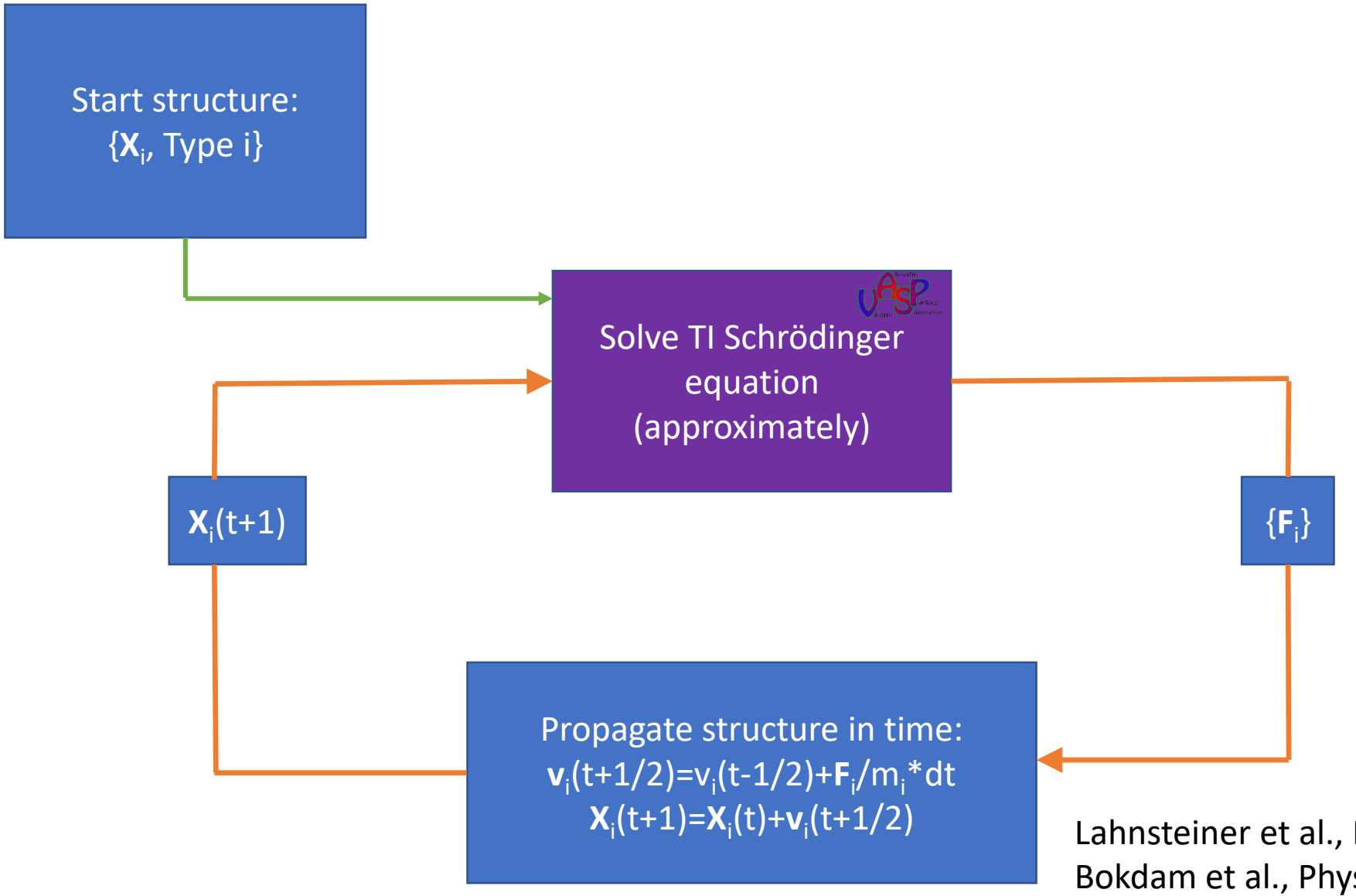
$\mathbf{X}_i(t+1)$

Propagate structure in time:
$\mathbf{v}_i(t+1/2)=v_i(t-1/2)+\mathbf{F}_i/m_i*dt$
$\mathbf{X}_i(t+1)=\mathbf{X}_i(t)+\mathbf{v}_i(t+1/2)$

NVT !!

Lahnsteiner et al., Physical Review B, **94**, 214114 (2016)
Bokdam et al., Phys. Rev. Lett. **119**, 145591 (2017)
Lahnsteiner et al., Phys. Rev. Mat., **2**, 073604 (2018)

Ok, so let's do first principles Molecular Dynamics



Advantage:

- High Accuracy
- Predictive value
- Flexibility

Disadvantage:

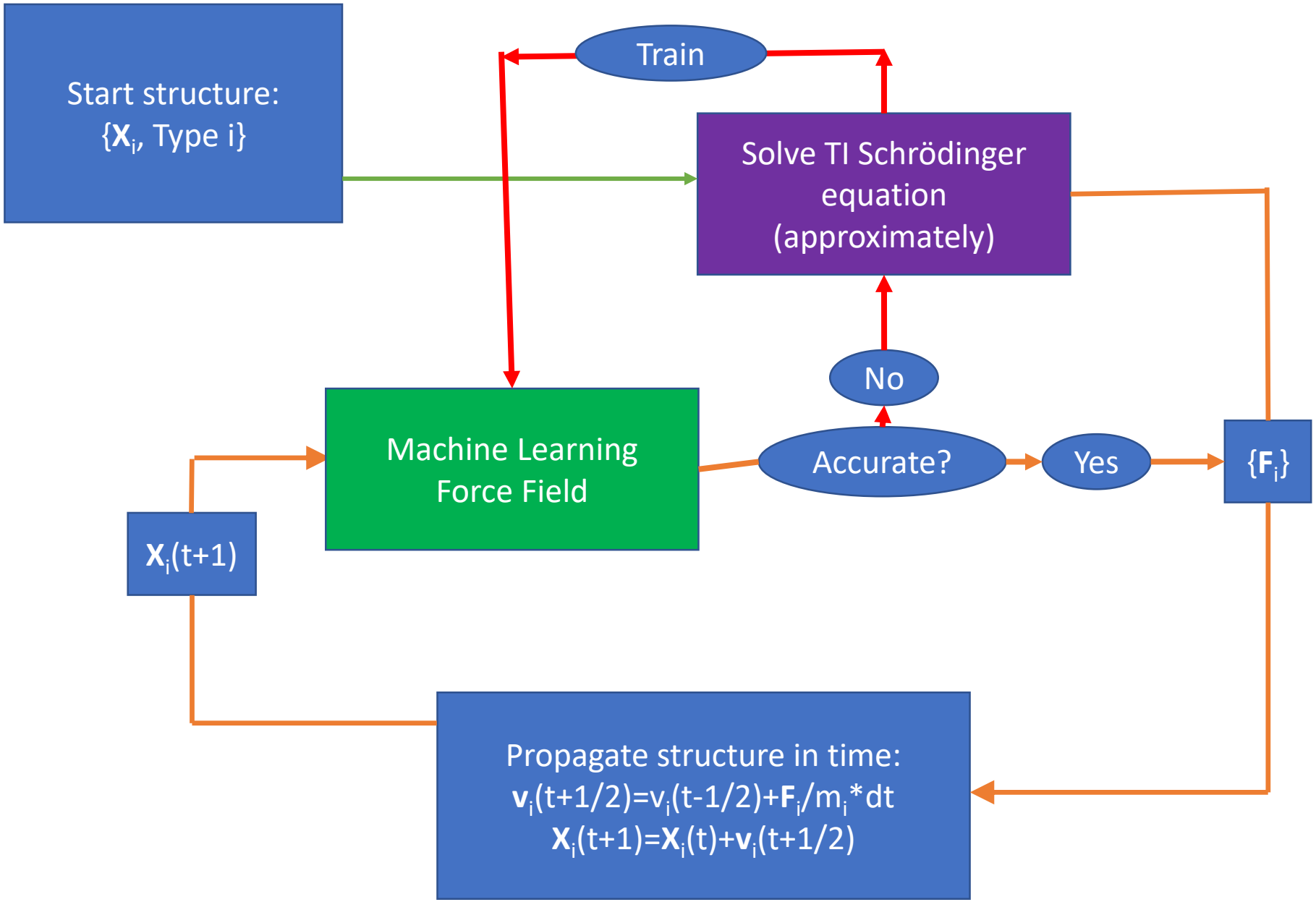
- Compute intensive
- Slow
- Bad system size scaling

Consequence:

- No access to: thermal conductivity, phase transitions, non-equilibrium MD, etc…

Lahnsteiner et al., Physical Review B, **94**, 214114 (2016)
Bokdam et al., Phys. Rev. Lett. **119**, 145591 (2017)
Lahnsteiner et al., Phys. Rev. Mat., **2**, 073604 (2018)

Include ML in first principles Molecular Dynamics



Advantage:

- High Accuracy
- Predictive value
- Flexibility

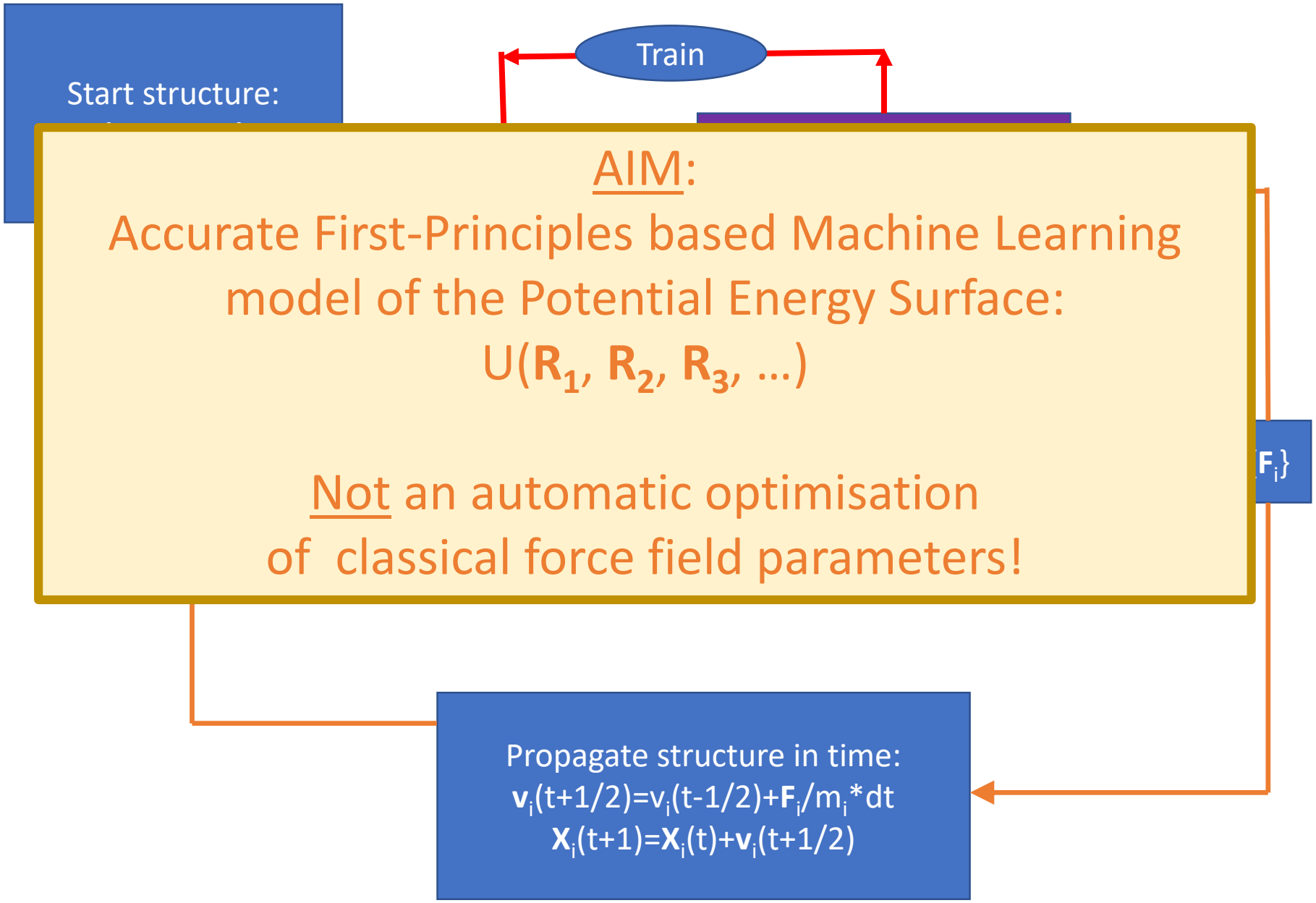
Disadvantage:

- ~~Compute intensive~~
- ~~Slow~~
- Bad system size scaling **(only in training!)**

Consequence:

- Access to: thermal conductivity, phase transitions, non-equilibrium MD, etc…

Include ML in first principles Molecular Dynamics



Advantage:

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- Flexibility

Disadvantage:

- ~~Compute intensive~~
- ~~Slow~~
- Bad system size scaling **(only in training!)**

Consequence:

- Access to: thermal conductivity, phase transitions, non-equilibrium MD, etc…

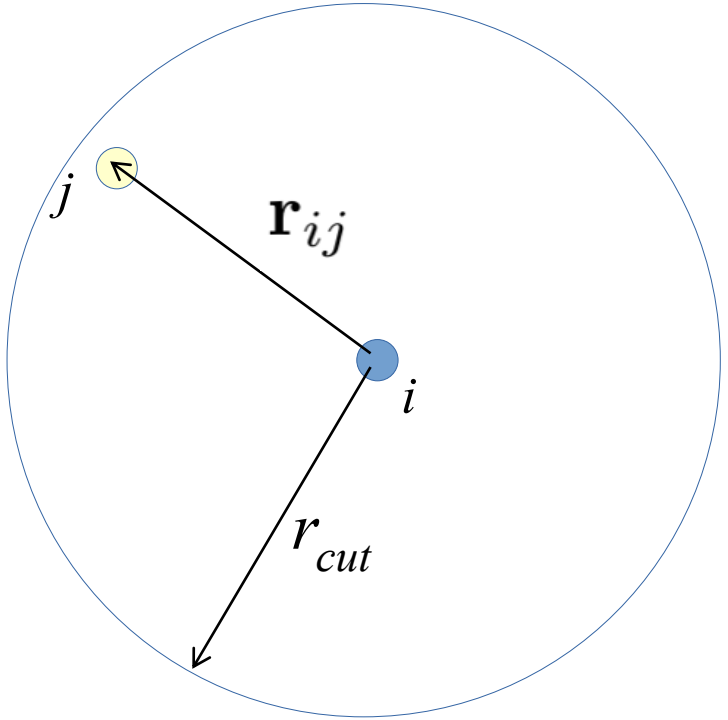
Attempt to describe (a smoothened version of) the Potential Energy Surface

$$U = \sum_{i=1}^{N_\mathrm{a}} U_i$$

$$\rho_i(\mathbf{r}) = \sum_{j=1}^{N_\mathrm{a}} f_\mathrm{cut}(r_{ij})\, g(\mathbf{r} - \mathbf{r}_{ij})$$

$$g(\mathbf{r}) = \frac{1}{\sqrt{2\sigma_\mathrm{atom}\pi}} \exp\left(-\frac{|\mathbf{r}|^2}{2\sigma_\mathrm{atom}^2}\right)$$

$$U_i = F[\rho_i(\mathbf{r})]$$



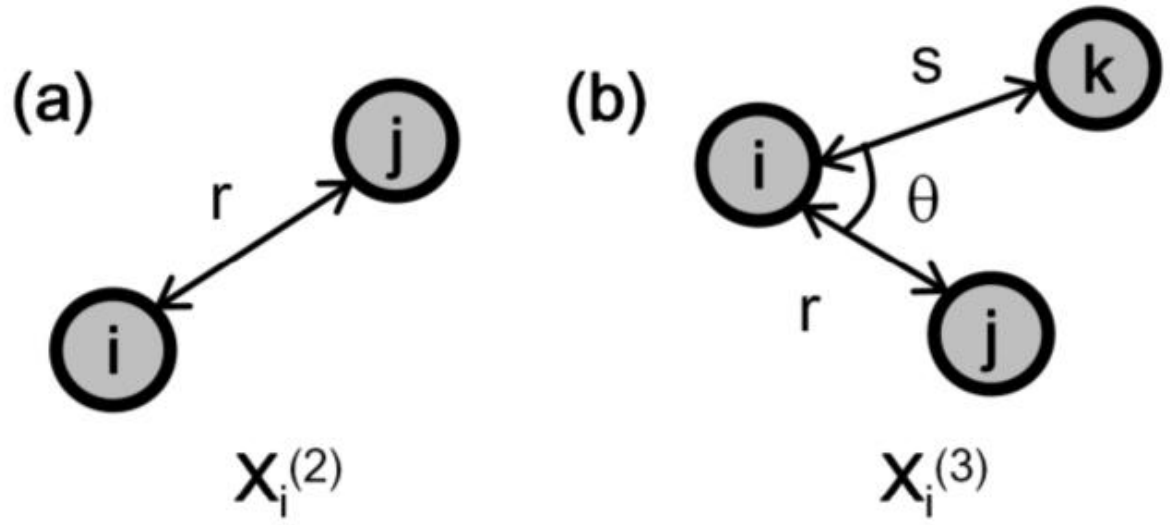
Drawback, *F* does not have rotational invariance!

Gaussian Approximation Potential (GAP):
Bartok *et al.,* Phys. Rev. Lett. **104**, 136403 (2010)

Attempt to describe the Potential Energy Surface

For **descriptors X_i** and kernel K, we adapt a variant of the Smooth Overlap Atomic Positions (SOAP)

SOAP: Bartok et al., Phys. Rev. B **87**, 184115 (2013)



$X_i^{(2)}$ $X_i^{(3)}$

$$\rho_i^{(2)}(r) = \frac{1}{4\pi}\int \rho_i(r\hat{\mathbf{r}})\, d\hat{\mathbf{r}}$$

$$\rho_i^{(3)}(r,s,\theta) = \iint \delta(\hat{\mathbf{r}}\cdot\hat{\mathbf{s}} - \cos\theta)\, \rho_i(r\hat{\mathbf{r}})\, \rho_i^*(s\hat{\mathbf{s}})\, d\hat{\mathbf{r}} d\hat{\mathbf{s}}$$

$$\rho_i(\mathbf{r}) = \sum_{l=1}^{L_{\max}} \sum_{m=-l}^{l} \sum_{n=1}^{N_R^l} c_{nlm}^i \chi_{nl}(r)\, Y_{lm}(\hat{\mathbf{r}})$$

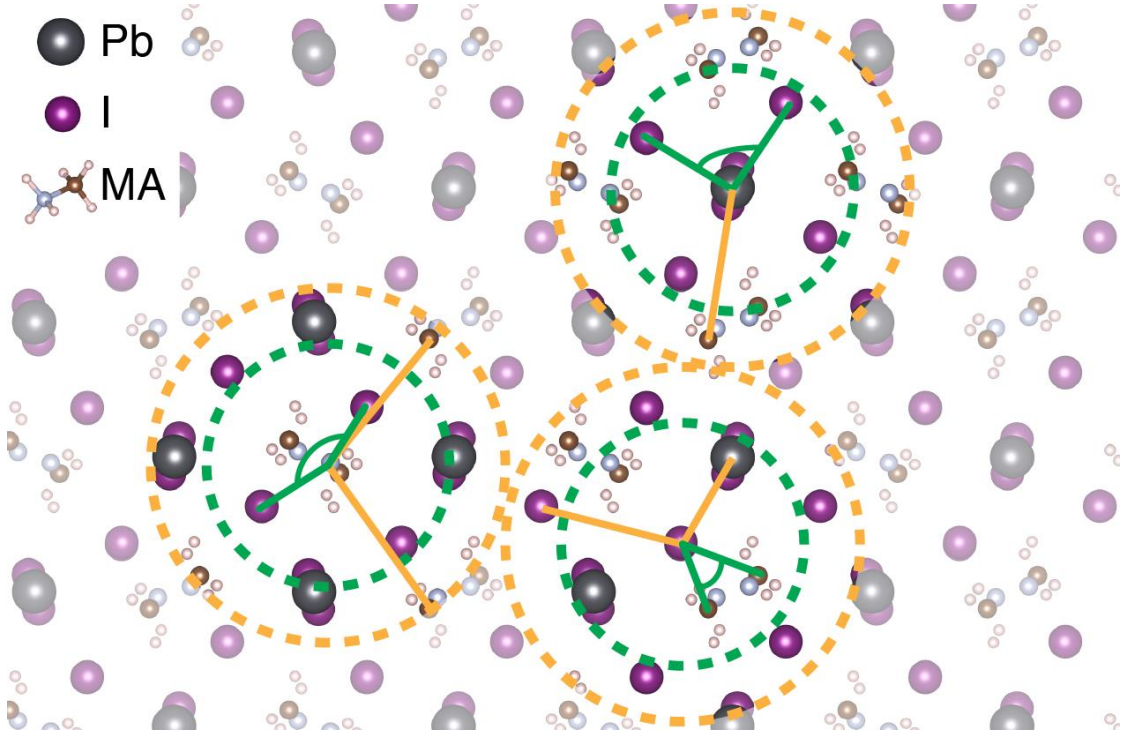
X_i

Increase until accuracy threshold is passed

$$U_i = F\left[\rho_i^{(2)}, \rho_i^{(3)}\right]$$

Machine-Learning Force Fields (MLLF)

$$U = \sum_{i=1}^{N_\mathrm{a}} U_i = \sum_{i=1}^{N_\mathrm{a}} \sum_{i_\mathrm{B}=1}^{N_\mathrm{B}} w_{i_\mathrm{B}} K\left(\mathbf{X}_i, \mathbf{X}_{i_\mathrm{B}}\right)$$



$$K\left(\mathbf{X}_i, \mathbf{X}_{i_\mathrm{B}}\right) = \beta^{(2)}\left(\mathbf{X}_i^{(2)} \cdot \mathbf{X}_{i_\mathrm{B}}^{(2)}\right) + \beta^{(3)}\left(\bar{\mathbf{X}}_i^{(3)} \cdot \bar{\mathbf{X}}_{i_\mathrm{B}}^{(3)}\right)^{\zeta^{(3)}}$$

Similarity measure

After fitting, the Energy, Forces and Stress (EFS) of structure with $\mathbf{X}_i$ can be calculated:

$$\mathbf{y} = \boldsymbol{\phi}\mathbf{w}$$

$\sum_i K(\mathbf{X}_i^\alpha, \mathbf{X}_{i_B})/N_a^\alpha$ $\quad w_{i_\mathrm{B}}$

Dimension of $\mathbf{y}$: $\quad m^\alpha = 1 + 3N_a^\alpha + 6$

Dimension of $\boldsymbol{\phi}$: $\quad m^\alpha \times N_B$

R. Jinnouchi *et al.*, Phys. Rev. Lett. **122**, 225701 (2019)
R. Jinnouchi *et al.*, Phys. Rev. B **100**, 014105 (2019)

On-the-fly training

The optimization of w_{iB} and the uncertainties are estimated by a regularised Bayesian linear-regression method.

Assumption: effect of movement of atoms outside of the cut-off radii can be modelled by Gaussian distributed noise in the FP data.

PHYSICAL REVIEW LETTERS **122,** 225701 (2019)

Editors' Suggestion

Phase Transitions of Hybrid Perovskites Simulated by Machine-Learning Force Fields Trained on the Fly with Bayesian Inference

Ryosuke Jinnouchi,[1,2] Jonathan Lahnsteiner,[1] Ferenc Karsai,[3] Georg Kresse,[1] and Menno Bokdam[1,*]
[1]*University of Vienna, Faculty of Physics and Center for Computational Materials Sciences, Sensengasse 8/12, 1090 Vienna, Austria*
[2]*Toyota Central R&D Labs, Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan*
[3]*VASP Software GmbH, Sensengasse 8, 1090 Vienna, Austria*

(Received 19 March 2019; published 7 June 2019)

Weights: $$\mathbf{w} = [\mathbf{I}/\sigma_w^2 + \mathbf{\Phi}^T\mathbf{\Phi}/\sigma_v^2]^{-1}\mathbf{\Phi}^T\mathbf{Y}/\sigma_v^2,$$

Uncertainty: $$\boldsymbol{\sigma} = \sigma_v^2\mathbf{I} + \boldsymbol{\phi}^T[\mathbf{I}/\sigma_w^2 + \mathbf{\Phi}^T\mathbf{\Phi}/\sigma_v^2]^{-1}\boldsymbol{\phi}.$$

Optimisation is important to prevent overfitting

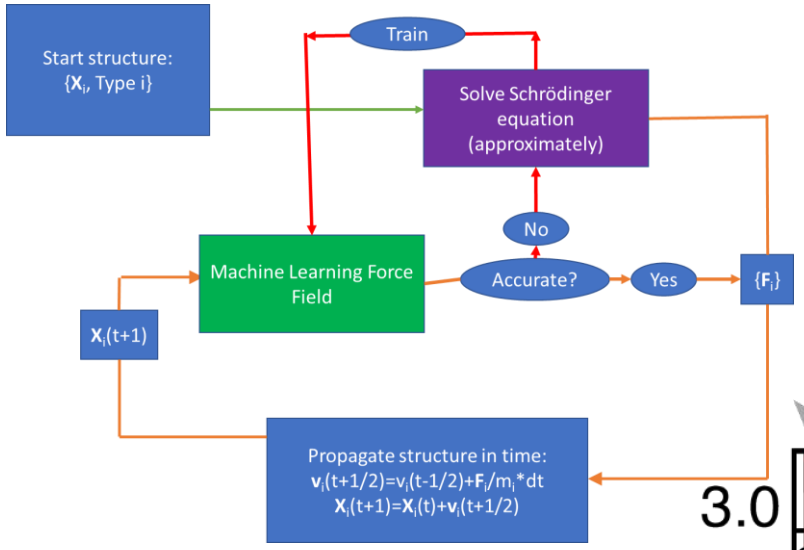
Design matrix, holds all $\boldsymbol{\phi}^\alpha$

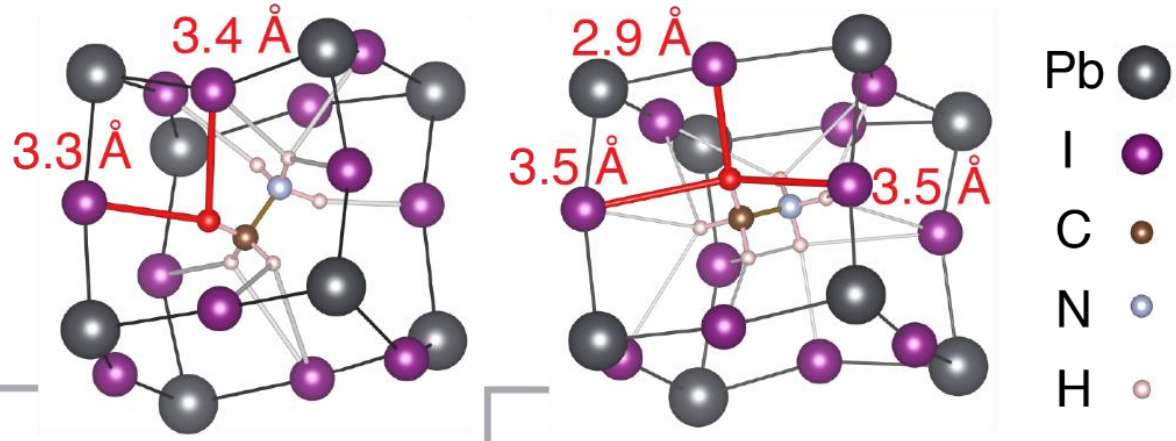
EFS data of all reference structures

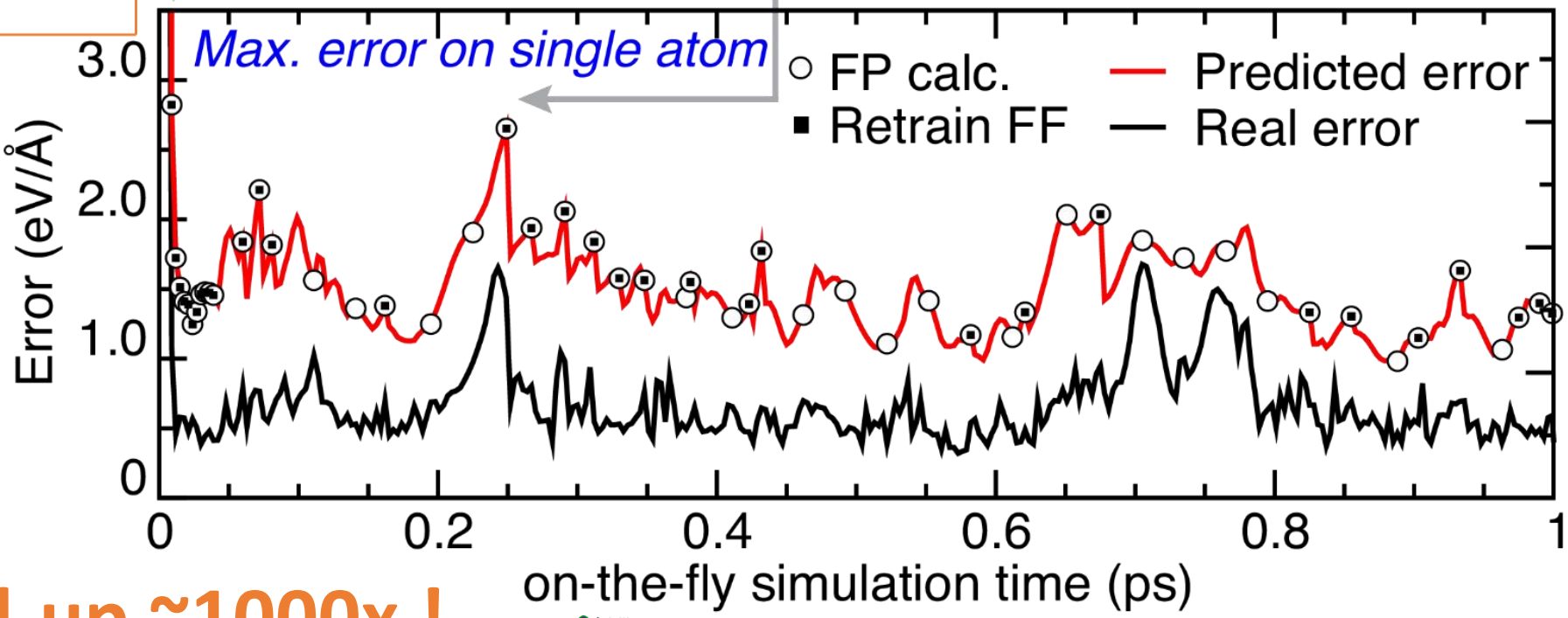
Further tech. specification: R. Jinnouchi *et al.*, Phys. Rev. Lett. **122**, 225701 (2019)
R. Jinnouchi *et al.*, Phys. Rev. B **100**, 014105 (2019)

Machine-Learning Force Fields (MLLF)

*Trained on-the-fly during **isothermal-isobaric** MD with SCAN DFA at 400 K*







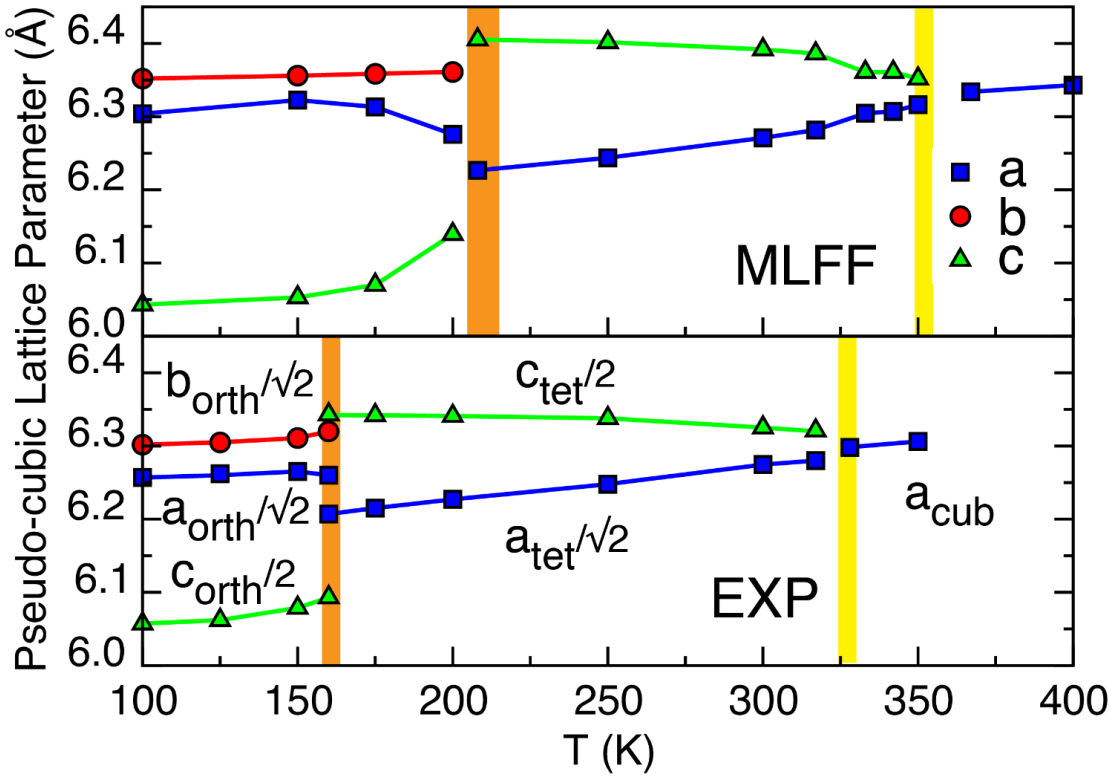
Effective speed-up ~1000x !

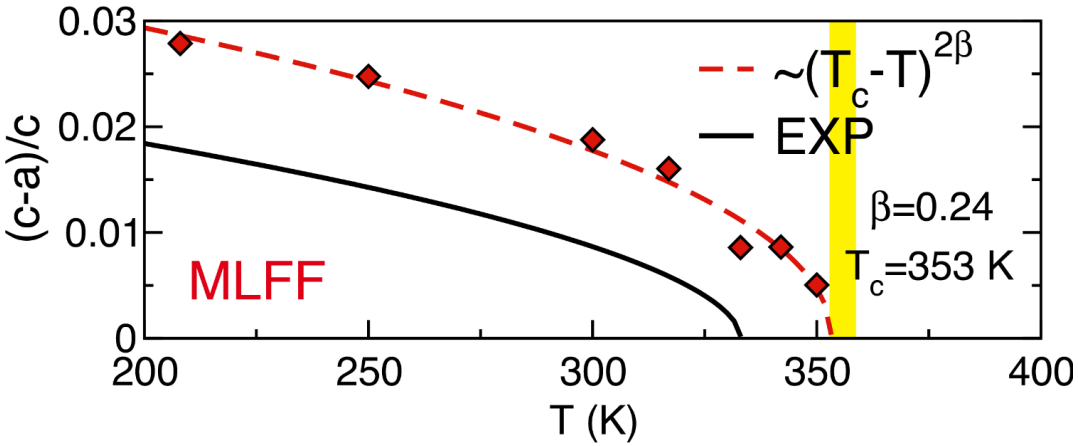
R. Jinnouchi *et al.*, Phys. Rev. Lett. **122**, 225701 (2019)

Machine-Learning Force Fields (MLLF)

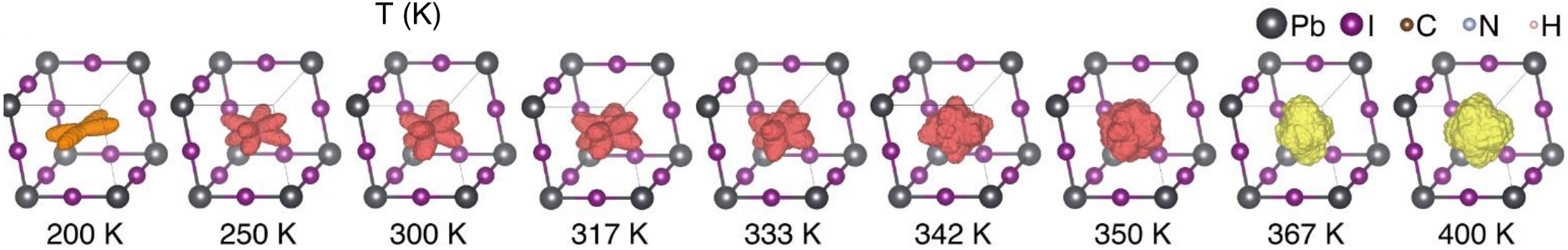
Trained on-the-fly during MD with SCAN DFA

Comparison to Experiment





- Near first-principles accuracy
- Large system sizes
- Nanosecond time scales



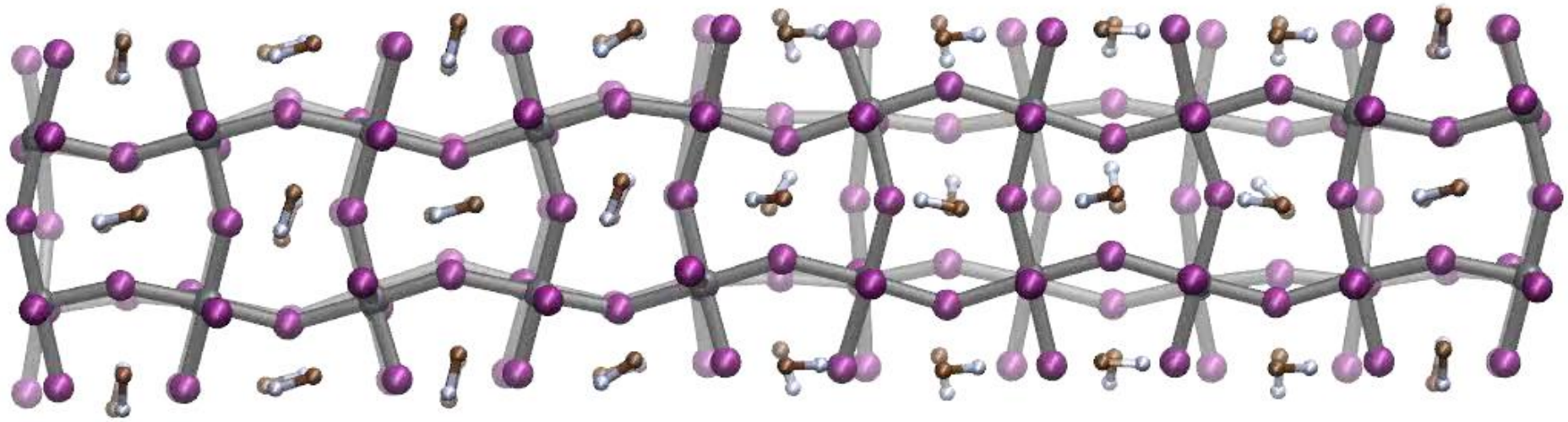
EXP: Whitfield et al., Sci. Rep. **6**, 35685 (2016)

Machine-Learning Force Fields (MLLF)

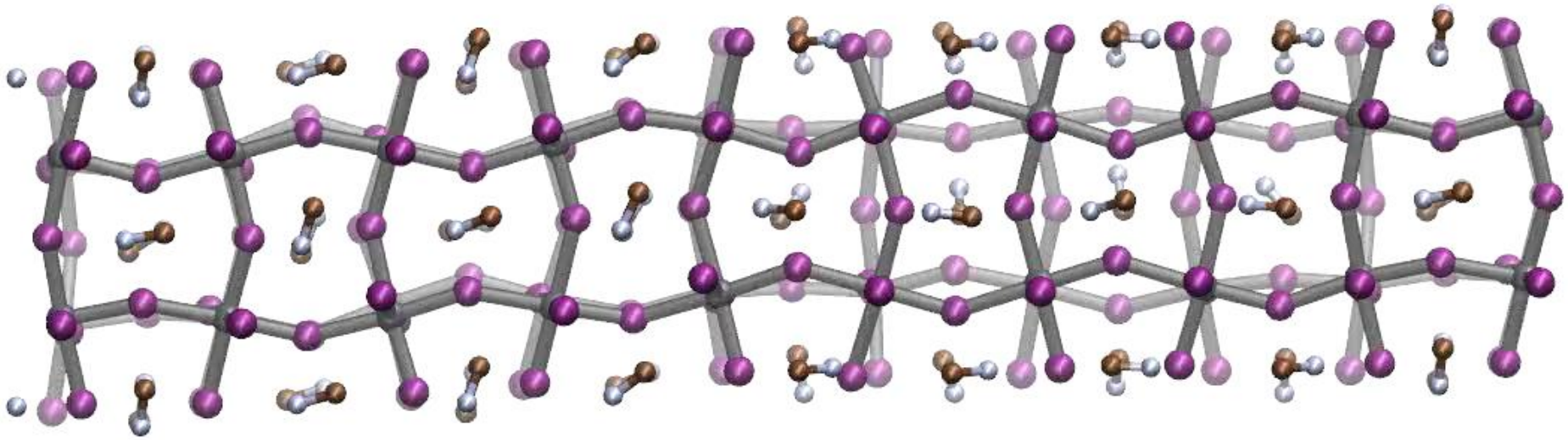
Trained on-the-fly during MD with SCAN DFA

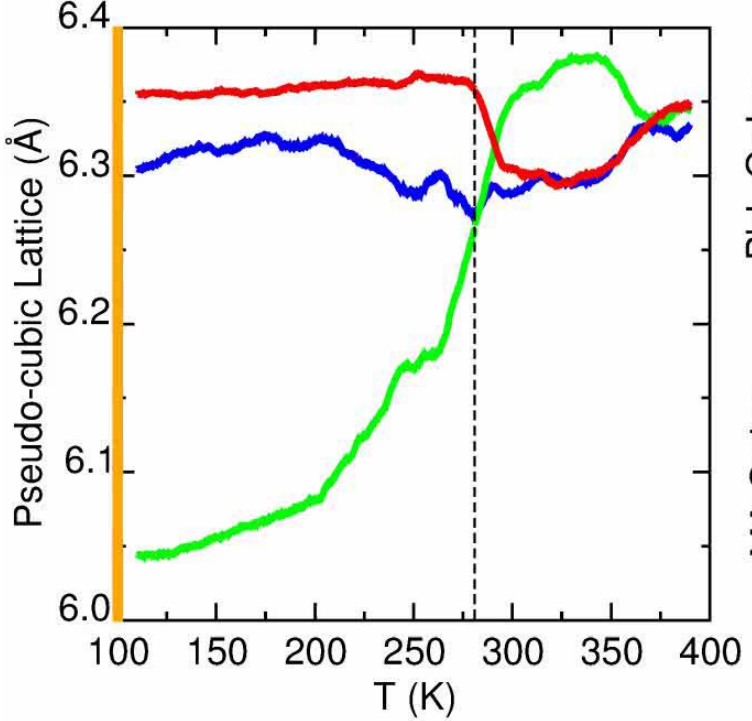
Movies:
dynamicsolids.net/sm/2019-mlff-perovskites

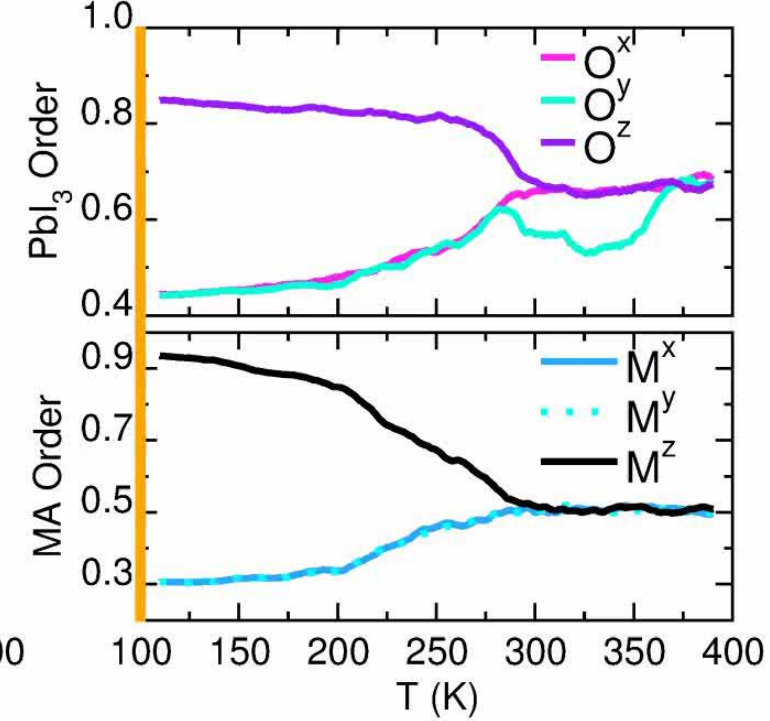
175 K

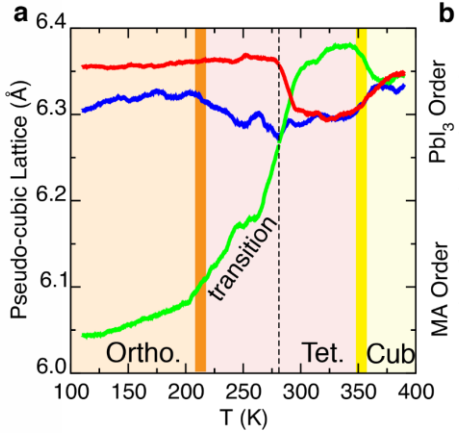


225 K

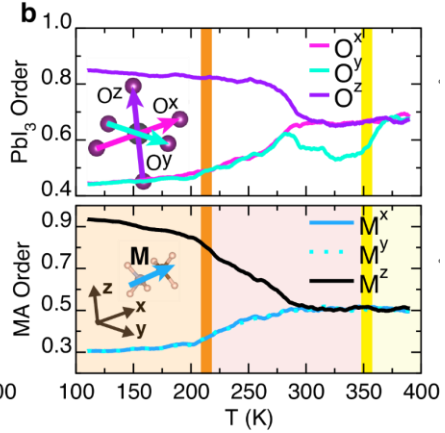






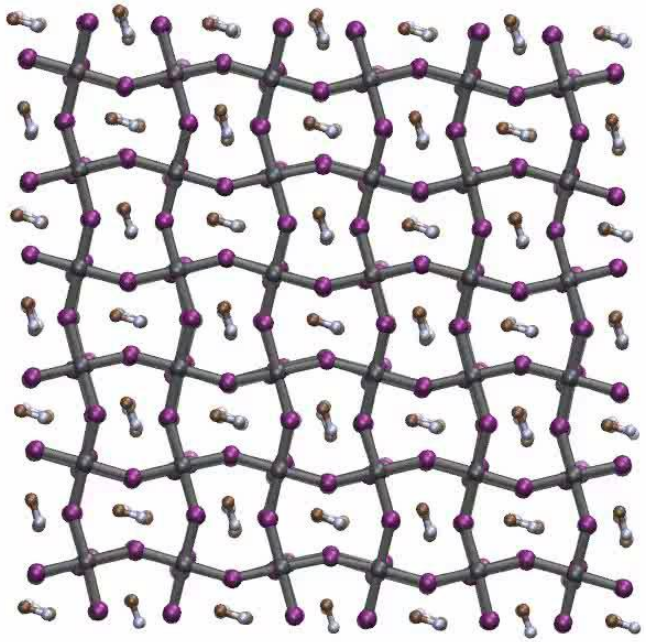


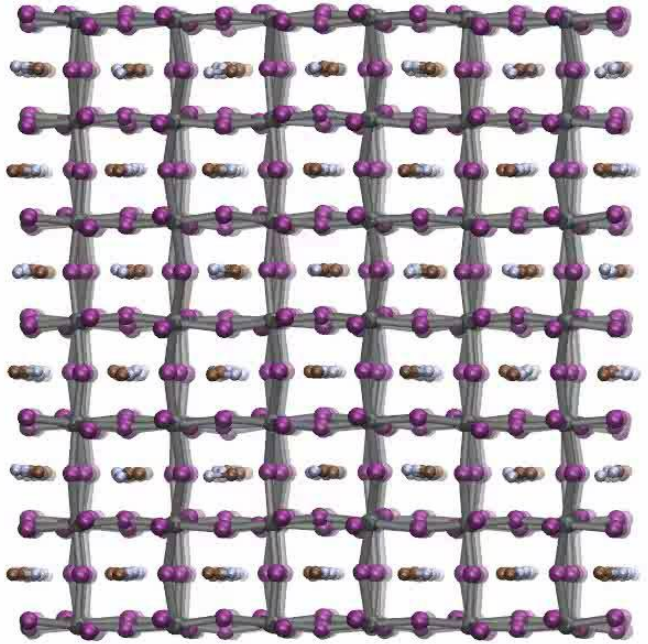
psuedo-cubic lattice constants



Order Parameters

XY plane



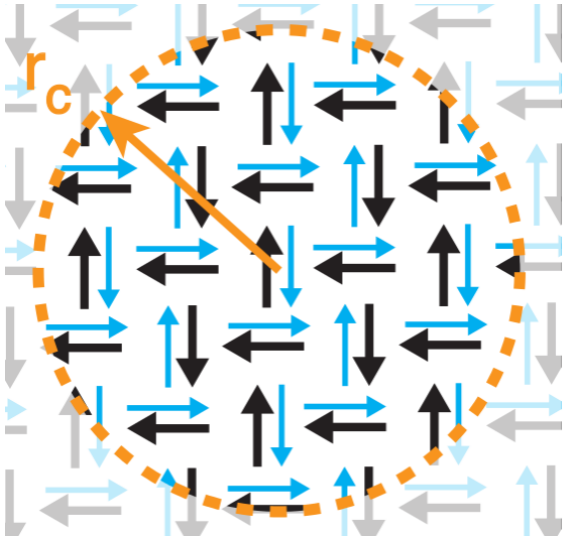


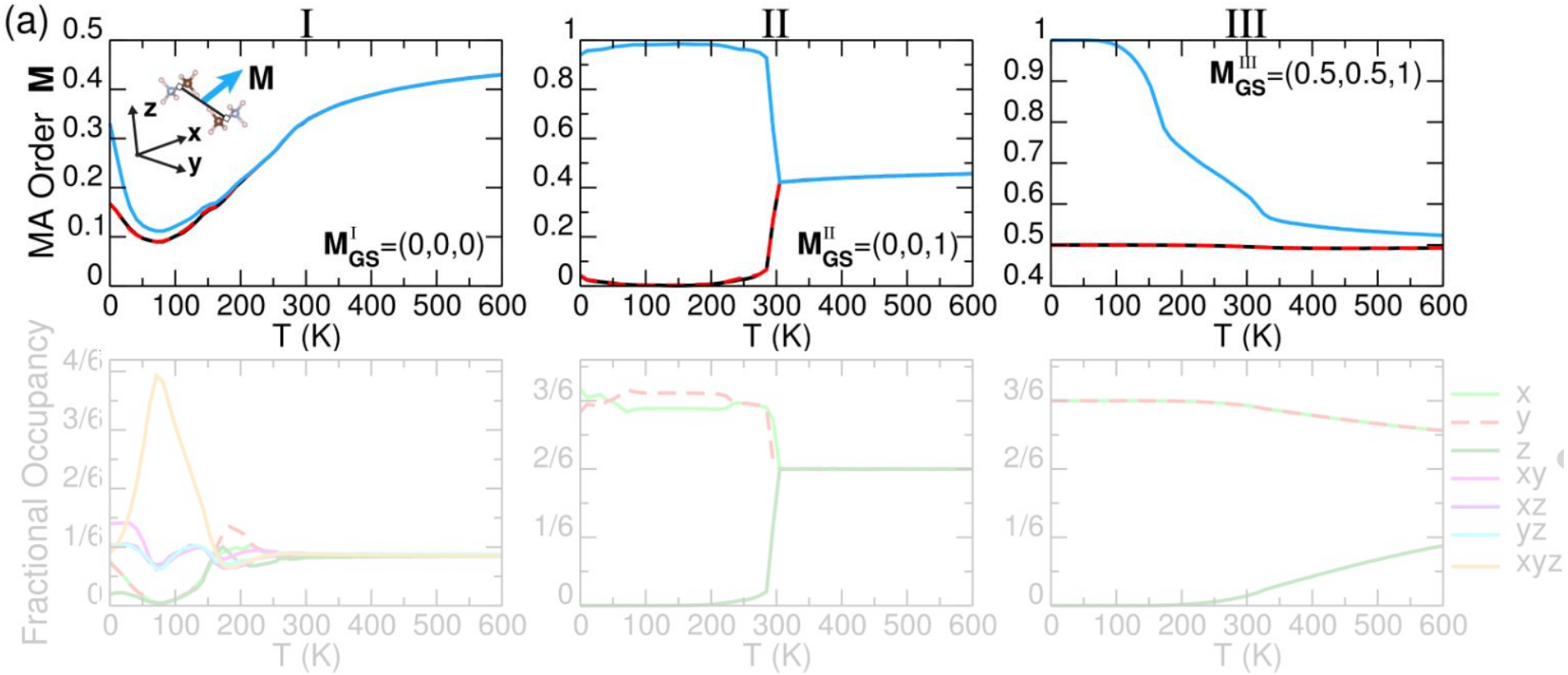
XZ plane

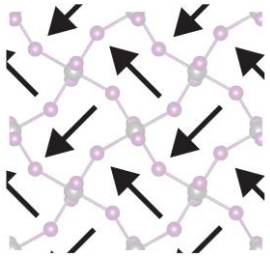
"Librational Pathways"

Movies:
dynamicsolids.net/sm/2019-mlff-perovskites

Monte-Carlo simulations analysed with order parameter **M**







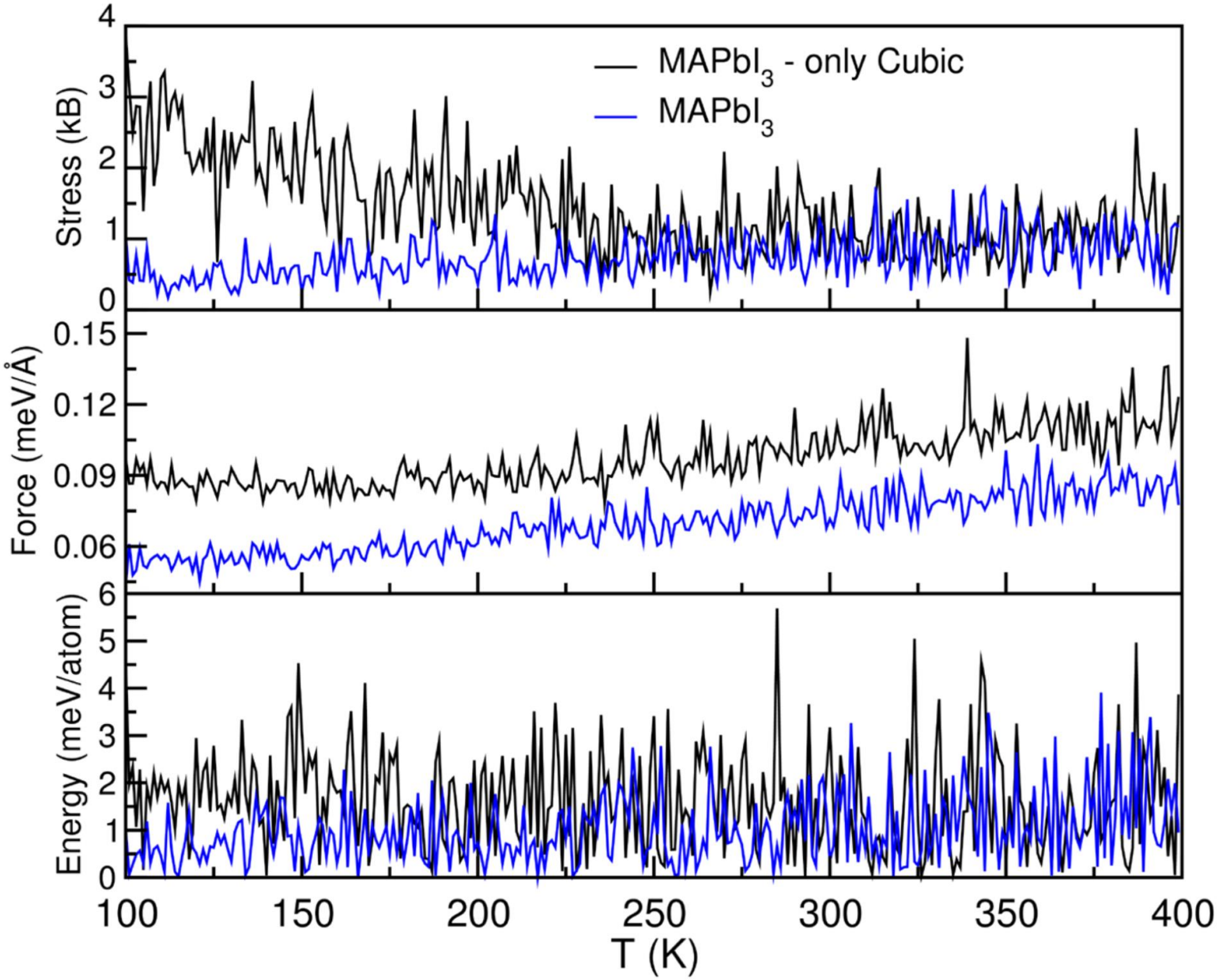
Lahnsteiner *et al.,* Phys. Rev. B **100**, 094106 (2019)

Model I: **Frost** *et al.*, APL Materials **2**, 081506 (2014) and Nature Comm. 6, 7124 (2015).
Model II: **Tan** *et al.*, ACS Energy Lett. **2**, 937 (2017).
Model III: **Simenas** *et al.*, J. Phys. Chem. Lett. **8**, 4906 (2017).

Machine-Learning Force Fields (MLLF)

Error estimation

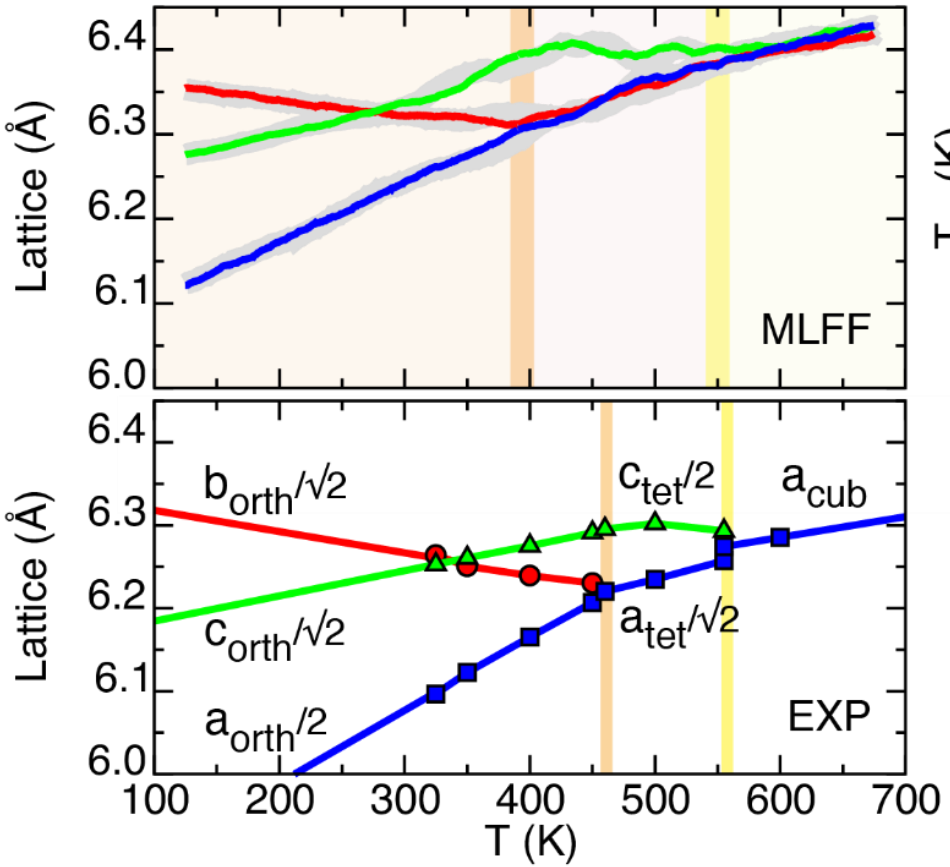
Can give new physical insight!

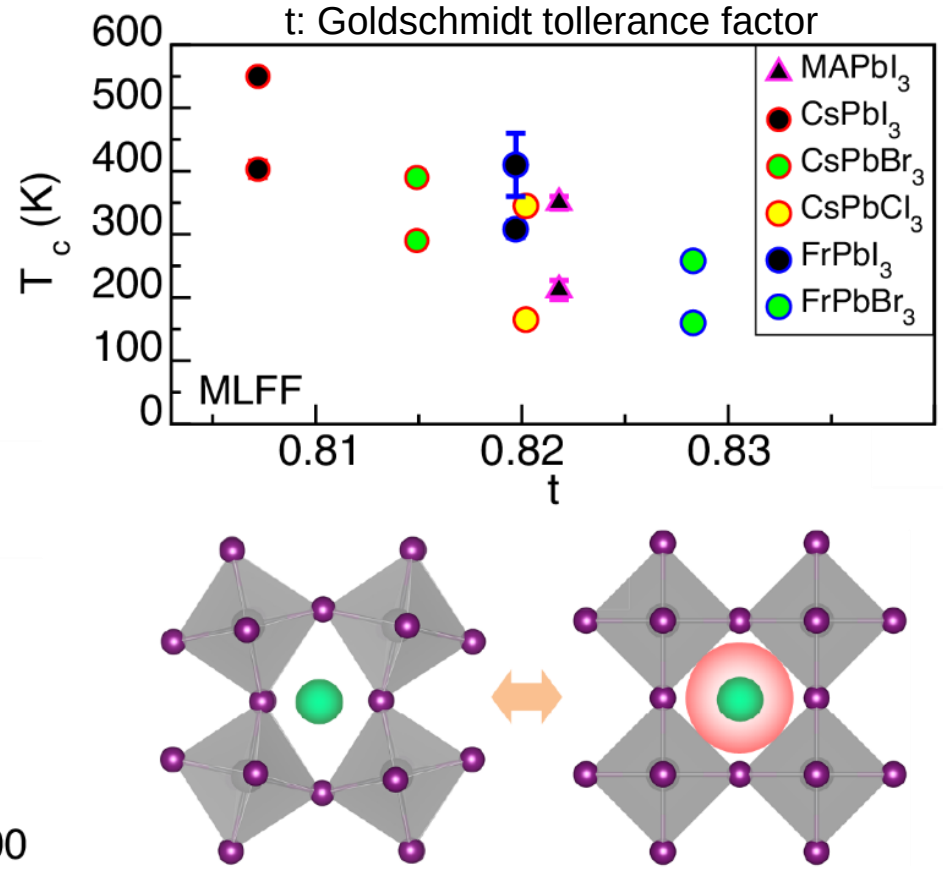


Machine-Learning Force Fields (MLLF)

Trained on-the-fly during MD with SCAN DFA

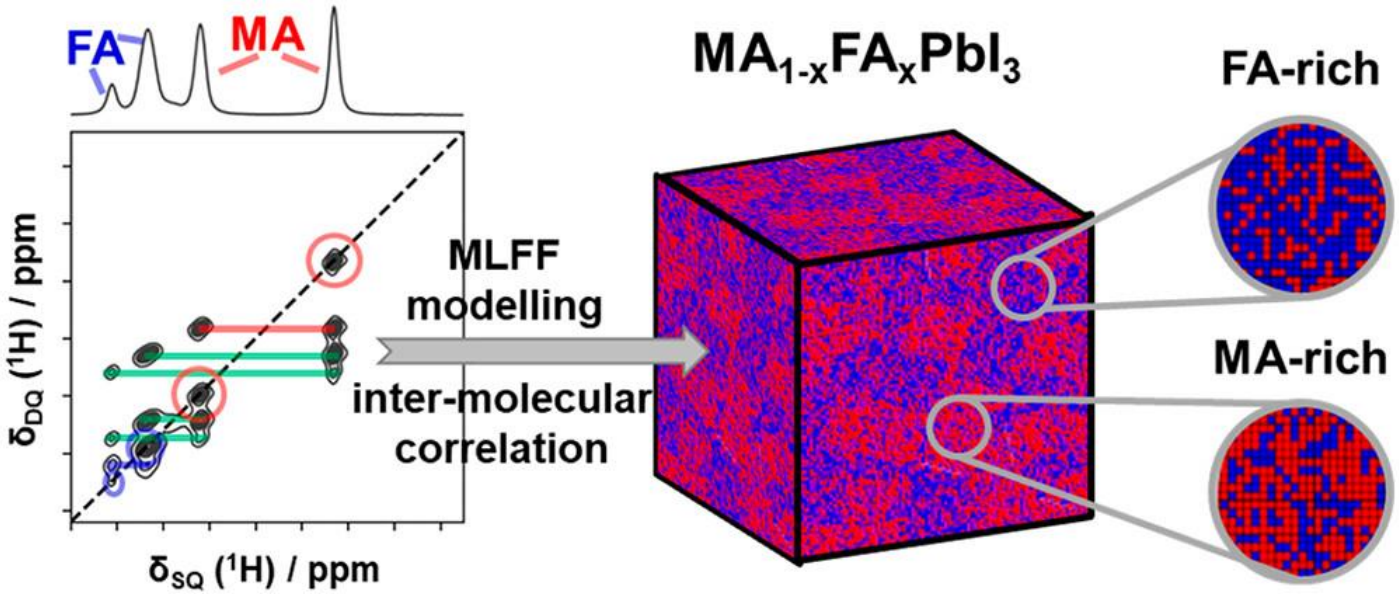
$CsPbI_3$ and other Inorganic perovskites

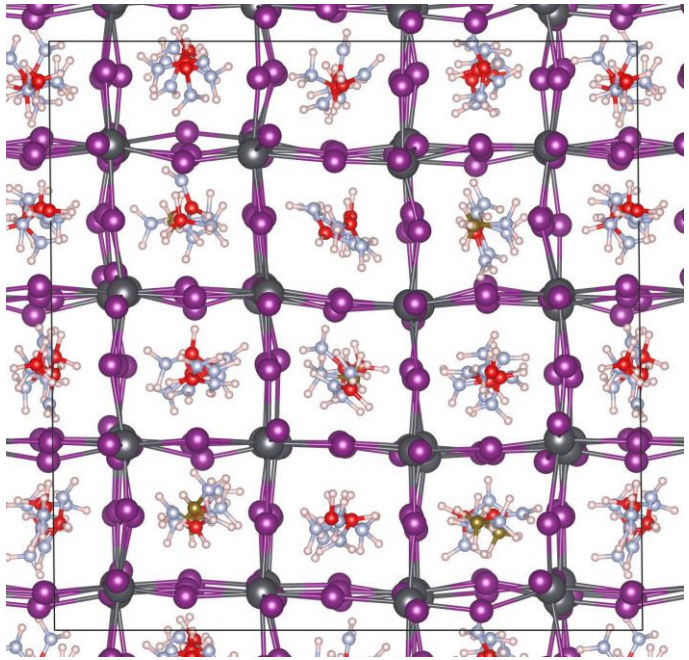




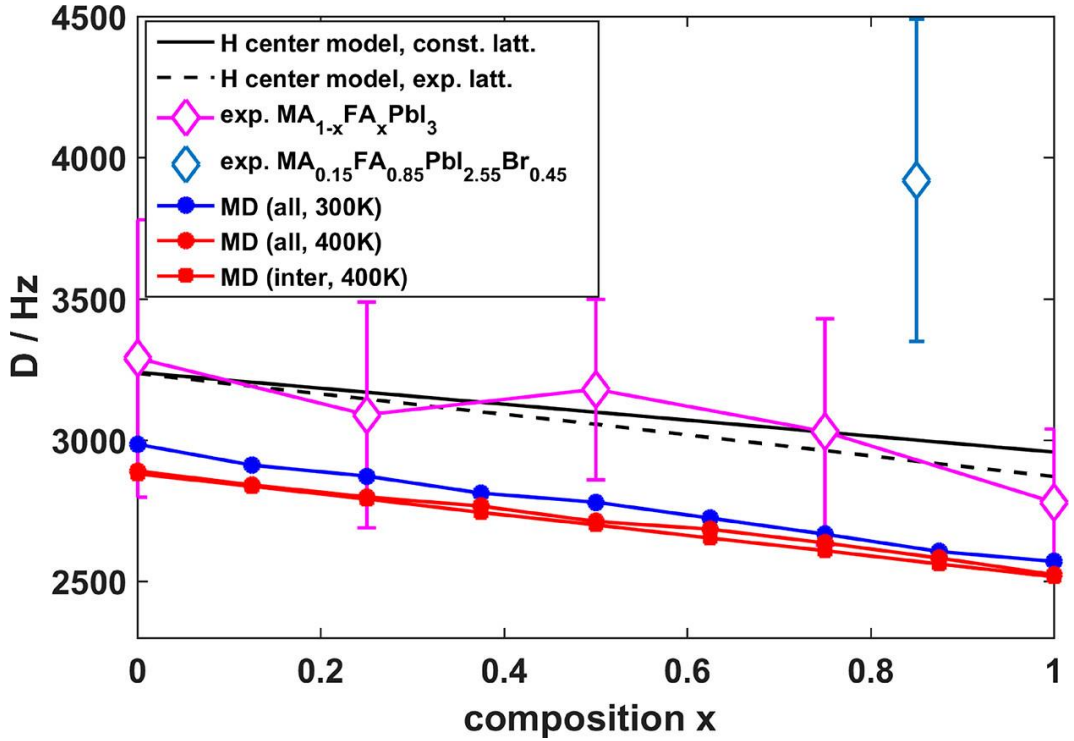
MLFF: Jinnouchi et al**.,** Phys. Rev. Lett. **122**, 225701 (2019)
EXP: A. Marronnier *et al*. ACS Nano 12, 3477 (2018)

MLLF and NMR experiments: resolving more complex crystal structure





Calculate the NMR ^{1}H-^{1}H dipolar coupling coefficient



Grueninger et al., J. Phys. Chem. C, **125**, 1742-1753 (2021)

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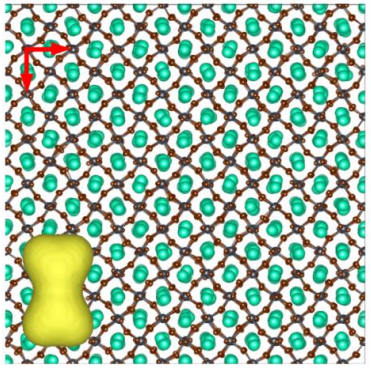
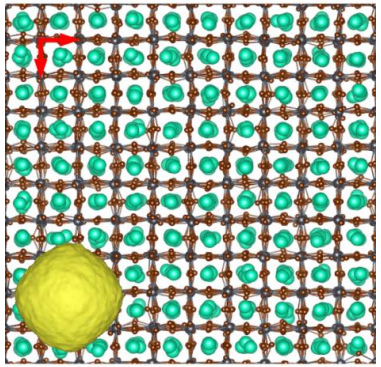
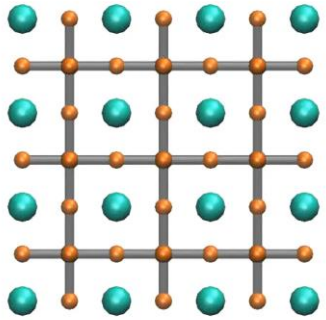
Outlook



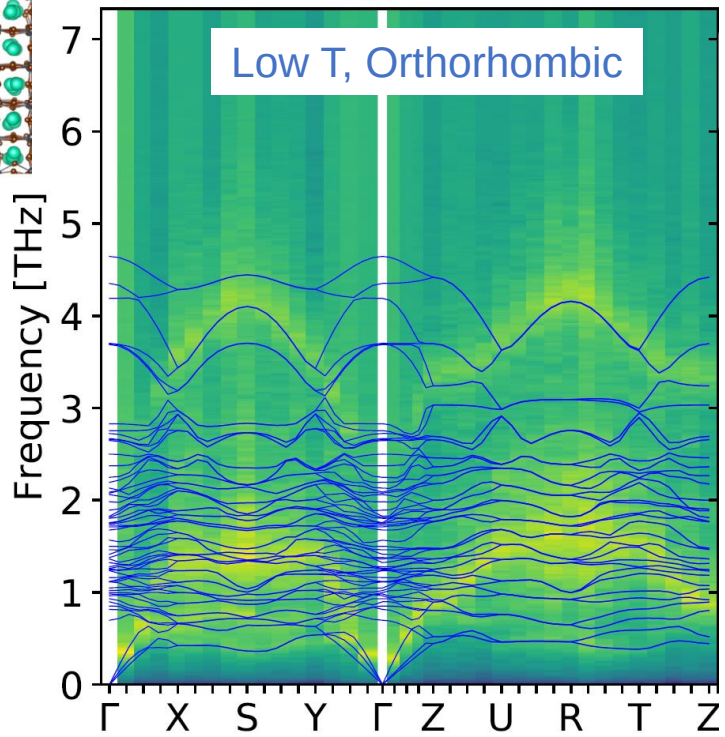


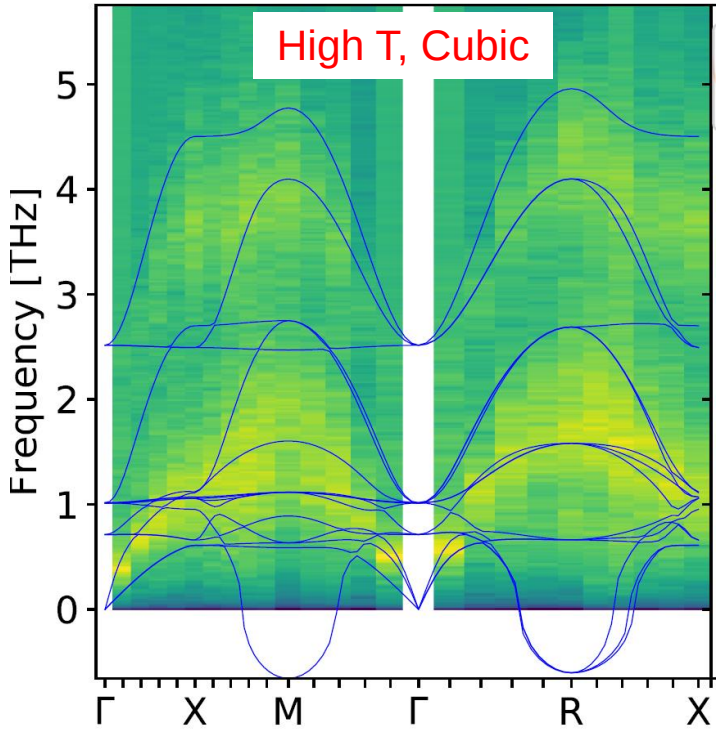
Near first-principles accuracy MLFFs allow us to go beyond the harmonic approximation and study lattice dynamics on the 'real' potential energy surface of complex Dynamic Solids by 'listening' to the system in large-scale molecular-dynamics simulations.



M

Example: $CsPbBr_3$ (10,240 atoms, nanoseconds, microcanonical)

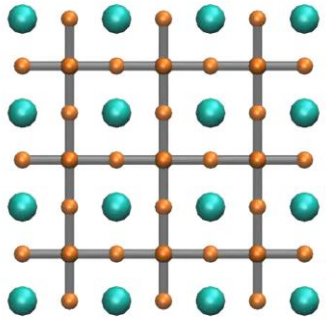




Dynamic Structure Factor $S(\mathbf{k}, \omega)$

Harmonic phonons (finite differences method)

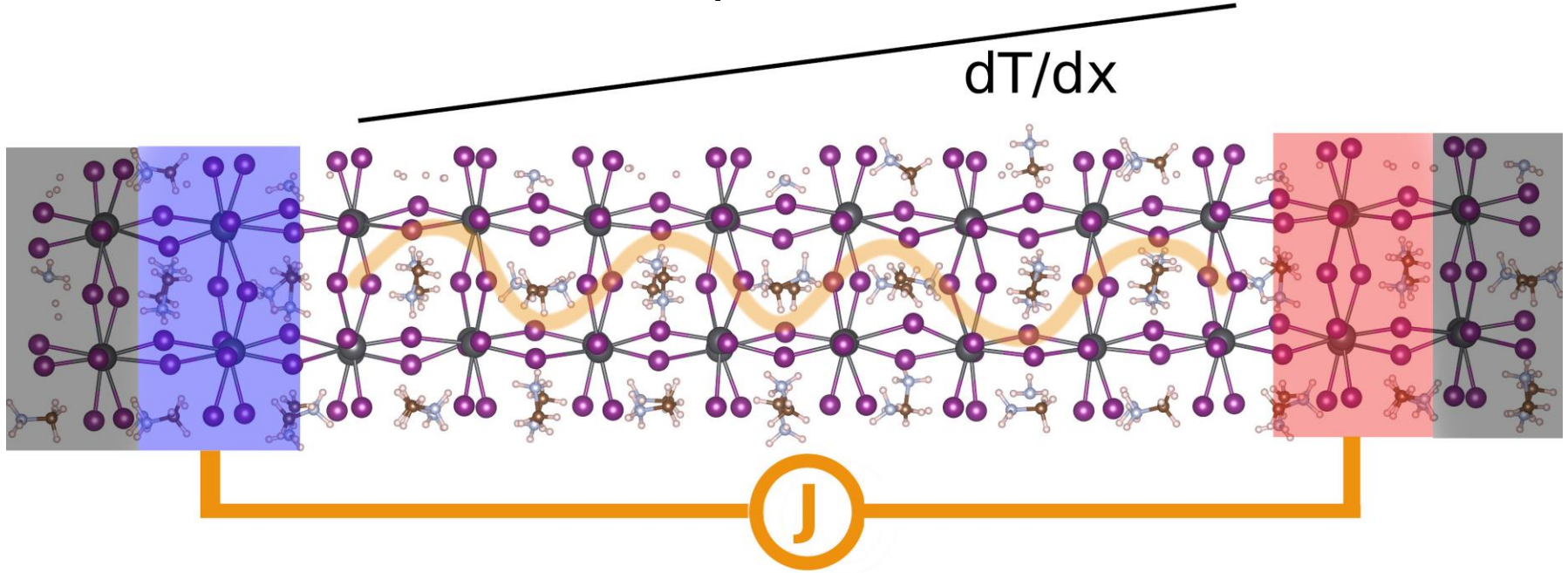
R



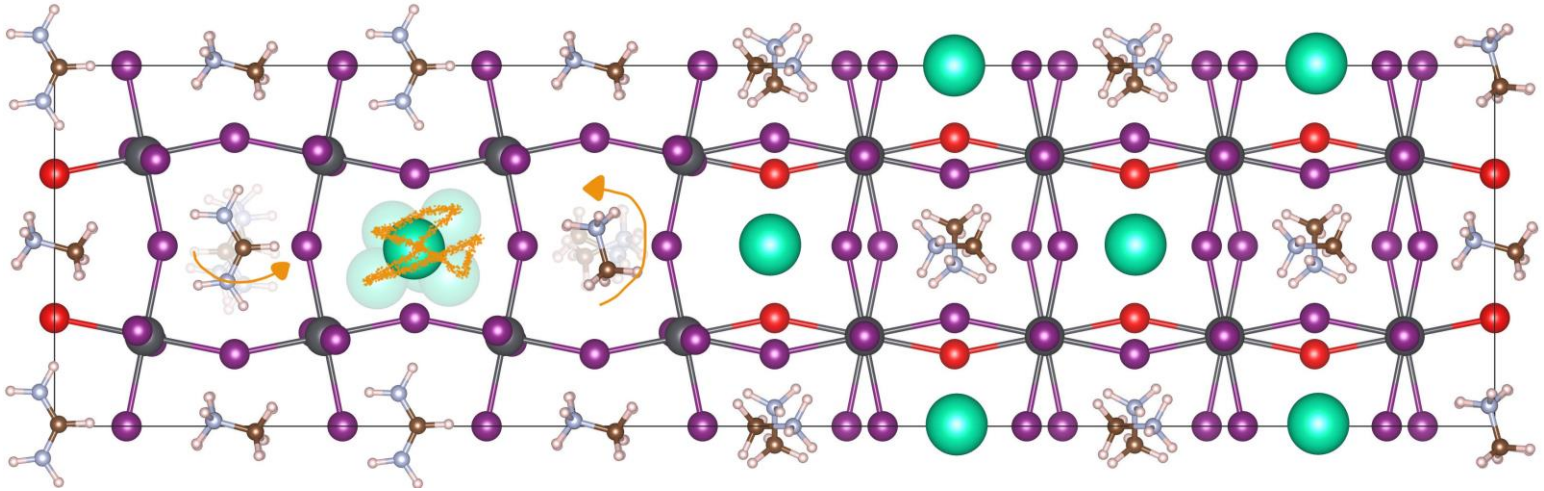
Unpublished, Lahnsteiner & Bokdam (2021)

Outlook

Thermal conductivity: an active measurement?



Increasing complexity, how far can we go?



- Ion transport in batteries
- Hydrogen storage
- Catalysis
- ….

Dynamic Solids

Thank you!

Questions?

Ryosuke Jinnouchi

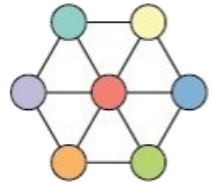
Jonathan Lahnsteiner

Ference Karsai

Georg Kresse

Menno Bokdam

dynamicsolids.net



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