Multibinit lattice part: From ab-initio data to predictive lattice potentials

ABINIT Developer Workshop 2021

M. Schmitt, L. Bastogne, J. Bieder and Ph. Ghosez

Theoretical Materials Physics, CESAM, Université de Liège, B-4000 Liège, Belgium

- Ab-Initio still limited to somewhat short time and length scales.
- State of the art for large scale MD: Reactive Force Fields, and empirical potentials.
- Current research effort: Effective potentials fitted on ab-initio data: Close the gap between ab-initio and effective potentials !
- Our approach: Reproduce the ab-initio potential energy surface (PES) by a polynomial fit $\rightarrow$ second-principles.

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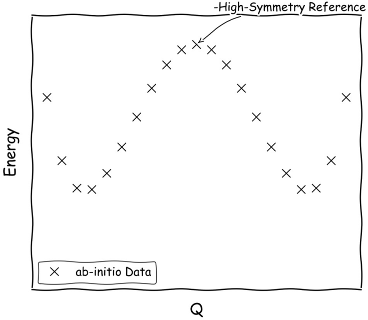

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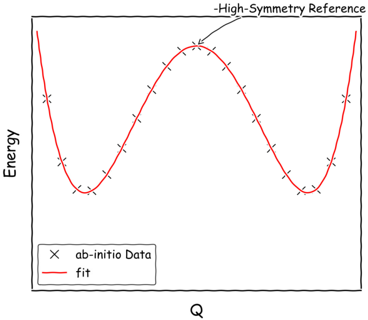

$$E = E_0 + c_2 Q^2 + c_3 Q^3 + c_4 Q^4 \ldots$$

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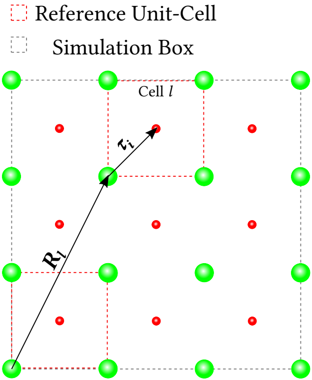
Reference Structure: $\{\mathbf{r}_0\}$



$$r_{0li\alpha} = R_{l\alpha} + \tau_{i\alpha}$$

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115
J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

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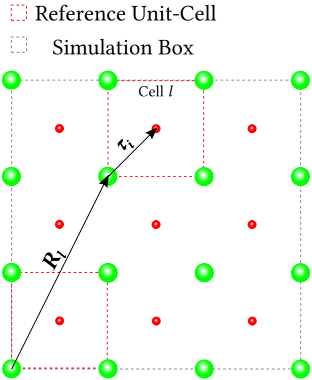

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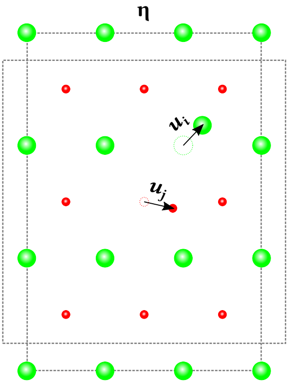
Distorted structure: $\{\mathbf{r}\}$



$$r_{li\alpha} = \sum_{\beta=1}^{3}(\delta_{\alpha\beta} + \eta_{\alpha\beta})r_{0li\beta} + u_{li\alpha}$$

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Modifications of the energy around the reference structure

$$E_{\text{tot}}\left(\{\mathbf{u}_i\},\eta\right) = E_0\left(\{\mathbf{r}_0\},0\right) + E_p\left(\{\mathbf{u}_i\}\right) + E_s(\eta) + E_{sp}\left(\{\mathbf{u}_i\},\eta\right)$$

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Atomic displacements

$$E_p\left(\{\mathbf{u}_i\}\right) = E_p^{Harm}\left(\{\mathbf{u}_i\}\right) + E_p^{Anharm}\left(\{\mathbf{u}_i\}\right)$$

$$K^{(n)}_{i\alpha j\beta\ldots} = \left.\frac{\partial^n E_{tot}}{\partial u_{i\alpha}\partial u_{j\beta}\cdots}\right|_{\eta=0}$$

$K^{(2)}$: Inter-atomic force constant

LIÈGE université

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$$E_s(\eta) = E_s^{Harm}(\eta) + E_s^{Anharm}(\eta)$$

$$C^{(m)}_{ab\ldots} = \frac{1}{N}\left.\frac{\partial^m E_{tot}}{\partial\eta_a\partial\eta_b\cdots}\right|_{u_i=0}$$

$C^{(2)}$: Elastic constant

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$$E_{sp}(\{\mathbf{u}_i\},\eta) = E_{sp}^{Harm}(\{\mathbf{u}_i\},\eta) + E_{sp}^{Anharm}(\{\mathbf{u}_i\},\eta)$$

$$\Lambda^{(m,n)}_{i\alpha a\ldots} = \frac{\partial^m E_{\text{tot}}}{\partial u_{i\alpha}\,\partial\eta_a\cdots}$$

$\Lambda^{(1,1)}$: force–response internal strain tensor

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$\Lambda^{(1,1)}$: force–response internal strain tensor

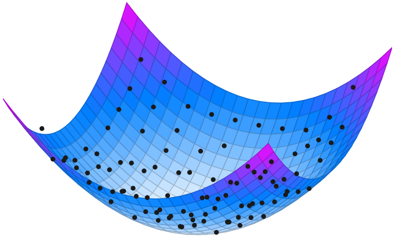
- All atomic degrees of freedom are included
- K^2, C^2, $\Lambda^{(1,1)}$ can be calculated **directly** from DFPT
- **Anharmonic** term parameters: fitted to reproduce representative ab-initio data (TS)

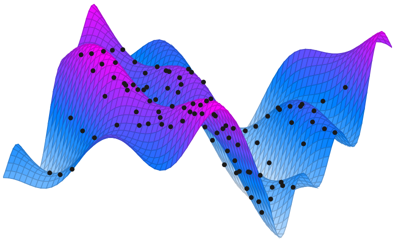
λ	1st order	2nd order		
		$\mathbf{u}$	η	$\mathcal{E}$
$\mathbf{u}$	f	K	Λ	Z^*
η	σ	Λ	C	e^0
$\mathcal{E}$	P	Z^*	e^0	ε^∞

Read from a .DDB file

Choice of TS generation strategy

Two scenarios





One minimum to explore

- Easy to explore with random structures

Several local minima to explore:

- Hard to explore all the minima with random structures

Choice of TS generation strategy

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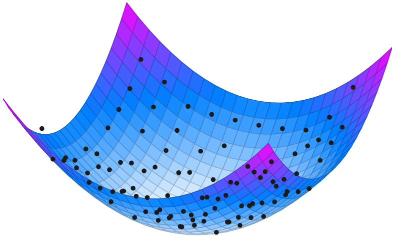

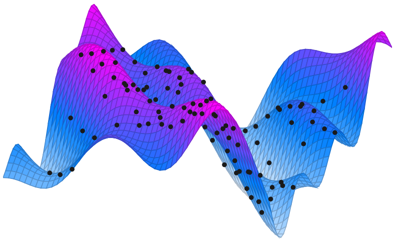

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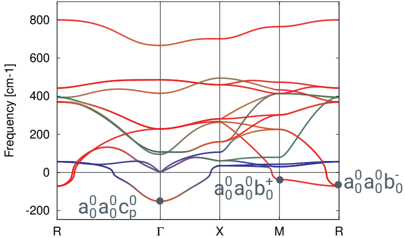
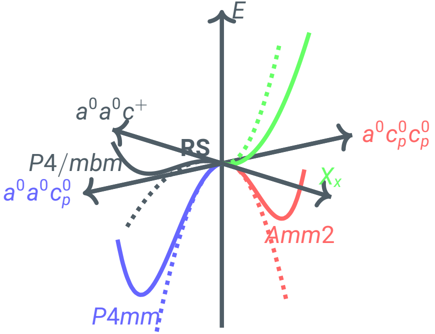
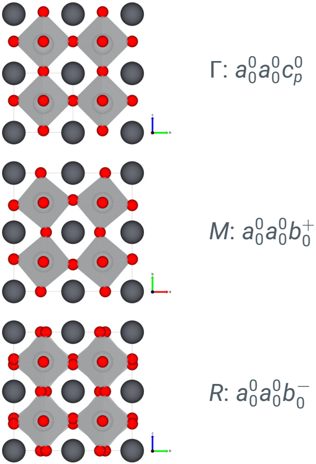
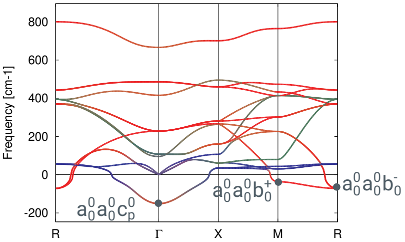
Training set generation | Indentification of instabilities

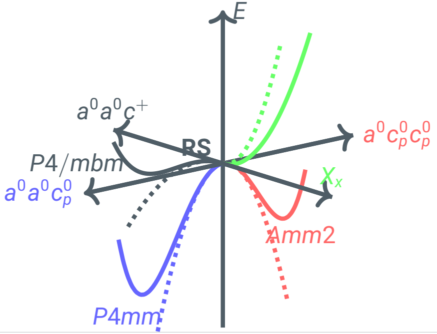


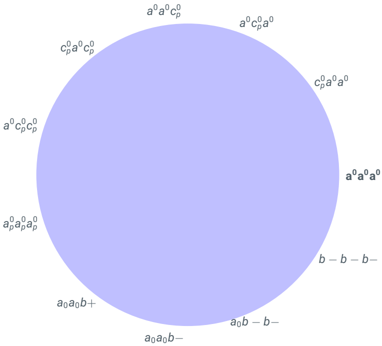




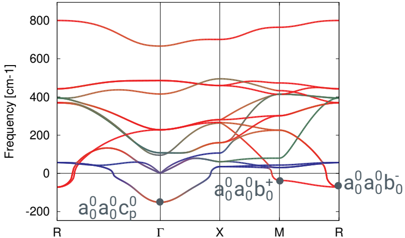
Identification of **instabilities** (negative curvature): anharmonicities are required to build a second-principles potential

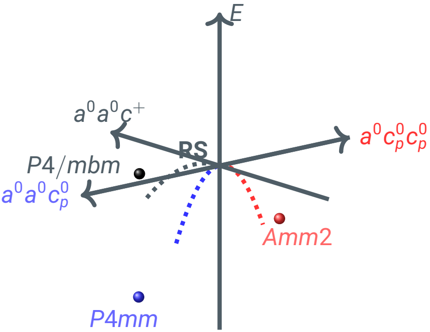


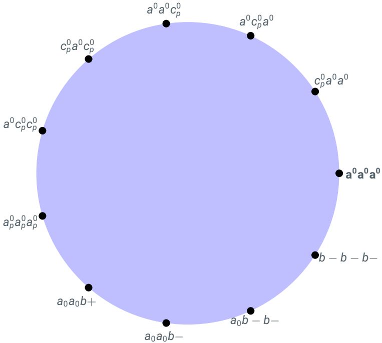




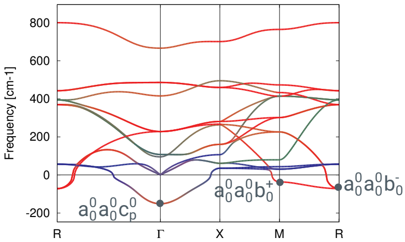
Identification of **instabilities** (negative curvature): reduce the complete B-O surface to the subspace of interest

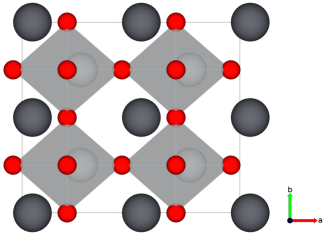


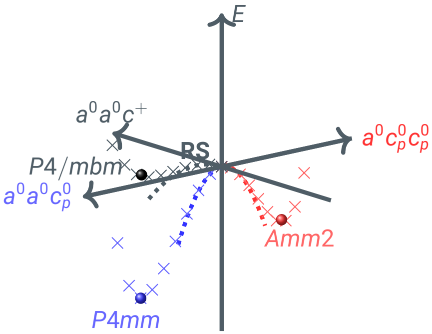




Identification of **instabilities** (negative curvature): Relaxation towards local minima



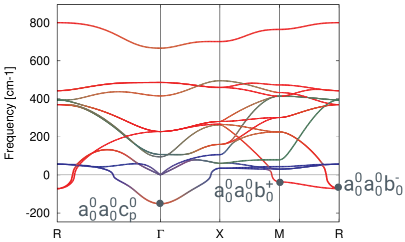


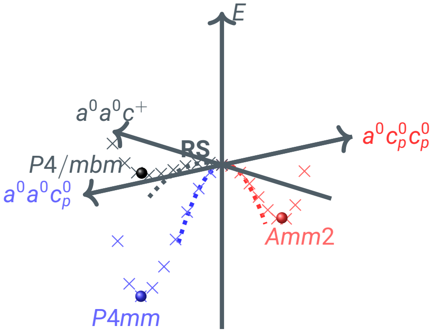


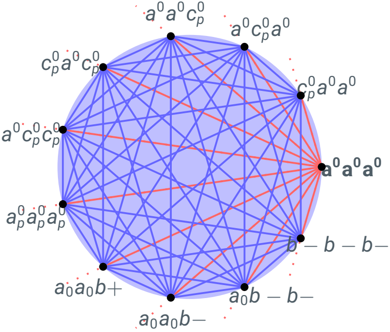
- Linear **Interpolation**: connecting all minima ($\alpha_{max} = 1$):

$$\alpha S_1 + \frac{(\alpha_{max} - \alpha)S_2}{\alpha_{max}}, \quad \alpha \in [0;\alpha_{max}[\qquad (1)$$

- **Extrapolation** after minima ($\alpha_{max} > 1$)



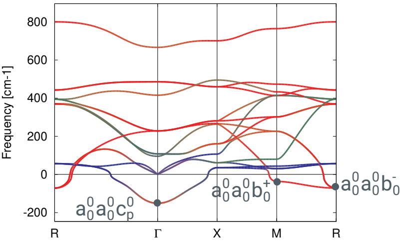


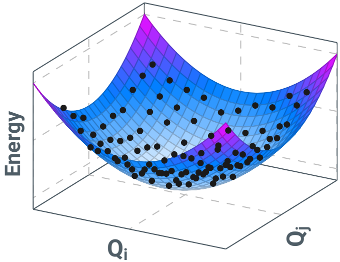


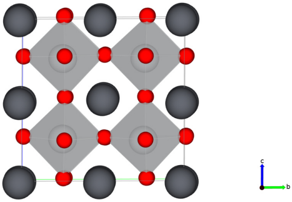
Command in AGATE

```
:interpolate npoints=· amplitude=·
```

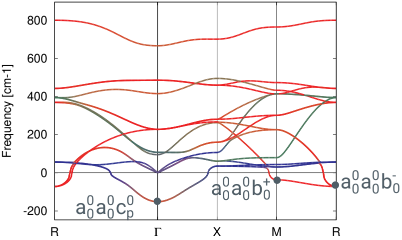
TS generation Phonon & strain noise

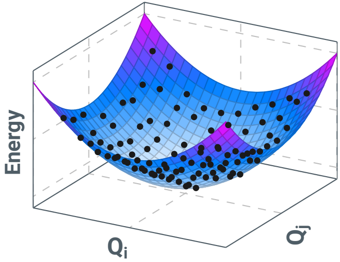


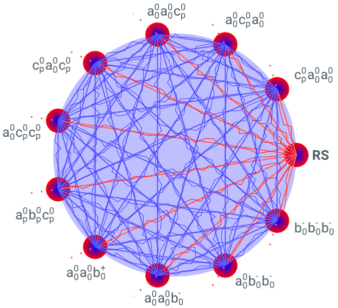




- Thermal population of **stable phonons modes** on minima and paths
- **Strain noise** on minima and paths







Command in AGATE

```
:thermalpop trajectory=·
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  • statistics=Classical/Quantum
  • iso=·:· tetra=·:· shear=·:·
  • temperature=·
```
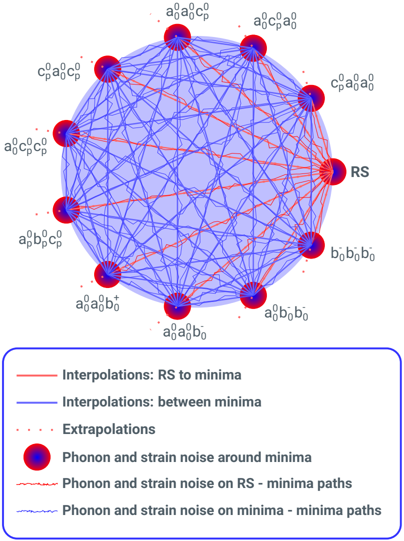
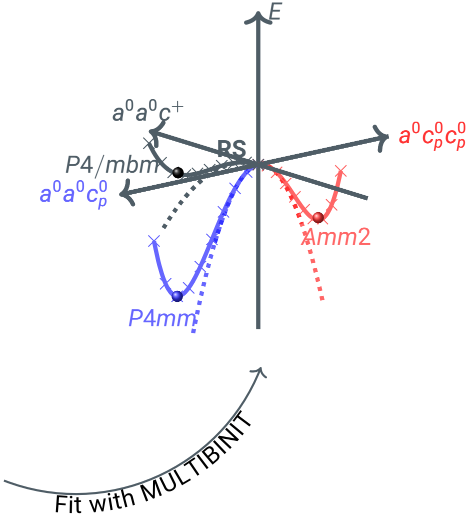


RS
Interpolations: RS to minima
Interpolations: between minima
Extrapolations
Phonon and strain noise around minima
Phonon and strain noise on RS - minima paths
Phonon and strain noise on minima - minima paths


E
RS
P4/mbm
P4mm
Amm2
Fit with MULTIBINIT

Anharmonic Polynomial Expansion

$$E_{tot}(\{\mathbf{u}_i\},\eta) = E_0(\{\mathbf{r}_0\},0) + E_p(\{\mathbf{u}_i\}) + E_s(\eta) + E_{sp}(\{\mathbf{u}_i\},\eta)$$

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$$+ K^{(4)}_{\substack{ijklmnop\\ \alpha\beta\gamma\delta}}(u_{i\alpha}-u_{j\alpha})(u_{k\beta}-u_{l\beta})(u_{m\gamma}-u_{n\gamma})(u_{o\delta}-u_{p\delta})$$

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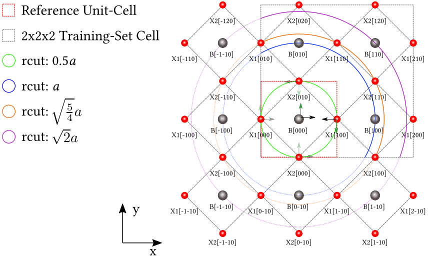
$$E_{sp}^{Anharm} = \Lambda^{(2,1)}_{\substack{ijkl\\ \alpha\beta\\ \gamma}}(u_{i\alpha}-u_{j\alpha})(u_{k\beta}-u_{l\beta})\eta_\gamma$$
$$+ \Lambda^{(1,2)}_{\substack{ij\\ \alpha\\ \beta\gamma}}(u_{i\alpha}-u_{j\alpha})\eta_\beta\eta_\gamma$$
$$+ \ldots$$

- Use symmetry to group terms to symmetry adapted terms: t

$$K^{(4)}_{\substack{BX\\x}}(u_{Bx}-u_{Xx})^4 = K^{(4)}_{\substack{BX[100]\\x}}(u_{Bx}-u_{X[100]x})^4 \in t$$



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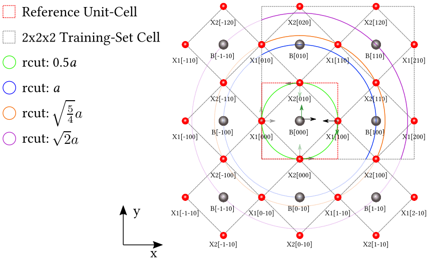
- Input:



Anharmonic Polynomial Expansion

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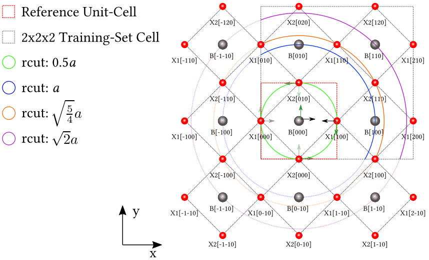
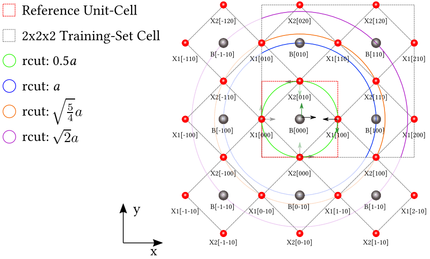
  $K^{(4)}_{\substack{BX\\x}}(u_{Bx}-u_{Xx})^4 = K^{(4)}_{\substack{BX[100]\\x}}(u_{Bx}-u_{X[100]x})^4 \in t$
- Input:
  - Order range of the expansion. Typically 3 to 4.



Anharmonic Polynomial Expansion

- Use symmetry to group terms to symmetry adapted terms: t

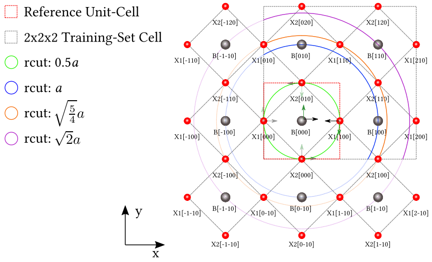
  $K^{(4)}_{\substack{BX\\x}}(u_{Bx}-u_{Xx})^4 = K^{(4)}_{\substack{BX[100]\\x}}(u_{Bx}-u_{X[100]x})^4 \in t$
- Input:
  - Order range of the expansion. Typically 3 to 4.
  - Interaction Range: Maximum distance for $(u_i - u_j)$ pairs



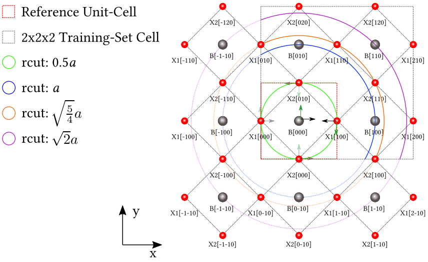
- Use symmetry to group terms to symmetry adapted terms: t

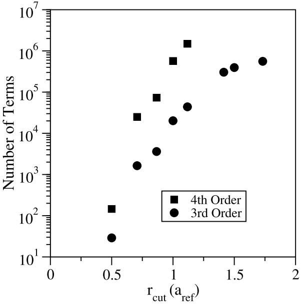
$$K^{(4)}_{\substack{BX\\x}}(u_{Bx}-u_{Xx})^4 = K^{(4)}_{\substack{BX[100]\\x}}(u_{Bx}-u_{X[100]x})^4 \in t$$

- Input:
  - Order range of the expansion. Typically 3 to 4.
  - Interaction Range: Maximum distance for $(u_i - u_j)$ pairs
  - Including Anharmonic strain and strain-phonon coupling



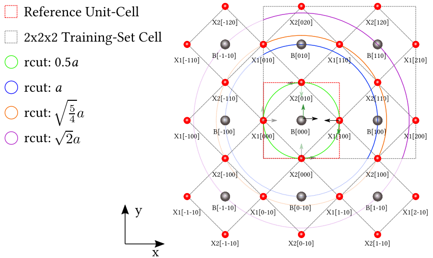
- Use symmetry to group terms to symmetry adapted terms: t
  $K^{(4)}_{\substack{BX\\x}}(u_{Bx}-u_{Xx})^4 = K^{(4)}_{\substack{BX[100]\\x}}(u_{Bx}-u_{X[100]x})^4 \in t$
- Input:
  - Order range of the expansion. Typically 3 to 4.
  - Interaction Range: Maximum distance for $(u_i - u_j)$ pairs
  - Including Anharmonic strain and strain-phonon coupling
  - Maximum order of strain in strain-phonon coupling

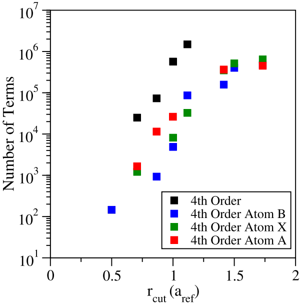




Anharmonic Polynomial Expansion

- Use symmetry to group terms to symmetry adapted terms: t
  $K^{(4)}_{\substack{BX\\x}}(u_{Bx}-u_{Xx})^4 = K^{(4)}_{\substack{BX[100]\\x}}(u_{Bx}-u_{X[100]x})^4 \in t$
- Input:
  - Order range of the expansion. Typically 3 to 4.
  - Interaction Range: Maximum distance for $(u_i - u_j)$ pairs
  - Including Anharmonic strain and strain-phonon coupling
  - Maximum order of strain in strain-phonon coupling
- Reduce number of terms by only including terms of form
  $K^{(3)}_{\substack{ijkl\\ \alpha\beta\gamma}}(u_{i\alpha}-u_{j\alpha})(u_{i\beta}-u_{k\beta})(u_{i\gamma}-u_{l\gamma})$





Fitting the anharmonic expansion

System of linear equations $B = AX$

System of linear equations $B = AX$

$$\begin{pmatrix} E^{DFT}(1) - E^{Har}(1) \\ E^{DFT}(2) - E^{Har}(2) \\ \vdots \\ E^{DFT}(N^{TS}) - E^{Har}(N^{TS}) \\ F^{DFT}_{1x}(1) - F^{Har}_{1x}(1) \\ F^{DFT}_{1y}(1) - F^{Har}_{1y}(1) \\ \vdots \\ F^{DFT}_{n^{TS}_{at}z}(N_{TS}) - F^{Har}_{n^{TS}_{at}z}(N_{TS}) \\ \vdots \\ S^{DFT}_{1}(1) - S^{Har}_{1}(1) \\ S^{DFT}_{2}(1) - S^{Har}_{2}(1) \\ \vdots \\ S^{DFT}_{6}(N_{TS}) - S^{Har}_{6}(N_{TS}) \end{pmatrix} = \begin{pmatrix} t_1(1) & t_2(1) & t_3(1) & \cdots & t_N(1) \\ t_1(2) & t_2(2) & t_3(2) & \cdots & t_N(2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ t_1(N^{TS}) & t_2(N^{TS}) & t_3(N^{TS}) & \cdots & t_N(N^{TS}) \\ \frac{\partial t_1}{\partial u_{1x}}(1) & \frac{\partial t_2}{\partial u_{1x}}(1) & \frac{\partial t_3}{\partial u_{1x}}(1) & \cdots & \frac{\partial t_N}{\partial u_{1x}}(1) \\ \frac{\partial t_1}{\partial u_{1y}}(1) & \frac{\partial t_2}{\partial u_{1y}}(1) & \frac{\partial t_3}{\partial u_{1y}}(1) & \cdots & \frac{\partial t_N}{\partial u_{1y}}(1) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\partial t_1}{\partial u_{n^{TS}_{at}z}}(N^{TS}) & \frac{\partial t_2}{\partial u_{n^{TS}_{at}z}}(N^{TS}) & \frac{\partial t_3}{\partial u_{n^{TS}_{at}z}}(N^{TS}) & \cdots & \frac{\partial t_N}{\partial u_{n^{TS}_{at}z}}(N^{TS}) \\ \frac{\partial t_1}{\partial \eta_1}(1) & \frac{\partial t_2}{\partial \eta_1}(1) & \frac{\partial t_3}{\partial \eta_1}(1) & \cdots & \frac{\partial t_N}{\partial \eta_1}(1) \\ \frac{\partial t_1}{\partial \eta_2}(1) & \frac{\partial t_2}{\partial \eta_2}(1) & \frac{\partial t_3}{\partial \eta_2}(1) & \cdots & \frac{\partial t_N}{\partial \eta_2}(1) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\partial t_1}{\partial \eta_6}(N^{TS}) & \frac{\partial t_2}{\partial \eta_6}(N^{TS}) & \frac{\partial t_3}{\partial \eta_6}(N^{TS}) & \cdots & \frac{\partial t_N}{\partial \eta_6}(N^{TS}) \end{pmatrix} \begin{pmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \\ \vdots \\ \theta_N \end{pmatrix}$$

System of linear equations $B = AX$

$$
\begin{pmatrix}
E^{DFT}(1) - E^{Har}(1) \\
E^{DFT}(2) - E^{Har}(2) \\
\vdots \\
E^{DFT}(N^{TS}) - E^{Har}(N^{TS}) \\
F^{DFT}_{1x}(1) - F^{Har}_{1x}(1) \\
F^{DFT}_{1y}(1) - F^{Har}_{1y}(1) \\
\vdots \\
F^{DFT}_{n^{TS}_{at}z}(N_{TS}) - F^{Har}_{n^{TS}_{at}z}(N_{TS}) \\
\vdots \\
S^{DFT}_1(1) - S^{Har}_1(1) \\
S^{DFT}_2(1) - S^{Har}_2(1) \\
\vdots \\
S^{DFT}_6(N_{TS}) - S^{Har}_6(N_{TS})
\end{pmatrix}
=
\begin{pmatrix}
t_1(1) & t_2(1) & t_3(1) & \cdots & t_N(1) \\
t_1(2) & t_2(2) & t_3(2) & \cdots & t_N(2) \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
t_1(N^{TS}) & t_2(N^{TS}) & t_3(N^{TS}) & \cdots & t_N(N^{TS}) \\
\frac{\partial t_1}{\partial u_{1x}}(1) & \frac{\partial t_2}{\partial u_{1x}}(1) & \frac{\partial t_3}{\partial u_{1x}}(1) & \cdots & \frac{\partial t_N}{\partial u_{1x}}(1) \\
\frac{\partial t_1}{\partial u_{1y}}(1) & \frac{\partial t_2}{\partial u_{1y}}(1) & \frac{\partial t_3}{\partial u_{1y}}(1) & \cdots & \frac{\partial t_N}{\partial u_{1y}}(1) \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\frac{\partial t_1}{\partial u_{n^{TS}_{at}z}}(N^{TS}) & \frac{\partial t_2}{\partial u_{n^{TS}_{at}z}}(N^{TS}) & \frac{\partial t_3}{\partial u_{n^{TS}_{at}z}}(N^{TS}) & \cdots & \frac{\partial t_N}{\partial u_{n^{TS}_{at}z}}(N^{TS}) \\
\frac{\partial t_1}{\partial \eta_1}(1) & \frac{\partial t_2}{\partial \eta_1}(1) & \frac{\partial t_3}{\partial \eta_1}(1) & \cdots & \frac{\partial t_N}{\partial \eta_1}(1) \\
\frac{\partial t_1}{\partial \eta_2}(1) & \frac{\partial t_2}{\partial \eta_2}(1) & \frac{\partial t_3}{\partial \eta_2}(1) & \cdots & \frac{\partial t_N}{\partial \eta_2}(1) \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\frac{\partial t_1}{\partial \eta_6}(N^{TS}) & \frac{\partial t_2}{\partial \eta_6}(N^{TS}) & \frac{\partial t_3}{\partial \eta_6}(N^{TS}) & \cdots & \frac{\partial t_N}{\partial \eta_6}(N^{TS})
\end{pmatrix}
\begin{pmatrix}
\theta_1 \\ \theta_2 \\ \theta_3 \\ \vdots \\ \theta_N
\end{pmatrix}
$$

$\rightarrow$ Way too many independent coefficients to determine.
$\rightarrow$ Select *some important* terms and fit their coefficients.

Step forward selection procedure

$$min||B - AX||^2 \text{ and } min\ \theta_i \neq 0$$

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

Step forward selection procedure

$$min||B - AX||^2 \text{ and } min\ \theta_i \neq 0$$

$$G(\Theta_p, TS) = \frac{1}{N_1}\sum_s \frac{1}{\Omega^1(s)}(E^{Anh}_{DFT}(s) - E^{Anh}(\Theta_p, s))^2 + \frac{1}{N_2}\sum_{si\alpha}(F^{Anh}_{DFTi\alpha}(s) - F^{Anh}_{i\alpha}(\Theta_p, s))^2$$
$$+ \frac{1}{N_3}\sum_{s\kappa}\Omega^2(s)(S^{Anh}_{DFT,\kappa}(s) - S^{Anh}_{\kappa}(\Theta_p, s))^2$$

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

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$$+ \frac{1}{N_3}\sum_{s\kappa}\Omega^2(s)(S^{Anh}_{DFT,\kappa}(s) - S^{Anh}_{\kappa}(\Theta_p, s))^2$$

Start with the set of p coefficients θ_p

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

Step forward selection procedure

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$$+\frac{1}{N_3}\sum_{s\kappa}\Omega^2(s)(S^{Anh}_{DFT,\kappa}(s) - S^{Anh}_{\kappa}(\Theta_p, s))^2$$

Start with the set of p coefficients θ_p

↓

$min\ \ G(\Theta^i_1, TS)\ \forall\ i\ in\ p$ $\longrightarrow$ select term θ_i with $\arg\min_i(G(\Theta^i_1, TS))$

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

Step forward selection procedure

$$min||B - AX||^2 \text{ and } min\ \theta_i \neq 0$$

$$G(\Theta_p, TS) = \frac{1}{N_1}\sum_s \frac{1}{\Omega^1(s)}(E^{Anh}_{DFT}(s) - E^{Anh}(\Theta_p, s))^2 + \frac{1}{N_2}\sum_{si\alpha}(F^{Anh}_{DFTi\alpha}(s) - F^{Anh}_{i\alpha}(\Theta_p, s))^2$$
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Start with the set of p coefficients θ_p

↓

$min\ G(\Theta^i_1, TS)\ \forall\ i\ in\ p$ → select term θ_i with $\arg\min_i(G(\Theta^i_1, TS))$

↓

$min\ G(\Theta^i_2, TS)\ \forall\ i\ in\ p - 1$ → select term θ_i with $\arg\min_i(G(\Theta^i_2, TS))$

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

Step forward selection procedure

$$min||B - AX||^2 \text{ and } min\ \theta_i \neq 0$$

$$G(\Theta_p, TS) = \frac{1}{N_1}\sum_s \frac{1}{\Omega^1(s)}(E^{Anh}_{DFT}(s) - E^{Anh}(\Theta_p, s))^2 + \frac{1}{N_2}\sum_{si\alpha}(F^{Anh}_{DFTi\alpha}(s) - F^{Anh}_{i\alpha}(\Theta_p, s))^2$$
$$+\frac{1}{N_3}\sum_{s\kappa}\Omega^2(s)(S^{Anh}_{DFT,\kappa}(s) - S^{Anh}_{\kappa}(\Theta_p, s))^2$$

Start with the set of p coefficients θ_p

↓

$$min\ G(\Theta^i_1, TS)\ \forall\ i\ in\ p \quad \rightarrow \text{ select term } \theta_i \text{ with } \arg\min_i(G(\Theta^i_1, TS))$$

↓

$$min\ G(\Theta^i_2, TS)\ \forall\ i\ in\ p - 1 \quad \rightarrow \text{ select term } \theta_i \text{ with } \arg\min_i(G(\Theta^i_2, TS))$$

↓

$$min\ G(\Theta^i_3, TS)\ \forall\ i\ in\ p - 2 \quad \rightarrow \text{ select term } \theta_i \text{ with } \arg\min_i(G(\Theta^i_3, TS))$$

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

Step forward selection procedure

$$min||B - AX||^2 \text{ and } min\ \theta_i \neq 0$$

$$G(\Theta_p, TS) = \frac{1}{N_1}\sum_s \frac{1}{\Omega^1(s)}(E^{Anh}_{DFT}(s) - E^{Anh}(\Theta_p, s))^2 + \frac{1}{N_2}\sum_{si\alpha}(F^{Anh}_{DFTi\alpha}(s) - F^{Anh}_{i\alpha}(\Theta_p, s))^2$$
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Start with the set of p coefficients θ_p

↓

$min\ G(\Theta^i_1, TS)\ \forall\ i\ in\ p$ $\rightarrow$ select term θ_i with $\arg\min_i(G(\Theta^i_1, TS))$

↓

$min\ G(\Theta^i_2, TS)\ \forall\ i\ in\ p - 1$ $\rightarrow$ select term θ_i with $\arg\min_i(G(\Theta^i_2, TS))$

↓

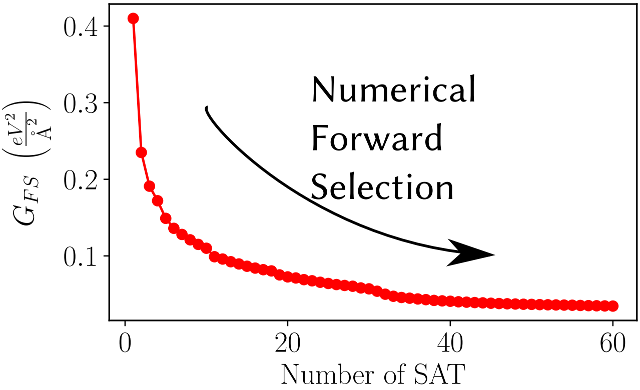
$min\ G(\Theta^i_3, TS)\ \forall\ i\ in\ p - 2$ $\rightarrow$ select term θ_i with $\arg\min_i(G(\Theta^i_3, TS))$

↓

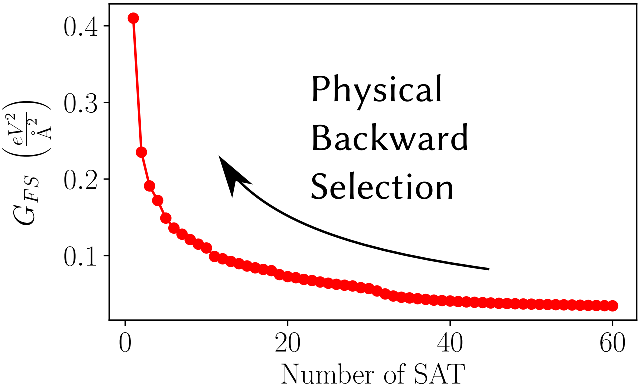
$min\ G(\Theta^i_4, TS)\ \forall\ i\ in\ p - 3$ $\rightarrow$ select term θ_i with $\arg\min_i(G(\Theta^i_4, TS))$...

Escorihuela-Sayaler et al., Phys. Rev. B **95**, 094115

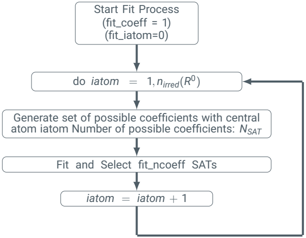
Step forward selection procedure

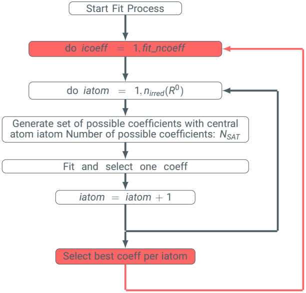


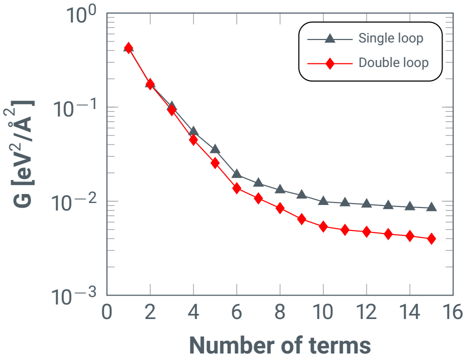
Step forward selection procedure



Different fitting schemes







Outlook: Learn from machine learning

- Use methods known in **compressive sensing** techniques: LASSO and Elastic/Net Penalizations
- Add penalization term to least squares operator, rewarding solutions with few non zero coefficients.
- Use filtering techniques to eject terms with little corelation to the ab-inito data from fit and selection procedure.

LASSO

$$\hat{X} = \arg\min_{X}(||B - AX||^2 + \alpha||X||_1)$$

Elastic Net

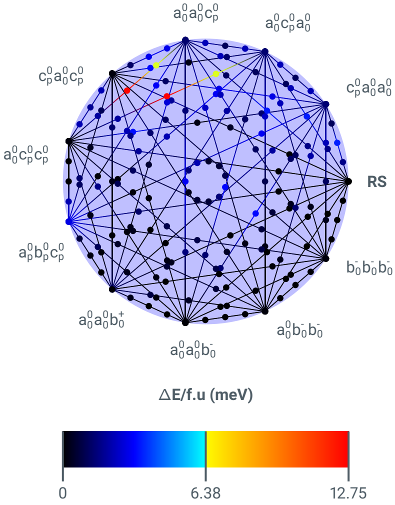
$$\hat{X} = \arg\min_{X}(||B - AX||^2 + \alpha_1||X||_1 + \alpha_2||X||^2)$$

Pearson Correlation

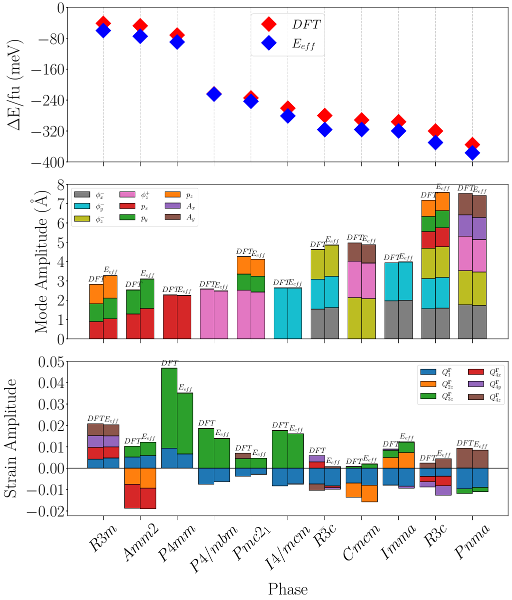
$$r_{xy} = \frac{\sum_i^N (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i^N (x_i - \bar{x})^2}\sqrt{(\sum_i^N y_i - \bar{y})^2}}$$

Training set reproduction

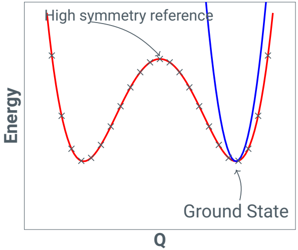
Energy difference: DFT vs. Model.



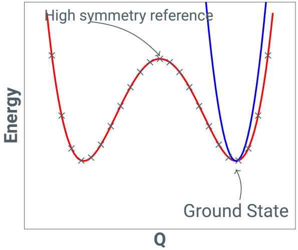
Relaxations

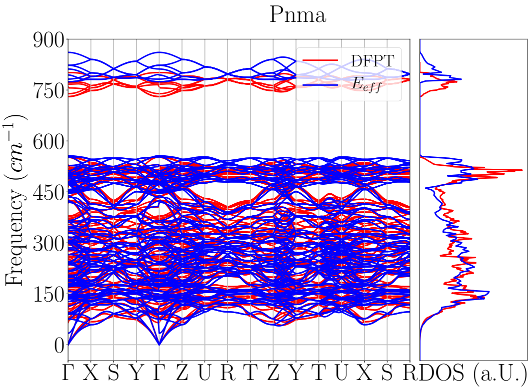


Phonon dispersion curves



Phonon dispersion curves





1 Model definition

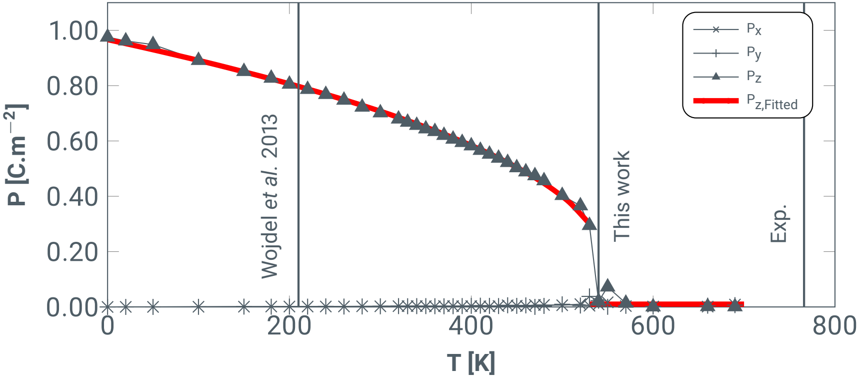
2 Training set generation

3 Model Generation & Fit

4 Testing/validation

5 Predictions & analysis tools

- Lead titanate ($PbTiO_3$)
- Calcium titanate ($CaTiO_3$)



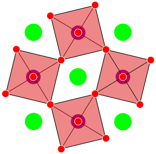
- T_c in better agreement with experiment than previous work
- **First order** phase transition:
  - Discontinuity at T_c
  - $P \sim (T_c - T)^{1/4}$

Command in AGATE

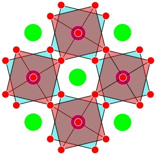
- `:average`
- `:plot xy x=T y="polarization ddb=."`

$CaTiO_3$ Virtual Heating Experiment

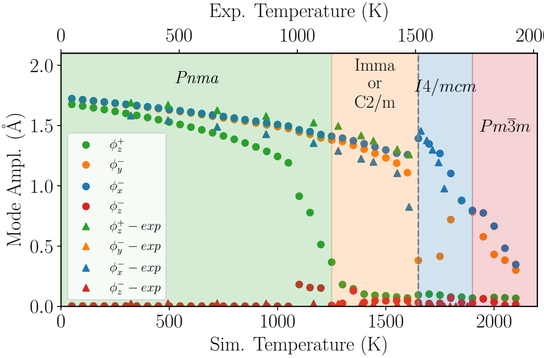
In-Phase Rotation ϕ_z^+



Anti-Phase Rotation ϕ_z^-



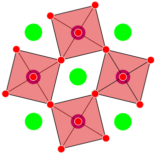
16x16x16 cells, 20480 atoms
Hybrid Monte Carlo Sampling
40000 steps per temperature



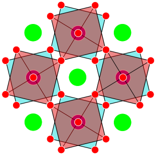
Experimental Transitions: *Pnma* $\rightarrow$ 1512K *I4/mcm* $\rightarrow$ 1636K *Pm$\bar{3}$m*

Yashima, M. & Ali, R., Solid State Ionics, 2009, **180**, 120 - 126

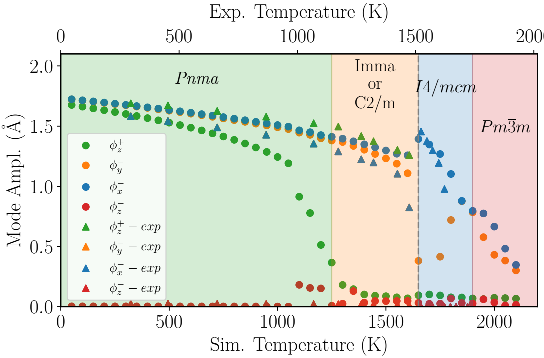
In-Phase Rotation ϕ_z^+



Anti-Phase Rotation ϕ_z^-



16x16x16 cells, 20480 atoms
Hybrid Monte Carlo Sampling
40000 steps per temperature

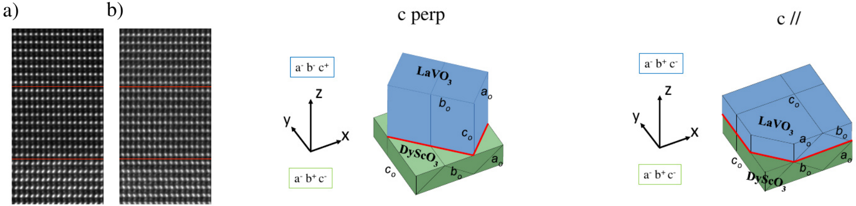


Experimental Transitions: *Pnma* → 1512K *I4/mcm* → 1636K *Pm$\bar{3}$m*

Yashima, M. & Ali, R., Solid State Ionics, 2009, **180**, 120 - 126

→ But phase transition sequence debated. *Imma* intermediate has been proposed

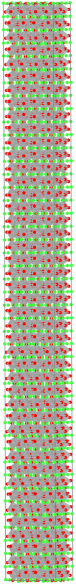
Carpenter M., American Mineralogist (2007) **92** (2-3): 309–327



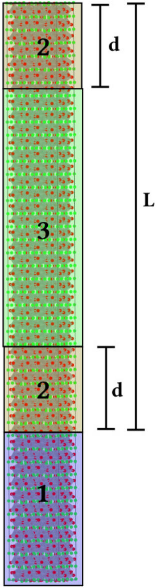
- Thin films (<60 u.c.): only c ||.
- Thick films (>60 u.c.): Mostly c perp. but intermediate layer of about 10 u.c. c ||.
- Elastically favored c perp.

→ Competition between elastic and interface energy at the origin of intermediate layer formation.

Reprodcution of $LaVO_3$/$DyScO_3$ interface

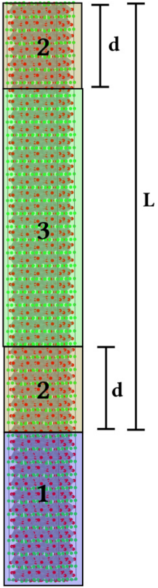


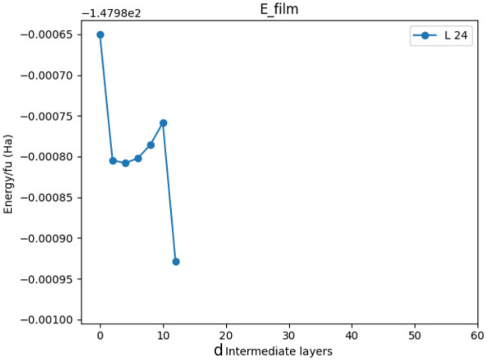
$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface

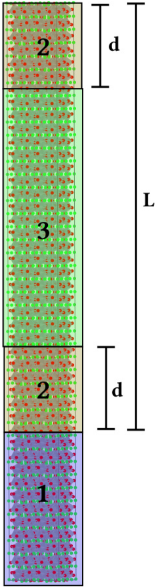


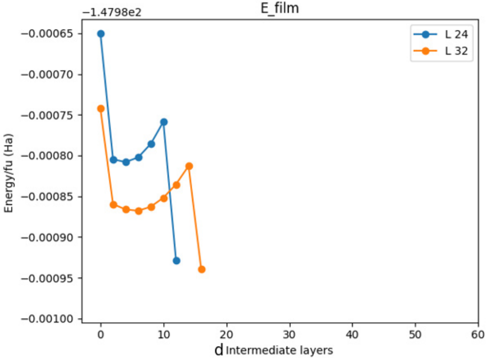
- **1**: *"substrate"* c || with exageratted distortions
- **2**: c || free to relax
- **3**: c perp free to relax

$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface

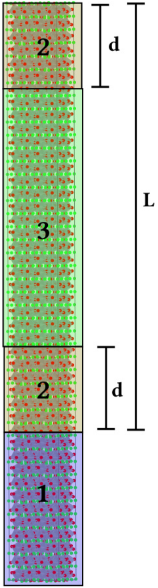


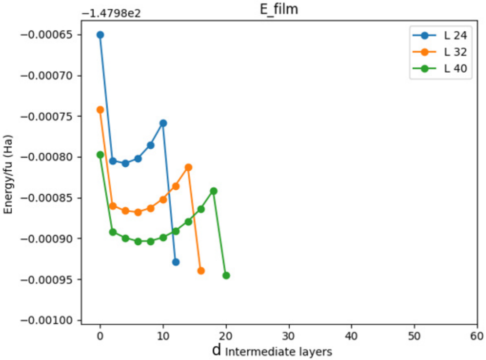



2
d
3
L
2
d
1

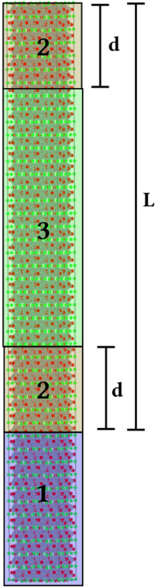

E_film
−1.4798e2
Energy/fu (Ha)
−0.00065
−0.00070
−0.00075
−0.00080
−0.00085
−0.00090
−0.00095
−0.00100
0
10
20
30
40
50
60
d Intermediate layers
L 24
L 32

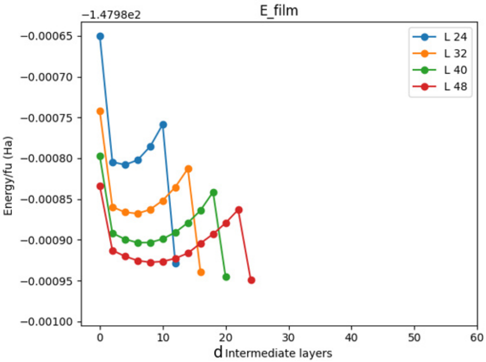
$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface



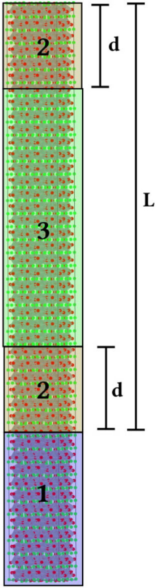


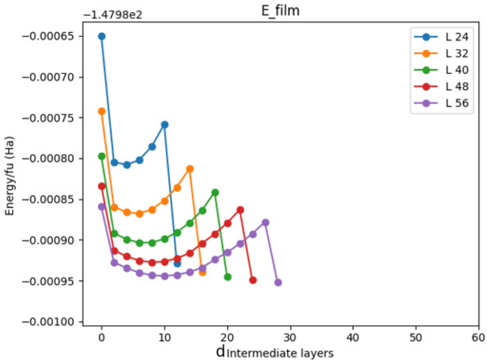
$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface



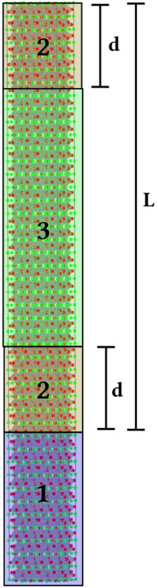


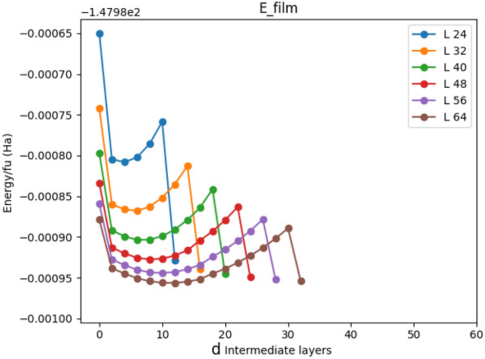
$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface



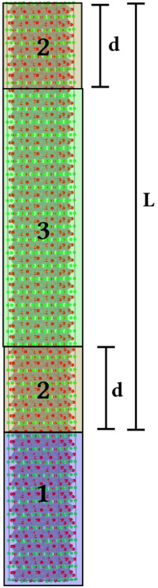


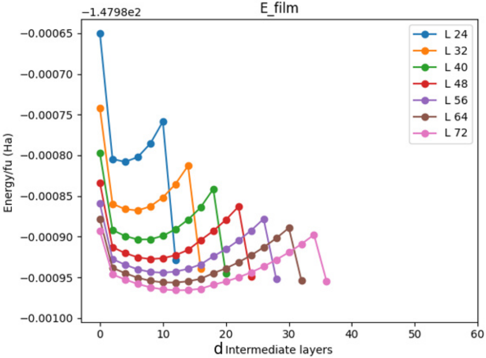
$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface



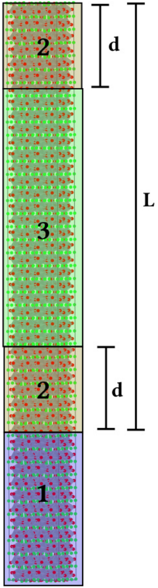


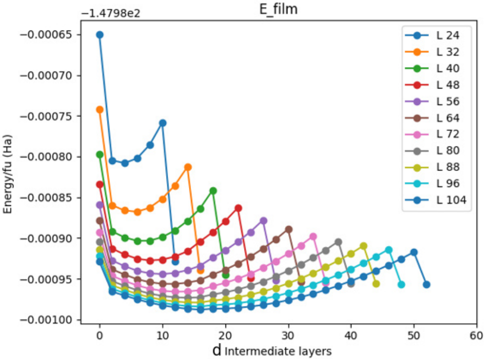
$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface

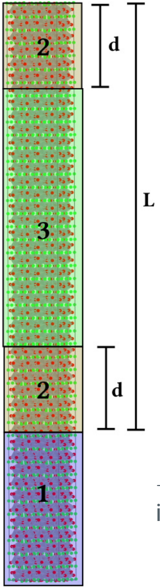


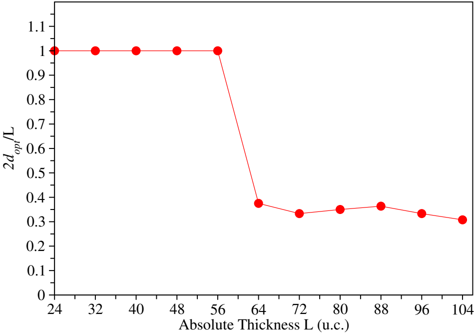


$CaTiO_3$ Reprodcution of $LaVO_3/DyScO_3$ interface









→ CaTiO$_3$ second-principles model is able to qualitatively reproduce interemediate layer formation at LaVO$_3$/DyScO$_3$ interface.

Conclusions

Summary

- Automated procedure for generating fitting polynomial expansions
- New test set generation strategy can help to effectively sample **important** parts of the Born-Oppenheimer PES
- Use of effective potentials for finite temperature and advanced thin film studies.

Outlook

- Implementation of combining different effective potentials in different zones of the simulation box
- New fitting strategies borrowed from machine learning.
- Effective Potentials as background lattice model for electron-lattice, or spin-lattice models