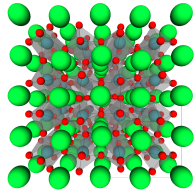
The Multibinit project



Marcus Schmitt†, Jordan Bieder, Fabio Riccii Alexande Martin, Xu He, Nicole Helbig and Philippe Ghosez

†PhyTheMa - ULG
CESAM / Q-MAT

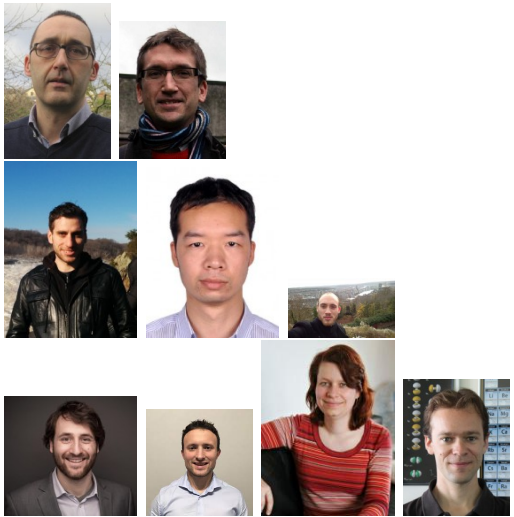
Abinit School Prague 2019

September 06*st*, 2019

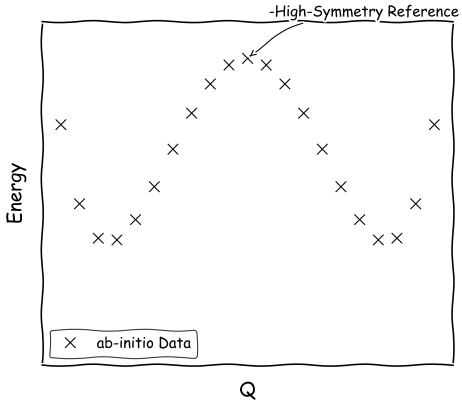
What is Multibinit ?

Who is Multibinit ?

Philippe Ghosez
Philippe.Ghosez@uliege.be
Matthieu Verstraete
matthieu.verstraete@uliege.be
Jordan Bieder
Jordan.Bieder@uliege.be
He Xu
X.He@uliege.be
Alexandre Martin
Michael Marcus Schmitt
MMN.Schmitt@doct.uliege.be
William Lafargue dit Hauret
william.lafargue-dit-hauret@uliege.be
Nicole Helbig
nehelbig@gmail.com
Eric Bousquet
eric.bousquet@uliege.be

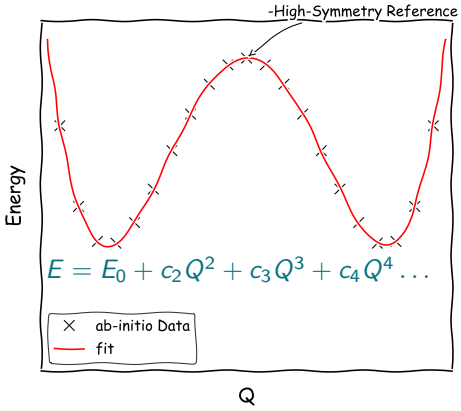


Transform Ab-Initio Data into Polynomial Description



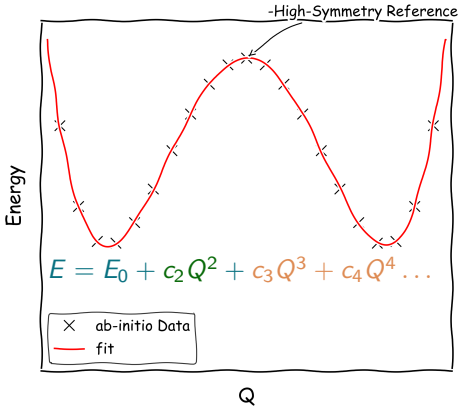
Q: A direction of displacements $(\mathbf{u}, \eta)$

Transform Ab-Initio Data into Polynomial Description



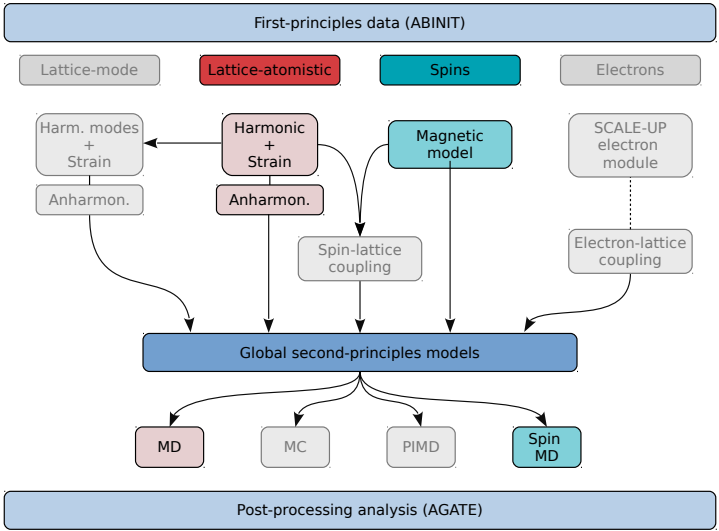
Q: A direction of displacements $(\mathbf{u}, \eta)$

Transform Ab-Initio Data into Polynomial Description



Q: A direction of displacements $(\mathbf{u}, \eta)$

Harmonic part extracted from DFPT - Higher order Fitted


First-principles data (ABINIT)
Lattice-mode
Lattice-atomistic
Spins
Electrons
Harm. modes + Strain
Harmonic + Strain
Magnetic model
SCALE-UP electron module
Anharmon.
Anharmon.
Spin-lattice coupling
Electron-lattice coupling
Global second-principles models
MD
MC
PIMD
Spin MD
Post-processing analysis (AGATE)

Multibinit in the package

- Multibinit is a new executable included in the main directory: *src*/98_*main*/*multibinit*
- Source to be found in *src*/78_*effpot*
- New input have been created (mix between anaddb and ABINIT)
- XML files are used for storing model informations (Fast reading)
- MPI Parallelization
- Abinit movers for Molecular Dynamics
- Documentation with tutorials and topics on Abinit Website (Work in progress..!)

Basic Procedure

- Express energy as low order Taylor expansion
  - Use high-symmetry reference structure
  - Variables: selected local modes and strains
- Determine coefficients from a limited number of DFT calculations
- Resulting energy expansion allows for finite temperature Monte Carlo

Successful results already for many oxide systems.
However identifying a small set of degrees of fredom is often difficult.

We need a general description of the energetics of all the atomic degress of freedom

K. Rabe and J. Joannopoulos, PRL 59, 570 (1987); PRB 36, 6631 (1987)
W. Zhong et al., PRL 73, 1861 (1994); PRB 52, 6301 (1995)

Energy changes around reference structure due to distortions

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

$$E_{eff}(\{\mathbf{u}_i\},\eta) = E_p(\{\mathbf{u}_i\}) + E_s(\eta) + E_{sp}(\{\mathbf{u}_i\},\eta)$$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Energy changes around reference structure due to distortions

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

$$E_{eff}(\{\mathbf{u}_i\},\eta) = E_p(\{\mathbf{u}_i\}) + \boxed{E_s(\eta)} + E_{sp}(\{\mathbf{u}_i\},\eta)$$

Energy change due to strain only

$$E_s^{Harm}(\eta)$$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Energy changes around reference structure due to distortions

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

$$E_{eff}(\{\mathbf{u}_i\},\eta) = E_p(\{\mathbf{u}_i\}) + E_s(\eta) + E_{sp}(\{\mathbf{u}_i\},\eta)$$

Energy change from atomic displacements

Energy change due to strain only

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

$E_s^{Harm}(\eta)$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Energy changes around reference structure due to distortions

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

$$E_{eff}(\{\mathbf{u}_i\},\eta) = E_p(\{\mathbf{u}_i\}) + E_s(\eta) + E_{sp}(\{\mathbf{u}_i\},\eta)$$

Energy change from atomic displacements

Energy change due to strain only

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

$E_s^{Harm}(\eta)$

$E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Energy changes around reference structure due to distortions

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

$$E_{eff}(\{\mathbf{u}_i\},\eta) = E_p(\{\mathbf{u}_i\}) + E_s(\eta) + E_{sp}(\{\mathbf{u}_i\},\eta)$$

- $E_p(\{\mathbf{u}_i\})$: Energy change from atomic displacements
  - $E_p^{Harm}(\{\mathbf{u}_i\}) + E_p^{Anharm}(\{\mathbf{u}_i\})$
    - $E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$
- $E_s(\eta)$: Energy change due to strain only
  - $E_s^{Harm}(\eta)$
- $E_{sp}(\{\mathbf{u}_i\},\eta)$: Strain-phonon coupling
  - $E_{sp}^{Harm}(\{\mathbf{u}_i\},\eta) + E_{sp}^{Anharm}(\{\mathbf{u}_i,\eta\})$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Energy changes around reference structure due to distortions

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

$$E_{eff}(\{\mathbf{u}_i\},\eta) = E_p(\{\mathbf{u}_i\}) + E_s(\eta) + E_{sp}(\{\mathbf{u}_i\},\eta)$$

- $E_p(\{\mathbf{u}_i\})$: Energy change from atomic displacements
  - $E_p^{Harm}(\{\mathbf{u}_i\}) + E_p^{Anharm}(\{\mathbf{u}_i\})$
    - $E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$
- $E_s(\eta)$: Energy change due to strain only
  - $E_s^{Harm}(\eta)$
- $E_{sp}(\{\mathbf{u}_i\},\eta)$: Strain-phonon coupling
  - $E_{sp}^{Harm}(\{\mathbf{u}_i\},\eta) + E_{sp}^{Anharm}(\{\mathbf{u}_i,\eta\})$

Same framework as H_{eff} but includes all-atomic degrees of freedom.

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Phonon term $E_p(\{\mathbf{u}_i\}) = E_p^{Harm}(\{\mathbf{u}_i\}) + E_p^{Anharm}(\{\mathbf{u}_i\})$

Taylor development around the reference structure

$$E_p(\{\mathbf{u}_i\}) = \underbrace{\frac{1}{2}\sum_{i\alpha j\beta} K^{(2)}_{i\alpha j\beta} u_{i\alpha} u_{j\beta}}_{\text{Harmonic terms}} + \underbrace{\frac{1}{6}\sum_{i\alpha j\beta k\gamma} K^{(3)}_{i\alpha j\beta k\gamma} u_{i\alpha} u_{j\beta} u_{k\gamma}}_{\text{Anharmonic terms}} + \mathcal{O}(u^4)$$

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

- Must comply the Acoustic Sum Rule $\rightarrow$ difficulte to enforce for $n > 2$
- Use displacement differences $\rightarrow$ ASR satisfied by construction

$$E_{\text{Harm}}(\{u_i\}) = \frac{1}{2}\sum_{\substack{i,j,k,h\\ \alpha,\beta}} \tilde{K}^{(2)}_{ij\alpha kh\beta}(u_{i\alpha} - u_{j\alpha})(u_{k\beta} - u_{h\beta})$$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

2. Lattice Effective Hamiltonians

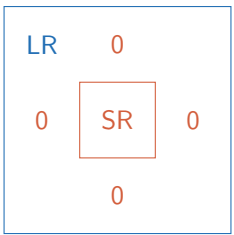
$$E_p^{Harm}(\{\mathbf{u}_i\}) = E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$$

$$\begin{aligned} E_p^{Harm}(\{\mathbf{u}_i\}) &= \frac{1}{2}\sum_{i\alpha j\beta} K^{(2)}_{i\alpha j\beta} u_{i\alpha} u_{j\beta} = \frac{1}{2}\sum_{i\alpha j\beta} \left(S_{i\alpha j\beta} + L_{i\alpha j\beta}\right) u_{i\alpha} u_{j\beta} \\ &= \frac{1}{2}\sum_{\substack{i\in SC\\ \alpha}} u_{i\alpha} \sum_{\substack{j\in SR\\ \beta}} S_{i\alpha j\beta} u_{j\beta} + \frac{1}{2}\sum_{\substack{i\in SC\\ \alpha}} u_{i\alpha} \sum_{\substack{j\in SC\\ \beta}} \underbrace{\left(\sum_{b}^{\infty} L_{i\alpha j\beta}(b)\right)}_{\tilde{L}_{i\alpha j\beta(\mathbf{q}=0)}} \underbrace{u^b_{j\beta}}_{u^0_{j\beta}} \end{aligned}$$

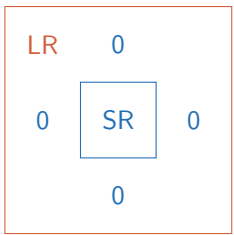
$$E_p^{Harm}(\{\mathbf{u}_i\}) = E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$$

$$\begin{aligned} E_p^{Harm}(\{\mathbf{u}_i\}) &= \frac{1}{2}\sum_{i\alpha j\beta} K^{(2)}_{i\alpha j\beta} u_{i\alpha} u_{j\beta} = \frac{1}{2}\sum_{i\alpha j\beta} \left(S_{i\alpha j\beta} + L_{i\alpha j\beta}\right) u_{i\alpha} u_{j\beta} \\ &= \frac{1}{2}\sum_{\substack{i\in SC\\ \alpha}} u_{i\alpha} \sum_{\substack{j\in SR\\ \beta}} S_{i\alpha j\beta} u_{j\beta} + \frac{1}{2}\sum_{\substack{i\in SC\\ \alpha}} u_{i\alpha} \sum_{\substack{j\in SC\\ \beta}} \underbrace{\left(\sum_{b}^{\infty} L_{i\alpha j\beta}(b)\right)}_{\tilde{L}_{i\alpha j\beta(\mathbf{q}=0)}} \underbrace{u^b_{j\beta}}_{u^0_{j\beta}} \end{aligned}$$

SR<LR



LR<SR



$E_p^{Anharm}(\{\mathbf{u}_i\})$

- Anharmonicity degree : chose from maximum order: 3, 4, 5, 6,...
- For each order build the possible terms

$$E_p^{(n)}(\{\mathbf{u}_i\} = \frac{1}{!n} \sum_{\substack{i,j,k,l,m,n,\cdots \\ \alpha,\beta,\gamma,\cdots}} K_{ijklmn}^{(n)\alpha\beta\gamma}(u_{i\alpha} - u_{j\alpha})(u_{k\beta} - u_{l\beta})(u_{m\gamma} - u_{n\gamma})\cdots$$

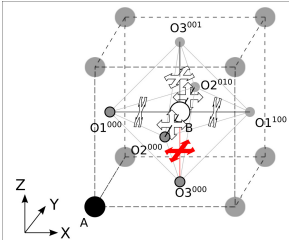
- ASR enforces by using differences
- Use symmetries to reduce de number of coefficients

$E_p^{Anharm}(\{\mathbf{u}_i\})$

Symmetry considerations: "Symmetry adapted terms"

The operations of the space group can generate a collection of symmetry related terms which reduces the number of *independent* parameters. In practice :

- Define range or cutoff radius
- Build all terms within this range
- Apply all symmetries to find relations between terms :



$(u_{0Bx} - u_{0O3x})^2(u_{0By} - u_{0O3y})^2 + \frac{\pi}{2}$ rotation about the y-axis transforms to $(u_{0Bz} - u_{0O1z})^2(u_{0By} - u_{0O1y})^2$
$\rightarrow$ **15 independent parameters**
(1^{st} nearest neighbors at 3^{rd} and 4^{th} order in u) for the anharmonic phonon part.

Phonon term $E_p(\{\mathbf{u}_i\}) = E_p^{Harm}(\{\mathbf{u}_i\}) + E_p^{Anharm}(\{\mathbf{u}_i\})$

Harmonic terms

- $K^{(2)}$ obtained by DFPT as the back-Fourier-transformed dynamical matrix
- Remove dipole-dipole interaction in real space to obtain the SR only.
- Use ewald summation to compute the exact dipole-dipole interaction.

$\Rightarrow$ Harmonic terms exact by construction and include all phonon branches

Phonon term $E_p(\{\mathbf{u}_i\}) = E_p^{Harm}(\{\mathbf{u}_i\}) + E_p^{Anharm}(\{\mathbf{u}_i\})$

Harmonic terms

- $K^{(2)}$ obtained by DFPT as the back-Fourier-transformed dynamical matrix
- Remove dipole-dipole interaction in real space to obtain the SR only.
- Use ewald summation to compute the exact dipole-dipole interaction.

$\Rightarrow$ Harmonic terms exact by construction and include all phonon branches

Anharmonic terms

- Displacement differences expression allows for an unconstrained optimization of $\tilde{K}^{(n)}$
- Determined by fitting key quantites to limited number of DFT calculations (training set)

Strain term $E_s(\eta)$

Taylor development around the reference structure

$$E_s(\eta) = \frac{N}{2} \sum_{ab} C^{(2)}_{ab} \eta_a \eta_b + \frac{N}{6} \sum_{abc} C^{(3)}_{abx} \eta_a \eta_b \eta_c + \mathcal{O}(\eta^4)$$

with $C^{(m)}_{ab\ldots} = \frac{1}{N} \frac{\partial^m E_{eff}}{\partial \eta_a \partial \eta_b \cdots}\Big|_{u_i=0}$

- Harmonic term calculated directly : the frozen ion elastic constants (DFPT)
- Anharmonic terms : in practice not required for semi-quantitative results

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Strain-Phonon coupling $E_{sp}(\{u_i\}, \eta)$

Taylor development also subject to ASR

$$E_{sp}(\{u_i\}, \eta) = \underbrace{\frac{1}{2}\sum_a \sum_{i\alpha} \Lambda^{(1,1)}_{ai\alpha}\eta_a u_{i\alpha}}_{\text{Forces at homogeneous strain}} + \underbrace{\frac{1}{6}\sum_a \sum_{i\alpha j\beta} \Lambda^{(1,2)}_{ai\alpha j\beta}\eta_a u_{i\alpha} u_{j\beta}}_{\text{Change in force csts with strain}} + \dots$$

- The $\Lambda^{(m,n)}$ must comply with a set of ASRs
- Use displacement differences

$$E_{sp}(\{u_i\}, \eta) = \frac{1}{2}\sum_a \sum_{ij\alpha} \Lambda^{(1,1)}_{ai\alpha}\eta_a(u_{i\alpha} - u_{j\alpha}) + \frac{1}{6}\sum_a \sum_{ij\alpha kh\beta} \Lambda^{(1,2)}_{ai\alpha j\beta}\eta_a(u_{i\alpha} - u_{j\alpha})(u_{k\beta} - u_{h\beta}) + \dots$$

J. Wojdel et al., J. Phys. Condens. Matter 25 (2013) 305401

Fitting anhamonic terms

Fit is performed on both Phonon and Strain-phonon terms.

- For a set (TS) of configurations (s) from DFT calculations, we fit with least squares method, the goal function is defined as:

$$G[\lambda_p, TS] = \frac{1}{M_1} \sum_{s,\alpha,j} \left(F^{TS}_{\alpha_j}(s) - F_{\alpha_j}[\lambda_p](s)\right)^2 + \frac{1}{M_2} \sum_{s,j} \Omega^2(s) \left(\sigma^{TS}_j(s) - \sigma_j[\lambda_p](s)\right)^2$$

- where $\Omega(s) = \left(V(s)\sqrt{(N)}\right)^{(-1/3)}$
- The goal function has to satisfy $\frac{\partial G[\lambda_p, TS]}{\partial \lambda_\mu} = 0 \quad \forall \mu$ and $\frac{\partial^2 G[\lambda_p, TS]}{\partial \lambda_\mu \partial \lambda_\nu} \geq 0 \quad \forall \mu\nu$
- We solve the system of p linear equations in order to get the set of coefficients λ_p

3. Fitting the Anharmonic part


```
prt_model = 1

#-------------------------------------------------------------
#Inputs for the fitted coefficients
#-------------------------------------------------------------

fit_coeff = 1

fit_generateCoeff = 1
fit_rangePower = 3 4    #  Range for the powers of the polynomial (default 3 to 4 )
fit_ncoeff = 7          #  Number of  coefficients to consider for the fit
fit_cutoff = 8          #  Cutoff for the interactions
fit_anhaStrain = 0
fit_SPCoupling = 1

ts_option = 1
```

Problem: We create much more terms than we can fit !

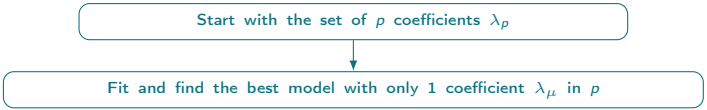
Perovskite:

- 1st neighbor($0.5a$): 20-terms
- 2nd neighbor($a/\sqrt{2}$): 278-terms
- 3rd neighbor(a): 1504-terms

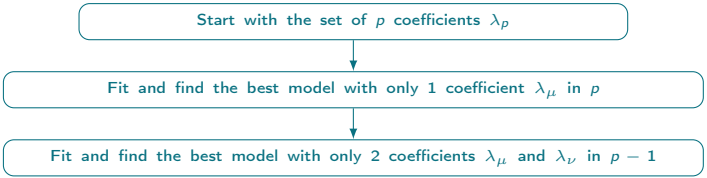
4. FIT PROCESS: GENERAL PROCEDURE

Start with the set of p coefficients λ_p

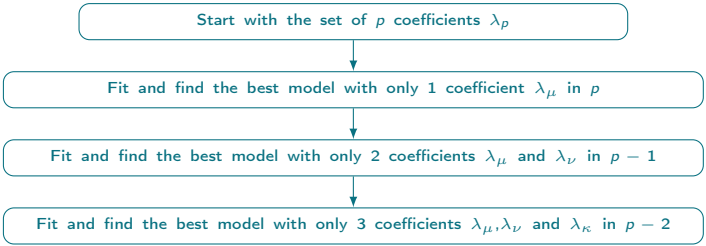
4. FIT PROCESS: GENERAL PROCEDURE



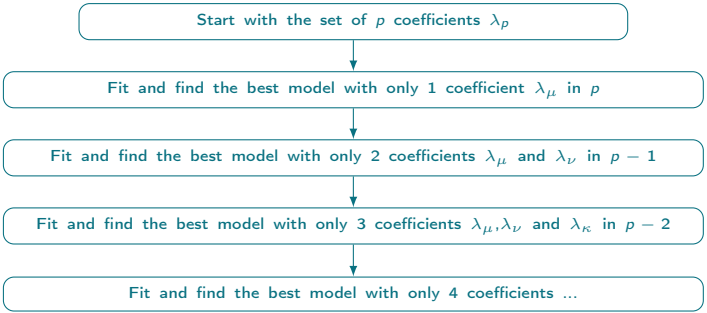
4. FIT PROCESS: GENERAL PROCEDURE



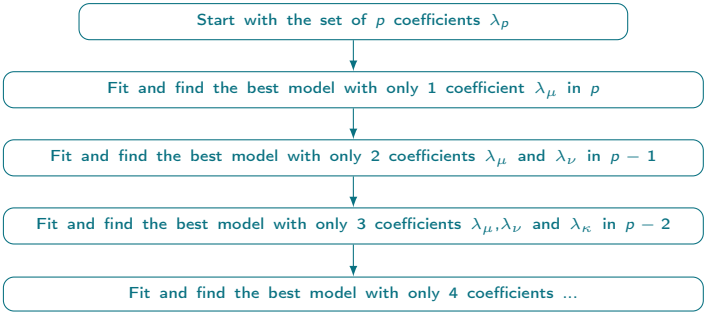
4. FIT PROCESS: GENERAL PROCEDURE



4. FIT PROCESS: GENERAL PROCEDURE

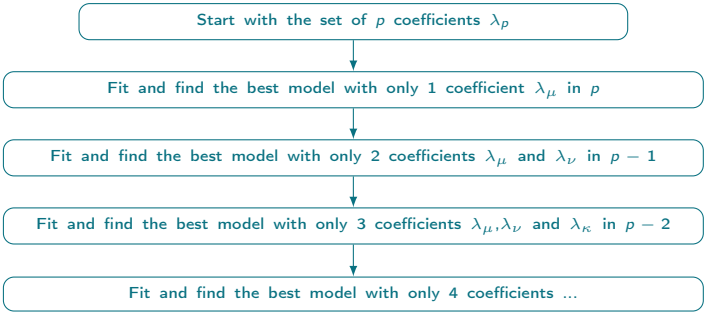


4. FIT PROCESS: GENERAL PROCEDURE



Problems:

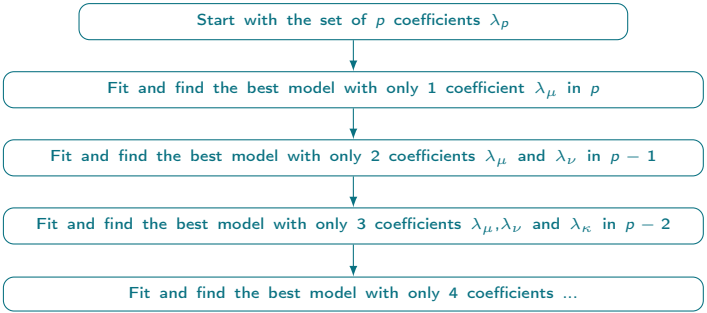
4. FIT PROCESS: GENERAL PROCEDURE



Problems:

- We need to define convergence criterion to stop the fit process (specific phase, energy, forces...)

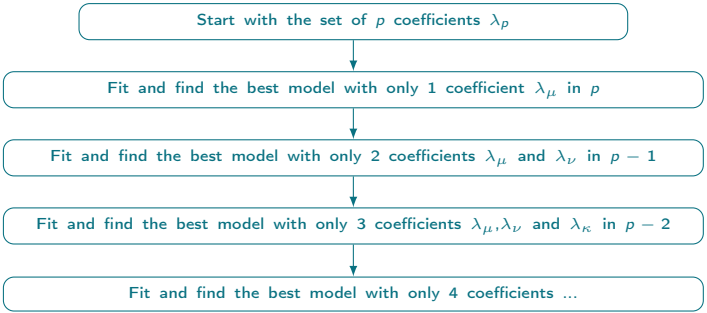
4. FIT PROCESS: GENERAL PROCEDURE



Problems:

- We need to define convergence criterion to stop the fit process (specific phase, energy, forces...)
- We need to define a good training set

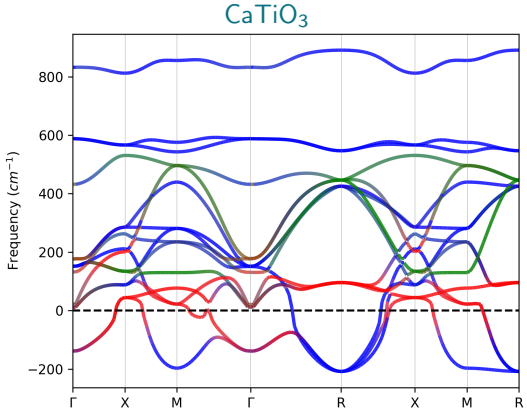
4. FIT PROCESS: GENERAL PROCEDURE



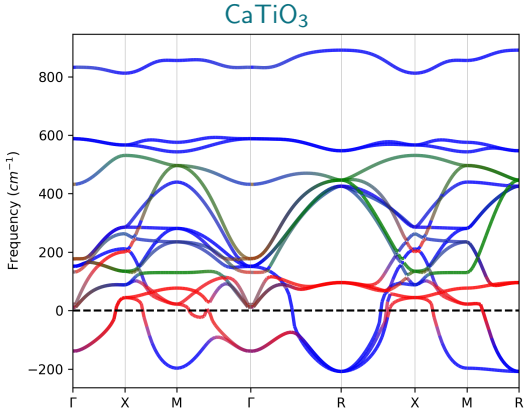
Problems:

- We need to define convergence criterion to stop the fit process (specific phase, energy, forces...)
- We need to define a good training set
- We need to bound the model

Real Materials Might Have Many Instabilities and Complex Ground-State Structures

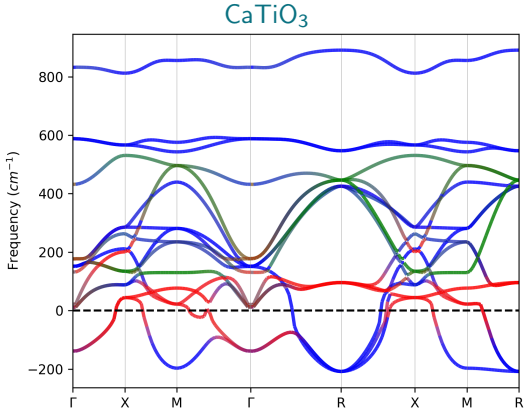


Real Materials Might Have Many Instabilities and Complex Ground-State Structures



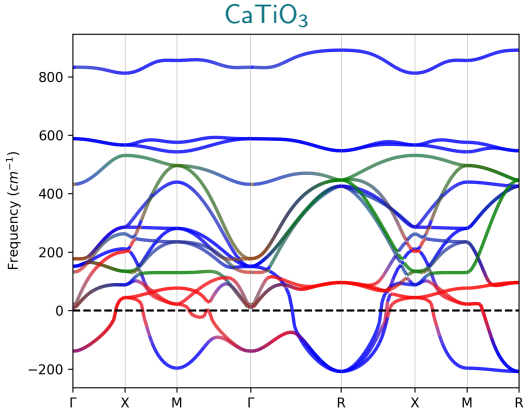
Ground-State Structure *Pnma*: Composed of 5 modes and 2 strains

Real Materials Might Have Many Instabilities and Complex Ground-State Structures



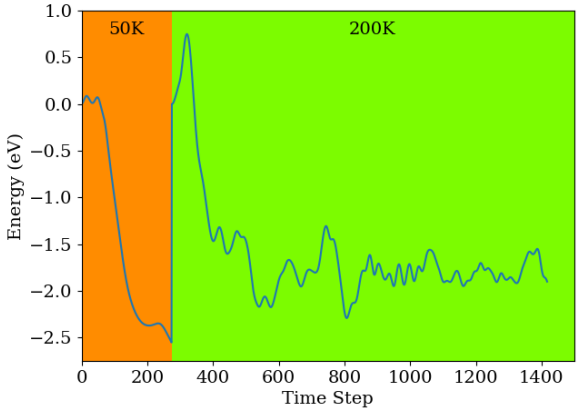
Ground-State Structure *Pnma*: Composed of 5 modes and 2 strains
Largest displacement about 0.4 Å≈ 10% of LC

Real Materials Might Have Many Instabilities and Complex Ground-State Structures

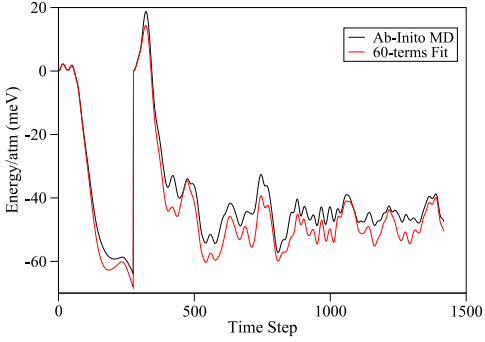


Ground-State Structure *Pnma*: Composed of 5 modes and 2 strains
Largest displacement about 0.4 Å≈ 10% of LC
Competing Phases $R\bar{3}c$,$I4/mcm$, $P4/mbm$, $Cmcm$

Use Ab-Initio Molecular Dynamics to Sample Instable Paths

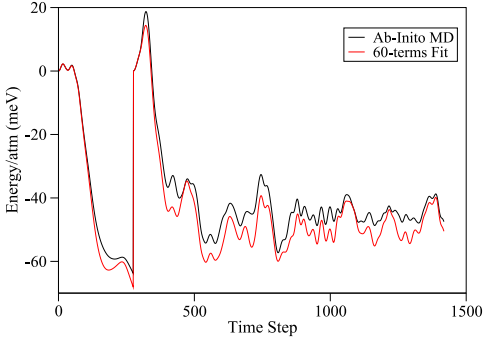


A First Free Fit Using Multibinit




```
Mean Standard Deviation values of the effective_potential (meV/atm):
  Energy           :    4.0803665397763584E+00
Goal function values of the effective_potential
with respect to the test_set (eV^2/A^2):
  Forces+Stresses  :    2.4466967954928562E-02
  Forces           :    2.0260908611633852E-02
  Stresses         :    4.2060593432947067E-03
```

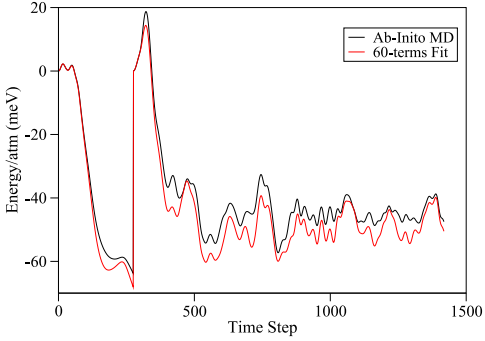
A First Free Fit Using Multibinit



At T=50K Model goes to the *Pnma*-phase

```
Mean Standard Deviation values of the effective_potential (meV/atm):
  Energy           :   4.0803665397763584E+00
Goal function values of the effective_potential
with respect to the test_set (eV^2/A^2):
  Forces+Stresses :   2.4466967954928562E-02
  Forces          :   2.0260908611633852E-02
  Stresses        :   4.2060593432947067E-03
```

A First Free Fit Using Multibinit



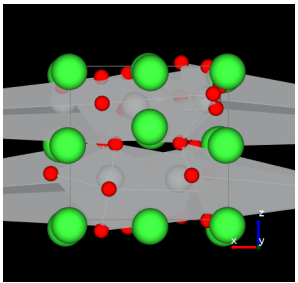
At T=50K Model goes to the *Pnma*-phase

5000-steps,40-atoms
≈ 70s on 4 cores

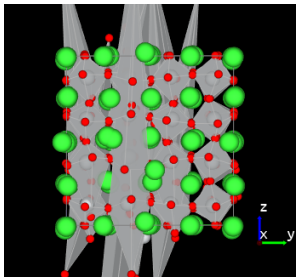
```
Mean Standard Deviation values of the effective_potential (meV/atm):
  Energy           :    4.0803665397763584E+00
Goal function values of the effective_potential
with respect to the test_set (eV^2/A^2):
  Forces+Stresses  :    2.4466967954928562E-02
  Forces           :    2.0260908611633852E-02
  Stresses         :    4.2060593432947067E-03
```

"Boundedness" is a Big Problem

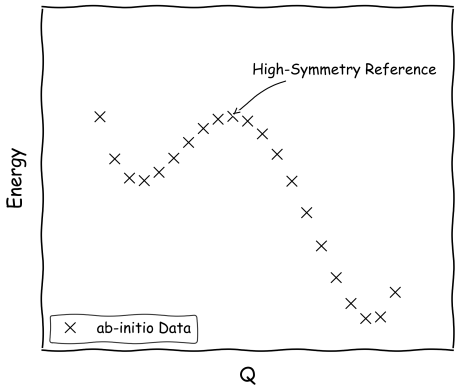
T = 300K



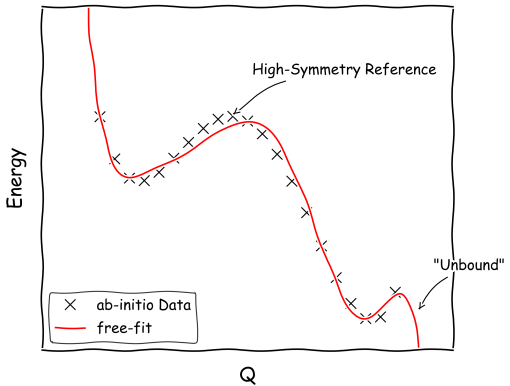
ncell = 4x4x4



5. Lattice Model of $CaTiO_3$

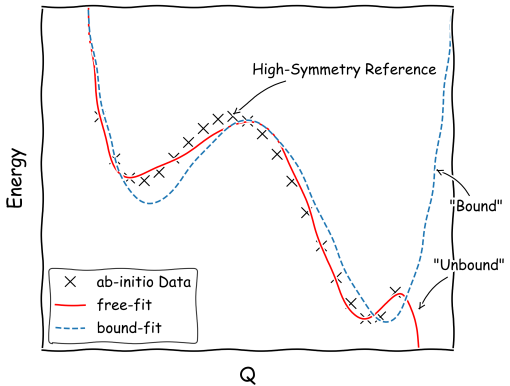


"UnBoundedness" - Negative Divergence in The Effective Potential



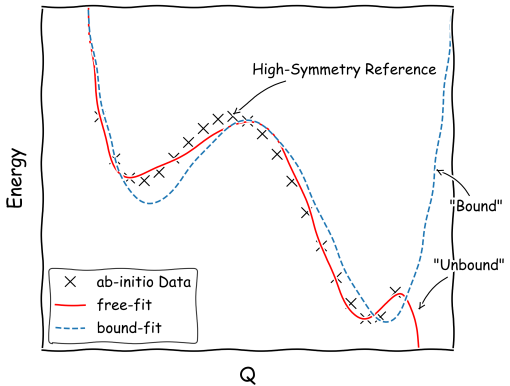
Appears if highest order term in Q is odd or even with negative coeffcient

"UnBoundedness" - Negative Divergence in The Effective Potential



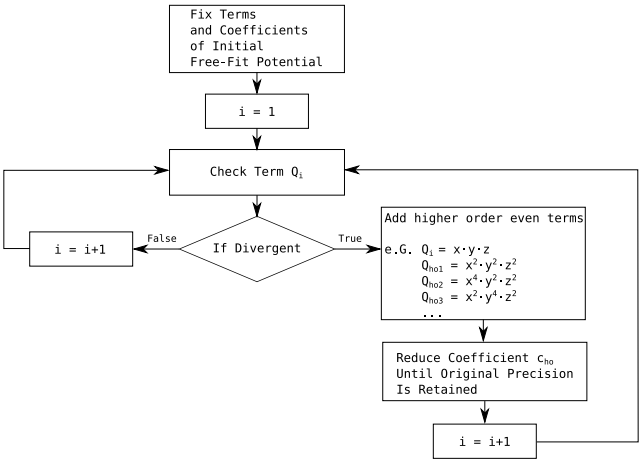
Appears if highest order term in Q is odd or even with negative coeffcient

"UnBoundedness" - Negative Divergence in The Effective Potential



Appears if highest order term in Q is odd or even with negative coeffcient
Add higher order terms to bound in direction Q! How to keep precision?

A Simple Algorithm to Impose Boundedness



5. Lattice Model of $CaTiO_3$

Free Fit
60 terms

```
Mean Standard Deviation values of the effective-potential (meV/atm):
  Energy           :    4.0803665397763584E+00
Goal function values of the effective potential
with respect to the test-set (eV^2/A^2):
  Forces+Stresses  :    2.4466967954928562E-02
  Forces           :    2.0260908611633852E-02
  Stresses         :    4.2060593432947067E-03
```

5. Lattice Model of $CaTiO_3$

Free Fit
60 terms

57 *diverging* terms →

Bound Fit
283 terms

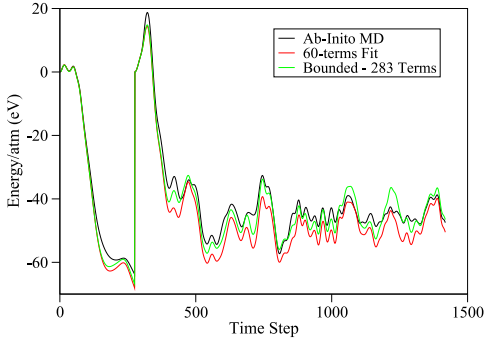
```
Mean Standard Deviation values of the effective-potential (meV/atm):
  Energy           :   4.0803665397763584E+00
Goal function values of the effective_potential
with respect to the test-set (eV^2/A^2):
  Forces+Stresses  :   2.4466967954928562E-02
  Forces           :   2.0260908611633852E-02
  Stresses         :   4.2060593432947067E-03
```

5. Lattice Model of $CaTiO_3$

Free Fit
60 terms

57 *diverging* terms →

Bound Fit
283 terms




```
Mean Standard Deviation values of the effective-potential (meV/atm):
  Energy          :   2.1664871069774949E+00
Goal function values of the effective_potential
with respect to the test-set (eV^2/A^2):
  Forces+Stresses :   2.7889442532740654E-02
  Forces          :   2.3225875500530173E-02
  Stresses        :   4.6635670322104803E-03
```

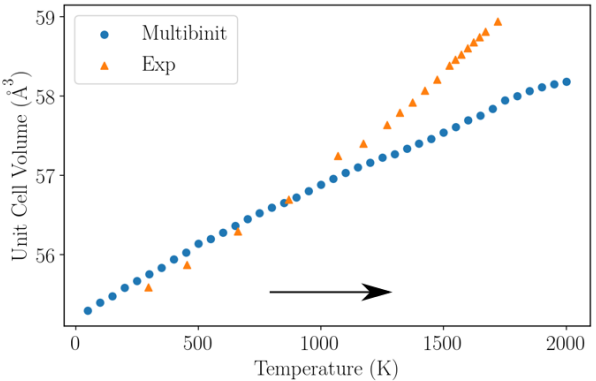
5. Lattice Model of $CaTiO_3$

The model is bound

16x16x16 cells, 20480 atoms

6000-steps per temperature

96-cores $\approx$ 1h15min per temperature



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

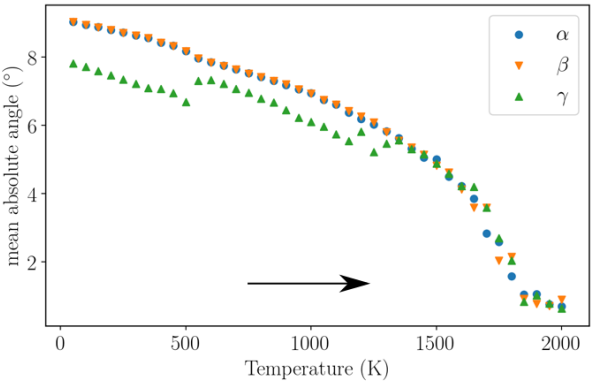
5. Lattice Model of $CaTiO_3$

The model is bound

16x16x16 cells, 20480 atoms

6000-steps per temperature

96-cores $\approx$ 1h15min per temperature



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

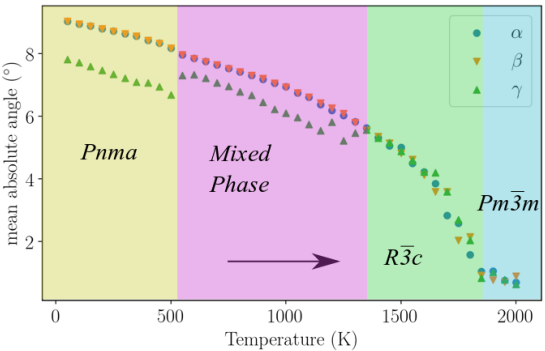
5. Lattice Model of $CaTiO_3$

The model is bound

16x16x16 cells, 20480 atoms

6000-steps per temperature

96-cores ≈ 1h15min per temperature



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

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

6. Electronic + Lattice Effective Model

The Information about the electronic states are hidden in the lattice effective potential parameters

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0) + E(\mathbf{u},\eta)$$

$$E(u,\eta) = E^{phonon}(u) + E^{strain}(\eta) + E^{strain-phonon}(u,\eta)$$

$$E^{ph}(\mathbf{u}) = \sum_{ijkh\alpha\beta} K^{(2)}_{ijkh\alpha\beta}(u_{i\alpha}-u_{j\alpha})(u_{k\beta}-u_{h\beta}) + \sum_{ikhrt\alpha\beta\gamma} K^{(3)}_{ikhrt\alpha\beta\gamma}(u_{i\alpha}-u_{j\alpha}) \times (u_{k\beta}-u_{h\beta})(u_{r\gamma}-u_{t\gamma})\ldots$$

$$E^{s}(\eta) = \sum_{ab} C_{ab}\eta_a\eta_b$$

$$E^{s-ph}(\{\mathbf{u}\},\eta) = \sum_a \sum_{ij\alpha} \Lambda^{(1,1)}_{aij\alpha}\eta_a(u_{i\alpha}-u_{j\alpha}) + \sum_a \sum_{ijhk\alpha\beta} \Lambda^{(1,2)}_{aijhk\alpha\beta}\eta_a(u_{i\alpha}-u_{j\alpha}) \times (u_{k\beta}-u_{h\beta})\ldots$$

6. Electronic + Lattice Effective Model

The Information about the electronic states are hidden in the lattice effective potential parameters

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0) + E(\mathbf{u},\eta)$$

$$E(u,\eta) \;=\; E^{phonon}(u) \;+ E^{strain}(\eta) + E^{strain-phonon}(u,\eta)$$

$$E^{ph}(\mathbf{u}) = \sum_{ijkh\alpha\beta} K^{(\mathbf{2})}_{ijkh\alpha\beta}(u_{i\alpha}-u_{j\alpha})(u_{k\beta}-u_{h\beta}) + \sum_{ikhrt\alpha\beta\gamma} K^{(\mathbf{3})}_{ikhrt\alpha\beta\gamma}(u_{i\alpha}-u_{j\alpha}) \times(u_{k\beta}-u_{h\beta})(u_{r\gamma}-u_{t\gamma})\dots$$

$$E^{s}(\eta) = \sum_{ab} C_{ab}\eta_a\eta_b$$

$$E^{s-ph}(\{\mathbf{u}\},\eta) = \sum_{a}\sum_{ij\alpha} \Lambda^{(\mathbf{1},\mathbf{1})}_{aij\alpha}\eta_a(u_{i\alpha}-u_{j\alpha}) + \sum_{a}\sum_{ijhk\alpha\beta} \Lambda^{(\mathbf{1},\mathbf{2})}_{aijhk\alpha\beta}\eta_a(u_{i\alpha}-u_{j\alpha}) \times(u_{k\beta}-u_{h\beta})\dots$$

Reintroduce some electronic states of interest with SCALE-UP

Garcia-Fernandez, P. *et al* Phys. Rev. B, 2016, **93** 195137

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0)) + E(\mathbf{u},\eta) + E_{el}(\mathbf{u},\eta)$$

$$E_{el}(\mathbf{u},\eta) = \sum_{ab} D^U_{ab}\gamma_{ab}(\mathbf{u},\eta) + 1/2\sum_{ab}\sum_{a'b'} D^U_{ab}D^U_{a'b'}U_{aba'b'} - D^I_{ab}D^I_{a'b'}I_{aba'b'}$$

6. Electronic + Lattice Effective Model

The Information about the electronic states are hidden in the lattice effective potential parameters

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0) + E(\mathbf{u},\eta)$$

$$E(u,\eta) \;=\; E^{phonon}(u) \;+ E^{strain}(\eta) + E^{strain-phonon}(u,\eta)$$

$$E^{ph}(\mathbf{u}) = \sum_{ijkh\alpha\beta} K^{(\mathbf{2})}_{ijkh\alpha\beta}(u_{i\alpha}-u_{j\alpha})(u_{k\beta}-u_{h\beta}) + \sum_{ikhrt\alpha\beta\gamma} K^{(\mathbf{3})}_{ikhrt\alpha\beta\gamma}(u_{i\alpha}-u_{j\alpha}) \times(u_{k\beta}-u_{h\beta})(u_{r\gamma}-u_{t\gamma})\dots$$

$$E^{s}(\eta) = \sum_{ab} C_{ab}\eta_a\eta_b$$

$$E^{s-ph}(\{\mathbf{u}\},\eta) = \sum_a \sum_{ij\alpha} \Lambda^{(\mathbf{1},\mathbf{1})}_{aij\alpha}\eta_a(u_{i\alpha}-u_{j\alpha}) + \sum_a \sum_{ijhk\alpha\beta} \Lambda^{(\mathbf{1},\mathbf{2})}_{aijhk\alpha\beta}\eta_a(u_{i\alpha}-u_{j\alpha}) \times(u_{k\beta}-u_{h\beta})\dots$$

Reintroduce some electronic states of interest with SCALE-UP

Garcia-Fernandez, P. *et al* Phys. Rev. B, 2016, **93** 195137

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0)) + E(\mathbf{u},\eta) + E_{el}(\mathbf{u},\eta)$$

$$E_{el}(\mathbf{u},\eta) = \sum_{ab} D^U_{ab}\gamma_{ab}(\mathbf{u},\eta) + 1/2\sum_{ab}\sum_{a'b'} D^U_{ab}D^U_{a'b'}U_{aba'b'} - D^I_{ab}D^I_{a'b'}I_{aba'b'}$$

With the central quantity: $D_{ab} = d_{ab} - d^{(0)}_{ab}$

6. Electronic + Lattice Effective Model

The Information about the electronic states are hidden in the lattice effective potential parameters

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0) + E(\mathbf{u},\eta)$$

$$E(u,\eta) \;=\; E^{phonon}(u) \;+ E^{strain}(\eta) + E^{strain-phonon}(u,\eta)$$

$$E^{ph}(\mathbf{u}) = \sum_{ijkh\alpha\beta} K^{(\mathbf{2})}_{ijkh\alpha\beta}(u_{i\alpha}-u_{j\alpha})(u_{k\beta}-u_{h\beta}) + \sum_{ikhr t\alpha\beta\gamma} K^{(\mathbf{3})}_{ikhrt\alpha\beta\gamma}(u_{i\alpha}-u_{j\alpha}) \times(u_{k\beta}-u_{h\beta})(u_{r\gamma}-u_{t\gamma})\dots$$

$$E^{s}(\eta) = \sum_{ab} C_{ab}\eta_a\eta_b$$

$$E^{s-ph}(\{\mathbf{u}\},\eta) = \sum_a \sum_{ij\alpha} \Lambda^{(\mathbf{1},\mathbf{1})}_{aij\alpha}\eta_a(u_{i\alpha}-u_{j\alpha}) + \sum_a \sum_{ijhk\alpha\beta} \Lambda^{(\mathbf{1},\mathbf{2})}_{aijhk\alpha\beta}\eta_a(u_{i\alpha}-u_{j\alpha}) \times(u_{k\beta}-u_{h\beta})\dots$$

Reintroduce some electronic states of interest with SCALE-UP

Garcia-Fernandez, P. *et al* Phys. Rev. B, 2016, **93** 195137

$$E_{tot}(\mathbf{u},\eta) = E_0(\mathbf{r_0},0)) + E(\mathbf{u},\eta) + E_{el}(\mathbf{u},\eta)$$

$$E_{el}(\mathbf{u},\eta) = \sum_{ab} D^U_{ab}\gamma_{ab}(\mathbf{u},\eta) + 1/2\sum_{ab}\sum_{a'b'} D^U_{ab}D^U_{a'b'}U_{aba'b'} - D^I_{ab}D^I_{a'b'}I_{aba'b'}$$

With the central quantity: $D_{ab} = d_{ab} - d^{(0)}_{ab}$

And the electron-lattice coupling expressed in $\gamma_{ab}(\mathbf{u},\eta)$

The Information about the electronic states are hidden in the lattice effective

$E^{ph}(\mathbf{u}) =$ α)

+

×

Access

- Electronic Structure at Finite T
- Electronic Structure of Large Scale Objects
- $D_{ab} \neq 0$: Magnetic States, Polarons, Excitons

Reintroduce some electronic states of interest with SCALE-UP

Garcia-Fernandez, P. *et al* Phys. Rev. B, 2016, **93** 195137

$$E_{tot}(\mathbf{u}, \eta) = E_0(\mathbf{r_0}, 0)) + E(\mathbf{u}, \eta) + E_{el}(\mathbf{u}, \eta)$$

$$E_{el}(\mathbf{u}, \eta) = \sum_{ab} D^U_{ab} \gamma_{ab}(\mathbf{u}, \eta) + 1/2 \sum_{ab} \sum_{a'b'} D^U_{ab} D^U_{a'b'} U_{aba'b'} - D^I_{ab} D^I_{a'b'} I_{aba'b'}$$

With the central quantity: $D_{ab} = d_{ab} - d^{(0)}_{ab}$

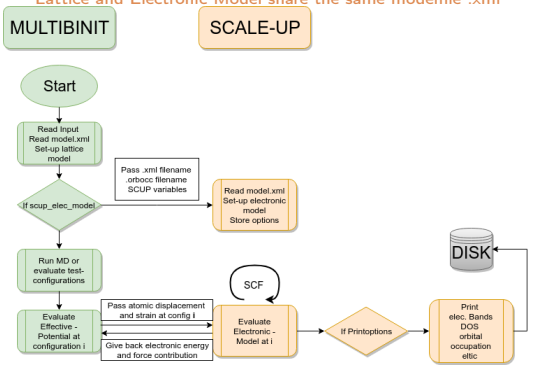
And the electron-lattice coupling expressed in $\gamma_{ab}(\mathbf{u}, \eta)$

THE MULTIBINIT - SCALE-UP INTERFACE

Multibinit incorporates SCALE-UP as a library

```
FC_LIBS="-L/path/to/scaleup/build/src/.libs/ -lscaleup"
```

Lattice and Electronic Model share the same modelfile .xml

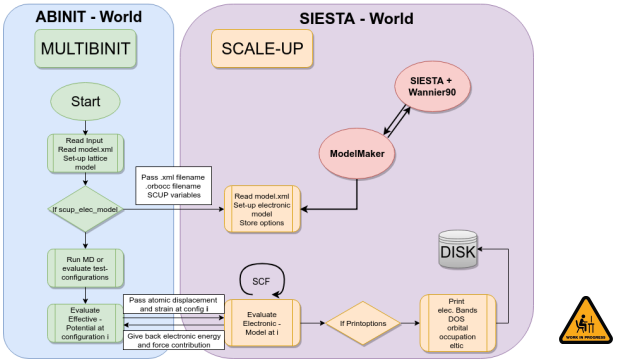


THE MULTIBINIT - SCALE-UP INTERFACE

Multibinit incorporates SCALE-UP as a library

```
FC_LIBS="-L/path/to/scaleup/build/src/.libs/ -lscaleup"
```

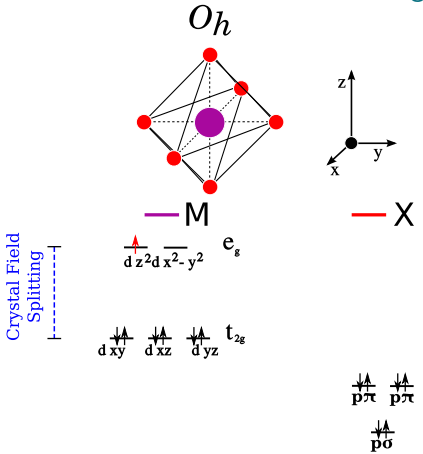
Lattice and Electronic Model share the same modelfile .xml



Transferability assured by PSML Pseudopotential-Format.

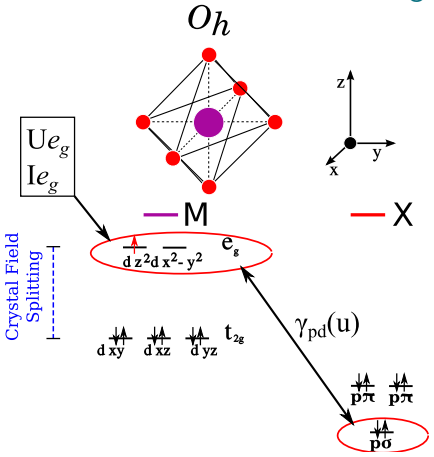
A first model using electron-lattice coupling

Classical Problem of cooperative Jahn-Teller Effect in Perovskites
Corner shared transition metal octahedra with double-degenerate electronic state



A first model using electron-lattice coupling

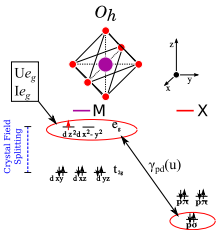
Classical Problem of cooperative Jahn-Teller Effect in Perovskites
Corner shared transition metal octahedra with double-degenerate electronic state



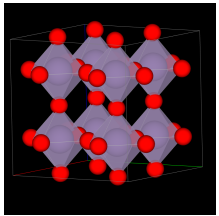
6. Electronic + Lattice Effective Model

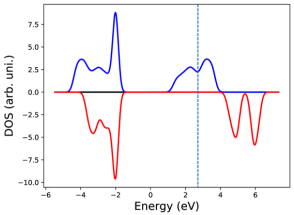
Electron-Lattice Coupling - Investigate Band-Structure and DOS

$U_{e_g} = 3eV$, $I_{e_g} = 1.5eV$, $\gamma_{pd} = 1.5eV$



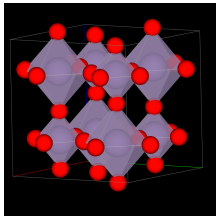
Cubic

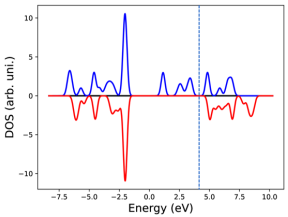




↑ Spin-up

Q_1^R





↓ Spin-Down

Multibinit is

But first interesting results arrive !

Thank You !

- ULiège : Marcus Schmitt, He Xu, Nicole Helbig, Fabio Ricci, Matthieu Verstraete, Eric Bousquet, Philippe Ghosez
- UCLouvain : Gian-Marco Rignanese, Xavier Gonze
- Others : Alexandre Martin, Sergeï Prokhorenko, Andrés Camilo García Castro

Interactions also with :

- USantander : Javier Junquera and Pablo García-Fernández
- LIST : Jorge Íñiguez