

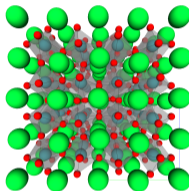


LIÈGE université
CESAM



AbiDev 2019

The Multibinit project



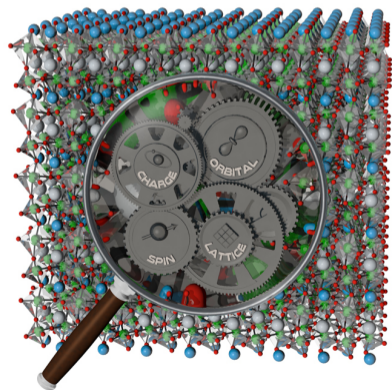
† Jordan Bieder, Alexandre Martin, Xu He, Marcus Schmitt, Nicole Helbig and
Philippe Ghosez

† PhyTheMa - ULG
CESAM / Q-MAT

May 21st, 2019

Motivations

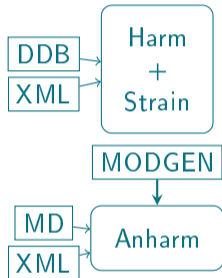
Understanding and engineering functional properties often require understanding materials at the atomic scale.

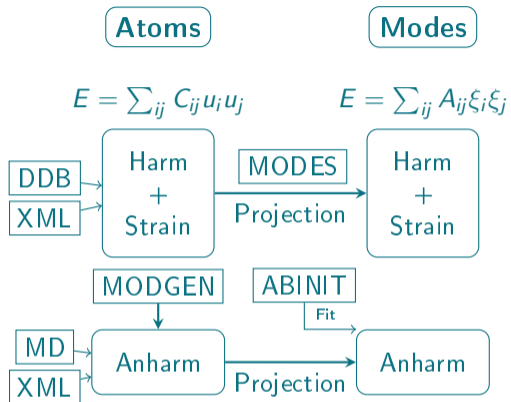


- From *ab-initio* data to second-principles.
- Integrate some degree of freedom.
- Access relevant properties at operating conditions from different length-scales.

Atoms

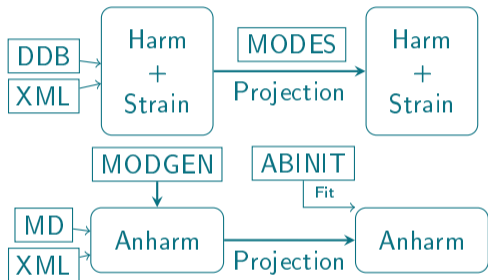
$$E = \sum_{ij} C_{ij} u_i u_j$$





Atoms

$$E = \sum_{ij} C_{ij} u_i u_j$$

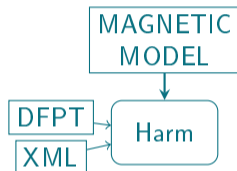


Modes

$$E = \sum_{ij} A_{ij} \xi_i \xi_j$$

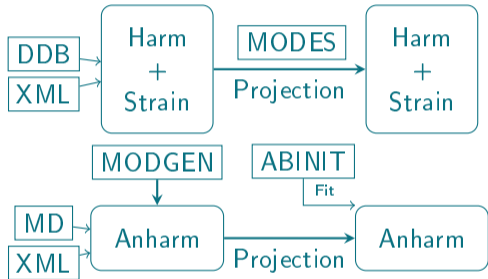
Spins

$$E = \sum_{ij} J_{ij} S_i S_j$$



Atoms

$$E = \sum_{ij} C_{ij} u_i u_j$$

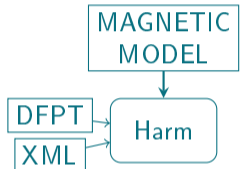


Modes

$$E = \sum_{ij} A_{ij} \xi_i \xi_j$$

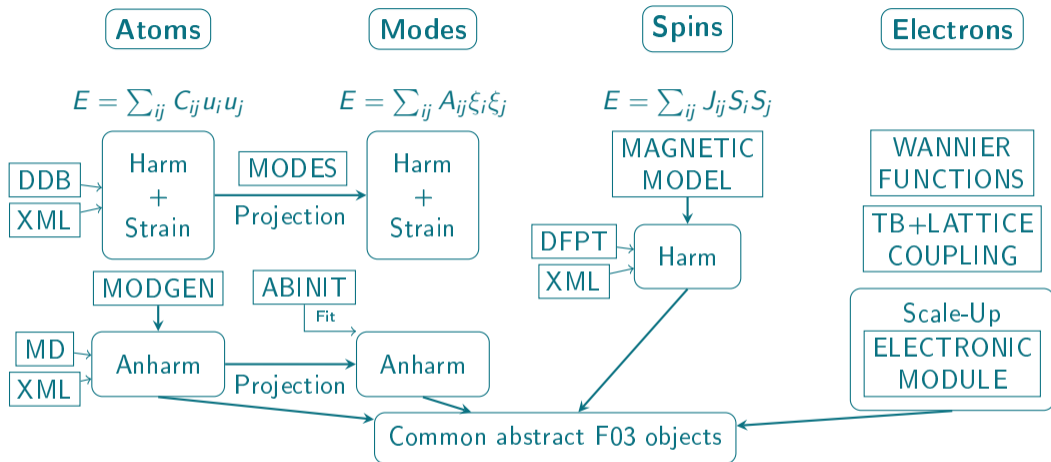
Spins

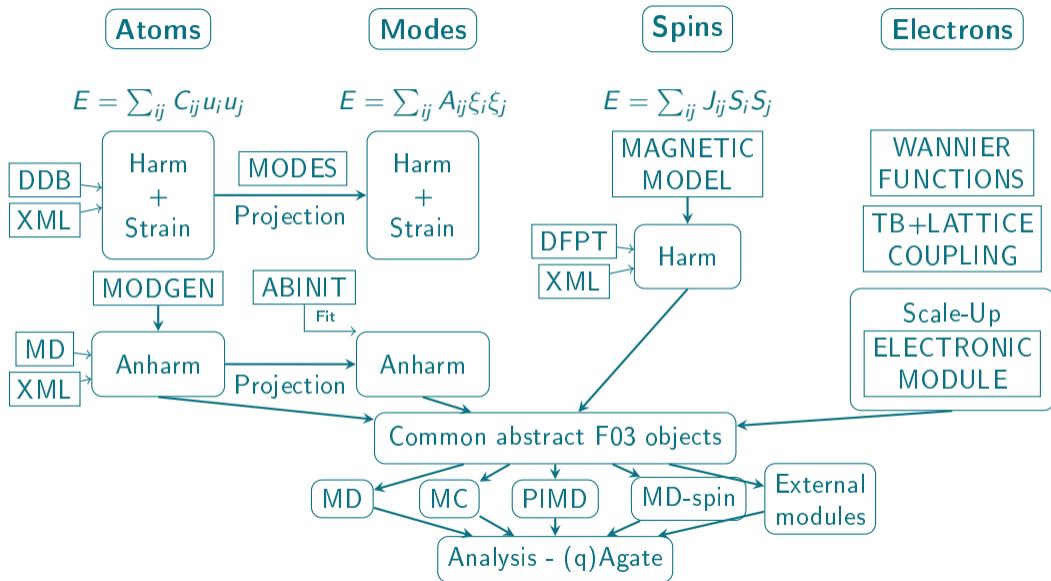
$$E = \sum_{ij} J_{ij} S_i S_j$$

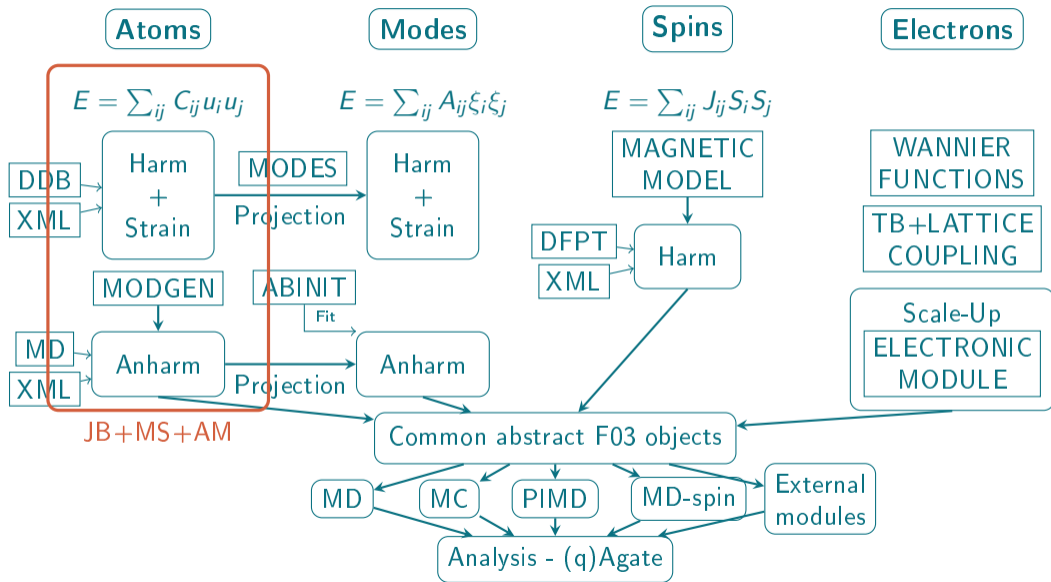


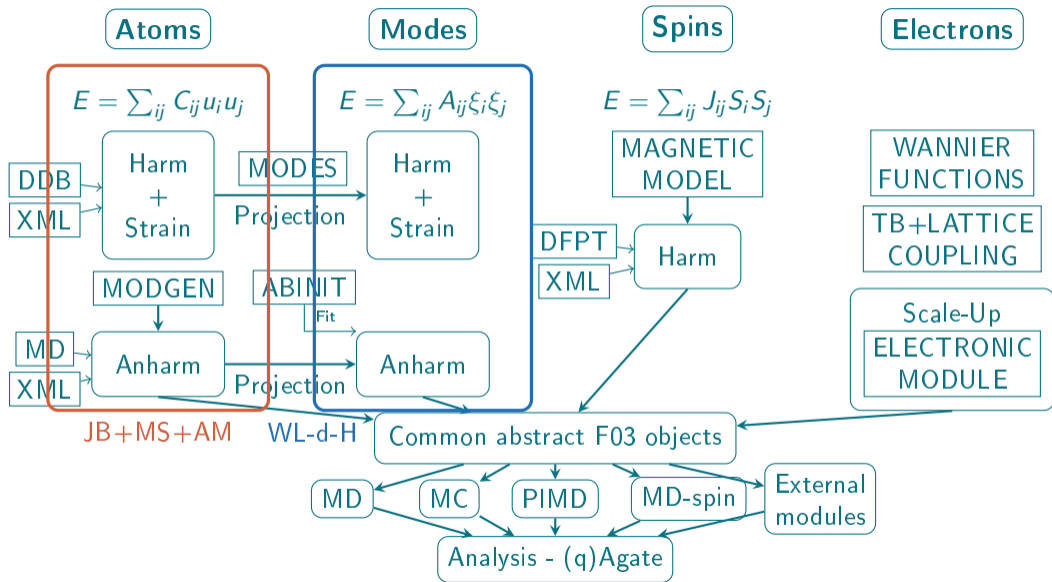
Electrons

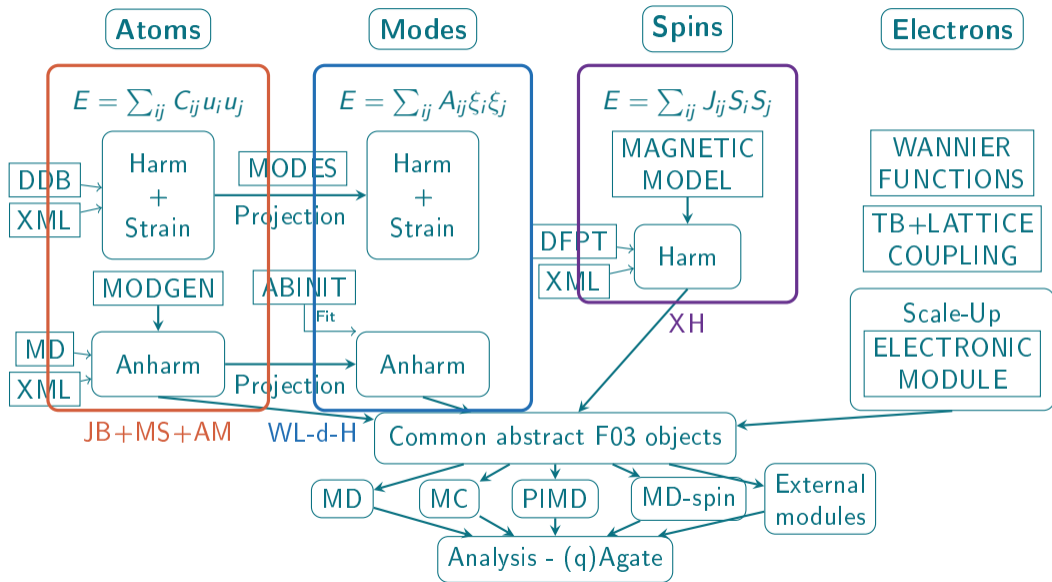
WANNIER
FUNCTIONSTB+LATTICE
COUPLINGScale-Up
ELECTRONIC
MODULE

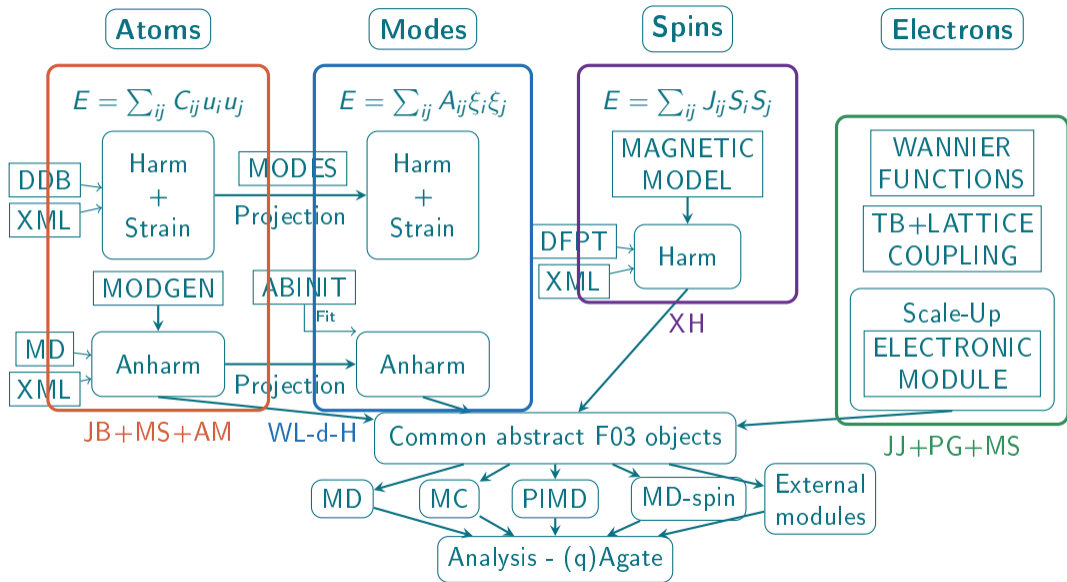












Multibinit in the package

- Multibinit is a new executable included in the `src/98_main/multibinit`
- New directory `src/78_effpot` have been created with many new files !
 - New directory structure is planned to better organize the code
 - Split abstract layer from each potential
 - Split the mover from the potentials
- New input have been created (mix between `anaddb` and `ABINIT`)
- The parsing of the XML file is done with Fortran or LibXML (more efficient...)
- MPI Parallelization
- Hybrid Monte Carlo is implemented
- Some of `abinit` movers are used
- New automatic tests in the version 8
- New documentation with a topic on the website.
- New tutorial to learn how to use `multibinit` (lattice and spin)



Basic Procedure

- Express energy as low order Taylor expansion
 - Use high-symmetry reference structure
 - Variables: 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 freedom is often difficult.

We need a general description of the energetics of all the atomic degrees 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

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

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



Energy changes around reference structure due to distortions

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

↓
Energy change due to
strain only

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

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



Energy changes around reference structure due to distortions

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

Energy change from atomic displacements

Energy change due to strain only

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

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

Energy changes around reference structure due to distortions

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

Energy change from
atomic displacements

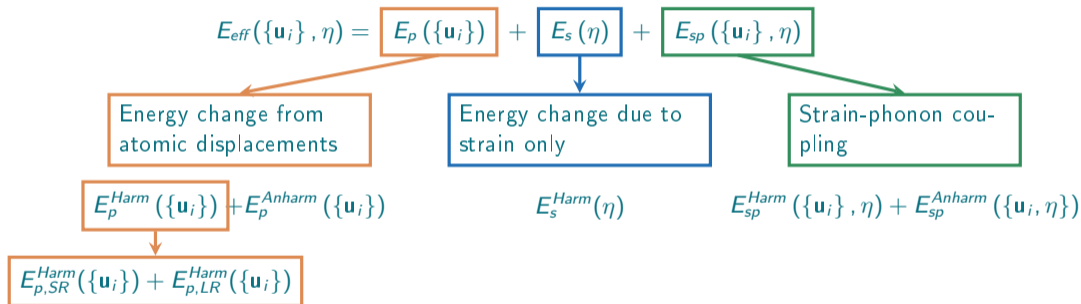
Energy change due to
strain only

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

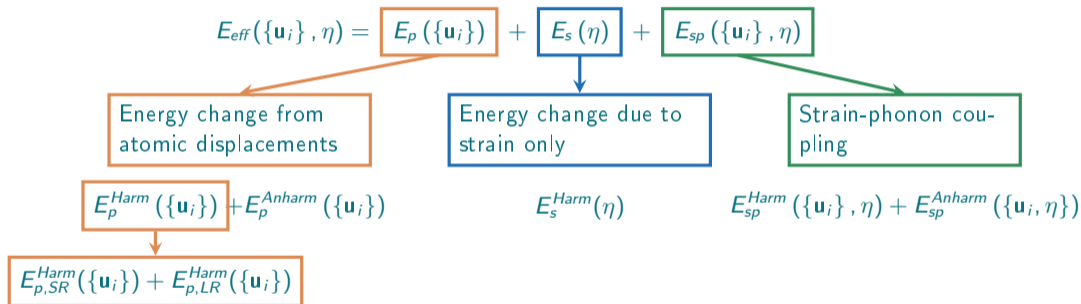
$$E_s^{\text{Harm}}(\eta)$$

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

Energy changes around reference structure due to distortions



Energy changes around reference structure due to distortions



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

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

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

Taylor development around the reference structure

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

$$\text{with } K_{i\alpha j\beta\dots}^n = \left. \frac{\partial^n E_{\text{eff}}}{\partial u_{i\alpha} \partial u_{j\beta} \dots} \right|_{\eta=0}$$

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

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

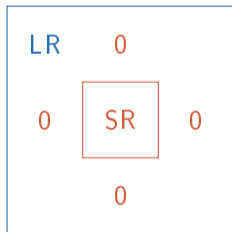
$$E_p^{Harm}(\{\mathbf{u}_i\}) = E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$$

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

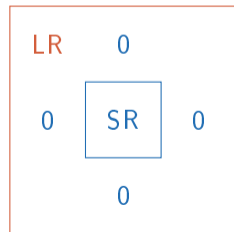
$$E_p^{Harm}(\{\mathbf{u}_i\}) = E_{p,SR}^{Harm}(\{\mathbf{u}_i\}) + E_{p,LR}^{Harm}(\{\mathbf{u}_i\})$$

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

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

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

- ASR enforces by using differences
- Too many terms for “hight” orders
- Use symmetries to reduce de number of coefficients

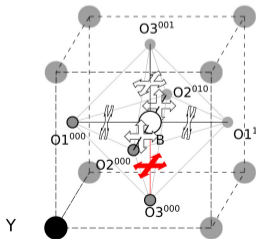


$$E_p^{Anharm}(\{\mathbf{u}_i\})$$

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 $(u_{0Bz} - u_{0O1z})^2(u_{0By} - u_{0O1y})^2$
 → **15 independent parameters**
 (1st nearest neighbors at 3rd and 4th order in u) for the
 anharmonic phonon part.

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

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.
- ⇒ Harmonic terms exact by construction and include all phonon branches

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

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.
- ⇒ 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 quantities to limited number of DFT calculations (training set)

Strain term $E_s(\eta)$

Taylor development around the reference structure

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

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

- 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

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

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

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

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:

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

- where $\Omega(s) = (V(s)\sqrt{(N)})^{(-1/3)}$
- 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

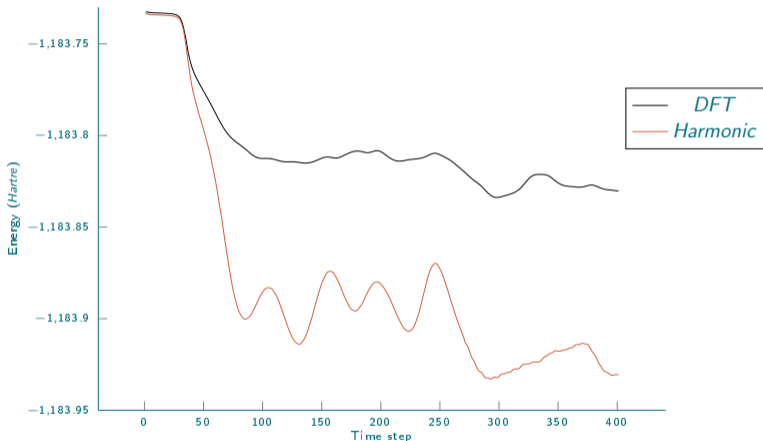
```
prt_model = 1

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

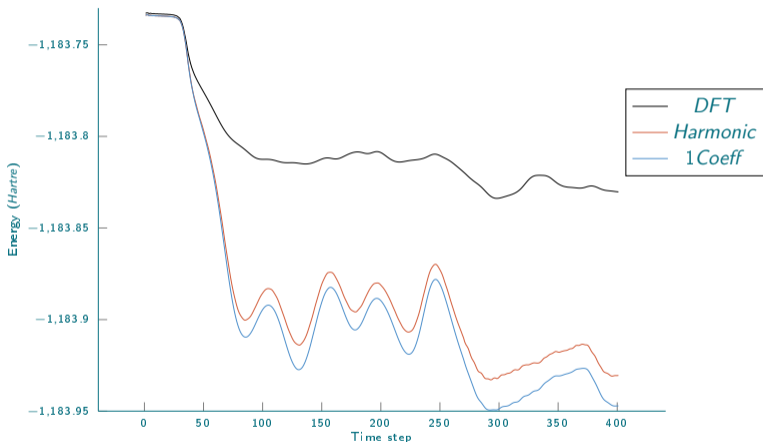
fit_coeff = 1

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

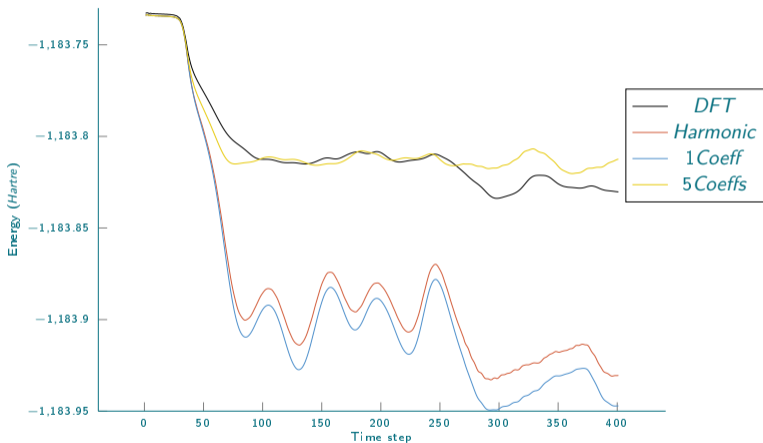
ts_option = 1
```

Example of CaTiO_3 cubic phase


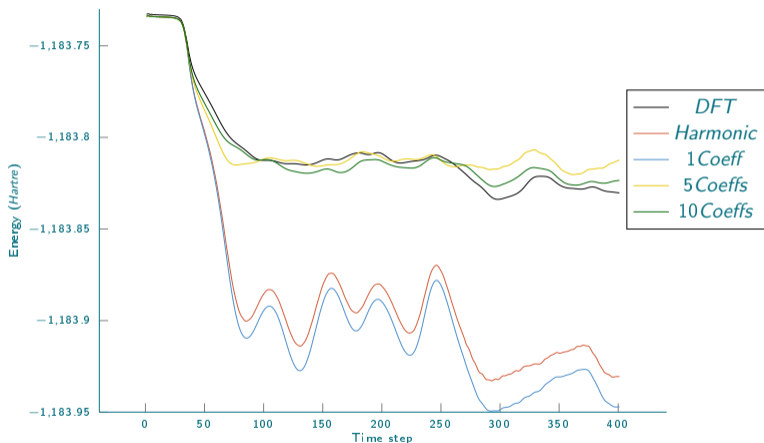
- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.

Example of CaTiO_3 cubic phase


- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 1 Coeff: 284.70 meV/f.u.

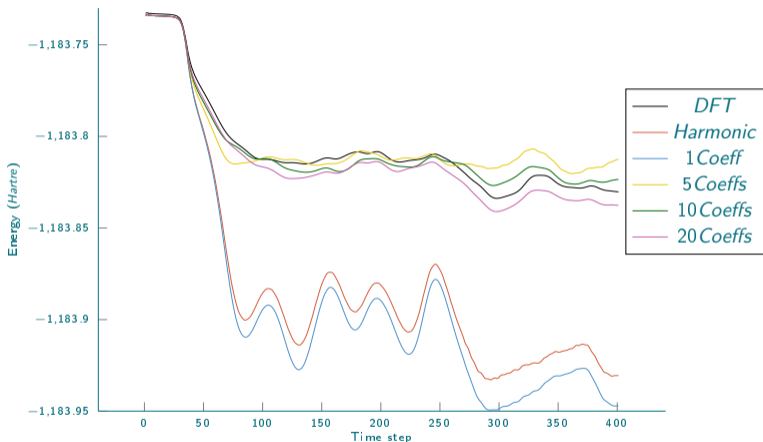
Example of CaTiO_3 cubic phase


- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 5 Coeffs: 21.28 meV/f.u.

Example of CaTiO_3 cubic phase


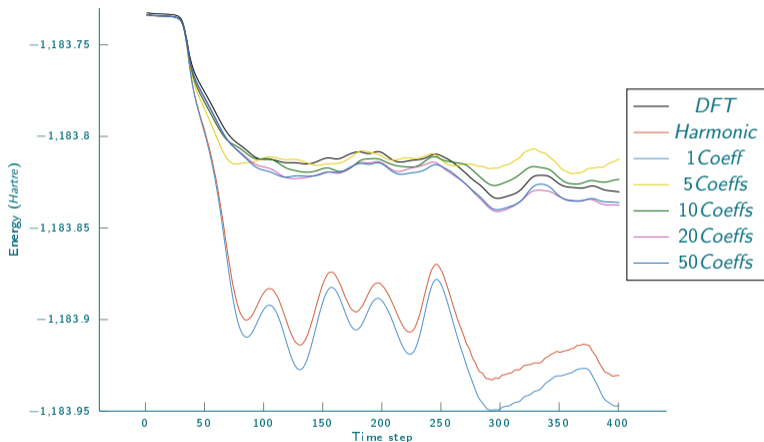
- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 10 Coeffs: 12.75 meV/f.u.

Example of CaTiO_3 cubic phase



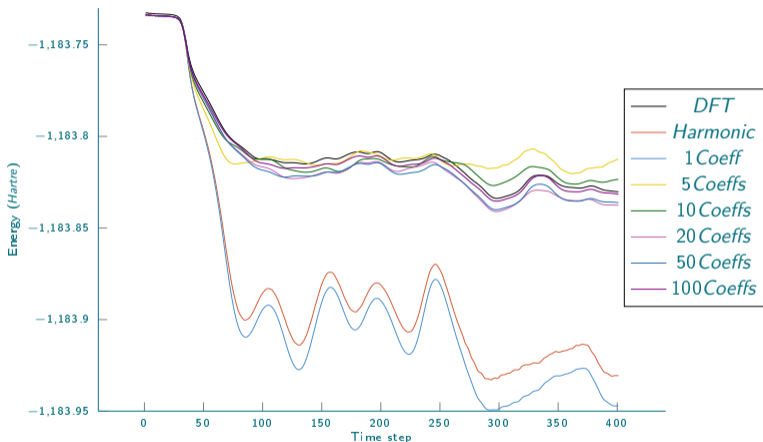
- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 20 Coeffs: 19.37 meV/f.u.

Example of CaTiO_3 cubic phase

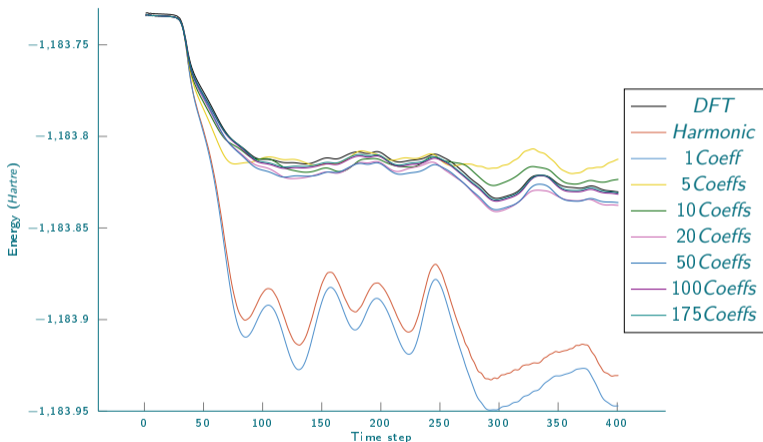


- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 50 Coeffs: 19.03 meV/f.u.

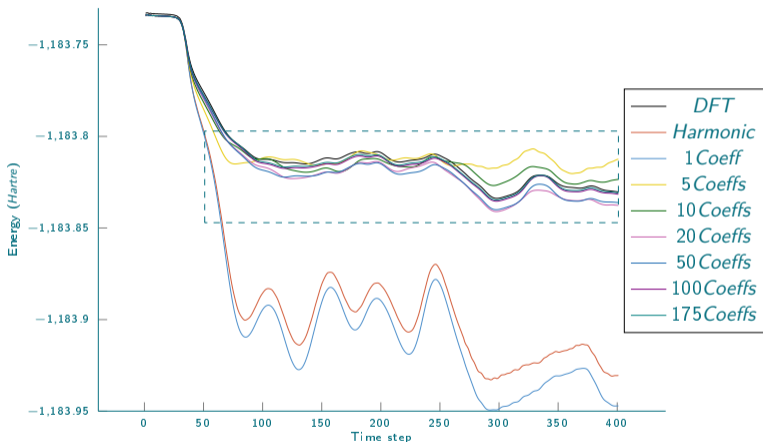
Example of CaTiO_3 cubic phase



- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 100 Coeffs: 6.46 meV/f.u.

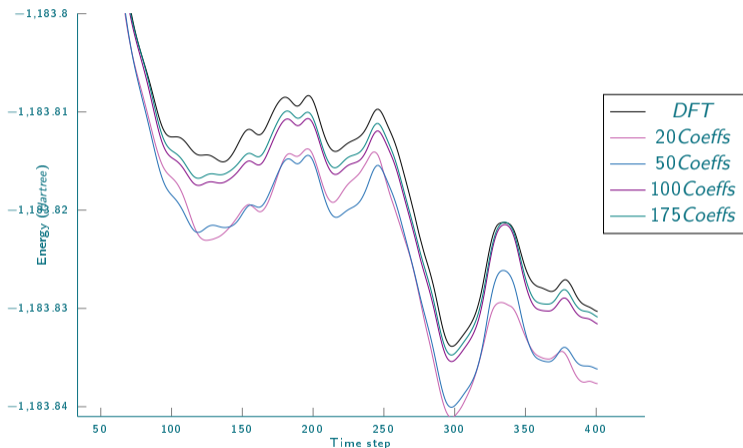
Example of CaTiO_3 cubic phase


- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 175 Coeffs: 4.45 meV/f.u.

Example of CaTiO_3 cubic phase


- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 175 Coeffs: 4.45 meV/f.u.

Example of CaTiO_3 cubic phase



- Mean Standard Deviation of the Energy with only Harmonic: 250.58 meV/f.u.
- Mean Standard Deviation of the Energy with 175 Coeffs: 4.45 meV/f.u.



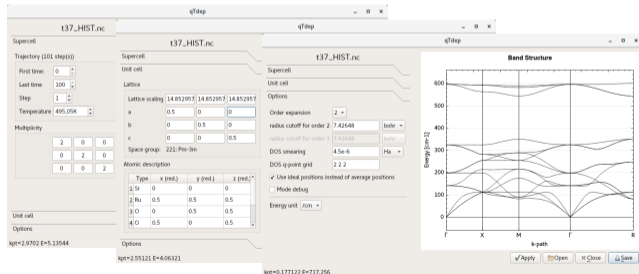
Bounding the potential

- If the highest order is odd
 - If the highest order is even and the coefficient negative
- ⇒ The potential might be unstable !!
- Add artificial physics with maths to bound the process.
- See M. Schmitt presentation.



Analyzing the results q(Agate)

- Visualize the trajectory
- Perform all “MD” analysis (PDF, T, P, V, ...)
- Extract phonons at finite temperature (with a-TDEP see F. Bottin talk)
- Project on modes and follow phase transitions



Lattice part

- Multibinit is able to make interface between first principles calculations and mesoscopic simulations for \hat{A} «any \hat{A} » system
- Automatic construction of the models with harmonic and anharmonic contributions from first principles
- Automatic bound process
- Tool able to run dynamics (Monte Carlo or Molecular dynamics)
- Good tools for result analysis and post-processing of data ((q)Agate)
- New ionmov in abinit to generate the training set



Miscellaneous

- Spin potential available (X. He talk)
- Spin dynamics available (X. He Talk)
- Spin-lattice coupling (N. Helbig)
- Effective Hamiltonian WIP (W. Lafargue-dit-Hauret poster)
- Coupling with electronic potential (M. Schmitt and previous talks)
- Common data structure for ease of use and interfacing



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