Theoretical Materials Physics
Q-MAT - CESAM

The MULTIBINIT software project

Philippe GHOSEZ

Philippe.Ghosez@ulg.ac.be

Fréjus, May 2017

MULTIBINIT collaborators

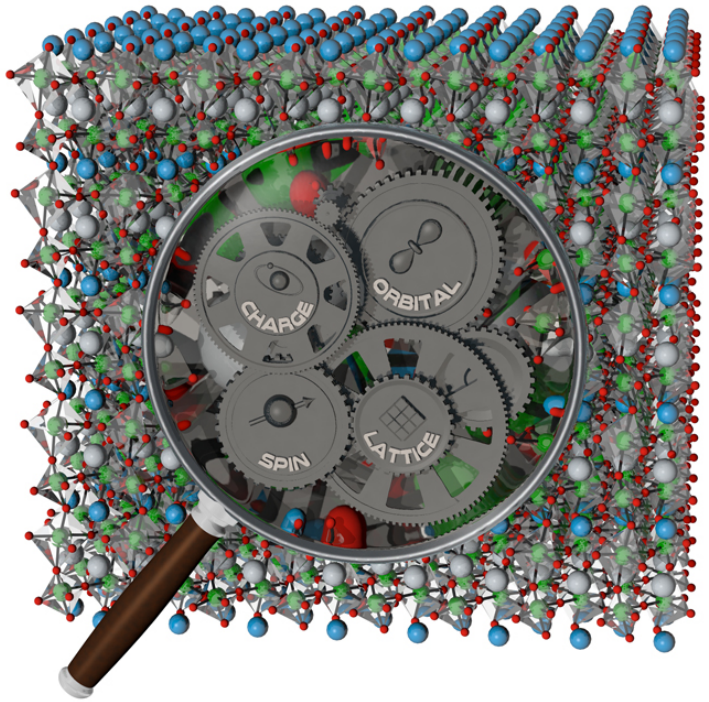
- **ULiège** : Alexandre Martin, Sergeï Prokhorenko, He Xu, Matthieu Verstraete, Eric Bousquet, Philippe Ghosez
- **UCLouvain** : Gian-Marco Rignanese
- **CEA** : Jordan Bieder

Interactions also with :

- **USantander** : Javier Junquera and Pablo Garcia-Fernandez
- **LIST** : Jorge Iniguez

Motivation

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



First-principles modelling has become a **standard** tool :

- Speed (compatible with needs)
- Accuracy (tiny effects)
- Reliabilty (predictive)
- Automaticity (high-throughput)
- « Cheap » (compared to exp)

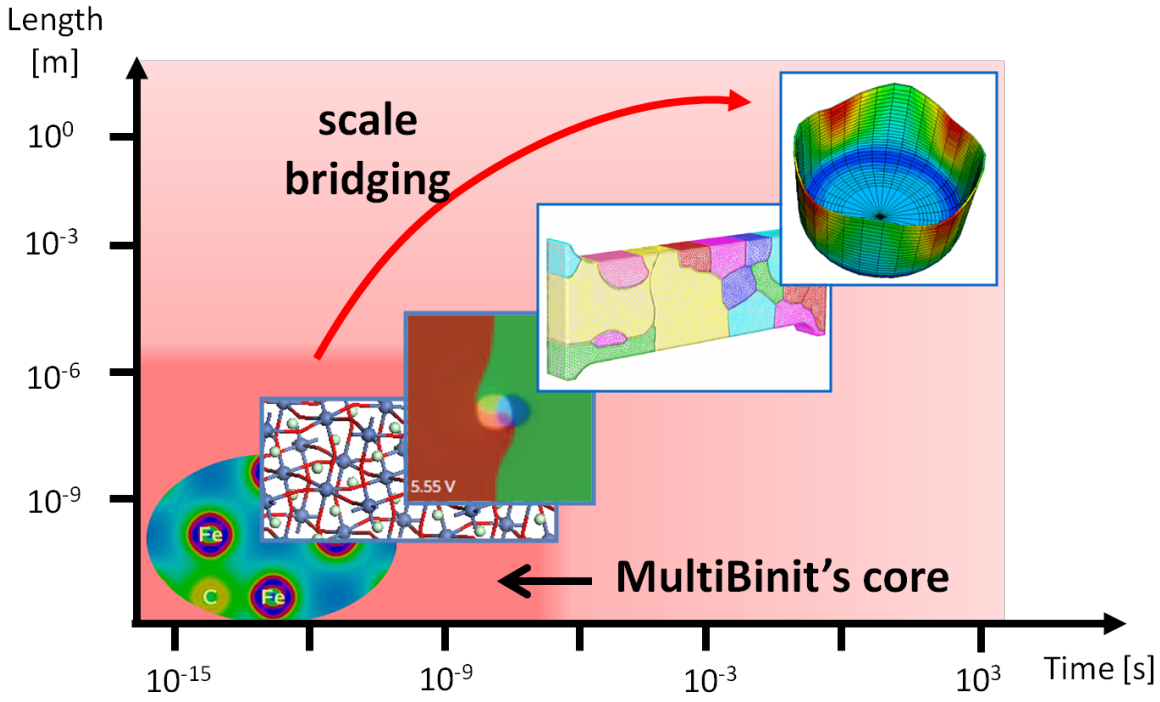
From academia to industry …

Motivation

Different scales

- Micro-macro scale :

Well established continuous models



- Nanoscale:

First-principles but limited to relatively small length-scale (nm, 100-1000 atoms) and small time-scale (few ps).

- Mesoscale:

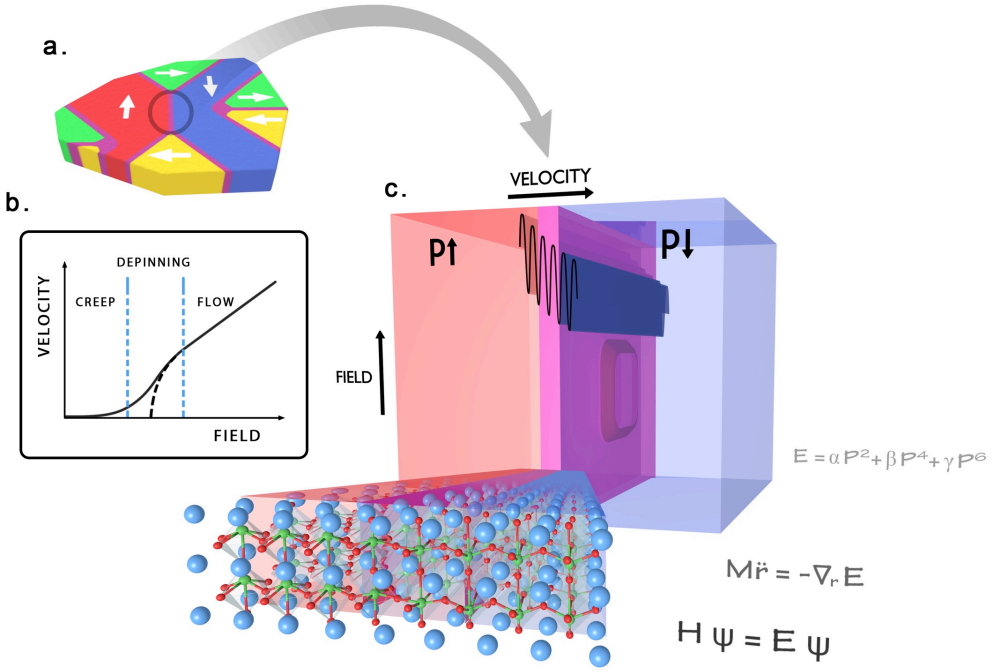
Often needs to keep atomistic description.

Various types of atomistic models but no standard yet.

Second-principles

- **Multi-scale**:

Accessing relevant properties at operating conditions (finite-T, mechanical constraints…) often needs **to bridge different length-scales**.



Domain-wall motion in $PbTiO_3$

- « **Second-principles** » :

- *Effective models* integrating out some degrees of freedom.
- All parameters extracted from first-principles data (two options: computed directly or fitted)

Motivation

- **First-principles**

ACADEMIA

1990 — Various methods and home-made codes with specific features.

2000 — Joint development of unified packages with multifunctionalities : **ABINIT**, …

2010 — Definition of standards, compatibility, robustness Reliability,…

INDUSTRY

Motivation

- **First-principles**
- **Second-principles**

ACADEMIA

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2000 — Joint development of unified packages with multifunctionalities : **ABINIT**, …

2010 — Definition of standards, compatibility, robustness reliability

INDUSTRY

Various methods and home-made codes with specific features.

Joint development of unified packages with multifunctionalities : **MULTIBINIT**!

Steps and objectives

- **Steps**:

1. Generation of models systematically improvable and adapted to the geometry

2. Determination of parameters from first-principles data

3. Finite temperature simulations of various quantities

4. Efficient result analysis (AGATE)

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- **Objectives**:

- *Generic tool* valid for « any » system.

- *Automatic construction* of models and determination of parameters (high-throughput)

- *Compatibility* with various FP packages.

- Integrated tool gathering *various modes and functionalities*.

- Good *tools for result analysis* and post-processing of data.

What is MULTIBINIT ?

MULTIBINIT

- **At first : model atomic potentials for lattice dynamics simulations.**

- Various possible approaches (Lennard-Jones, shell-models, bond-valence models, Tersoff, reactive force-fields …).

- *Our choice* : generalisation of « effective Hamiltonian » approach developed for ferroelectrics.

- Based on a **« *low-order* » expansion** around a **reference structure** : limited to « *small »* displacements and *fixed bonding topology* !

- Inclusion of all *atomic degrees of freedom* (reduced coordinates) and *homogeneous strains*.

MULTIBINIT - Lattice

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

$$E^{harm}(u) + E^{anharm}(u)$$

$$E^{SR}(u) + E^{DD}(u)$$

$$E_{\mathrm{p}}(\{\boldsymbol{u}_i\}) = \tfrac{1}{2}\sum_{i\alpha j\beta} K^{(2)}_{i\alpha j\beta} u_{i\alpha} u_{j\beta} + \tfrac{1}{6}\sum_{i\alpha j\beta k\gamma} K^{(3)}_{i\alpha j\beta k\gamma} u_{i\alpha} u_{j\beta} u_{k\gamma} + \cdots,$$

(up to arbitrary orders)

$$E^{harm}(\eta)$$

$$E_{\mathrm{s}}(\boldsymbol{\eta}) = \frac{N}{2}\sum_{ab} C^{(2)}_{ab}\eta_a\eta_b$$

$$E^{harm}(\eta) + E^{anharm}(\eta)$$

$$E_{\mathrm{sp}}(\{\boldsymbol{u}_i\},\boldsymbol{\eta}) = \tfrac{1}{2}\sum_{a}\sum_{i\alpha}\Lambda^{(1,1)}_{ai\alpha}\eta_a u_{i\alpha} + \tfrac{1}{6}\sum_{a}\sum_{i\alpha j\beta}\Lambda^{(1,2)}_{ai\alpha j\beta}\eta_a u_{i\alpha} u_{j\beta} + \tfrac{1}{6}\sum_{ab}\sum_{i\alpha}\Lambda^{(2,1)}_{abi\alpha}\eta_a\eta_b u_{i\alpha} + \cdots$$

See *Alex's talk*

- Harmonic terms directly computed from first-principles (physical quantities)
- Anharmonic terms directly fitted on first-principles (effective parameters)

Example : $PbTiO_3$

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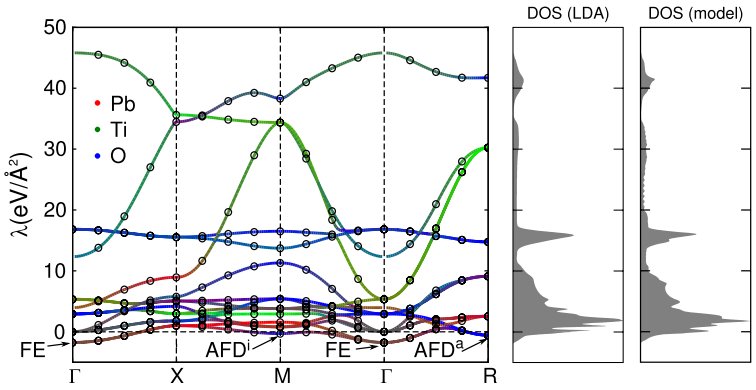
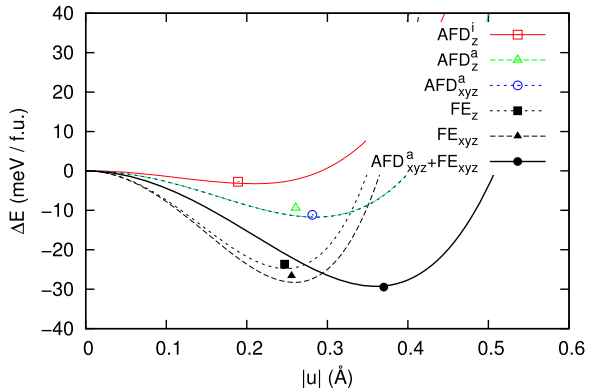
Force-constant matrix eigenvalues



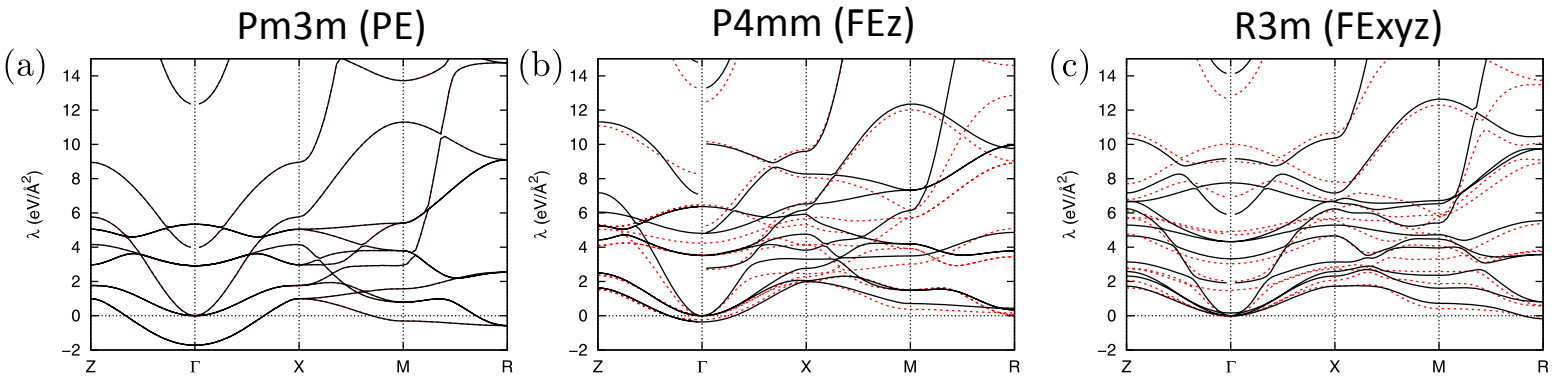
Effective anharmonicities



Keep first-principles accuracy at the harmonic level

Effective treatment of the anharmonicities at low orders

Force-constant matrix eigenvalues for distinct metastable phases



Proper description of the dispersion curves even well away from the reference for highly anharmonic systems

Example : $PbTiO_3$

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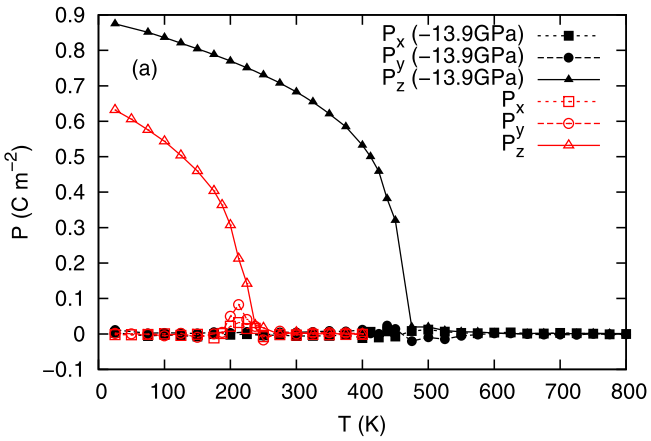
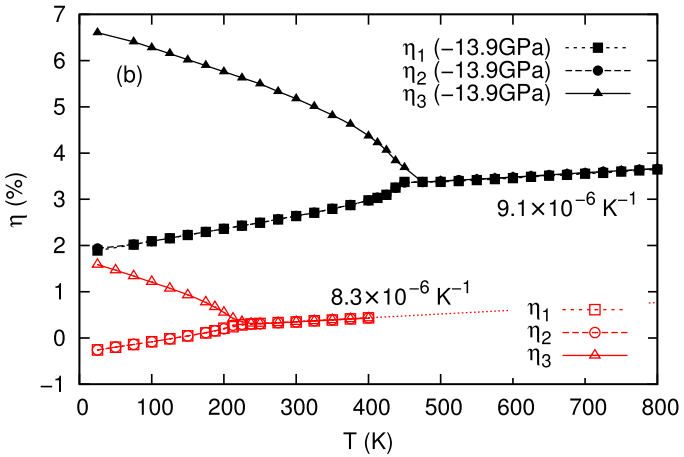
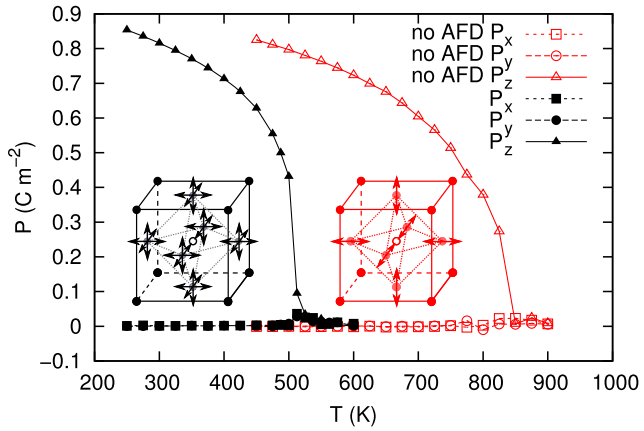




It properly captures the ferroelectric phase transition
(although some renormalization of T is required)



New physics accessible:
It reveals the crucial role of hidden
and competing oxygen AFD motions

MULTIBINIT

Beyond effective atomic potentials

Perspective on MULTIBINIT structure and expected future developments

MULTIBINIT

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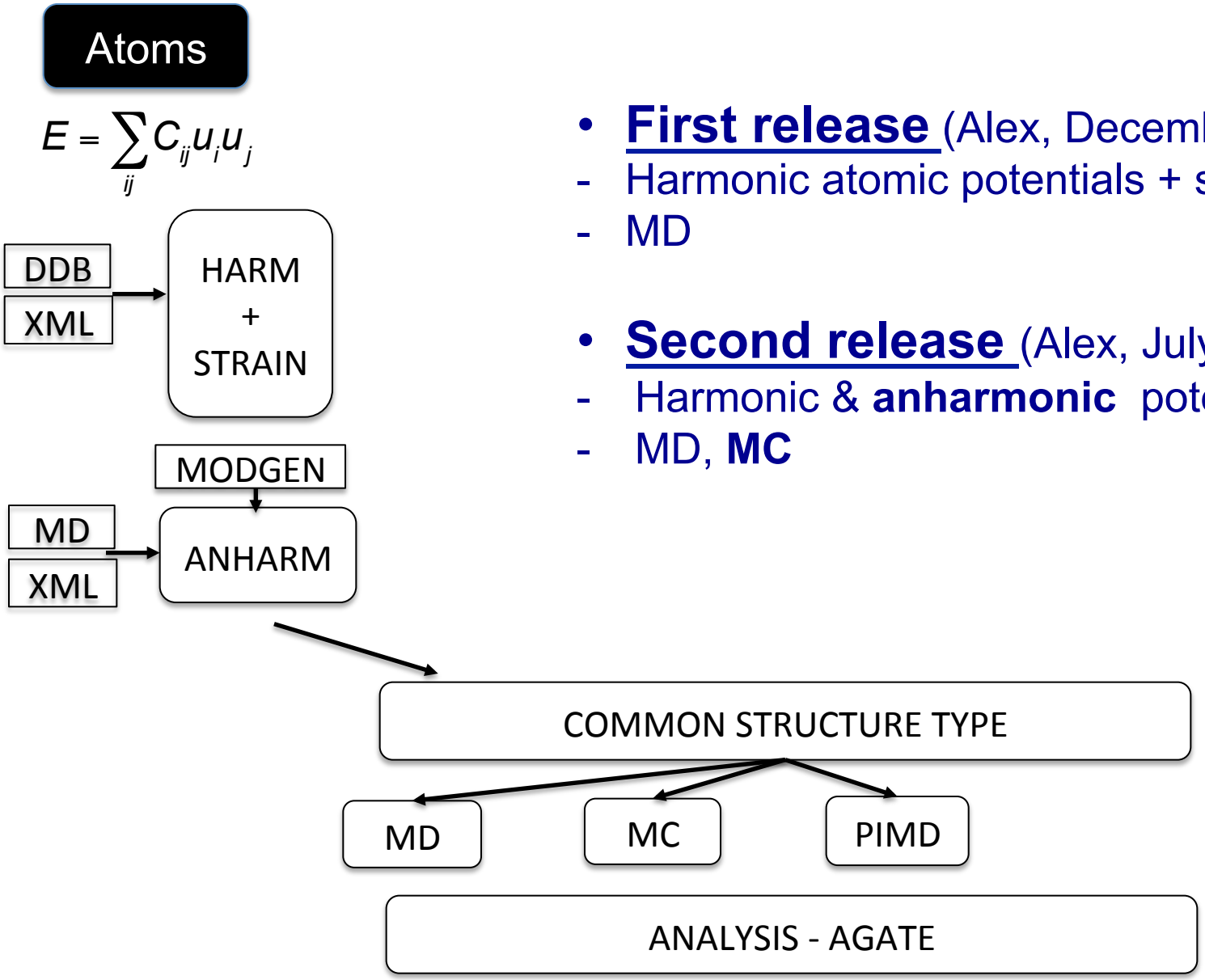
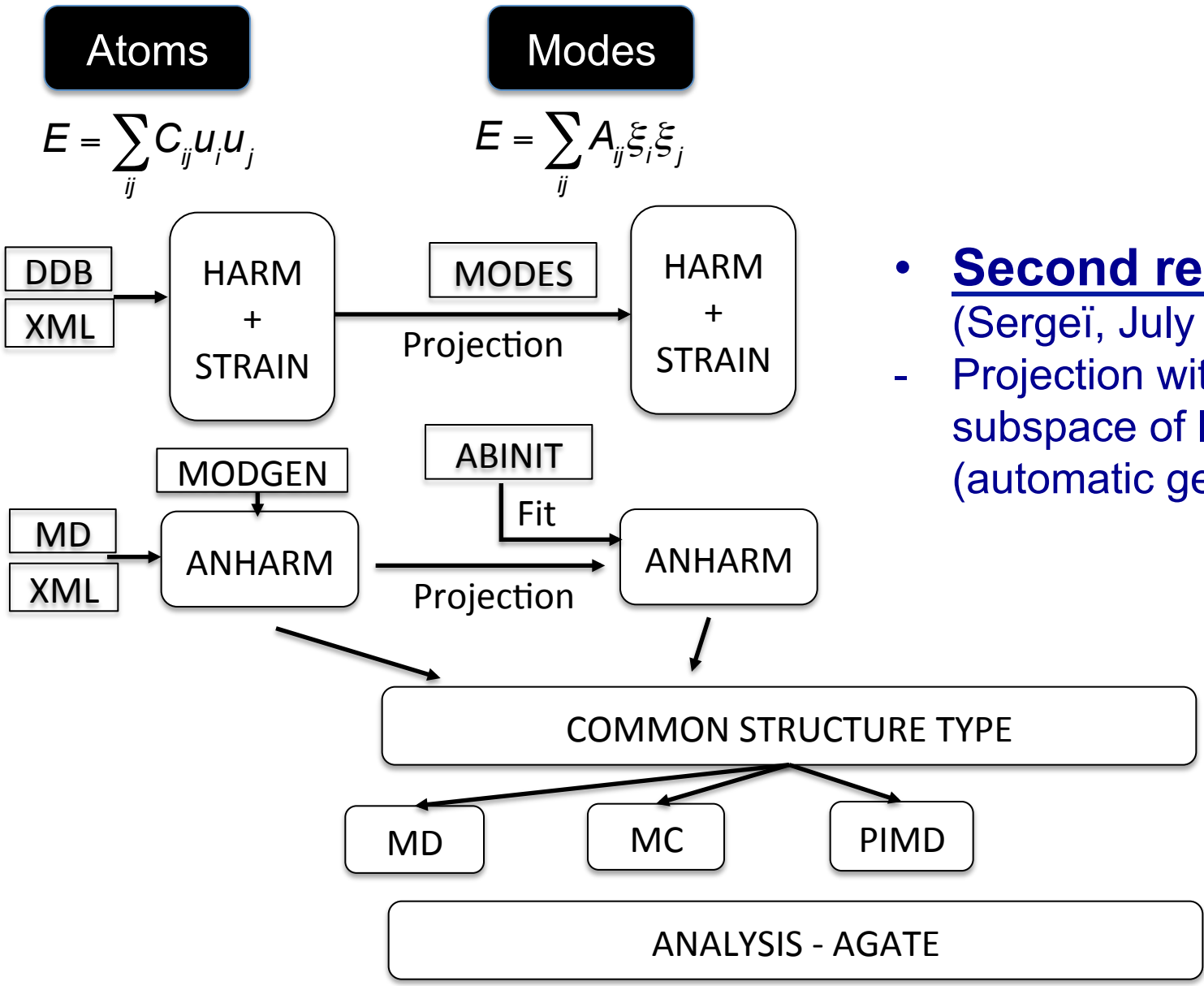


- **First release** (Alex, December 16):
  - Harmonic atomic potentials + strain
  - MD

- **Second release** (Alex, July 17):
  - Harmonic & **anharmonic** potentials + strain
  - MD, **MC**

See Jordan

MULTIBINIT



- **Second release** (Sergeï, July 17):
  - Projection within a given subspace of lattice modes (automatic generation H_{eff})

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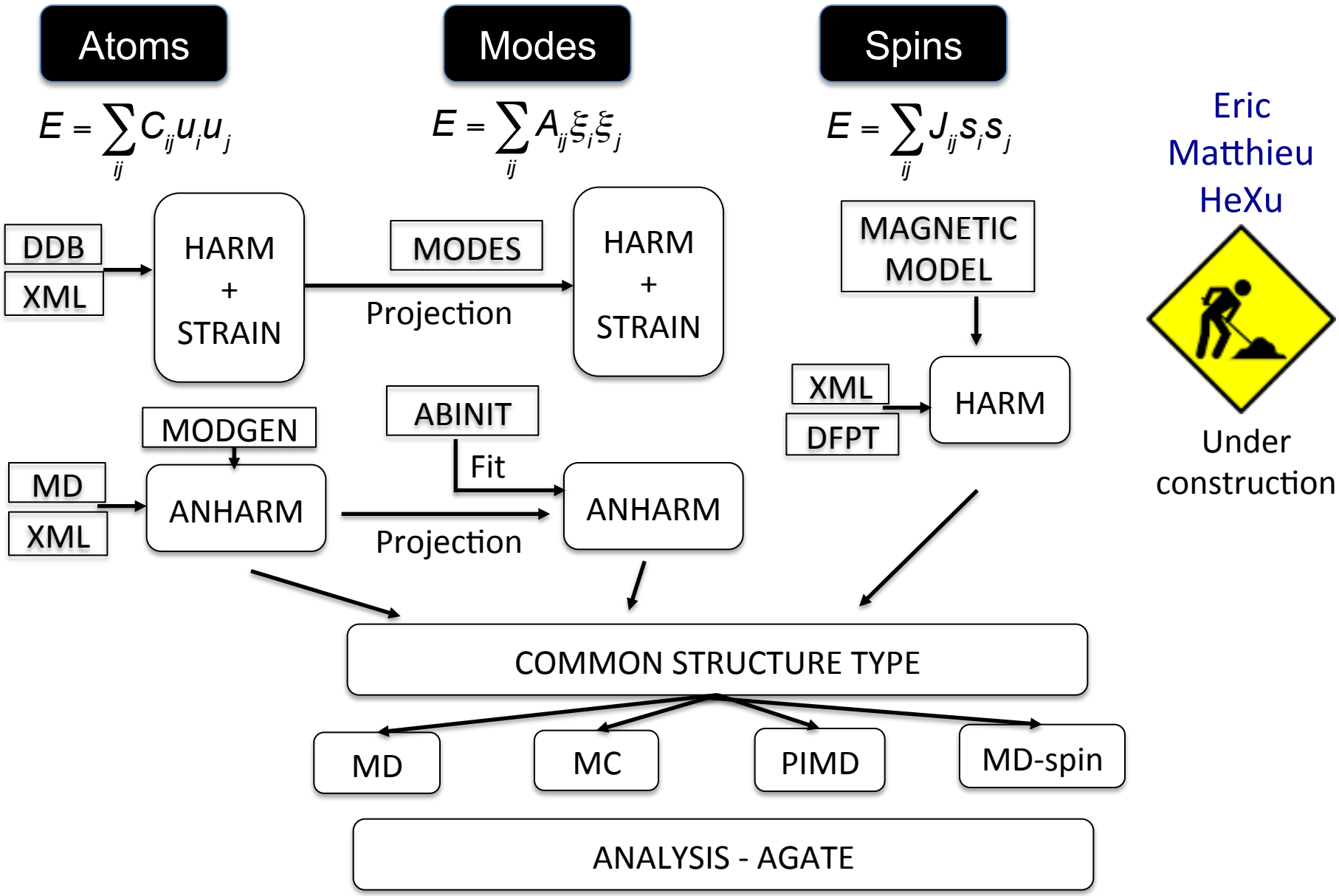
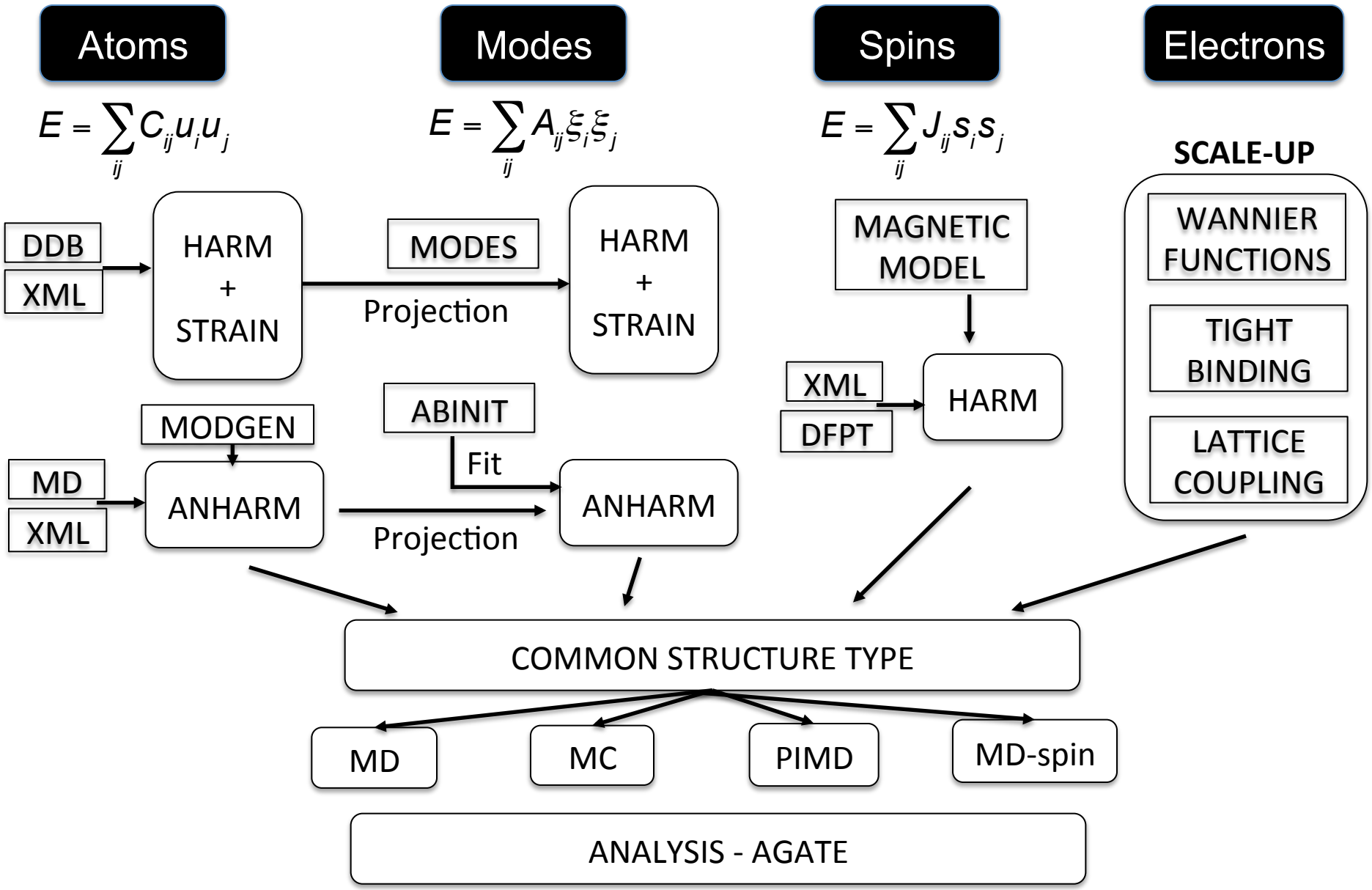


Eric
Matthieu
HeXu

Under construction

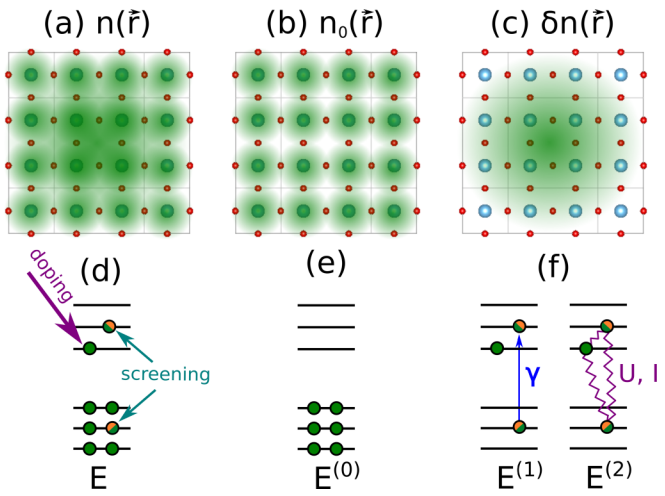
MULTIBINIT


Atoms
Modes
Spins
Electrons
$E = \sum_{ij} C_{ij} u_i u_j$
$E = \sum_{ij} A_{ij} \xi_i \xi_j$
$E = \sum_{ij} J_{ij} s_i s_j$
SCALE-UP
DDB
XML
HARM + STRAIN
MODES
Projection
HARM + STRAIN
MAGNETIC MODEL
WANNIER FUNCTIONS
TIGHT BINDING
LATTICE COUPLING
XML
DFPT
HARM
MODGEN
ABINIT
Fit
MD
XML
ANHARM
Projection
ANHARM
COMMON STRUCTURE TYPE
MD
MC
PIMD
MD-spin
ANALYSIS - AGATE

MULTIBINIT – Electronic part

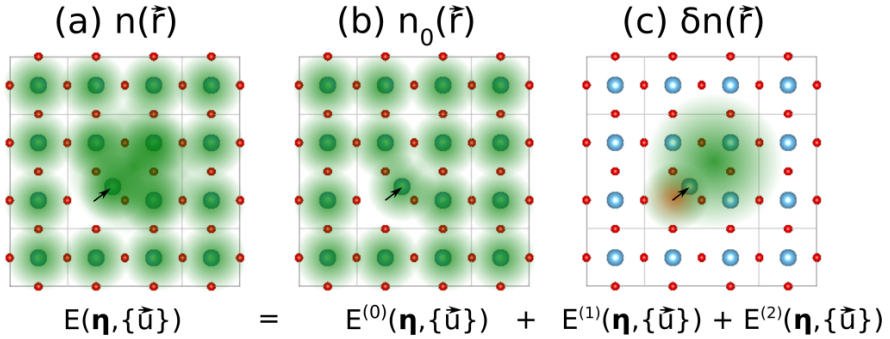
- **Interface with SCALE-UP module (P. Garcia & J. Junquera)**

- Sometimes necessary to reintroduce electronic degrees of freedom.



- « Extra » tight-binding model based on Wannier functions **coupled** to the effective atomic potentials

- Only **deviations** with respect to reference electronic configuration are taken into account !



- Suitable for MIT, orbital and charge orderings, polarons, conducting domain walls …

Summary

- **MULTIBINIT** :

- A unified tool designed for the second-principles modelling of large systems (up to a few 100.000 of atoms) at finite temperatures and operating conditions (external pressure, finite fields …). (but restricted to fixed bonding topology)

- A well intergrated package, with automatic construction of models from first-principles data.

- Various mixed modes: atoms/modes – strain – spin/electrons
- Various schemes : MD, MC, (PIMD), …

- Good post-processing tools for data analysis (AGATE) !