MULTIBINIT:

How to scale up simulations from second principles models

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1. MULTIBINIT AND THE LATTICE MODEL
How to compute the energy from second principles?

- The energy of this new system is not \( E_0 \) due to the small displacement \( u \).
- Application of a strain \( \eta \) or an electric field will also change the energy.

We compute the energy with the response functions from first principles.
How to compute the energy from second principles?

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ENERGY FROM SECOND PRINCIPLES

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**We compute the energy with the response functions from first principles**
Energy from second principles

\[ E(u, \eta) = E_{\text{phonon}}(u) + E_{\text{strain}}(\eta) + E_{\text{strain-phonon}}(u, \eta) \]

- Harmonic parts are computed with DFT/DFPT calculations.
- Anharmonic parts of the strain coupling can be computed with finite differences with respect to strain or can be fitted.
- The anharmonic part involving atomic displacements is more complex...
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2. Harmonic part of the potential
Harmonic part $E^{\text{harm}}(u, \eta)$ of the potential

Harmonic part of the potential $^1$: $E^{\text{harm}}(u, \eta) = E^{\text{harm}}(u) + E^{\text{harm}}(u, \eta) + E^{\text{harm}}(\eta)$

- In the model, the harmonic part is computed from *ab initio* calculations
- This model requires DFPT calculations or finite differences...
- Computation of the phonon response:
  $$E^{\text{harm}}(u) = \frac{\partial^2 E}{\partial u^2} + \frac{\partial^2 E}{\partial \varepsilon^2} + \frac{\partial^2 E}{\partial \varepsilon \partial u}$$
  Inter-atomic force constants Dielectric tensor Effective charges

- Computation of the strain response:
  $$E^{\text{harm}}(\eta) = \frac{\partial^2 E}{\partial \eta^2}$$
  Elastic constants

- Computation of the strain-phonon coupling:
  $$E^{\text{harm}}(u, \eta) = \frac{\partial^2 E}{\partial \eta \partial u}$$
  Internal strain

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Harmonic part $E^{harm}(u, \eta)$ of the potential

Special treatment of the interatomic force constants

- Generation of a supercell and 1 cell as reference
- Get the short range part in real space
- Computation of the dipole dipole interaction in reciprocal space for supercell in gamma (Ewald summation)

- Application of the acoustic sum rule
Harmonic part $E^{harm}(u, \eta)$ of the potential

Creation of the XML file with all the harmonic information

- Generation and/or use of XML file compatible with SPLD (Monte Carlo software)

```xml
<?xml version="1.0" ?>
<System_definition>
  <energy units="hartree">
    -1.62101128523
  </energy>
  <unit_cell units="bohrradius">
    7.3029865  0.000000  0.000000
    0.000000  7.3029865  0.000000
    0.000000  0.000000  7.3029865
  </unit_cell>
  <epsilon_inf units="epsilon0">
    6.352933  0.000000  0.000000
    0.000000  6.352933  0.000000
    0.000000  0.000000  6.352933
  </epsilon_inf>
  <elastic units="hartree">
    5.14090062749  1.47408623715  1.47408623715
    1.47408623715  5.14090062749  1.47408623715
    1.47408623715  1.47408623715  5.14090062749
    0.00000000000  0.00000000000  0.00000000000
    0.00000000000  0.00000000000  0.00000000000
  </elastic>
</System_definition>
```
Harmonic part $E^{\text{harm}}(u, \eta)$ of the potential

Creation of the XML file with all the harmonic information

- Generation and/or use of XML file compatible with SPLD (Monte Carlo software)

```xml
<atom mass="47.867" massunits="atomicmassunit">
   <position units="bohrradius">
      3.6515000 3.6515000 3.6515000
   </position>
   <borncharge units="abs(e)">
      7.33264 0.00000 0.00000
      0.00000 7.33263 0.00000
      0.00000 0.00000 7.33253
   </borncharge>
</atom>

<atom mass="87.62" massunits="atomicmassunit">
   <position units="bohrradius">
      0.0000000 0.0000000 0.0000000
   </position>
   <borncharge units="abs(e)">
      2.55338 0.00000 0.00000
      0.00000 2.55438 0.00000
      0.00000 0.00000 2.55438
   </borncharge>
</atom>
```
Harmonic part $E^{\text{harm}}(u, \eta)$ of the potential

Creation of the XML file with all the harmonic information

- Generation and/or use of XML file compatible with SPLD (Monte Carlo software)

```xml
<local_force_constant units="hartree/bohrradius**2">
  <data>
    5.41194389e-01 0.00000000e+00 1.70259891e-19 -1.07108103e-03 -2.74008600e-03
    -2.74008600e-03 -2.95745144e-01 0.00000000e+00 0.00000000e+00 3.11837486e-02
    0.00000000e+00 0.00000000e+00 3.11837486e-02 0.00000000e+00 0.00000000e+00
    0.00000000e+00 5.41194389e-01 0.00000000e+00 -2.74008600e-03 -1.07108103e-03
    -2.74008600e-03 0.00000000e+00 3.11837486e-02 0.00000000e+00 0.00000000e+00
    -2.95745144e-01 0.00000000e+00 0.00000000e+00 3.11837486e-02 0.00000000e+00
    1.70259891e-19 0.00000000e+00 5.41194389e-01 -2.74008600e-03 -2.74008600e-03
    -1.07108103e-03 0.00000000e+00 3.11837486e-02 0.00000000e+00 0.00000000e+00
    0.00000000e+00 3.11837486e-02 0.00000000e+00 0.00000000e+00 -2.95745144e-01
    1.07108103e-03 -2.74008600e-03 -2.74008600e-03 2.72371689e-02 0.00000000e+00
    1.36207913e-18 5.19603800e-03 0.00000000e+00 0.00000000e+00 -3.43714097e-03
  </data>
  <cell>
    0 0 0
  </cell>
</local_force_constant>
```
3. Anharmonic part of the potential
General form of the Anharmonic part $E^{anhar} (u, \eta)$ of the potential

Anharmonic part of the potential: $E^{anhar} (u, \eta) = E^{anhar} (u) + E^{anhar} (u, \eta)$

There is 2 models in multibinit for the anharmonic part:

- Compute strain-coupling $E^{anhar} (u, \eta)$ with finite differences and fit the phonon part $E^{anhar} (u)$

- Fit both $E^{anhar} (u, \eta)$ and $E^{anhar} (u)$ $^2$:
  - The phonon anharmonic part can be expressed as a sum of polynomial terms:
    $$E^{anhar} (u) = \sum_{n \alpha \beta i} \lambda_{\alpha i \beta i} (u_{\alpha i} - u_{\beta i})^n$$
  - The strain-phonon coupling anharmonic part of the energy can be expressed as:
    $$E^{anhar} (u, \eta) = \sum_{mn \alpha \beta i j} \lambda_{\alpha i \beta i k j} (u_{\alpha i} - u_{\beta i})^m (\eta_j)^n$$
  - The form $(u_{\alpha i} - u_{\beta i})^n$ ensures that the acoustic sum rule is always applied
  - Use the symmetries of the system in order to reduce the number of terms

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FIT PROCESS: DEFINITION OF THE GOAL FUNCTION

- With the set of terms, we can write the energy, forces and stresses as:

\[
E[\lambda_p](u, \eta) = E^{\text{harm}}(u, \eta) + \sum_i \lambda_i t_i(u, \eta)
\]

\[
F_{\alpha_j}[\lambda_p](u, \eta) = F^{\text{harm}}_{\alpha_j}(u, \eta) + \sum_i \lambda_i \frac{\partial t_i(u, \eta)}{\partial u_{\alpha j}}
\]

\[
\sigma_j[\lambda_p](u, \eta) = \sigma^{\text{harm}}_j(u, \eta) + \sum_i \lambda_i \frac{\partial t_i(u, \eta)}{\partial \eta_j}
\]

- We are now able to compute energy, for a given configuration of \((u, \eta) \Rightarrow s\)
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F_{\alpha_j}[\lambda_p](u, \eta) = F_{\alpha_j}^{\text{harm}}(u, \eta) + \sum_i \lambda_i \frac{\partial t_i(u, \eta)}{\partial u_{\alpha_j}}
\]

\[
\sigma_j[\lambda_p](u, \eta) = \sigma_j^{\text{harm}}(u, \eta) + \sum_i \lambda_i \frac{\partial t_i(u, \eta)}{\partial \eta_j}
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• We are now able to compute energy, for a given configuration of \((u, \eta) \Rightarrow s\)
FIT PROCESS: DEFINITION OF THE GOAL FUNCTION

- For a set $TS$ of configurations $s$ from DFT calculations (Molecular dynamics), we can define the goal function $^3$ as:

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

- where $\Omega(s) = \left[V(s)\sqrt{(N)}\right]^{(-1/3)}$ $^4$

- The goal function has to satisfy $\frac{\partial G[\lambda_p, TS]}{\partial \lambda_\mu} = 0 \ \forall \mu$ and $\frac{\partial^2 G[\lambda_p, TS]}{\partial \lambda_\mu \partial \lambda_\nu} \geq 0 \ \forall \mu \nu$

- We solve the system of $p$ linear equations in order to get the set of coefficients $\lambda_p$

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$^3$ Carlos Escorihuela-Sayalero, Jacek C. Wojdeł, and Jorge Iniguez. “Efficient systematic scheme to construct second-principles lattice dynamical models”. In: Phys. Rev. B 95, 094115 (2017)

FIT PROCESS: GENERAL PROCEDURE

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

Start with the set of $p$ coefficients $\lambda_p$

1. Fit and find the best model with only 1 coefficient $\lambda_\mu$ in $p$
2. Fit and find the best model with only 2 coefficients $\lambda_\mu$ and $\lambda_\nu$ in $p$
3. Fit and find the best model with only 3 coefficients $\lambda_\mu, \lambda_\nu$ and $\lambda_\kappa$ in $p$
4. Fit and find the best model with only 4 coefficients...
FIT PROCESS: GENERAL PROCEDURE

- Start with the set of \( p \) coefficients \( \lambda_p \)

- Fit and find the best model with only 1 coefficient \( \lambda_\mu \) in \( p \)

- Fit and find the best model with only 2 coefficients \( \lambda_\mu \) and \( \lambda_\nu \) in \( p \)

- Fit and find the best model with only 3 coefficients \( \lambda_\mu, \lambda_\nu \) and \( \lambda_\kappa \) in \( p \)

- Fit and find the best model with only 4 coefficients ...

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Fit and find the best model with only 4 coefficients ...

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FIT PROCESS: GENERATION OF THE XML FILE

Creation of XML file with all the anharmonic informations

- Generation and/or use of XML file compatible with SPLD (Monte Carlo software)

```xml
<?xml version="1.0" ?>
<Heff_definition>
  <coefficient number="1" text="(O1_x-O2_x)^1(O1_y-O2_y)^1(eta_2)^1",value="2.326695479e-01">
    <term weight="1.000000">
      <displacement_diff atom_a="2" atom_b="3" direction="x" power="1">
        <cell_a>0 0 0</cell_a>
        <cell_b>0 0 0</cell_b>
      </displacement_diff>
      <displacement_diff atom_a="2" atom_b="3" direction="y" power="1">
        <cell_a>0 0 0</cell_a>
        <cell_b>0 0 0</cell_b>
      </displacement_diff>
      <strain power="1" voigt="2"/>
    </term>
    <term weight="-1.000000">
      <displacement_diff atom_a="2" atom_b="3" direction="x" power="1">
        <cell_a>0 0 0</cell_a>
        <cell_b>0 1 0</cell_b>
      </displacement_diff>
      <displacement_diff atom_a="2" atom_b="3" direction="y" power="1">
        <cell_a>0 0 0</cell_a>
        <cell_b>0 1 0</cell_b>
      </displacement_diff>
      <strain power="1" voigt="2"/>
    </term>
  </coefficient>
  ....
</Heff_definition>
```
4. MULTIBINIT
Multibinit is a new executable included in the `src/98_main/multibinit`.

New directory `src/78_effpot` has been created with:

```plaintext
m_multibinit_dataset.F90
m_effective_potential_file.F90
m_effective_potential.F90
m_anharmonics_terms.F90
m_harmonics_terms.F90
m_polynomial_coeff.F90
m_polynomial_term.F90
m_polynomial_conf.F90
m_fit_polynomial_coeff.F90
compute_anharmonics.F90
m_effpot_mpi.F90
effpot_mpi.c
```

New input has been created (mix between anaddb and ABINIT)

The parsing of the XML file is done with Fortran or LibXML (more efficient...)

MPI Parallelization over the cell

MD from abinit and new Monte Carlo

New automatic tests in the version 8
energy_reference = -173.5214880971  # Set the energy of the structure

prteffpot = -1  # Print the effective potential in the XML

#---------------------------------------------------------------
# Generation of the IFC (only for DDB file)
#---------------------------------------------------------------
dipdip = 1  # Recompute the dipole-dipole interaction

ngqpt = 1 1 1  # Number of Grids points for Q Points
nqshft 2  # Number of shifts
q1shft 0.00000000E+00 0.00000000E+00 0.00000000E+00 5.00000000E-01 5.00000000E-01 5.00000000E-01

#---------------------------------------------------------------
# Inputs for the fitted coefficients
#---------------------------------------------------------------
ncoeff = 11
coefficients = 2.57647e-02 -5.02737e-03 -4.88691e-02 1.09467e-03 -1.53765e-02 1.82874e-03 2.41786e-03 1.64082e-04 8.64944e-04 6.61714e-01 1.76231e-01

#---------------------------------------------------------------
# Monte carlo / molecular dynamics
#---------------------------------------------------------------
dynamics = 13
optcell = 2
restartf = -1
n_cell = 16 16 16
ntime = 5000
temperature = 400
strtarget = 3+0 3+0
DDB file comes directly from ABINIT with a lot of informations...
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MULTIBINIT

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5. PHASE TRANSITION OF SrTiO$_3$ FROM $Pm\bar{3}m$ TO $Pnma$ WITHIN SECOND PRINCIPLES
Computational details

- Supercell (16x16x16) of SrTiO₃ perovskite in cubic phase with 5 atoms per unitcell
- NPT simulations from 50 to 500K at 0 and -4GPa
- The harmonic part is build with DFPT calculations in LDA
- The anharmonic part is fitted with molecular dynamics of 2x2x2 supercell at 10K:

\[
\begin{align*}
(01_x-02_x)^1(01_y-02_y)^1(eta_2)^1 \\
(02_z-03_z[1 1 0]) \\
(Sr_z-01_z)^1(eta_4)^1(Sr_y-01_y)^1 \\
(Ti_x-02_x)^2(01_y-03_y)^2 \\
(Ti_z[0 1 0]-01_z[0 1 0])^1(Ti_z-01_z[0 1 0])^1(Ti_y-01_y[0 1 0])^1 \\
(Sr_x-02_x)^2(Sr_z-03_z)^1 \\
(01_z-Sr_z[0 1 0]) \\
(01_z-02_z)^6 \\
(Sr_x-02_x)^6 \\
(eta_4)^2(Sr_y-01_y)^2 \\
(Ti_z-02_z)^2(eta_3)^2
\end{align*}
\]
Visualization and extraction of quantities with AGATE

• Follow the evolution of lattice parameters as a function of the temperature
Visualization and extraction of quantities with AGATE

- Follow the evolution of lattice parameters as a function of the temperature
PHASE TRANSITION OF SrTiO$_3$

Visualization and extraction of quantities with AGATE

- Follow the evolution of the AFD rotation ($a^0a^0c^-$) as function of the temperature

![Graph showing the evolution of AFD rotation as a function of temperature.](chart)

Evolution of the soft mode in R

- Get the phonons in temperature with TDEP

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PHASE TRANSITION OF SrTiO₃

Evolution of the soft mode in R

- Get the phonons in temperature with TDEP

![Graph showing the evolution of the soft mode in R](image)

6. Conclusion
MULTIBINIT is open source code available in the ABINIT package

- Multibinit constructs effective potential from first principle calculations and run dynamics
- Multibinit takes advantage of ABINIT (DFPT, molecular dynamics, GilLab, farm test, community...)
- Read the XML with LIBXML (C language) or FORTRAN
- MPI Parallelization and “Oriented object programming spirit”
- Tests are provided for the farm test
- Run over 80 000 atoms on 50CPUS (30sec/MD step)
Perspectives:

- Compute phonons, elastic tensor, thermal conductivity... in temperature
- Add automatic fit process for anharmonic part
- Add electric field treatment
- Add effective Hamiltonian model
- Add Spin model
- Add the coupling with electrons model (Tight bindings)
- Improve memory consuming of the molecular dynamics
Thanks for your attention