

ABINIT School on ground state, linear response properties and dynamics  
Prague, Sept. 2-6, 2019



FROM RESEARCH TO INDUSTRY



# Density-Functional Perturbation Theory: response to electric field and strain

*Marc Torrent*

*CEA, DAM, DIF, Arpajon, F-91297 France*

## REFERENCES - AKNOWLEDGEMENTS

- X. Gonze (UCL, Belgium) *and team*  
DFPT in ABINIT, response to electric field, NC pseudopotentials
- D. Hamann (Mat-Sim, US) *and team*  
elastic and piezoelectric tensor tensor, NC pseudopotentials
- M. Torrent (CEA, France)  
DFPT+PAW
- A. Martin (CEA, France)  
Elastic and piezoelectric tensors within PAW
- D. Vanderbilt and team (Rutgers, US)  
Various contributions to DFPT, clarification on formalisms
- And others...

*D. Hamann and X. Gonze are acknowledged for having inspired several slides of this presentation*

*Metric tensor formulation of strain in density-functional perturbation theory*

Hamann, Wu, Rabe, Vanderbilt, Phys. Rev. B 71, 035117 (2005).

*Generalized-gradient-functional treatment of strain in density-functional perturbation theory*

Hamann, Rabe, Vanderbilt, Phys. Rev. B 72, 033102 (2005).

*Systematic treatment of displacements, strains, and electric fields in density-functional perturbation theory*

Wu, Vanderbilt, Hamann, Phys. Rev. B 72, 035105 (2005).

See *vanderbilt-anaddb-notes.pdf* and *elasticity-oganov.pdf* in  
~abinit/doc/theory

*Projector augmented-wave approach to density-functional perturbation theory*

Audouze, Jollet, Torrent, Gonze, Phys. Rev. B 73, 235101 (2006)

*Projector augmented-wave formulation of response to strain and electric-field perturbation within DFPT*

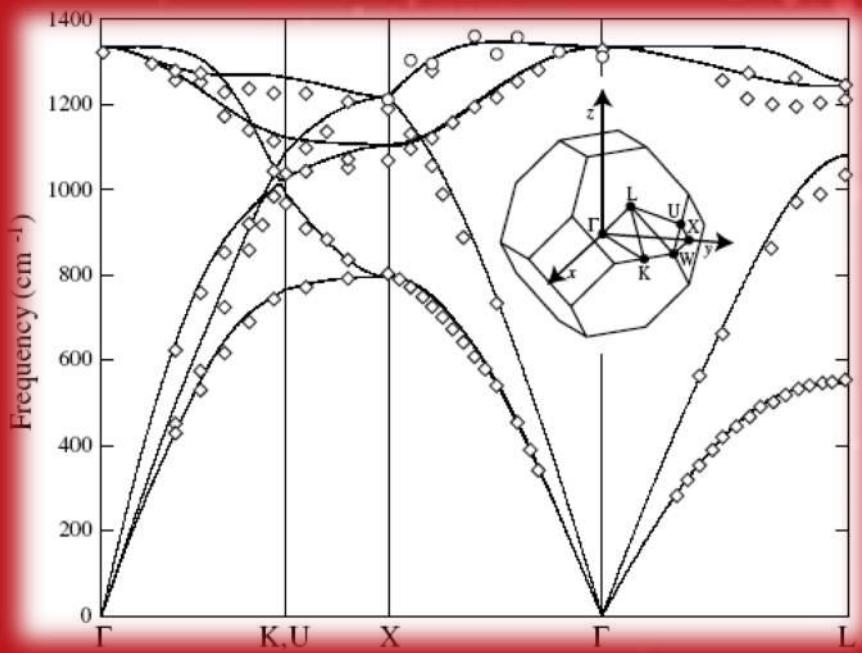
Martin, Torrent, Caracas, Phys. Rev. B 99, 094112 (2019).

*1st-principles responses of solids to atomic displacements & homogeneous electric fields: Implementation of a conjugate-gradient algorithm*

Gonze, Phys. Rev. B 55, 10337 (1997).

Gonze, Lee, Phys. Rev. B 55, 10355 (1997).

- DDFT – Recap
- **Response to homogeneous electric field**
  - Long wavelength limit
- **Response to strain**
  - Metric tensor formulation
  - Technical issues
- **Example - Real application**
  - Application to geophysics
  - Performances



## Density-functional perturbation theory Quick recap...

- All quantities are expanded in **power series** in a DF energy parameter  $\lambda$ :

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \dots, \quad X = E_{el}, T, V_{ext}, \psi_\alpha(\mathbf{r}), n(\mathbf{r}), \varepsilon_\alpha, H$$

- Solutions  $\psi^{(0)}$  of Kohn-Sham equation minimize the usual DFT functional  $E^{(0)}$

$$H^{(0)} |\psi_\alpha^{(0)}\rangle = \varepsilon_\alpha^{(0)} |\psi_\alpha^{(0)}\rangle$$

- The variational functional for  $E^{(2)}$  is minimized by solutions  $\psi^{(1)}$  of the self-consistent Sternheimer equation:

$$P_c(H^{(0)} - \varepsilon_\alpha^{(0)})P_c |\psi_\alpha^{(1)}\rangle = -P_c H^{(1)} |\psi_\alpha^{(0)}\rangle$$

- where  $P_c$  is the projector on unoccupied states and:

$$H^{(1)} = T^{(1)} + V_{ext}^{(1)} + V_{Hxc}^{(1)}, \quad V_{Hxc}^{(1)} = \frac{\partial}{\partial \lambda} \frac{\delta E_{Hxc}}{\delta n(\mathbf{r})} \Big|_{n^{(0)}} + \int \frac{\delta^2 E_{Hxc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}') d\mathbf{r}',$$

$$n^{(1)}(\mathbf{r}) = \sum_{\alpha}^{\text{occ}} [\psi_{\alpha}^{*(1)}(\mathbf{r}) \psi_{\alpha}^{(0)}(\mathbf{r}) + \psi_{\alpha}^{*(0)}(\mathbf{r}) \psi_{\alpha}^{(1)}(\mathbf{r})].$$

- We consider here the following perturbations  $\lambda$ :
- An uniform and proportional deformation (strain).

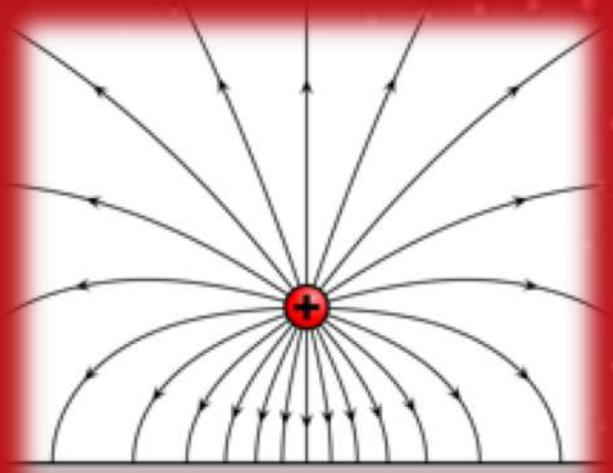
Notation:

$$X \xrightarrow{\text{strain } \varepsilon_{\alpha\beta}} X^{(\alpha\beta)}$$

- A change of a homogeneous, static electric field.

Notation:

$$X \xrightarrow{\text{field } \varepsilon_j} X^{(\varepsilon_j)}$$



## Density-functional perturbation theory Response to homogeneous electric field

- Electric field Hamiltonian:  $V_{\mathcal{E}} = \vec{\mathcal{E}} \cdot \vec{r}$ 
  - Linear potential

$$V_{\mathcal{E}} = \vec{\mathcal{E}} \cdot \vec{r}$$

Position operator  
Electric field

- Breaks the **periodic boundary conditions**!
- To apply DFPT with the electric field perturbation, one needs at least:

$$\langle u_{c,k} | \vec{r} | u_{v,k} \rangle \quad \text{or} \quad P_{ck} [\vec{r} | u_{v,k} \rangle]$$

conduction state      valence state      projection on conduction states

periodic part of Bloch wf

- These quantities are not accessible within the periodic boundary conditions.  
**How to deal with that ?**

*Standard approach to deal with the periodicity issue...*

- Electric field potential:

$$V_{\varepsilon} = \vec{\varepsilon} \cdot \vec{r} = \sum_j \varepsilon_j r_j = \sum_j \varepsilon_j |\mathbf{r}\rangle_j \langle \mathbf{r}| = \sum_j \varepsilon_j r_j |\mathbf{r}\rangle \langle \mathbf{r}|$$

- We deduce:

$$\frac{\partial \mathcal{H}}{\partial \varepsilon_j} = r_j |\mathbf{r}\rangle \langle \mathbf{r}|$$

- Key idea : replace the position operator  $\mathbf{r}_j$  by:

$$\mathbf{r}_j = \lim_{q_j \rightarrow 0} \left( \frac{1}{2iq_j} (e^{iq_j r_j} - e^{-iq_j r_j}) \right)$$

$$\frac{\partial \mathcal{H}}{\partial \varepsilon_j} = \lim_{q_j \rightarrow 0} \left( \frac{1}{2iq_j} (e^{iq_j r_j} |\mathbf{r}\rangle\langle\mathbf{r}| - e^{-iq_j r_j} |\mathbf{r}\rangle\langle\mathbf{r}|) \right)$$

- Using:

$$\frac{\partial \mathcal{H}_{\mathbf{k}, \mathbf{k} \mp \mathbf{q}}}{\partial \varepsilon} |u_{n, \mathbf{k} \mp \mathbf{q}}\rangle \equiv e^{-i(\mathbf{k} \mp \mathbf{q})\mathbf{r}} |\mathbf{r}\rangle\langle\mathbf{r}| e^{i(\mathbf{k} \mp \mathbf{q})\mathbf{r}'} |u_{n, \mathbf{k} \mp \mathbf{q}}\rangle = |u_{n, \mathbf{k} \mp \mathbf{q}}\rangle$$

- We deduce:

$$\begin{aligned} \frac{\partial \mathcal{H}_{\mathbf{k}, \mathbf{k}}}{\partial \varepsilon} |u_{n, \mathbf{k}}\rangle &= \lim_{\mathbf{q} \rightarrow 0} \frac{1}{2iq} \left( \frac{\partial \mathcal{H}_{\mathbf{k}, \mathbf{k}-\mathbf{q}}}{\partial \varepsilon} |u_{n, \mathbf{k}-\mathbf{q}}\rangle - \frac{\partial \mathcal{H}_{\mathbf{k}, \mathbf{k}+\mathbf{q}}}{\partial \varepsilon} |u_{n, \mathbf{k}+\mathbf{q}}\rangle \right) \\ &= -i \lim_{\mathbf{q} \rightarrow 0} \left( \frac{|u_{n, \mathbf{k}-\mathbf{q}}\rangle - |u_{n, \mathbf{k}+\mathbf{q}}\rangle}{2q} \right) \end{aligned}$$

- Going to the limit:

$$\frac{\partial \mathcal{H}_{\mathbf{k}, \mathbf{k}}}{\partial \varepsilon} |u_{n, \mathbf{k}}\rangle = i \frac{d|u_{n, \mathbf{k}}\rangle}{d\mathbf{k}}$$

Periodic part  
of WF

$$\frac{\partial \mathcal{H}_{\mathbf{k},\mathbf{k}}}{\partial \varepsilon} |u_{n,\mathbf{k}}\rangle = i \vec{\nabla}_{\mathbf{k}} |u_{n,\mathbf{k}}\rangle$$

- Applying the 1<sup>st</sup>-order electric field Hamiltonian on a wave function is identical as **applying the gradient with respect to k**
- The treatment of homogeneous electric field is thus mapped onto the original periodic system.

- The derivative of the wave function with respect to  $\mathbf{k}$  can be computed within the DFPT formalism,  
*Solving the Sternheimer equation:*

$$P_{c\mathbf{k}} \left( H^{(0)} - \varepsilon_{n,\mathbf{k}}^{(0)} \right) P_{c\mathbf{k}} | \psi_{n,\mathbf{k}}^{(\mathbf{k})} \rangle = -P_{c\mathbf{k}} \mathbf{H}^{(\mathbf{k})} | \psi_{n,\mathbf{k}}^{(0)} \rangle$$

- Note that 1<sup>st</sup>-order Hamiltonian  $\mathbf{H}^{(\mathbf{k})}$  is non self-consistent  
*The density does not depend on  $\mathbf{k}$*
- ABINIT input flag : **rfddk**  
Need **iscf=-3** (non-self-consistent computation)
- 1<sup>st</sup>-order wave function is saved in a “DDK” file that can be used in a response to electric field DFPT run.

- Electronic part of dielectric tensor

- Proportionnality coefficient between polarization  $P_\gamma$  and electric field
- Linked to a second derivative of total energy

$$P_\gamma = -\frac{1}{V} \frac{\partial E}{\partial \mathcal{E}_\gamma}$$

$$\epsilon_{\gamma\nu}^\infty = \delta_{\gamma\nu} + 4\pi \frac{\partial P_\gamma}{\partial \mathcal{E}_\nu}$$

$$\epsilon_{\gamma\nu}^\infty = \delta_{\gamma\nu} - \frac{4\pi}{V} \frac{\partial^2 E}{\partial \mathcal{E}_\gamma \partial \mathcal{E}_\nu}$$

## ■ Born effective charges

- Proportionality coefficient:
  - between polarisation and atomic displacement
  - between force and electric field
- Linked to a **mixed** second derivative of total energy

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \left. \frac{\partial P_\alpha}{\partial \tau_{\kappa\beta}} \right|_{\delta \vec{E}=0} = \frac{\partial F_{\kappa\beta}}{\partial \mathcal{E}_\alpha}$$

$$Z_{\kappa,\alpha\beta}^* = -\frac{\Omega_0}{V} \frac{\partial^2 E}{\partial \mathcal{E}_\alpha \partial \tau_{\kappa\beta}}$$

## ■ Piezoelectric tensor

- Proportionality coefficient:
  - between polarisation and strain
  - between stress and electric field
- Linked to a **mixed** second derivative of total energy

$$e_{\alpha\beta\gamma} = - \left. \frac{\partial P_\alpha}{\partial \epsilon_{\beta\gamma}} \right|_{\delta \vec{E}=0} = -\Omega \left. \frac{\partial \sigma_{\beta\gamma}}{\partial \epsilon_\alpha} \right|$$

$$e_{\alpha\beta\gamma} = - \frac{\partial^2 E}{\partial \epsilon_\alpha \partial \epsilon_{\beta\gamma}}$$

- To get 2<sup>nd</sup>-order total energy, just replace 1<sup>st</sup>-order Hamiltonian  $H^{(\varepsilon)}$  by its expression depending on  $i\nabla_k$
- Here example of a mixed perturbation electric field +  $\lambda_1$

$$\begin{aligned}\frac{\partial^2 E_{var}}{\partial \lambda_1 \mathcal{E}_j} = & 2 \left[ \frac{\Omega_0}{(2\pi)^3} \int d\mathbf{k} \sum_n \left( \langle \psi_{n,\mathbf{k}}^{(0)} | \frac{\partial^2 \mathcal{H}}{\partial \lambda_1 \partial \mathcal{E}_j} \Big|_{\psi_n^{(0)}} | \psi_{n,\mathbf{k}}^{(0)} \rangle + \langle \psi_{n,\mathbf{k}}^{(\lambda_1)} | \mathcal{H}^{(0)} - \epsilon_n^{(0)} | \psi_{n,\mathbf{k}}^{(\mathcal{E}_j)} \rangle \right. \right. \\ & + \langle \psi_{n,\mathbf{k}}^{(\lambda_1)} | i \frac{d}{dk_j} | \psi_{n,\mathbf{k}}^{(0)} \rangle + \langle \psi_{n,\mathbf{k}}^{(0)} | \frac{\partial \mathcal{H}}{\partial \lambda_1} \Big|_{\psi_n^{(0)}} | \psi_{n,\mathbf{k}}^{(\mathcal{E}_j)} \rangle) \Big) \\ & \left. + \frac{1}{2} \int_{\Omega} \frac{dV_{xc}}{d\rho} \Big|_{\rho^{(0)}} \rho^{(\lambda_1)}(\mathbf{r}) \rho^{(\mathcal{E}_j)}(\mathbf{r}) d\mathbf{r} + 2\pi\Omega \sum_{\mathbf{G} \neq 0} \frac{\rho^{(\lambda_1)}(\mathbf{G}) \rho^{(\mathcal{E}_j)}(\mathbf{G})}{G^2} \right]\end{aligned}$$

- To get non-variational expression of 2<sup>nd</sup>-order total energy, just suppose that one of the two 1st-order wave function is zero.
- This expression is non-stationary (i.e., 1<sup>st</sup>-order in convergence errors).
- We obtain two different expressions.

$$\frac{\partial^2 E_{nonvar}}{\partial \lambda_1 \mathcal{E}_j} = 2 \frac{\Omega_0}{(2\pi)^3} \int d\mathbf{k} \sum_n \langle \psi_{n,\mathbf{k}}^{(\lambda_1)} | i \frac{d}{dk_j} | \psi_{n,\mathbf{k}}^{(0)} \rangle$$

$$\frac{\partial^2 E_{nonvar}}{\partial \mathcal{E}_j \lambda_1} = 2 \frac{\Omega_0}{(2\pi)^3} \int d\mathbf{k} \sum_n \langle \psi_{n,\mathbf{k}}^{(0)} | \frac{\partial \mathcal{H}}{\partial \lambda_1} \Big|_{\psi_n^{(0)}} | \psi_{n,\mathbf{k}}^{(\mathcal{E}_j)} \rangle$$

```
# First dataset : Self-consistent run

# Second dataset : Non-self-consistent run for full k point set

# Third dataset : d/dk response calculation
getwfk3 -1          # Uses as input the output wf of the previous dataset
getden3 1
rfddk3 1            # Activate the calculation of the d/dk perturbation
# We can also use rfelfd=2
iscf3 -3            # The d/dk perturbation must be treated
# in a non-self-consistent way
rfdir3 1 1 1         # Directions for perturbation

# Fourth dataset : Response Function calculation : electric field perturbation
getwfk4 -2          # Uses as input wfs the output wfs of the dataset 1
getddk4 -1          # Uses as input ddk wfs the output of the dataset 3
rfelfd4 3            # Activate the the electric field perturbation
rfdir4 1 1 1         # All directions are selected. However, symmetries
# will be used to decrease the # of pert.

# Common data
nqpt 1 qpt 0.0 0.0 0.0 # This is a calculation at the Gamma point
kptopt 2              # Generation of k points, using only the TR symmetry
```

```
Perturbation wavevector (in red.coord.) 0.000000 0.000000 0.000000
Perturbation : derivative vs k along direction 1
[...]

iter 2DEtotal(Ha)      deltaE(Ha)  residm    vres2
-ETOT 1 -8.3114099083037 -8.311E+00 2.709E-02 0.000E+00
ETOT 2 -8.3153468866281 -3.937E-03 1.678E-05 0.000E+00
ETOT 3 -8.3153482602104 -1.374E-06 4.304E-09 0.000E+00
ETOT 4 -8.3153482610322 -8.218E-10 6.755E-12 0.000E+00
ETOT 5 -8.3153482610330 -8.296E-13 9.994E-15 0.000E+00
ETOT 6 -8.3153482610330 3.375E-14 1.690E-17 0.000E+00
ETOT 7 -8.3153482610329 1.599E-14 2.558E-20 0.000E+00
ETOT 8 -8.3153482610329 8.882E-15 9.941E-23 0.000E+00
At SCF step 8 max residual= 9.94E-23 < tolwfr= 1.00E-22 =>converged.
[...]

Eight components of 2nd-order total energy (hartree) are
1,2,3: 0th-order hamiltonian combined with 1st-order wavefunctions
kin0= 2.21582275E+01 eigvalue= -1.19796310E+00 local= -1.73372853E+01
4,5,6: 1st-order hamiltonian combined with 1st and 0th-order wfs
kin1= -1.68814512E+01 Hartree= 0.00000000E+00 xc= 0.00000000E+00
7,8,9: eventually, occupation + non-local contributions
edocc= 0.00000000E+00 enl0= 4.69236920E+00 enl1= 2.50754707E-01
1-9 gives the relaxation energy (to be shifted if some occ is /=2.0)
erelax= -8.31534826E+00
No Ewald or frozen-wf contrib.: the relaxation energy is the total one
2DEtotal= -0.8315348261E+01 Ha. Also 2DEtotal= -0.226272133461E+03 eV
( non-var. 2DEtotal : -8.3153482610E+00 Ha)
[...]
respfm : d/dk was computed, but no 2DTE, so no DDB output.
```

Dielectric tensor, in cartesian coordinates,				matrix element	
j1	j2	dir	pert	real part	imaginary part
dir	pert	dir	pert		
1	4	1	4	9.7606052146	-0.0000000000
1	4	2	4	-0.0000000000	-0.0000000000
1	4	3	4	-0.0000000000	-0.0000000000
2	4	1	4	-0.0000000000	-0.0000000000
2	4	2	4	9.7606052146	-0.0000000000
2	4	3	4	-0.0000000000	-0.0000000000
3	4	1	4	-0.0000000000	-0.0000000000
3	4	2	4	-0.0000000000	-0.0000000000
3	4	3	4	9.7606052146	-0.0000000000

**Effective charges, in cartesian coordinates,**

(from electric field response)

if specified in the inputs, asr has been imposed

j1	j2	matrix element
dir pert	dir pert	real part      imaginary part

1	1	1	4	2.1043565138	0.0000000000
---	---	---	---	--------------	--------------

2	1	1	4	-0.0000000000	0.0000000000
---	---	---	---	---------------	--------------

3	1	1	4	0.0000000000	0.0000000000
---	---	---	---	--------------	--------------

1	2	1	4	-2.1272284702	0.0000000000
---	---	---	---	---------------	--------------

2	2	1	4	0.0000000000	0.0000000000
---	---	---	---	--------------	--------------

3	2	1	4	-0.0000000000	0.0000000000
---	---	---	---	---------------	--------------

1	1	2	4	-0.0000000000	0.0000000000
---	---	---	---	---------------	--------------

2	1	2	4	2.1043565138	0.0000000000
---	---	---	---	--------------	--------------

3	1	2	4	0.0000000000	0.0000000000
---	---	---	---	--------------	--------------

1	2	2	4	0.0000000000	0.0000000000
---	---	---	---	--------------	--------------

2	2	2	4	-2.1272284702	0.0000000000
---	---	---	---	---------------	--------------

3	2	2	4	-0.0000000000	0.0000000000
---	---	---	---	---------------	--------------

1	1	3	4	0.0000000000	0.0000000000
---	---	---	---	--------------	--------------

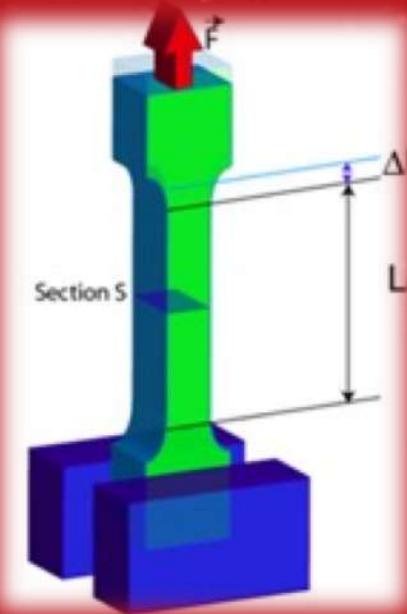
2	1	3	4	-0.0000000000	0.0000000000
---	---	---	---	---------------	--------------

3	1	3	4	2.1043565138	0.0000000000
---	---	---	---	--------------	--------------

1	2	3	4	0.0000000000	0.0000000000
---	---	---	---	--------------	--------------

2	2	3	4	-0.0000000000	0.0000000000
---	---	---	---	---------------	--------------

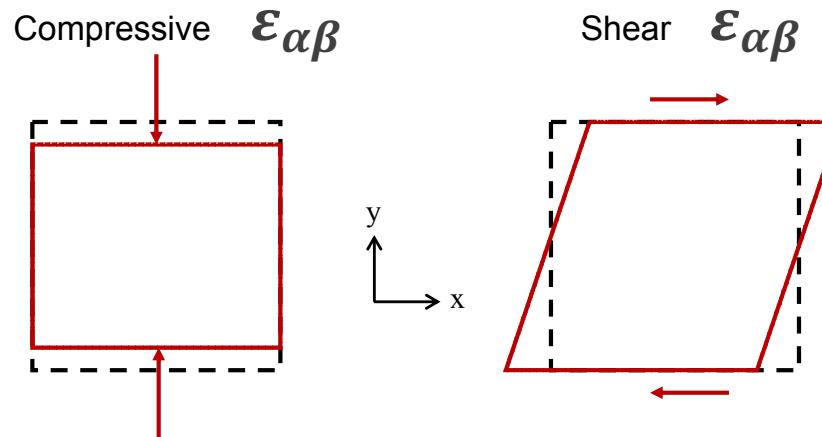
3	2	3	4	-2.1272284702	0.0000000000
---	---	---	---	---------------	--------------



## Density-functional perturbation theory Response to strain

- Concept from **continuum mechanics**
- Uniform, proportional deformation of a solid

- Described by dimensionless second-rank tensor  $\boldsymbol{\varepsilon}$



- Stress:  $\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{dE}{d\varepsilon_{\alpha\beta}}$  Force per unit area

Cartesian	xx	yy	zz	yz	xz	xy
Cartesian	1 1	2 2	3 3	2 3	1 3	1 2
Voigt	1	2	3	4	5	6
ipert, idir	natom+3, 1	natom+3, 2	natom+3, 3	natom+4, 1	natom+4, 2	natom+4, 3

$$\begin{pmatrix} 1 + \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{12} & 1 + \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{13} & \varepsilon_{23} & 1 + \varepsilon_{33} \end{pmatrix} = \begin{pmatrix} 1 + \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1 + \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & 1 + \varepsilon_3 \end{pmatrix}$$

- Only the symmetric part of the strain tensor matters.  
Antisymmetric strains are simply rotations.
- In ABINIT, all these forms are used at various places internally and in the output.
- Strain and related properties are expressed in cartesian coordinates throughout ABINIT.  
Other perturbations are expressed in reduced coordinates.

```
At SCF step 21      vres2 = 3.07E-19 < tolvrs= 1.00E-18 =>converged.
```

```
Cartesian components of stress tensor (hartree/bohr^3)
sigma(1 1)= -3.32496227E-05  sigma(3 2)=  0.00000000E+00
sigma(2 2)= -3.32496227E-05  sigma(3 1)=  0.00000000E+00
sigma(3 3)= -2.34717014E-05  sigma(2 1)=  0.00000000E+00
```

- Stress is ground-state property,  
Output for all ABINIT GS runs.
- Can be used as a “force” to optimize unit cell size and shape  
along with internal atomic coordinates.
- Numerical differentiation by  $\epsilon_{\alpha\beta}$  yields elastic tensor.

- Uniform strain changes the positions of the atomic potentials proportionally to their distances from the origin:

$$\begin{aligned} V(\mathbf{r}) &= \sum_{Cell} \sum_{\mathbf{R} Atom} V_\tau[\mathbf{r} - \boldsymbol{\tau} - \mathbf{R}] \\ &\xrightarrow{\text{strain } \varepsilon} \sum_{Cell} \sum_{\mathbf{R} Atom} V_\tau[\mathbf{r} - (1 + \varepsilon)\boldsymbol{\tau} - (1 + \varepsilon)\mathbf{R}] \end{aligned}$$

- This causes unique problems for perturbation expansions:
  - From the point of view of a single unit cell, strain changes the periodic boundary conditions, so wave functions of the strained lattice cannot be expanded in terms of those of the unstrained lattice.
  - Discretization grids change under deformation : take into account a contribution from the derivative of the grid?

## « METRIC TENSOR FORMULATION »

“Elegant” formulation proposed by Hamann et al., PRB 71, 035117 (2005)

- Every lattice, unstrained or strained, is a unit cube in reduced coordinates.
- Primitive real and reciprocal lattice vectors define the transformations:

$$X_\alpha = \sum_i R_{\alpha i}^P \tilde{X}_i, \quad K_\alpha \equiv (k_\alpha + G_\alpha) = \sum_i G_{\alpha i}^P \tilde{K}_i, \quad \sum_\alpha R_{\alpha i}^P G_{\alpha j}^P = 2\pi \delta_{ij}$$

– Cartesian indices  $\alpha, \beta, \dots = 1, 3$  and reduced indices  $i, j, \dots = 1, 3$

- Every term in the plane-wave DFT functional can be expressed in terms of dot products and the unit cell volume  $\Omega$ .
- Dot products and  $\Omega$  in reduced coordinates are computed with metric tensors:

$$\mathbf{X}' \cdot \mathbf{X} = \sum_{ij} \tilde{X}'_i \Xi_{ij} \tilde{X}_j, \quad \mathbf{K}' \cdot \mathbf{K} = \sum_{ij} \tilde{K}'_i \Upsilon_{ij} \tilde{K}_j, \quad \Omega = (\det[\Xi_{ij}])^{1/2}, \quad \mathbf{K} \cdot \mathbf{X} = \tilde{\mathbf{K}} \cdot \tilde{\mathbf{X}}$$

- This trick reduces strain to a “simple” parameter of a density functional whose wave functions have invariant boundary conditions.
- The only strain dependence of DFT functional is in the metric tensors.

- Strain derivatives of the metric tensor are straightforward.

$$\Xi_{ij}^{(\alpha\beta)} = \frac{\partial \Xi_{ij}}{\partial \varepsilon_{\alpha\beta}} = R_{\alpha i}^P R_{\beta j}^P + R_{\beta i}^P R_{\alpha j}^P$$

$$\Xi_{ij}^{(\alpha\beta\gamma\delta)} = \frac{\partial^2 \Xi_{ij}}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\delta}} = \delta_{\alpha\gamma} (R_{\beta i}^P R_{\delta j}^P + R_{\delta i}^P R_{\beta j}^P) + \delta_{\beta\gamma} (R_{\alpha i}^P R_{\delta j}^P + R_{\delta i}^P R_{\alpha j}^P)$$

- In cartesian coordinates, volume  $\Omega$  has simple derivatives:

$$\frac{\partial \Omega}{\partial \varepsilon_{\alpha\beta}} = \delta_{\alpha\beta} \Omega \quad \frac{\partial^2 \Omega}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\delta}} = \delta_{\alpha\beta} \delta_{\gamma\delta} \Omega$$

- Consequence : derivative of integrals over the volume:

$$\frac{\partial}{\partial \varepsilon_{\alpha\beta}} \int_{\Omega} f(\mathbf{r}) d\mathbf{r} = \int_{\Omega} \frac{\partial f(\mathbf{r})}{\partial \varepsilon_{\alpha\beta}} d\mathbf{r} + \delta_{\alpha\beta} \int_{\Omega} f(\mathbf{r}) d\mathbf{r}$$

$$\begin{aligned}
E_{el}^{(2)} \left\{ \psi^{(0)}; \psi^{(1)} \right\} = & \sum_{\alpha}^{occ} \left[ \left\langle \psi_{\alpha}^{(1)} \left| T^{(0)} + V_{Har+loc}^{(0)} + V_{non-loc}^{(0)} - \mathcal{E}_{\alpha}^{(0)} \right| \psi_{\alpha}^{(1)} \right\rangle \right. \\
& + \left\langle \psi_{\alpha}^{(1)} \left| T^{(1)} + V_{loc}^{(1)} + V_{non-loc}^{(1)} + V_{Har}^{(1)} + V_{xc}^{(1)} \right| \psi_{\alpha}^{(0)} \right\rangle \\
& + \left\langle \psi_{\alpha}^{(0)} \left| T^{(1)} + V_{loc}^{(1)} + V_{non-loc}^{(1)} + V_{Har}^{(1)} + V_{xc}^{(1)} \right| \psi_{\alpha}^{(1)} \right\rangle \\
& \left. + \left\langle \psi_{\alpha}^{(0)} \left| T^{(2)} + V_{loc}^{(2)} + V_{non-loc}^{(2)} \right| \psi_{\alpha}^{(0)} \right\rangle \right] \\
& + \frac{1}{2} \frac{d^2 E_{Har}}{d \lambda^2} \Bigg|_{n^{(0)}} + \frac{1}{2} \frac{d^2 E_{xc}}{d \lambda^2} \Bigg|_{n^{(0)}} + \frac{1}{2} \frac{d^2 E_{Ion-Ion}}{d \lambda^2}
\end{aligned}$$

- All these terms can be found in **ABINIT output file**.
  - There are additional terms in case of Projector Augmented-Wave approach.
  - ABINIT computes also a **non-variational** expression for  $E^{(2)}$ .  
If convergence is reached it has to be equal to the variational one.

Seventeen components of 2nd-order total energy (hartree) are

**1,2,3:** 0th-order hamiltonian combined with 1st-order wavefunctions  
kin0= 5.45759309E+00 eigvalue= -4.64795287E-01 local= -3.43266023E+00

**4,5,6,7:** 1st-order hamiltonian combined with 1st and 0th-order wfs  
loc psp = 1.38229987E+00 Hartree= 1.08631683E+00 xc= -4.86887660E-01  
kin1= -5.29050571E+00

**8,9,10:** eventually, occupation + non-local contributions  
edocc= 0.00000000E+00 enl0= 2.22543400E+00 enl1= -4.92230408E+00

1-10 gives the relaxation energy (to be shifted if some occ is /=2.0)  
erelax= -4.44550918E+00

**11,12,13** Non-relaxation contributions : frozen-wavefunctions and Ewald  
fr.hart= -5.37096135E-01 fr.kin= 4.17616081E+00 fr.loc= 2.61961436E+00

**14,15,16** Non-relaxation contributions : frozen-wavefunctions and Ewald  
fr.nonl= 3.24102985E+00 fr.xc= -2.30295282E-01 Ewald= -3.20692684E+00

**17** Non-relaxation contributions : pseudopotential core energy  
pspcore= -2.77394479E-01

Resulting in :

**2DEtotal= 0.1339583111E+01 Ha.** Also **2DEtotal= 0.364519096295E+02 eV**  
**(2DErelax= -4.4455091757E+00 Ha. 2DENonrelax= 5.7850922867E+00 Ha)**  
**( non-var. 2DEtotal : 1.3395938195E+00 Ha)**

- We need second derivative with respect to strain  $\varepsilon_{\alpha\beta}$ , electric field  $\mathcal{E}_j$  and atomic coordinates  $\tau_{\kappa i}$  to obtain:

Interatomic force constants  $\partial^2 E / \partial \tau_{\kappa i} \partial \tau_{\kappa' j}$

Clamped-atom elastic tensor  $\partial^2 E / \partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\delta}$

Clamped-atom dielectric tensor  $\partial^2 E / \partial \mathcal{E}_j \partial \mathcal{E}_{j'}$

- We need combinations of strain  $\varepsilon_{\alpha\beta}$ , electric field  $\mathcal{E}_j$  and atomic coordinates  $\tau_{\kappa i}$  derivatives to obtain:

Force-response internal strain tensor  $\partial^2 E / \partial \varepsilon_{\alpha\beta} \partial \tau_{\kappa i}$

Clamped-atom piezoelectric tensor  $\partial^2 E / \partial \varepsilon_{\alpha\beta} \partial \mathcal{E}_j$

Born effective charges  $\partial^2 E / \partial \tau_{\kappa i} \partial \mathcal{E}_j$

- Calculating mixed 2<sup>nd</sup> derivatives of the energy with respect to pairs of perturbations.
- By the “2n+1” theorem, these only require one set of 1<sup>st</sup>-order wave functions.
- This expression is non-stationary.  
(i.e., 1<sup>st</sup>-order in convergence errors)

$$\begin{aligned} E_{el}^{(\lambda_1\lambda_2)} = & \sum_{\alpha}^{\text{occ}} \left\langle \psi_{\alpha}^{(\lambda_2)} \left| (T^{(\lambda_1)} + V_{ext}^{(\lambda_1)} + V_{Hxc0}^{(\lambda_1)}) \right| \psi_{\alpha}^{(0)} \right\rangle \\ & + \sum_{\alpha}^{\text{occ}} \left\langle \psi_{\alpha}^{(0)} \left| (T^{(\lambda_1\lambda_2)} + V_{ext}^{(\lambda_1\lambda_2)}) \right| \psi_{\alpha}^{(0)} \right\rangle + \frac{1}{2} \frac{\partial^2 E_{Hxc}}{\partial \lambda_1 \partial \lambda_2} \Big|_{n^{(0)}}, \end{aligned}$$

**Non-self-consistent**

## ■ Strain – atomic coordinate derivatives

- Use 1<sup>st</sup>-order strain wave functions  $\psi_{\mathbf{km}}^{(\alpha\beta)}$
- Use 1<sup>st</sup>-order atomic-coordinate Hamiltonian  $H^{(\tau_{ki})}$
- Calculate non-variational expression of  $E^{(2)}$   
*All terms: kinetic, local, hartree, XC, non-local*

## ■ Strain – electric field derivatives

- Use special simpler non-variational expression with 1<sup>st</sup>-order wave–vector wave functions and 1<sup>st</sup>-order strain wave functions:

$$\frac{\partial^2 E}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_j} = 2 \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} \sum_m \left\langle i\psi_{\mathbf{km}}^{(k_j)} \middle| \psi_{\mathbf{km}}^{(\alpha\beta)} \right\rangle$$

	ipert	idir	type	coord	$_1\text{WF}^*$	Voigt	File
Index of perturbation	1	1	$\partial/\partial\tilde{\tau}$	$\mathbf{R}_1^P$	1		
Direction	1	2	$\partial/\partial\tilde{\tau}$	$\mathbf{R}_2^P$	2		
	1	3	$\partial/\partial\tilde{\tau}$	$\mathbf{R}_3^P$	3		
	2	1	$\partial/\partial\tilde{\tau}$	$\mathbf{R}_1^P$	4		
	2	2	$\partial/\partial\tilde{\tau}$	$\mathbf{R}_2^P$	5		
	2	3	$\partial/\partial\tilde{\tau}$	$\mathbf{R}_3^P$	6		
	...				...		
	natom+1	1	$\partial/\partial\tilde{\mathbf{k}}$	$\mathbf{G}_1^P$	3*natom+1		
	natom+1	2	$\partial/\partial\tilde{\mathbf{k}}$	$\mathbf{G}_1^P$	3*natom+2		
	natom+1	3	$\partial/\partial\tilde{\mathbf{k}}$	$\mathbf{G}_1^P$	3*natom+3		
	natom+2	1	$\partial/\partial\mathcal{E}$	$\mathbf{R}_1^P$	3*natom+4		
	natom+2	2	$\partial/\partial\mathcal{E}$	$\mathbf{R}_2^P$	3*natom+5		
	natom+2	3	$\partial/\partial\mathcal{E}$	$\mathbf{R}_3^P$	3*natom+6		
	natom+3	1	$\partial/\partial\varepsilon_{\alpha\beta}$	xx	3*natom+7	1	
	natom+3	2	$\partial/\partial\varepsilon_{\alpha\beta}$	yy	3*natom+8	2	
	natom+3	3	$\partial/\partial\varepsilon_{\alpha\beta}$	zz	3*natom+9	3	
	natom+4	1	$\partial/\partial\varepsilon_{\alpha\beta}$	yz	3*natom+10	4	
	natom+4	2	$\partial/\partial\varepsilon_{\alpha\beta}$	xz	3*natom+11	5	
	natom+4	3	$\partial/\partial\varepsilon_{\alpha\beta}$	xy	3*natom+12	6	

# ABINIT INPUT FILE FOR RF RUN WITH STRAIN

```
# First dataset : Self-consistent run

# Second dataset : Non-self-consistent run
#                   for full k point set

# Third dataset : d/dk response calculation
#this section is omitted if
#only the elastic tensor is
#wanted
getwfk3 2
getden3 1
iscf3 -3
rfelfd3 2
rfdir3 1 1 1

# Fourth dataset : phonon, strain, and homogeneous
#                   electric field response

diemix4 0.85
diemac4 1.0
getwfk4 2
getddk4 3      #omitted for ELT only
iscf4 3
rfelfd4 3      #omitted for ELT only
rfatpol4 1 2
rfdir4 1 1 1
rfphon4 1
rfstrs4 3      #only this is new for strain

# Common data          #stresses and forces should
nqpt 1              #(in general) be relaxed
qpt 0 0 0            #beforehand
```

- With natom=2, electric field ipert=4 and strain ipert=5
- Only a sample of the complete matrix shown
- Careful: mix of reduced and Cartesian coordinates!

```
2nd-order matrix (non-cartesian coordinates, masses not included,
asr not included)
cartesian coordinates for strain terms (1/ucvol factor
for elastic tensor components not included)
      j1          j2          matrix element
    dir pert dir pert      real part      imaginary part

      1      1      2      2      -2.8200006186      0.0000000000
      1      1      3      2      -2.8654826400      interatomic force constant (red-red)
      1      1      1      4      -4.1367712586      Born effective charge (red-red)
      1      1      2      5      -0.0238530938      internal strain (red-cart)
      1      4      3      4      46.0269881204      dielectric tensor (red-red)
      1      4      3      5      -0.2214090328      piezoelectric tensor (red-cart)
      1      5      2      6      -0.0103809572      elastic tensor (cart-cart)
```

## Elastic

```
Rigid-atom elastic tensor , in cartesian coordinates,
      j1      j2          matrix element
      dir pert dir pert    real part   imaginary part

1 7 1 7 0.0056418387 0.00000000000
1 7 2 7 0.0013753709 0.00000000000
1 7 3 7 0.0007168444 0.00000000000
1 7 1 8 0.00000000000 0.00000000000
1 7 2 8 0.00000000000 0.00000000000
1 7 3 8 0.00000000006 0.00000000000

2 7 1 7 0.0013753707 0.00000000000
2 7 2 7 0.0056418385 0.00000000000
```

## Piezoelectric

```
Rigid-atom proper piezoelectric tensor, in cartesian
coordinates,
      j1      j2          matrix element
      dir pert dir pert    real part   imaginary part

1 6 1 7 0.00000000000 0.00000000000
1 6 2 7 0.00000000000 0.00000000000
1 6 3 7 0.00000000000 0.00000000000
1 6 1 8 0.00000000000 0.00000000000
1 6 2 8 0.0076114623 0.00000000000
1 6 3 8 0.00000000000 0.00000000000

2 6 1 7 0.00000000000 0.00000000000
2 6 2 7 0.00000000000 0.00000000000
```

## Internal strain

```
Internal strain coupling parameters, in cartesian coordinates,
zero average net force deriv. has been imposed
      j1      j2          matrix element
      dir pert dir pert    real part   imaginary part

1 1 1 7 0.1249319229 0.00000000000
1 1 2 7 -0.1249319272 0.00000000000
1 1 3 7 0.00000000000 0.00000000000
1 1 1 8 0.00000000000 0.00000000000
1 1 2 8 -0.1016111210 0.00000000000
1 1 3 8 0.00000000003 0.00000000000

2 1 1 7 0.00000000000 0.00000000000
2 1 2 7 0.00000000000 0.00000000000
2 1 3 7 0.00000000000 0.00000000000
2 1 1 8 -0.1016109573 0.00000000000
2 1 2 8 0.00000000000 0.00000000000
2 1 3 8 -0.1249319425 0.00000000000
```

- We are treating here strain as an independent variable, but, in a laboratory, only stress is applied.
- Strain will change the reduced atomic coordinates, not just the metric tensors.
- Atomic relaxation makes modest changes the the elastic constants for “normal” solids, huge changes for special cases (molecular solids).
- There are large relaxation changes in the piezoelectric constants for most piezoelectric materials.

- Introduce a model energy function quadratic in atomic displacements  $\Delta\tau_{ki}$ , strain  $\varepsilon_{\alpha\beta}$ , and electric field  $\mathcal{E}_j$ :

$$H(\Delta\tau, \varepsilon_{\alpha\beta}, \mathcal{E}) = (\Delta\tau \ \varepsilon \ \mathcal{E}) \left[ \begin{pmatrix} -\mathbf{F}/\Omega \\ \boldsymbol{\sigma} \\ -\mathbf{P} \end{pmatrix} + \begin{pmatrix} \mathbf{K}/\Omega & -\mathbf{\Lambda}/\Omega & -\mathbf{Z}/\Omega \\ -\mathbf{\Lambda}^T/\Omega & \mathbf{C} & -\mathbf{e} \\ -\mathbf{Z}^T/\Omega & \mathbf{e}^T & \boldsymbol{\chi} \end{pmatrix} \begin{pmatrix} \Delta\tau \\ \varepsilon \\ \mathcal{E} \end{pmatrix} \right]$$

- « Clamped » quantities:,

$F_{m\alpha}$	Atomic forces	$C_{\alpha\beta,\gamma\delta}$	Elastic tensor
$\sigma_{\alpha\beta}$	Stress	$Z_{m\alpha,\gamma}$	Born effective charges
$P_\alpha$	Electric polarization	$e_{\alpha,\gamma\delta}$	Piezoelectric tensor
$K_{m\alpha,ny}$	Interatomic force constants	$\chi_{\alpha,\gamma}$	Dielectric susceptibility
$\Lambda_{m\alpha,\gamma\delta}$	“Force” internal strain tensor		

$$C_{\alpha\beta\delta\gamma} = \bar{C}_{\alpha\beta\delta\gamma} - \Omega^{-1} \Lambda_{\kappa k \alpha \beta} (K^{-1})_{\kappa k \kappa' k'} \Lambda_{\kappa' k' \gamma \delta},$$

$$e_{j\alpha\beta} = \bar{e}_{j\alpha\beta} + \Omega^{-1} Z_{\kappa k j} (K^{-1})_{\kappa k \kappa' k'} \Lambda_{\kappa' k' \alpha \beta},$$

$$\chi_{jj'} = \bar{\chi}_{jj'} + \Omega^{-1} Z_{\kappa k j} (K^{-1})_{\kappa k \kappa' k'} Z_{\kappa' k' j'}.$$

- We assume the forces are zero (relaxed structure).
- Strain and electric field 2<sup>nd</sup> derivatives of  $\mathbf{H}$  yield the relaxed-atom elastic piezoelectric and dielectric tensors.
- $K^{-1}$  is the pseudo-inverse of the interatomic force constant matrix.

- Need to use **anaddb** script as a post-processor of ABINIT results
- All the needed 2<sup>nd</sup> derivatives must be present in the **\_DDB** file (from several RF ABINIT runs).
- Results are converted to conventional units rather than atomic units.
- Various other tensors corresponding — such as fixed or zero polarization or stress, etc. — can be calculated using the same approach.
- See **elaflag**, **instrflag**, **dieflag**, **piezoflag**, **polflag** in the **anaddb** help file.

## Input file

```
dieflag  3 !flag for relaxed-ion dielectric tensor
elaflag  3 !flag for the elastic tensor
piezoflag 3 !flag for the piezoelectric tensor
instrflag 1 !flag for the internal strain tensor

!the effective charge part
    asr 1
    chneut 1

!Wavevector list number 1

    nph11  1
    qph11  0.0 0.0 0.0 1.0

!Wave vector list no. 2

    nph21  1
    qph21  0.0 0.0 1.0 0.0
```

## Output file

Elastic Tensor (relaxed ion) (Unit:10^2GP, VOIGT notation) :

1.2499151	0.6699976	0.6835944	0.0022847	-0.0113983	-0.0001512
0.6699976	1.6217899	0.5566207	0.0194005	-0.0055653	-0.0055915
0.6835944	0.5566207	1.5896839	-0.0207927	0.0107924	0.0080825
0.0022847	0.0194005	-0.0207927	0.6659339	0.0077398	-0.0056845
-0.0113983	-0.0055653	0.0107924	0.0077398	0.7283916	0.0014049
-0.0001512	-0.0055915	0.0080825	-0.0056845	0.0014049	0.7222881

proper piezoelectric constants (relaxed ion) (Unit:c/m^2)

0.01714694	0.05107080	-0.00883676
0.00828454	0.03716812	-0.00810176
0.01882065	0.05180658	-0.00576393
-0.03872154	-0.01245206	0.01902693
-0.01424058	0.00757132	-0.00294782
0.01566436	-0.00054740	0.00218470

- Also in output
  - Clamped-ion versions of tensors in standard units
  - Clamped and relaxed compliance tensors
  - “Force-response” and “displacement response” internal strain tensors
  - More tensors corresponding to different boundary conditions
- An important check is that the tensors have symmetry appropriate to the point group of the material.



## **DFPT + strain + electric field**

## **Technical issues**

- Back to the basics:

Stress-strain definition of elastic tensor is:

$$\sigma_{\alpha\beta} = C_{\alpha\beta\gamma\delta}^{ss} \varepsilon_{\gamma\delta}$$

- Elastic tensor computed from DFPT  
→ “Proper” elastic tensor :

$$C_{\alpha\beta\gamma\delta}^{\text{proper}} = \frac{d^2 E}{d\varepsilon_{\alpha\beta} d\varepsilon_{\gamma\delta}} = \frac{1}{V_0} \frac{d}{d\varepsilon_{\alpha\beta}} (V \sigma_{\gamma\delta})$$

Volume    Volume  
  undeformed crystal                            changed by strain

- The definitions differ:

*If the reference  
structure is under stress*

$$C_{\alpha\beta\gamma\delta}^{\text{proper}} = C_{\alpha\beta\gamma\delta}^{ss} + \delta_{\gamma\delta} \sigma_{\alpha\beta}^0$$

Stress reference structure

- The polarization  $P_\alpha$  is defined within a “polarization quantum” due to the freedom to choose the phase of *Bloch* wave functions.

We have different polarization “branches”:

$$\mathbf{P}^{(b')} = \mathbf{P}^{(b)} + \frac{e}{\Omega} \mathbf{R}$$

Lattice vector 

- Strain-induced changes:

$$d\mathbf{P}^{(b')} = d\mathbf{P}^{(b)} - \frac{e}{\Omega^2} \mathbf{R} d\Omega + \frac{e}{\Omega} d\mathbf{R}$$

- The proper piezoelectric tensor is independent of the branch:

$$e_{\alpha\beta\gamma}^{\text{Proper}} = e_{\alpha\beta\gamma} + \delta_{\beta\gamma} P_\alpha - \delta_{\alpha\beta} P_\gamma$$

Vanderbilt, J. Phys. Chem. Solids 61, 147 (2000)

## ■ Numerous numerical issues

- Amplitude of increment of the finite differences (system dependent)
- Number of points in the finite difference scheme
- Changes of real space grid when manual deformation is applied
- Numerical scheme for real space integrals when the center moves
- Slow convergence of “finite electric field” computations  
(within “Berry phase” formalism”)

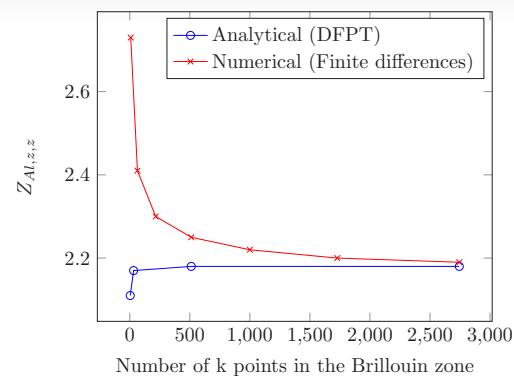


FIG. 1. Convergence of the effective charges in AlAs with respect to the Brillouin zone sampling as obtained in both finite differences and in DFPT.

Martin, Torrent, Caracas, PRB 99, 094112 (2019)

- Al and AlAs crystals. Projector Augmented-Wave approach
- Ground state calculations of stress and polarization with clamped atomic coordinates
- Finite-difference d/dk for best consistency with polarization calculations
- 5-point numerical derivatives with strain increment  $10^{-4}$

TABLE IV. Elastic tensor of fcc Al in GPa, obtained with DFPT and FD.

Elastic constant	$C_{11}$	$C_{12}$	$C_{44}$
FD	114.36042	60.01343	34.00284
DFPT	114.35981	60.01364	34.00364
Exp. [29]	114.30	61.92	31.62

TABLE I. Clamped-ion force-strain coupling parameters of AlAs in reduced coordinates, in Ha. Comparison of the numerical values obtained with DFPT and FD:  $-\Omega \frac{\partial^2 E_{\text{vol}}}{\partial \tau_{kk} \partial \varepsilon_{\alpha\beta}}$  [Eq. (48)].

$\varepsilon_{\alpha\beta}$	$\kappa$	$k$	FD+PAW	DFPT+PAW
1	Al	x	0.84452759	0.84452677
2	Al	x	-0.84452759	-0.84452679
3	Al	x	0.00000000	0.00000000
4	Al	x	-0.40239908	-0.40239911
5	Al	x	-0.69697561	-0.69697569
6	Al	x	-0.48758797	-0.48758777

TABLE II. Born effective charges of AlAs in units of charge [Eq. (47)]. Comparison between the two nonvariational expressions, Eqs. (30)–(32) and Eq. (86), in DFPT.

$\kappa$	$k$	$-\Omega \frac{\partial^2 E_{\text{vol}}}{\partial \tau_{kk} \partial \tilde{\varepsilon}_k}$	$-\Omega \frac{\partial^2 E_{\text{vol}}}{\partial \tilde{\varepsilon}_k \partial \tau_{kk}}$
Al	x	2.07482486	2.07482525
Al	y	2.07482486	2.07482525
Al	z	2.22353351	2.22353327
As	x	-2.07485811	-2.07485849
As	y	-2.07485811	-2.07485849
As	z	-2.22341484	-2.22341461

TABLE III. Piezoelectric tensor of AlAs in units of charge/Bohr<sup>2</sup> [Eq. (46)]. Comparison between the two nonvariational expressions, Eqs. (30)–(32) and Eq. (86), in DFPT.

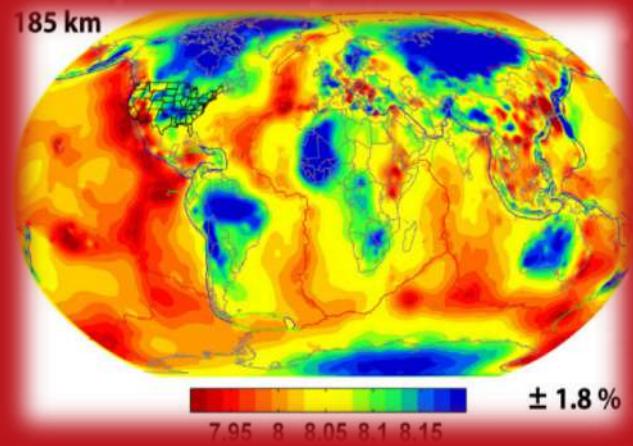
$\varepsilon_{\alpha\beta}$	$k$	$-\frac{\partial^2 E_{\text{vol}}}{\partial \varepsilon_{\alpha\beta} \partial \tilde{\varepsilon}_k}$	$-\frac{\partial^2 E_{\text{vol}}}{\partial \tilde{\varepsilon}_k \partial \varepsilon_{\alpha\beta}}$
5	x	0.01036757	0.01036757
4	y	0.01036986	0.01036831
1	z	0.00645215	0.00645173
2	z	0.00645215	0.00645173
3	z	-0.00991493	-0.00991383

- The Hellmann-Feynman theorem (or 2N+1 theorem) is only valid for the complete basis set.
- If the plane wave basis set is not complete with respect to changes of the volume, the terms in theorem's expression containing derivatives of the wavefunction persist.
- Unless absolute convergence with respect to the basis set has been achieved - the diagonal components of the stress tensor are incorrect.

$$\begin{aligned}\frac{dE}{d\varepsilon_{\alpha\beta}} &= \sum_n \frac{d}{d\varepsilon_{\alpha\beta}} \langle \psi_n | H | \psi_n \rangle \\ &= \sum_n \left\langle \psi_n \left| \frac{dH}{d\varepsilon_{\alpha\beta}} \right| \psi_n \right\rangle + \epsilon_n \underbrace{\left( \left\langle \psi_n \left| \frac{d\psi_n}{d\varepsilon_{\alpha\beta}} \right| \psi_n \right\rangle + \left\langle \psi_n \left| \frac{d\psi_n}{d\varepsilon_{\alpha\beta}} \right| \psi_n \right\rangle \right)}_{\text{zero if basis is complete}}\end{aligned}$$

- To avoid the *Pulay stress*, use of **ecutsm** ABINIT input variable is mandatory.
- It allows one to define an effective kinetic energy for plane waves, obtained by multiplying the kinetic energy by a smooth smearing function.
- Using a non-zero **ecutsm**, the total energy curves as a function of **ecut** can be smoothed, keeping consistency with the stress and automatically including the *Pulay stress*.
- The recommended value is 0.5 Ha.

See: Bernasconi et al., J. Phys. Chem. Solids 56, 501 (1995)

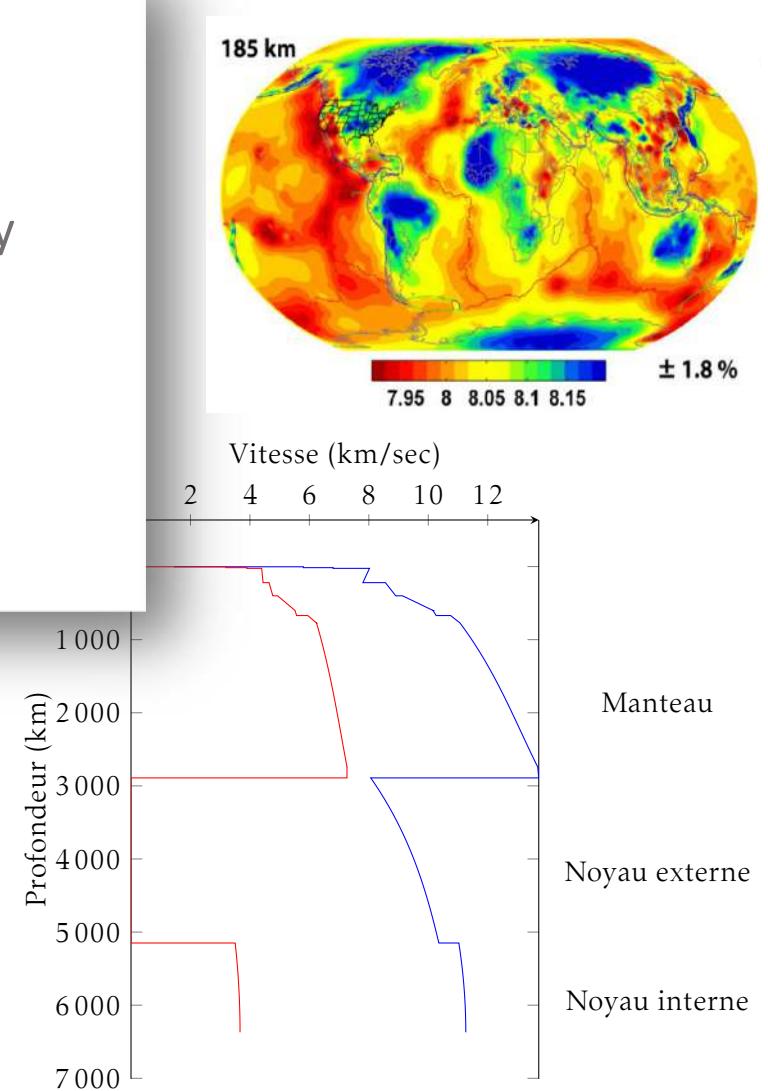
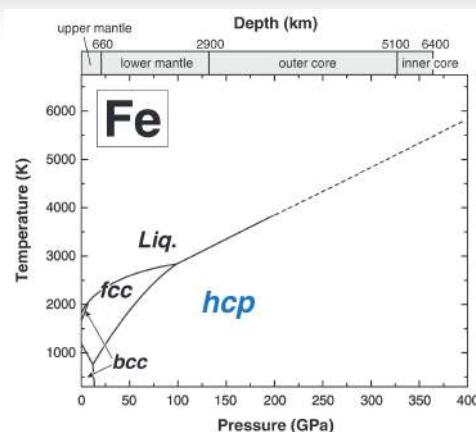


## DFPT + strain + electric field Real applications

## Impurities in iron at extreme conditions

A. Martin, PhD thesis (2015)

- Earth inner core is made of iron and impurities
- Its real composition is unknown
- Observable: seismic waves, giving the sound velocity
- Try several chemical compositions, compute elastic tensor, deduce sound velocity...  
... and compare with PREM model (Preliminary Reference Earth Model).

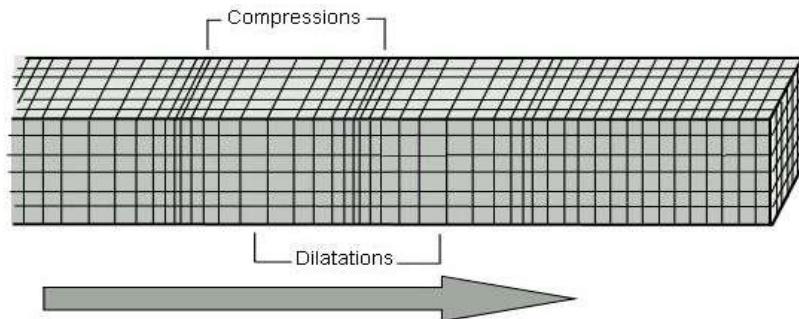


## Impurities in iron at extreme conditions

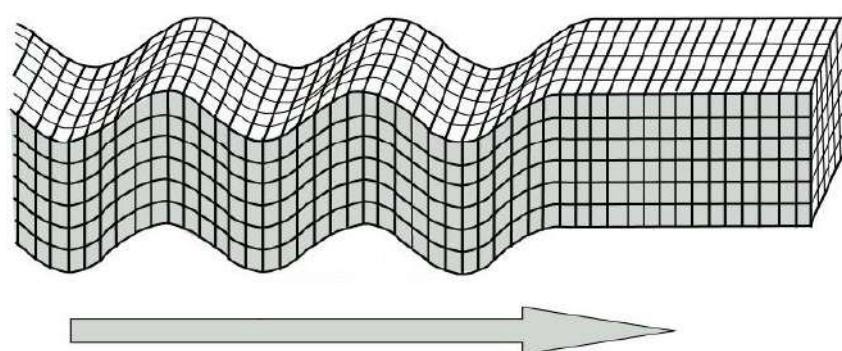
A. Martin, PhD thesis (2015)

### ■ Seismic waves

Longitudinal  $\rightarrow V_p$



Transverse  $\rightarrow V_s$

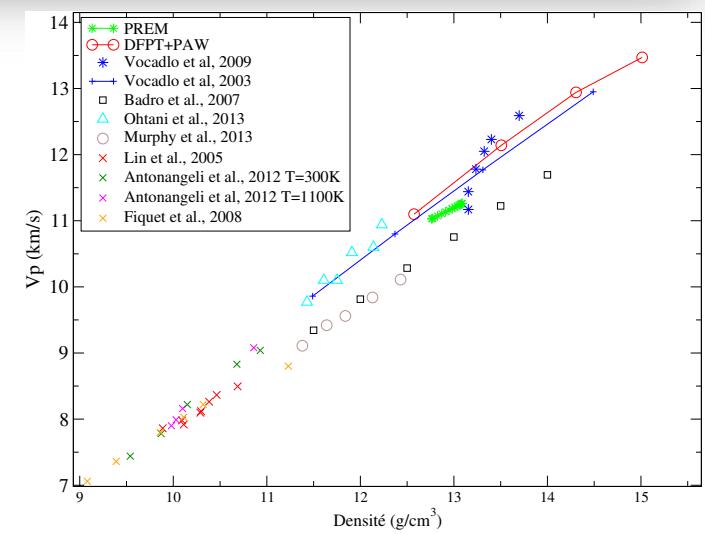


$$V_p = \sqrt{K + \left(\frac{4G}{3}\right)}$$

$$V_s = \sqrt{\frac{G}{\rho}}$$

$$K_v = \frac{(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{13} + C_{23})}{9}$$

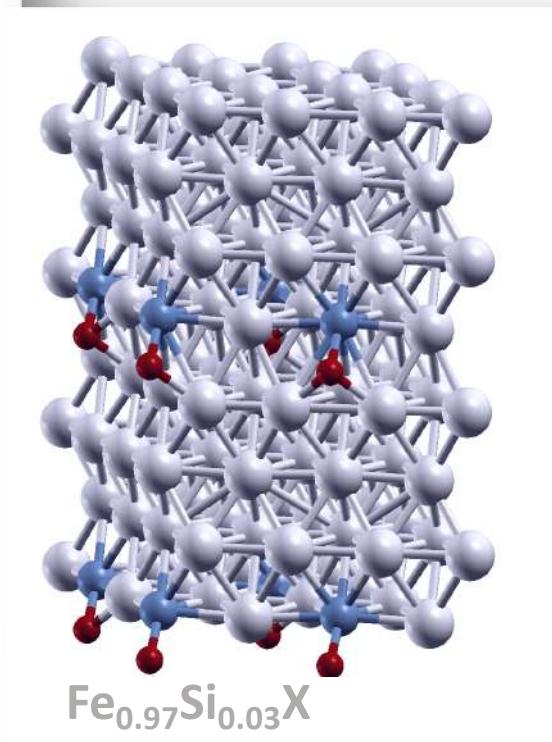
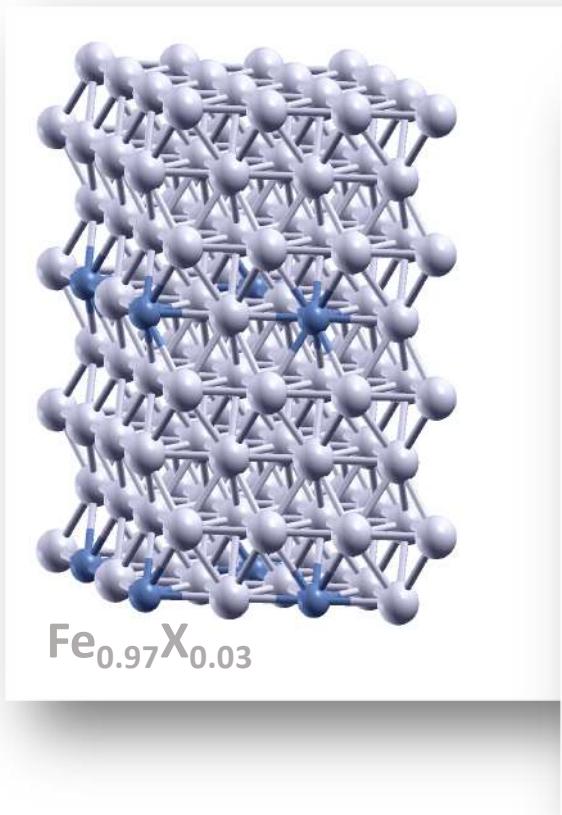
$$G_v = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})}{15}$$



## Impurities in iron at extreme conditions

A. Martin, PhD thesis (2015)

- Try various simulation cells  
With impurities in substitution or interstitial



### PAW formalism

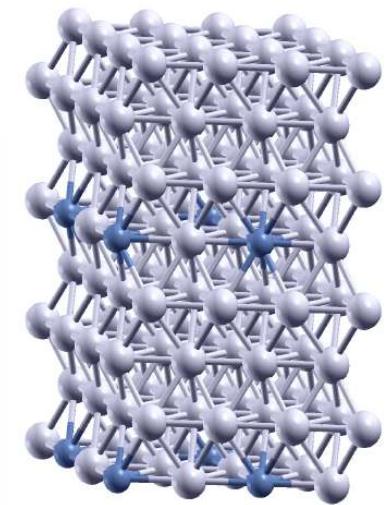
Élément	[cœur]	valence
H	[]	$1s^1$
C	$[1s^2]$	$2s^2 2p^2$
O	$[1s^2]$	$2s^2 2p^4$
Si	$[1s^2 2s^2 2p^6]$	$3s^2 3p^2$
S	$[1s^2 2s^2 2p^6]$	$3s^2 3p^4$
Fe	$[1s^2 2s^2 2p^6]$	$3s^2 3p^6 4s^1 3d^7$

## Impurities in iron at extreme conditions

- Simulation cell :  $\text{Fe}_{16}\text{C}$

TABLE V. Relaxed-ion elastic tensors of  $\text{Fe}_{16}\text{C}$  (in GPa) at 320 GPa. The comparison between the perturbative approach (DFPT) and the finite difference approach (FD) shows differences on the order of tens of MPa or less.

	$C_{11}$	$C_{22}$	$C_{33}$	$C_{44}$	$C_{55}$
FD	127.409	127.444	47.284	25.254	25.244
DFPT	127.428	127.428	47.295	25.244	25.244
	$C_{66}$	$C_{12}$	$C_{13}$	$C_{14}$	$C_{56}$
FD	41.037	45.339	31.510	-2.739	-2.739
DFPT	41.038	45.351	31.522	-2.739	-2.739

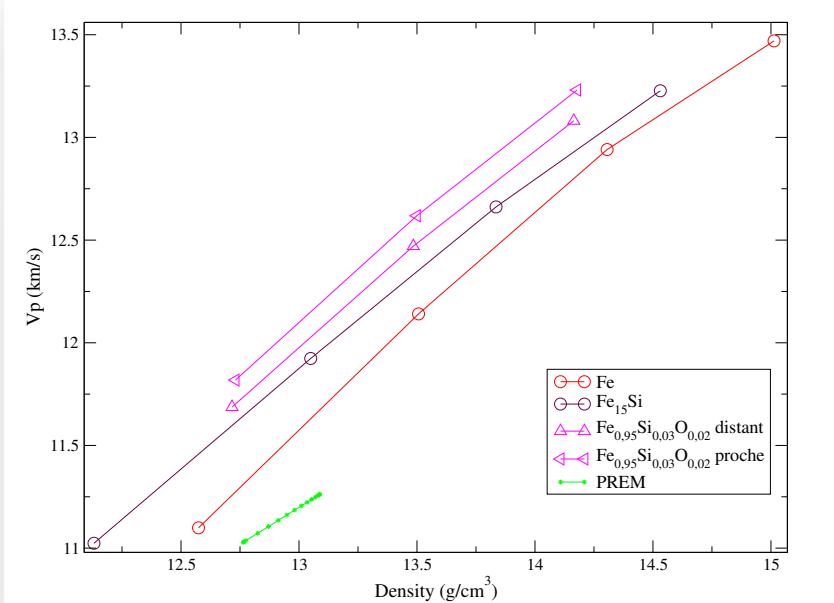
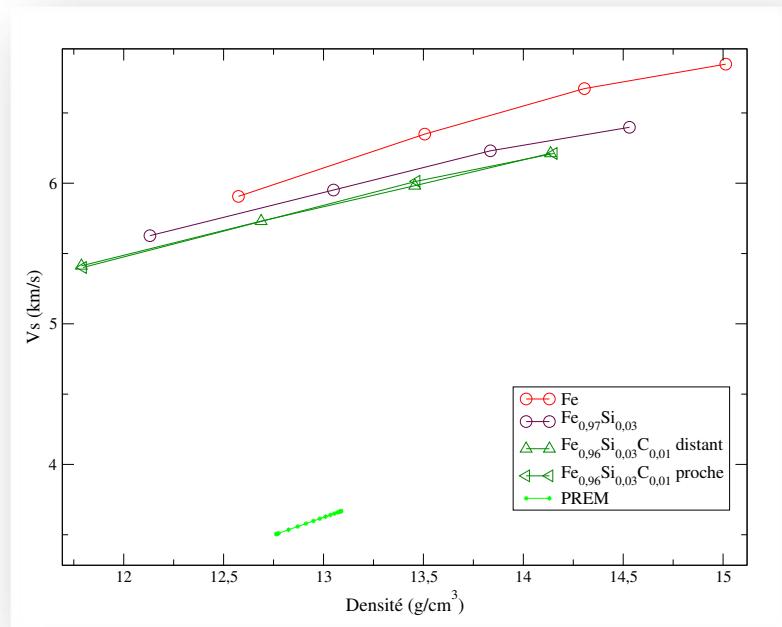


Martin, Torrent, Caracas, PRB 99, 094112 (2019)

## Impurities in iron at extreme conditions

A. Martin, PhD thesis (2015)

### ■ Sound velocities



## Impurities in earth mantel

A. Martin, PhD thesis (2015)

### ■ Elastic tensor of $\text{MgSiO}_3$ perovskite

TABLE VI. Elastic constants (in GPa) and sound velocities (in km/s) of  $\text{MgSiO}_3$  perovskite at 0 GPa.

$C_{ij}$	$C_{11}$	$C_{22}$	$C_{33}$	$C_{44}$	$C_{55}$
DFPT+NC	512	579	488	213	181
FD+PAW	482	549	457	201	176
DFPT+PAW	482	549	457	201	176
S.V. Sinogeikin (exp.)[31]	481	528	456	200	182
Y.Haeri (exp.)[32]	482	537	485	186	186
$C_{ij}$	$C_{66}$	$C_{13}$	$C_{32}$	$C_{12}$	$V_p$
DFPT+NC	166	153	167	162	11.21
FD+PAW	156	137	150	137	10.85
DFPT+PAW	156	137	150	137	10.85
S.V. Sinogeikin (exp.)[31]	147	139	146	125	10.84
Y.Haeri (exp.) [32]	147	147	146	144	11.04
				$V_s$	
					6.63
					6.49
					6.49
					6.47
					6.57

Martin, Torrent, Caracas, PRB 99, 094112 (2019)

## Impurities in earth mantel

A. Martin, PhD thesis (2015)

- MgSiO<sub>3</sub> perovskite with Al impurities at 120GPa

### Born effective charges

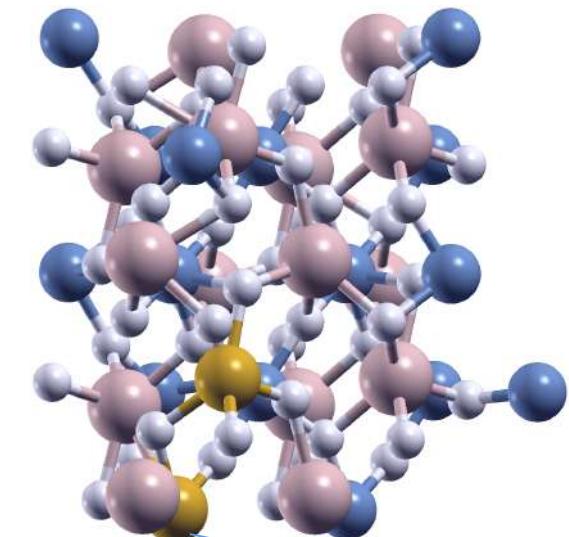
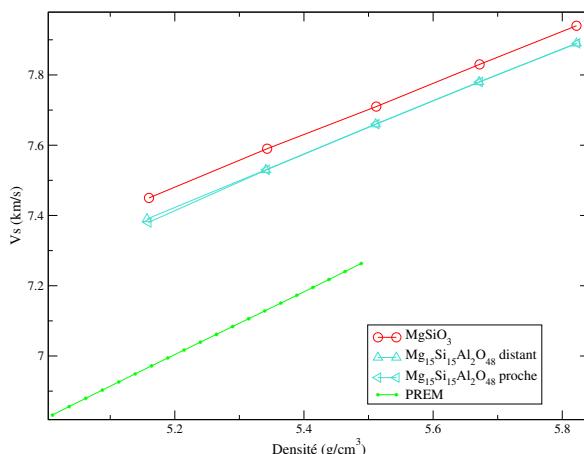
Atome :	x	y	z
Al <sub>1</sub>	3,03	2,90	3,20
Al <sub>2</sub>	2,80	2,91	2,82
Mg	2,03	1,85	2,13
Si	3,63	3,72	3,67
O <sub>1</sub>	-1,73	-1,53	-2,44
O <sub>2</sub>	-2,00	-2,12	-1,68
O <sub>3</sub>	-2,01	-2,08	-1,68

(c) Mg<sub>15</sub>Si<sub>15</sub>Al<sub>2</sub>O<sub>48</sub> configuration proche

Atome :	x	y	z
Al <sub>1</sub>	2,97	2,90	3,20
Al <sub>2</sub>	2,83	2,85	2,79
Mg	2,06	1,91	2,12
Si	3,59	3,77	3,69
O <sub>1</sub>	-1,73	-1,51	-2,42
O <sub>2</sub>	-2,01	-2,06	-1,68
O <sub>3</sub>	-1,89	-2,02	-1,71

(d) Mg<sub>15</sub>Si<sub>15</sub>Al<sub>2</sub>O<sub>48</sub> configuration distante

### Sound velocity



- Fe<sub>16</sub>C unit cell at 320 Gpa, trigonal symmetry
- 7 independent elastic constants to compute
- *Curie* supercomputer (french TGCC computing center)
- 512 CPUs

## Finite differences

- 5-point formula
- 29 independent structural relaxations
- 1400 CPU walltime hours per relaxation

**Total : 40 000 CPU hours**

## DFPT

- 1 structural relaxation
- 1400 CPU walltime hours per relaxation
- 6 strain RF calculations (80 hours)

**Total : 2 200 CPU hours**

*Ratio can change according to the number of symmetries...*



## Conclusion

- Response to electric field and strain almost fully available in ABINIT
- ABINIT is the only DFT code giving access to an analytical calculation of elastic and piezoelectric tensors
- Easy to use (no q-points, etc.)
- Norm-conserving pseudo-potentials  
Projector Augmented-Wave  
(Elastic tensor+GGA not available within PAW)
- Try “*Hands on*” on *Elastic Properties* tutorial to learn more...



Commissariat à l'énergie atomique et aux énergies alternatives - [www.cea.fr](http://www.cea.fr)