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First-principles calculations of insulators in a finite electric field

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Outline

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- 1st part: Structural response to macroscopic electric fields
  - Formalism
  - Berry phase calculation of **P** and the ddk
  - Implementation
  - In practice: how to optimize the structure for a fixed polarization
  - Applications
- 2nd part: First-principles approach to insulators in finite electric fields
  - Formalism
    - Definition of an electric field dependent energy functional
    - For $E < E_c$: minimization of the energy functional
    - Computation of forces and stresses
  - Implementation in ABINIT
  - In practice: how to do a finite electric field calculation
  - Applications
- Conclusions

Electric field perturbation: difficulties

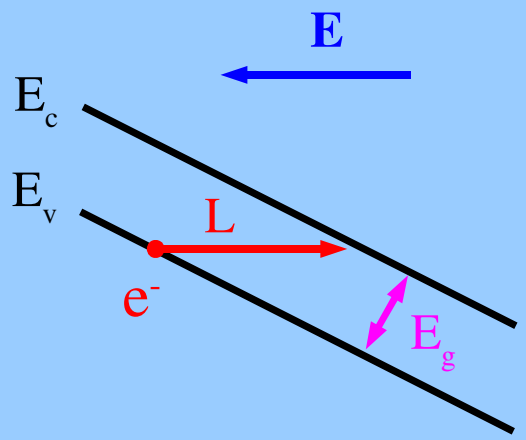
The perturbation $-\mathbf{E}\cdot\mathbf{r}$ is nonperiodic and unbound from below

- Nonperiodic

  Methods based on Bloch's theorem and eigenstates ψ_{nk} do not apply

- Unbound from below

  Energy can always be lowered by transferring charge from valence states in one region to conduction states in a distant region



Electric field "bends" the energy bands

→ Dielectric breakdown by interband (Zener) tunneling

→ An infinite crystal in the presence of an electric field does not have a ground-state

1st Method: Structural response to macroscopic electric fields

Electric field derivatives of arbitrary order can be computed from DFPT

*R. W. Nunes and X. Gonze, PRB **63**, 155107 (2001)*

- Low-order Taylor expansion of the energy with respect to the electric field
- Dependence of the energy on the structural degrees of freedom is preserved to all orders
- Two step approach:
  1) Map out the energy as a function of the polarization
  2) Use this energy surface & field-coupling term to compute the ground state structure in the presence of the electric field
- More informations

*Na Sai, K. M. Rabe and D. Vanderbilt, PRB **66**, 104108 (2002)*
*H. Fu and R. E. Cohen, Nature **403**, 281 (2000)*

Constrained polarization approach: formalism

- Structural response at constant electric field **E**

$$F(\boldsymbol{E}) = \min_{\boldsymbol{R},\eta} F(\boldsymbol{R},\eta,\boldsymbol{E}) \Rightarrow \begin{cases} \boldsymbol{R}_{eq}(\boldsymbol{E}) \\ \eta_{eq}(\boldsymbol{E}) \end{cases}$$

Strain η and atomic positions **R** at fixed electric field **E**

- Polarization: thermodynamic conjugate of **E:** $P_\alpha = \frac{-1}{\Omega}\frac{\partial F}{\partial E_\alpha}$
- Legendre transformation ($\lambda = \Omega \mathbf{E}$):

$$\left.\begin{aligned} \widetilde{F}(\boldsymbol{R},\eta,\boldsymbol{P}) &= \min_{\lambda}[F(\boldsymbol{R},\eta,\lambda) + \lambda\cdot\boldsymbol{P}] \\ \widetilde{F}(\boldsymbol{P}) &= \min_{\boldsymbol{R},\eta}\widetilde{F}(\boldsymbol{R},\eta,\boldsymbol{P}) \end{aligned}\right\}$$

Strain and atomic positions at fixed polarization:

$$\boldsymbol{R}_{eq}(\boldsymbol{P}) \;\&\; \eta_{eq}(\boldsymbol{P})$$

- Inverse Legendre transformation

$$F(\boldsymbol{E}) = \min_{\boldsymbol{P}}[\widetilde{F}(\boldsymbol{P}) - \Omega\,\boldsymbol{E}\cdot\boldsymbol{P}]$$

Constrained polarization approach: formalism

- Taylor expansion of F(**R**,η,**E**) around **E** = 0

$$F(\boldsymbol{R},\eta,\boldsymbol{E}) = F(\boldsymbol{R},\eta,0) + \sum_{\alpha} E_{\alpha} \frac{\partial F(\boldsymbol{R},\eta,\boldsymbol{E})}{\partial E_{\alpha}}\Big|_{E=0} + \frac{1}{2}\sum_{\alpha,\beta} E_{\alpha} E_{\beta} \frac{\partial^2 F(\boldsymbol{R},\eta,\boldsymbol{E})}{\partial E_{\alpha} E_{\beta}}\Big|_{E=0} + \ldots$$

- Truncation of the Taylor expansion at the lowest order

$$F_1(\boldsymbol{R},\eta,\boldsymbol{E}) = F(\boldsymbol{R},\eta,0) - \Omega\, \boldsymbol{E}\cdot\boldsymbol{P}(\boldsymbol{R},\eta,0)$$

Approximation is supposed to be valid in systems where the ionic contribution to the polarization dominates (f. ex. ferroelectrics)

- Resulting expression

$$\widetilde{F}(\boldsymbol{P}) = \min_{\lambda,\boldsymbol{R},\eta} \left[F(\boldsymbol{R},\eta,0) + \lambda\cdot(\boldsymbol{P} - \boldsymbol{P}(\boldsymbol{R},\eta,0))\right]$$

Constrained polarization approach: formalism

- System of equations to be solved

$$\frac{\partial F(\boldsymbol{R},\eta,0)}{\partial R} - \frac{\partial P(\boldsymbol{R},\eta,0)}{\partial R}\lambda = 0$$

$$\frac{\partial F(\boldsymbol{R},\eta,0)}{\partial \eta} - \frac{\partial P(\boldsymbol{R},\eta,0)}{\partial \eta}\lambda = 0$$

$$\boldsymbol{P}(\boldsymbol{R},\eta,0) = \boldsymbol{P}$$

- In practice: Taylor expansion of F(**R**,η,0) and P(**R**,η,0)

$$F(\boldsymbol{R},\eta,0) = F(\boldsymbol{R_0},\eta_0,0) - f\,\delta\boldsymbol{R} + \Omega\,\sigma\,\delta\eta + \frac{1}{2}K\,\delta\boldsymbol{R}^2 + \frac{\Omega}{2}C\,\delta\eta^2 + \gamma\,\delta\boldsymbol{R}\,\delta\eta$$

$$\boldsymbol{P}(\boldsymbol{R},\eta,0) = \boldsymbol{P}(\boldsymbol{R_0},\eta_0,0) + \frac{1}{\Omega}Z^*\,\delta\boldsymbol{R} + e\,\delta\eta$$

$\mathbf{R}_0$, η_0	:	trial guess of the initial coordinates and strains ($\delta\mathbf{R} = \mathbf{R} - \mathbf{R}_0$ & $\delta\eta = \eta - \eta_0$)
f, σ	:	Hellmann-Feynmann forces and stresses
K	:	interatomic force constants
C	:	rigid atom elastic constants
γ	:	coupling parameters between **R** and η
Z^*	:	Born effective charges
e	:	clamped ion piezoelectric tensor

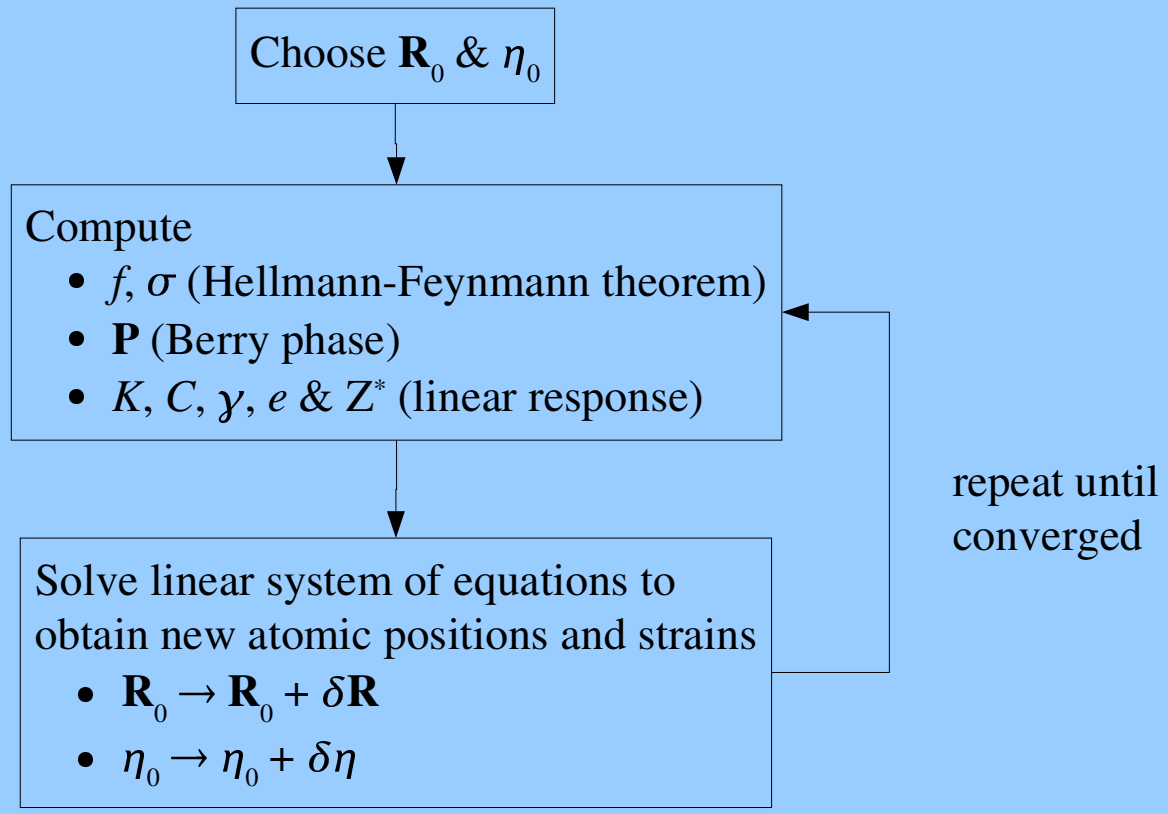
Constrained polarization approach: formalism

- Linear systems of equations

$$\begin{pmatrix} K & \gamma & -1/\Omega Z^* \\ \gamma & \Omega C & -e \\ -1/\Omega Z^* & -e & 0 \end{pmatrix} \begin{pmatrix} \delta \boldsymbol{R} \\ \delta \eta \\ \lambda \end{pmatrix} = \begin{pmatrix} f \\ -\Omega \sigma \\ \Delta \boldsymbol{P} \end{pmatrix}$$

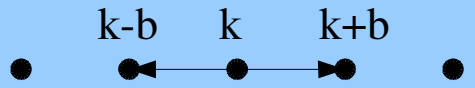
$\Delta\mathbf{P}$ = difference between initial and target values of **P**

- Iterative solution



Berry phase calculation of P and the ddk

- Definition of the Born effective charges $Z^* = \Omega \frac{\partial P}{\partial R}$
- Computation of **P**: string averaged Berry phase



$$P = \frac{-2e}{(2\pi)^3} \int dk_{\perp} \, \Im \ln \left(\prod det \, S(k, k+b) \right)$$

- Computation of Z^* (linear response, non-stationarry expression)

$$Z^* = \frac{2ie\Omega}{(2\pi)^3} \int dk \sum_{m}^{occ} \langle \frac{\partial u_{nk}}{\partial R} | \frac{\partial u_{nk}}{\partial k} \rangle$$

- **PROBLEM:** If the ddk is computed from linear response, the relation between Z^* and **P** is only satisfied in a the limit of a dense k-point mesh
- Finite k-point grid: finite difference formula of the ddk

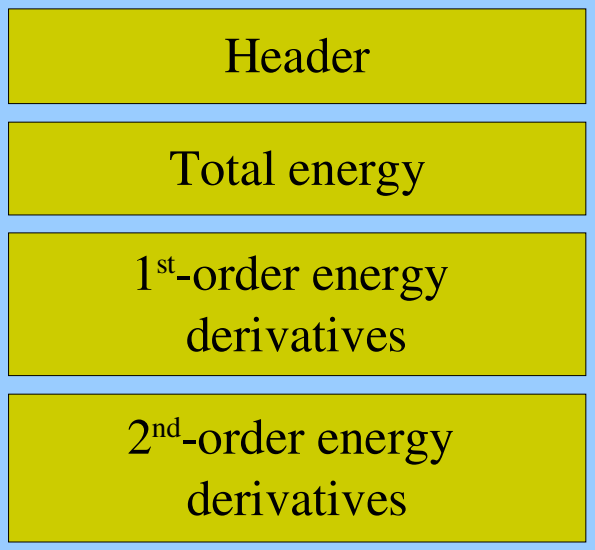
$$\frac{\partial u_{nk}}{\partial k} = \frac{1}{2b} \left[\frac{u_{nk+b}}{\langle u_{nk} | u_{nk+b} \rangle} - \frac{u_{nk-b}}{\langle u_{nk} | u_{nk-b} \rangle} \right]$$

- Comments:
  - No violoation of the charge neutrality
  - Same arguments in case of the piezoelectric tensor

Implementation

- ABINIT: new Berry phase routine (berryphase_new.f)
  - Easier to use
  - Polarization in cartesian coordinates
  - MPI parallelization over k-points
- ANADDB:

Structure of the DDB



New routine relaxpol.f

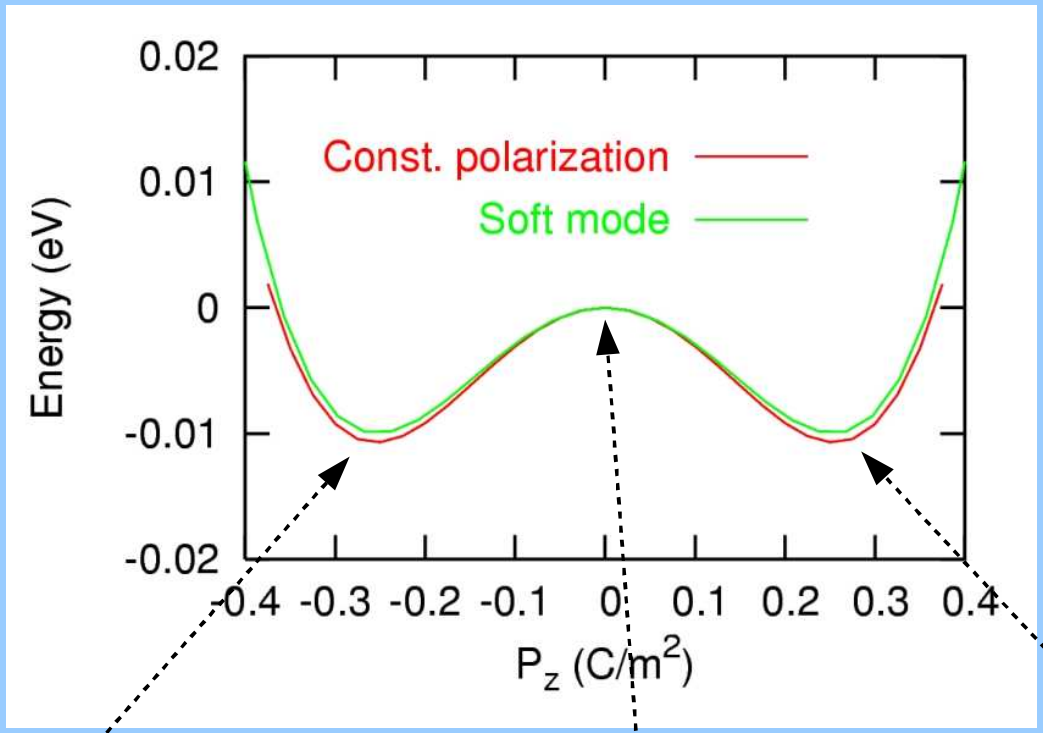
- Called from anaddb.f
- Compute **P** in cartesian coordinates
- Solve linear system of equations
- Compute λ, residual forces and stresses
- Update atomic positions and lattice constants

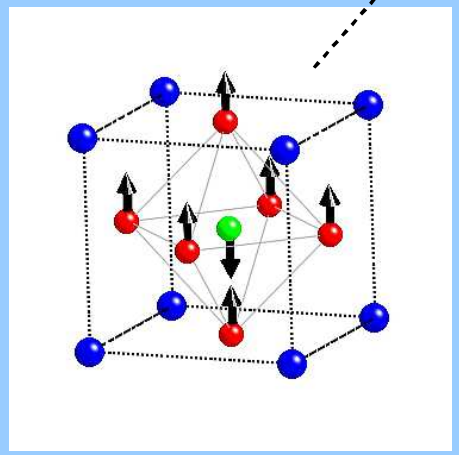
In practice (v.4.3.x)

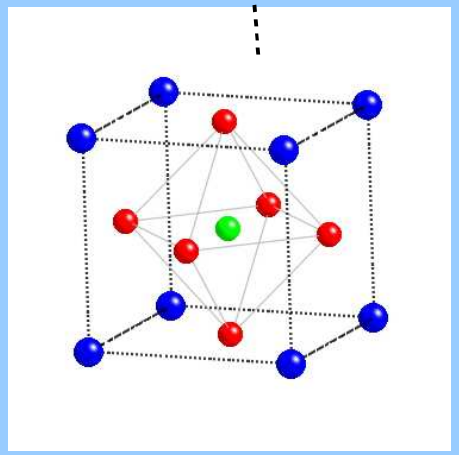
- **1st step:** Ground state calculation of the forces and the stress tensor
- **2nd step:** Berryphase calculation of **P** and the ddk
  - *kptopt* = 3
  - *berryopt* = -3: use berryphase_new.f routine
  - *rfdir* = 1 1 1: compute projection of **P** & ddk along x, y and z
  - *nband* = number of occupied bands
- **3th step:** Linear response calculation
- **4th step:** Use ANADDB to compute new atomic positions and lattice constants
  - *polflag* = 1
  - *targetpol* = target value of the polarization (cartesian coordinates & C/m^2)
  - relaxat, relaxstr
  - natfix, iatfix, istrfix

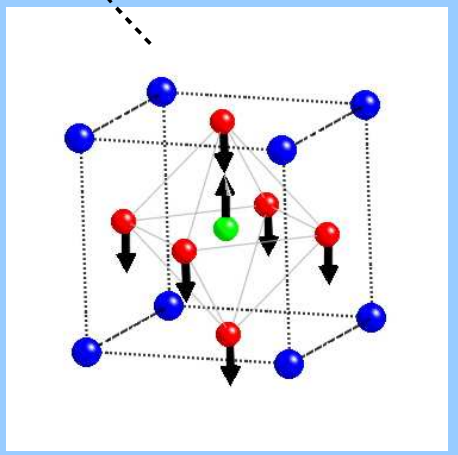
  } specify which degrees of freedom are allowed to relax
- Repeat steps 1, 2, 3 & 4 until convergence is reached

Application: double well in $BaTiO_3$



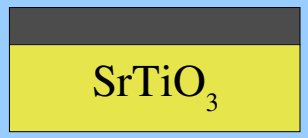






Application: c/a of $PbTiO_3$ as a function of P

Motivation: $PbTiO_3$ thin films grown on a $SrTiO_3$ substrate



Experiment:

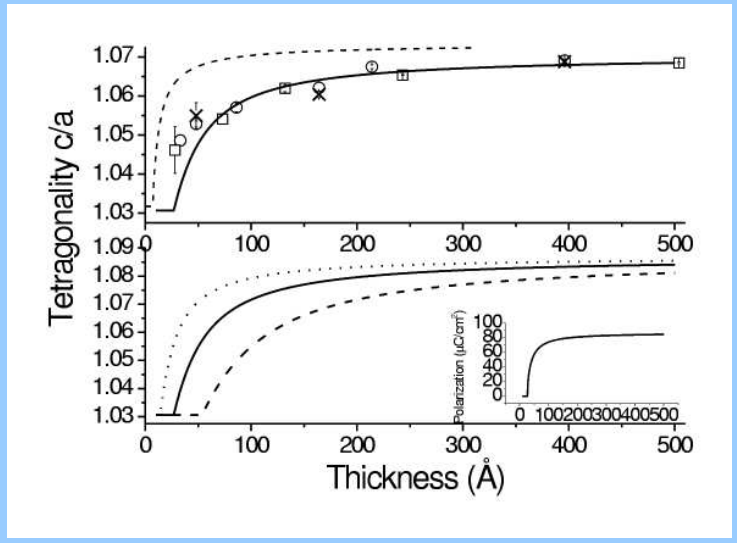
c/a decreases with decreasing film thickness

Theory (effective hamiltonian):

depolarizing electric field

→ reduction of the polarization

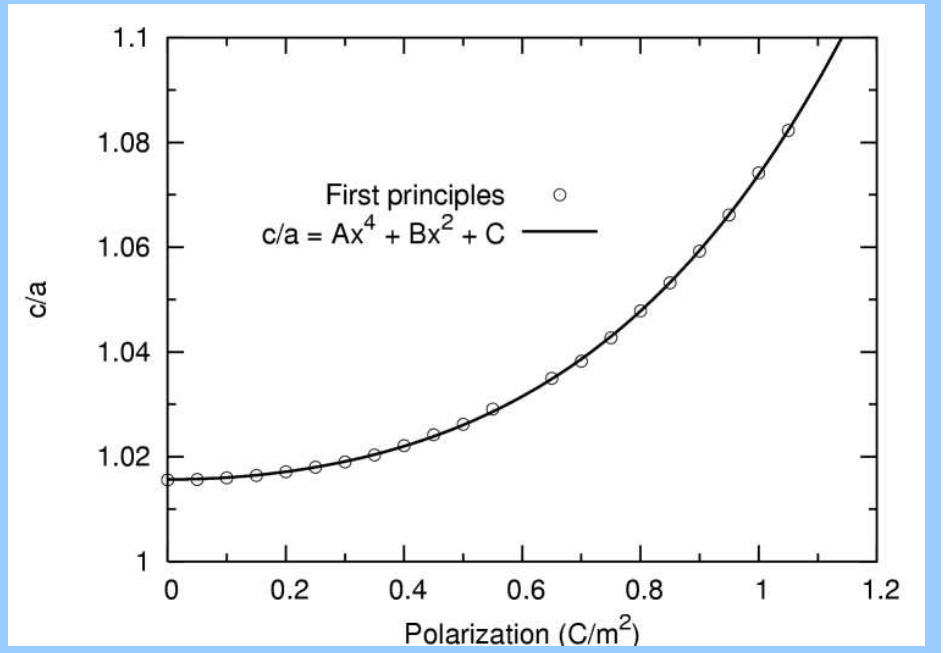
→ reduction of c/a



C. Lichtensteiger et al., cond-mat/0404228

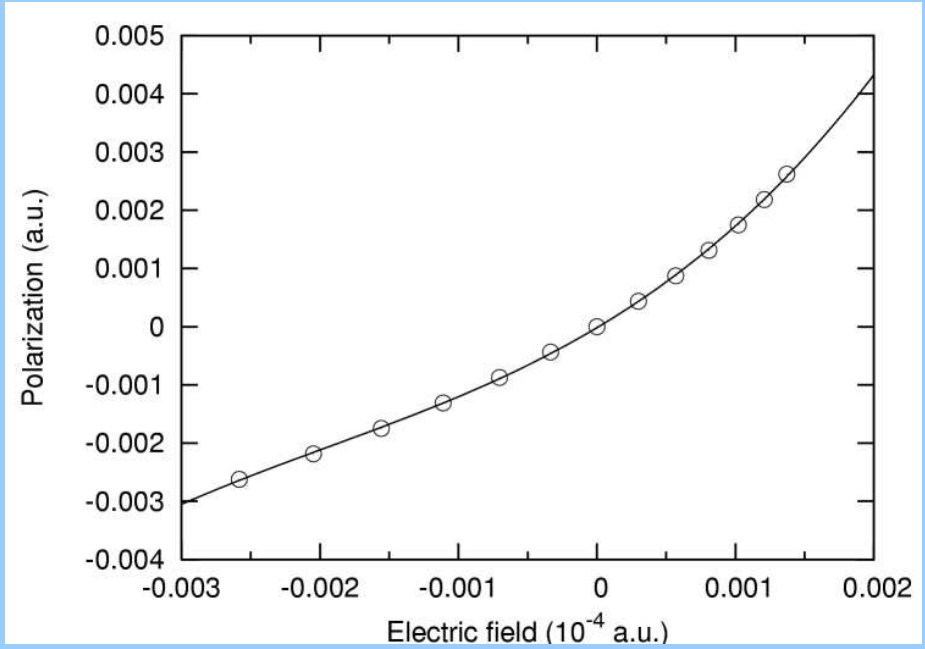
Result

a has been fixed at the theoretical lattice constant of $SrTiO_3$



Application: non-linear dielectric response of tetragonal $PbTiO_3$

P_z as a function of an electric field along z



Ionic dielectric constant:

$\varepsilon = 17.82$

(linear response $\varepsilon = 17.37$)

Tunability:

$$\frac{d\chi_{zz}}{dE_z} = 13711\ pm/V$$

2nd method: First-principles approach to insulators in finite electric fields

For a supercell of size $L = N_k a$ (a = unit cell size, N_k = number of k-points), use only fields smaller than $E_c \sim \frac{E_g}{N_k a}$

- For $E < E_c$, we can minimize the energy functional

$$F\left[\{u_{nk}\}\right] = F_{KS} - a^3 \boldsymbol{E} \cdot \boldsymbol{P}$$

  - F_{KS} = Kohn-Sham energy at zero electric field
  - **P** = macroscopic polarization that is computed as a Berry phase of "field polarized" Bloch functions u_{nk}
  - Long-lived metastable state
- For $E > E_c$, F has no minimum
- More informations

I. Souza, J. Íñiguez and D. Vanderbilt, Phys. Rev. Lett. ***89****, 117602 (2002)*

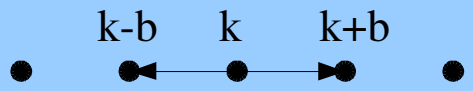
Minimization of the energy functional F

- Strategy: use the preconditione cg minimization implemented in ABINIT to minimiez F_{KS}
- Gradient of the energy functional F $\quad |G_{nk}\rangle = \dfrac{\delta F}{\delta \langle u_{nk}|}$

$$|G_{nk}\rangle = H_{KS}(\boldsymbol{k})|u_{nk}\rangle + |W_{nk}\rangle$$

usual zero-field term — electric field term

- Electric field term



$$|W_{nk}\rangle = C(E)\sum_{m}\left[S^{-1}_{mn}(\boldsymbol{k},\boldsymbol{k}+\boldsymbol{b})|u_{mk+b}\rangle - S^{-1}_{mn}(\boldsymbol{k},\boldsymbol{k}-\boldsymbol{b})|u_{mk-b}\rangle\right]$$

- Transform $|G_{nk}\rangle$ into a preconditioned cg search direction $|D_{nk}\rangle$

Minimization of the energy functional F

- Update of a state $|u_{nk}\rangle$

$$|u_{nk}\rangle^{(new)} = \cos(\theta)\,|u_{nk}\rangle^{(old)} + \sin(\theta)\,|D_{nk}\rangle$$

- Minimize $F(\theta)$
  - $E = 0$: analytic formula for θ_{min}

    M. C. Payne et al., Rev. Mod. Phys. ***64****, 1045 (1992)*

  - $E \neq 0$: no analytic formula for θ_{min}, line minimization must be performed numerically

Computation of forces and stresses

- Field polarized Bloch functions are stationary points of F, the Hellmann-Feynmann theorem yields for the force on atom j

$$f_j = -\frac{dF}{dr_j} = -\frac{\partial F}{\partial r_j}$$

(no implicit dependence on r_j via the wavefunctions)

$$F\left[\{u_{nk}\}\right] = F_{KS} - a^3 \boldsymbol{E} \cdot (\boldsymbol{P}_{el} + \boldsymbol{P}_{ion})$$

no explicit dependence on r_j

$$\longrightarrow \quad f_j = -\frac{\partial F_{KS}}{\partial r_j} + eZ_j E$$

- Similar arguments show that the expression used to compute the stress under zero electric field remains valid

Implementation in ABINIT (4.3.x)

gstate.f

- **initberry.f**

  Initialization of Berry phase calculation:
  - Polarization, ddk & electric field
  - store informations in the *efield_type* structured datatype

- **scfcv.f**
  - **berryphase_new.f** Initialize polarization *pel_cg(1:3)* & Initialize overlap matrices

    Start SCF optimization of wavefunctions
  - **vtorho.f**
    - **vtowfk.f**
      - **cgwf.f**

        Non-SCF line minimizations. For each iteration
        - update overlap matrices
        - add the electric field contribution to the gradient
        - perform line minimization numerically (**linemin.f**)
  - Update polarization: add change in Berry phase to *pel_cg(1:3)*

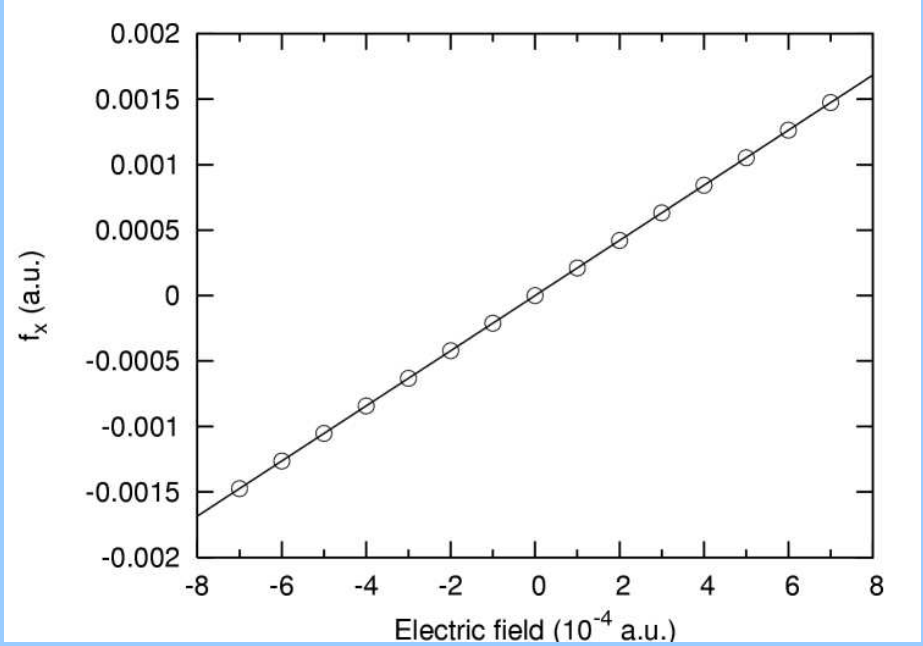
    End SCF optimization of wavefunctions
  - **berryphase_new.f** Recompute polarization, check that it is consistent with the value obtained from the update of the wavefuntions

In practice (4.3.x)

- **1st step:** Perform a calculation under zero electric field
- **2nd step:** Electric fiel calculation (use wavefunctions computed during the first step to initialize the calculation)
  - *berryopt* = 4
  - *efield(1:3)* = cartesian coordinates of the electric field in atomic units
  - *nsym* = 1
  - *kptopt* = 3
  - *nband* = number of valence bands
- **COMMENTS:**
  - insulators only
  - MPI parallelization not yet implemented
  - no spin polarization (spin polarization probably available in ABINITv4.4.x)
  - You should increase the amplitude of the electric field in small steps
  - Suggestion: use multiple datasets. For each dataset, use a slightly larger value of the electric field and take wavefunctions of the previous dataset to initialize the SCF cycle.

Applications: AlAs, electric field along x

Force on Al along the x direction



Born effective charges:

$$Z^* = \Omega \frac{\partial P}{\partial \tau} = \frac{\partial f}{\partial E}$$

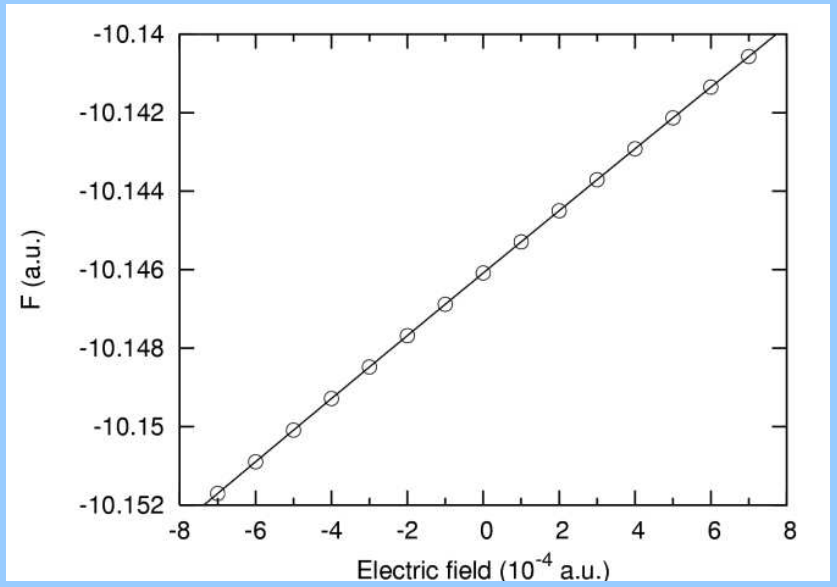
Finit electric field calculation:

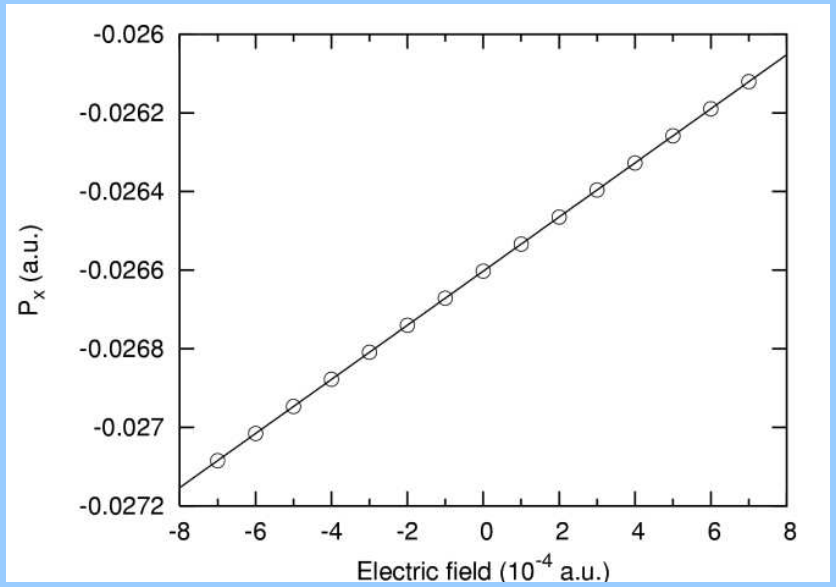
$Z^* = 2.1057$

Linear response calculation:

$Z^* = 2.1019$

Applications: AlAs, electric field along x





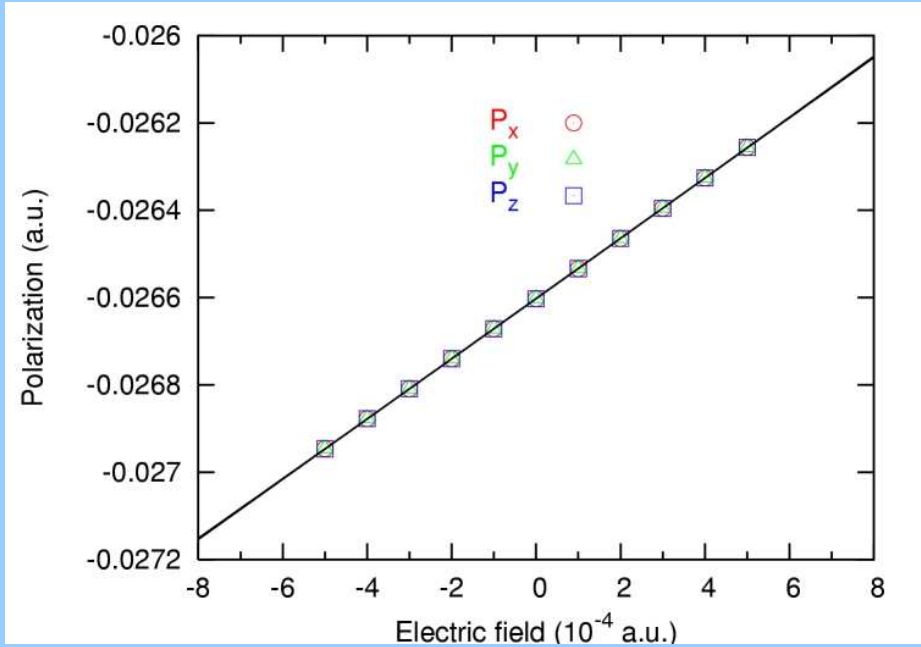
Optical dielectric constant

$$\varepsilon = 1 - \frac{4\pi}{\Omega}\frac{\partial^2 F}{\partial E^2} = 1 + 4\pi\frac{\partial P}{\partial E}$$

Method	Value
F(E)	9.6517
P(E)	9.6539
linear response	9.9417

Applications: AlAs, electric field along (1,1,1)

Polarziation as a function of **E** = E*(1,1,1)



Non-linear optical susceptibilities

$$\chi^{(2)} = \frac{1}{2}\frac{\partial^2 P}{\partial E^2}$$

Finite electric field calculation:

$\chi^{(2)}$ = 70.1393 pm/V

Non-linear response calculation:

$\chi^{(2)}$ = 69.6073 pm/V

Application to cubic semiconductors

Black = Theory

Blue = Experiment

	GaAs	AlAs	GaP	AlP
a (a.u.)	10.45 (10.68)	10.59 (10.69)	10.11 (10.28)	10.24 (10.33)
Z^*_{cation}	2.00 (2.16)	2.14 (2.18)	2.10 (2.04)	2.24 (2.28)
ϵ_∞	11.9 (10.9)	9.6 (8.2)	9.4 (9.0)	8.1 (7.5)
ϵ_{static}	13.5 (13.1)	11.5 (10.1)	11.2 (11.1)	10.2 (9.8)
$\chi^{(2)}$ (pm/V)	134 (166)	64	66 (74)	39
$\overline{\gamma}_{14}$	−0.40 (−0.32)	−0.10	−0.25 (−0.18)	0.05

I. Souza et al., PRL ***89****, 117602 (2002)*

Conclusions

First-principles calculations of insulators in finite electric fields

- **1st method:** structural response to macroscopic electric fields
  - Derivatives of the energy with respect to the electric field can be accurately computed from DFPT
  - Low order Taylor expansion of the energy with respect to the electric field
  - Map out the energy as a function of the polarization
  - Iterative optimization of the structure under the constrained of a fixed polarization
- **2nd method:** first-principles approach to insulators in finite electric fields
  - Practical scheme for computing the electronic structure of insulators under a finite bias
  - For $E < E_c$: minimization of a modified energy functional
  - Accurate computation of the total energy, the polarization, the forces and stresses
  - Finite difference calculation of electric field derivatives