Calculating the flexoelectric tensor with ABINIT

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EXCELENCIA SEVERO OCHOA

Outline

I INTRODUCTION

II BULK FLEXOELECTRICITY

- First-principles theory of flexoelectricity
- Usage of the ABINIT implementation
- Numerical example: bulk flexoelectric tensor of $SrTiO_3$

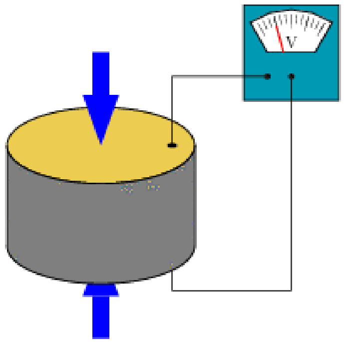
III FINITE SIZE SAMPLES

- Surface piezoelectricity
- Flexural deformation in practice
- Numerical example: total flexovoltage response of 2D materials

V SUMMARY AND CONCLUSIONS

Electromechanical Response

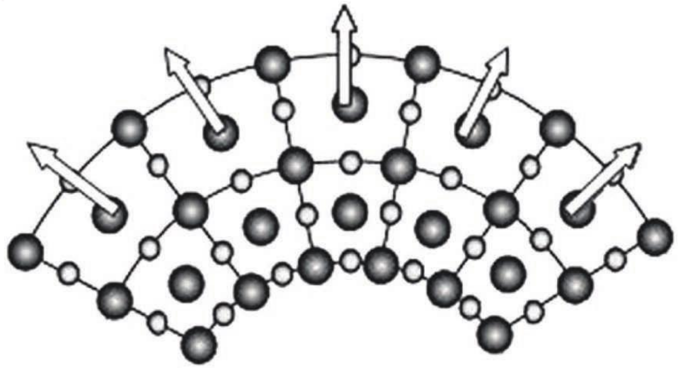
PIEZOELECTRICITY



$$P_\alpha = e_{\alpha\beta\gamma}\,\varepsilon_{\beta\gamma}$$

- **P** response to uniform strain
- Few materials display this effect
- Size-independent property

FLEXOELECTRICITY



$$P_\alpha = \mu_{\alpha\lambda,\beta\gamma}\frac{\partial\varepsilon_{\beta\gamma}}{\partial r_\lambda}$$

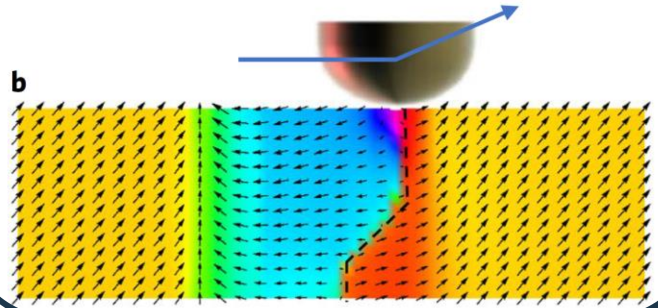
- **P** response to strain gradient
- Universal property of all materials
- Scales as the inverse of the sample size

Why Does Flexoelectricity Matter?

MECHANICAL MANIPULATION OF POLARIZATION

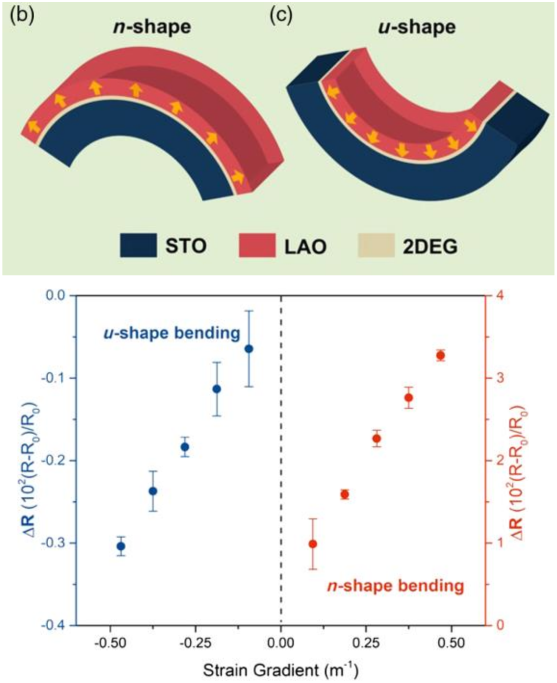
Lu *et al.*, Science (2012)

Park *et al.*, Nat. Nano (2018)



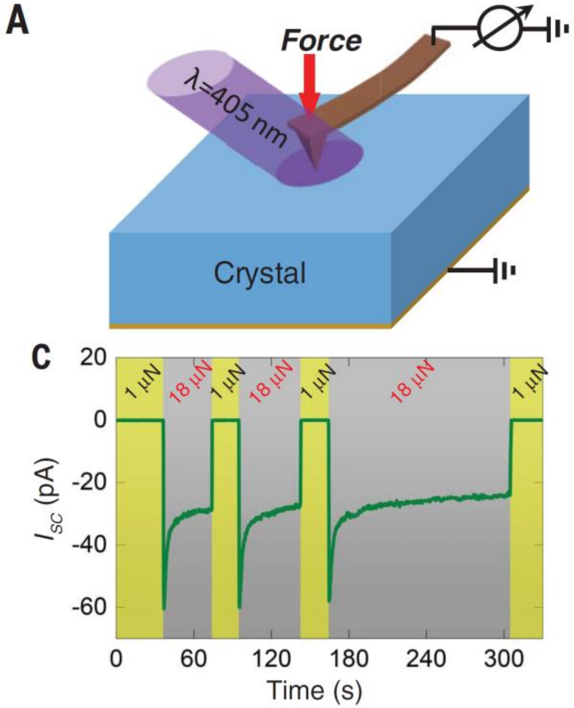
FLEXOELECTRONICS

Zhang *et al.*, PRL (2019)



FLEXOFOTOVOLTAICS

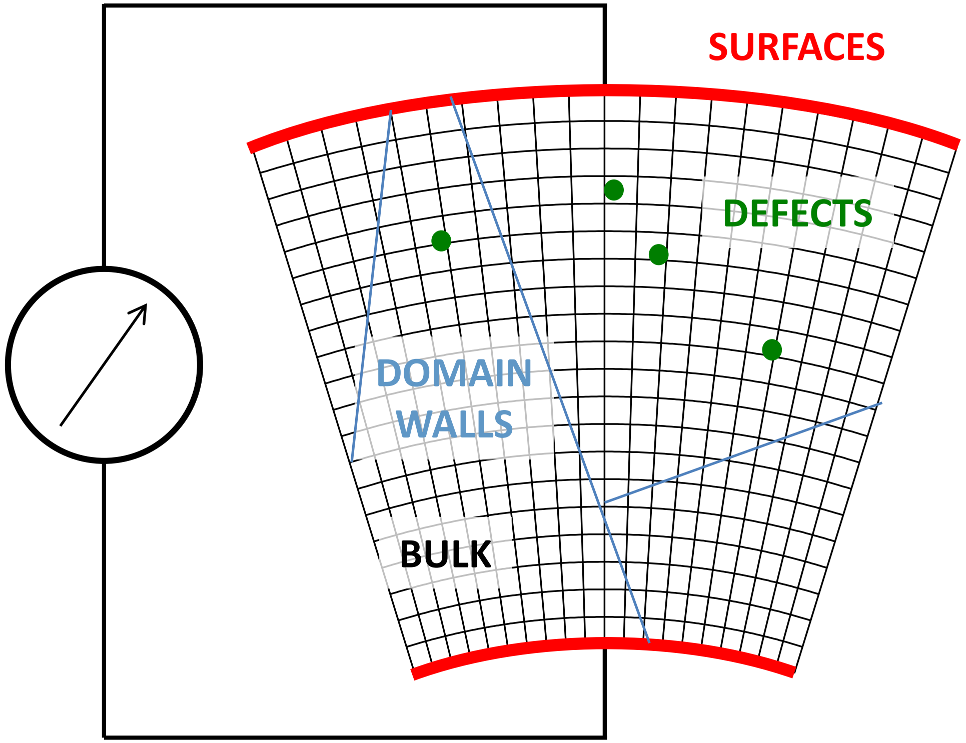
Yang *et al.*, Science (2018)



Fundamental Interest: study of curvature effects on material properties

Necessity of a First-Principles Theory

First-principles ("*ab initio*"): using fundamental quantum mechanics to calculate the properties of real materials



EXPERIMENT
Bend the sample & measure the transient current

OUTCOME
Lots of different contributions…
…only their overall sum is accessible!

Density Functional Theory (DFT) is a powerful "theoretical microscope" that can isolate the individual effects

PROBLEM: Translational symmetry is broken!

Cannot use Bloch theorem, plane waves, etc.?

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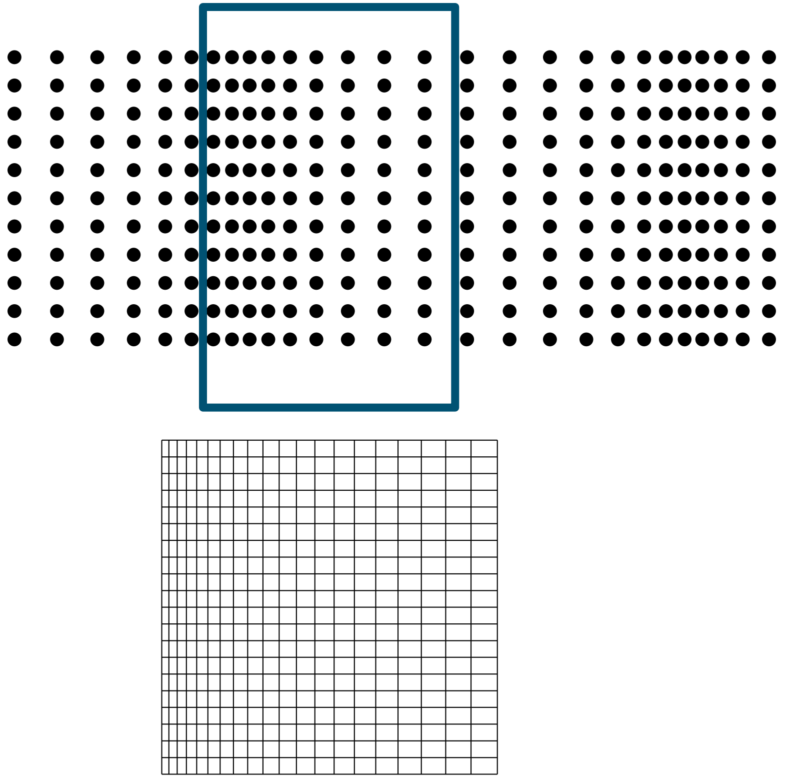
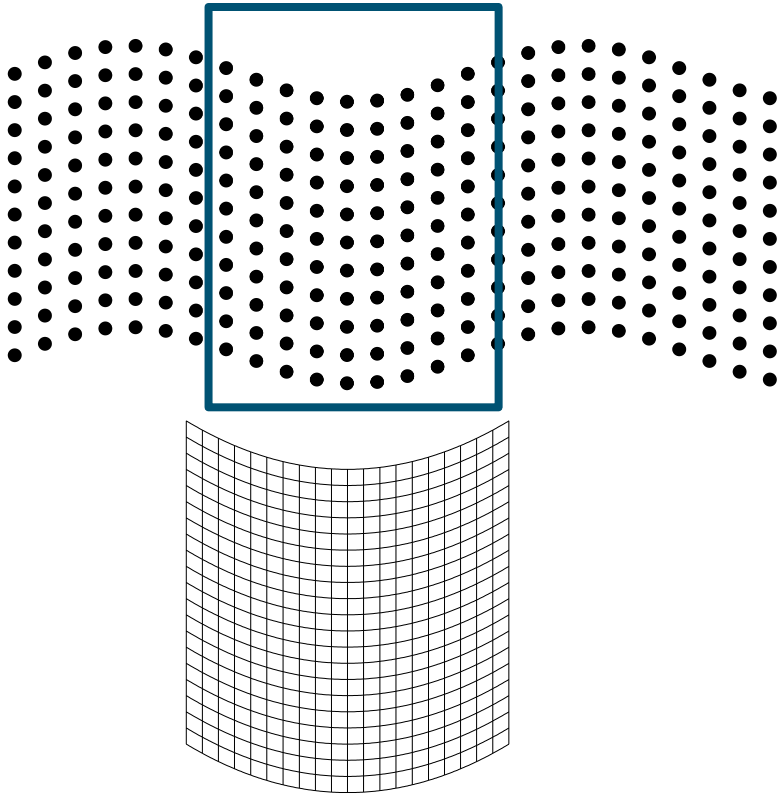
Solution Via Acoustic Phonons

LONGITUDINAL



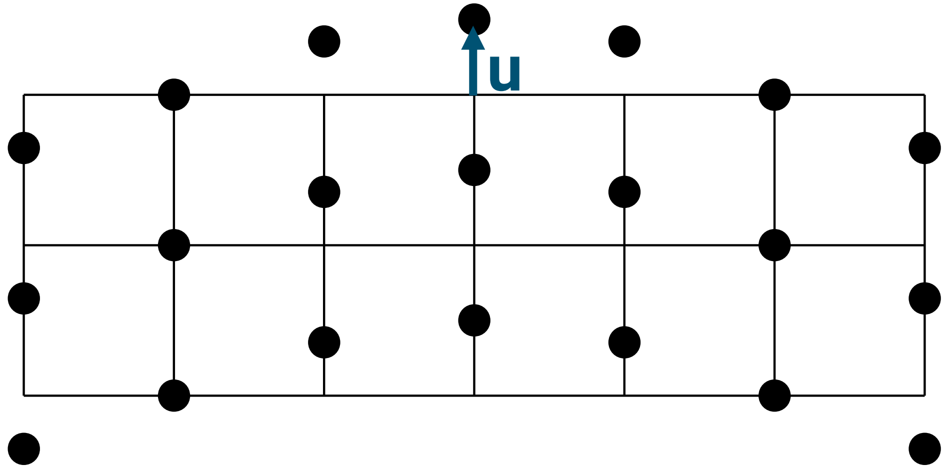
SHEAR



Martin **PRB** 5, 1607 (1972) → PIEZOELECTRICITY

Resta **PRL** 105, 127601 (2010)
Stengel **PRB** 88, 174106 (2013)
Hong & Vanderbilt **PRB** 88, 174107 (2013) → FLEXOELECTRICITY

Solution Via Acoustic Phonons



Modulated displacement field **u**
(deformation wave)

$$u_\beta(\mathbf{r}) = \lambda e^{i\mathbf{q}\cdot\mathbf{r}}$$

- Can recast gradient effects as a long-wave expansion in the wave vector **q**

$$P_\alpha(\mathbf{r}) = \underbrace{\varepsilon_{\beta\gamma}(\mathbf{r})e_{\alpha\beta\gamma}}_{\text{PIEZO}} + \frac{\partial \varepsilon_{\beta\gamma}(\mathbf{r})}{\partial r_\delta}\underbrace{\mu_{\alpha\delta,\beta\gamma}}_{\text{FLEXO}} + \cdots \Rightarrow P_\alpha(\mathbf{q}) = i\lambda q_\gamma e_{\alpha\beta\gamma} - \lambda q_\gamma q_\delta \mu_{\alpha\delta,\beta\gamma} + \cdots$$

$O(q^0)$: rigid translation, **P** vanishes due to ASR

$O(q^1)$: uniform strain

$O(q^2)$: strain gradient

- Allows to perform calculations on a primitive cell by using DFPT

Towards a Practical Scheme

- Intermediate "low-level" quantities

	TRANSLATION	PIEZO	FLEXO		
$\bar{P}_\alpha(\mathbf{q}) =$		$+i\lambda q_\gamma \; \bar{e}_{\alpha\beta\gamma}$	$-\lambda q_\gamma q_\delta \; \bar{\mu}_{\alpha\delta,\beta\gamma} \; + \cdots$	*electronic polarization*	
$\vert f(\mathbf{q})\rangle =$		$\vert\Lambda_{\beta\gamma}\rangle$	$\vert C_{\delta,\beta\gamma}\rangle$	*atomic forces*	
$\vert u(\mathbf{q})\rangle =$	$\vert\beta\rangle$	$\vert\Gamma_{\beta\gamma}\rangle$	$\vert L_{\delta,\beta\gamma}\rangle$	*atomic displacements*	$\langle\kappa\alpha\vert\beta\rangle = \delta_{\alpha\beta}$

- Notation convention: bra/ket (N = number of basis atoms)

$$Z^{(\alpha)}_{\kappa\rho} = \langle\kappa\rho|Z^{(\alpha)}\rangle$$ *Born effective charges (3N-dimensional vector)*

$$\Phi_{\kappa\rho\kappa'\sigma} = \langle\kappa\rho|\Phi|\kappa'\sigma\rangle.$$ *force-constants matrix (3N x 3N operator)*

κ, κ'	sublattice indices
$\alpha, \beta, \ldots$	Cartesian directions

Piezo vs. Flexo Tensors: similar...

$$e_{\alpha\beta\gamma} = \underbrace{\bar{e}_{\alpha\beta\gamma}}_{electronic} + \underbrace{\frac{1}{\Omega}\langle Z^{(\alpha)}|\Gamma_{\beta\gamma}\rangle}_{lattice-mediated} \Longleftrightarrow \mu_{\alpha\lambda,\beta\gamma} = \underbrace{\mu^{\mathrm{el}}_{\alpha\lambda,\beta\gamma}}_{electronic} + \underbrace{\frac{1}{\Omega}\langle Z^{(\alpha)}|L_{\lambda,\beta\gamma}\rangle}_{lattice-mediated}.$$

Atomic Displacements

$$|\Gamma_{\beta\gamma}\rangle = \Phi^{-1}|\Lambda_{\beta\gamma}\rangle. \Longleftrightarrow |L_{\lambda,\beta\gamma}\rangle = \Phi^{-1}|C_{\lambda,\beta\gamma}\rangle.$$

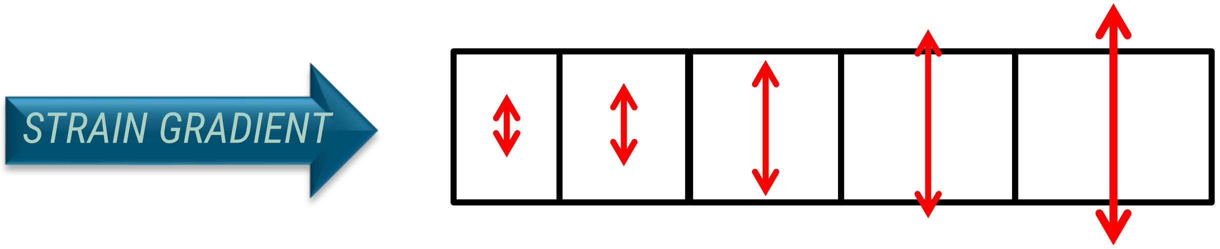
Atomic Forces

... but different:

$$\begin{aligned} \mu^{\mathrm{el}}_{\alpha\lambda,\beta\gamma} &= \bar{\mu}_{\alpha\lambda,\beta\gamma} - \langle P^{(1,\lambda)}_{\alpha}|\Gamma_{\beta\gamma}\rangle, \\ |C_{\lambda,\beta\gamma}\rangle &= \underbrace{|\bar{C}_{\lambda,\beta\gamma}\rangle}_{\text{CLAMPED-ION}} + \underbrace{\Phi^{(1,\lambda)}|\Gamma_{\beta\gamma}\rangle}_{\text{NEW TERMS (??)}}. \end{aligned}$$

Interpretation of new terms

A strain gradient induces a gradient of the optical mode "$\updownarrow$"



$$\frac{\partial \varepsilon}{\partial x} \longrightarrow \langle \Gamma | \updownarrow \rangle \boxed{\frac{\partial \updownarrow}{\partial x}}$$

$$\rightarrow \langle P^{(1)} | \updownarrow \rangle$$ electronic **P**

$$\rightarrow \Phi^{(1)} | \updownarrow \rangle$$ atomic forces

$\updownarrow$ = Raman-active "gerade" mode (even under space inversion)

Basic Ingredients: Classification

Uniform Response

Second derivatives of the energy w.r.t. electric field $(\mathbf{E})$, phonon $(\boldsymbol{\tau})$ or strain $(\boldsymbol{\varepsilon})$

	$\mathbf{E}$	$\boldsymbol{\tau}$	$\boldsymbol{\varepsilon}$
$\mathbf{E}$	ϵ	$\lvert\mathbf{Z}^*\rangle$	$\bar{\mathrm{e}}$
$\boldsymbol{\tau}$		$\boldsymbol{\Phi}$	$\lvert\boldsymbol{\Lambda}\rangle$
$\boldsymbol{\varepsilon}$			$\boldsymbol{\mathcal{C}}$

$\boldsymbol{\epsilon}$ = dielectric tensor

$\boldsymbol{\mathcal{C}}$ = elastic tensor

Spatial Dispersion (1st order)

Third derivatives of the energy w.r.t. two perturbations and the momentum wave-vector $(\mathbf{q})$

	$\mathbf{E}$	$\boldsymbol{\tau}$	$\boldsymbol{\varepsilon}$
$\mathbf{E}$	$\mathbf{G}$	$\lvert\mathbf{P}^{(1)}\rangle$	$\bar{\boldsymbol{\mu}}$
$\boldsymbol{\tau}$		$\boldsymbol{\Phi}^{(1)}$	$\lvert\bar{\mathrm{C}}\rangle$
$\boldsymbol{\varepsilon}$			$\boldsymbol{\mathcal{D}}$

$\mathbf{G}$ = natural optical activity

$\boldsymbol{\mathcal{D}}$ = acoustical activity

Theory and ABINIT implementation:
M. Royo and M. Stengel, Phys. Rev. X **9**, 021050 (2019)
M. Royo and M. Stengel, *in preparation*.

Example of long-wave DFPT ABINIT run

```
# Cubic STO: computation of the FxE Tensor

ndtset        5

#Set 1: Ground state self-consistency

getwfk1       0
kptopt1       1
nqpt1         0
tolvrs1       1.0d-18

#Set 2: Response function calculation of d/dk

iscf2         -3
kptopt2       2
rfelfd2       2
tolwfr2       1.0d-22
rfdir2        1 1 1

#Set 3: Response function calculation of d2/dkdk

getddk3       2
iscf3         -3
kptopt3       2
rf2_dkdk3     1
tolwfr3       1.0d-22

#Set 4 : Response function calculation of q=0 phonons,
# electric field and strain perturbations

getddk4       2
kptopt4       2
rfelfd4       3
rfphon4       1
rfatpol4      1 5
rfdir4        1 1 1
tolvrs4       1.0d-10
prepalw4      1        # Deactivates symmetries for the lw routines

#Set 5: Long-wave magnitudes calculation

optdriver5    10       # Activates long-wave driver
kptopt5       2
get1wf5       4
get1den5      4
getddk5       2
getdkdk5      3
lw_flexo5     1        # Calculates flexoelectric tensor ingredients

#Common input variables
getwfk        1
useylm        1
nqpt          1
qpt           0.0d+00  0.0d+00  0.0d+00
…
```

Postprocessing with MRGDDB and ANADDB

MRGDDB input

```
STO.ddb.out
#Total DDB for complete STO FxE tensor
3
STO_o_DS1_DDB
STO_o_DS4_DDB
STO_o_DS5_DDB
```

STO_o_DS1_DDB → *FORCES AND STRESS*

STO_o_DS4_DDB → *UNIFORM RESPONSE FUNCTIONS*

STO_o_DS5_DDB → *GRADIENT RESPONSE FUNCTIONS*

ANADDB input

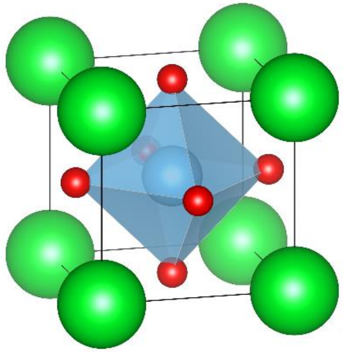
```
flexoflag  1    # flexoelectric tensor

  dieflag  3     # ion-relaxed dielectric tensor
    nph2l  1

piezoflag  3    # piezoelectric tensor
 instrflag 1    # internal strain tensor
   elaflag 3    # elastic tensor
```

Bulk Flexoelectric Coefficients of $SrTiO_3$

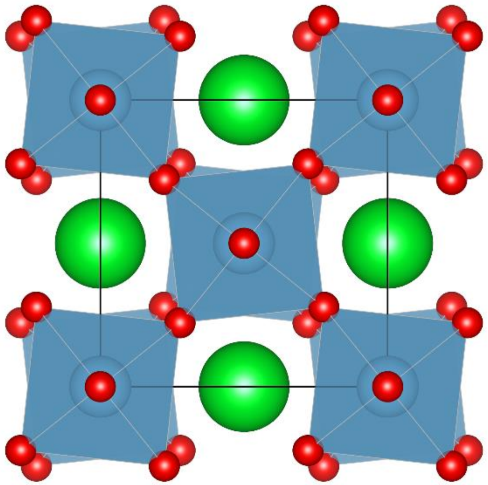
CUBIC



	$\bar{\mu}$	$P^{(1)}\Gamma$	$\bar{C}$	$\Phi^{(1)}\Gamma$	μ
xx, xx	-0.891	0.0	-181.950	0.0	$\mathbf{-182.841}$
xx, yy	-0.832	0.0	-157.953	0.0	$\mathbf{-158.785}$
xy, xy	-0.083	0.0	-19.310	0.0	$\mathbf{-19.392}$

ill defined (xx, xx and xx, yy)

TETRAGONAL



	$\bar{\mu}$	$P^{(1)}\Gamma$	$\bar{C}$	$\Phi^{(1)}\Gamma$	μ
xx, xx	-0.946	0.056	-68.865	3.516	$\mathbf{-66.239}$
zz, zz	-0.898	-0.013	-55.841	-2.507	$\mathbf{-59.259}$
xx, yy	-0.786	0.052	-55.977	3.416	$\mathbf{-53.294}$
xx, zz	-0.830	-0.041	*ill defined*	-2.626	$\mathbf{-61.631}$
zz, xx	-0.841	0.017	-49.897	3.308	$\mathbf{-47.413}$
xy, xy	-0.028	0.002	-4.091	0.313	$\mathbf{-3.805}$
xz, xz	-0.079	0.023	-6.796	-1.292	$\mathbf{-8.144}$
zx, zx	-0.081	0.013	-5.468	-1.706	$\mathbf{-7.242}$

ill defined (xx, xx and zz, zz)

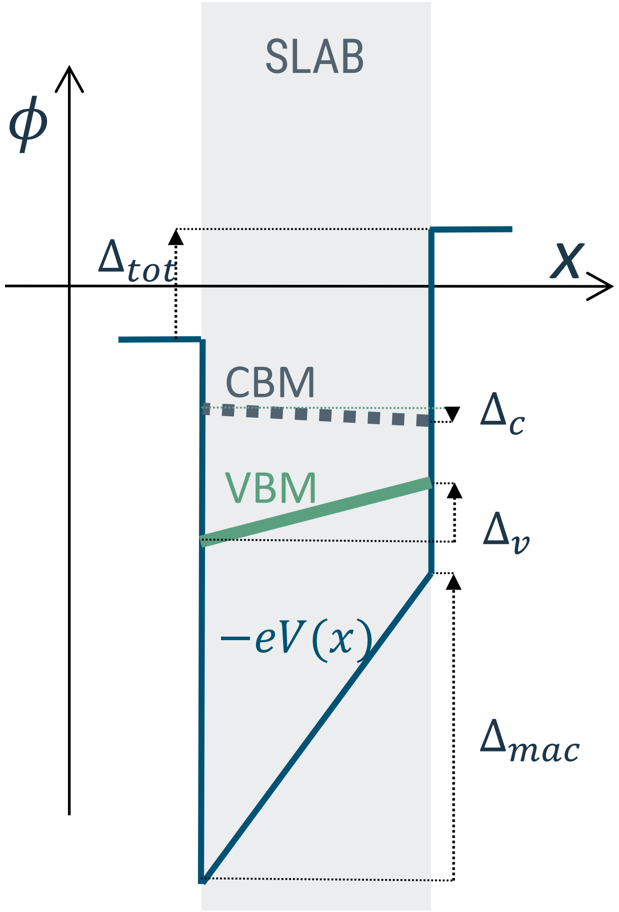
Arbitrariness in the Longitudinal and Transverse Coefficients

Bulk flexoelectric coefficients are only defined modulo a constant

$$\Delta\mu_{\alpha\lambda,\beta\gamma} = \chi_{\alpha\lambda}\frac{\partial V}{\partial \varepsilon_{\beta\gamma}}$$

$\chi_{\alpha\lambda}$ Dielectric susceptibility

V Potential



- Necessity of removing the macroscopic electric fields associated to long-wavelength phonons
- Dependence on which reference potential is taken to impose short-circuit EBCs (the macroscopic electrostatic potential in the implementation)
- Direct link to the theory of **absolute deformation potentials**

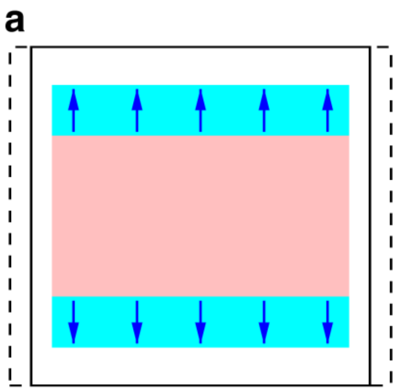
$$D_{n\kappa}^{\beta\gamma,\hat{\mathbf{q}}} = \underbrace{\frac{dE_{n\mathbf{k}}}{d\varepsilon_{\beta\gamma}}}_{\text{Band structure}} - \underbrace{\frac{e}{\epsilon_0\epsilon_{\hat{\mathbf{q}}}}\mu^{\mathrm{II}}_{\alpha\lambda,\beta\gamma}\,\hat{q}_\alpha\hat{q}_\lambda}_{\text{Macroscopic electrostatics}}$$

M. Stengel, PRB **92**, 205115 (2015)

Outline

Surface Piezoelectricity

UNIFORM STRAIN

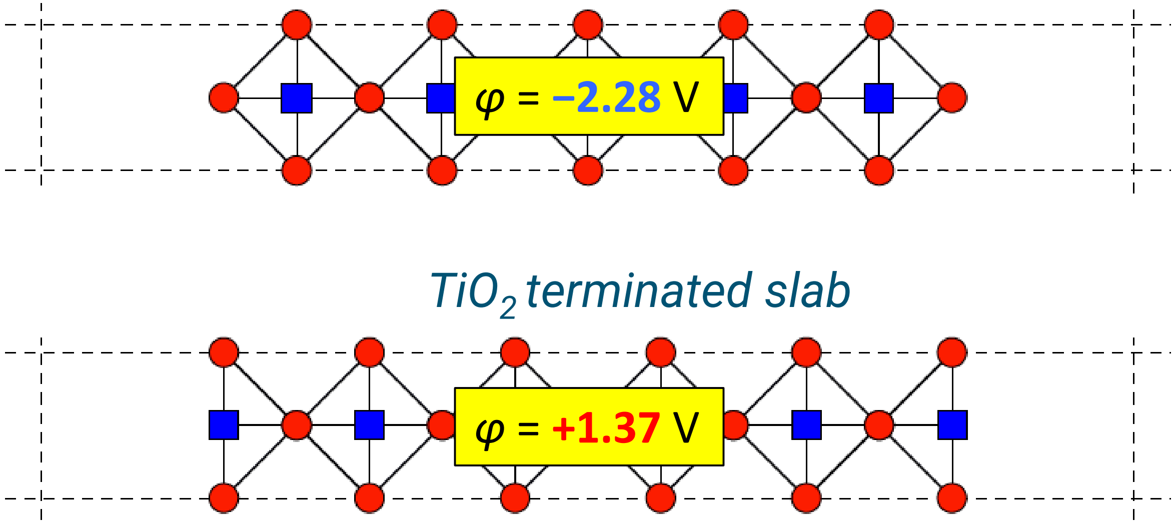


Surface contributions are as important as bulk ones at any thickness of the sample

$\approx \frac{\partial \phi}{\partial \varepsilon_{\beta\gamma}}$ ϕ (potential offset) suffers from the same reference potential ambiguity and cancels de bulk one

SrO terminated slab

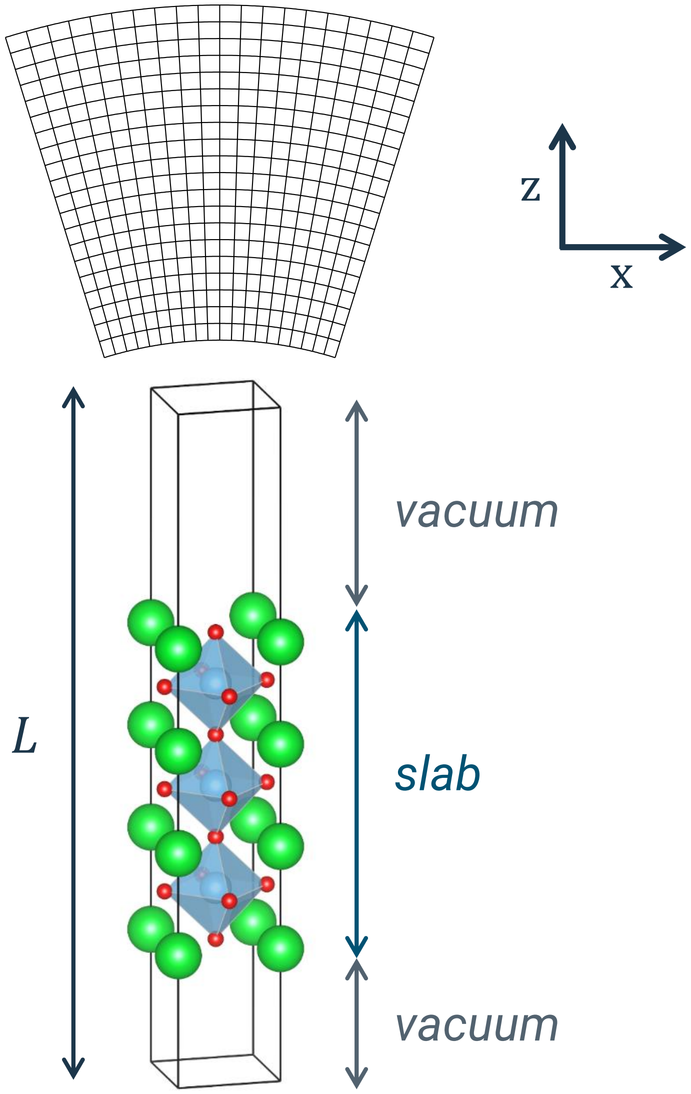
TiO_2 terminated slab



M. Stengel, PRB 90, 220103(R) (2014)

The surface determines the sign of the total response!

Flexural Deformation in Practice



- **Important considerations:**
  - Open-circuit EBCs need to be imposed
  - Voltage response rather than polarization response
  - Additional surface piezoelectricity contributions

Springolo, Royo & Stengel, arXiv:2010.08470

TOTAL FLEXOVOLTAGE

$$\varphi = \frac{\partial V}{\partial \varepsilon_{xx,z}} = \underbrace{\frac{L}{\epsilon_0 \epsilon_{zz}} \mu_{zz,xx}}_{\text{Bulk}} + \underbrace{\frac{\mathcal{Q}[\rho^{\mathrm{U}}_{xx}]}{2\ \epsilon_0} - \frac{\mathcal{Q}[\rho^0]}{2\ \epsilon_0}}_{\text{Surface}}$$

ρ^{U}_{xx}: Density response to a uniform strain

ρ^0: Ground-state density

$\mathcal{Q}[\rho] = \int d^3\boldsymbol{r}\ z^2 \rho(\boldsymbol{r})$

Flexovoltages of several 2D materials

BULK vs. SURFACE

(units: nV·m)

	φ^{G}	φ^{M}	φ^{U}	φ
C	-2.4658	3.8456	-1.4932	-0.1134
Si	-1.9448	3.5106	-1.5073	0.0585
P (zigzag)	-5.1229	6.4059	-1.0655	0.2175
P (armchair)	-5.2086	6.4059	-1.2564	-0.0591
BN	-2.4433	3.5744	-1.3320	-0.2009
MoS_2	-9.3319	10.2987	-1.2937	-0.3269
WSe_2	-11.1874	12.0630	-1.2655	-0.3899
SnS_2	-6.8832	8.3647	-1.1223	0.3592

Bulk

Surface

Large cancelation between bulk and metric contributions

CLAMPED-ION vs. LATTICE-MEDIATED

(units: nV·m)

	φ^{CI}	φ^{LM}	φ
C	-0.1134	0.0000	-0.1134
Si	0.0585	0.0000	0.0585
P (zigzag)	0.2320	-0.0151	0.2170
P (armchair)	-0.0130	-0.0461	-0.0591
BN	-0.0381	-0.1628	-0.2009
MoS_2	-0.2704	-0.0565	-0.3269
WSe_2	-0.3158	-0.0742	-0.3899
SnS_2	0.1864	0.1728	0.3592

Rich variety in magnitude and sign

Springolo, Royo & Stengel, arXiv:2010.08470

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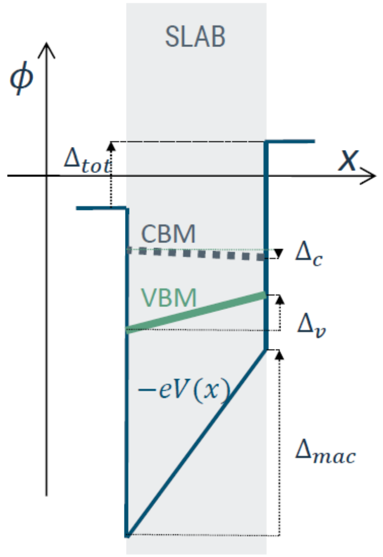
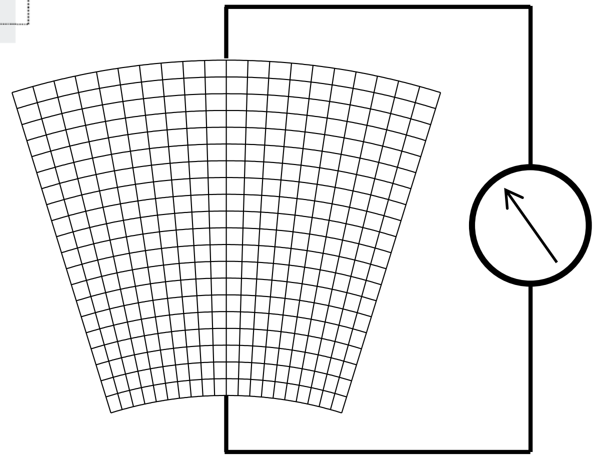
Summary and Conclusions

- **Bulk flexoelectric tensor μ in the official ABINIT code (since v.9.0.2)**



- **μ not a physical observable, we need to add:**
  - Band term ➡ *Absolute deformation potentials*
  - Surface contribution ➡ *Total voltage response to a deformation gradient*



Outlook for the Longwave Driver

- **Work in progress**
  - Extension to GGA functionals
  - Facilitate calculating absolute deformation potentials
- **Short term**
  - Extension to PSPs with XC non-linear core corrections
  - Incorporation of surface piezoelectricity terms in ANADDB
  - Optimizing performance: use of symmetries and reduction in the number of I/O operations

MERGE WITH NONLINEAR DRIVER?

- **Long term**
  - New spatial dispersion quantities

$\mathbf{G}$ = natural optical activity

$\mathcal{D}$ = acoustical activity

Long-Wave DFPT First-Order Gradient Formula

$$E_{\gamma}^{\lambda_1^* \lambda_2} = s \int_{\mathrm{BZ}} [d^3 k] \sum_m E_{m\mathbf{k},\gamma}^{\lambda_1^* \lambda_2}$$
$$+ \frac{1}{2} \int_{\Omega} \int K_{\gamma}(\mathbf{r}, \mathbf{r}') n^{\lambda_1 *}(\mathbf{r}) n^{\lambda_2}(\mathbf{r}') d^3 r d^3 r'$$
$$+ \frac{1}{2} \frac{\partial}{\partial q_{\gamma}} \left(\frac{\partial^2 E}{\partial \lambda_1^* \partial \lambda_2} \right) \Big|_{\mathbf{q}=0},$$

$$E_{m\mathbf{k},\gamma}^{\lambda_1^* \lambda_2} = \langle u_{m\mathbf{k}}^{\lambda_1} | \partial_{\gamma} \hat{H}_{\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\lambda_2} \rangle$$
$$+ \langle u_{m\mathbf{k}}^{\lambda_1} | \partial_{\gamma} \hat{Q}_{\mathbf{k}} \, \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | \left(\hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_1} \right)^{\dagger} \partial_{\gamma} \hat{Q}_{\mathbf{k}} | u_{m\mathbf{k}}^{\lambda_2} \rangle$$
$$+ \langle u_{m\mathbf{k}}^{\lambda_1} | \hat{H}_{\mathbf{k},\gamma}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | \left(\hat{H}_{\mathbf{k},\gamma}^{\lambda_1} \right)^{\dagger} | u_{m\mathbf{k}}^{\lambda_2} \rangle.$$

- Only response functions to uniform perturbations are necessary
- *One-shot* Γ-point calculation
- Minimal computational resources and time

Theory and ABINIT implementation:
M. Royo and M. Stengel, Phys. Rev. X **9**, 021050 (2019)