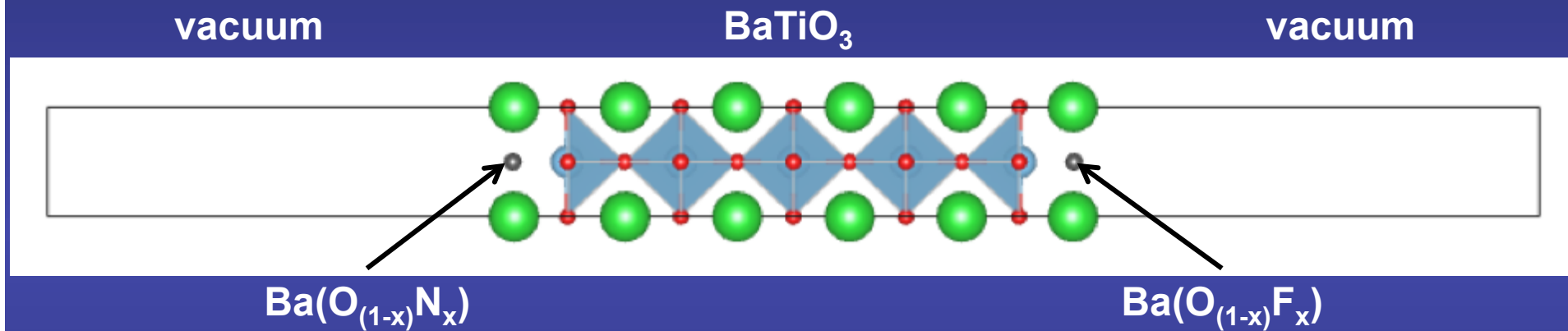


# Simulations of a ferroelectric slab under constrained electric displacement



Javier Junquera

# Most important reference followed in this lecture

## ARTICLES

PUBLISHED ONLINE: 1 FEBRUARY 2009 | DOI: 10.1038/NPHYS1185

nature  
physics

## Electric displacement as the fundamental variable in electronic-structure calculations

Massimiliano Stengel<sup>1\*</sup>, Nicola A. Spaldin<sup>1</sup> and David Vanderbilt<sup>2</sup>

Nature Physics 5, 304 (2009)

PHYSICAL REVIEW B 83, 235112 (2011)



## Band alignment at metal/ferroelectric interfaces: Insights and artifacts from first principles

Massimiliano Stengel,<sup>1</sup> Pablo Aguado-Puente,<sup>2</sup> Nicola A. Spaldin,<sup>3</sup> and Javier Junquera<sup>2</sup>

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(Received 2 March 2011; published 7 June 2011)

Section III C

# Macroscopic Maxwell equations in materials

From basic electrostatic, the macroscopic Maxwell equation in materials

$$\nabla \cdot \vec{D}(\vec{r}) = \rho_{\text{ext}}(\vec{r})$$

Encompasses all bound-charged effects  
*that can be referred to the properties of  
periodically repeated primitive bulk unit*

Contains all the rest:

- Delta-doping layers
- Metallic free charges
- Charged adsorbates
- Variations in local stoichiometry
- ...

If we assume that the interface is oriented along the  $z$  axis,  
and each material is periodic in the plane parallel to the interface  $(x, y)$

$$\frac{dD(z)}{dz} = \rho_{\text{ext}}(z)$$

# Relation between the normal component of the displacement field at the interface of different media

We start from the Maxwell equation in macroscopic media

SI units

$$\nabla \cdot \vec{D}(\vec{r}) = \rho_{\text{ext}}(\vec{r})$$

Let  $V$  be a finite volume in space,  $S$  the closed surface bounding it,  $da$  an element of area on the surface, and  $\vec{n}$  a unit normal to the surface at  $da$  pointing outward from the enclosed volume

Integrating the Maxwell equation over the volume

$$\int_V \nabla \cdot \vec{D}(\vec{r}) d\vec{r} = \int_V \rho_{\text{ext}}(\vec{r}) d\vec{r}$$

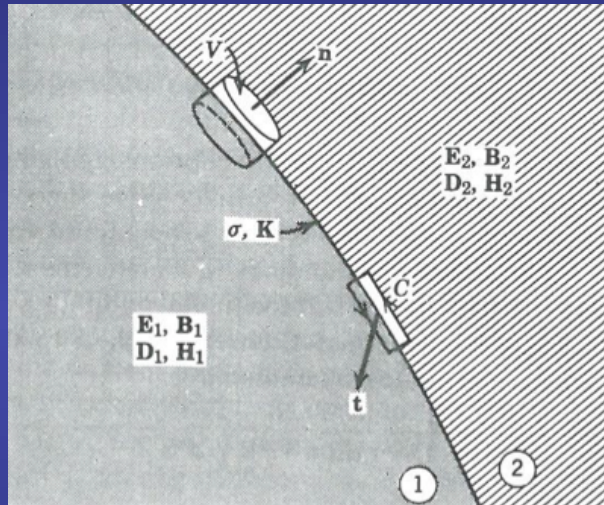
Then, we apply the divergence theorem

$$\int_V \nabla \cdot \vec{D}(\vec{r}) d\vec{r} = \oint_S \vec{D} \cdot \vec{n} da$$

$$\oint_S \vec{D} \cdot \vec{n} da = \int_V \rho_{\text{ext}}(\vec{r}) d\vec{r}$$

# Relation between the normal component of the displacement field at the interface of different media

An infinitesimal Gaussian pillbox straddles the boundary surface between two media



J. D. Jackson  
Classical Electrodynamics, John Wiley and sons  
Second Edition

In the limit of a very shallow pillbox, the side surfaces do not contribute to the integral

If the top and bottom are parallel, tangent to the surface, and of area  $\Delta a$ , then

$$\oint_S \vec{D} \cdot \vec{n} da = (\vec{D}_2 - \vec{D}_1) \cdot \vec{n} \Delta a$$

If the charge density  $\rho_{\text{ext}}$  is singular at the interface so as to produce an idealized surface charge density  $\sigma_{\text{ext}}$

$$\int_V \rho_{\text{ext}}(\vec{r}) d\vec{r} = \sigma_{\text{ext}} \Delta a$$

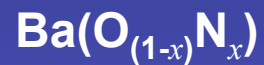
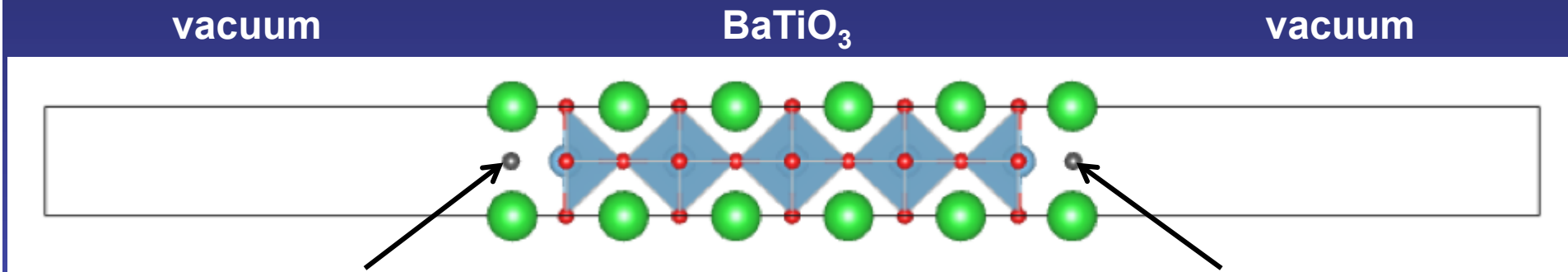
So the normal component of  $\vec{D}$  on either side of the boundary surface is related according to

$$(\vec{D}_2 - \vec{D}_1) \cdot \vec{n} = \sigma_{\text{ext}}$$

The discontinuity of the normal component of  $\vec{D}$  at any point is equal to the surface charge density at that point

# “Constrained- $\sigma$ ” method

Adopt a vacuum/insulator/vacuum geometry



Pseudos generated  
with the virtual  
crystal  
approximation



Replace the O by a fictitious  
atom of fractional atomic charge

Replace the O by a fictitious  
atom of fractional atomic charge

$$Z = 8 - x$$

$$Z = 8 + x$$

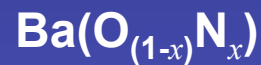
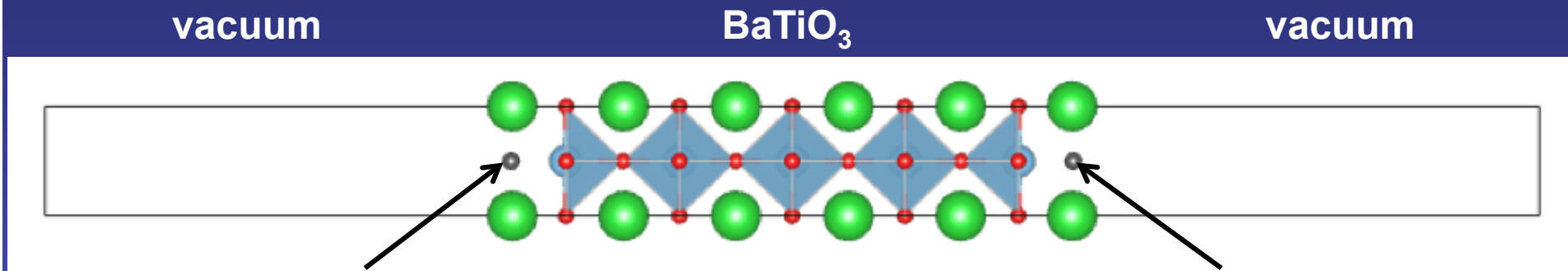
If  $x = 0 \Rightarrow$  the “fictitious atom” is oxygen at both surfaces

Nominal net charge at the left surface = 0

Nominal net charge at the right surface = 0

# “Constrained- $\sigma$ ” method

Adopt a vacuum/insulator/vacuum geometry



Replace the O by a fictitious atom of fractional atomic charge

$$Z = 8 - x$$

Pseudos generated with the virtual crystal approximation



Replace the O by a fictitious atom of fractional atomic charge

$$Z = 8 + x$$

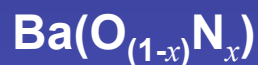
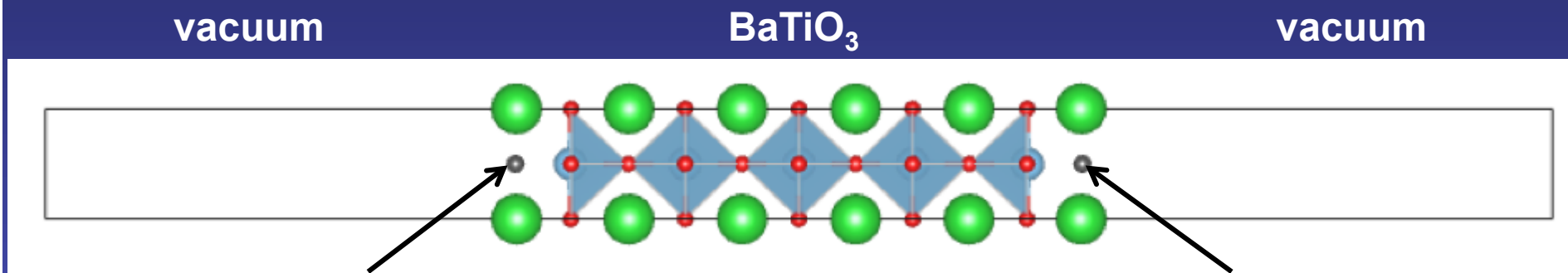
If  $x = 1 \Rightarrow$  the “fictitious atom” is Nitrogen at the left and Fluorine at the right surface

Nominal net charge at the left surface = -1

Nominal net charge at the right surface = +1

# “Constrained- $\sigma$ ” method

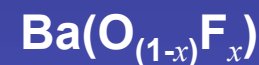
Adopt a vacuum/insulator/vacuum geometry



Replace the O by a fictitious atom of fractional atomic charge

$$Z = 8 - x$$

Pseudos generated with the virtual crystal approximation



Replace the O by a fictitious atom of fractional atomic charge

$$Z = 8 + x$$

For fractional values of  $x$ ,

Nominal charge of the “fictitious atom”:

$$-2 - x$$

Nominal net charge at the left surface

$$+2 - 2 - x = -x \quad \text{Negative}$$

Nominal charge of the “fictitious atom”:

$$-2 + x$$

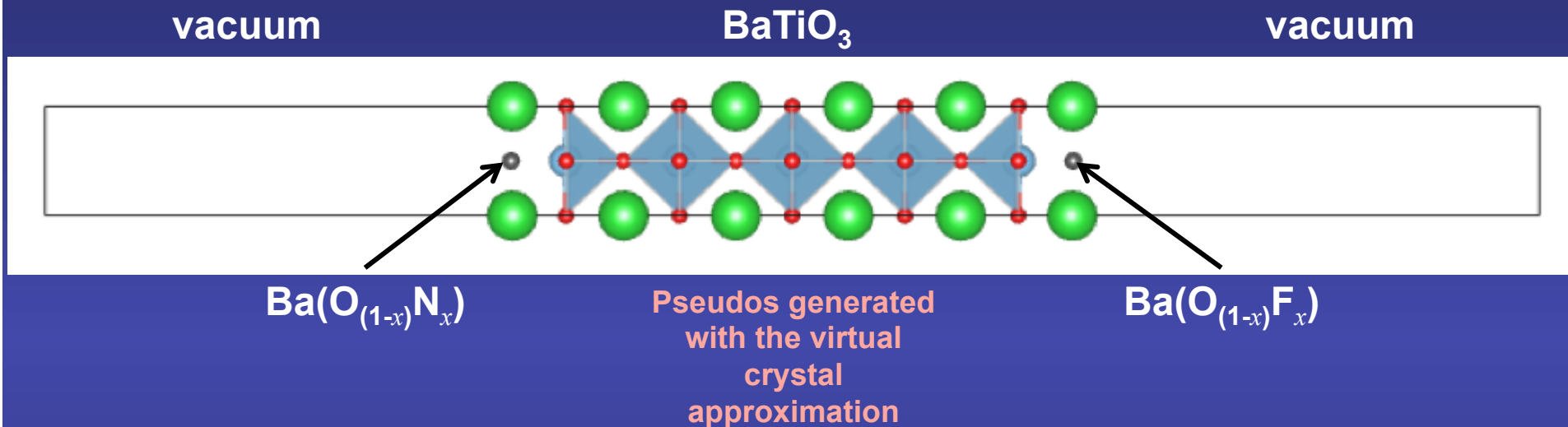
Nominal net charge at the right surface

$$+2 - 2 + x = +x \quad \text{Positive}$$



# “Constrained- $\sigma$ ” method

Adopt a vacuum/insulator/vacuum geometry



Therefore, the surface charge density at each termination amounts to

$$\sigma_{\text{ext}} = \frac{Q}{S} = -\frac{x}{S} \qquad \sigma_{\text{ext}} = \frac{Q}{S} = +\frac{x}{S}$$

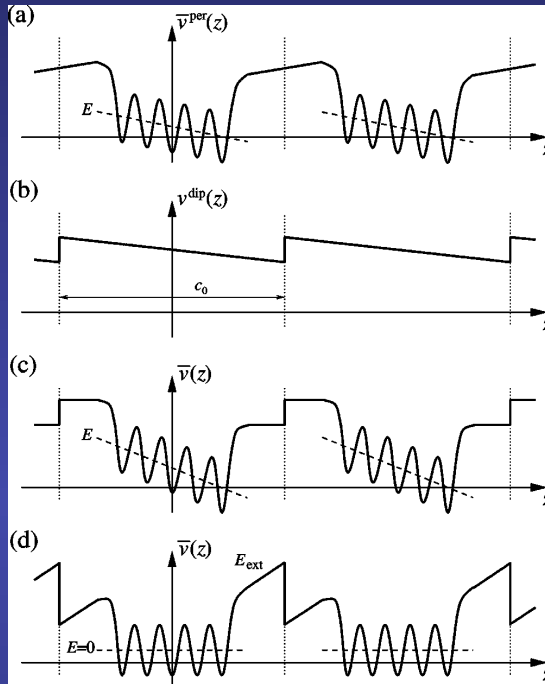
As we have seen previously  $\left(\vec{D}_2 - \vec{D}_1\right) \cdot \vec{n} = \sigma_{\text{ext}}$

If we particularize this for the left surface (1 = vacuum; 2 = BaTiO<sub>3</sub>)

$$D_2 - D_1 = \sigma_{\text{ext}} \Rightarrow D_{\text{BaTiO}_3} - D_{\text{vacuum}} = \frac{Q}{S} = -\frac{x}{S}$$

# The dipole correction in the vacuum region is required to ensure that $D = 0$ in the vacuum side

B. Meyer and D. Vanderbilt  
 Phys. Rev. B 63, 205426 (2001)



← That is what we are looking for.  
 Zero electric field in the vacuum region

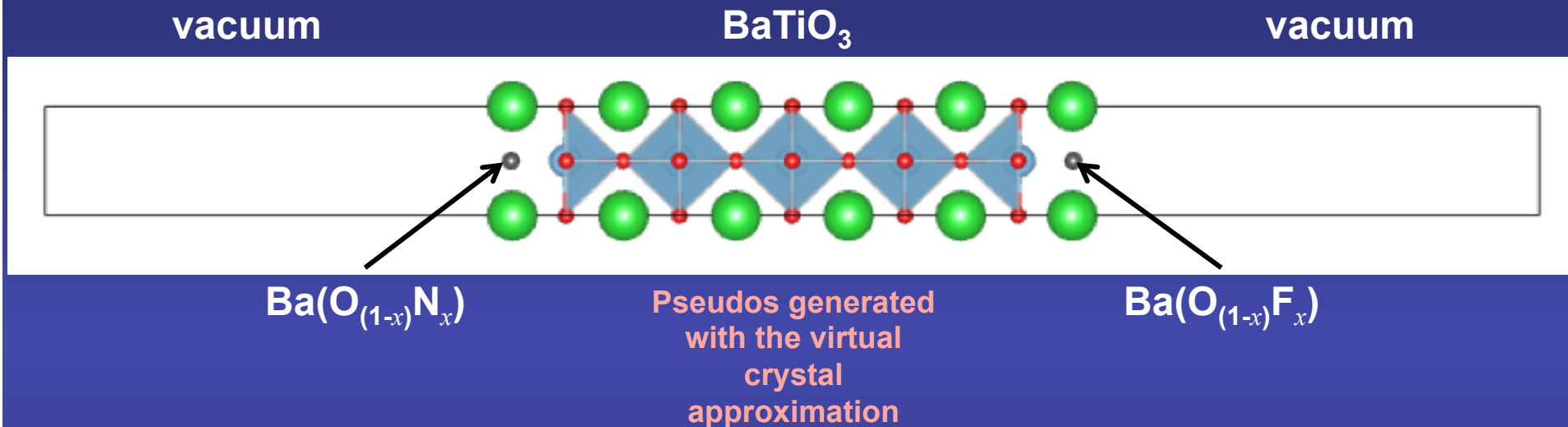
If there is no electric field in vacuum, then

$$D_{\text{vacuum}} = 0$$

```
#
# Variables to run a calculation at constant displacement field, D
#
SlabDipoleCorrection .true. # SIESTA calculates the electric field
                             # required to compensate the dipole of
                             # the system at every iteration of
                             # the self-consistent cycle.
                             # The potential added to the grid
                             # corresponds to that of a dipole layer
                             # at the middle of the vacuum layer.
                             # For slabs, this exactly compensates
                             # the electric field at the vacuum
                             # created by the dipole moment of
                             # the system.
```

# “Constrained- $\sigma$ ” method

Adopt a vacuum/insulator/vacuum geometry



Therefore, the surface charge density at each termination amounts to

$$\sigma_{\text{ext}} = \frac{Q}{S} = -\frac{x}{S}$$

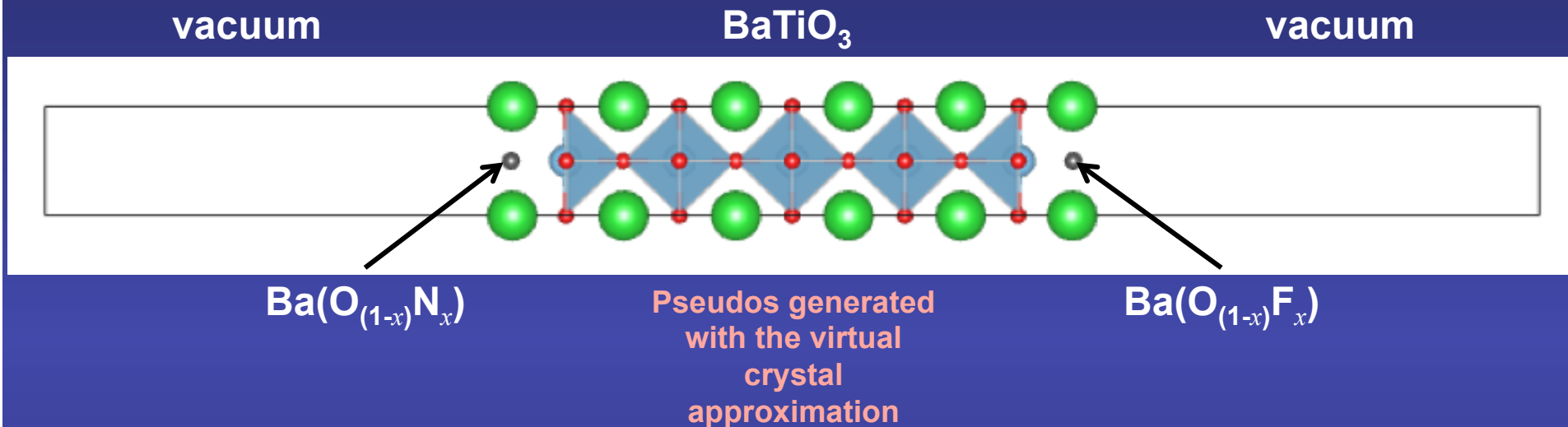
$$\sigma_{\text{ext}} = \frac{Q}{S} = +\frac{x}{S}$$

$$D_2 - D_1 = \sigma_{\text{ext}} \Rightarrow D_{\text{BaTiO}_3} - D_{\text{vacuum}} = \frac{Q}{S} = -\frac{x}{S}$$

$$\text{If } D_{\text{vacuum}} = 0 \Rightarrow D_{\text{BaTiO}_3} = \frac{Q}{S} = -\frac{x}{S}$$

# “Constrained- $\sigma$ ” method

Adopt a vacuum/insulator/vacuum geometry



$$D_{\text{BaTiO}_3} = \frac{Q}{S} = -\frac{x}{S}$$

We can monitor the value of the displacement field with an external parameter  $x$

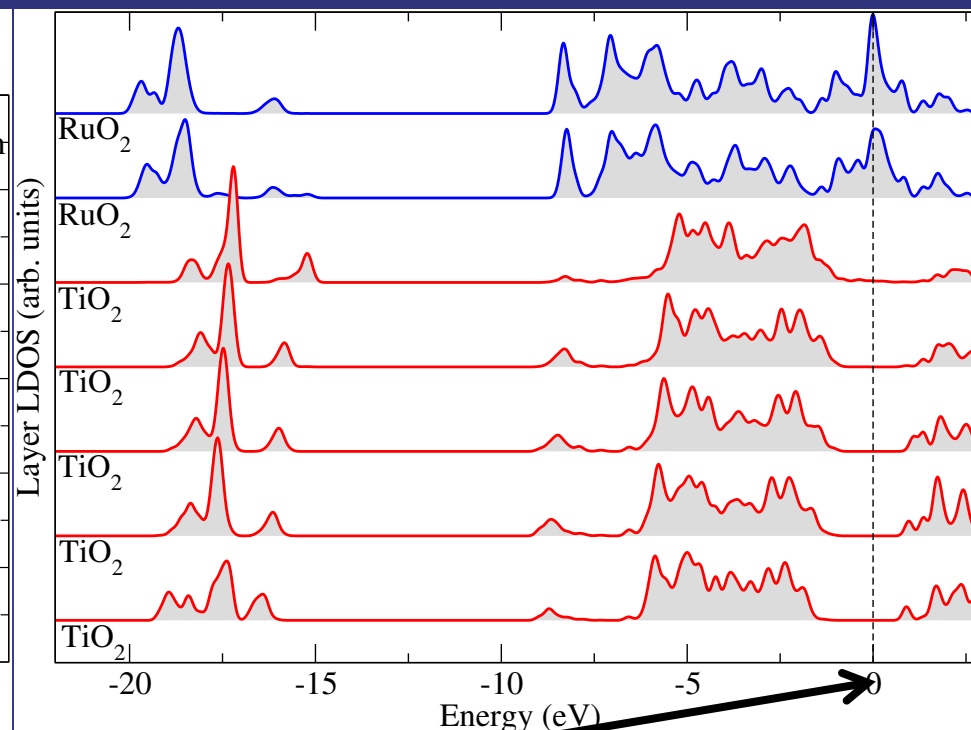
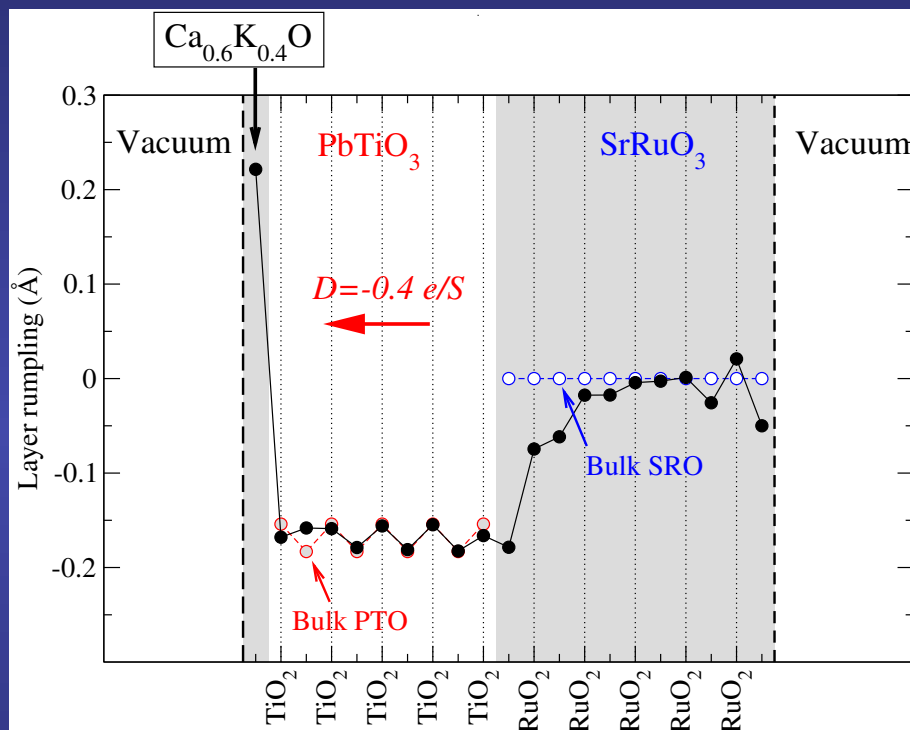
In many ferroelectric materials, we can assume that  $D \approx P$ , with errors of 1%

Largest electric field that can be applied without dielectric breakdown  $\mathcal{E} \sim 0.1 \text{ GV/m}$

$$\Rightarrow \epsilon_0 \mathcal{E} \sim 10^{-3} \text{ C/m}^2 \ll \text{typical polarizations} \sim 0.1 - 1.0 \text{ C/m}^2$$

# “Constrained- $\sigma$ ” method in capacitors

Adopt a vacuum/insulator/metal/vacuum geometry



Induce a layer of bound charges at its free surface  
(  $Q$  per surface unit cell  $S$  )

$$\sigma_{\text{ext}} = \frac{Q}{S}$$

$\Rightarrow$

$$D_2 = D_{\text{PbTiO}_3} = \frac{Q}{S}$$

If the surface region remains locally insulating

# Comparison of the “constrained- $\sigma$ ” method with the existing methods based on applied fields

## Useful alternative to the already existing “constrained- $D$ ” method

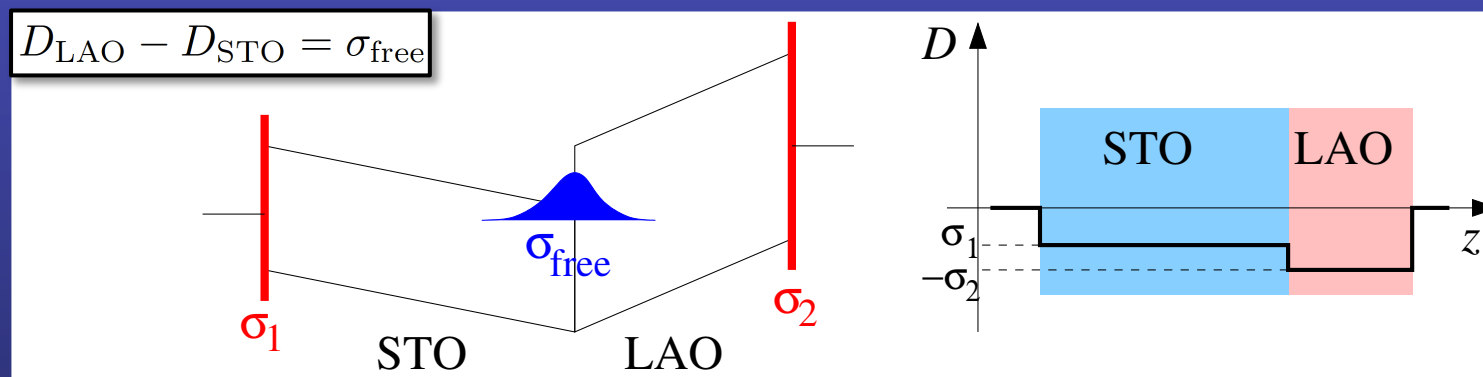
M. Stengel, N. A. Spaldin and D. Vanderbilt, Nature Physics 5, 304 (2009)

### Advantages:

No need for a specialized code

Practical for interfaces (esp. metal/insulator)

Can constrain  $D$  to two different values at the opposite boundaries of the slab



M. Stengel, Phys. Rev. Lett. 106, 136803 (2011)

### Disadvantages:

Cumbersome for bulk calculations

# How to apply the constrained- $\sigma$ method in SIESTA (easily transferable to any other code)

1. Generate pseudopotential and basis set for alchemical atoms
2. Check that the free surface remains locally insulating
3. Relax the structure and check (at least one time) how the displacement vector within the slab is the same as the one enforced by the external charge

# Generate pseudopotentials for alchemy atoms

Follow the instructions given in the lecture

How to generate a mixed pseudopotential.  
The Virtual Crystal Approximation in SIESTA

You can download it from:

[http://personales.unican.es/junqueraj/JavierJunquera\\_files/Metodos/Pseudos/Pseudos.html](http://personales.unican.es/junqueraj/JavierJunquera_files/Metodos/Pseudos/Pseudos.html)



# For each pseudoatom, a new species has to be defined

```
%block ChemicalSpeciesLabel
  1      56      Ba
  2      22      Ti
  3       8       O
  4     201  ON-0.95000
  5     202  OF-0.95000
%endblock ChemicalSpeciesLabel

%block SyntheticAtoms
4
  2  2  3  4
    2.000000  3.950000  0.000000  0.000000
5
  2  2  3  4
    2.000000  4.050000  0.000000  0.000000
%endblock SyntheticAtoms
```

Each pseudoatom has to be included as a new Chemical Specie.

The chemical specie number should start at 201 and then numbered consecutively

The name of the chemical specie of the pseudoatom should be that provided by the VCA util

Then, a new block is required for the pseudoatoms. It should contain the information contained in the name.synth file provided by the VCS util.

Remember to change the integer in the first line to point to the right specie in the ChemicalSpeciesLabel block

# Basis set for the pseudoatoms

```
ON-0.95000      3      -0.28
n=2      0      2      E      40.58      3.95
  4.95272270428712      3.60331408800389
  1.000000000000000      1.000000000000000
n=2      1      2      E      36.78      4.35
  4.99990228025066      3.89745395068600
  1.000000000000000      1.000000000000000
n=3      2      1      E      21.69      0.93
  2.73276990670788
  1.000000000000000
OF-0.95000      3      -0.28
n=2      0      2      E      40.58      3.95
  4.95272270428712      3.60331408800389
  1.000000000000000      1.000000000000000
n=2      1      2      E      36.78      4.35
  4.99990228025066      3.89745395068600
  1.000000000000000      1.000000000000000
n=3      2      1      E      21.69      0.93
  2.73276990670788
  1.000000000000000
```

Since the pseudoatoms are close to O, we chose as the basis set for the pseudoatoms the same basis as for O.

The blocks have to be included in the PAO.Basis block, but changing the line to point to the corresponding chemical specie

# The additional charge density is introduced by replacing oxygens at the surface by fictitious atoms

Oxygen atoms at surfaces  
are replaced by

An atom of fractional charge 5.95

This layer will have a formal  
charge of -0.05

This layer will have a formal  
charge of +0.05

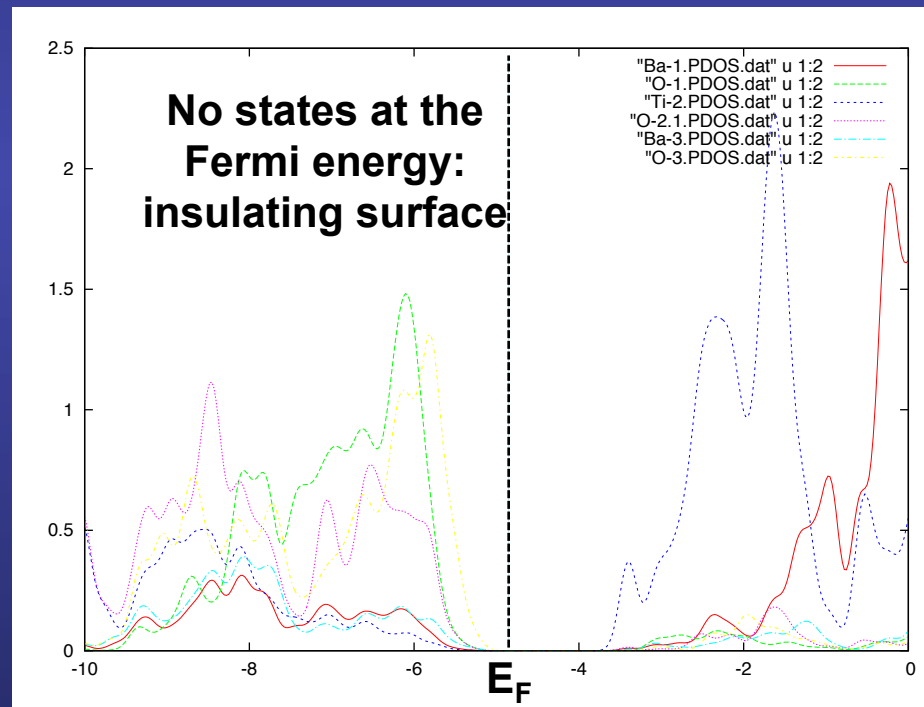
An atom of fractional charge 6.05

```
%block AtomicCoordinatesAndAtomicSpecies
 0.000000000 0.000000000 31.263511472 1
 3.660400960 3.660400960 31.183163575 4
 3.660400960 3.660400960 34.823972352 2
 3.660400960 0.000000000 34.861985781 3
 0.000000000 3.660400960 34.861985781 3
 0.000000000 0.000000000 38.716237575 1
 3.660400960 3.660400960 38.692193436 3
 3.660400960 3.660400960 42.455760764 2
 3.660400960 0.000000000 42.457692504 3
 0.000000000 3.660400960 42.457692504 3
 0.000000000 0.000000000 46.234251560 1
 3.660400960 3.660400960 46.233589773 3
 3.660400960 3.660400960 50.000000000 2
 3.660400960 0.000000000 50.000000000 3
 0.000000000 3.660400960 50.000000000 3
 0.000000000 0.000000000 53.765748440 1
 3.660400960 3.660400960 53.766410227 3
 3.660400960 3.660400960 57.544239236 2
 3.660400960 0.000000000 57.542307496 3
 0.000000000 3.660400960 57.542307496 3
 0.000000000 0.000000000 61.283762425 1
 3.660400960 3.660400960 61.307806564 3
 3.660400960 3.660400960 65.176027648 2
 3.660400960 0.000000000 65.138014219 3
 0.000000000 3.660400960 65.138014219 3
 0.000000000 0.000000000 68.736488528 1
 3.660400960 3.660400960 68.816836425 5
%endblock AtomicCoordinatesAndAtomicSpecies
```

# Check that the free surface remains locally insulating

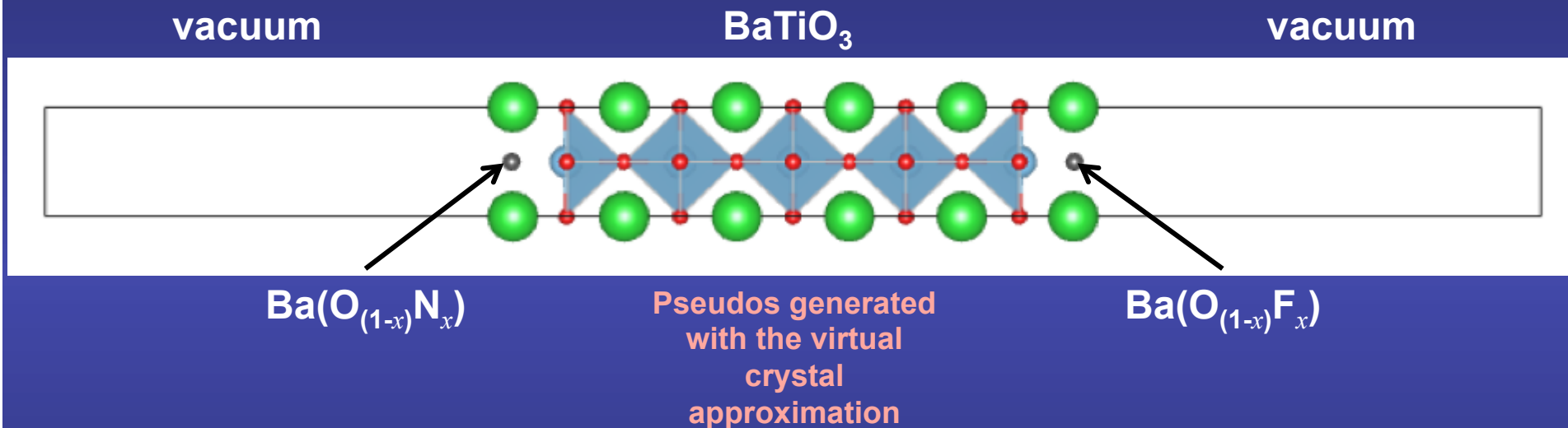
See below the lecture

How to compute the projected density of states (PDOS)



Check that the displacement vector within the slab is the same as the one enforced by the external charge

$$D = \epsilon_0 \mathcal{E} + P$$



$$\text{If } D_{\text{vacuum}} = 0 \Rightarrow D_{\text{BaTiO}_3} = \frac{Q}{S} = -\frac{x}{S}$$

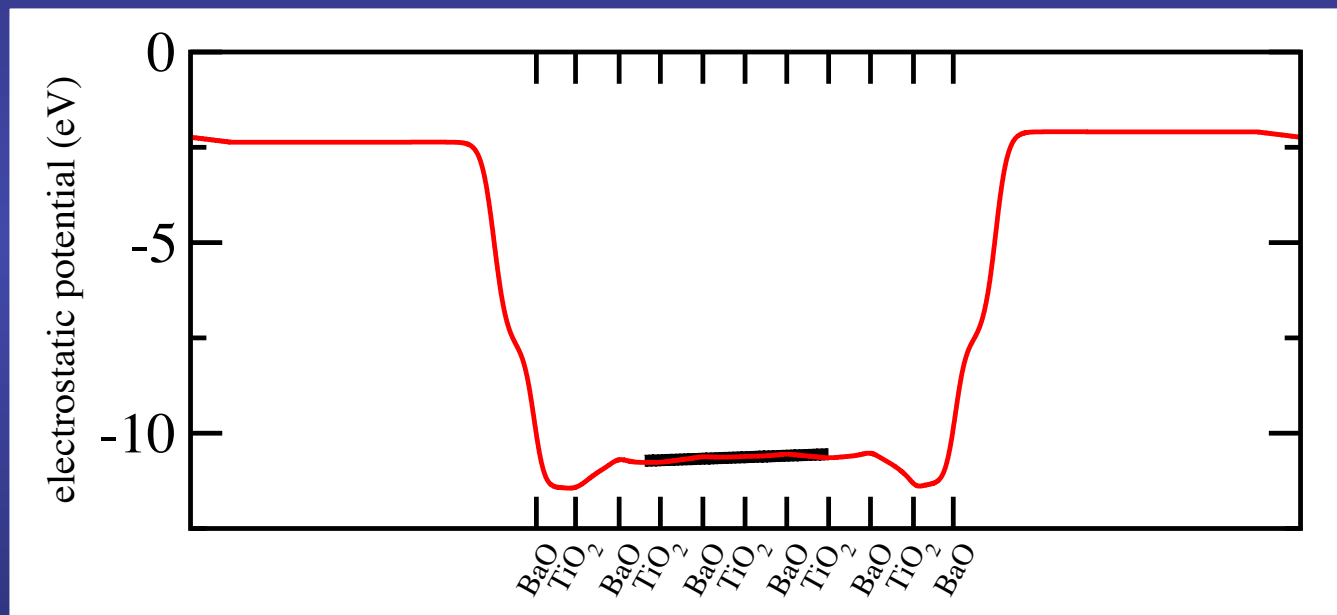
In our example,  $x = 0.05$ , and the in-plane lattice constant is the theoretical one of an hypothetical SrTiO<sub>3</sub> substrate ( $a = 3.874 \text{ \AA}$ )

$$D_{\text{BaTiO}_3} = -\frac{0.05 \text{ electrons}}{(3.874 \text{ \AA})^2} \times \left(\frac{10^{10} \text{ \AA}}{1 \text{ m}}\right)^2 \times \frac{1 \text{ C}}{6.2415 \times 10^{18} \text{ electrons}} = -5.338 \times 10^{-2} \frac{\text{C}}{\text{m}^2}$$

Check that the displacement vector within the slab is the same as the one enforced by the external charge

$$D = \epsilon_0 \mathcal{E} + P$$

We compute the macroscopic internal electric field within BaTiO<sub>3</sub> slab  
(see the tutorial “how to compute the internal electric field” below)



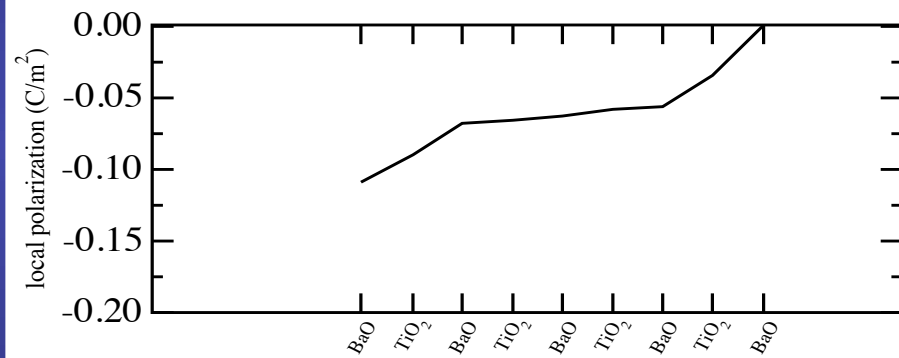
$$\epsilon_{\text{BaTiO}_3} = 0.0104 \frac{\frac{\text{eV}}{e}}{\text{Bohr}} \times \frac{1 \text{ Bohr}}{0.529177 \text{ \AA}} \times \frac{1 \text{ \AA}}{10^{-10} \text{ m}} = 1.974 \times 10^8 \frac{\text{V}}{\text{m}}$$

$$\epsilon_0 \epsilon_{\text{BaTiO}_3} = 8.854 \times 10^{-12} \frac{\text{F}}{\text{m}} \times 1.974 \times 10^8 \frac{\text{V}}{\text{m}} = 1.747 \times 10^{-3} \frac{\text{C}}{\text{m}^2}$$

Check that the displacement vector within the slab is the same as the one enforced by the external charge

$$D = \epsilon_0 \mathcal{E} + P$$

We compute the local polarization within BaTiO<sub>3</sub> slab  
(see the tutorial “how to compute the local polarization” below)



#	z (Ang)	Px (C/m <sup>2</sup> )	Py (C/m <sup>2</sup> )	Pz (C/m <sup>2</sup> )
18	18.376660873	-0.000000001	-0.000000001	-0.105472570
20	20.457428928	-0.000000001	-0.000000001	-0.088640898
22	22.418271761	-0.000000001	-0.000000001	-0.066930676
24	24.445287373	-0.000000001	-0.000000001	-0.064462693
26	26.424394483	-0.000000001	-0.000000001	-0.062514460
28	28.440715634	-0.000000001	-0.000000001	-0.058916991
30	30.432055406	-0.000000001	-0.000000001	-0.057296090
32	32.424608718	-0.000000001	-0.000000001	-0.035671478
34	34.469210930	-0.000000001	-0.000000001	-0.000880223

In SIESTA,  $\frac{\chi_{\text{tot}}}{\chi_{\text{ion}}} = 0.859$

$$\tilde{P}_j^Z = \left(1 + \frac{\chi_{\infty}}{\chi_{\text{ion}}}\right) P_j^Z = \frac{\chi_{\text{tot}}}{\chi_{\text{ion}}} P_j^Z$$

Taking a value around the center of the slab

$$P_j^Z \approx -0.064 \frac{\text{C}}{\text{m}^2} \Rightarrow \tilde{P}_j^Z \approx -5.498 \times 10^{-2} \frac{\text{C}}{\text{m}^2}$$

**Check that the displacement vector within the slab is the same as the one enforced by the external charge**

$$D = \varepsilon_0 \mathcal{E} + P$$

**Compare the value enforced by the external charge**

$$D_{\text{BaTiO}_3} = -\frac{0.05 \text{ electrons}}{(3.874 \text{ \AA})^2} \times \left(\frac{10^{10} \text{ \AA}}{1 \text{ m}}\right)^2 \times \frac{1 \text{ C}}{6.2415 \times 10^{18} \text{ electrons}} = -5.338 \times 10^{-2} \frac{\text{C}}{\text{m}^2}$$

**With the value obtained from the macroscopic field and the local polarization**

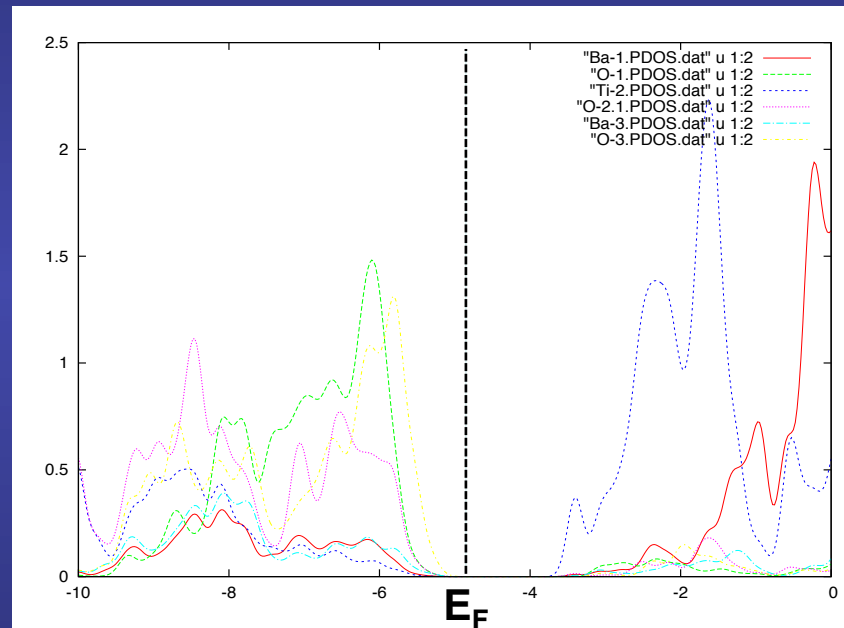
$$\varepsilon_0 \mathcal{E}_{\text{BaTiO}_3} = 8.854 \times 10^{-12} \frac{\text{F}}{\text{m}} \times 1.974 \times 10^8 \frac{\text{V}}{\text{m}} = 1.747 \times 10^{-3} \frac{\text{C}}{\text{m}^2}$$

$$P_j^Z \approx -0.064 \frac{\text{C}}{\text{m}^2} \Rightarrow \tilde{P}_j^Z \approx -5.498 \times 10^{-2} \frac{\text{C}}{\text{m}^2}$$

$$D_{\text{BaTiO}_3} = \varepsilon_0 \mathcal{E}_{\text{BaTiO}_3} + \tilde{P}_{\text{BaTiO}_3}^Z \approx 1.747 \times 10^{-3} \frac{\text{C}}{\text{m}^2} - 5.498 \times 10^{-2} \frac{\text{C}}{\text{m}^2} = -5.332 \times 10^{-2} \frac{\text{C}}{\text{m}^2}$$



# How to compute the projected density of states (PDOS)



Javier Junquera

**To check that the interface is insulating,  
compute the layer by layer projected density of states**

```
%block ProjectedDensityOfStates
  -70.00  5.00  0.150 3000  eV
%endblock ProjectedDensityOfStates

%PDOS.kgrid_Monkhorst_Pack
  60  0  0  0.5
   0 60  0  0.5
   0  0  2  0.5
%end PDOS.kgrid_Monkhorst_Pack
```

**A separate set of k-points, usually on a finer grid  
than the one used to achieve self-consistency.  
Same format as the Monkhorst-Pack grid.**

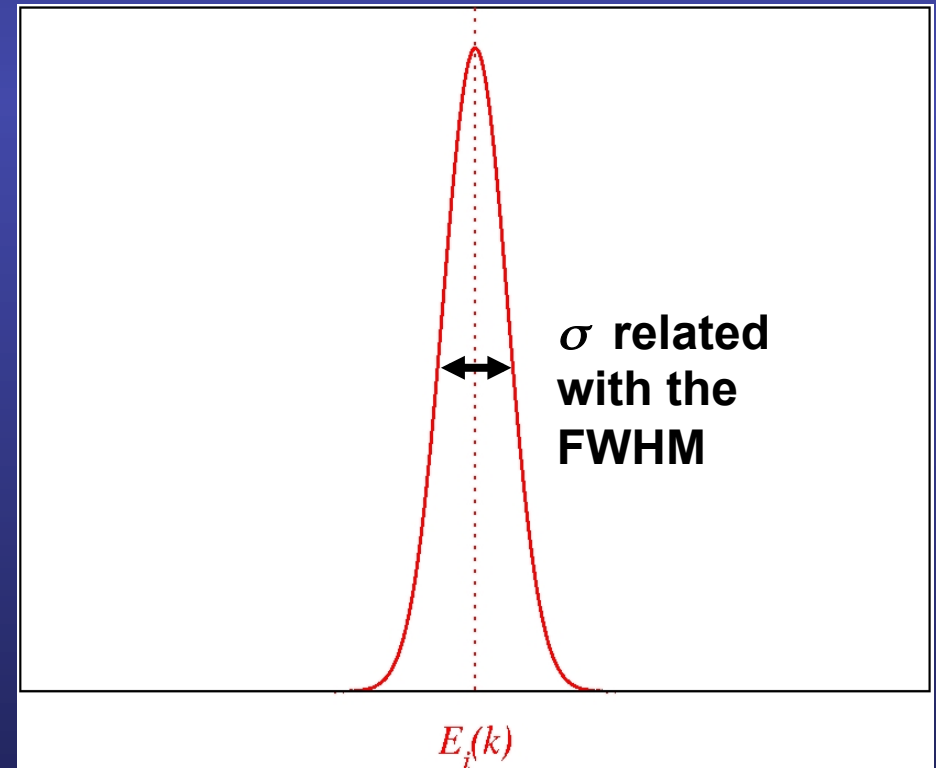
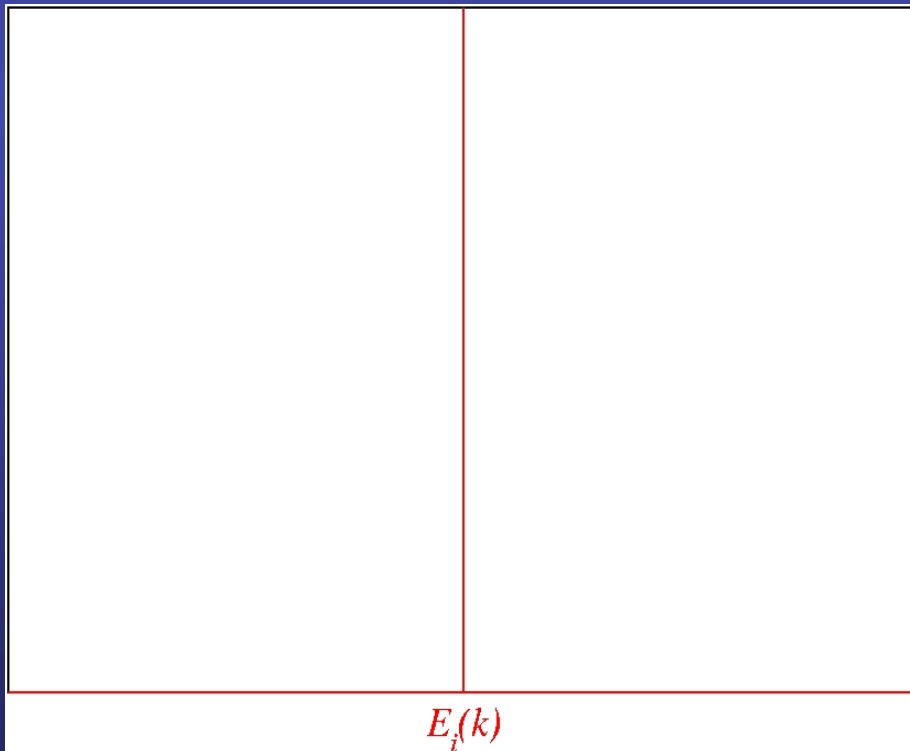
# How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates  
-70.0 5.0 0.150 3000 eV  
%endblock ProjectedDensityOfStates
```

**-70.0 5.0** : Energy window where the DOS and PDOS will be computed  
(relative to the program's zero, i.e. the same as the  
eigenvalues printed by the program)

# The eigenvalues are broadening by a gaussian to smooth the shape of the DOS and PDOS

$$\delta \left( E - E_i(\vec{k}) \right) \rightarrow \frac{1}{\sigma \sqrt{\pi}} e^{-\frac{(E - E_i(\vec{k}))^2}{\sigma^2}}$$



# How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates  
-70.0 5.0 0.150 3000 eV  
%endblock ProjectedDensityOfStates
```

**-70.0 5.0** : Energy window where the DOS and PDOS will be computed  
(relative to the program's zero, i.e. the same as the  
eigenvalues printed by the program)

**0.150** : Peak width of the gaussian used to broad the eigenvalues (energy)

**It should be twice as large as the fictitious electronic  
temperature used during self-consistency**

(see Appendix B of M. Stengel et al. Phys. Rev. B 83, 235112 (2011))

# How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates  
-70.0 5.0 0.150 3000 eV  
%endblock ProjectedDensityOfStates
```

**-70.0 5.0** : Energy window where the DOS and PDOS will be computed  
(relative to the program's zero, i.e. the same as the  
eigenvalues printed by the program)

**0.150** : Peak width of the gaussian used to broad the eigenvalues (energy)

**It should be twice as large as the fictitious electronic  
temperature used during self-consistency**

(see Appendix B of M. Stengel et al. Phys. Rev. B 83, 235112 (2011))

**3000** : Number of points in the histogram

# How to compute the DOS and PDOS

```
%block ProjectedDensityOfStates  
-70.0 5.0 0.150 3000 eV  
%endblock ProjectedDensityOfStates
```

**-70.0 5.0** : Energy window where the DOS and PDOS will be computed  
(relative to the program's zero, i.e. the same as the  
eigenvalues printed by the program)

**0.150** : Peak width of the gaussian used to broad the eigenvalues (energy)

**It should be twice as large as the fictitious electronic  
temperature used during self-consistency**

(see Appendix B of M. Stengel et al. Phys. Rev. B 83, 235112 (2011))

**3000** : Number of points in the histogram

**eV** : Units in which the previous energies are introduced

# Output for the Density Of States

SystemLabel.DOS

## Format

Energy (eV)      DOS Spin Up (eV<sup>-1</sup>)      DOS Spin Down (eV<sup>-1</sup>)

-69.99993	0.00000	0.00000
-69.97492	0.00000	0.00000
-69.94991	0.00000	0.00000
.	.	.
.	.	.
.	.	.



# Output for the Projected Density Of States

SystemLabel.PDOS

Written in XML

```
<pdos>
<nspin>1</nspin>
<norbitals> 387</norbitals>
<energy_values units="eV">
  -69.99993
  -69.97492
  -69.94991
  .
  .
  .
</energy_values>
<orbital
  index="          1"
  atom_index="          1"
  species="Ba"
  position=" 0.000000  0.000000  31.156083"
  n="          5"
  l="          0"
  m="          0"
  z="          1"
>
<data>
  0.00000
  0.00000
  0.00000
  .
  .
  .
</data>
</orbital>
</pdos>
```

Energy Window

One element `<orbital>` for every atomic orbital in the basis set

# How to digest the SystemLabel.PDOS file

## fmpdos (by Andrei Postnikov)

Go to the directory Util/Contrib/Apostnikov, or download from

<http://www.home.uni-osnabrueck.de/apostnik/download.html>

Compile the code (in the Util directory, simply type \$ make)

Execute fmpdos and follow the instructions at run-time

```
$ <your_siesta_directory_path>/Util/Contrib/Apostnikov/fmpdos
  Input file name (PDOS):
Surface.PDOS
  Output file name :
Ba-1.PDOS.dat
  Extract data for atom index (enter atom NUMBER, or 0 to select all),
  or for all atoms of given species (enter its chemical LABEL):
1
  Extract data for n= ... (0 for all n ):
0
```

**Repeat this for all the atoms you might be interested in, specially those at the surface layers**

# How to digest the SystemLabel.PDOS file

## Plot the layer by layer Projected Density of States

```
$ gnuplot
```

```
G N U P L O T
```

```
Version 4.2 patchlevel 5
```

```
last modified Mar 2009
```

```
System: Darwin 11.4.2
```

```
Copyright (C) 1986 - 1993, 1998, 2004, 2007 - 2009
```

```
Thomas Williams, Colin Kelley and many others
```

```
Type 'help' to access the on-line reference manual.
```

```
The gnuplot FAQ is available from http://www.gnuplot.info/faq/
```

```
Send bug reports and suggestions to <http://sourceforge.net/projects/gnuplot>
```

```
Terminal type set to 'aqua'
```

```
gnuplot> plot "Ba-1.PDOS.dat" u 1:2 w l, "O-1.PDOS.dat" u 1:2 w l,
```

```
"Ti-2.PDOS.dat" u 1:2 w l, "O-2.1.PDOS.dat" u 1:2 w l,
```

```
"Ba-3.PDOS.dat" u 1:2 w l, "O-3.PDOS.dat" u 1:2 w l
```

```
gnuplot> set xrange [-10:0]
```

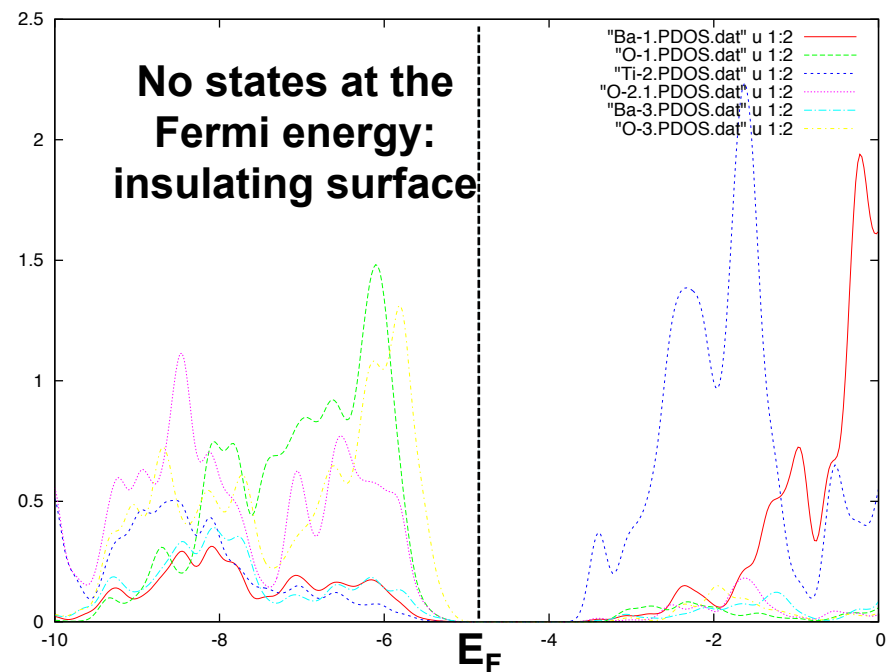
```
gnuplot> replot
```

Plot an interval of energies around the Fermi energy, that can be found in the following lines of the output file

```
scf: iscf   Eharris(eV)   E_KS(eV)   FreeEng(eV)   dDmax   Ef(eV)
scf:   1   -19120.0592   -19120.0592 -19120.0592   0.00001 -4.7719
```

For the bottom interface  
(repeat the same for the top interface)

Plot the PDOS for the atoms of  
the three first layers starting  
from the bottom



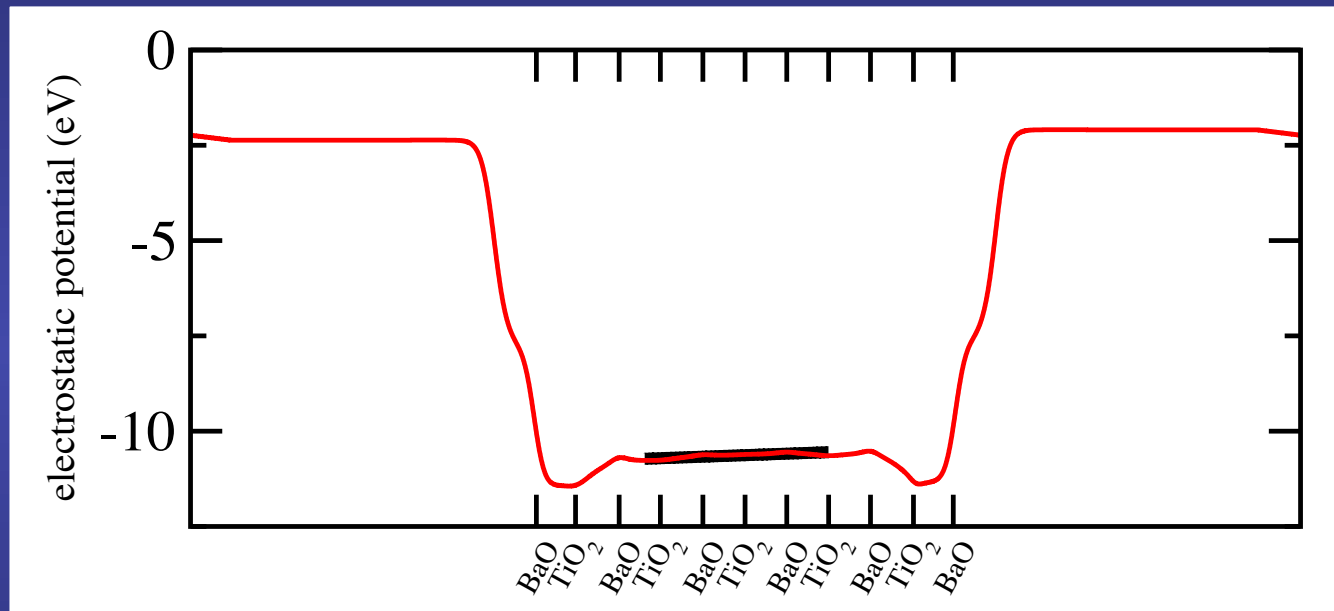
# Normalization of the DOS and PDOS

$$\int_{-\infty}^{+\infty} g(E) dE = \text{Number of bands per k-point} = \text{Number of atomic orbitals in the unit cell}$$

$$\int_{-\infty}^{+\infty} g(E) n(E) dE = \text{Number of electrons in the unit cell}$$

↑  
Occupation factor at energy  $E$

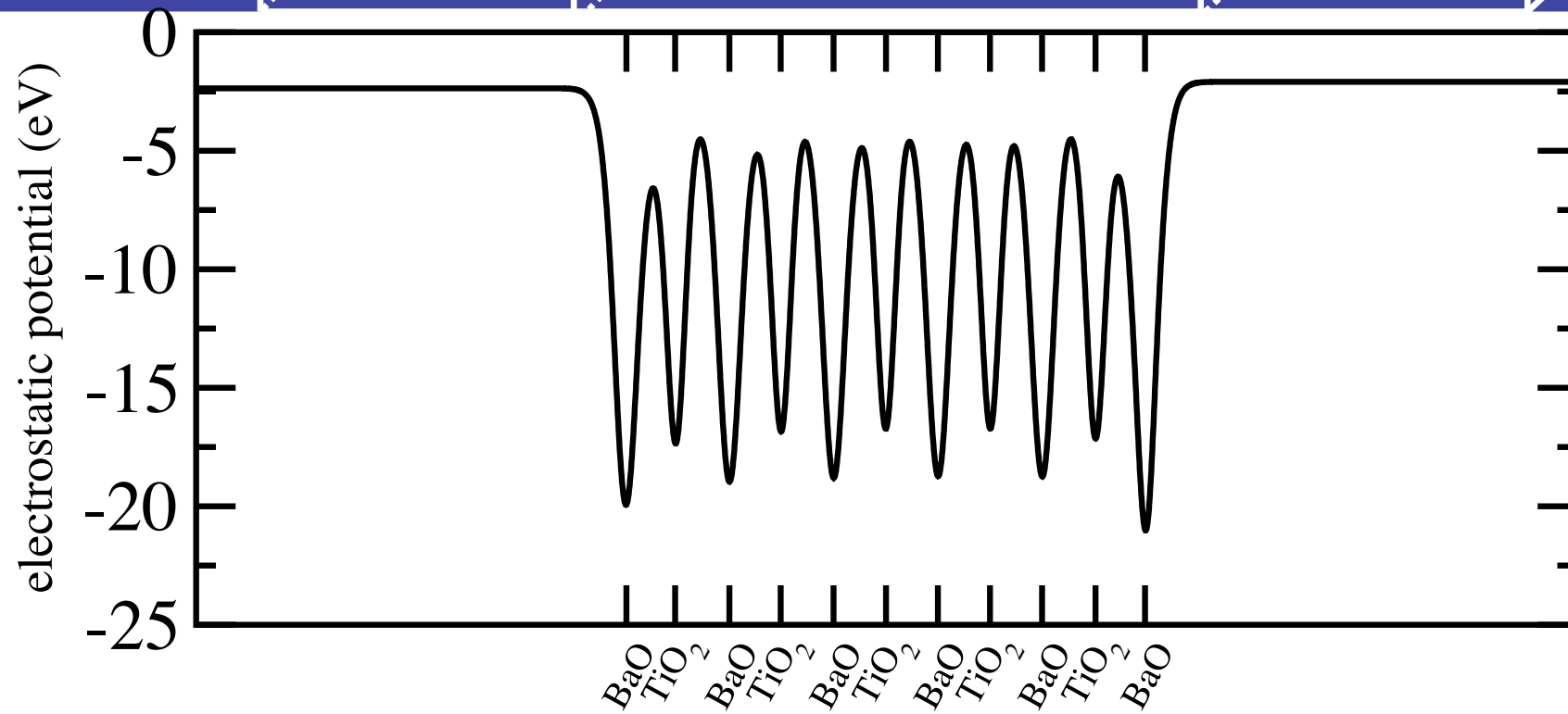
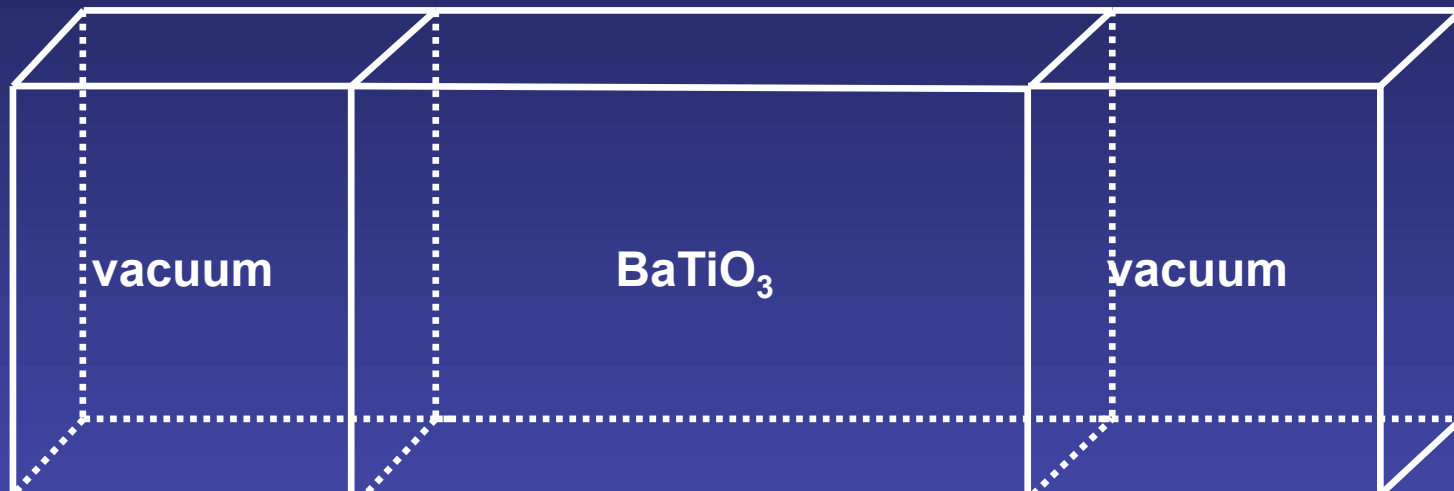
# How to compute the macroscopic electric field within the slab



Javier Junquera

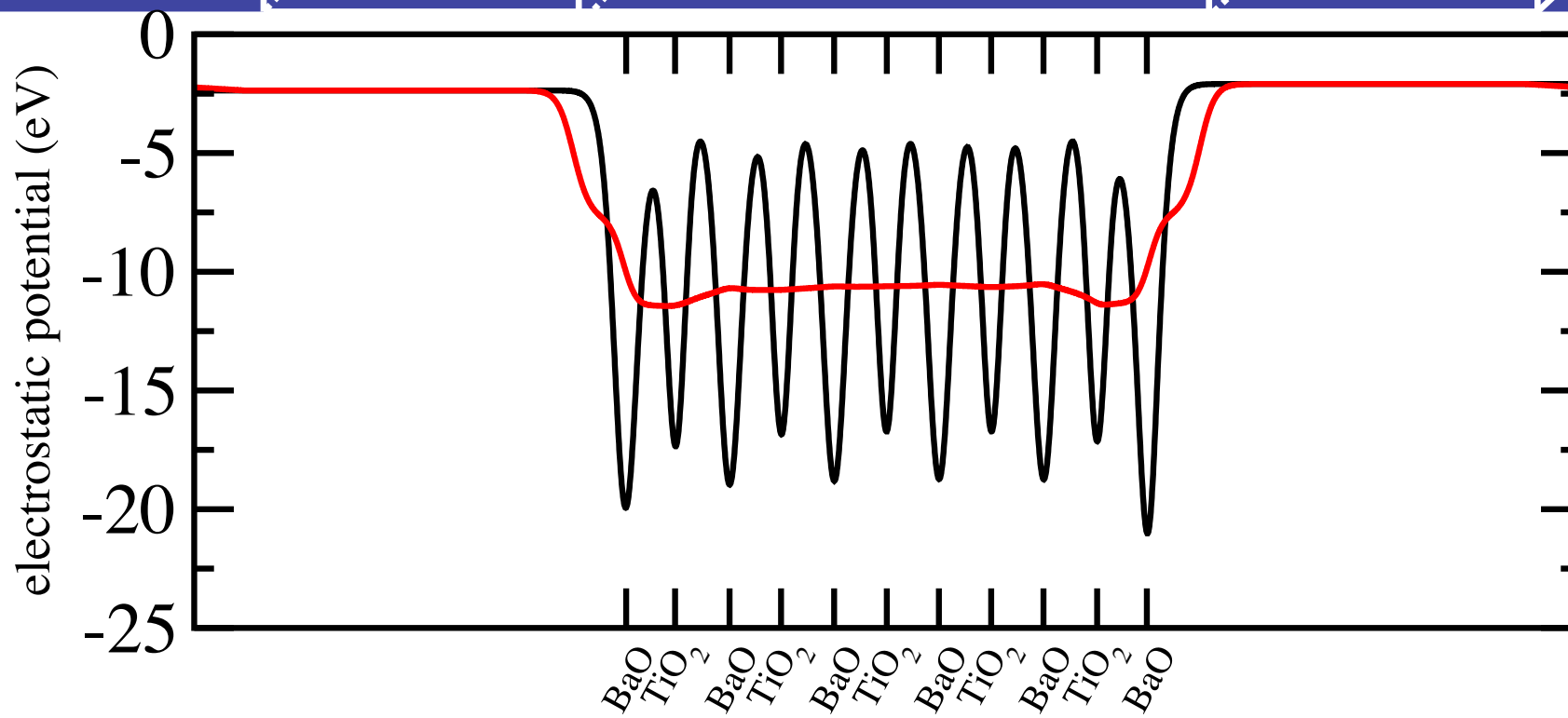
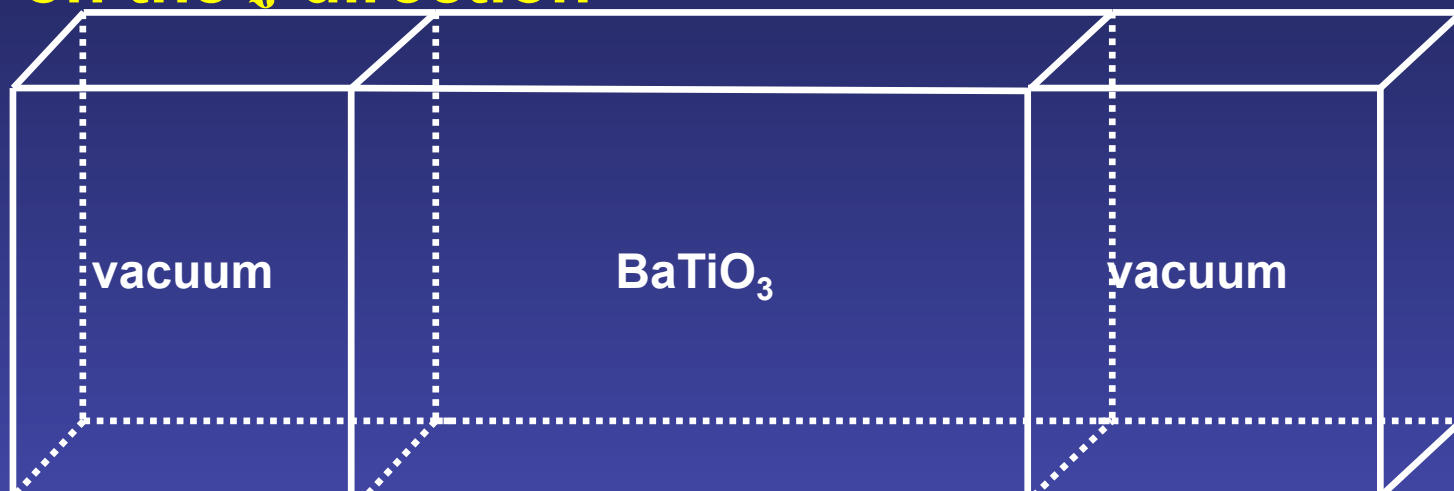
# First step: average in the plane

$$\bar{V}(z) = \frac{1}{S} \int_S dx dy V(\vec{r})$$



Second step: nanosmooth the planar  
average on the  $z$ -direction

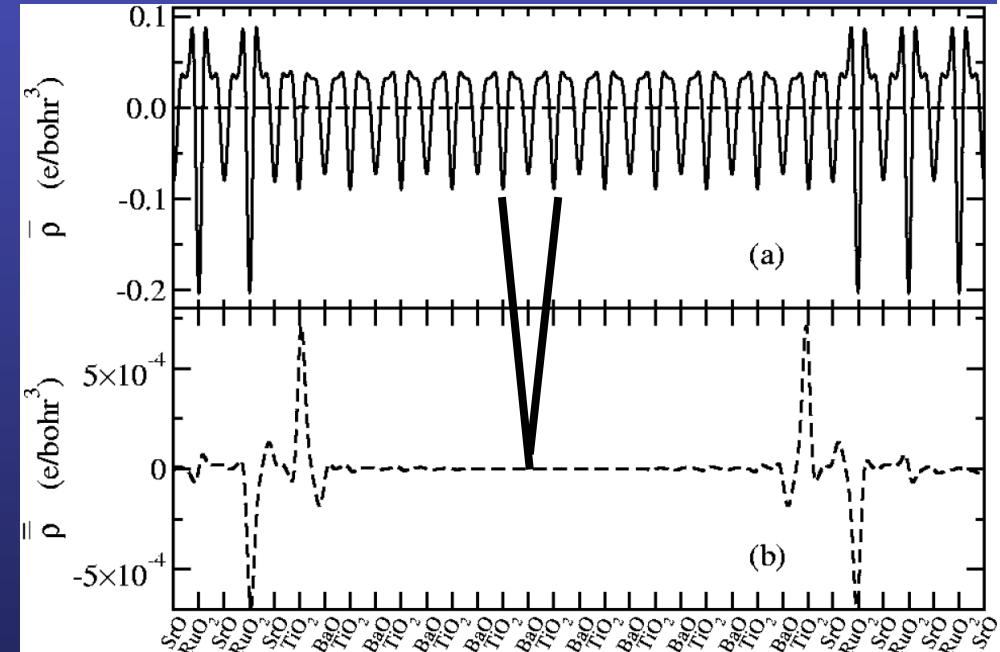
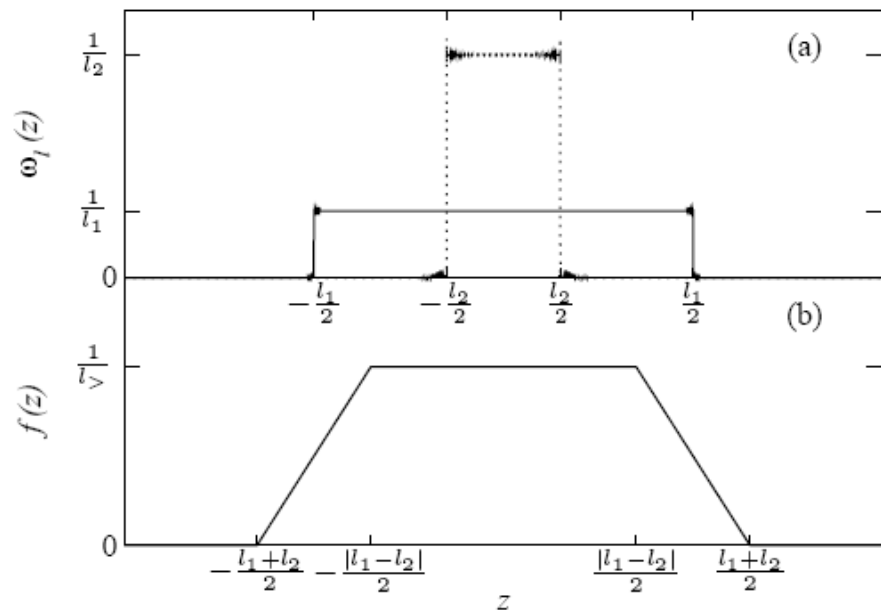
$$\bar{V}(z) = \int dz' f(z - z') \bar{V}(z')$$



Atomic scale fluctuations are washed out by filtering the magnitudes via convolution with smooth functions

$$\bar{\rho}(z) = \int dz' f(z - z') \bar{\rho}(z')$$

$$f(z - z') = \int dz'' \omega_{l_1}(z - z'') \omega_{l_2}(z'' - z')$$





## How to compile MACROAVE...

```
$ cd ~/siesta/Util/Macroave/Src/  
$ make  
ifort -c -O3 defs_basis.f90  
ifort -c -O3 defs_common.f90  
ifort -c -O3 io.f  
ifort -c -O3 iorho.f  
ifort -c -O3 paste.f  
ifort -c -O3 macroave.f  
ifort -c -O3 thetaft.f  
ifort -c -O3 surpla.f  
ifort -c -O3 volcel.f  
ifort -c -O3 recipes.f  
ifort -c -O3 hdr_io.f90  
ifort -o macroave.x \  
    defs_basis.o defs_common.o io.o iorho.o paste.o macroave.o thetaft.o  
    surpla.o volcel.o recipes.o hdr_io.o
```

Automaticallu uses the **same arch.make** file as for the compilation  
of **SIESTA**

**...and where to find the User's Guide and some Examples**

```
$ cd ~/siesta/Util/Macroave  
$ ls  
Docs  Examples  Src
```

# How to run MACROAVE

## SIESTA

```
SaveRho .true.  
SaveTotalCharge .true.  
SavelonicCharge .true.  
SaveDeltaRho .true.  
SaveElectrostaticPotential .true.  
SaveTotalPotential .true.
```

Depending on what you want  
to nanosmooth

## Output of SIESTA required by MACROAVE

```
SystemLabel.RHO  
SystemLabel.TOCH  
SystemLabel.IOCH  
SystemLabel.DRHO  
SystemLabel.VH  
SystemLabel.VT
```

## MACROAVE

```
Prepare the input file macroave.in  
$ ~/siesta/Util/Macroave/Src/macroave.x
```

You **do not** need to rerun SIESTA to run  
MACROAVE as many times as you want

# Input of MACROAVE: macroave.in

Siesta	# Which code have you used to get the input data?
Potential	# Which is the input microscopic data?
Surface	# Name of the file where the input data is stored
1	# Number of convolutions required to calculate the macro. ave.
7.557853043	# First length for the filter function in macroscopic average
7.47614934	# Second length for the filter function in macroscopic average
216	# Total charge
spline	# Type of interpolation

The same code with the same input runs with information provided by

**SIESTA**

or

**ABINIT**

(indeed it should be quite straight forward to generalize to any other code)

# Input of MACROAVE: macroave.in

```
Siesta          # Which code have you used to get the input data?
Potential       # Which is the input microscopic data?
Surface         # Name of the file where the input data is stored
1              # Number of convolutions required to calculate the macro. ave.
7.557853043    # First length for the filter function in macroscopic average
7.47614934     # Second length for the filter function in macroscopic average
216            # Total charge
spline         # Type of interpolation
```

## Name of the magnitude that will be nanosmoothed

**Potential:**

**SystemLabel.VH**

**Charge:**

**SystemLabel.RHO**

**TotalCharge:**

**SystemLabel.TOCH**

# Input of MACROAVE: macroave.in

```
Siesta          # Which code have you used to get the input data?
Potential       # Which is the input microscopic data?
Surface         # Name of the file where the input data is stored
1              # Number of convolutions required to calculate the macro. ave.
7.557853043    # First length for the filter function in macroscopic average
7.47614934     # Second length for the filter function in macroscopic average
216            # Total charge
spline         # Type of interpolation
```

**SystemLabel**

# Input of MACROAVE: macroave.in

```
Siesta           # Which code have you used to get the input data?
Potential        # Which is the input microscopic data?
Surface          # Name of the file where the input data is stored
1                # Number of convolutions required to calculate the macro. ave.
7.557853043     # First length for the filter function in macroscopic average
7.47614934      # Second length for the filter function in macroscopic average
216              # Total charge
spline           # Type of interpolation
```

## Number of square filter functions used for nanosmoothing

**1**

**Surfaces**

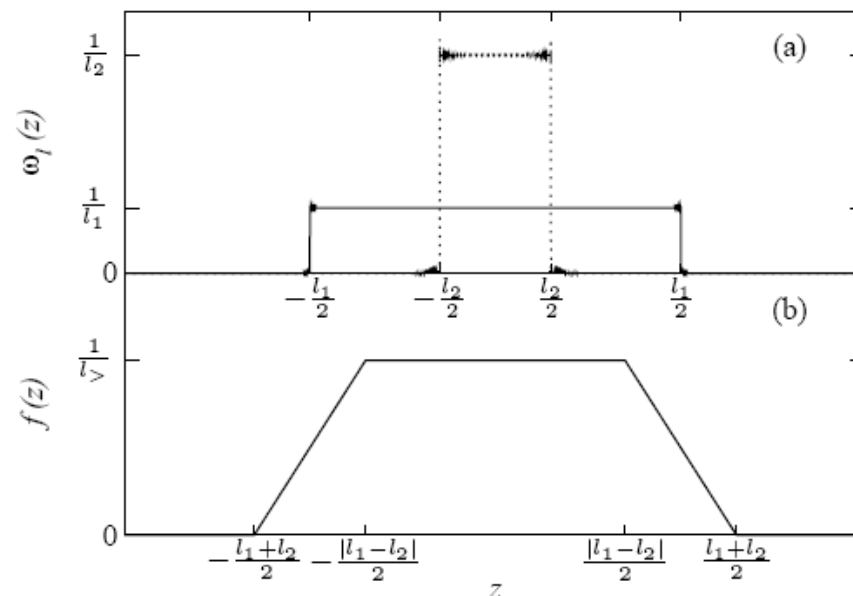
**2**

**Interfaces and superlattices**

# Input of MACROAVE: macroave.in

```
Siesta           # Which code have you used to get the input data?
Potential        # Which is the input microscopic data?
Surface         # Name of the file where the input data is stored
1               # Number of convolutions required to calculate the macro. ave.
7.557853043     # First length for the filter function in macroscopic average
7.47614934      # Second length for the filter function in macroscopic average
216            # Total charge
spline          # Type of interpolation
```

## Length of the different square filter functions (in Bohrs)



# Input of MACROAVE: macroave.in

```
Siesta           # Which code have you used to get the input data?
Potential        # Which is the input microscopic data?
Surface          # Name of the file where the input data is stored
1                # Number of convolutions required to calculate the macro. ave.
7.557853043     # First length for the filter function in macroscopic average
7.47614934     # Second length for the filter function in macroscopic average
216              # Total charge
spline          # Type of interpolation
```

## Total number of electrons

(used only to renormalize if we nanosmooth the electronic charge)



# Input of MACROAVE: macroave.in

```
Siesta           # Which code have you used to get the input data?
Potential        # Which is the input microscopic data?
Surface          # Name of the file where the input data is stored
1               # Number of convolutions required to calculate the macro. ave.
7.557853043     # First length for the filter function in macroscopic average
7.47614934     # Second length for the filter function in macroscopic average
216             # Total charge
spline          # Type of interpolation
```

Type of interpolation from the SIESTA mesh to a FFT mesh

**Spline**

or

**Linear**

# Output of MACROAVE

## Planar average

$$\bar{\rho}(z) = \frac{1}{S} \int_S dx dy \rho(\vec{r})$$

SystemLabel.PAV

## Nanosmoothed

$$\bar{\bar{\rho}}(z) = \int dz' f(z - z') \bar{\rho}(z')$$

SystemLabel.MAV

## Format

$z$		average
0.000000000000		0.000000000000
0.000095367432		0.000000000000
0.000190734863		0.000000000000
.	.	.
.	.	.
.	.	.

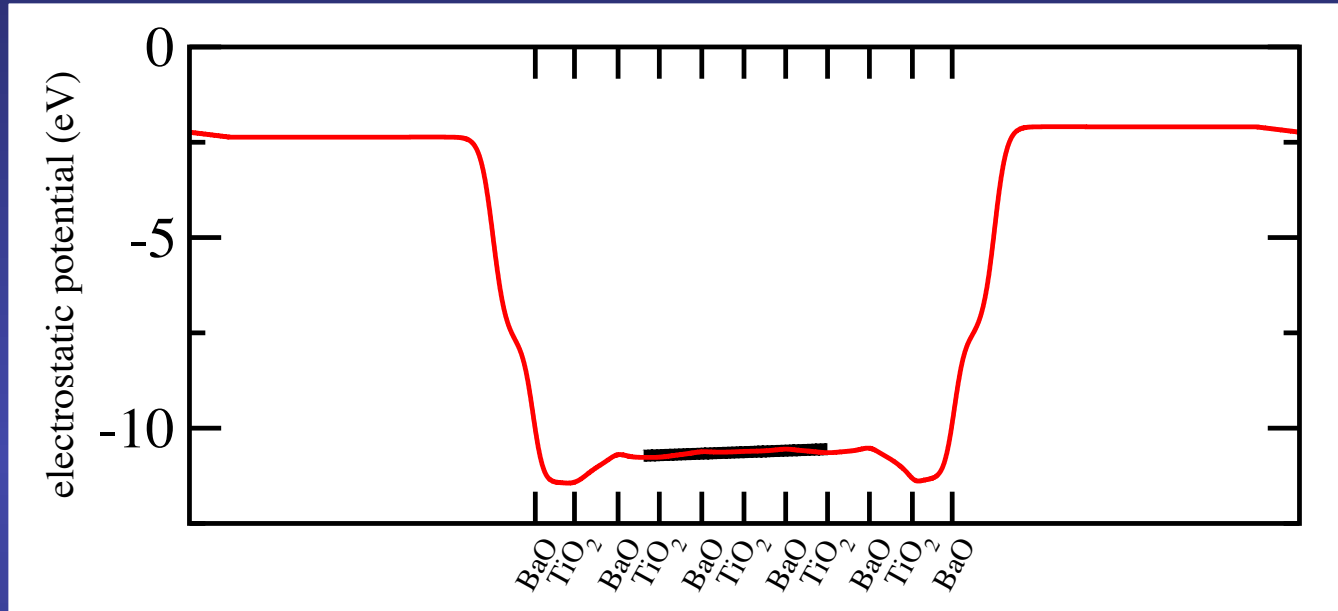
## Units

Coordinates: Bohr

Potential: eV

Charge density: electrons/Bohr<sup>3</sup>

To compute the electric field, plot the nanosmoothed pot. and perform a linear regression at the center of the slab



Note how the electric field in vacuum is zero, as imposed by the slab dipole correction

In our example, for  $\sigma = 0.05 \frac{\text{electrons}}{\text{surface unit cell}}$

$$\frac{dV}{dz} = 0.010444 \frac{\text{eV}}{\text{Bohr}} = 0.010444 \frac{\text{eV}}{\text{Bohr}} \times \frac{1 \text{ Ha}}{2 \times 13.6058 \text{ eV}} = 3.838 \times 10^{-4} \frac{\text{Ha}}{\text{Bohr}}$$

$$\mathcal{E} = -\frac{dV}{dz} = -3.838 \times 10^{-4} \frac{\text{Ha}}{\text{Bohr}}$$

# To learn more on nanosmoothing and how to compute work functions and band offsets with SIESTA

IOP PUBLISHING

JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 213203 (34pp)

[doi:10.1088/0953-8984/19/21/213203](https://doi.org/10.1088/0953-8984/19/21/213203)

TOPICAL REVIEW

## Nanoscale smoothing and the analysis of interfacial charge and dipolar densities

Javier Junquera<sup>1,2</sup>, Morrel H Cohen<sup>2,3</sup> and Karin M Rabe<sup>2</sup>

PHYSICAL REVIEW B **67**, 155327 (2003)

## First-principles calculation of the band offset at BaO/BaTiO<sub>3</sub> and SrO/SrTiO<sub>3</sub> interfaces

Javier Junquera,<sup>1</sup> Magali Zimmer,<sup>1</sup> Pablo Ordejón,<sup>2</sup> and Philippe Ghosez<sup>1</sup>

# How to compute the layer by layer polarization

**Javier Junquera**



# How to compute the local value of the “effective polarization”

Ubiquitous formula to compute the **dipole density** of layer  $j$ :

$$p_j^Z = \frac{1}{S} \sum_{\alpha \in j} Z_\alpha^* R_{\alpha z}$$

Surface cell area  $\nearrow$   $\uparrow$   $\longleftarrow$  Position of atom  $\alpha$  along  $z$

Bulk Born effective charges associated with atom  $\alpha$

Note that:

- we sum only over all the atoms that belong to that particular layer  $j$
- we assume a one-dimensional problem (the atoms are allowed to move only along the  $z$  direction, so we do not need to consider off-diagonal terms in the Born effective charges).

# How to compute the local value of the “effective polarization”

Ubiquitous formula to compute the **dipole density** of layer  $j$ :

$$p_j^Z = \frac{1}{S} \sum_{\alpha \in j} Z_\alpha^* R_{\alpha z}$$

**This formula is typically ill-defined**

Since the acoustic sum rule is usually not satisfied by individual layers

$$\sum_{\alpha \in j} Z_\alpha^* \neq 0$$

Then the formula is origin dependent

**To circumvent this problem:**

perform an average with the neighboring layers (so the acoustic sum rule is satisfied when summing the weighted effective charges in all these layers)

**For instance, in perovskites**

[valid for II-IV ( $\text{PbTiO}_3$  or  $\text{BaTiO}_3$ ), I-V ( $\text{KNbO}_3$ ), and III-III ( $\text{LaAlO}_3$ )]

$$\bar{p}_j^Z = \frac{1}{4} p_{j-1}^Z + \frac{1}{2} p_j^Z + \frac{1}{4} p_{j+1}^Z$$

# How to compute the local value of the “effective polarization”

Ubiquitous formula to compute the **dipole density** of layer  $j$ :

$$\bar{p}_j^Z = \frac{1}{4}p_{j-1}^Z + \frac{1}{2}p_j^Z + \frac{1}{4}p_{j+1}^Z$$

The approximate **local polarization** immediately follows

$$P_j^Z = \frac{\bar{p}_j^Z}{\left(\frac{c}{2}\right)} = \frac{2}{c}\bar{p}_j^Z$$

Here we assume that every individual layer occupies only half the cell

Average out-of-plane lattice parameter

**Exact estimate:**

- **In the linear limit** (the dipole density is only linear in the positions)



This assumes small polar distortions

- **Under short-circuit electrical boundary conditions** (assuming that the electric field vanishes throughout the structural transformations). Remember that the Born effective charges assume zero electric-field



# How to compute the local value of the “effective polarization”

The approximate **local polarization** immediately follows

$$P_j^Z = \frac{\bar{p}_j^Z}{\left(\frac{c}{2}\right)} = \frac{2}{c} \bar{p}_j^Z$$

Exact estimate:

- In the linear limit (the dipole density is only linear in the positions)



This assumes small polar distortions

**Polar distortions in ferroelectric capacitors are generally large (close to the spontaneous polarization of the ferroelectric insulator)**

- Under short-circuit electrical boundary conditions (assuming that the electric field vanishes throughout the structural transformations). Remember that the Born effective charges assume zero electric-field

**There is generally an imperfect screening regime, with a macroscopic “depolarizing field”**

# How to compute the local value of the “effective polarization”

A corrected formula for the **local polarization**

$$P_j^Z = \frac{\bar{p}_j^Z}{\left(\frac{c}{2}\right)} = \frac{2}{c} \bar{p}_j^Z$$

Electronic susceptibility

$$\tilde{P}_j^Z = \left(1 + \frac{\chi_\infty}{\chi_{\text{ion}}}\right) P_j^Z = \frac{\chi_{\text{tot}}}{\chi_{\text{ion}}} P_j^Z$$

Ionic susceptibility

TABLE III. Values of the susceptibilities  $\chi$  and scaling factors  $\chi_{\text{tot}}/\chi_{\text{ion}}$  for the ferroelectric materials considered in this work.

	$\epsilon_{\text{tot}}$	$\epsilon_\infty$	$\chi_{\text{tot}}/\chi_{\text{ion}}$
BaTiO <sub>3</sub>	-48.87	6.48	0.90
PbTiO <sub>3</sub>	-96.54	8.33	0.93
KNbO <sub>3</sub>	-34.92	6.27	0.87

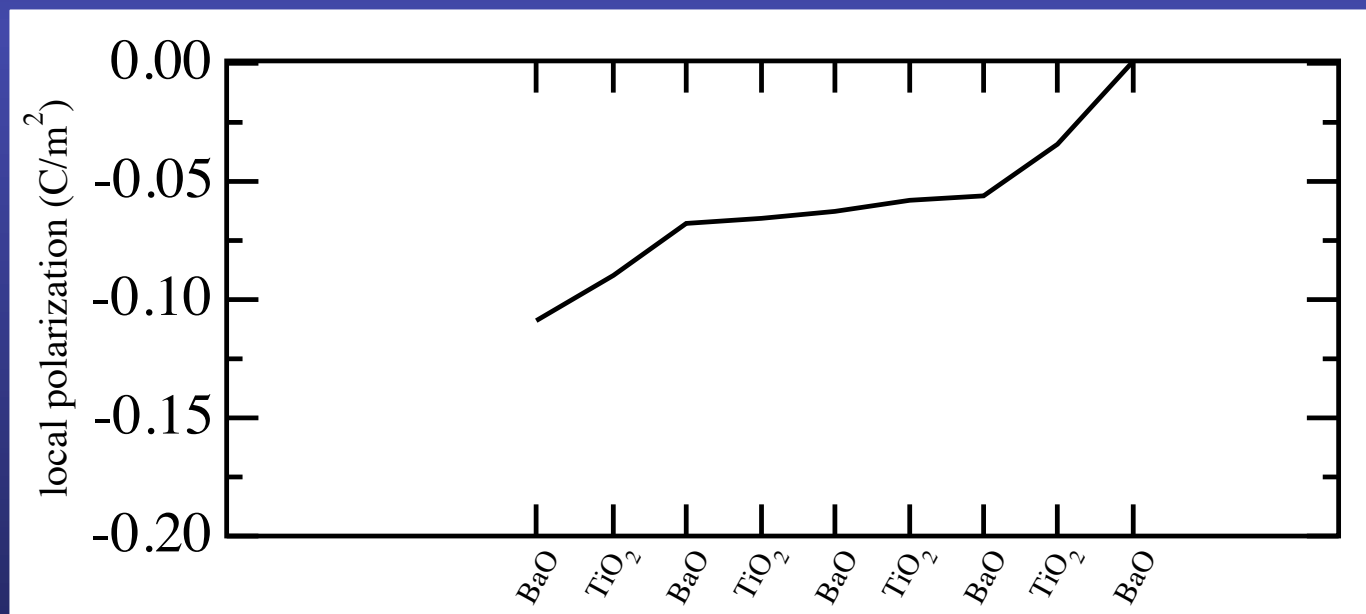
See Appendix A in  
M. Stengel *et al.* Phys. Rev. B 83, 235112 (2011)

# “Effective” layer-by-layer polarization in the BaTiO<sub>3</sub> slab

$$P_j^Z = \frac{\bar{p}_j^Z}{\left(\frac{c}{2}\right)} = \frac{2}{c} \bar{p}_j^Z$$

$$Z^*(\text{Ba}) = 2.6339978 \quad Z^*(\text{Ti}) = 7.189899 \quad Z^*(\text{O}_1) = -2.0946604 \quad Z^*(\text{O}_2) = -5.6345766$$

The acoustic sum rule is verified  $\sum_{\alpha} Z_{\alpha}^* = 0$



**Supporting slides**

# Relation between the normal component of the displacement field at the interface of different media

We start from the Maxwell equation in macroscopic media

**SI units**

$$\nabla \cdot \vec{D}(\vec{r}) = \rho_{\text{ext}}(\vec{r})$$

**atomic units**

$$\nabla \cdot \vec{D}(\vec{r}) = 4\pi\rho_{\text{ext}}(\vec{r})$$

Let  $V$  be a finite volume in space,  $S$  the closed surface bounding it,  $da$  an element of area on the surface, and  $\vec{n}$  a unit normal to the surface at  $da$  pointing outward from the enclosed volume

Integrating the Maxwell equation over the volume

$$\int_V \nabla \cdot \vec{D}(\vec{r}) d\vec{r} = \int_V \rho_{\text{ext}}(\vec{r}) d\vec{r} \qquad \int_V \nabla \cdot \vec{D}(\vec{r}) d\vec{r} = \int_V 4\pi\rho_{\text{ext}}(\vec{r}) d\vec{r}$$

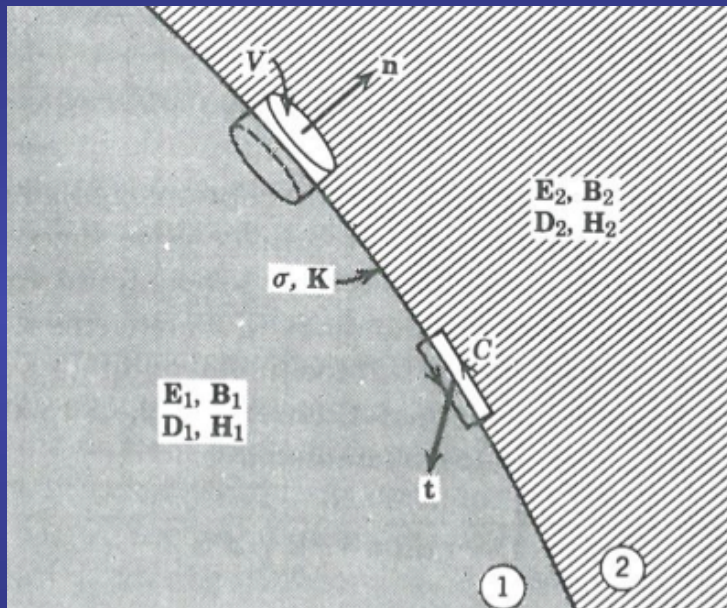
Then, we apply the divergence theorem

$$\int_V \nabla \cdot \vec{D}(\vec{r}) d\vec{r} = \oint_S \vec{D} \cdot \vec{n} da$$

$$\oint_S \vec{D} \cdot \vec{n} da = \int_V \rho_{\text{ext}}(\vec{r}) d\vec{r} \qquad \oint_S \vec{D} \cdot \vec{n} da = 4\pi \int_V \rho_{\text{ext}}(\vec{r}) d\vec{r}$$

# Relation between the normal component of the displacement field at the interface of different media

An infinitesimal Gaussian pillbox straddles the boundary surface between two media



In the limit of a very shallow pillbox, the side surfaces do not contribute to the integral

If the top and bottom are parallel, tangent to the surface, and of area  $\Delta a$ , then

$$\oint_S \vec{D} \cdot \vec{n} da = (\vec{D}_2 - \vec{D}_1) \cdot \vec{n} \Delta a$$

If the charge density  $\rho_{\text{ext}}$  is singular at the interface so as to produce an idealized surface charge density  $\sigma_{\text{ext}}$

$$\int_V \rho_{\text{ext}}(\vec{r}) d\vec{r} = \sigma_{\text{ext}} \Delta a \quad 4\pi \int_V \rho_{\text{ext}}(\vec{r}) d\vec{r} = 4\pi \sigma_{\text{ext}} \Delta a$$

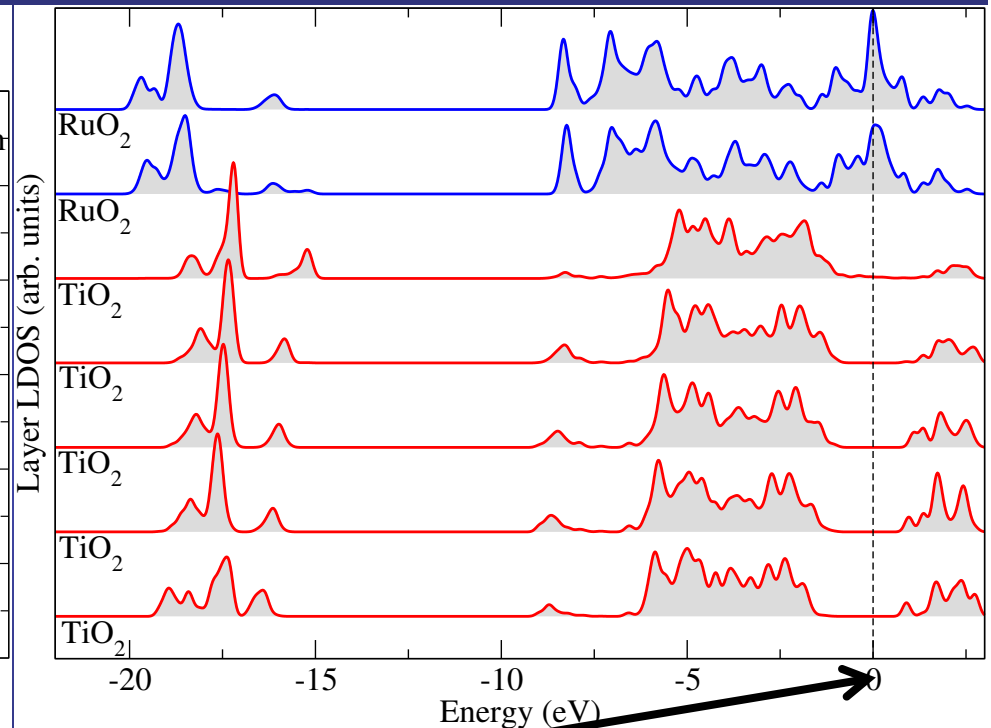
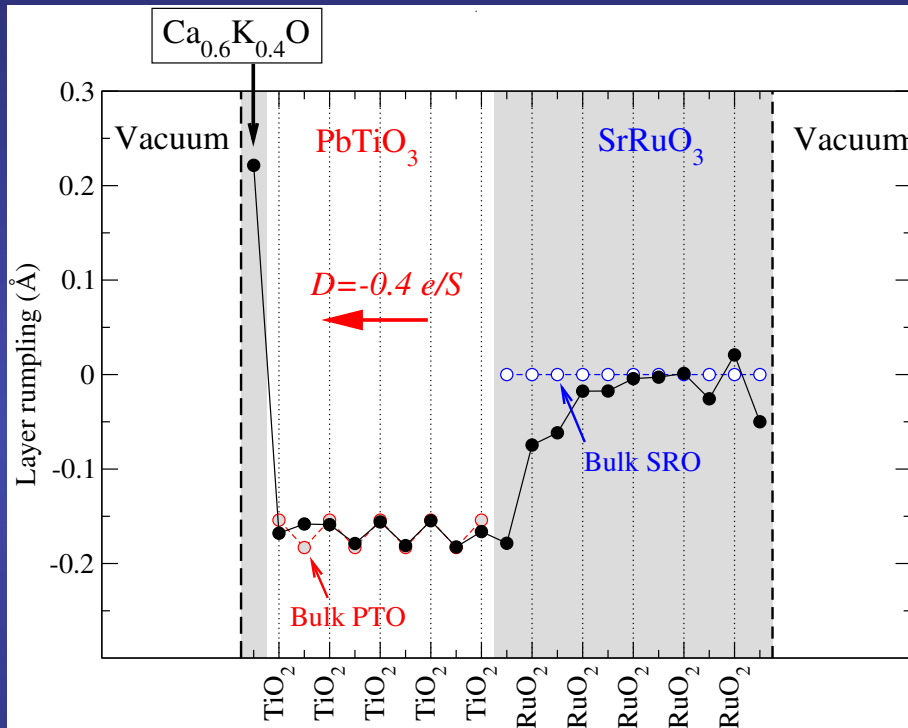
So the normal component of  $\vec{D}$  on either side of the boundary surface is related according to

$$\left( \vec{D}_2 - \vec{D}_1 \right) \cdot \vec{n} = \sigma_{\text{ext}} \quad \left( \vec{D}_2 - \vec{D}_1 \right) \cdot \vec{n} = 4\pi \sigma_{\text{ext}}$$

The normal component of  $\vec{D}$  at any point is equal to the surface charge density at that point

# “Constrained- $\sigma$ ” method

Adopt a vacuum/insulator/metal/vacuum geometry



Induce a layer of bound charges at its free surface  
(  $Q$  per surface unit cell  $S$  )

$$\rho_{\text{ext}} = \frac{Q}{S}$$

$$\Rightarrow D_2 - D_1 = D_{\text{PbTiO}_3} - D_{\text{vacuum}} = \rho_{\text{ext}} = \frac{Q}{S}$$

If the surface region remains locally insulating

In this example