Université de Liège

Macroscopic averages in Abinit

Javier Junquera

Département de Physique

Université de Liège

Macroscopic averages

Microscopic quantities

Macroscopic quantities

- Very rapidly functions of position
- Resembles the microscopic atomic structure
- Output of first-principles calculations (DEN, POT, …)

- Smooth variations with the position
- Magnitudes that enter in the discussion of dielectrics.
- Magnitudes measured experimentally.

Macroscopic Average Technique

Average over a region that is small on the macroscopic scale, but large compared with the atomic dimensions.

Macroscopic average technique

First step: Planar average

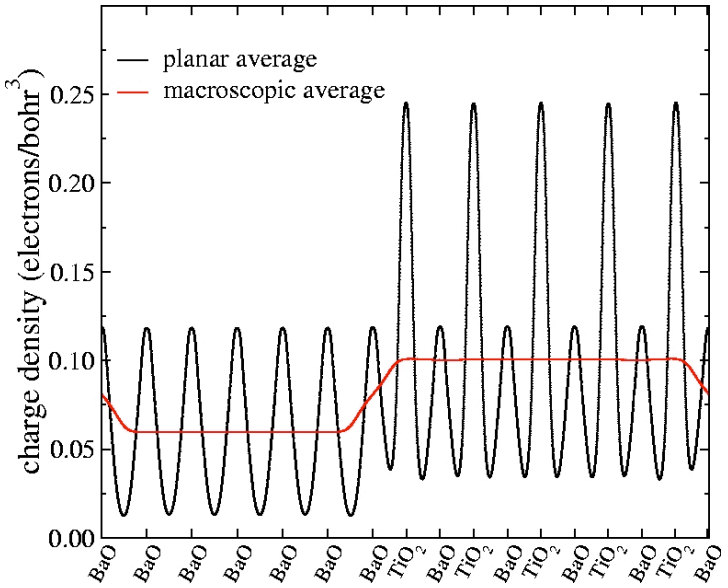
$$\overline{p}(z) = \frac{1}{S}\int_S p(x, y, z)\, dx dy$$

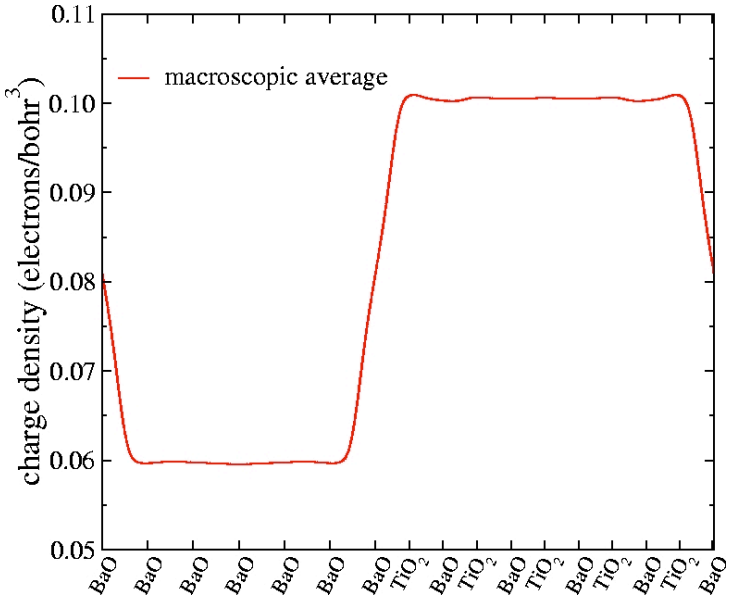
Second step: Averaging with a filter

(convolution with step functions)

$$\overline{\overline{p}}(z) = \int dz' \int dz'' \omega_{l_1}(z - z')\, \omega_{l_2}(z' - z'')\, \overline{p}(z'')$$

$$\omega_l = \frac{1}{l}\Theta\left(\frac{l}{2} - |z|\right)$$



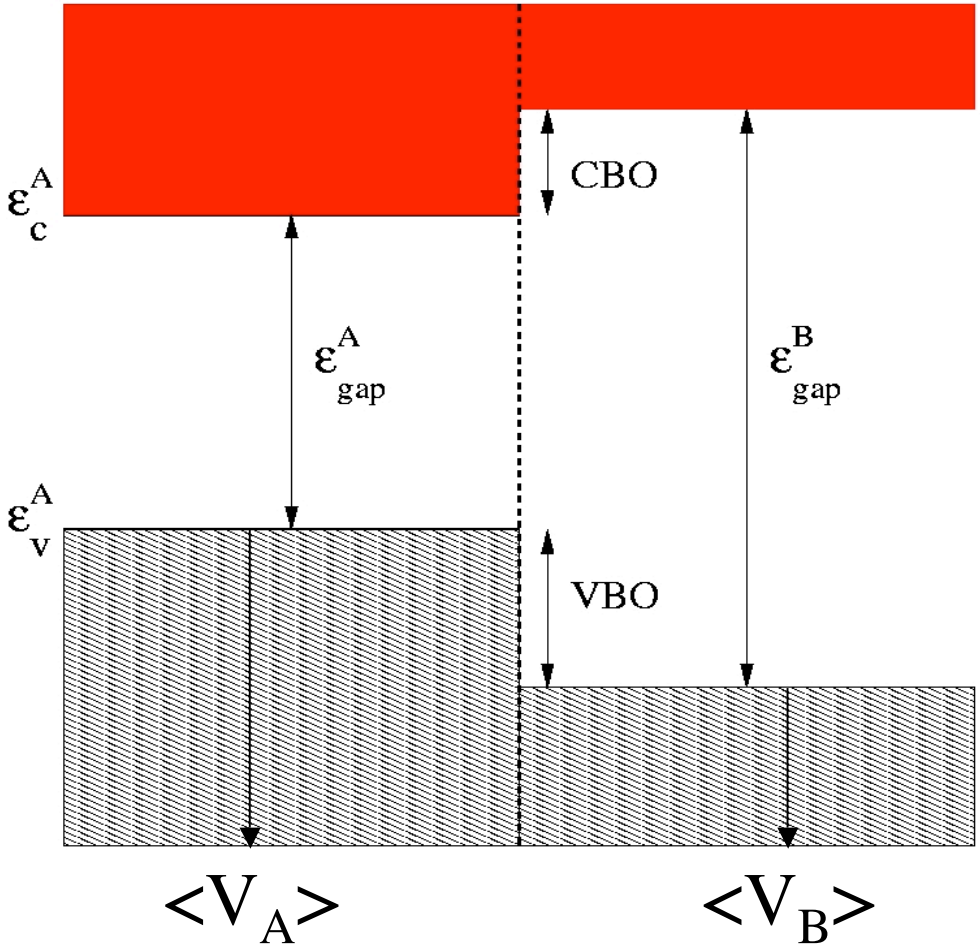


A. Baldereschi *et al.*, Phys. Rev. Lett., **61**, 734 (1988)

L. Colombo et. al., Phys. Rev. B, **44**, 5572 (1991)

Band offsets

BAND OFFSET: Relative position of the band gaps of both constituents at the interface



CBO: Conduction Band Offset

VBO: Valence Band Offset

$\langle V_{A,B} \rangle$ Arbitrary averages of the electrostatic potential

Relation $\langle V_A \rangle$? $\langle V_B \rangle$?

Band offset calculation

$$\Delta E_{VBO} = \Delta E_V + \Delta V$$

$\Delta E_V \equiv$ Band-structure term

Difference between the two valence band edges

Standard bulk structure calculations

$\Delta V \equiv$ Line-up of the electrostatic potential

Relates the average of the electrostatic potential in the two materials.

Can *only* be obtained from *a SCF calculation on the supercell*

Contains all the intrinsic effect of the interface

Obtained by macroscopic average technique

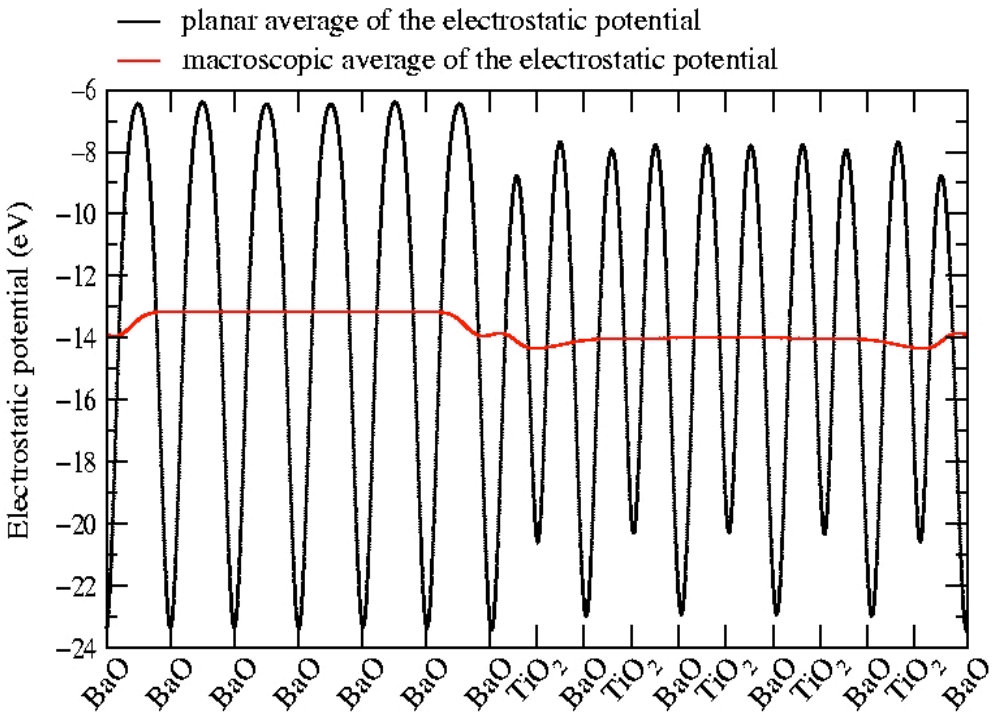
A. Baldereschi, S. Baroni and R. Resta, PRL **61**, 734 (1988)

Double-macroscopic average

$$\langle V \rangle = \frac{1}{\Omega} \int_{\Omega} d\vec{r}\, V_H(\vec{r})$$

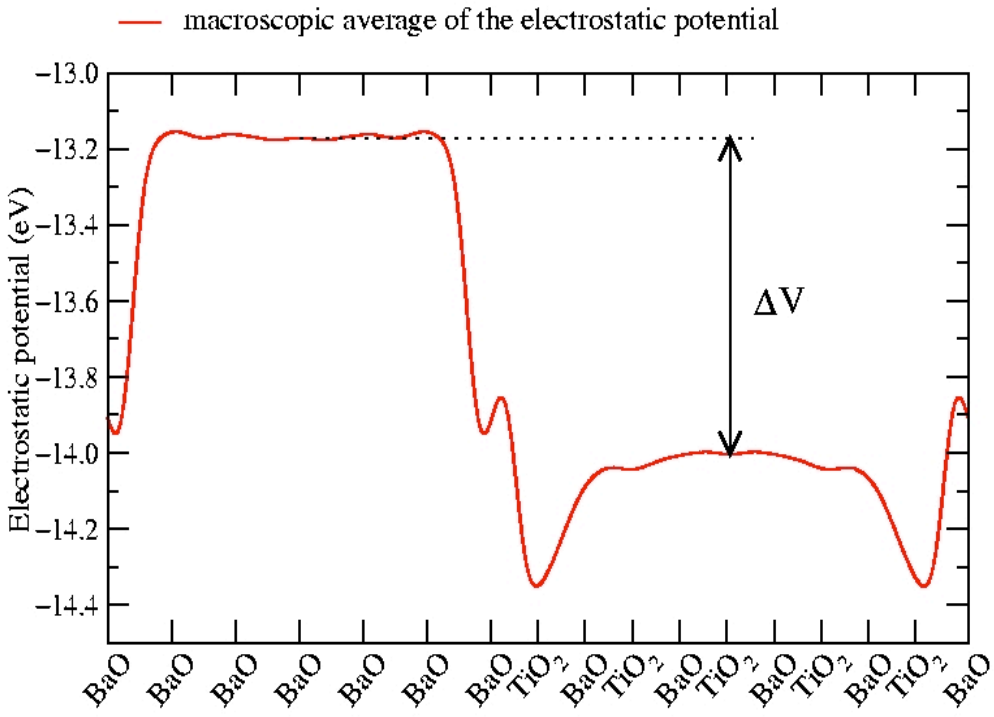
Planar average

$$\bar{V}(z) = \frac{1}{S} \int_{S} dx dy V(x, y, z)$$



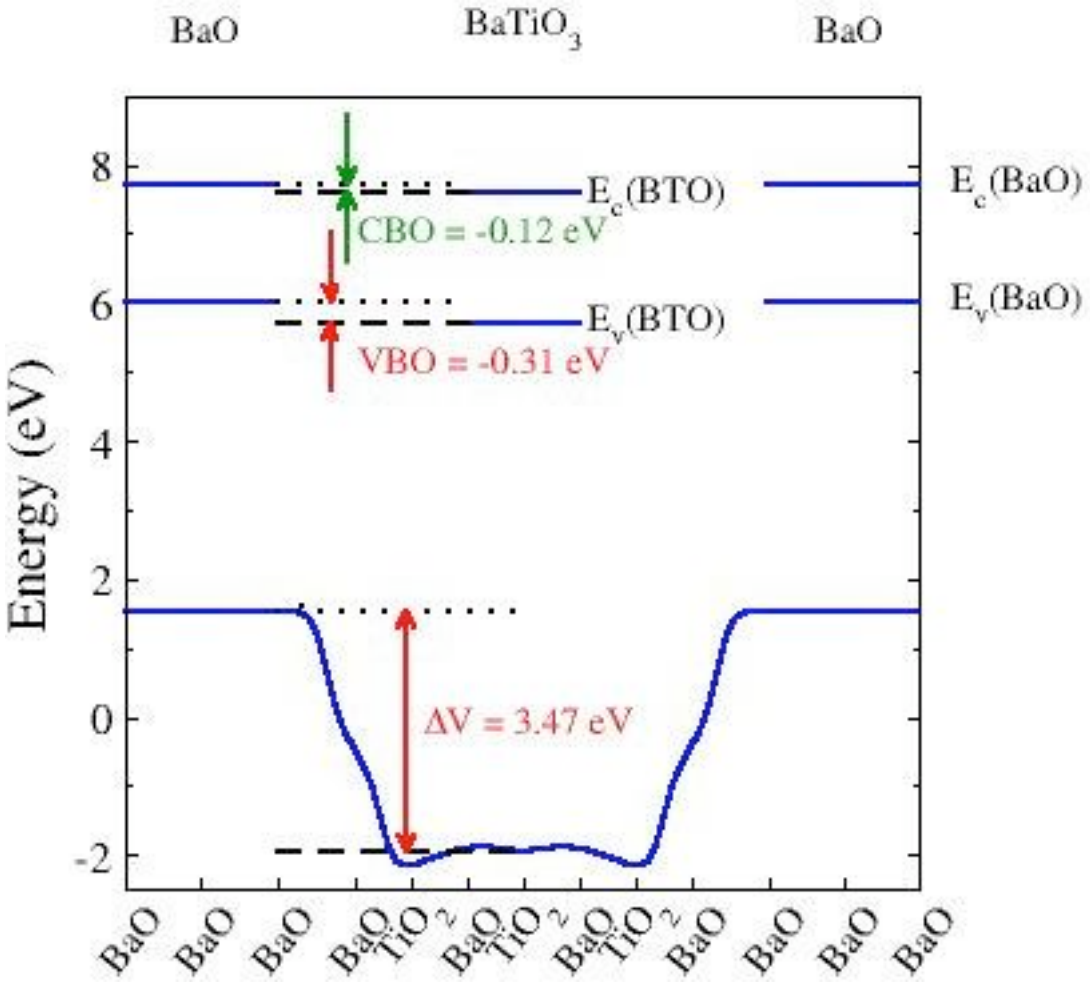
Average on normal direction

Convolution with two filter functions



L. Colombo *et al*, Phys. Rev. B, **44**, 5572 (1991)

$BaO/BaTiO_3$ band offset



ABINIT:

3 BaO / 3 $BaTiO_3$

VBO: -0.31 eV

SIESTA:

2 BaO / 3 $BaTiO_3$

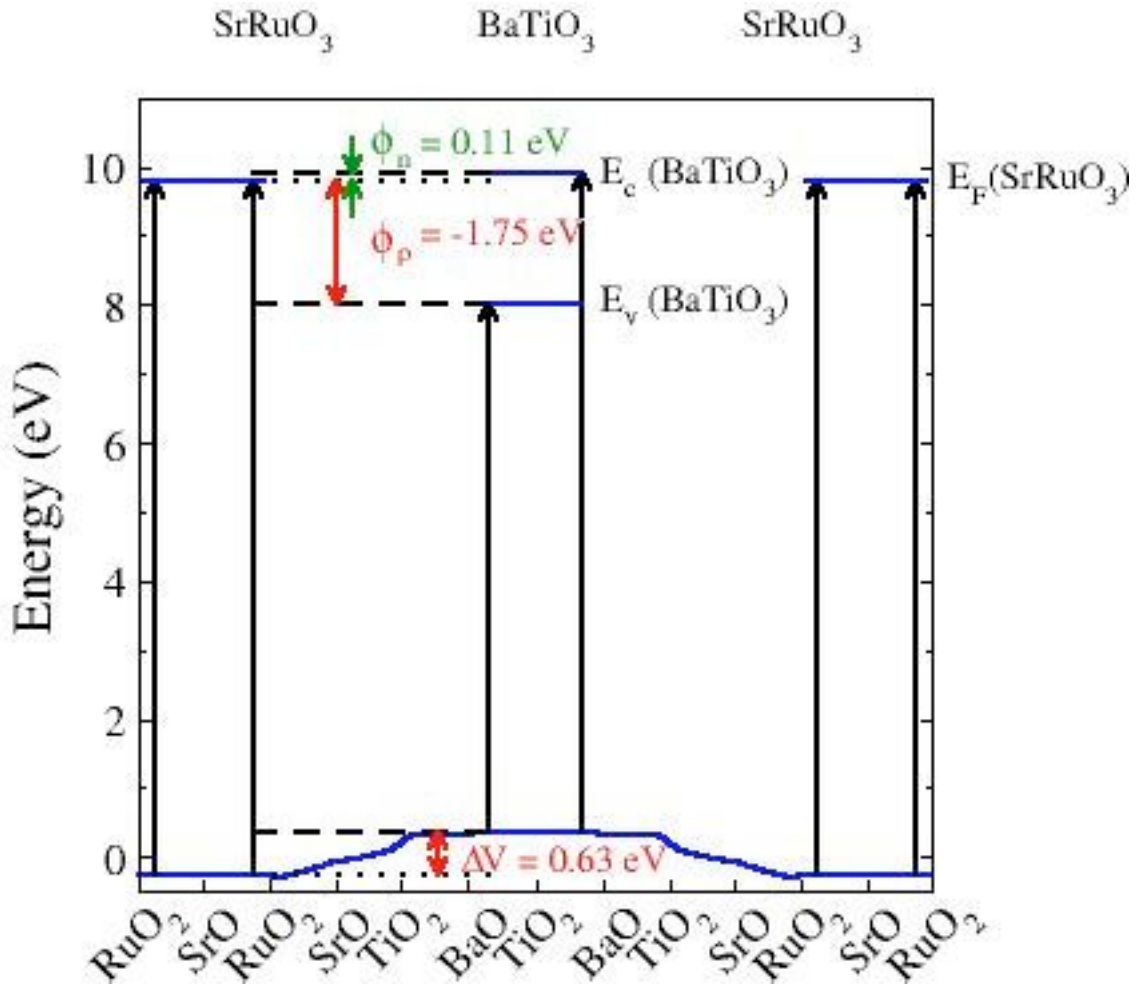
VBO: -0.21 eV

3 BaO / 5 $BaTiO_3$

VBO: -0.12 eV

Schottky barrier of $SrRuO_3/BaTiO_3$

$SrO\text{-}TiO_2$ interface



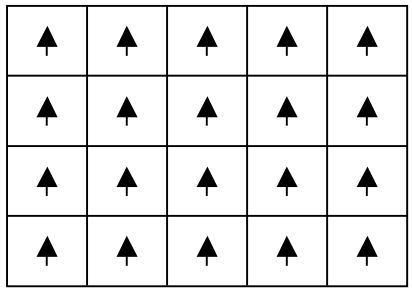
ABINIT:

3.5 $SrRuO_3$ / 2.5 $BaTiO_3$

ϕ_p: -1.75 eV

Dynamical charges

- Collective displacement: ⟶ macroscopic polarization *P*

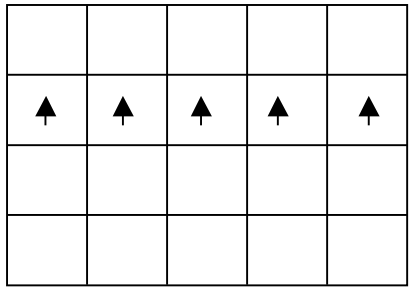


- Linear response :

$$Z_T^* = \Omega_o \left.\frac{\partial P}{\partial \Omega}\right|_{E=0}$$

$$Z_L^* = \Omega_o \left.\frac{\partial P}{\partial \Omega}\right|_{D=0} = \frac{Z_T^*}{\Omega}$$

- Individual displacement along z: ⟶ local dipole *p*



- Finite difference :
  - from the density :

$$Z_L^* = \frac{\Omega p}{\Omega\Omega} = \frac{\Omega \int \Omega(r).r\,dr}{\Omega\Omega}$$

  - from the potential :

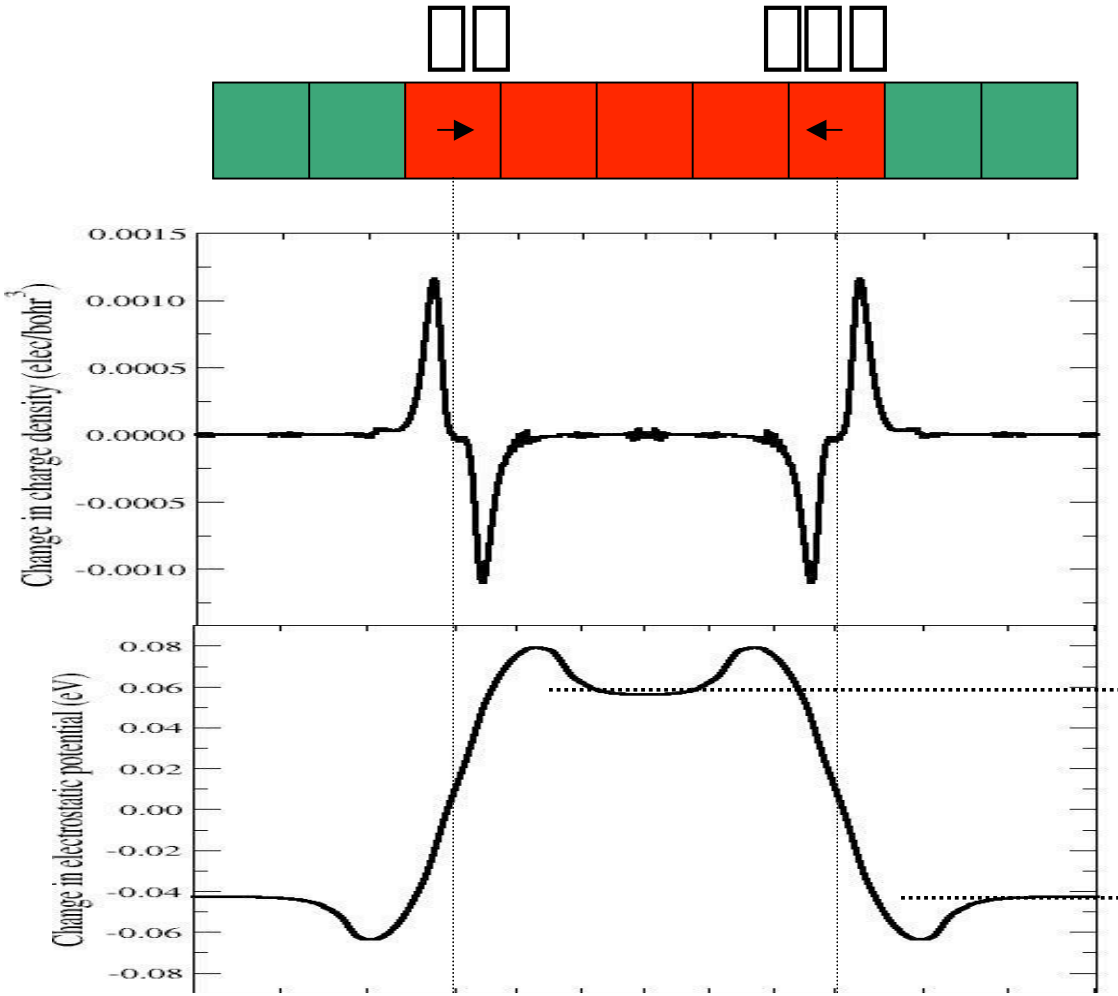
$$\frac{\Omega V}{\Omega\Omega} = \Omega \frac{4\pi}{A_0}\frac{\Omega p}{\Omega\Omega} = \Omega \frac{4\pi}{A_0} Z_L^*$$

R. Martin and K. Kunc,
PRB **24**, 2081 (1981)

Layer dependent quantity relevant for thin films: Z^*_L

Computation of longitudinal charges

□□(z)



□V(z)

□V

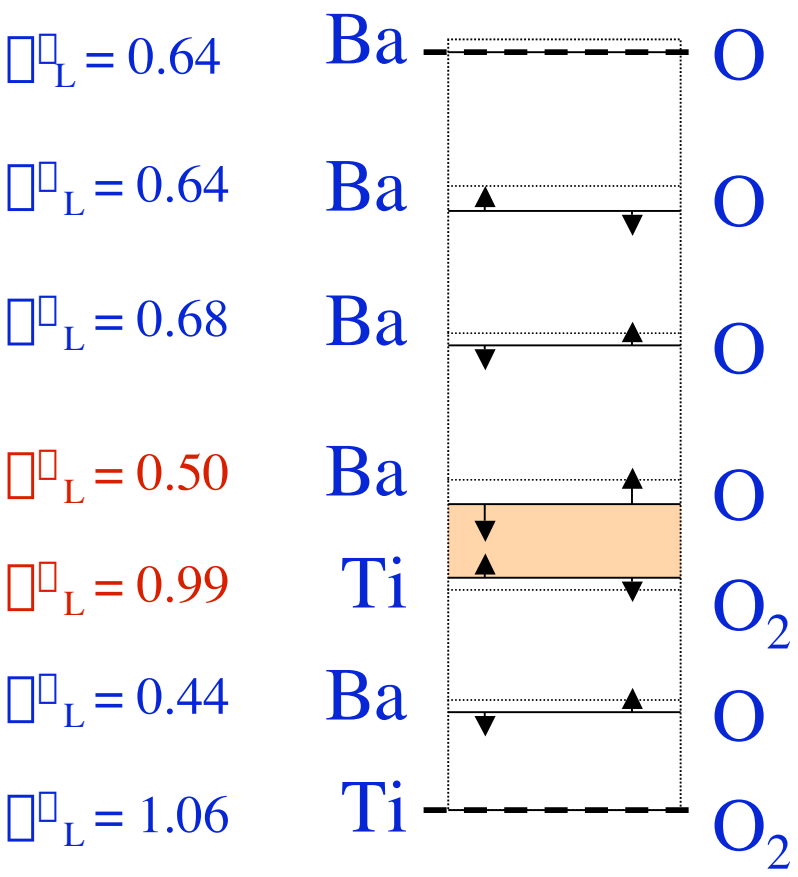
$$\frac{\square V}{\square \square} = \square \frac{4\square}{A_0} \frac{\square p}{\square \square} = \square \frac{4\square}{A_0} Z_L^*$$

BaO/BaTiO$_3$ interface: Z$^*_L$ along z

ΔZ^*_L(Ba)= 0.65

Bulk BO

ΔZ^*_L(O$_{||}$)= -0.65



ΔZ^*_L(Ba) = 0.43

ΔZ^*_L(Ti) = 1.06

Bulk BTO

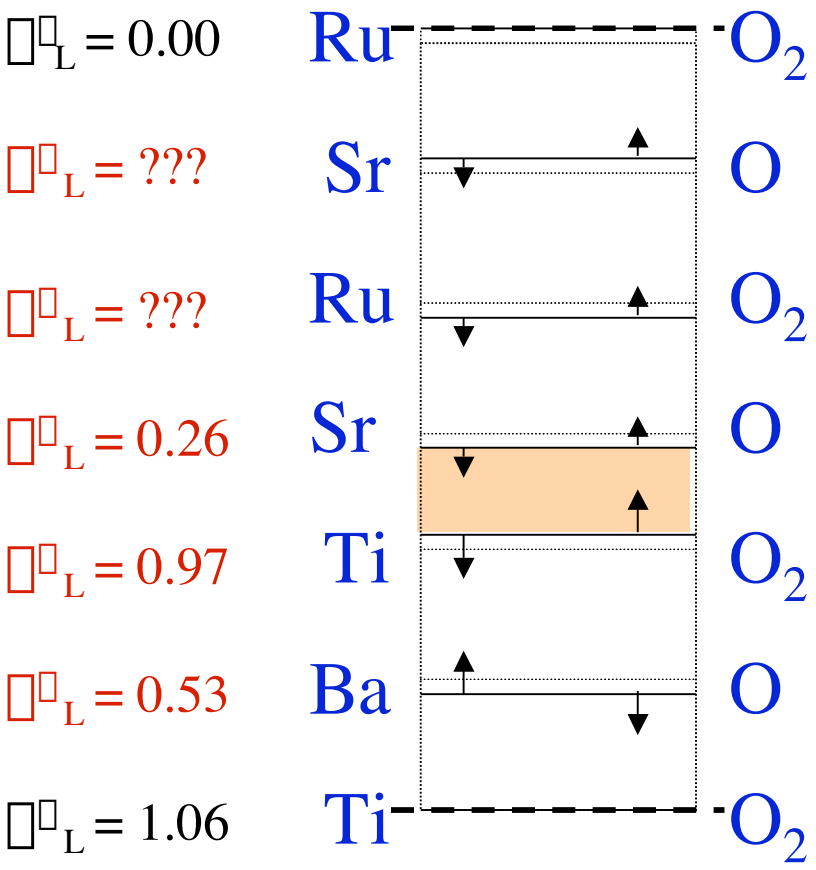
ΔZ^*_L(O$_{||}$) = -0.83

ΔZ^*_L(O$_{\perp}$) = -0.33

- linear response and finite differences techniques yield similar results
- sharp interface (for Z*)

$SrRuO_3/BaTiO_3$ interface: Z^*_L along z

ΔZ^*_L(Sr,Ru)= 0 — Bulk SRO — $\Delta Z^*_L(O_{\parallel})$= 0



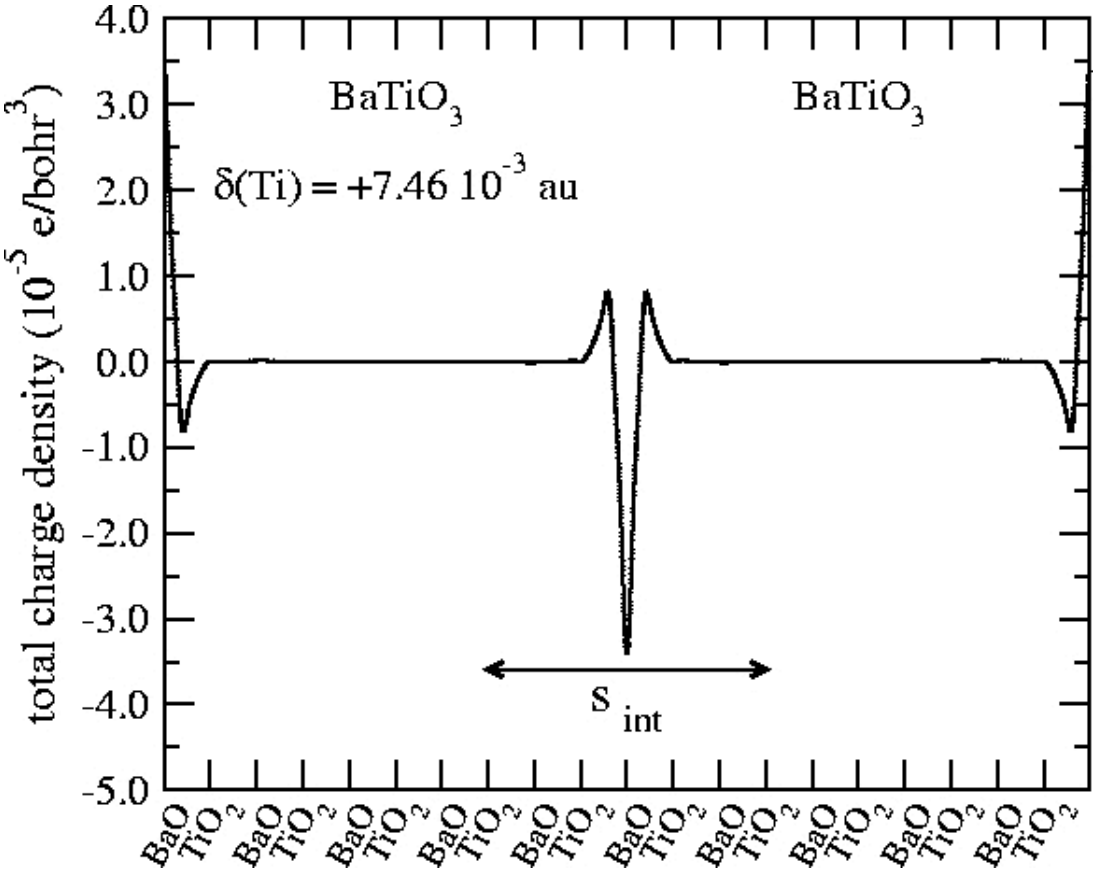
ΔZ^*_L(Ba) = 0.43 — Bulk BTO — $\Delta Z^*_L(O_{\parallel})$ = -0.83

ΔZ^*_L(Ti) = 1.06 — $\Delta Z^*_L(O_{\perp})$ = -0.33

- only finite differences technique
- broad interface (for Z*)

Electronic dielectric constants

F. Bernardini & V. Fiorentini, Phys. Rev. B, **58** 15292 (98)



$$\varepsilon^{\infty}(BaTiO_3) = 6.70$$

$$D_1 = E_1 + 4\pi P_1 = E_2 + 4\pi P_2 = D_2$$

$$\overline{\varepsilon^{\infty}} = \frac{(\varepsilon_1^{\infty} + \varepsilon_2^{\infty})}{2} = \frac{\left(P_2^{(0)} - P_1^{(0)}\right)}{\mathcal{E}_{int}}$$

$$\varepsilon^{\infty} = \lim_{\delta \to 0} \overline{\varepsilon^{\infty}}$$

Converge:

- Size of the supercell
- Atomic displacemets