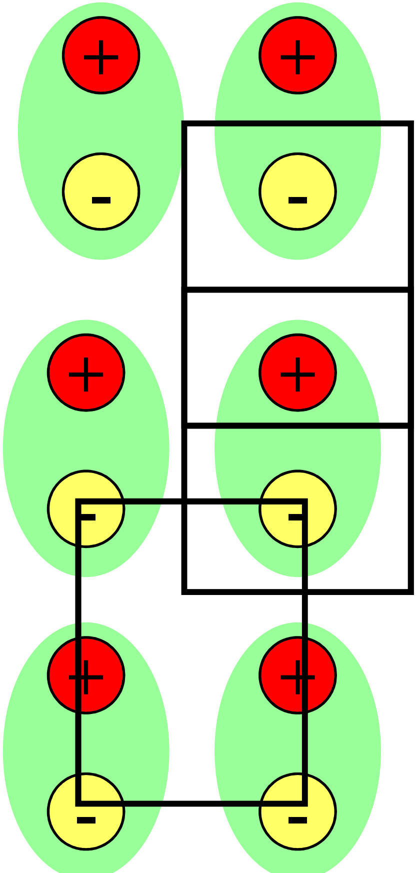
Electric polarization

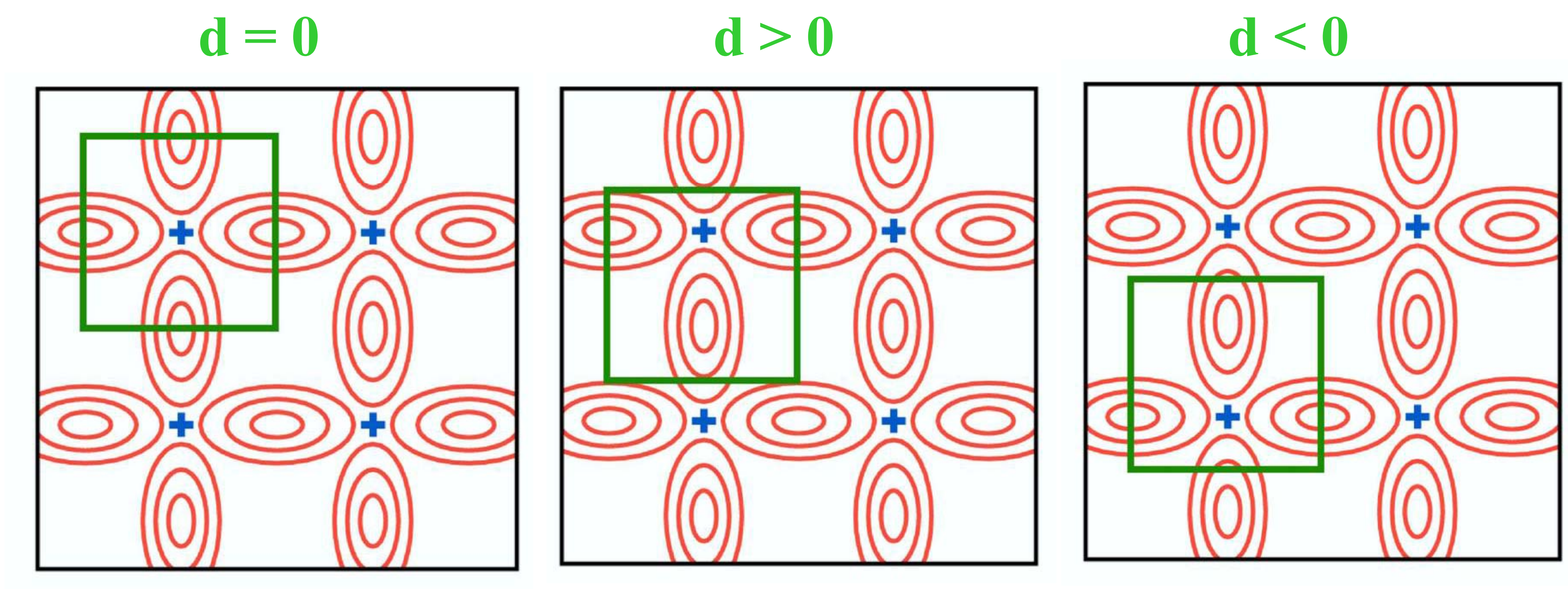


How to define the electric polarization in a solid?

Compose of molecules: $\vec{P} = \vec{d}_{mol} / V_{mol}$

Electric polarization cannot uniquely be defined from the charge distribution.

For a covalent solid the problem is even more clear...



Correct way: use currents

Use the current instead of density

$$\frac{d\vec{P}_e}{dt} = \frac{1}{V_{cell}} \int dr^3 \; j(\vec{r})$$

R. Resta 1992: changes in the electric polarization can be unambiguously defined and calculated

$$\Delta\vec{P}_e = \int dt \frac{d\vec{P}}{dt}$$

How to calculate polarization changes

King-Smith and Vanderbilt, 1993:

$$\Delta \mathbf{P} = \mathbf{P}(t_2) - \mathbf{P}(t_1)$$ where

$$\mathbf{P} = \frac{ie}{(2\pi)^3} \sum_n \int_{\mathrm{BZ}} d^3k \, \langle u_{nk} | \nabla_{\mathbf{k}} | u_{nk} \rangle$$

"Berry phase"

where $\psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{nk}(\mathbf{r})$

Ionic contribution

Of course, we have to add the contribution due the core of atoms or to the ions (i.e., core + core electrons):

$$\Delta\vec{P}_{tot} = \Delta\vec{P}_e + \sum_i Z^i{}_{val}\,\Delta\vec{R}_i$$

Equivalent formulation in terms of Wannier functions

$$\vec{P}_e = -\frac{2e}{V_{cell}} \sum_{i=1}^{N/2} < W_i \,|\, \vec{r} \,|\, W_i >$$

The centers of the Wanniers are defined modulo ***R***

$$\vec{r}_i \rightarrow \vec{r}_i + \vec{R} \quad \text{with} \quad \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

and, therefore, the polarization is defined modulo a "quantum" of polarization.

$$\vec{P}_e \rightarrow \vec{P}_e \pm \frac{2e\vec{R}}{V_{cell}}$$

Why is interesting to calculate ΔP ?

*You can study ferroelectricity

*You can calculate the dynamical or effective Born charges, Z

$$Z^*_{j\alpha\beta} = \frac{dP_\alpha}{dR_{j\beta}} \simeq \frac{\Delta P_\alpha}{\Delta R_{j\beta}}$$

*With Z you can calculate the IR absorption

*With Z you can calculate the long-range part of the dynamical matrix and LO-TO splitting

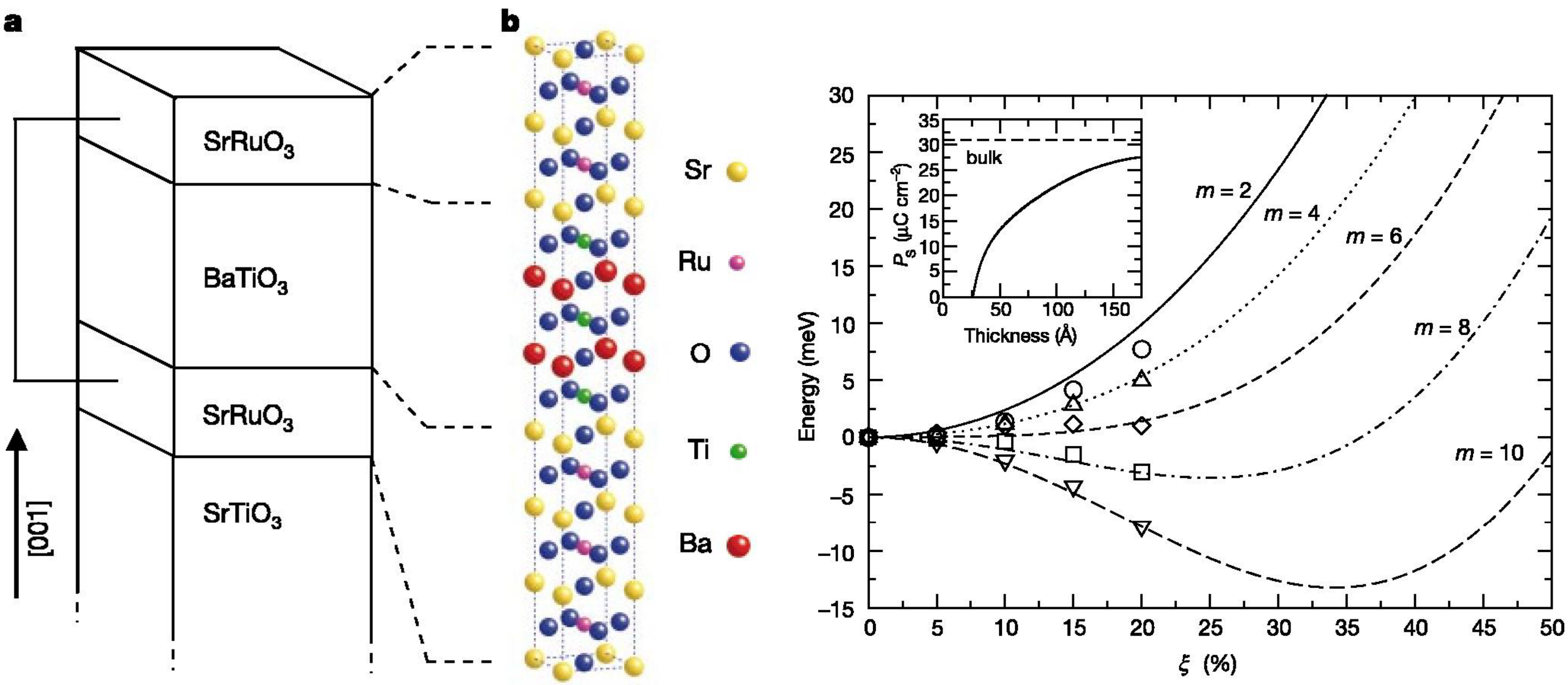
$$D_{\substack{mn\\ \mu\nu}}(\mathbf{q}) = D^{(0)}_{\substack{mn\\ \mu\nu}}(\mathbf{q}) + \frac{4\pi e^2}{\Omega} \frac{(\mathrm{Z}^*_m \cdot \hat{\mathbf{q}})_\mu (\mathrm{Z}^*_n \cdot \hat{\mathbf{q}})_\nu}{\epsilon_\infty(\mathbf{q})},$$

Dynamical charges in $BaTiO_3$

	$BaTiO_3$		
	SIESTA	PW[23]	PW[27]
$Z^{\star}_{A}$	+2.72	+2.74	+2.75
$Z^{\star}_{Ti}$	+7.60	+7.32	+7.16
$Z^{\star}_{O_{II}}$	-2.18	-2.14	-2.11
$Z^{\star}_{O_{I}}$	-5.96	-5.78	-5.69

Critical thickness of ferroelectric thin films

J. Junquera and P. Ghosez, Nature 422, 506 (2003)



SIESTA INPUT

PolarizationGrids:

$$P_{e,\|} = \frac{ifq_e}{8\pi^3} \int_A d\mathbf{k}_\perp \sum_{n=1}^{M} \int_0^{|G_\||} dk_\| \langle u_{\mathbf{k}n} | \frac{\delta}{\delta k_\|} | u_{\mathbf{k}n} \rangle$$

```
%block PolarizationGrids
    10    4    4
     4   10    4
     4    4   10
%endblock PolarizationGrids
```

SIESTA INPUT

BornCharge .true. (together with MD.TypeOfRun = FC)

The Born effective charge matrix is then written to the file SystemLabel.BC

We aware of the ambiguous definition of the polarization in the numerical calculation…..