

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

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# Acknowledgements

Nicola Spaldin  
UC Santa Barbara



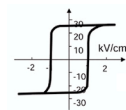
David Vanderbilt  
Rutgers University



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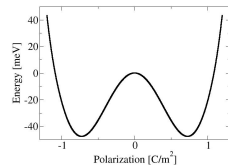
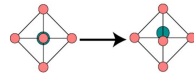
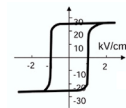
# Ferroelectrics: bulk

- Macroscopic description
  - Spontaneous  $P$ , switchable with  $\mathcal{E}$
- Microscopic mechanisms (e.g.  $\text{BaTiO}_3$ )
  - Unstable polar phonon mode
  - Subtle balance of long-range and short-range interactions



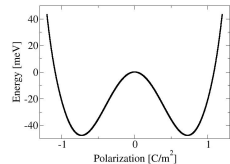
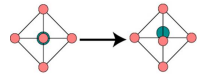
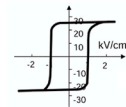
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*Collective phenomenon: does it survive in thin films?*

# Ferroelectrics: thin films

- Thin films desirable for applications
  - Ferroelectric memories
  - Gate dielectrics

However:

- Strong size effects
  - Polarization is reduced  
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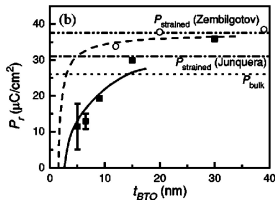
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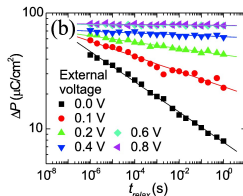
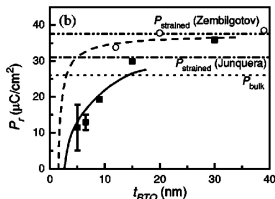


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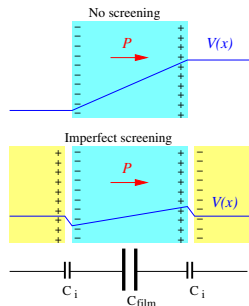
# What is the origin of the problem?

- Strong dependence on electrical boundary conditions
  - No screening: uniform  $P$  is suppressed by *depolarizing field*
  - Imperfect screening:  $P$  might be allowed *if thick enough*
  - Popular explanation: Intrinsic interface effect, Thomas-Fermi model

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## This talk:

- Interfacial capacitance  $C_i$  depends critically on **chemical bonding**
- We can make  $C_i$  **negative**!



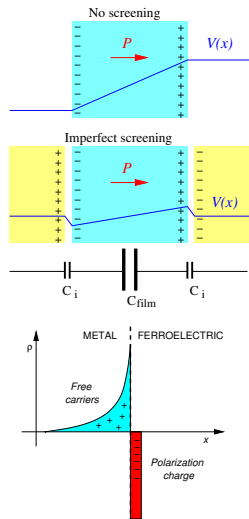
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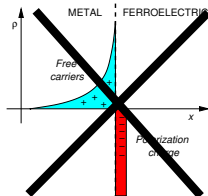
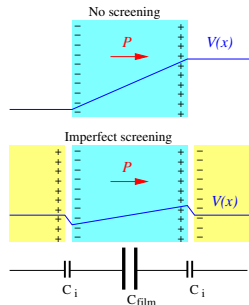
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# What theory to use?

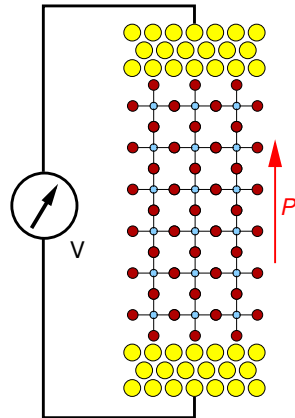
- Want a **microscopic** description of realistic metal-ferroelectric interfaces
  - Density-functional theory

$$E(\rho) = E_{Kinetic}(\rho) + E_{Hartree}(\rho) + E_{XC}(\rho)$$

- Want to calculate the **electrical properties** (e.g. polarization, capacitance, ...)
  - Finite electric fields, modern theory of polarization
  - Very recent developments...

M. Stengel and N. A. Spaldin, PRB 75, 205121 (2007).

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



# Outline

- 1 **Methods**
  - Finite electric fields
  - Metal/insulator heterostructures
  - Constrained- $D$  method
  
- 2 **Applications**
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# Finite fields in periodic solids

- Want to apply a uniform external electric field  $\mathcal{E}$
- **Idea:**

$$\mathcal{F}(\rho, \mathcal{E}) = E(\rho) + \int \rho(\mathbf{r}) V(\mathbf{r}) d^3r, \quad V(\mathbf{r}) = -\mathcal{E} \cdot \mathbf{r}$$

- The scalar potential is not periodic

- Finite potential drop  $\Delta V$

Solution:

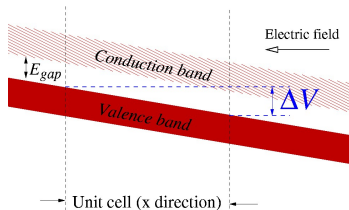
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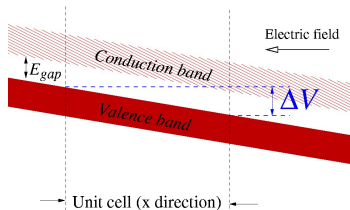
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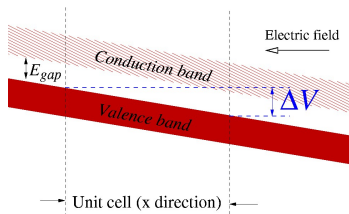
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- $P$  defined as a Berry phase

King-Smith and Vanderbilt, PRB 47, 1651 (1993); Resta, Ferroelectrics 136, 51 (1992).

# Finite fields in periodic solids



- The scalar potential is not periodic
  - Finite potential drop  $\Delta V$
- Solution:
  - Electric enthalpy:
 
$$\mathcal{F}(\mathcal{E}) = E_{KS} - \Omega \mathcal{E} \cdot \mathbf{P}$$
- There is no electronic ground state

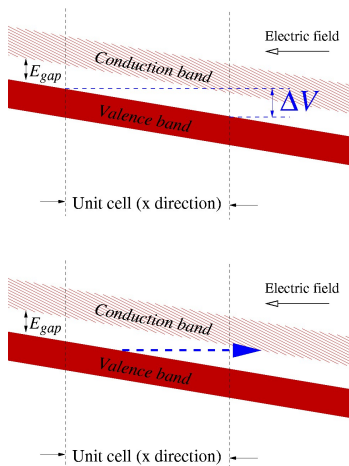
• Zener tunneling instability

Solution:

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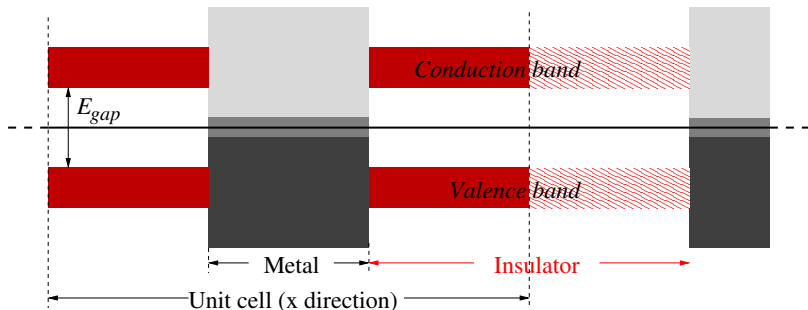
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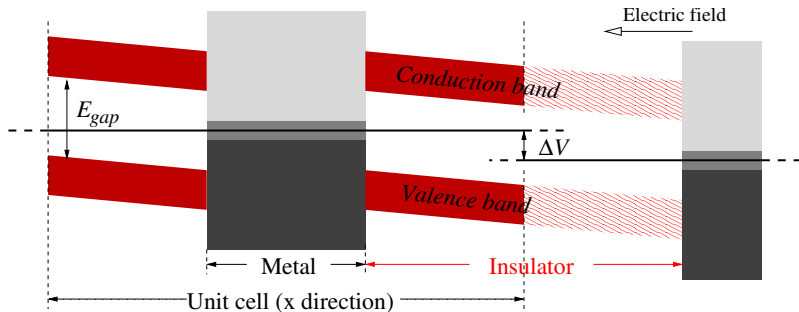
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  - Constrained- $D$  method
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# Metal-insulator heterostructures



- *Conducting* in plane, *insulating* along  $x$
- I should be able to apply a finite bias potential...

# Capacitors at finite $\mathcal{E}$



- $P$  and coupling to  $\mathcal{E}$  defined with Wannier functions
- The metastable polarized state is well defined as long as  $\Delta V < E_{gap}$  (no Schottky tunneling)

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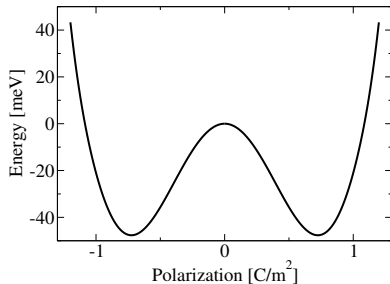
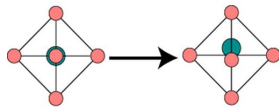
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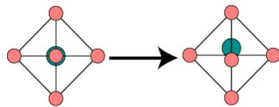
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- Double-well potential
  - Start from  $P = 0$
  - Apply a small  $\mathcal{E}$  field
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  - I cannot access the unstable region!

This region is necessary for modeling, so the answer is NO



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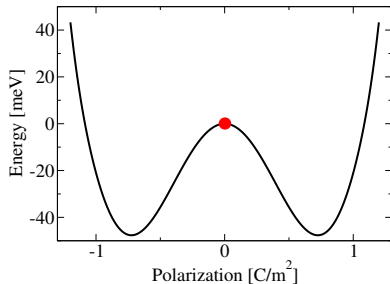
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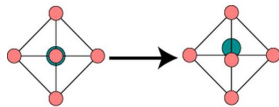
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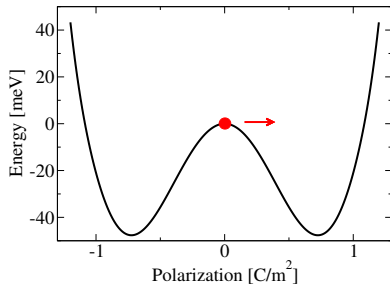
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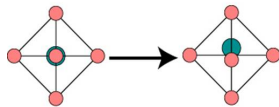
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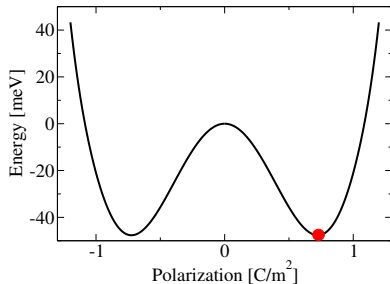
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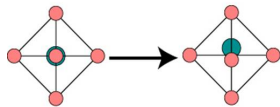
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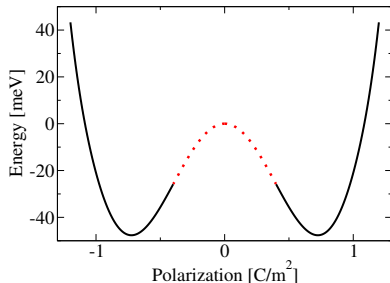
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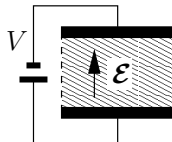


Idea: Try constraining  $D = \mathcal{E} + 4\pi P$  instead...

# Solution: Fixed- $D$ method

- Linear coupling  $\rightarrow$  Fixed- $\mathcal{E}$

- $\mathcal{F}(\mathcal{E}) = \min_v \left\{ E_{KS}(v) - \Omega \mathcal{E} \cdot \mathbf{P}(v) \right\}$
- Closed-circuit capacitor at given  $V$



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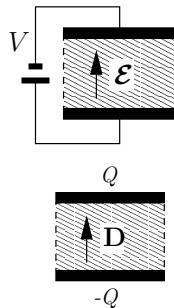
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M. Stengel, N. Spaldin and D. Vanderbilt, Nature Physics 5, 304 (2009).

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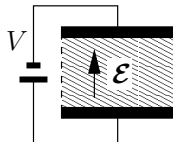
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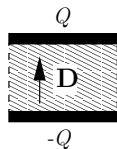
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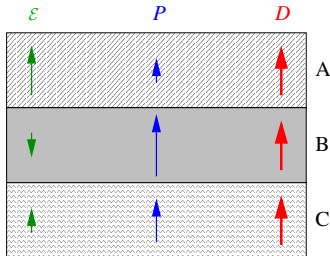
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# Further advantages of using $D$ : “locality principle”

- $D$  is **constant** throughout a layered heterostructure...

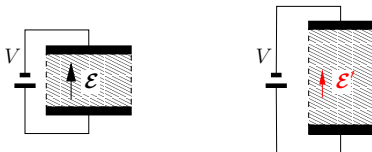


- ...if we know A, B and C we can predict ABC!

$$U_{ABC}(D) = U_A(D) + U_B(D) + U_C(D)$$

*Quantum theory + “old-school” electrostatics*

# Piezoelectricity: treatment of strains



- $V$  or  $Q$  remain constant under an applied strain, **not**  $\mathcal{E}$  or  $\mathbf{D}$ 
  - “Proper” treatment of piezoelectric effects
- Relationship to the fields:  $V = \mathcal{E} \cdot \mathbf{a}_3$ ,  $Q = \frac{\mathbf{D} \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}{4\pi}$
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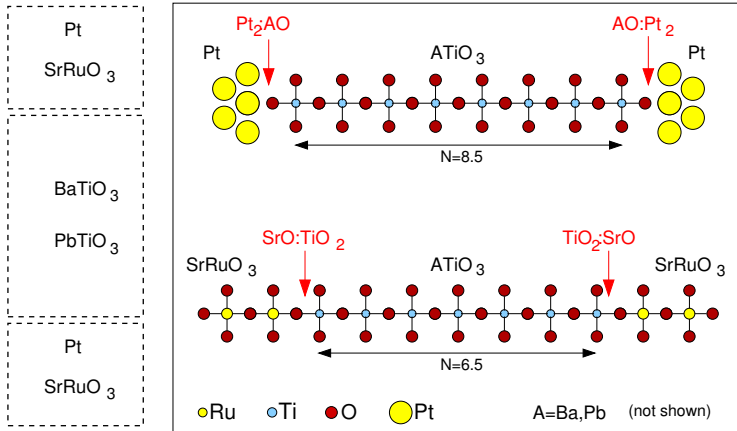


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# Computational models: four capacitors





# Stability of the paraelectric state

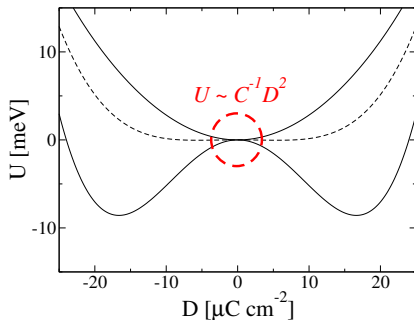
- Inverse capacitance

$$C^{-1} = \left( \frac{4\pi}{S} \right)^2 \frac{d^2 U}{dD^2} \Big|_{D=0}$$

- Stability against polar distortion
  - $C^{-1} > 0 \rightarrow$  stable
  - $C^{-1} < 0 \rightarrow$  unstable

- Results for  $C^{-1} S$  [ $\text{m}^2/\text{F}$ ]

*Impact of bulk vs. interface effects?*



	SrRuO <sub>3</sub>	Pt
PbTiO <sub>3</sub>	0.44	-1.43
BaTiO <sub>3</sub>	-1.55	-7.92

# Local dielectric response: ferroelectric regime

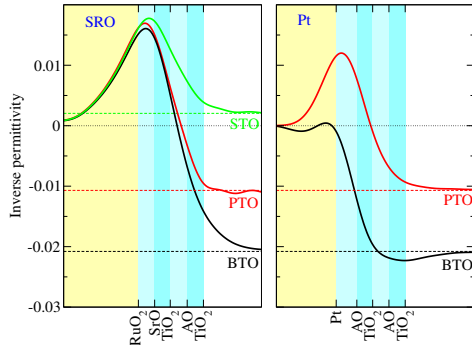
$$\text{Inverse permittivity profile: } \epsilon^{-1}(z) = \left. \frac{d\mathcal{E}(z)}{dD} \right|_{D=0}$$

- Strong intrinsic effect, localized at the interface
- Series capacitor model  

$$C^{-1} = 2C_I^{-1} + NC_{\text{bulk}}^{-1}$$
- Interface term  $C_I^{-1}$ :

	SrRuO <sub>3</sub>	Pt
PbTiO <sub>3</sub>	1.73	1.26
BaTiO <sub>3</sub>	2.28	0.04

Units of inv. capacitance density, m<sup>2</sup>/F



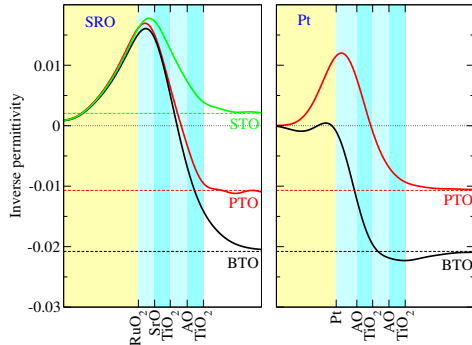
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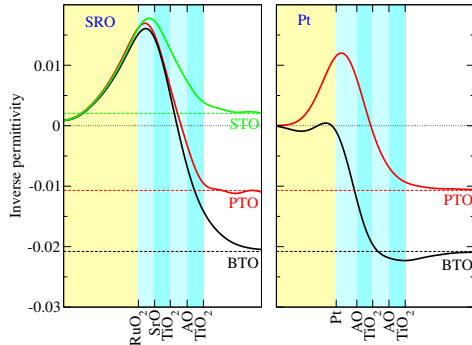
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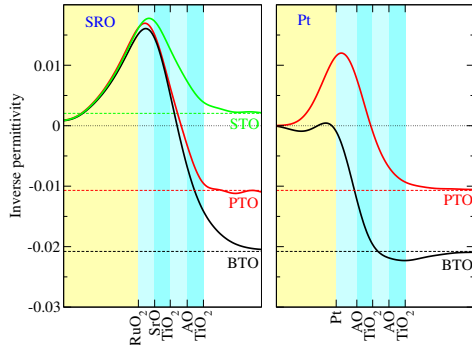
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# Critical thickness for ferroelectricity

- Series capacitor model:

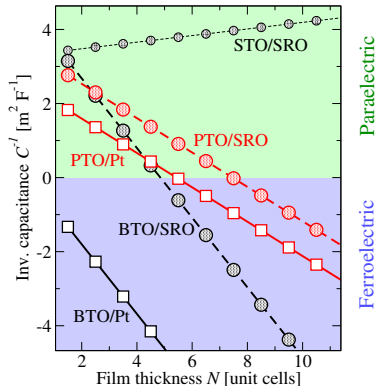
$$C^{-1}(N) = 2C_l^{-1} + NC_{\text{bulk}}^{-1}$$

- Critical thickness for FE:

$$C^{-1} = 0 \Rightarrow N_{\text{crit}} = -\frac{2C_l^{-1}}{C_{\text{bulk}}^{-1}}$$

	SRO	Pt
PbTiO <sub>3</sub>	8	6
BaTiO <sub>3</sub>	5	0

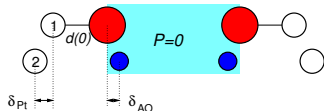
Thickness in number of unit cells



$N_{\text{crit}} = 0$  in BaTiO<sub>3</sub>/Pt?!

# Chemical bonding at the AO-Pt interface

- AO-terminated interfaces
  - Both O and A in the *atop* site
- Frustrated bonding environment, two competing effects:
  - Pt-O attraction (bonding)
  - Pt-A repulsion (non-bonding)



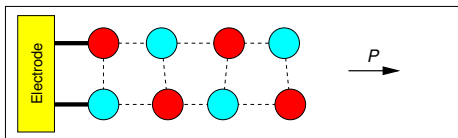
	$d$ (Å)	$\delta_{\text{Pt}}$ (Å)	$\delta_{\text{AO}}$ (Å)
A=Ba	2.26	0.46	0.12
A=Pb	2.11	0.34	0.19

Pt-O  $\sim$  2.0 Å in bulk oxide phases

# Interface bonding and ferroelectricity

## Idea:

- “Loose” interface bonds favor  $P$



- Force constants at the interface:

	PbTiO <sub>3</sub>	BaTiO <sub>3</sub>
$-K_{Pt-O}^L$	3.9	-0.1

$$(K_{ij} = \frac{\partial^2 U}{\partial z_i \partial z_j}, \text{ units of } 10^{-3} \text{ a.u.})$$

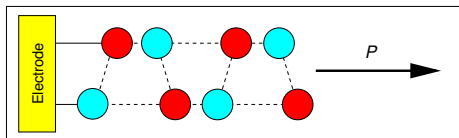
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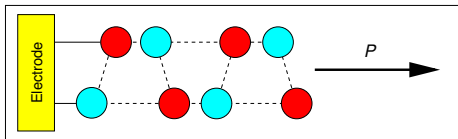
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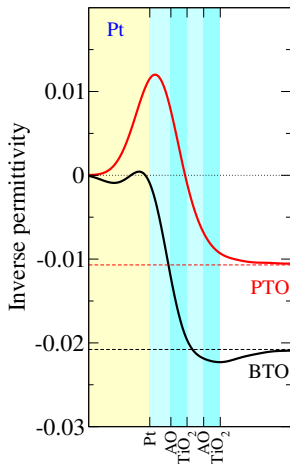


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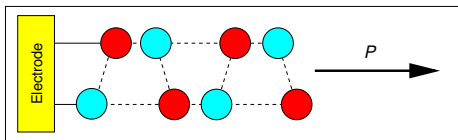
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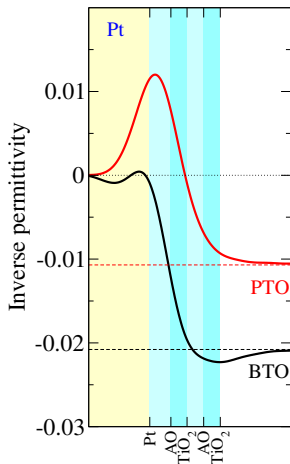


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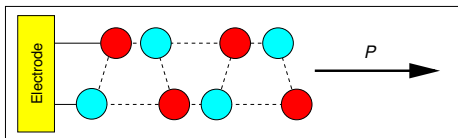
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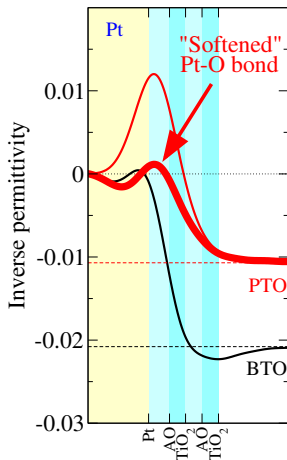


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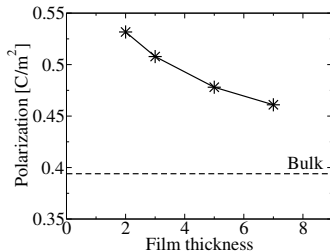
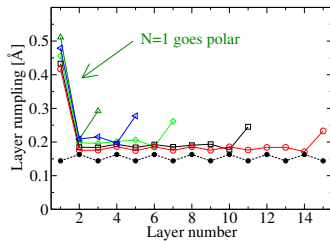
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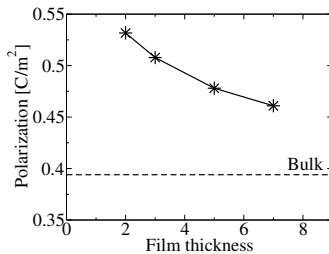
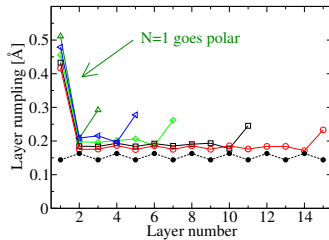
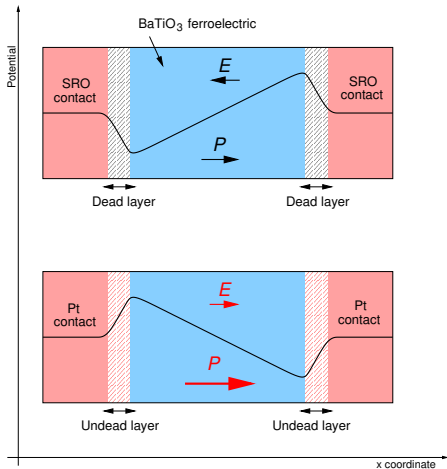
*Interface ferroelectricity driven by Pt-O bond!*

# What about the polar ground state?

- So far: paraelectric reference structure
- Out of curiosity: look at  $P$  in the ferroelectric state ( $\text{BaTiO}_3/\text{Pt}$ )
  - $N = 1, 2, 3, 5, 7$
  - Standard short-circuit
- Polarization and distortions **increase** the thinner the film
- Chemical bonding mechanism even **stronger in the FE state!**



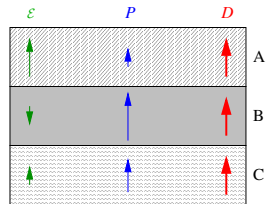
# “Negative dead layer” regime



# Summary

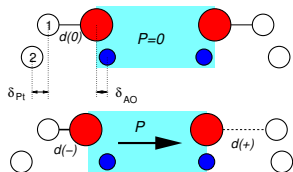
- Layer-by-layer device design via constrained- $D$  density-functional theory

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



- Enhancement of ferroelectricity driven by electrode-film bonding

M. Stengel, D. Vanderbilt and N. A. Spaldin,  
*Nature Materials* 8, 392 (2009).



# Microscopic analysis of $C^{-1}$

- Decomposition into LO polar modes

$$C^{-1} = (C^\infty)^{-1} - \left(\frac{4\pi}{S}\right)^2 \sum_{ij} Z_{i,x}^L (K^L)_{ij}^{-1} Z_{j,x}^L$$

- Three basic ingredients:

1. Electronic capacitance  $C^\infty$  (frozen ionic positions)
2. LO dynamical charges  $Z^L$  (lattice-electric field coupling)
3. Interatomic force constants  $K_{ij}^L$  (bond “stiffness”)



# Purely electronic effects ( $C^\infty$ and $Z^L$ )

- $C^\infty$  (frozen ions) depends on center of induced  $\rho$

*PTO/Pt better than BTO/Pt!*

- Dynamical charges are smaller near the interface

*PTO/Pt similar to BTO/Pt!*

