Electric fields, Wannier centers, and nonlinear dielectric response in perovskite superlattices

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Principal Collaborators

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Na Sai
Xifan Wu
Massimiliano Stengel

Karin Rabe

First-principles calculations

Throughout the talk:

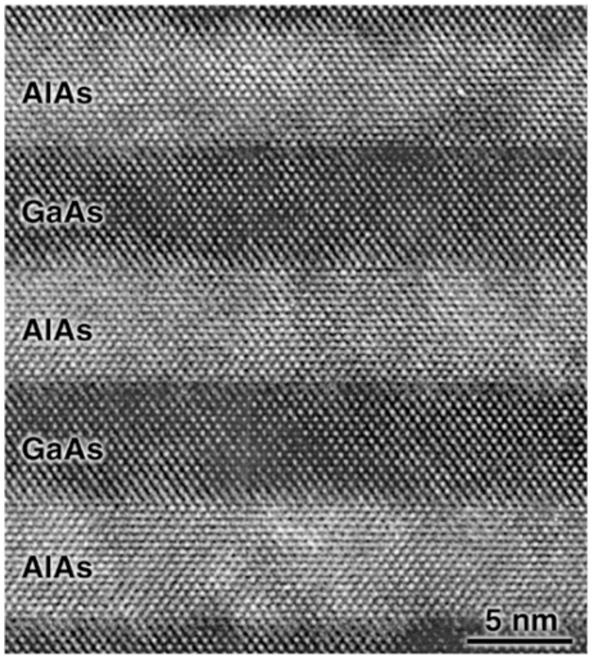
- Density-functional theory
- Local-density approximation
- Plane-wave pseudopotential approach
- ABINIT, VASP, PWSCF packages

Outline

- Introduction
  - Epitaxial perovskite superlattices
  - Unusual dielectric properties
- Theory of nonlinear dielectric behavior
  - Finite electric field $\mathcal{E}$
  - Mapping $E(P)$
  - Electric equations of state: $P(\mathcal{E})$, $\mathcal{E}(P)$, $P(D)$, etc.
  - Layer-by-layer spatial resolution of P
- Work in progress: Model for $P(D)$ of superlattice
- Summary and conclusions

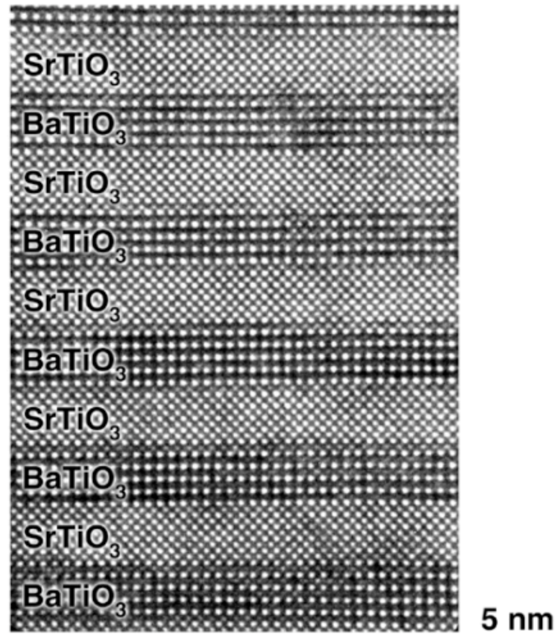
Advances in epitaxial growth

AlAs / GaAs Superlattice



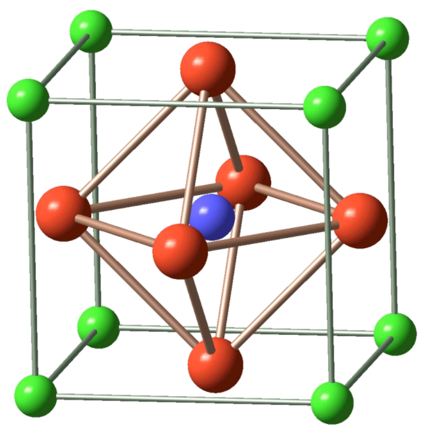
A. K. Gutakovskii *et al.*,
Phys. Stat. Sol. (a) **150** (1995) 127.

$BaTiO_3$ / $SrTiO_3$ Superlattice

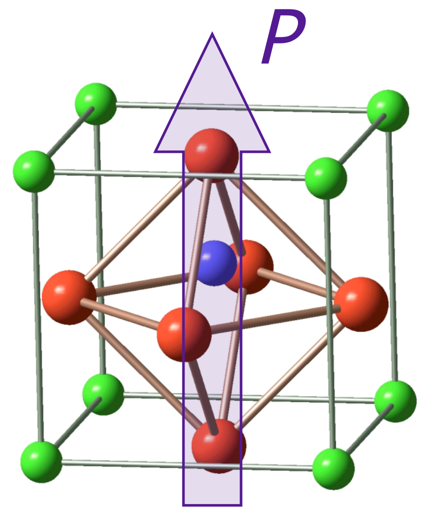


Film – Schlom Group (Penn State)
HRTEM – Pan Group (Univ. Michigan)

Cubic perovskite family



Paraelectric



Ferroelectric

<u>Examples</u>:

STO = $SrTiO_3$

BTO = $BaTiO_3$

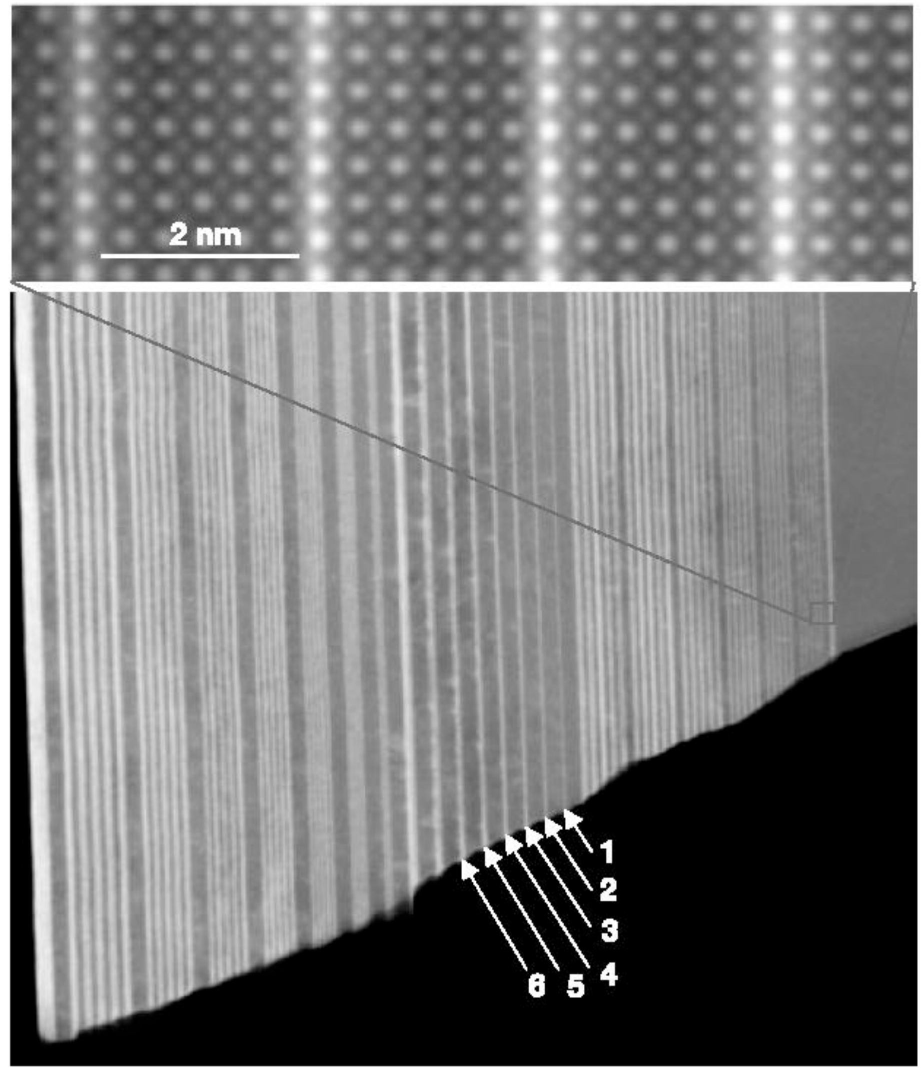
Advances in epitaxial growth

Artificial charge-modulation in atomic-scale perovskite titanate superlattices

A. Ohtomo, D. A. Muller, J. L. Grazul & H. Y. Hwang

Nature 419, 378 (2002).

$SrTiO_3$ / $LaTiO_3$

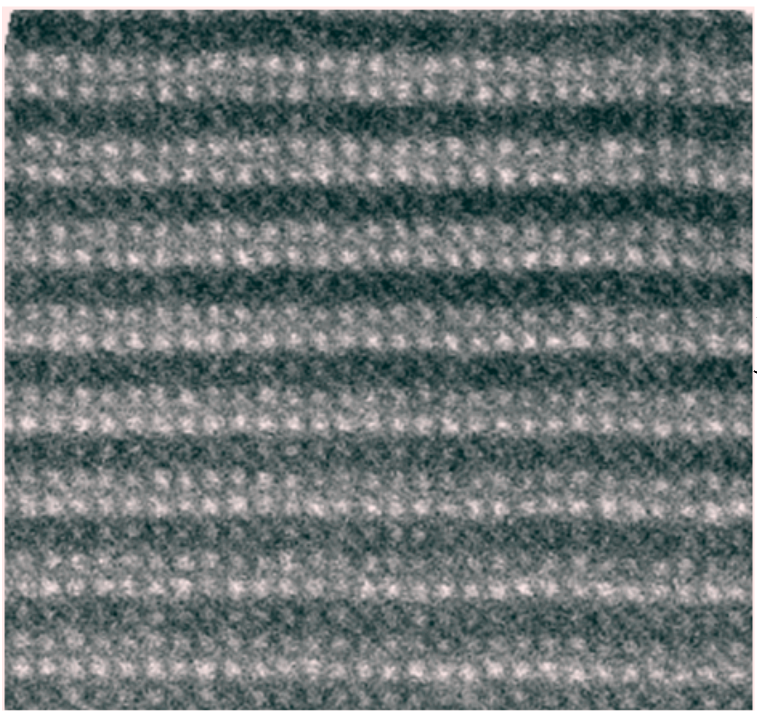


Advances in epitaxial growth

VOLUME 90, NUMBER 3 PHYSICAL REVIEW LETTERS week ending 24 JANUARY 2003

Artificial Dielectric Superlattices with Broken Inversion Symmetry

Maitri P. Warusawithana, Eugene V. Colla, J. N. Eckstein, and M. B. Weissman
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080
(Received 24 May 2002; published 24 January 2003)



High-resolution Z-contrast STEM:
J. Zuo and H. Chen, MSE at UIUC

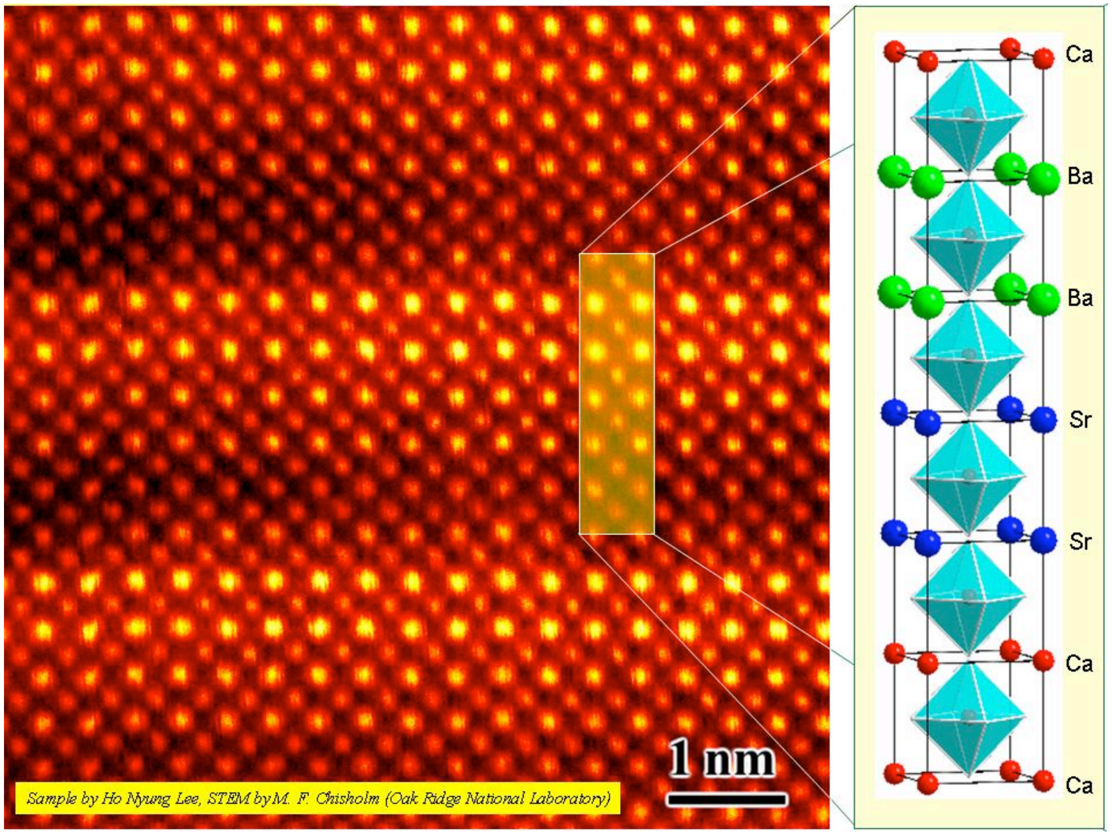
See also Sai, Meyer, and Vanderbilt, PRL **84**, 5636 (2000).

Advances in epitaxial growth

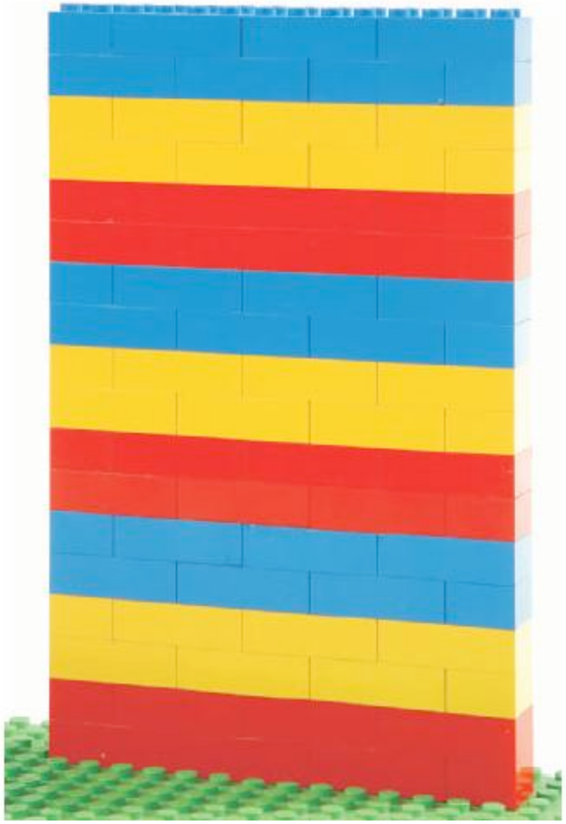
Strong polarization enhancement in asymmetric three-component ferroelectric superlattices

Ho Nyung Lee, Hans M. Christen, Matthew F. Chisholm, Christopher M. Rouleau & Douglas H. Lowndes

Nature 433, 395 (2005).



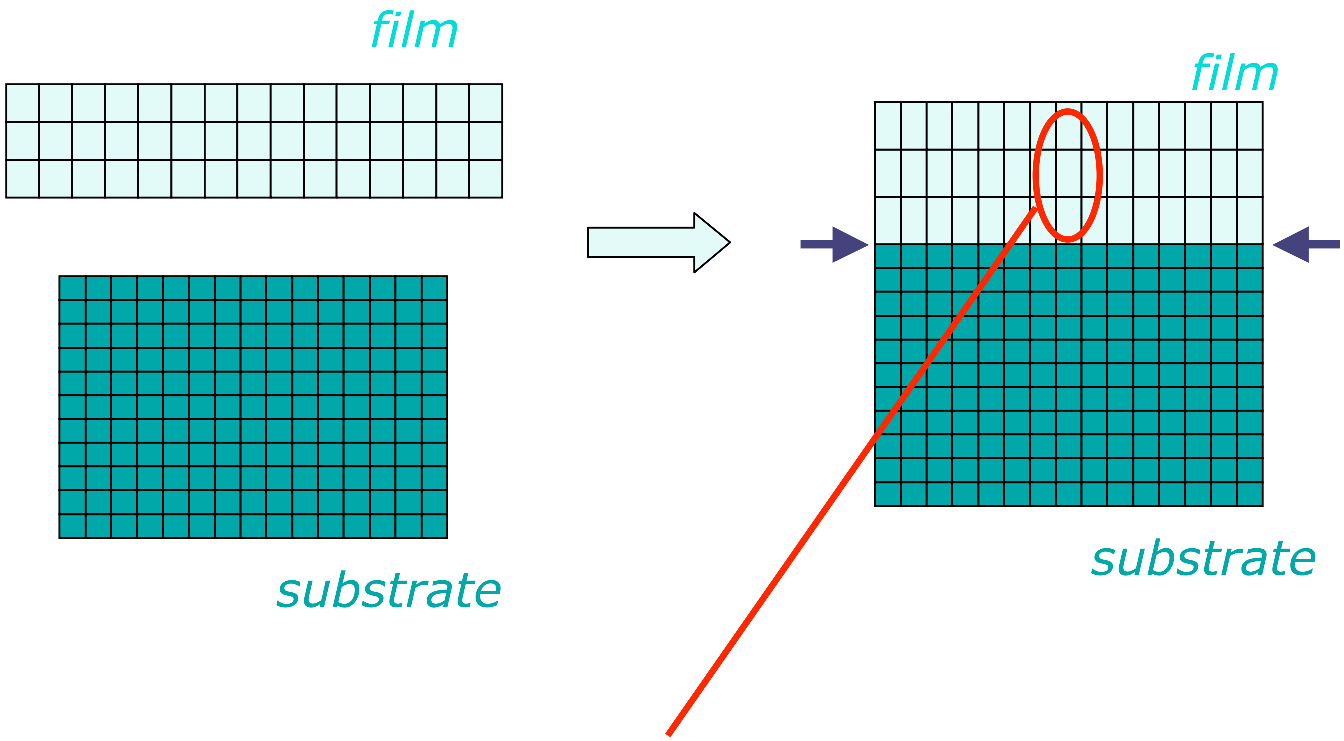
Advances in epitaxial growth



Courtesy H.-N. Lee

Exquisite control of epitaxy now possible !

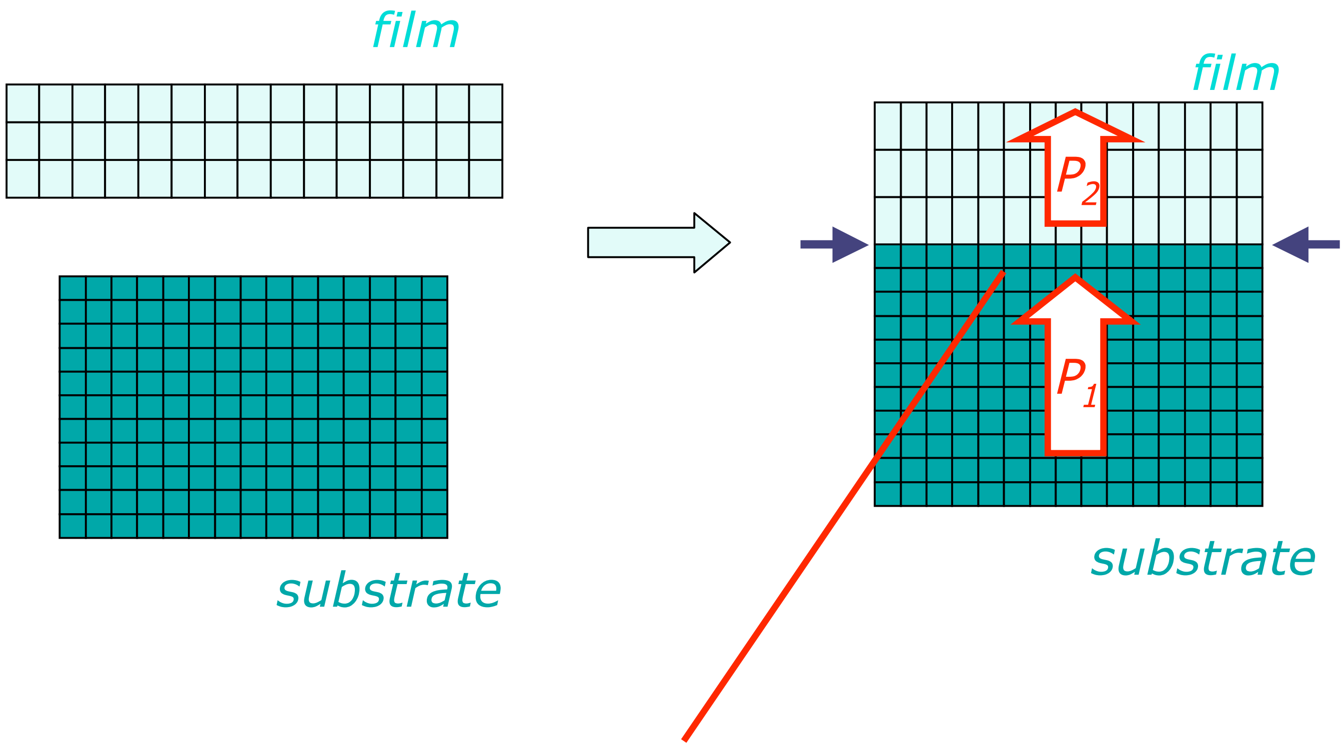
Epitaxy Constraints



Modifies ferroelectric behavior

(topic of another talk)

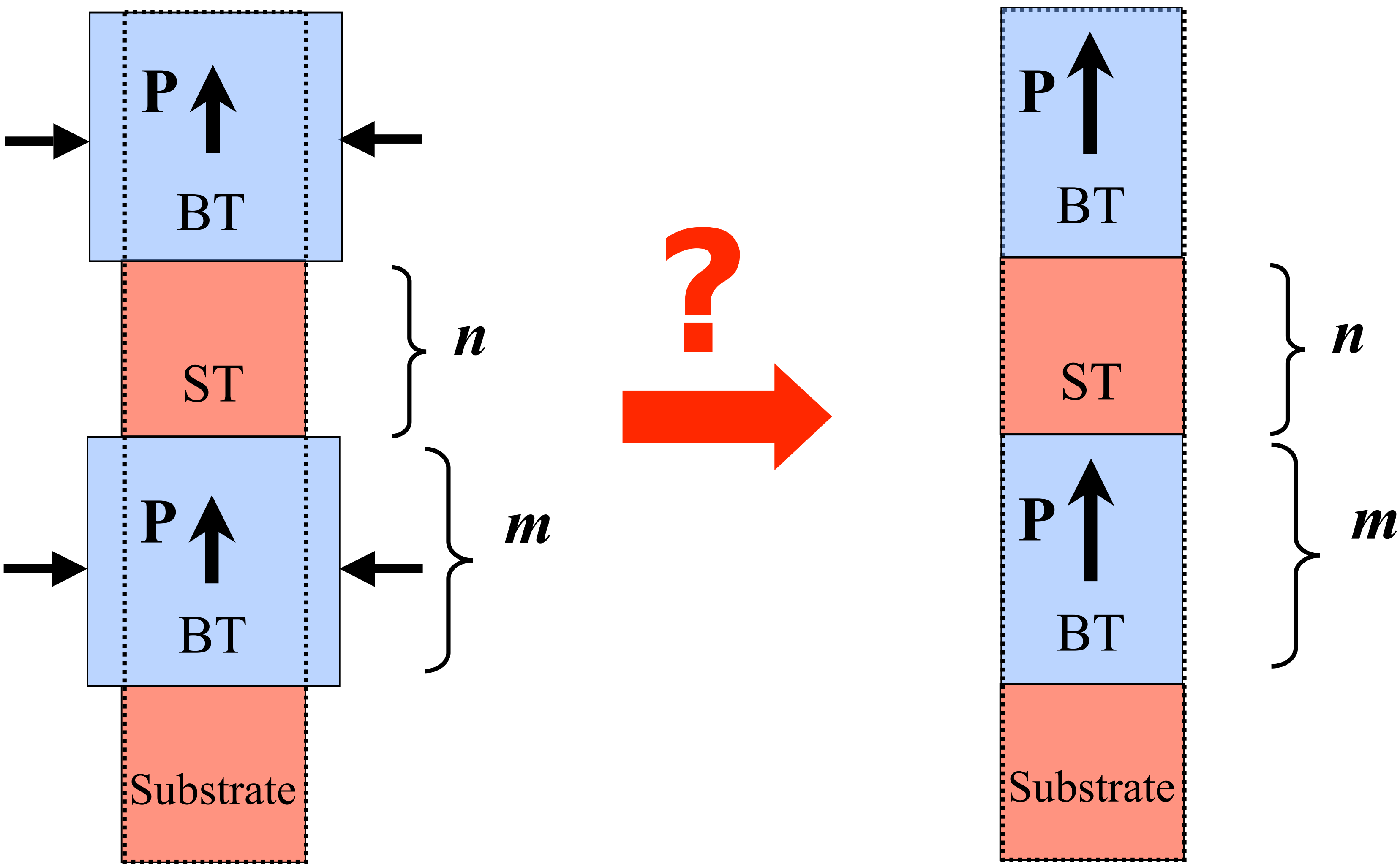
Electrical boundary conditions



Modifies ferroelectric behavior

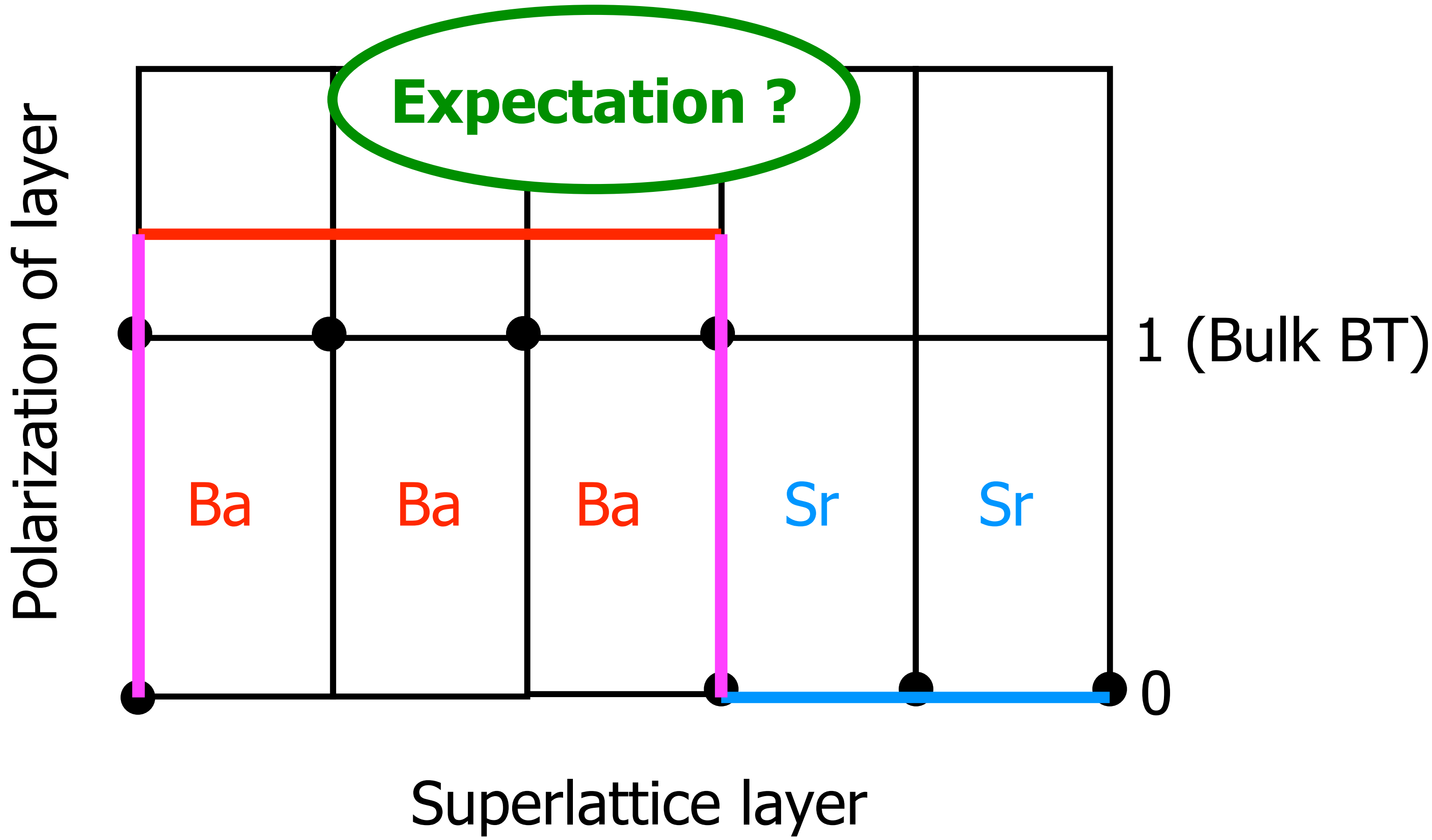
(topic of this talk!)

Example 1: BT/ST superlattices: Neaton & Rabe APL (2003)



Example 1: BT/ST superlattices: Neaton & Rabe APL (2003)

Example: m=3, n=2: …/Ba/Ba/Ba/Sr/Sr/…



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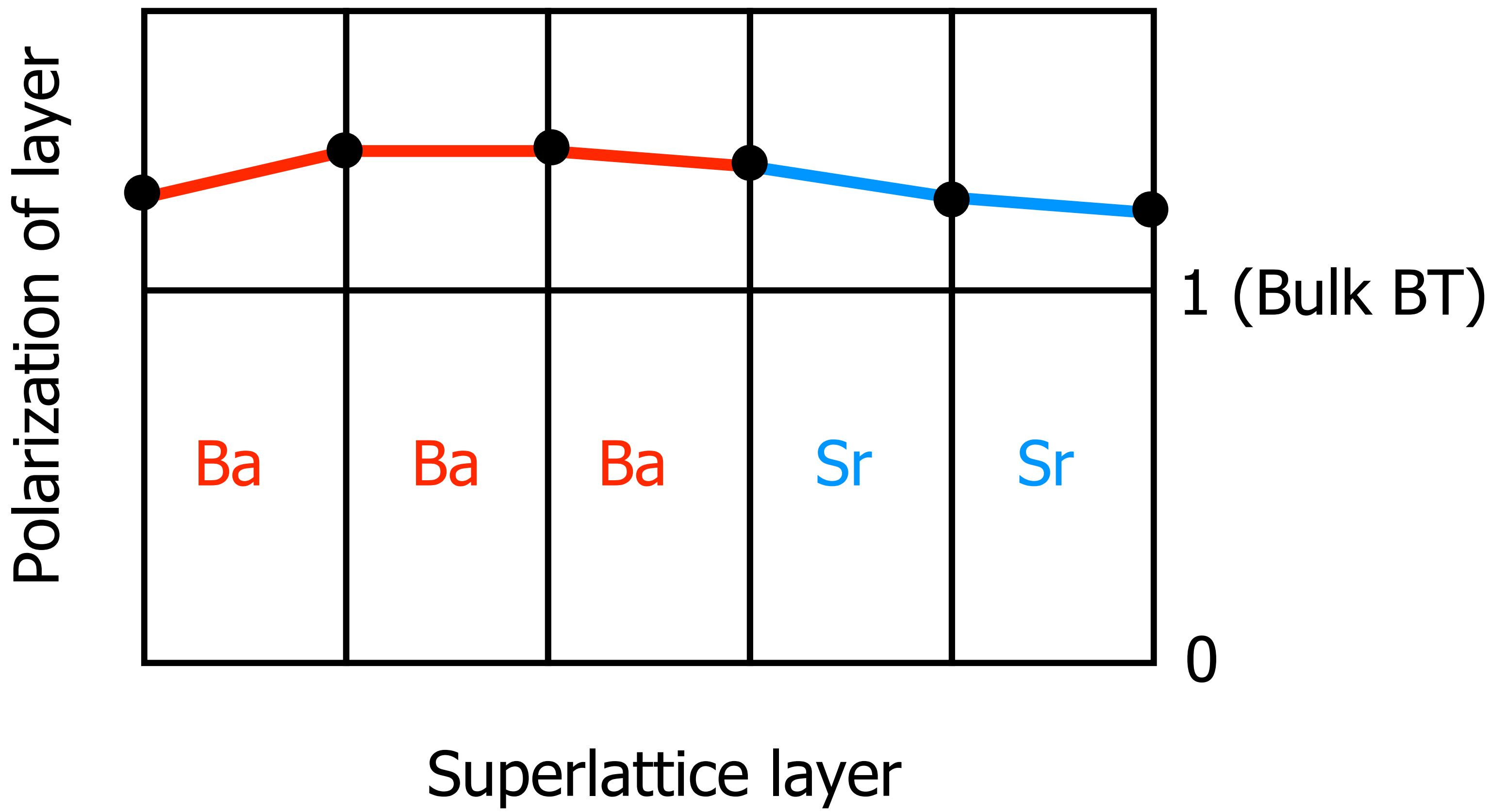
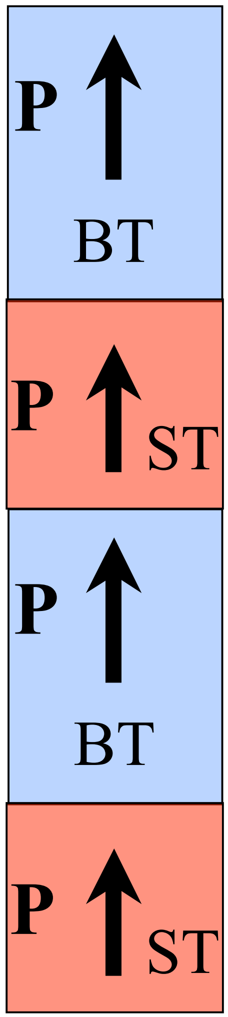
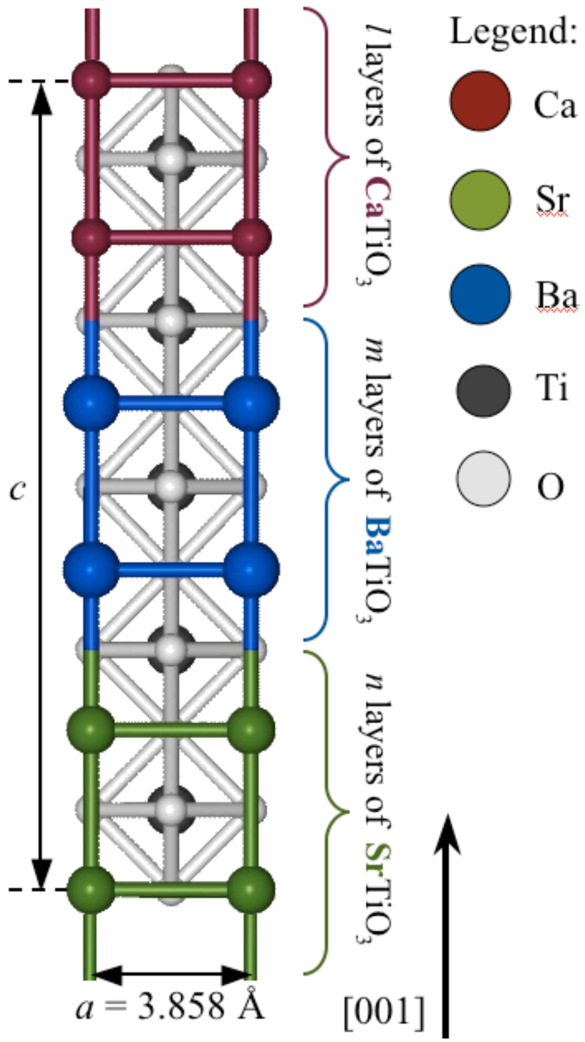


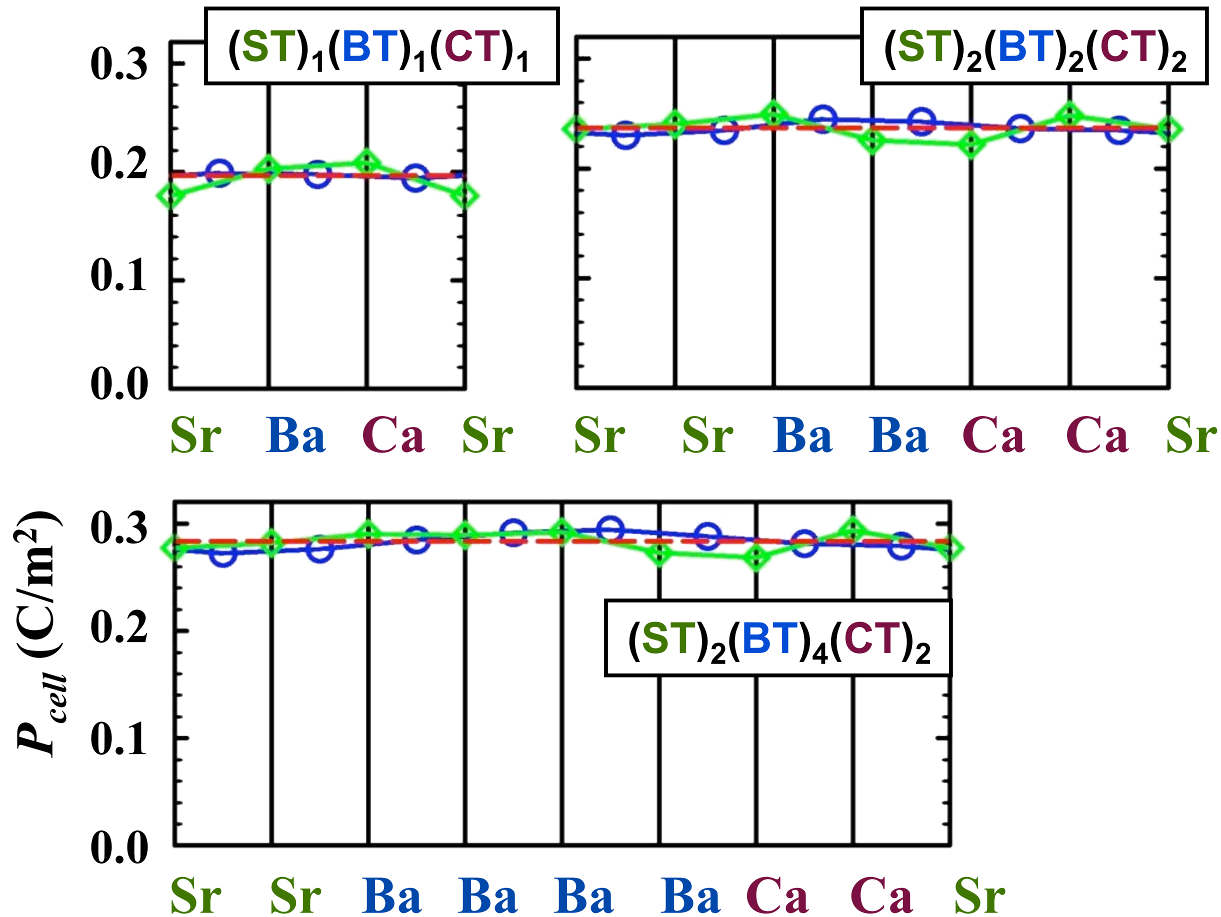
Example 1: BT/ST superlattices: Neaton & Rabe APL (2003)



$D_z = \varepsilon_0 \mathcal{E}_z + P_z$ constant

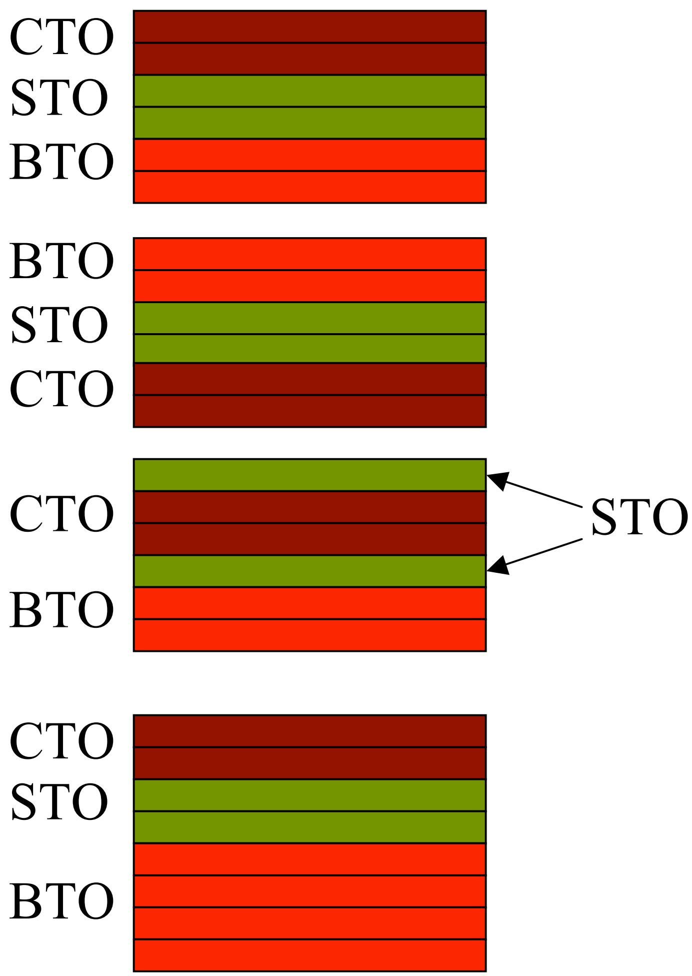
Nahkmanson, Rabe, & Vanderbilt, APL **87**, 102906 (2005).





$$P_{cell} \cong \frac{1}{V_{cell}} \sum_i Z_i^* \Delta u_i ,$$

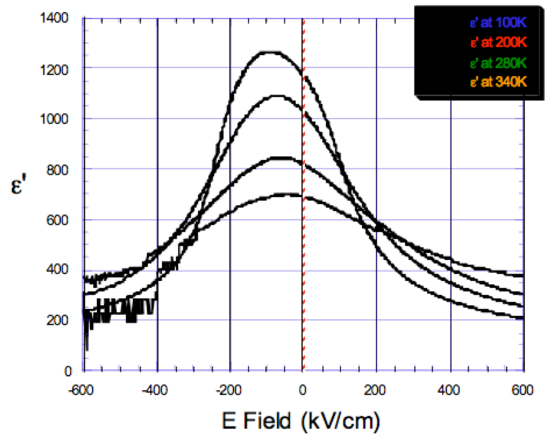
Example 2: Warusawithana, Colla, Eckstein, and Weissman, 2003



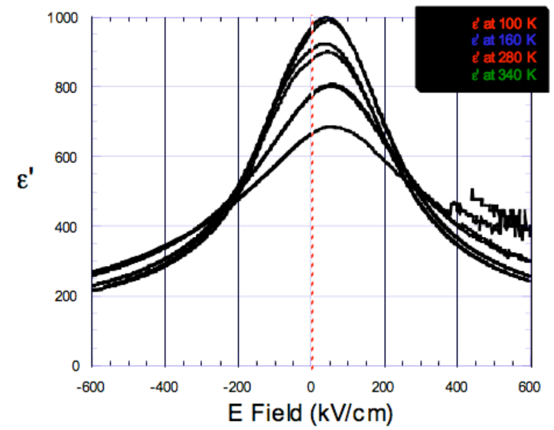
	Inversion symmetry?
222+	**NO**
222-	**NO**
1212	**YES**
422+	**NO**

Example 2: Warusawithana, Colla, Eckstein, and Weissman, 2003

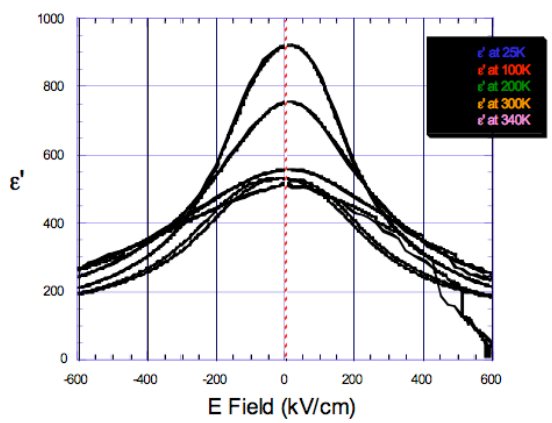
222+



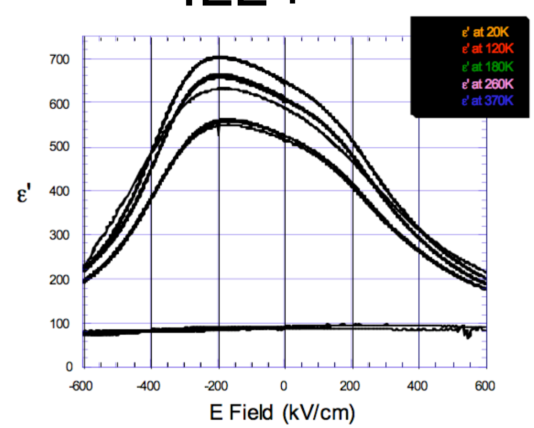
222-



1212



422+



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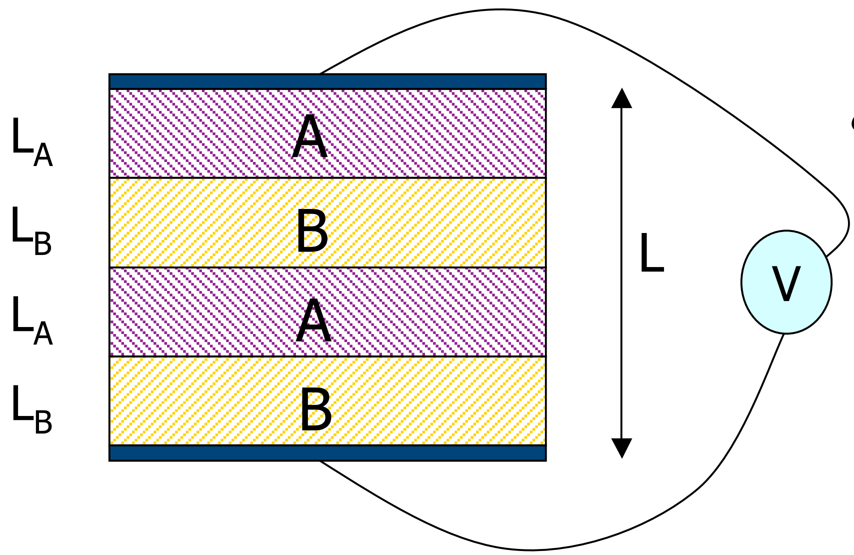
Desired theory should describe:



$$\mathcal{E} = \frac{V}{L}$$

P: Polarization
E: Energy
$\mathcal{E}$: Electric field
D: Displacement field

- Prediction of P_s by itself is not enough
- Want full $P(\mathcal{E})$ curve!

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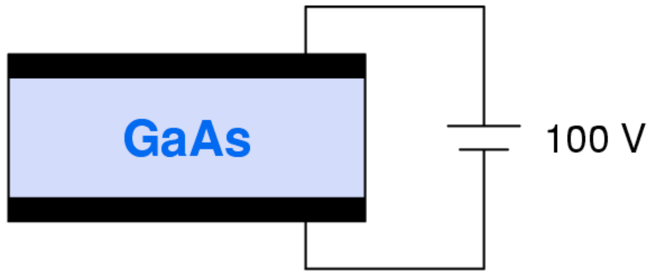
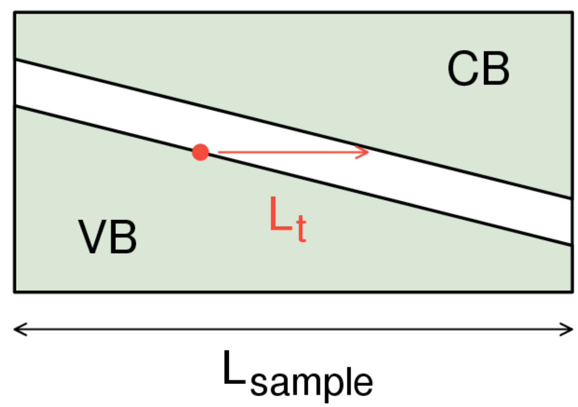
Electric Fields: The Problem

Easy to do in practice:



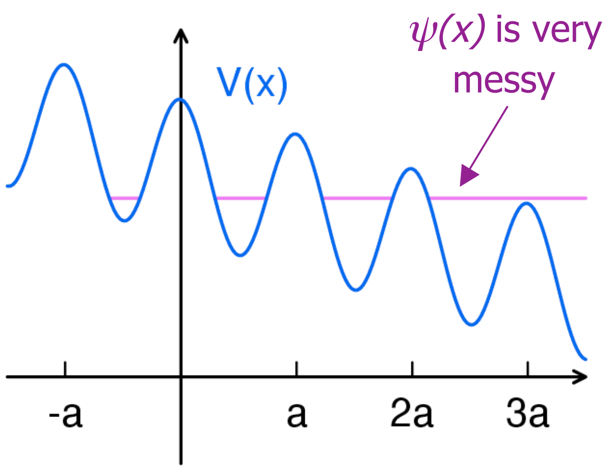
But ill-defined in principle:



Zener tunneling $\Rightarrow$ There is no ground state!

Electric Fields: The Problem

$$H = H_0 - e\,\mathcal{E}\,x$$
$$= \frac{P^2}{2m} + \widetilde{V}(x)\ , \quad \widetilde{V}(x) = V_{\rm per}(x) - e\,\mathcal{E}\,x$$

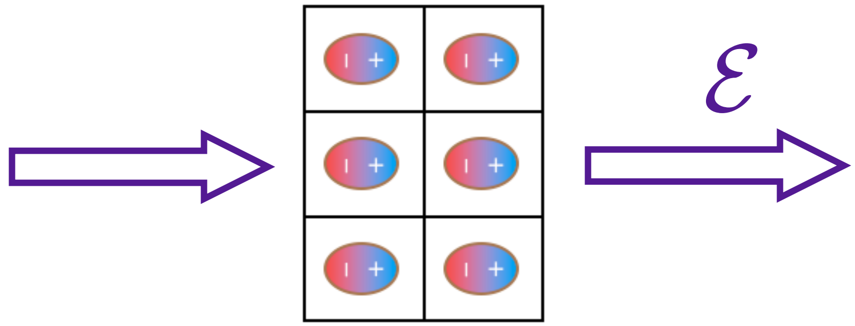


- $\widetilde{V}(x)$ is not periodic
- Bloch's theorem does not apply
- $\mathcal{E}$ acts as singular perturbation on eigenfunctions $\psi(x)$
- $\widetilde{V}(x)$ not bounded from below
- There is no ground state

Electric Fields: The Problem

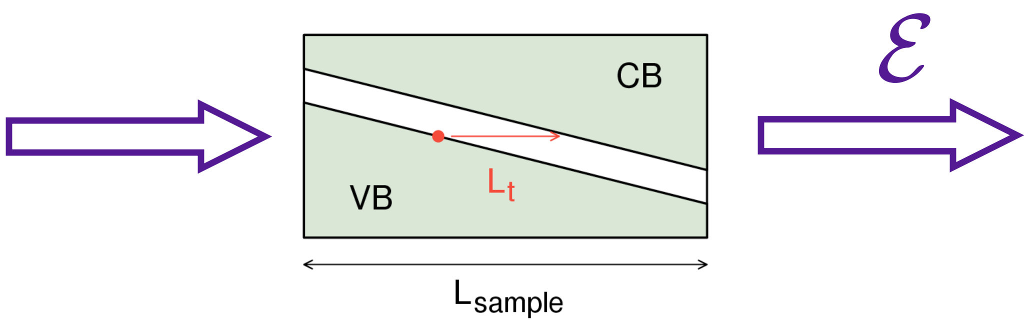
- Empirical and phenomenological approaches:

  No problem.



- First-principles approaches:

  Smart enough to become confused!



Electric Fields: The Solution

I. Souza, J. Iniguez, and D. Vanderbilt
"First-Principles Approach to Insulators in Finite Electric Fields"
Phys. Rev. Lett. 89, 117602 (2002).

- Seek long-lived resonance
- Described by Bloch functions
- Minimizing the electric enthalpy functional

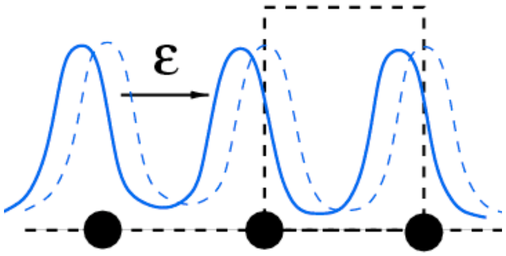
$$F = E - \mathcal{E} \cdot \mathbf{P}$$ *(Nunes and Gonze, 2001)*

$$E = \sum_{nk} \langle \psi_{nk} | T + V_{\mathrm{per}} | \psi_{nk} \rangle$$ ← Usual E_{KS}

$$\mathbf{P} = \mathbf{P}[\hat{n}] = \mathbf{P}[\{\psi_{nk}\}]$$ ← Berry phase polarization

- Justification:

Electric Fields: Justification



Seek long-lived metastable periodic solution

- Want periodic charge density:

$$\rho(\mathbf{r}) = \rho(\mathbf{r}+\mathbf{R})$$

- Want periodic one-particle density matrix:

$$n(\mathbf{r},\mathbf{r}') = n(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R})$$

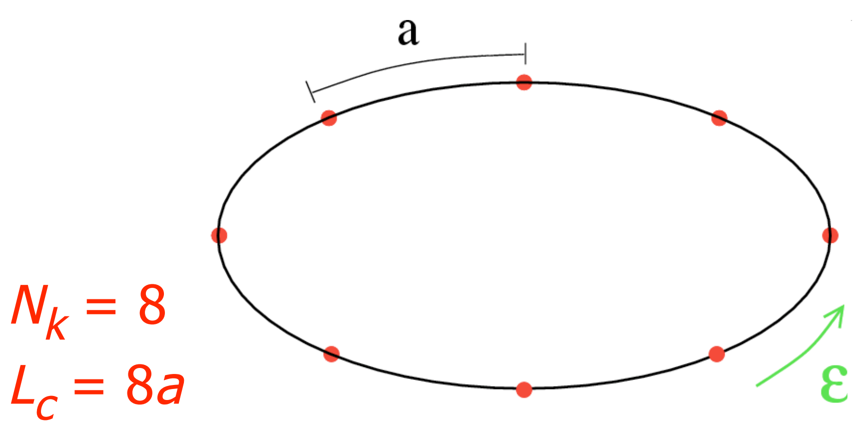
- Use Bloch representation of density matrix:

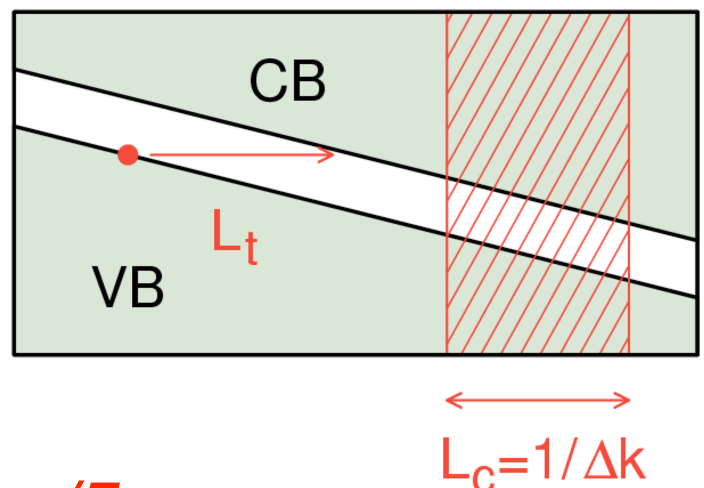
$$n(\mathbf{r},\mathbf{r}') = \sum_{n\mathbf{k}} \psi^*_{n\mathbf{k}}(\mathbf{r})\,\psi_{n\mathbf{k}}(\mathbf{r}')$$

even though $\psi_{n\mathbf{k}}$ are not eigenstates!

Electric Fields: Limitation

- There is a limitation!
- For given E-field, there is a limit on k-point sampling
- Length scale $L_C = 1/\Delta k$
- Meaning: L_C = supercell dimension



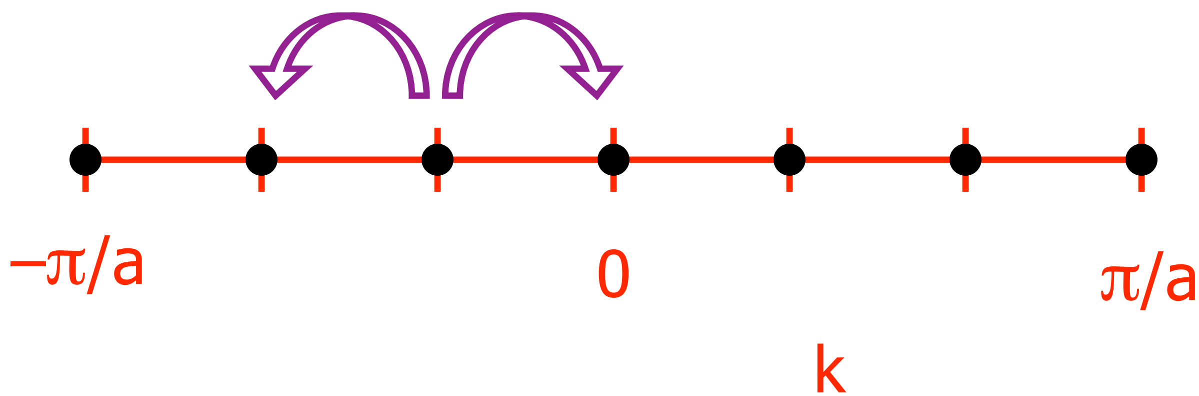


- Solution: Keep $\Delta k > 1/L_t = \varepsilon/E_g$

Electric Fields: Implementation

As long as Δk is not too small:

- Can use standard methods to find minimum
- The $\mathcal{E} \cdot P$ term introduces coupling between k-points



Sample Application: Born Z^*

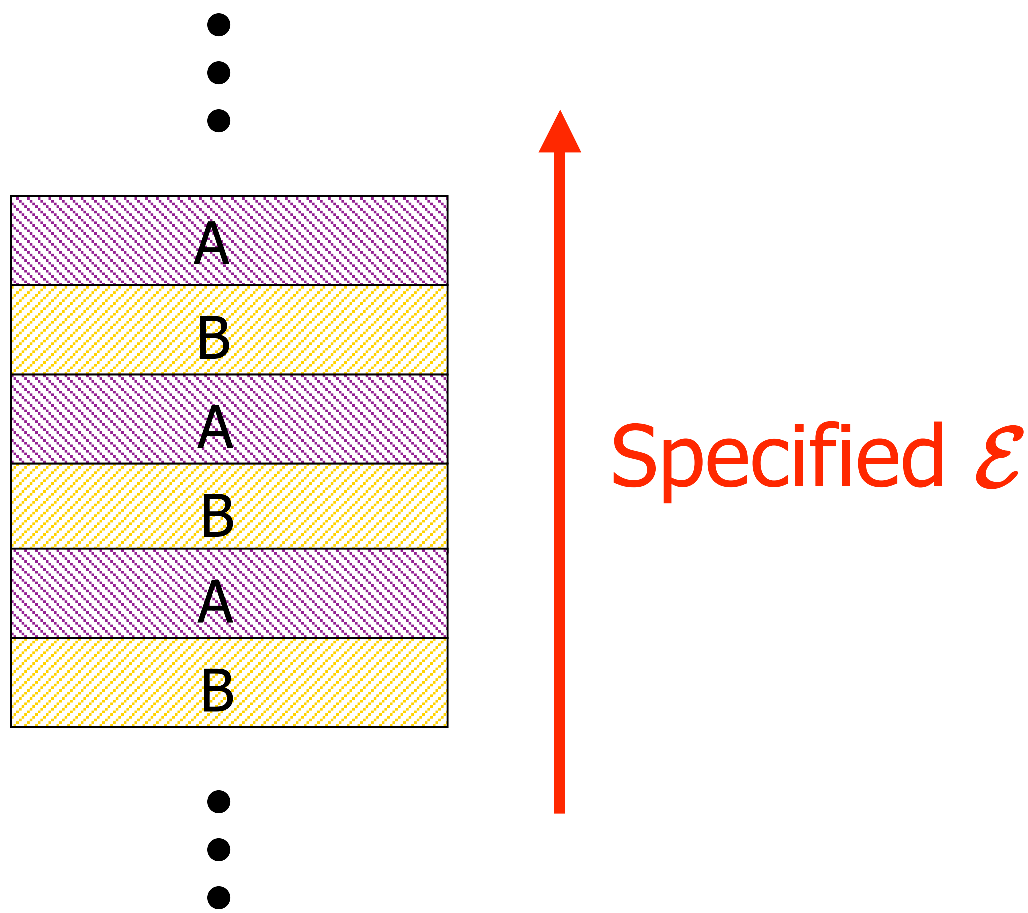
$$Z^*_{j\alpha\beta} = \frac{dP_\alpha}{dR_{j\beta}} \simeq \frac{\Delta P_\alpha}{\Delta R_{j\beta}}$$

$$Z^*_{j\alpha\beta} = \frac{dF_{j\beta}}{d\mathcal{E}_\alpha} \simeq \frac{\Delta F_{j\beta}}{\Delta \mathcal{E}_\alpha}$$

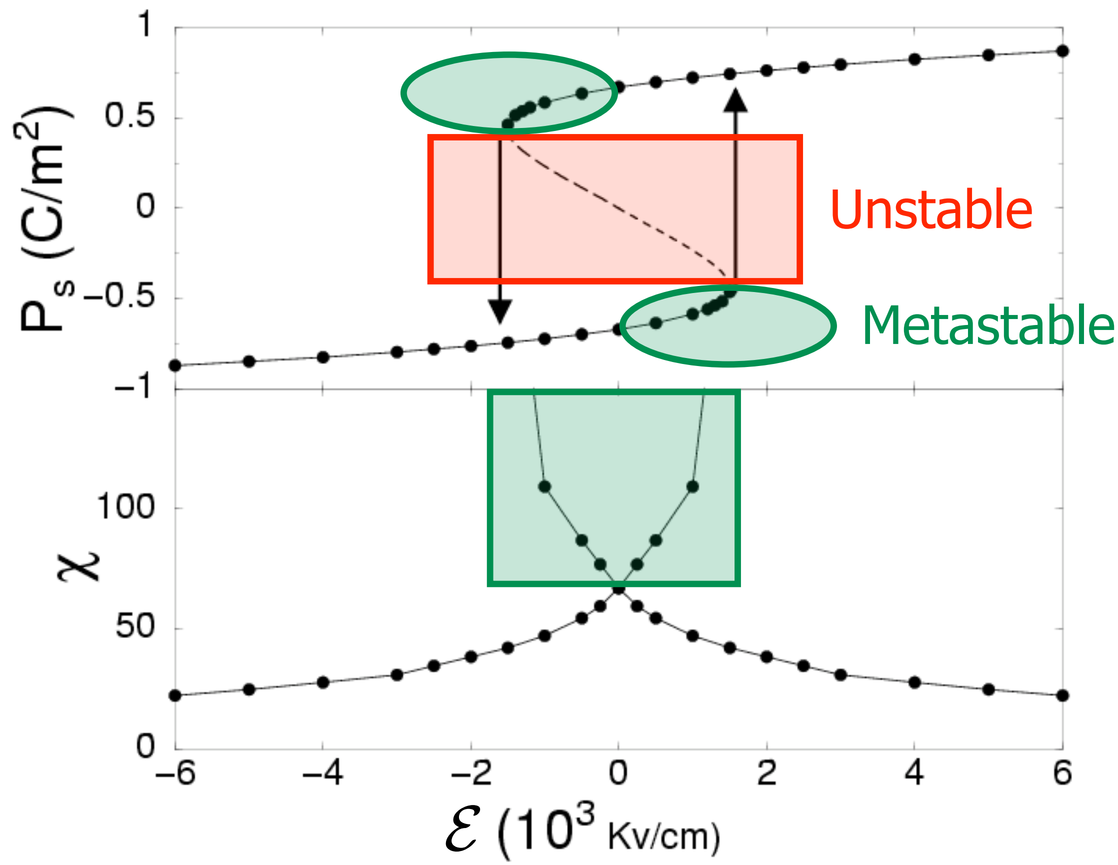
(Relation: $Z^*_{j\alpha\beta} = -\dfrac{d^2E}{d\mathcal{E}_\alpha\, dR_{j\beta}}$)

GaAs	AlAs	GaP	AlP	
2.07	2.18	2.04	2.28	(Literature values)
2.00	2.14	2.10	2.24	(Souza,Iniguez, & Vanderbilt, 2002)

We can now do calculations like this

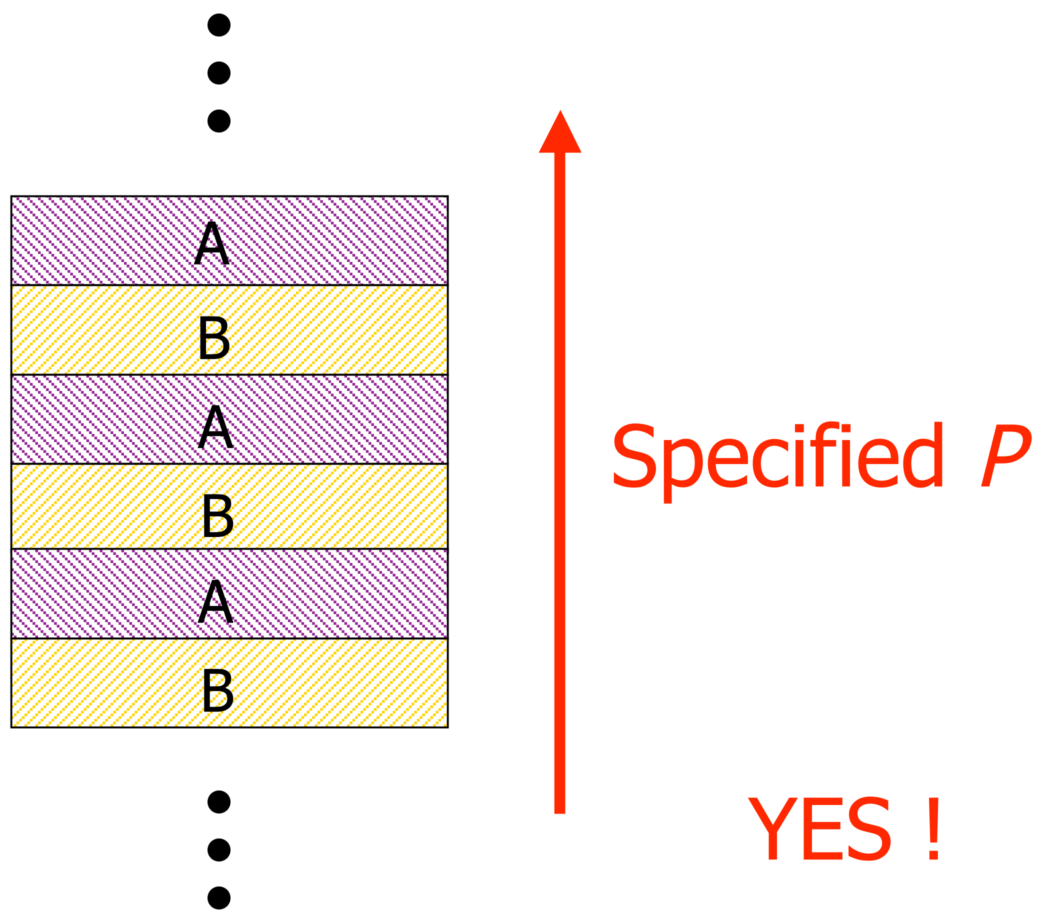


But $\mathcal{E}$ is not a good choice of dependent variable!



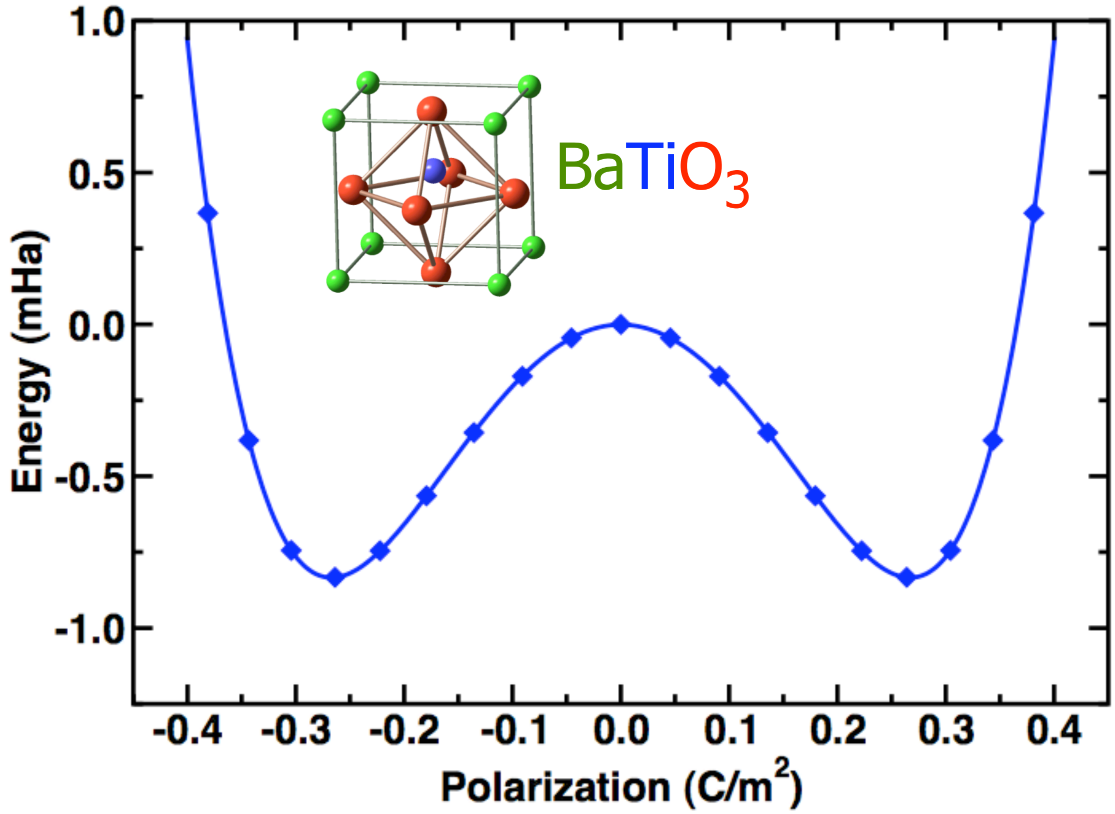
Sai, Rabe, and Vanderbilt, PRB **66**, 104108 (2002).

Can we do calculations like this?



YES !

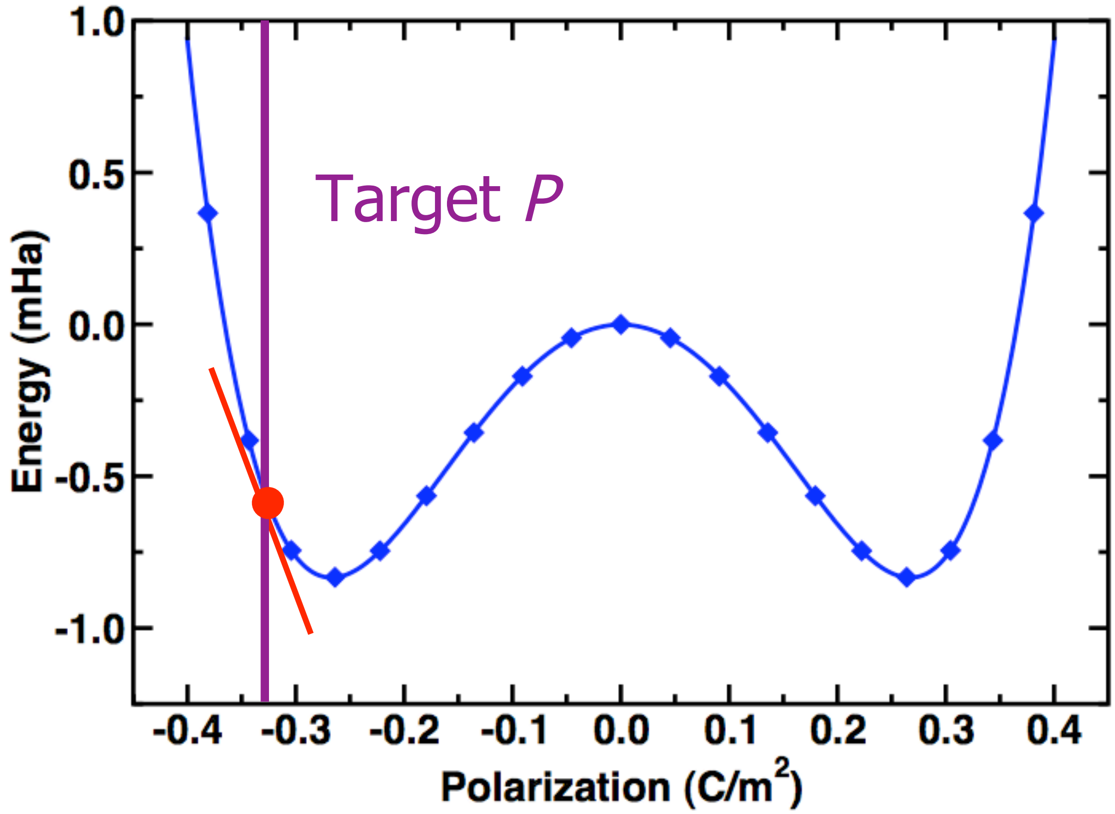
$E_{KS}(P)$



Minimize E_{KS}
with respect to
$\{\psi_{nk}\}$, $\{R_j\}$
subject to
$P(\{\psi_{nk}\},\{R_j\}) = P_{targ}$

Dieguez and Vanderbilt, PRL **96**, 056401 (2006).

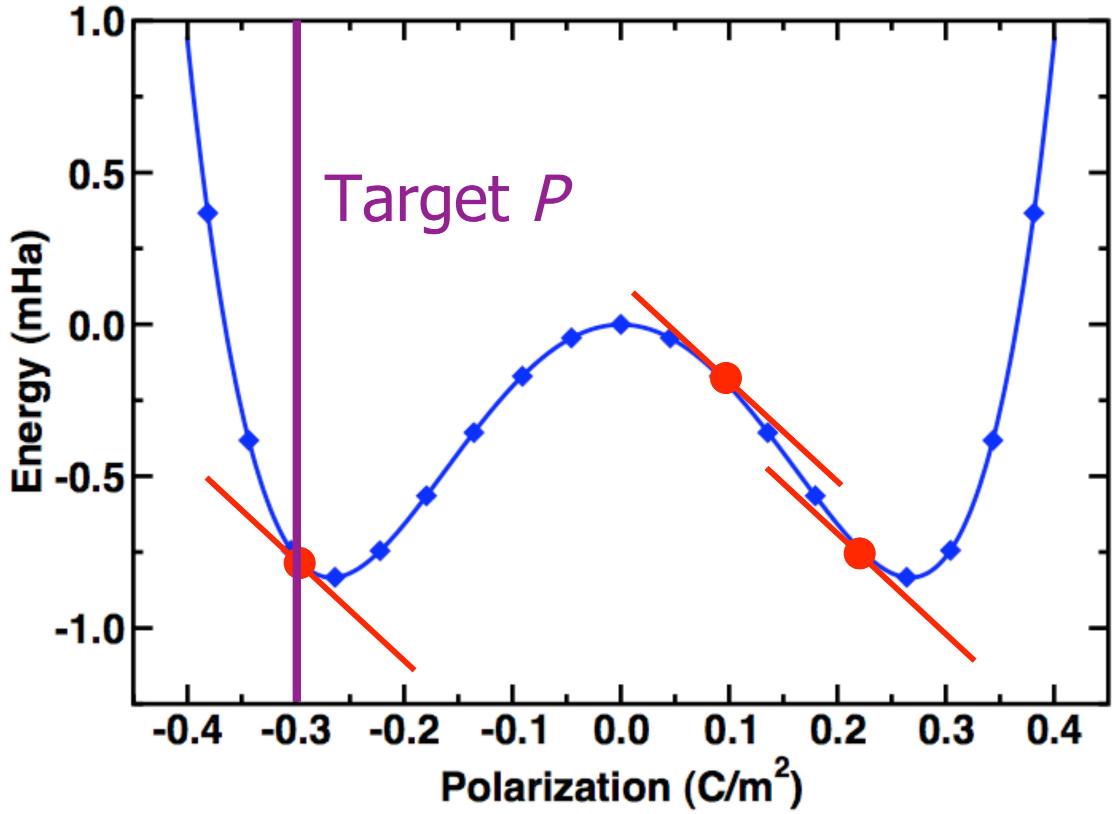
Lagrange mult.: *Min.* $E_{KS}(P)-\mathcal{E}\cdot P$



Electric field
$\mathcal{E} = dE/dP$

Dieguez and Vanderbilt, PRL **96**, 056401 (2006).

Lagrange mult.: *Min.* $E_{KS}(P)-\mathcal{E}\cdot P$



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Dieguez and Vanderbilt, PRL **96**, 056401 (2006).

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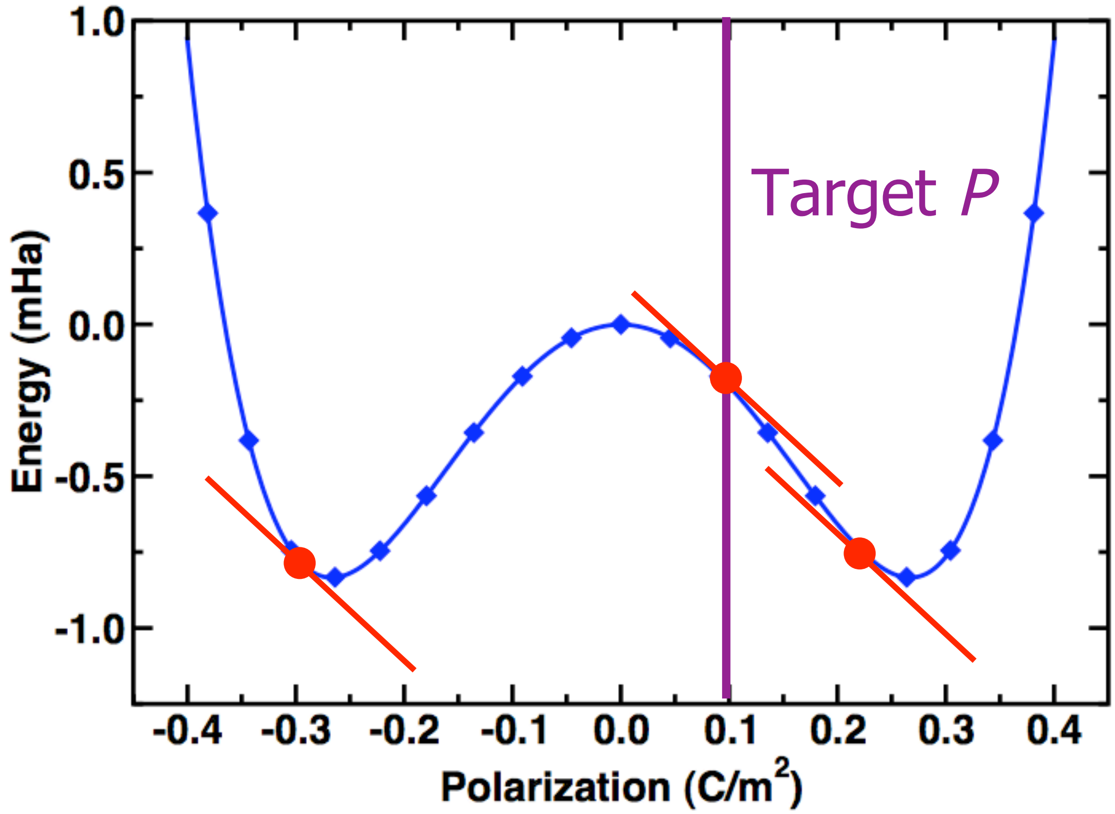
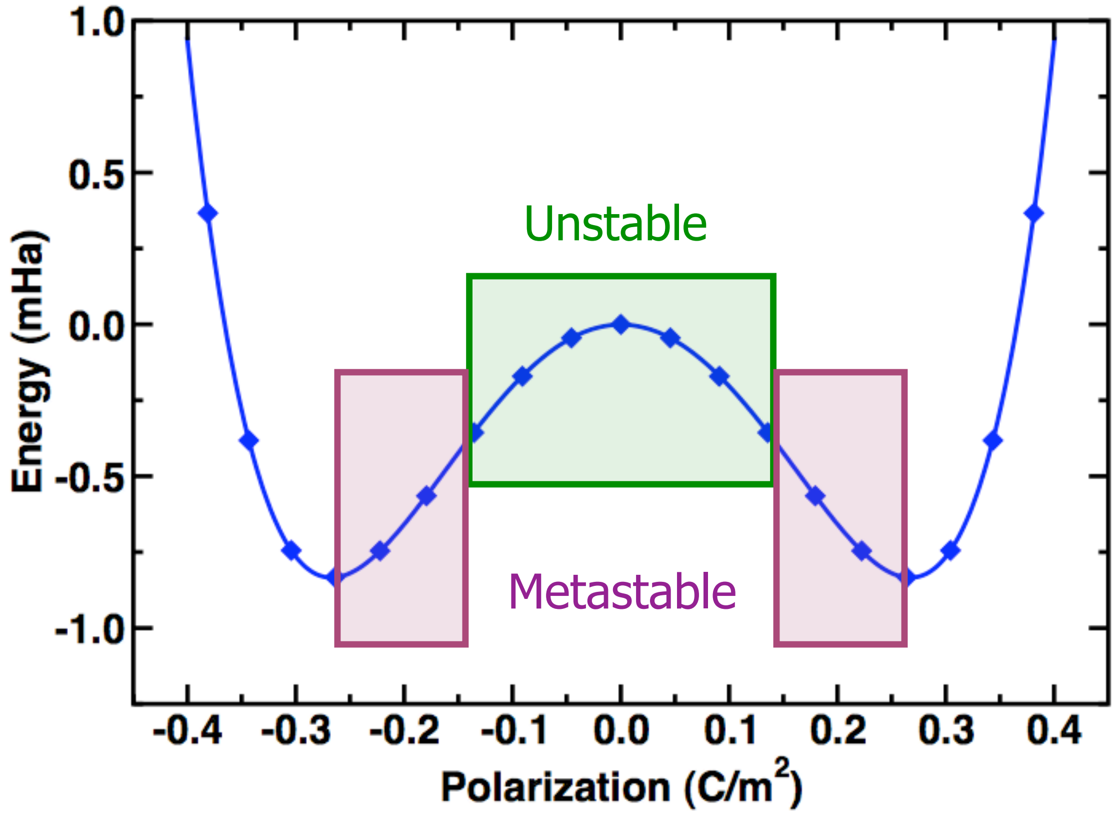


Electric field

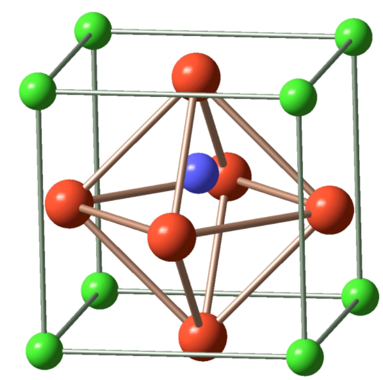
$\mathcal{E} = dE/dP$

Dieguez and Vanderbilt, PRL **96**, 056401 (2006).

Try to minimize at fixed $\mathcal{E}$

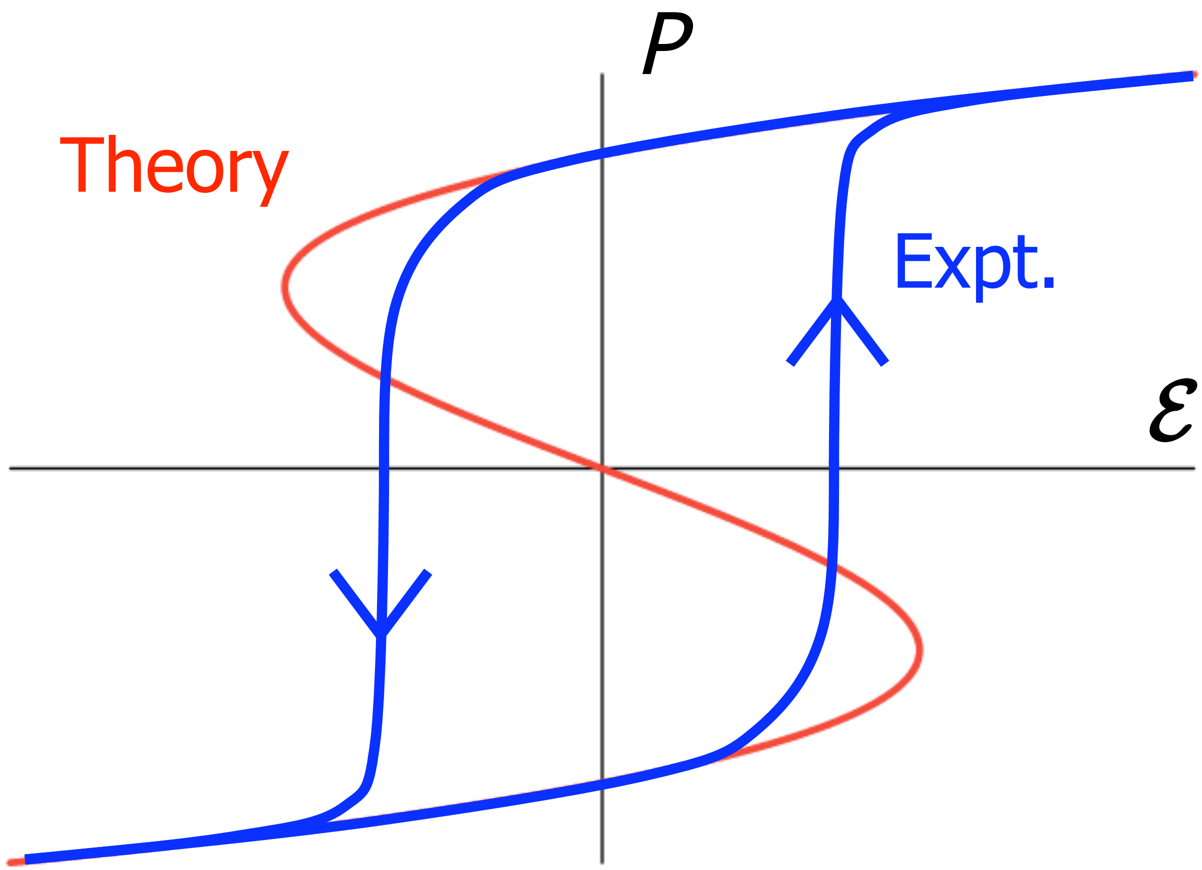


$BaTiO_3$



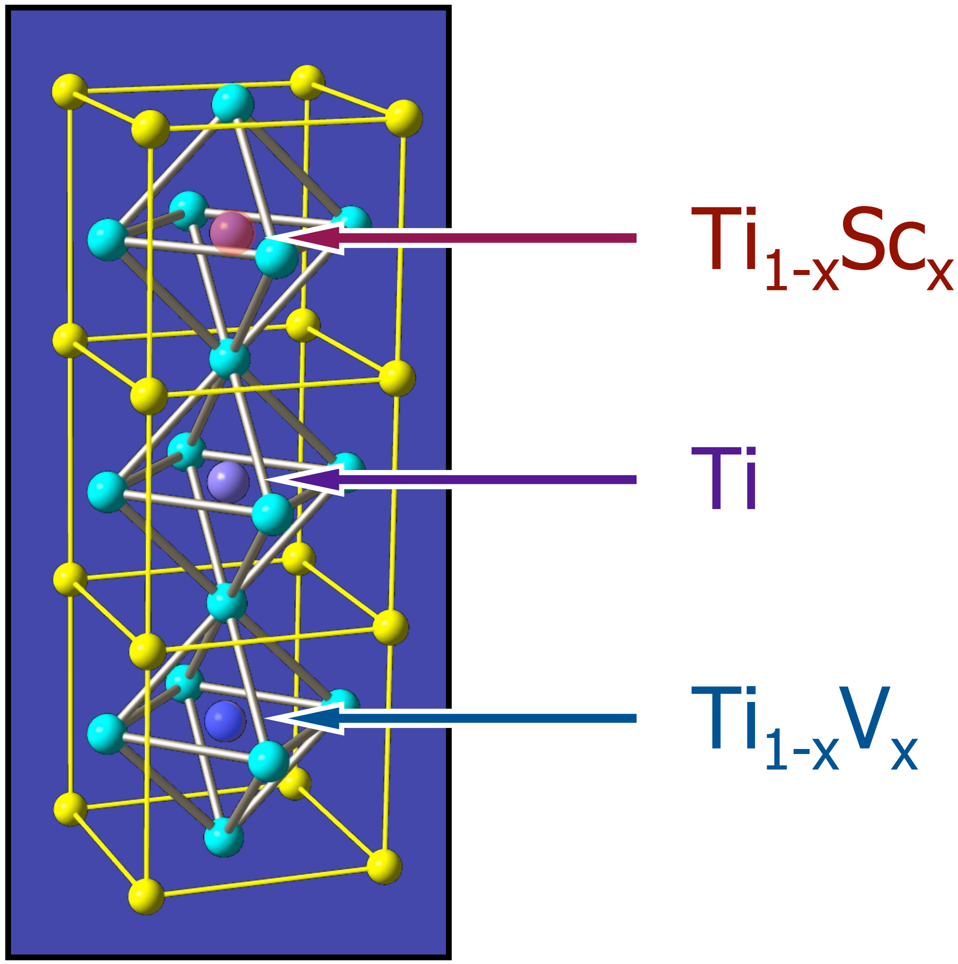
Dieguez and Vanderbilt, PRL **96**, 056401 (2006).

$\mathcal{E}(P)$ from $E(P)$



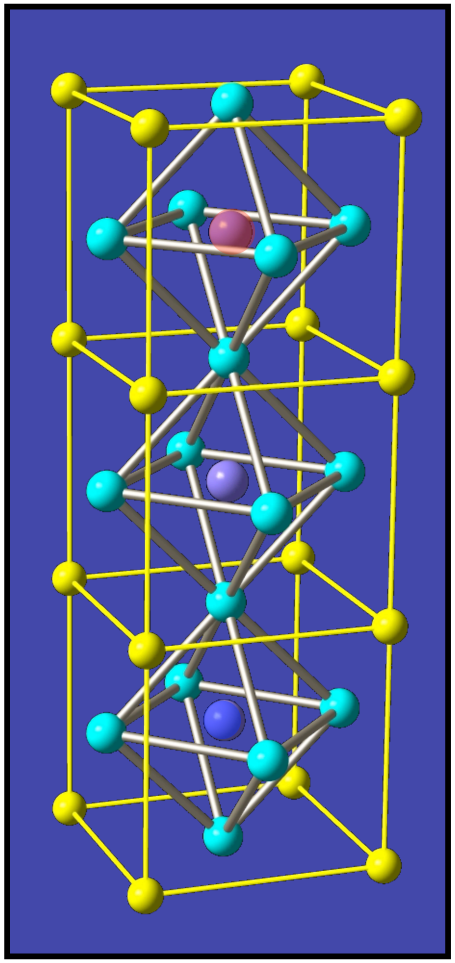
Dieguez and Vanderbilt, PRL **96**, 056401 (2006).

Example: Compositional breaking of inversion symmetry



Sc^{+3}	Ti^{+4}	V^{+5}

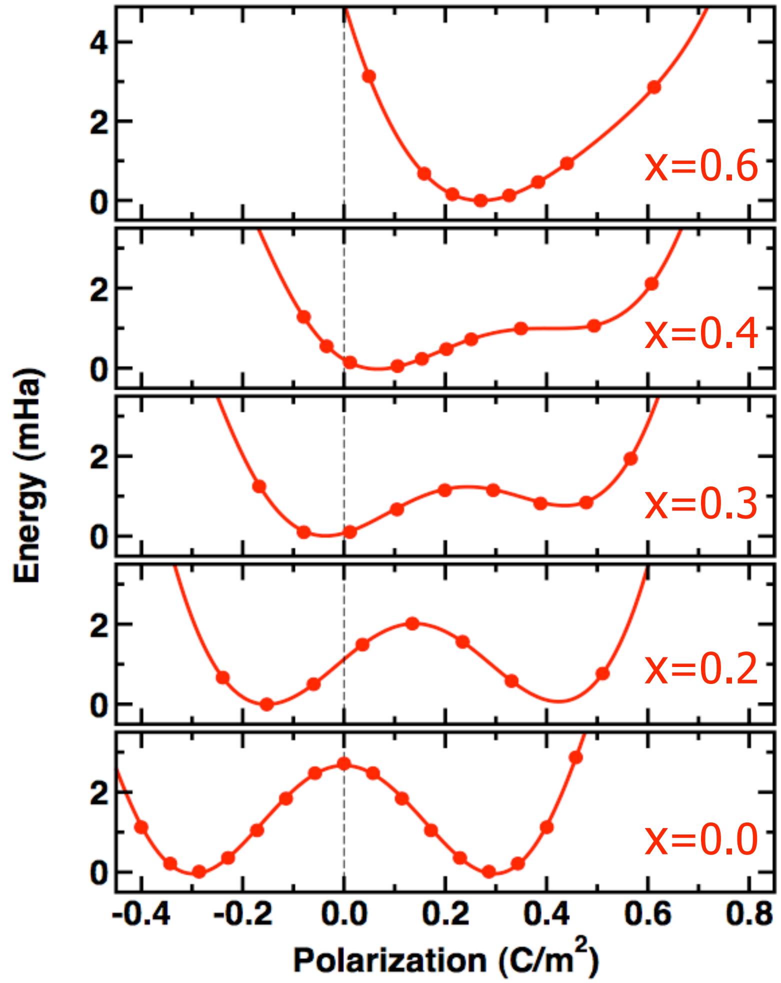
Example: Compositional breaking of inversion symmetry



Z=22-x

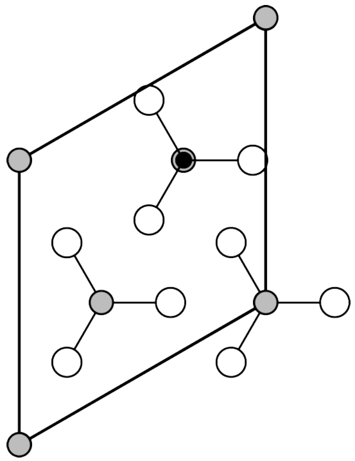
Z=22

Z=22+x

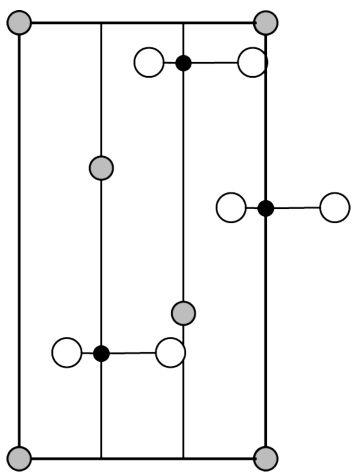


Dieguez and Vanderbilt, 2006

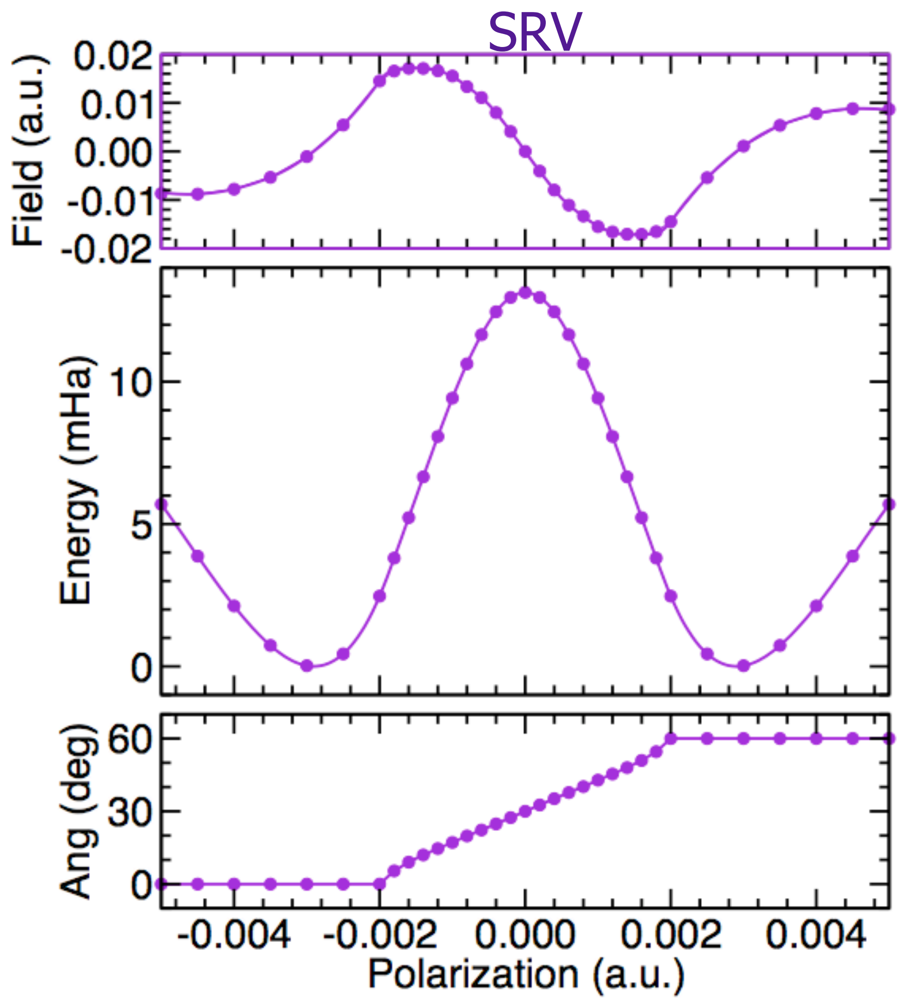
Example: Hexagonal KNO_3



Top view



Side view



Dieguez and Vanderbilt, 2006

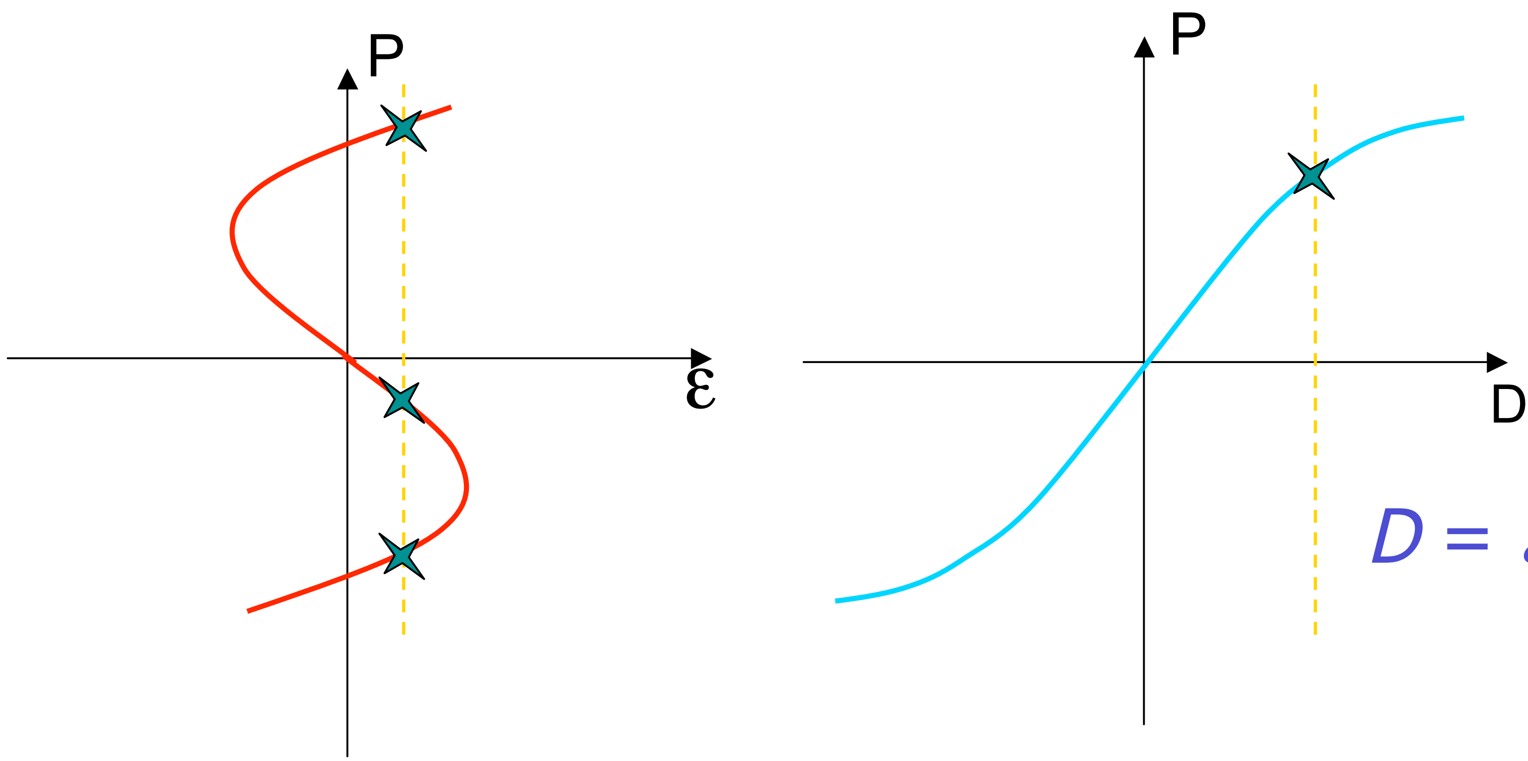
Electric equations of state

$$
\begin{tikzcd}
E(P) \arrow[d, "\text{Numerical derivative}"'] & & \\
\mathcal{E}(P) \arrow[rr, "\text{Numerical inversion}"] \arrow[d, "D=\varepsilon_0\mathcal{E}+P"'] & & P(\mathcal{E}) \\
D(P) \arrow[rr, "\text{Numerical inversion}"] & & \boxed{P(D)} \arrow[d, "D=\varepsilon_0\mathcal{E}+P"] \\
D(\mathcal{E}) & & \mathcal{E}(D) \arrow[ll, "\text{Numerical inversion}"']
\end{tikzcd}
$$

Best choice?

Why *P(D)* ?

1. *P(D)* is monotonic.



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

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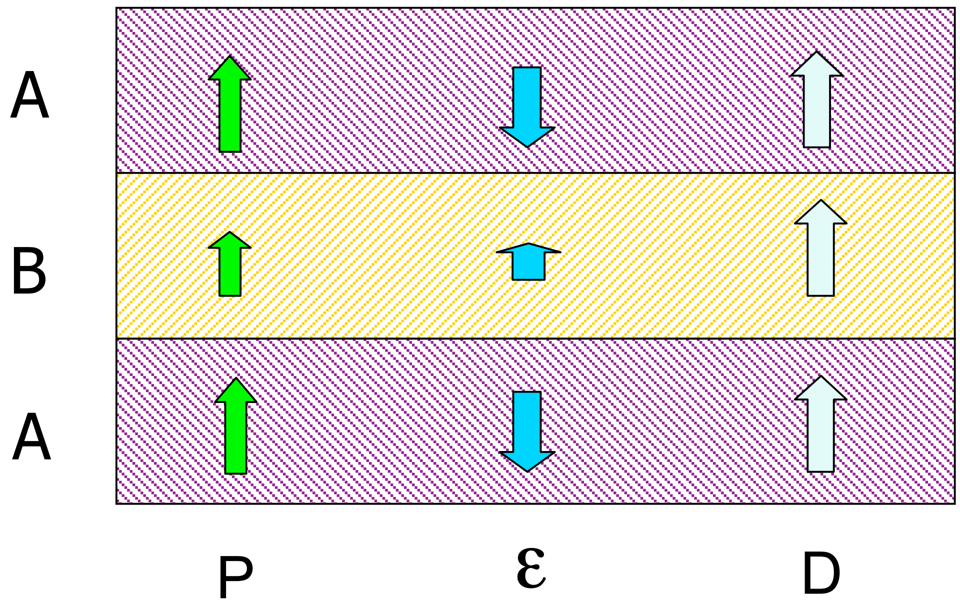
Why *P(D)* ?

2. *D* is uniform throughout superlattice.



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  - Unusual dielectric properties
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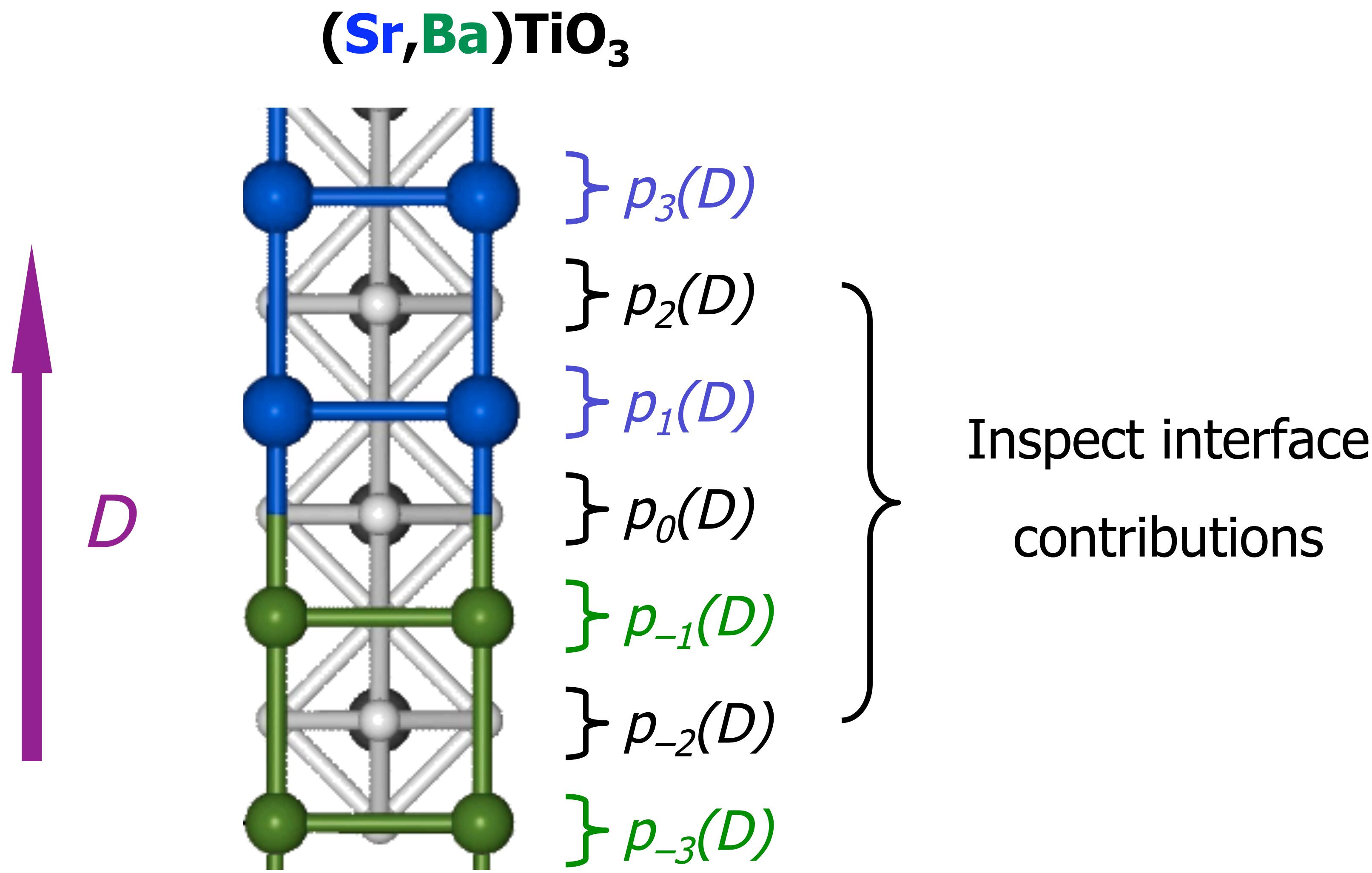
  - Finite electric field $\mathcal{E}$
  - Mapping $E(P)$
  - Electric equations of state: $P(\mathcal{E})$, $\mathcal{E}(P)$, $P(D)$, etc.
  - Layer-by-layer spatial resolution of P
- Work in progress: Model for $P(D)$ of superlattice
- Summary and conclusions

Look inside interface: layer polarizations



Definition of layer polarization

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Wannier-Based Definition of Layer Polarizations in Perovskite Superlattices

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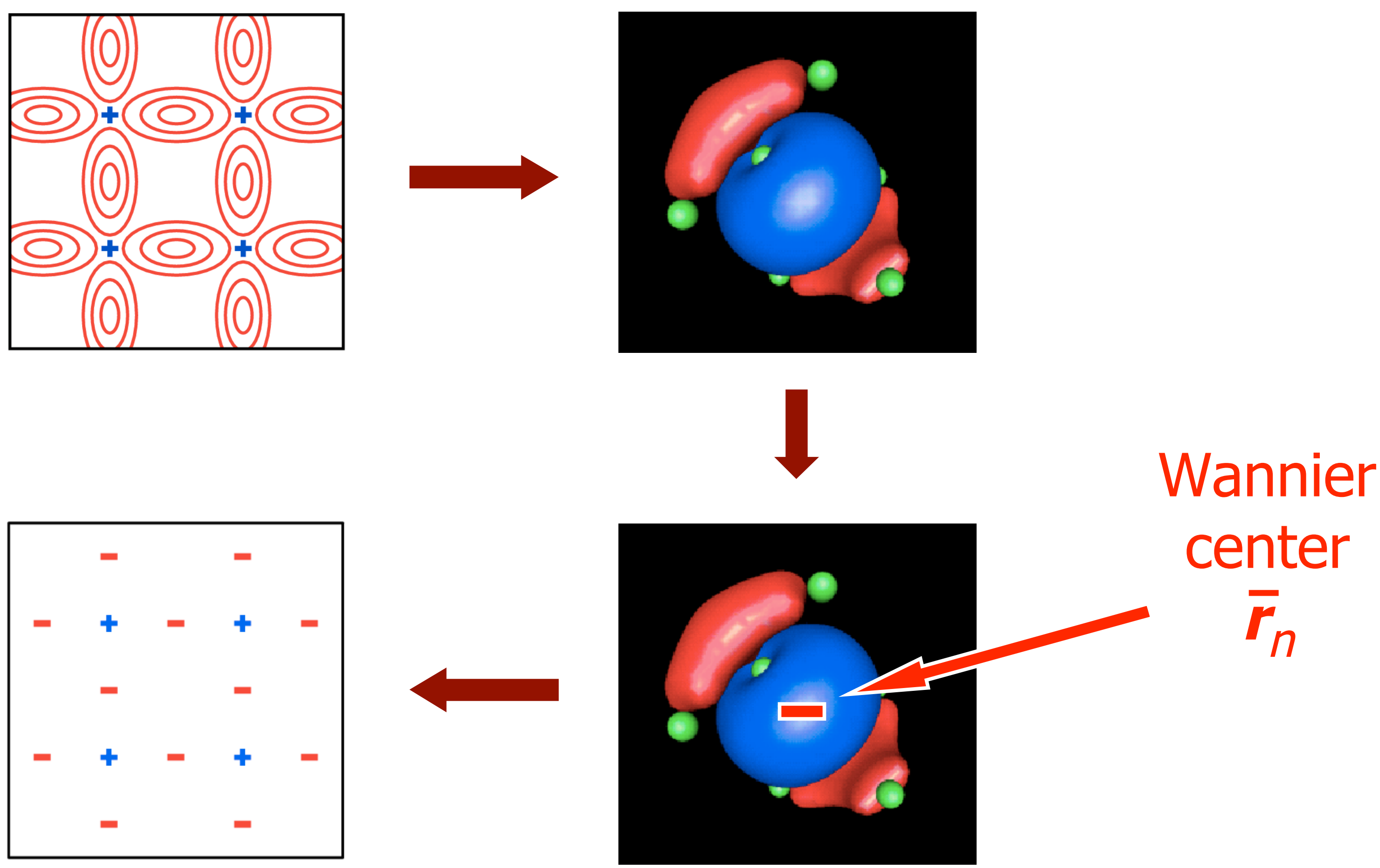
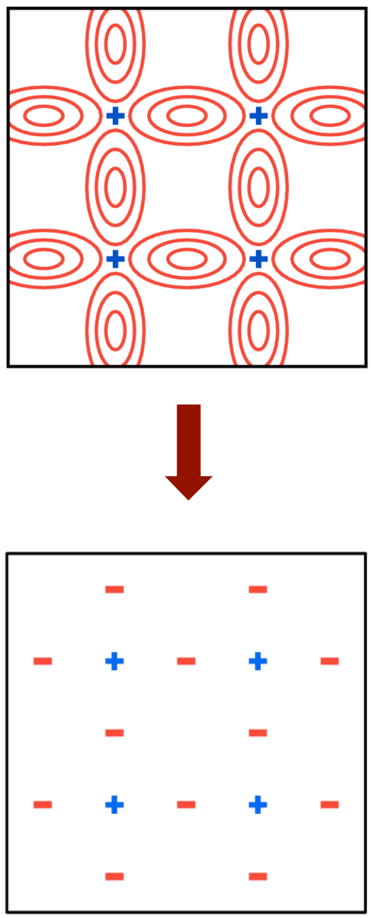
How to define layer polarizations?

Use Wannier function centers

Mapping to Wannier centers



Mapping to Wannier centers

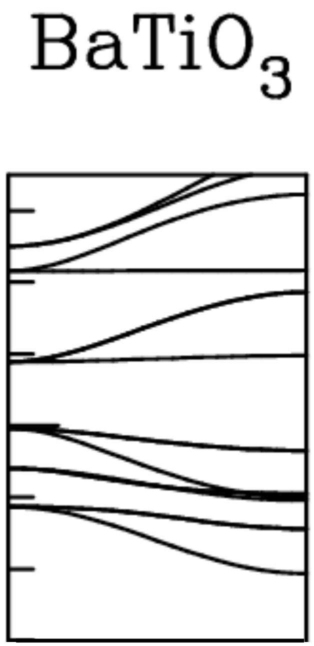


Wannier dipole theorem

$$\Delta \mathbf{P} = \Sigma_{ion}\, (Z_{ion} e)\, \Delta \mathbf{r}_{ion} + \Sigma_{wf}\, (-\,2e)\, \Delta \bar{\mathbf{r}}_{wf}$$

- Exact!
- Gives <u>local</u> description of dielectric response!

Wannier functions in $BaTiO_3$



Mainly Ti *3d*
(also some O *2p*)

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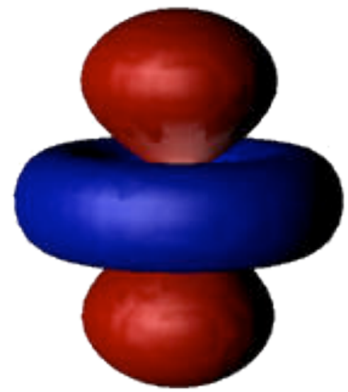
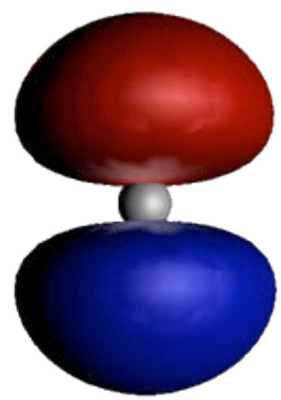
(also some Ti *3d*)

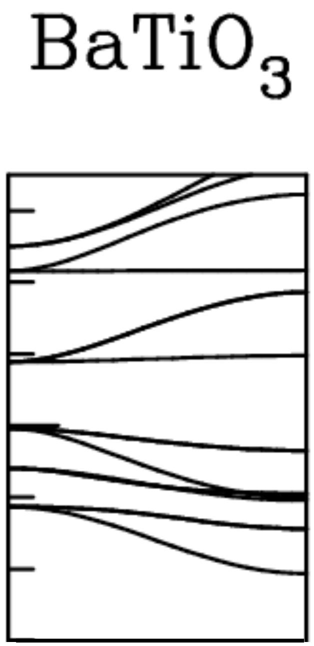


Ti *3d*



O *2p*

Wannier functions in $BaTiO_3$



Mainly O *2p*
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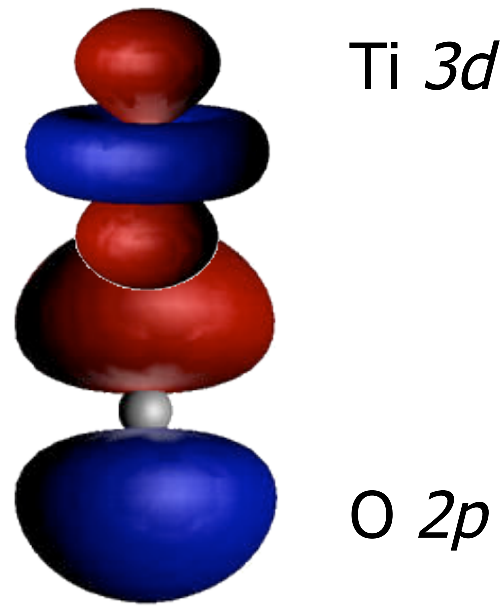
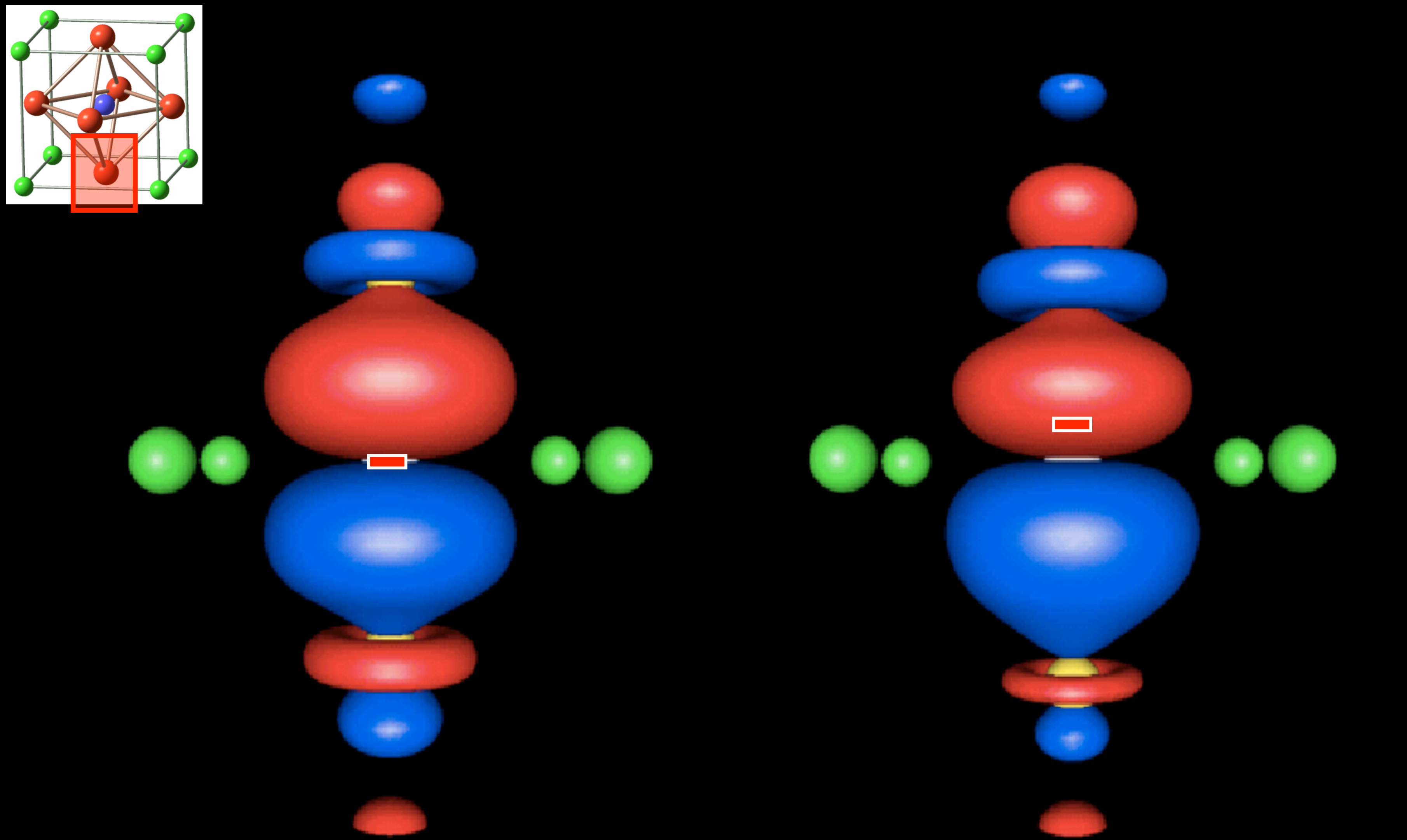
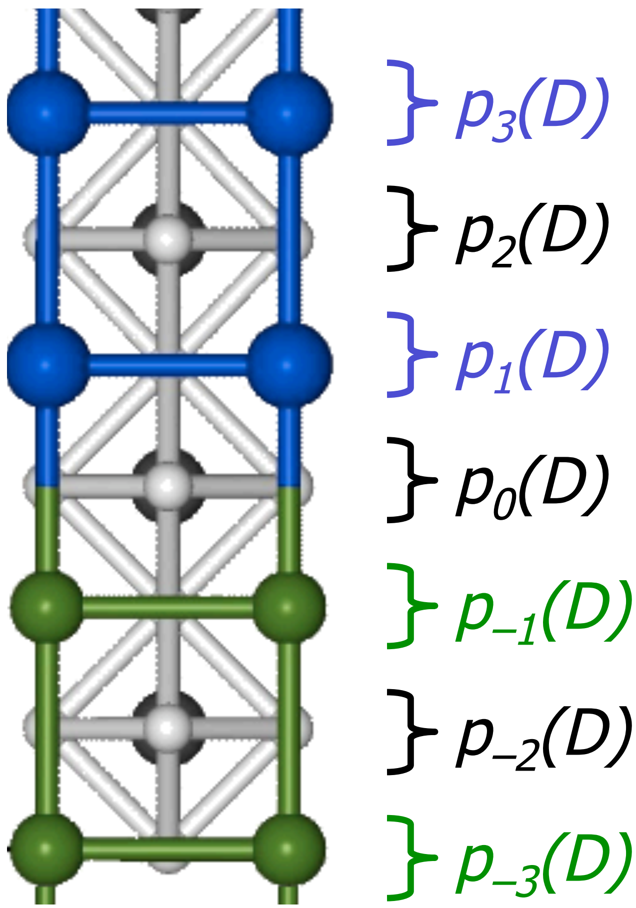




Ferroelectric $BaTiO_3$ (Courtesy N. Marzari)

Analysis of layer polarizations

(Sr,Ba)TiO$_3$

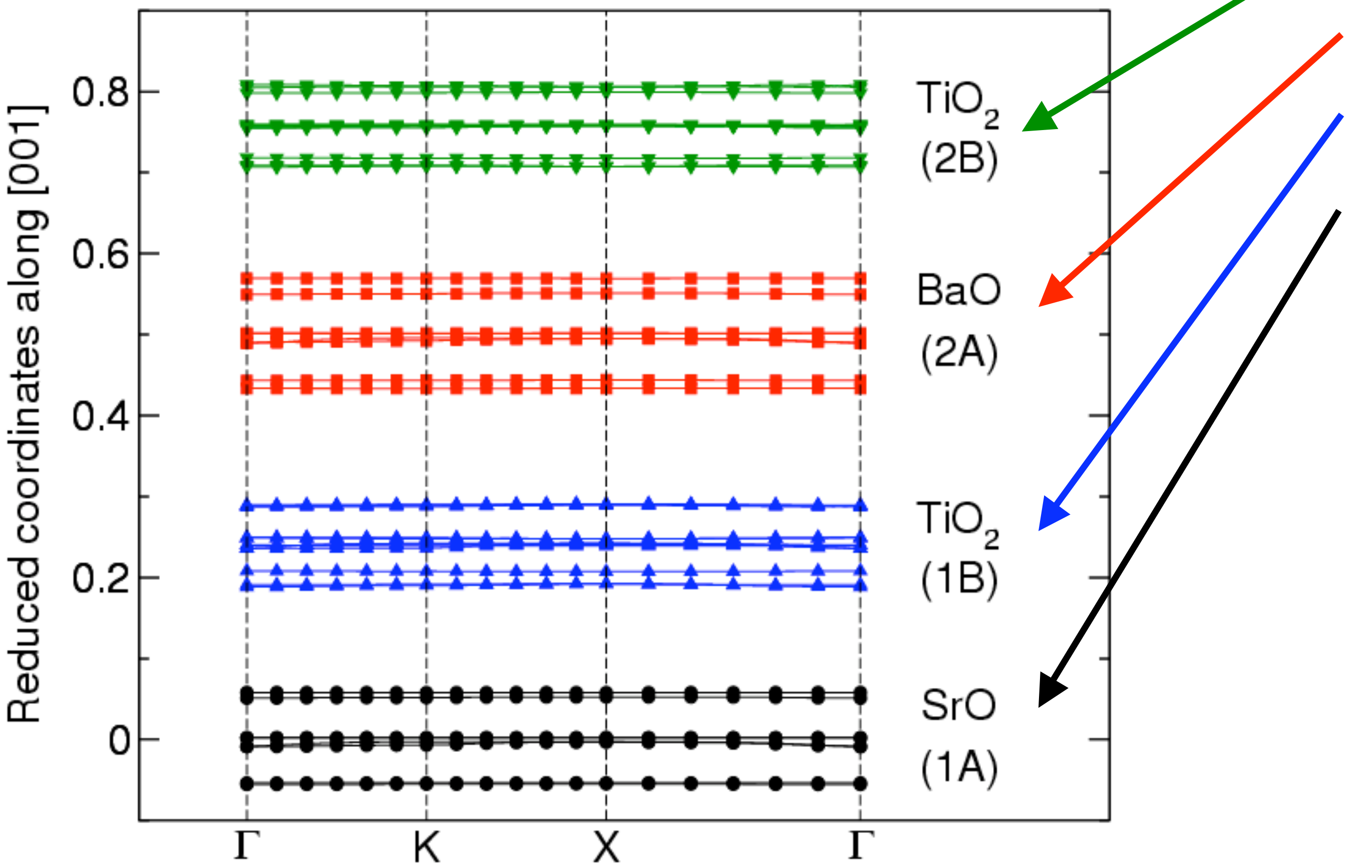


Ions can naturally be assigned to layers.

Can WF centers also be assigned to layers?

Analysis of layer polarizations

$(BT)_1$-$(ST)_1$ superlattice



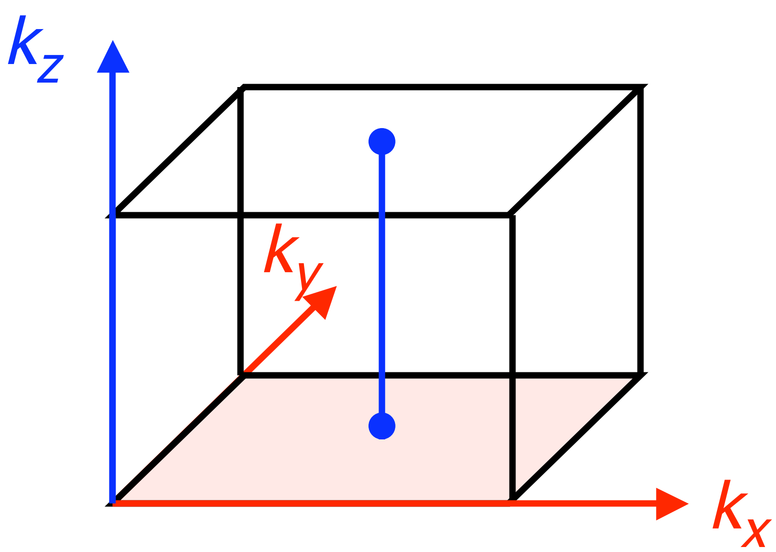
YES!

3D vs. 1D Wannier analysis

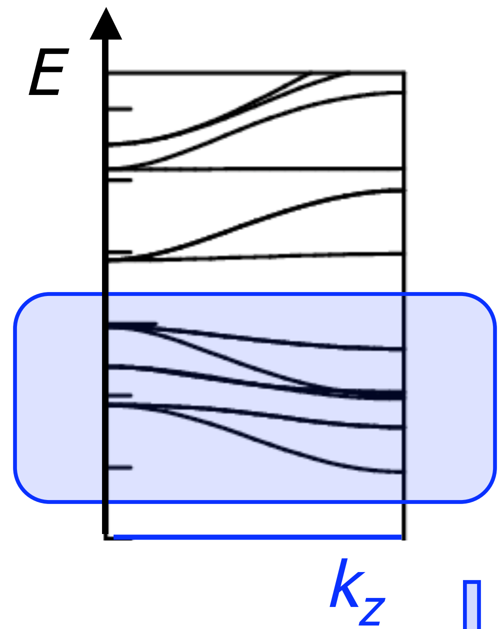
- 3D maximally localized Wannier functions
  - Marzari and Vanderbilt, PRB 56, 12847 (1997).
  - Requires iterative procedure
  - Compromise: maximum localization in *x*, *y*, and *z*
- Here keep (k_x, k_y) and work in 1D along k_z
  - Maximum localization along *z*
  - No iterative procedure needed
  - Only small matrix diagonalizations

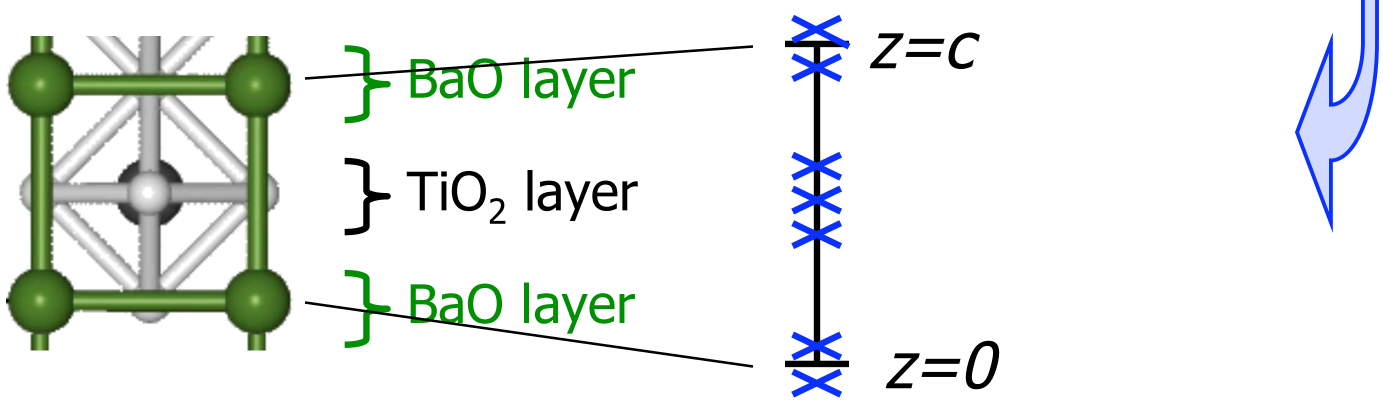
See also
Giustino, Umari, and Pasquarello, PRL 91, 267601 (2003);
Giustino and Pasquarello, PRB 71,144104 (2005).

1D analysis of layer polarizations



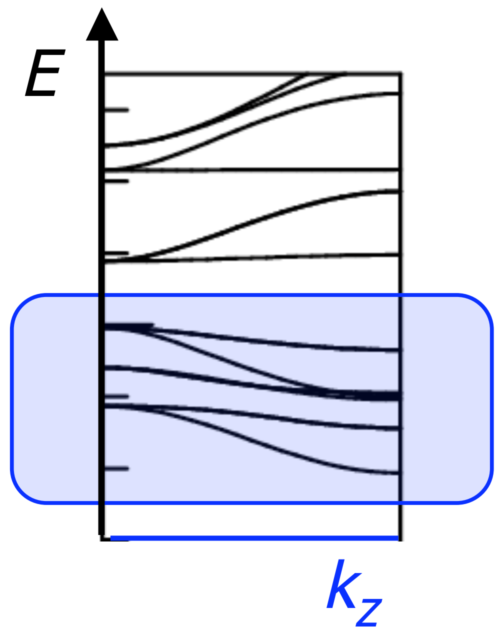
For given (k_x,k_y) :

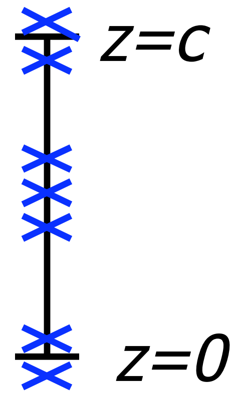




1D Wannier center analysis

For given (k_x,k_y) :





Choose unitary rotation

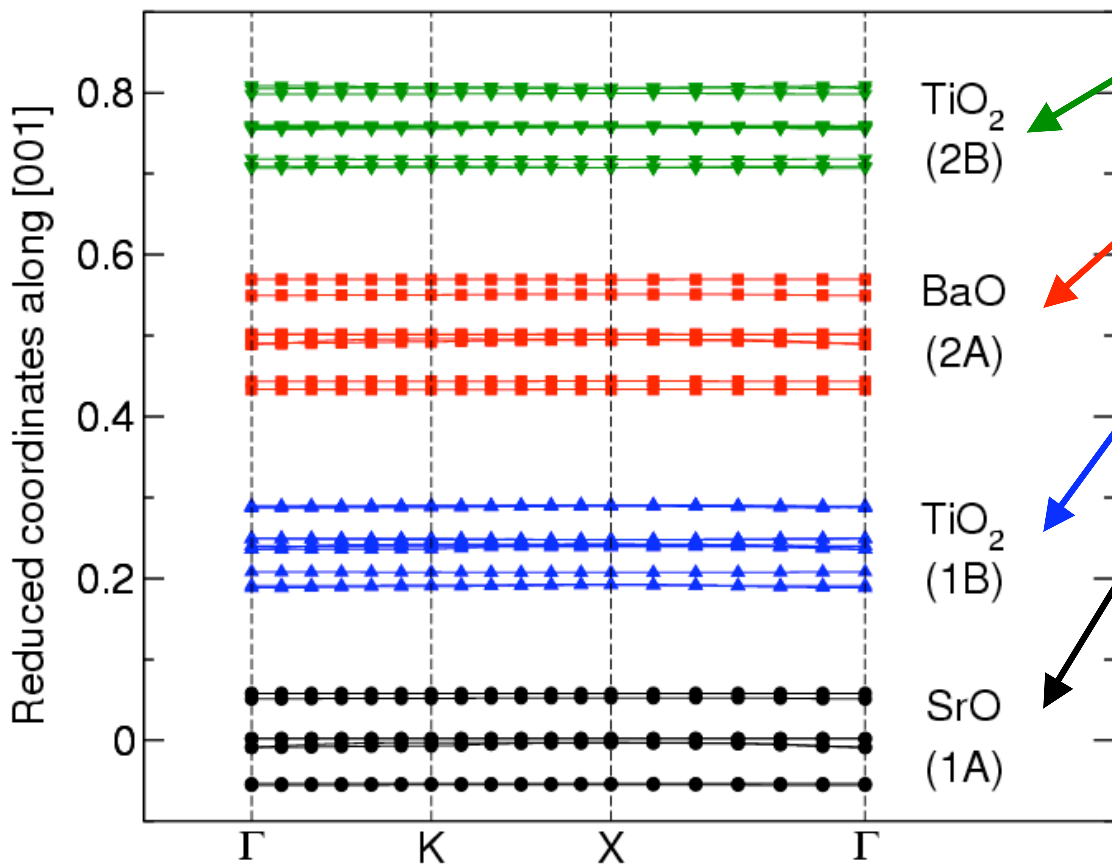
$$\psi_{n,k_z}^{k_x,k_y}(\mathbf{r}) \;\rightarrow\; w_{m,l}^{k_x,k_y}(\mathbf{r}) = w_{m,0}^{k_x,k_y}(\mathbf{r}-lc\hat{z})$$

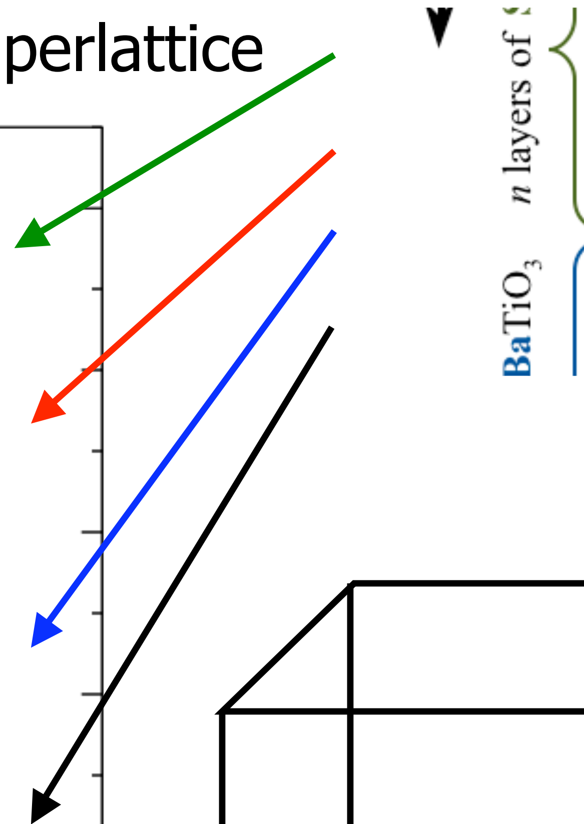
such that

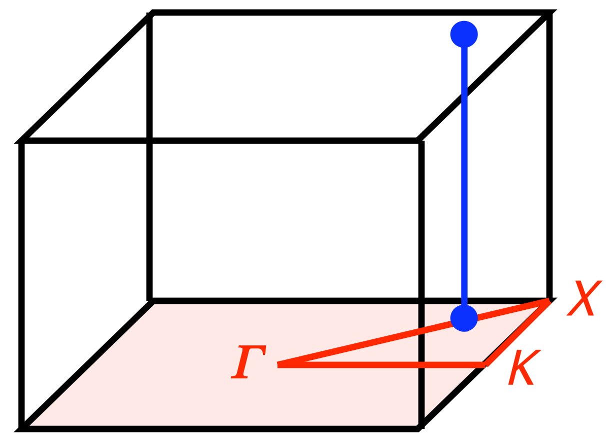
$$\langle w_{m,l}^{k_x,k_y}|z|w_{m',l'}^{k_x,k_y}\rangle = \bar{z}_{m,l}^{k_x,k_y}\,\delta_{mm'}\,\delta_{ll'}$$

Analysis of layer polarizations

$(BT)_1$-$(ST)_1$ superlattice







Analysis of layer polarizations

$$\mathbf{P} = \frac{1}{V}\sum_{\tau} Q_{\tau}\,\mathbf{R}_{\tau} - \frac{2e}{V}\sum_{m} \bar{\mathbf{r}}_{m}$$

Total

$$P_z = \frac{1}{c}\sum_{j} p_j$$

$$p_j = \frac{1}{S}\sum_{\tau\in j} Q_{\tau}\,R_{\tau z} - \frac{2e}{S}\sum_{m\in j} \bar{z}_{m}$$

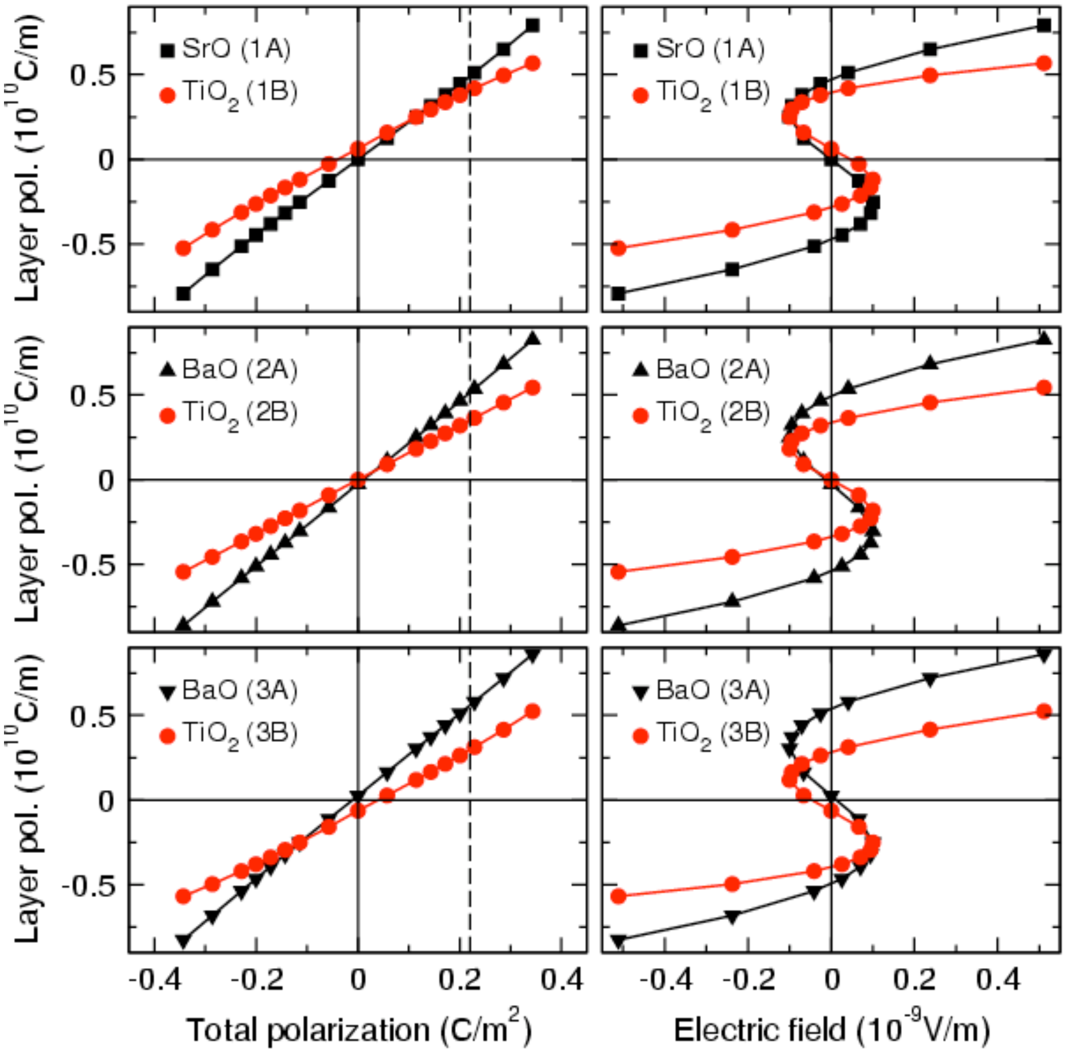
Layer decomposed

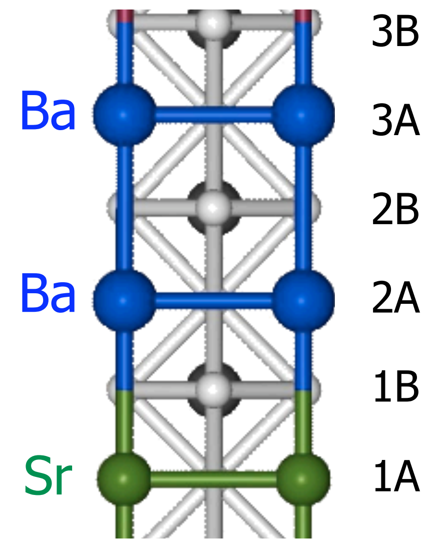
Ion contributions

Wannier ctr. contributions

$$V = cS$$

Analysis of layer polarizations





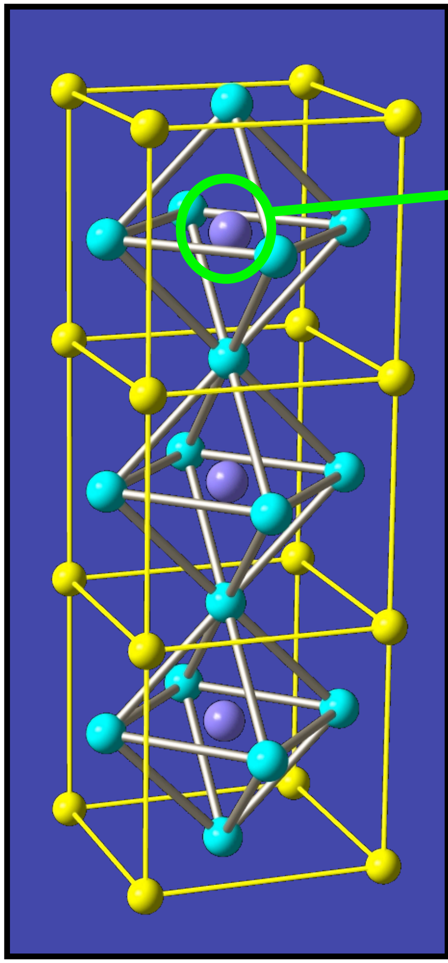
Wu, Dieguez, and Vanderbilt, PRL **97**, 107602 (2006).

Layer decomposition of *Z**

TABLE I: Layer decomposition of the [001] Born effective charges in a 3BT supercell. Total effective charges are given in the last row.

	Ti (1B)	Ba (1A)	$O_{\parallel}$ (1A)	$O_{\perp}$ (1B)
BaO (1A)	1.433	1.268	−2.448	−0.225
TiO_2 (1B)	1.872	0.148	−0.231	−0.930
BaO (2A)	1.262	0.434	−1.027	−0.191
TiO_2 (2B)	0.619	0.296	−0.542	−0.216
BaO (3A)	1.211	0.435	−1.046	−0.348
TiO_2 (3B)	0.636	0.191	−0.264	−0.217
Z^*	7.033	2.772	−5.557	−2.127

Layer decomposition of *Z**



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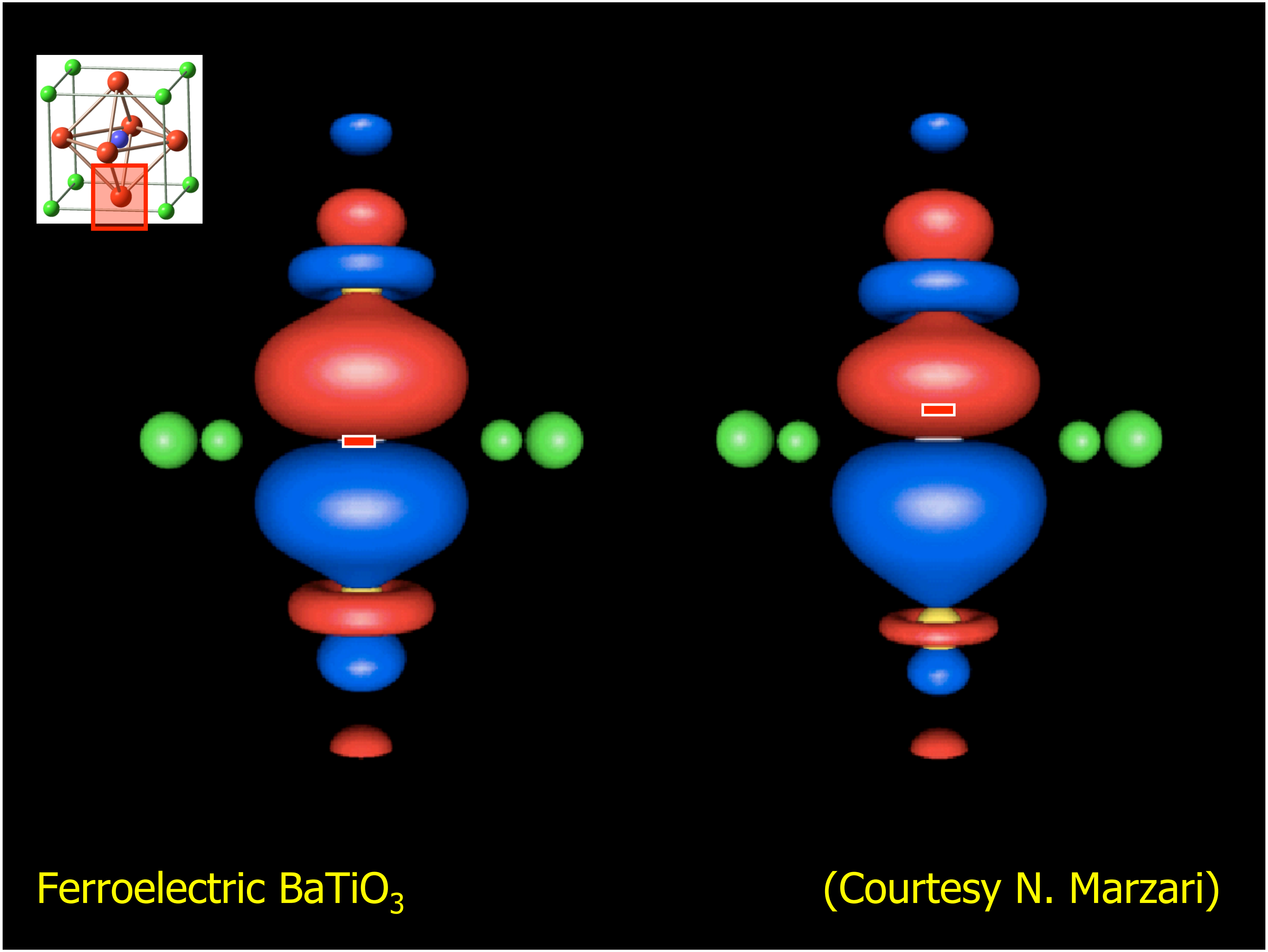
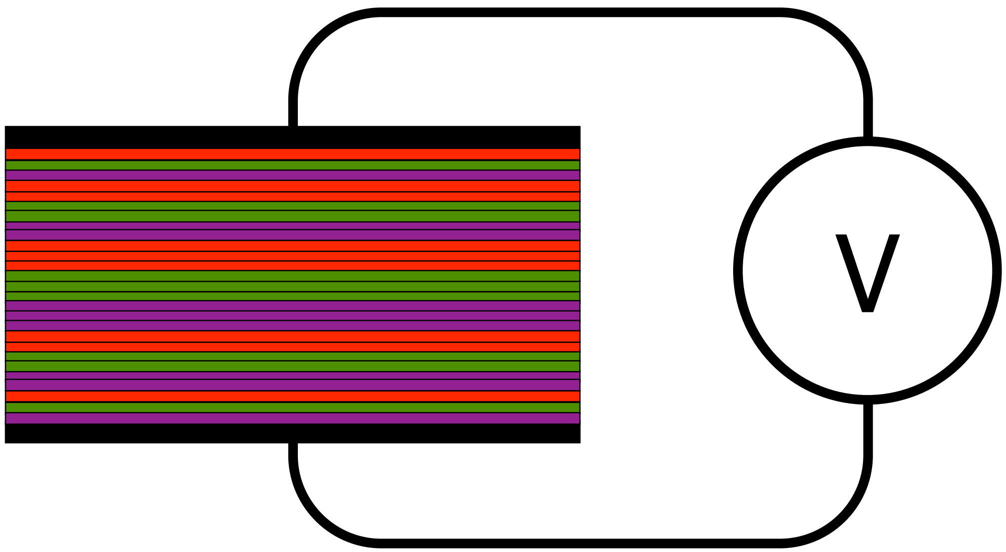

Ferroelectric $BaTiO_3$
(Courtesy N. Marzari)

Outline

- Introduction
  - Epitaxial perovskite superlattices
  - Unusual dielectric properties
- Theory of nonlinear dielectric behavior
  - Finite electric field $\mathcal{E}$
  - Mapping $E(P)$
  - Electric equations of state: $P(\mathcal{E})$, $\mathcal{E}(P)$, $P(D)$, etc.
  - Layer-by-layer spatial resolution of P
- Work in progress: Model for $P(D)$ of superlattice
- Summary and conclusions

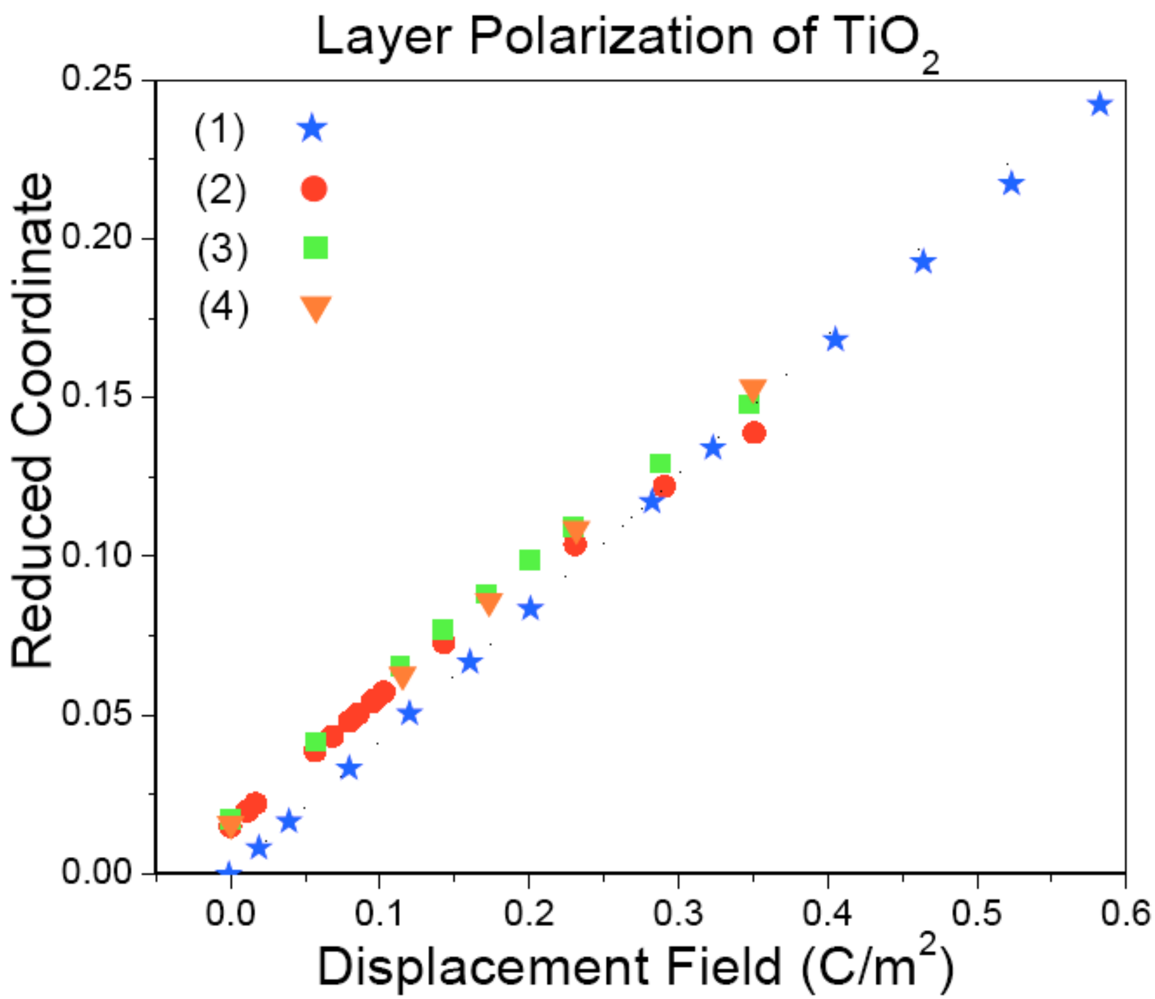
Desired theory: Non-linear C-V

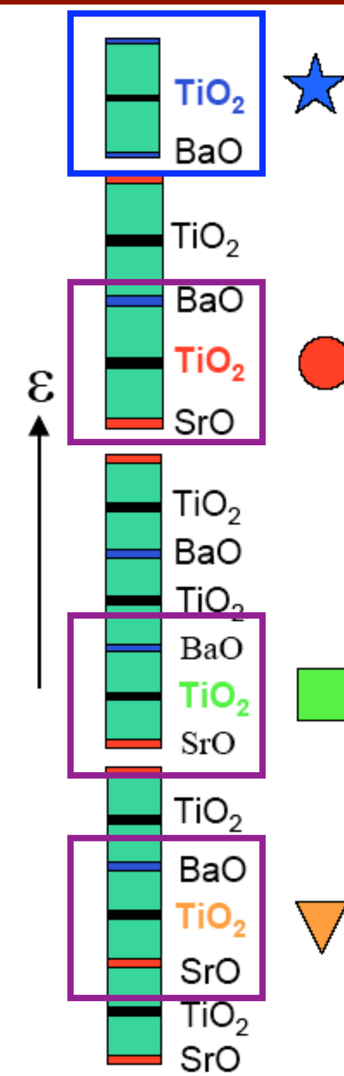
First-principles based model of electrostatics of arbitrary sequences?



Q-V and C-V characteristics?

Dependence of $p_j(D)$ on environment



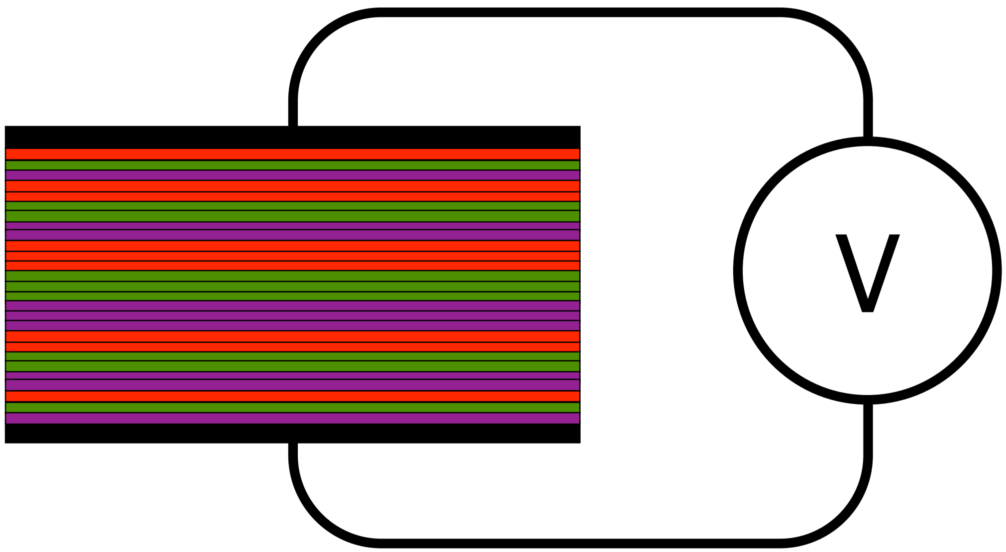


Work in progress: Improved model?

- Model: $P(D) = \sum_j p_j(D)$
- $P_j(D)$ depends on
  - — D field
  - — Chemical identity of layer itself
  - — Chemical identities of near neighbors
    (but dependence decays with distance)
- Use ab-initio $p_j(D)$ of short-period superlattices as database for fit
- Predict electrostatics of superlattices with arbitrary sequences

Desired theory: Non-linear C-V

First-principles based model of electrostatics of arbitrary sequences?



Q-V and C-V characteristics?

In Progress

Summary

- First-principles theory can now handle complex, nonlinear dielectric behavior
  - Finite electric field $\mathcal{E}$
  - Mapping $E(P)$
  - Electric equations of state: $P(\mathcal{E})$, $\mathcal{E}(P)$, $P(D)$, etc.
  - Layer-by-layer spatial resolution of P
- Applications
  - Here: Perovskite superlattices
  - Other dielectric, ferroelectric, piezoelectric systems