Polarization, electric fields, and dielectric response in insulators

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Outline

- Introduction
- Electric polarization
  - What is the problem?
  - What is the solution?
- Electric fields
  - What is the problem?
  - What is the solution?
- Localized description:
  - Wannier functions
- Dielectric and piezoelectric properties
  - Systematic treatment of E-fields and strains
  - Mapping energy vs. polarization
- Summary and prospects

Collaborators

Principal Contributors:

D. King-Smith	Polarization
N. Marzari	Wannier functions
R. Nunes	Electric fields
I. Souza	
J. Iniguez	
N. Sai	Mapping E vs. P
O. Dieguez	
K. Rabe	
X. Wu	Systematic DFPT in E and strain
D. Hamann	
X. Wang	DFPT in presence of E-field

Principal References

- Polarization
  - *R.D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).*
- Review on polarization
  - *R. Resta, Rev. Mod. Phys. 66, 899 (1994).*
- Dynamics of polarization
  - *I. Souza, J. Iniguez and D. Vanderbilt, Phys. Rev. B 69, 085106 (2004).*
- Finite electric field
  - *R.W. Nunes and X. Gonze, Phys. Rev. B 63, 155107 (2001).*
  - *I. Souza, J. Iniguez and D. Vanderbilt, Phys. Rev. Lett. 89, 117602 (2002).*
  - *P. Umari and A. Pasquarello, Phys. Rev. Lett. 89, 157602 (2002).*
- DFPT in E-field
  - *X. Wang and D. Vanderbilt, in preparation.*
- Mapping energy vs. polarization
  - *N. Sai, K.M. Rabe, and D. Vanderbilt, Phys. Rev. B 66, 104108 (2002).*
  - *O. Dieguez and D. Vanderbilt, in preparation.*
- Systematic DFPT for E-fields and strain
  - *X. Wu, D. Vanderbilt, and D.R. Hamann, submitted to Physical Review B.*
  - *D.R. Hamann, X. Wu, K.M. Rabe, and D. Vanderbilt, and, Phys. Rev. B. 71, 035117 (2005).*

Introduction

- Context: DFT (density functional theory)
- By mid-1990s, linear-response (DFPT) allowed calculation of:
  - Response of P to any perturbation
  - Response of anything to E-field perturbation
- However, it was not known how to:
  - Calculate P itself
  - Treat finite E-fields

Introduction

- Solutions of these problems are now in hand
  - Modern theory of polarization (1993)
  - Treatment of finite E-fields (2002)
- Allows routine calculation of non-linear dielectric, piezoelectric properties of complex materials

This talk:

Emphasis is on methods!

Touch only very briefly on applications

Theory of electric polarization

- Electric polarization:

  $\boldsymbol{P} = \boldsymbol{d}$ / volume

- How to define as a bulk quantity?

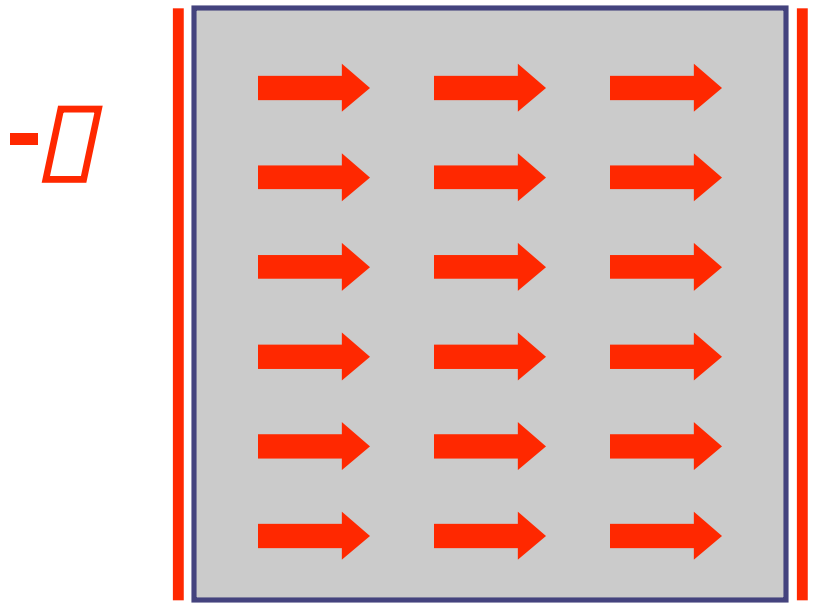
→ a) $\boldsymbol{P} = \boldsymbol{d}_{sample} / V_{sample}$?

b) $\boldsymbol{P} = \boldsymbol{d}_{cell} / V_{cell}$?

c) $\boldsymbol{P}$ $\square_{nk}$ $\square\square_{nk}\square\boldsymbol{r}\square\square_{nk}\square$?

$P = d_{sample} / V_{sample}$?

L x L x L sample:



$$\Delta P = (L^2 \Delta) . L / L^3$$

Theory of electric polarization

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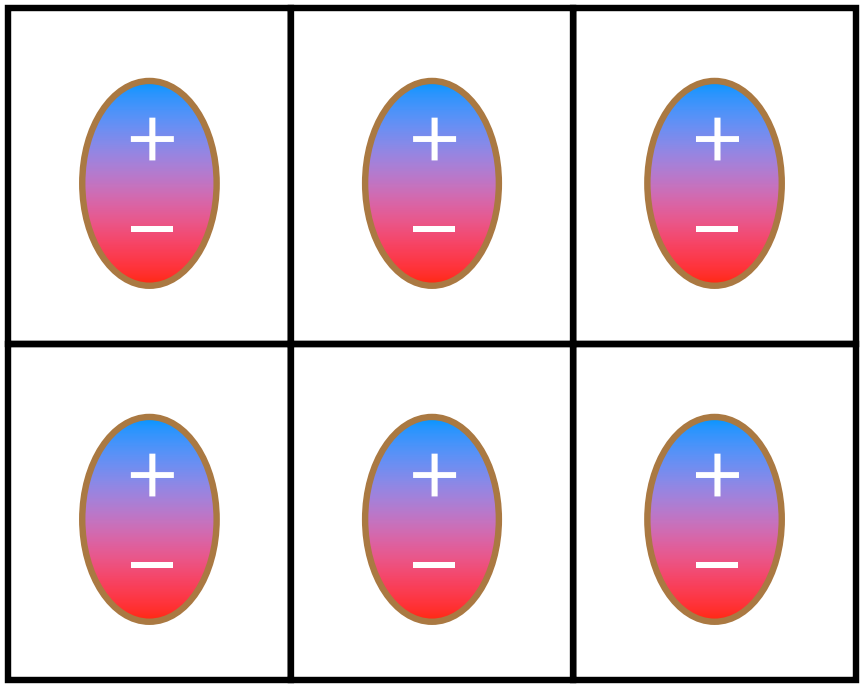
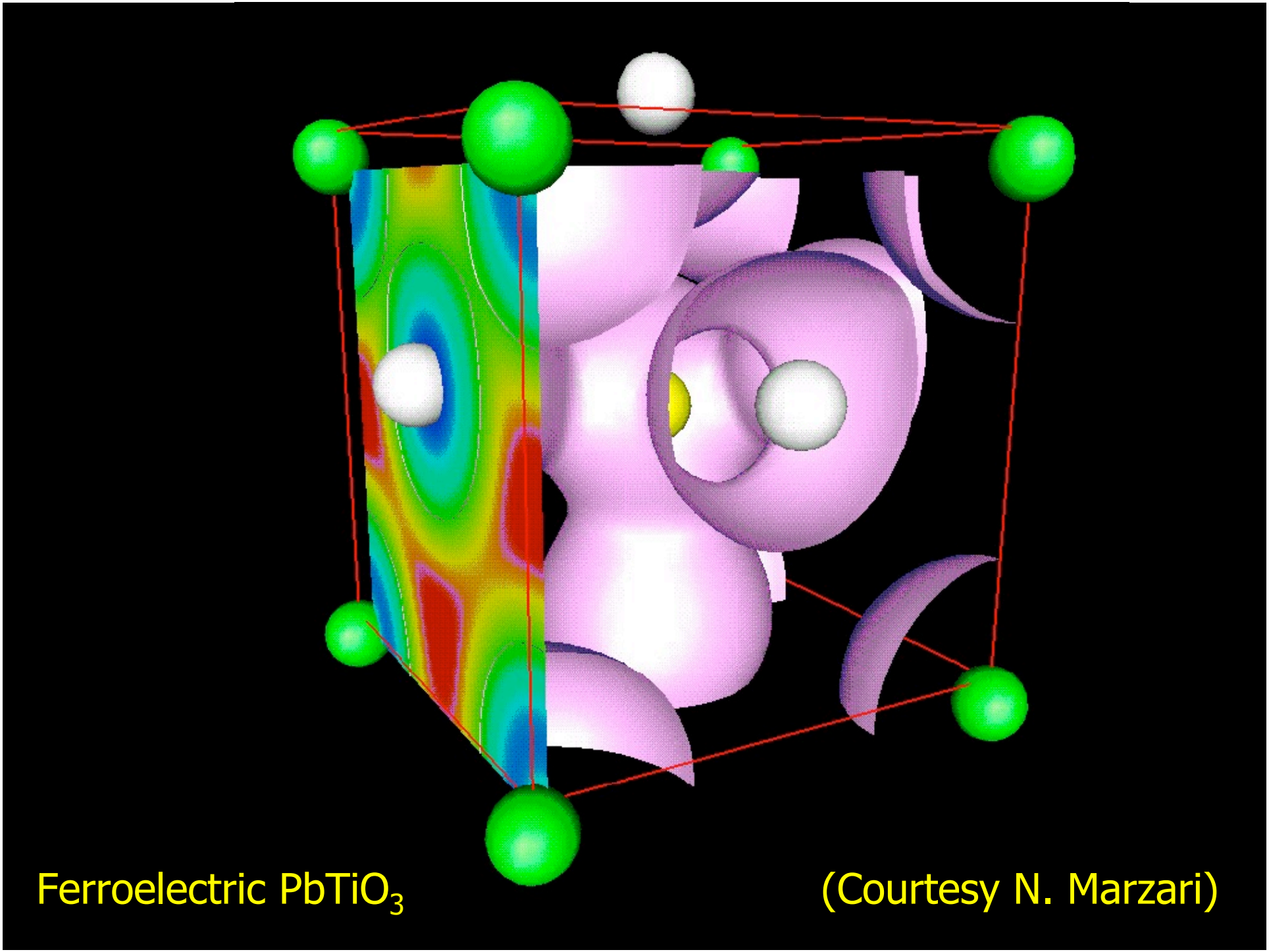
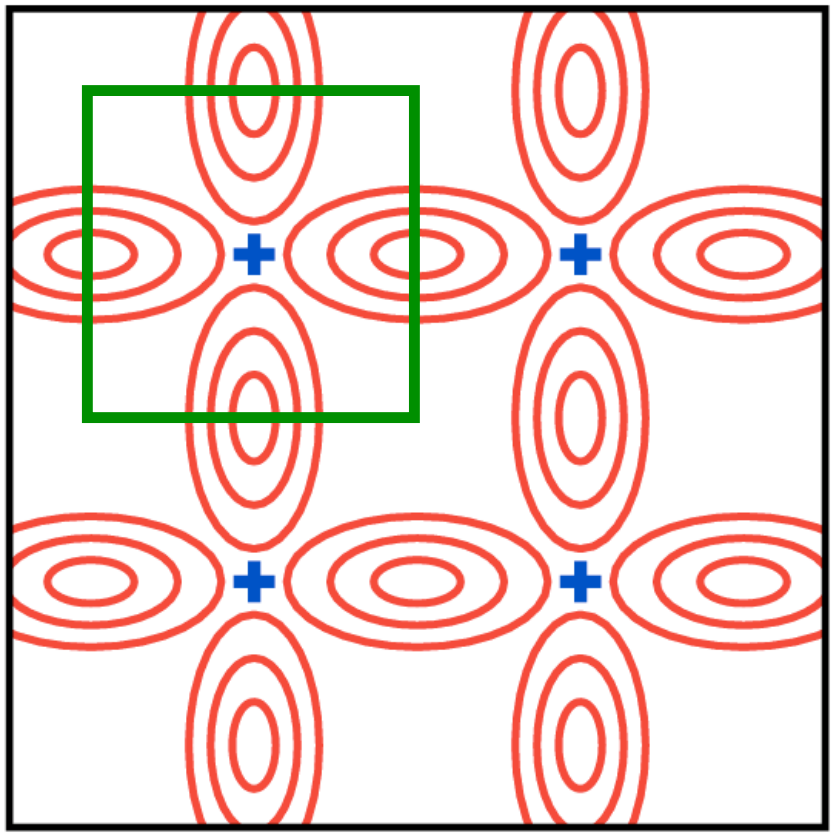
$P = d_{cell} / V_{cell}$?



- Textbook picture (Claussius-Mossotti)
- But does not correspond to reality!

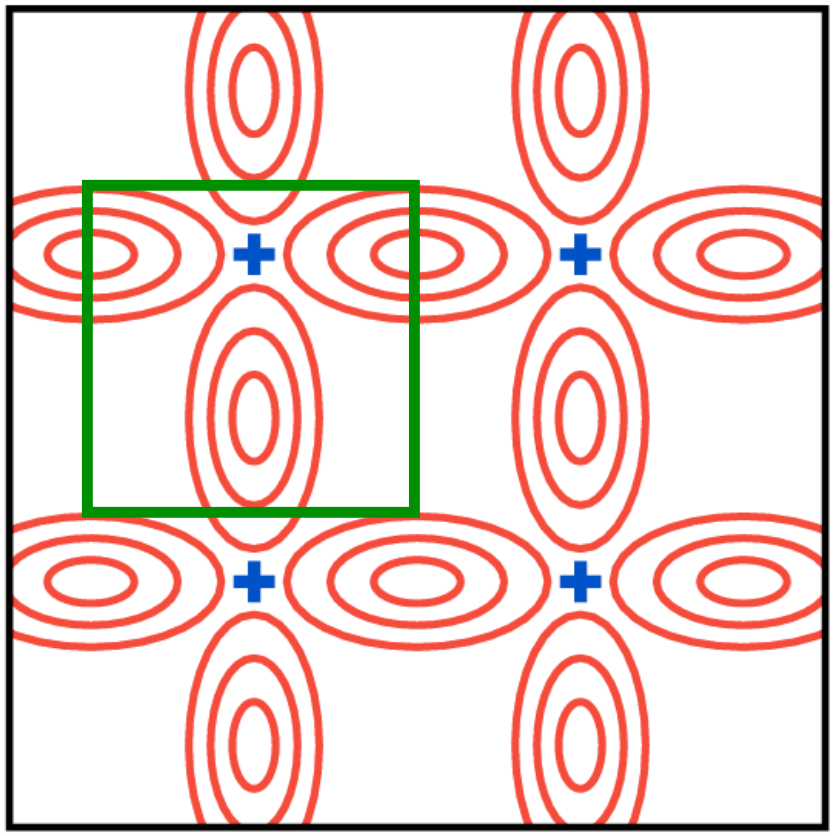

Ferroelectric $PbTiO_3$
(Courtesy N. Marzari)

$\boldsymbol{P = d_{cell} / V_{cell}}$?



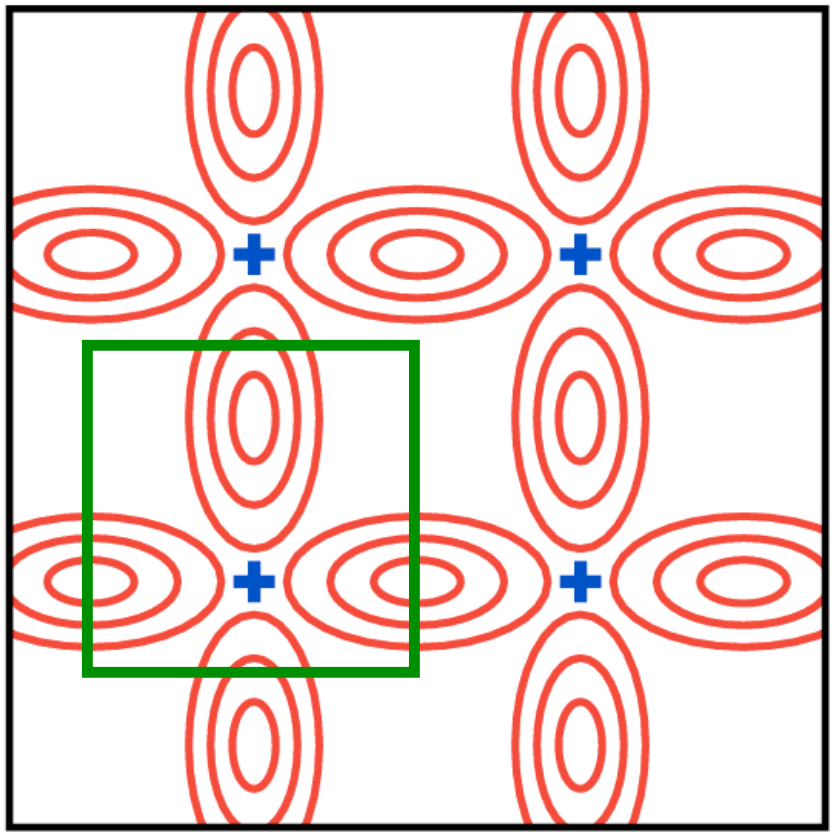
$\boldsymbol{d_{cell} = 0}$

$\boldsymbol{P} = \boldsymbol{d}_{cell} / V_{cell}$?



$\boldsymbol{d}_{cell} =$ ⬆

$\boldsymbol{P} = \boldsymbol{d}_{cell} / V_{cell}$?



$\boldsymbol{d}_{cell} =$ ⬇

Theory of electric polarization

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  c) ~~$\boldsymbol{P}$~~ $\int_{nk} \langle u_{nk} | \boldsymbol{r} | u_{nk} \rangle$?

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  c) ~~$\boldsymbol{P}$~~ $\Box_{nk} \Box\Box_{nk}\Box\boldsymbol{r}\Box\Box_{nk}\Box$?

  → d) $\boldsymbol{P}$ $\Box_{nk} \Box u_{nk}\Box\Box\Box_{\boldsymbol{k}}\Box u_{nk}\Box$?

Attempt 4

Attempt 4:

Use the current

$$\frac{d\mathbf{P}}{dt} = \frac{1}{V}\int_V d^3r\ \mathbf{j}(\mathbf{r})$$

instead of the density

$$\mathbf{P} = \frac{1}{V}\int_V d^3r\ \mathbf{r}\,\rho(\mathbf{r})$$

since $\mathbf{j}(\mathbf{r})$ is periodic but $\mathbf{r}\,\rho(\mathbf{r})$ is not.

Resta, 1992:

$$\Delta\mathbf{P} = \int \left(\frac{d\mathbf{P}}{dt}\right)\ dt$$

Resta, 1992:

$$\Delta \mathbf{P} = \int \left(\frac{d\mathbf{P}}{dt} \right) \, dt$$

King-Smith and Vanderbilt, 1993:

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

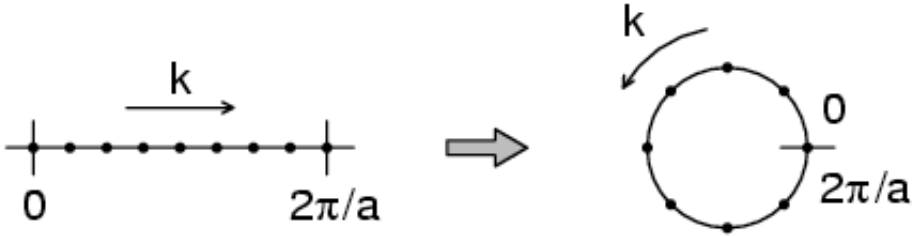
$$\mathbf{P} = \frac{ie}{(2\pi)^3} \sum_n \int_{\mathrm{BZ}} d^3k \, \langle u_{nk} | \, \nabla_{\mathrm{k}} \, | u_{nk} \rangle$$

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

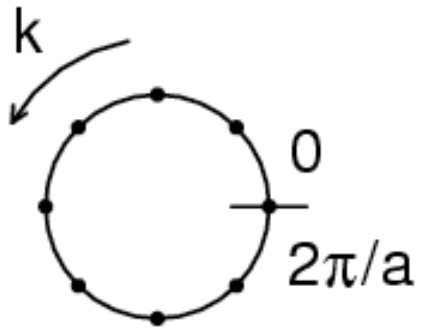
Simplify: 1 band, 1D

$$P = \frac{e}{2\pi} \int_{\mathrm{BZ}} dk \left\langle u_k \right| i \frac{d}{dk} \left| u_k \right\rangle$$

- Heuristically, $x \Rightarrow i \frac{d}{dk}$
- This is an example of a "Berry phase"
- The Brillouin zone is really a closed space:



Discrete sampling of k-space



$$P = -\frac{e}{2\pi} \operatorname{Arg} \prod_k \langle u_k | u_{k+\Delta k} \rangle$$

where

$$\operatorname{Arg}(z) = \tan^{-1}\left[\frac{\operatorname{Im}(z)}{\operatorname{Re}(z)}\right]$$

Gauge invariance

$$\ldots \langle u_{k_0} | u_{k_1} \rangle \langle u_{k_1} | u_{k_2} \rangle \langle u_{k_2} | u_{k_3} \rangle \ldots$$

is invariant under

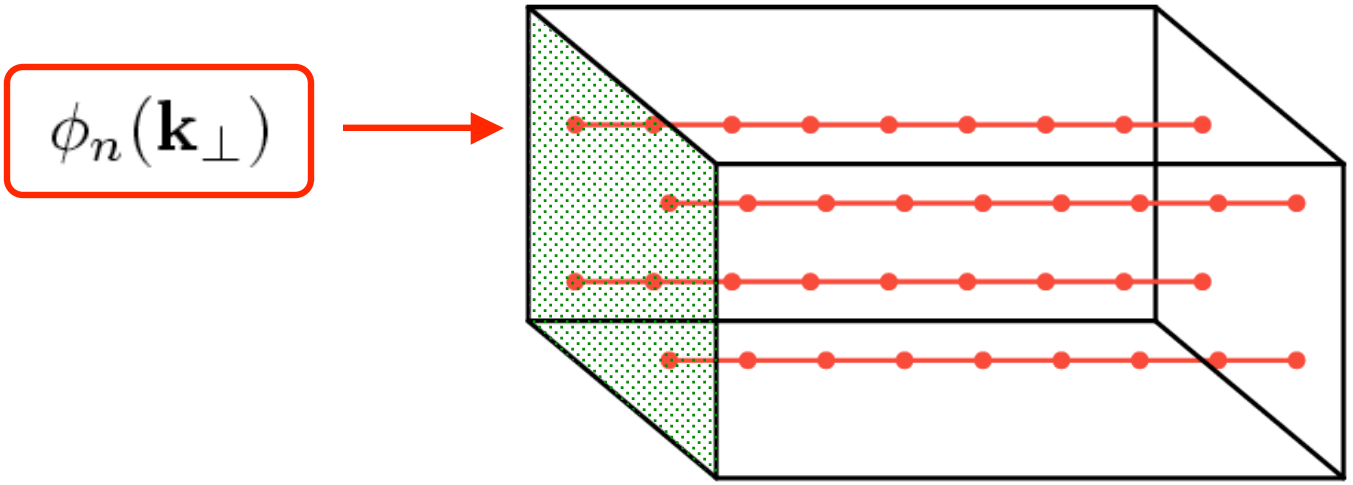
$$|u_{k_n}\rangle \rightarrow e^{i\beta_n} |u_{k_n}\rangle$$

So

$$P = -\frac{e}{2\pi} \operatorname{Arg} \prod_k \langle u_k | u_{k+\Delta k} \rangle$$

is a robust global property of closed manifold of states!

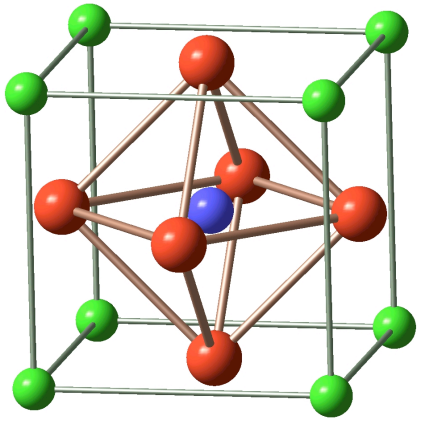
Discretized formula in 3D



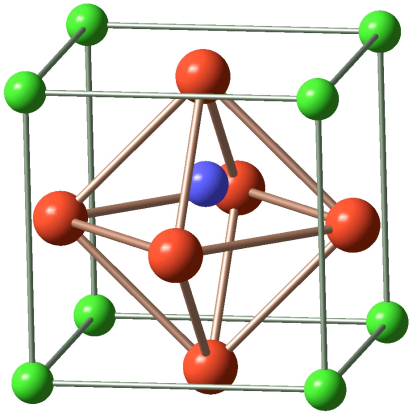
$$\mathbf{P}_n = \frac{1}{2\pi}\frac{e}{\Omega}\sum_j \phi_{n,j}\,\mathbf{R}_j \quad \text{where} \quad \phi_{n,j} = \frac{1}{N_{\mathbf{k}_\perp}}\sum_{\mathbf{k}_\perp}\phi_n(\mathbf{k}_\perp)$$

Sample Application: Born Z^*

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



Paraelectric



Ferroelectric

$Z^*(\mathrm{Ba}) = +2\ e$?

$Z^*(\mathrm{Ti}) = +4\ e$?

$Z^*(\mathrm{O_I}) = -2\ e$?

$Z^*(\mathrm{O_{II}}) = -2\ e$?

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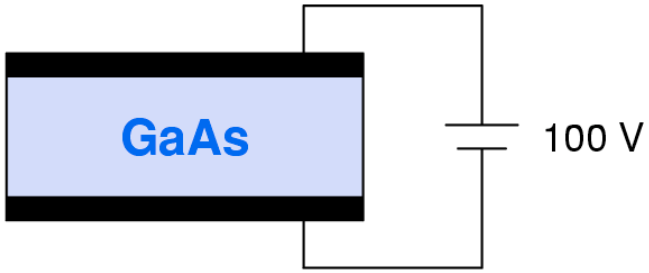
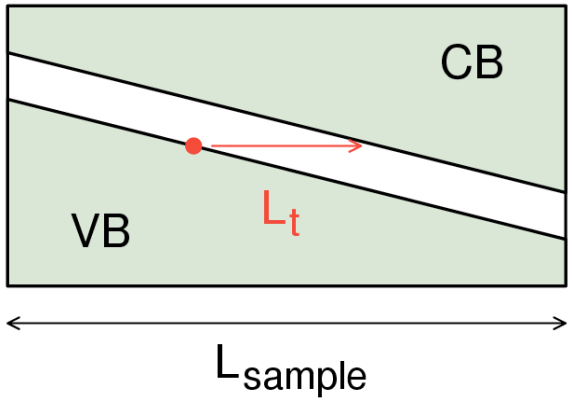
Electric Fields: The Problem

Easy to do in practice:



But ill-defined in principle:

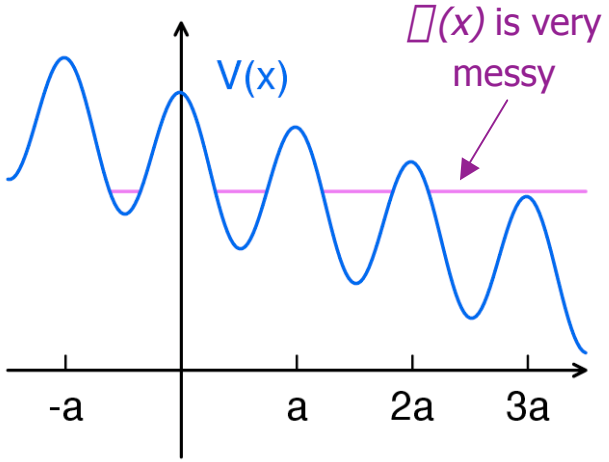


Zener tunneling

For small E-fields, $\tau_{Zener} >> \tau_{Universe}$; is it OK?

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 Solution

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

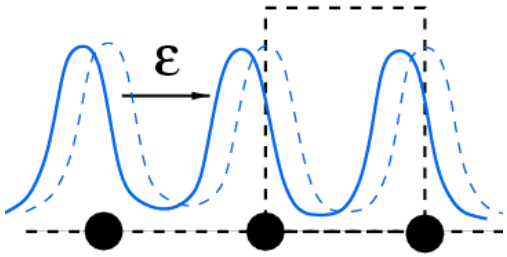
$$F = E - \mathcal{E} \cdot \mathbf{P}$$ *(Nunes and Gonze, 2001)*

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

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

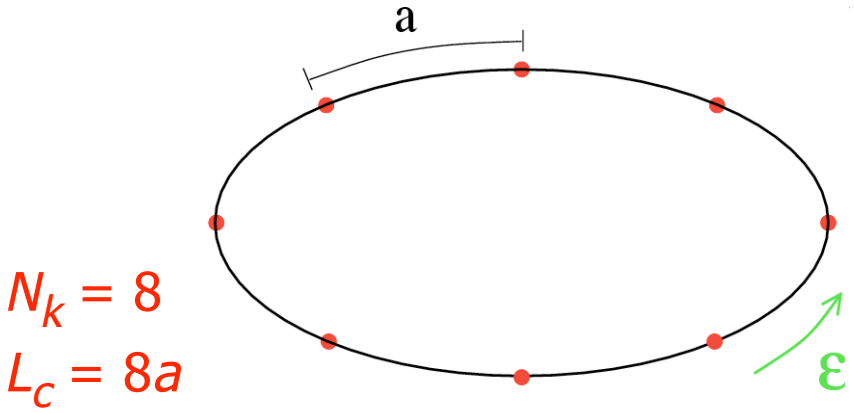
- Use Bloch representation of density matrix:

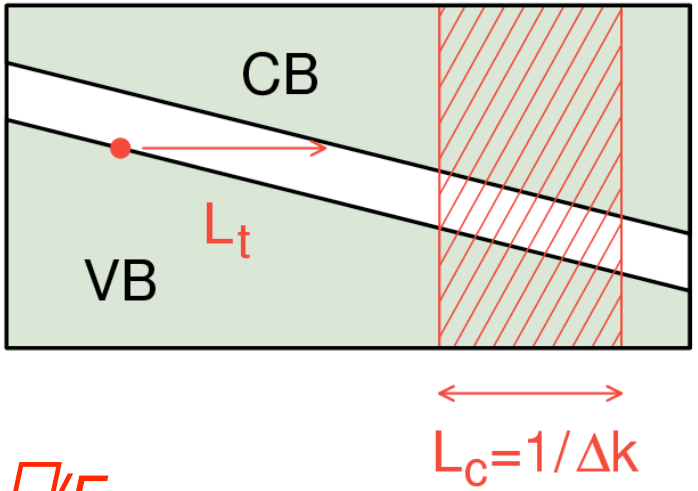
$$n(\mathbf{r}, \mathbf{r}') = \sum_{n\mathbf{k}} \psi^*_{n\mathbf{k}}(\mathbf{r})\, \psi_{n\mathbf{k}}(\mathbf{r}')$$

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

Electric Fields: The Hitch

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



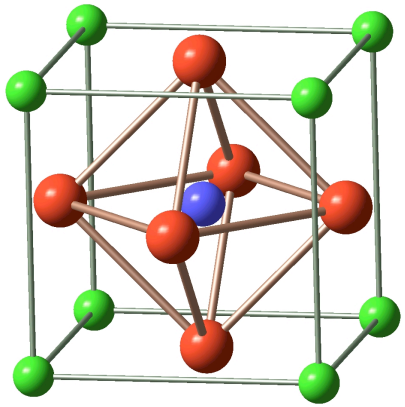


- Solution: Keep $\Delta k > 1/L_t = \Delta/E_g$

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

Can check that previous results for $BaTiO_3$ are reproduced

Sample Application: Born Z^*

	GaAs	AlAs	GaP	AlP
a (a.u.)	10.45	10.59	10.11	10.24
	(10.68)	(10.69)	(10.28)	(10.33)
Z^*_{cation}	2.00	2.14	2.10	2.24
	(2.07)	(2.18)	(2.04)	(2.28)
ϵ_∞	11.9	9.6	9.4	8.1
	(10.9)	(8.2)	(9.0)	(7.5)
$\epsilon_{\mathrm{static}}$	13.5	11.5	11.2	10.2
	(13.2)	(10.1)	(11.1)	(9.8)
$\chi^{(2)}$ (pm/V)	134	64	66	39
	(166)		(74)	
$(a^2/e)\,\gamma_{14}$	−0.40	−0.10	−0.25	0.05
	(−0.32)		(−0.18)	
$(a^2/e)\,\gamma_{14}^{(0)}$	−1.42	−1.40	−1.35	−1.31

(Souza,Iniguez, and Vanderbilt, 2002)

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Wannier function representation

Choose Wannier functions as

$$w_n(\mathbf{r}-\mathbf{R}) = \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

or, more precisely,

$$w_n(\mathbf{r}-\mathbf{R}) = \int_{BZ} e^{i\varphi_n(\mathbf{k})}\, \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

or, more precisely,

$$w_n(\mathbf{r}-\mathbf{R}) = \int_{BZ} \sum_m U^{(\mathbf{k})}_{mn}\, \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

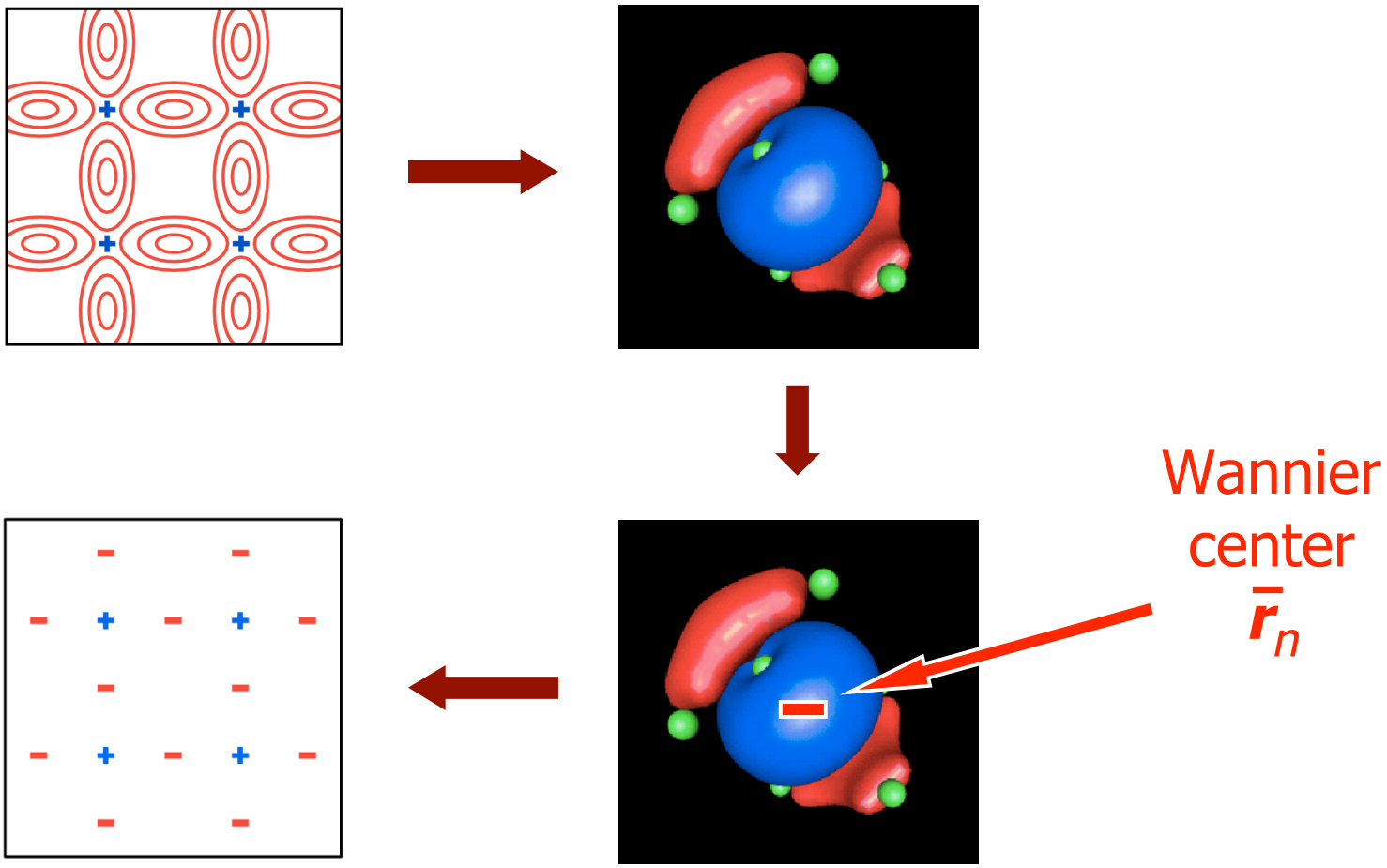
in order to minimize

$$\Omega = \sum_n \left[\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2\right]$$

(Marzari and Vanderbilt, 1997)

Here $\langle r^2\rangle_n = \langle 0n|r^2|0n\rangle$, $\boxed{\bar{\mathbf{r}}_n = \langle 0n|\mathbf{r}|0n\rangle}$ "Wannier center"

Mapping to Wannier centers



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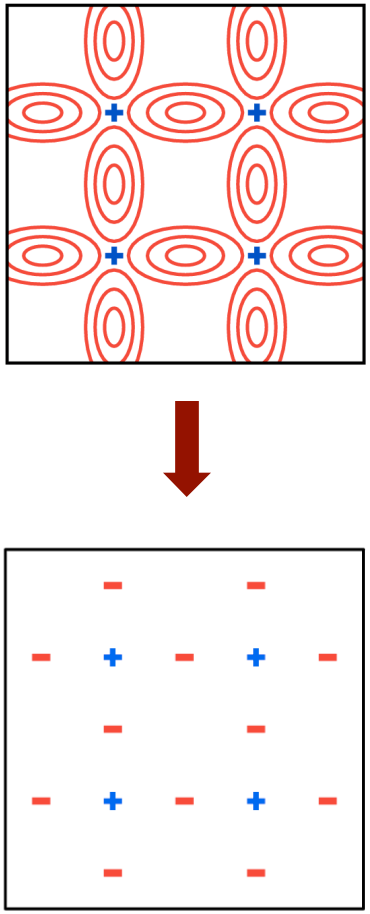
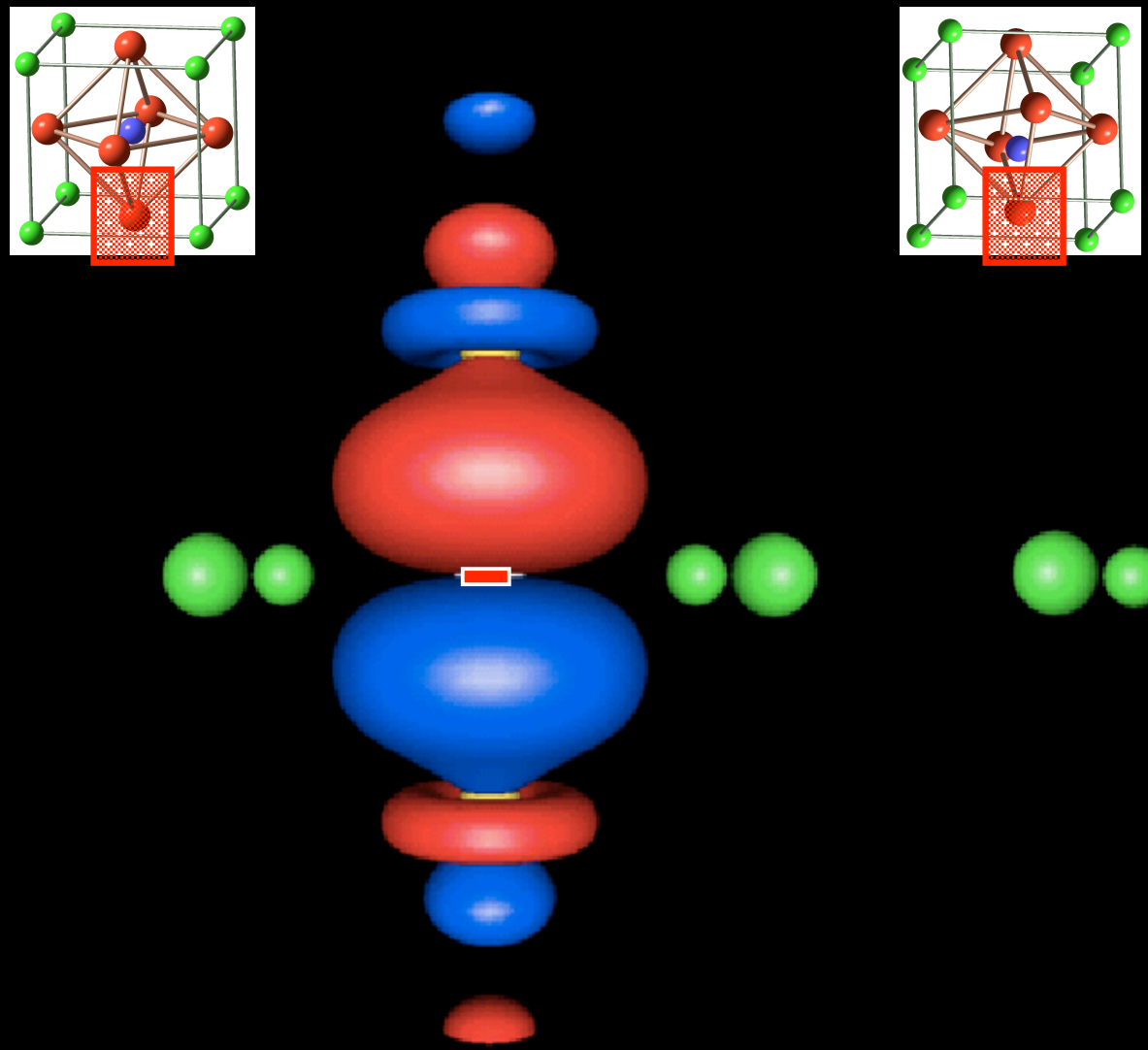


Wannier dipole theorem

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

- Exact!
- Gives local description of dielectric response!



$Z^*(\mathrm{Ba}) = +2.75\ e$

$Z^*(\mathrm{Ti}) = +7.16\ e$

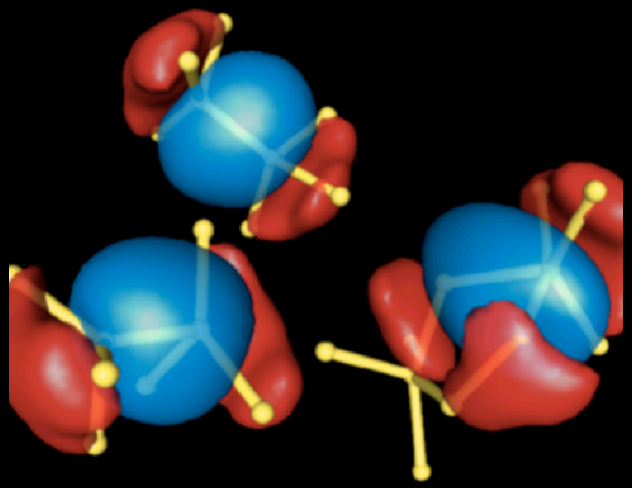
$Z^*(\mathrm{O_I}) = -5.69\ e$

$Z^*(\mathrm{O_{II}}) = -2.11\ e$

Ferroelectric $BaTiO_3$

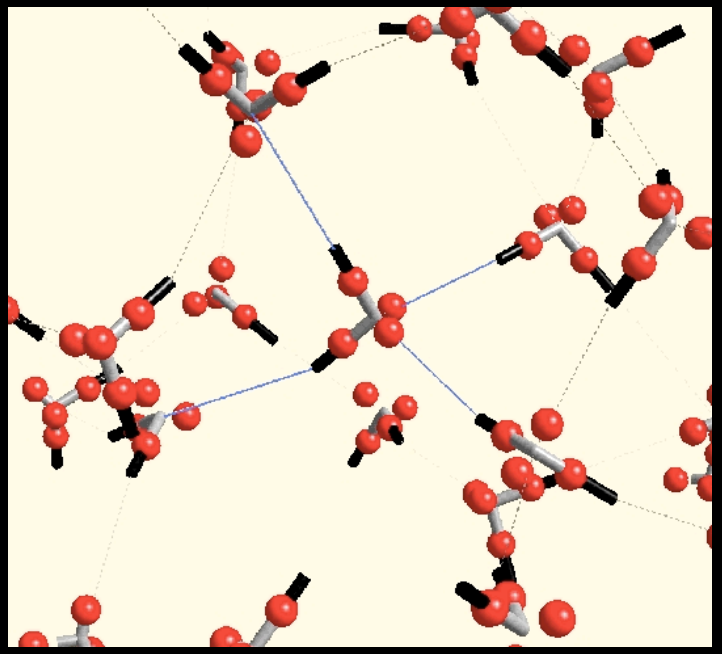
(Courtesy N. Marzari)

Wannier functions
in *a-Si*



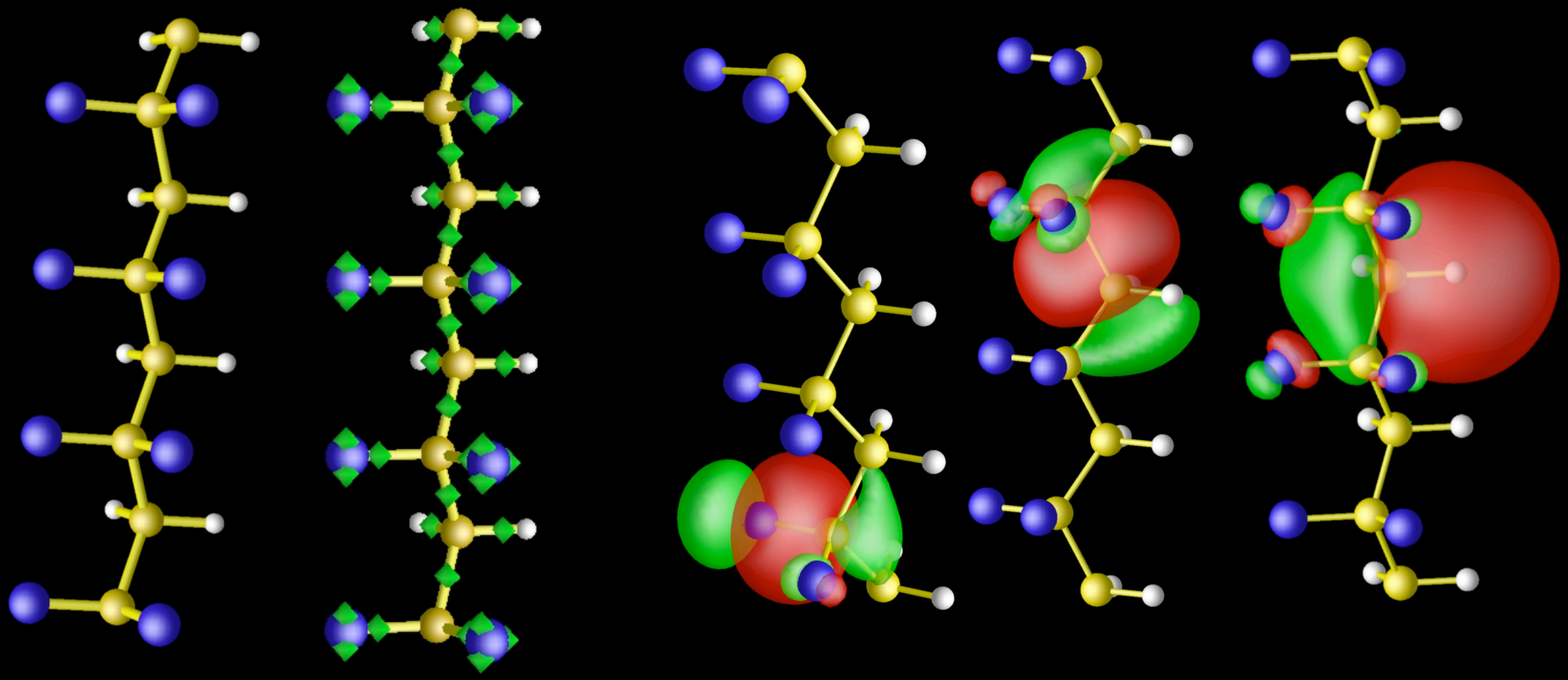
Fornari et al.

Wannier functions
in *l-H_2O*



Silvestrelli et al.

Wannier analysis of PVDF polymers and copolymers



S. Nakhmanson et al. (W26.3 2:54pm Thursday)

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Systematic treatment of E-fields and strain

(X. Wu, D. Vanderbilt, and D.R. Hamann, submitted to PRB)

We identify six needed *elementary tensors:*

$\square_{\square\square}$ = Frozen-ion dielectric tensor

$\overline{C}_{jk}$ = Frozen-ion elastic tnsor

K_{mn} = Force-constant matrix

$Z_{m\square}$ = Dynamical effective charge tensor

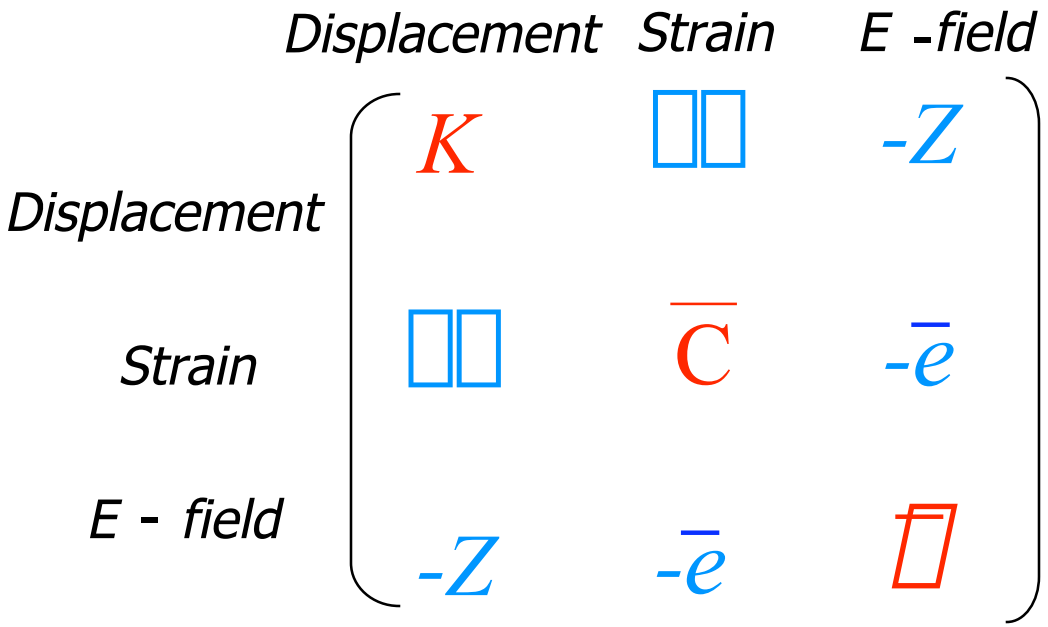
$\square_{mj}$ = Internal strain tensor

$\overline{e}_{\square j}$ = Frozen-ion piezoelectric tensor

These are computed within ABINIT using DFPT methods.

What are they?

They are elements of "big Hessian matrix"

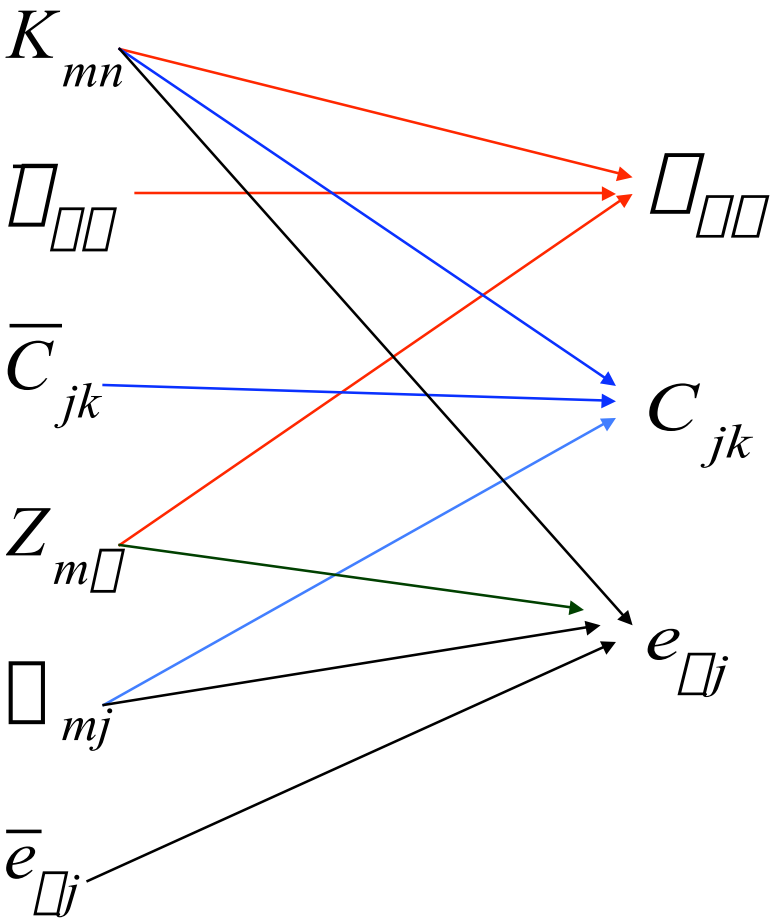


Build from

Elementary Tensors

To

Relaxed-ion tensors



Use relaxed ion $\Box_{\Box\Box}$, C_{jk}, $e_{\Box j}$ to compute

$$C_{jk}^{(D)} = C_{jk}^{(\Box)} + e_{\Box j}\Box_{\Box\Box}^{(\Box)}e_{\Box k}$$ ← *Elastic tensor at fixed D*

$$\Box_{\Box\Box}^{(\Box)} = \Box_{\Box\Box} + e_{\Box j}(C^{\Box 1})_{jk}e_{\Box k}$$ ← *Free-stress dielectric tensor*

$$S_{jk} = (C^{\Box 1})_{jk}$$ ← *Elastic compliance tensor*

$$\Box^{(\Box)} = (\Box^{(\Box)})^{(\Box 1)}$$ ← *Inverse dielectric tensor*

$$d_{\Box j} = S_{jk}^{(\Box)}e_{\Box k}$$

$$g_{\Box j} = \Box_{\Box\Box}^{(\Box)}d_{\Box j}$$

$$h_{\Box j} = \Box_{\Box\Box}^{(\Box)}e_{\Box j}$$

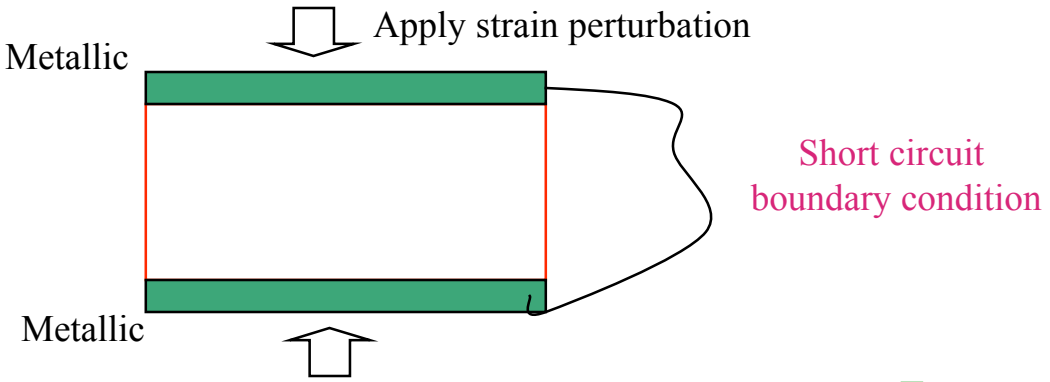
} *Various piezoelectric tensors*

$$k_{\Box j} = \frac{\left|d_{\Box j}\right|}{\sqrt{\Box_{\Box\Box}^{(\Box)}S_{jj}^{(\Box)}}}$$ ← *Electromechanical coupling*

Elastic tensors at different elec. BC's: ZnO

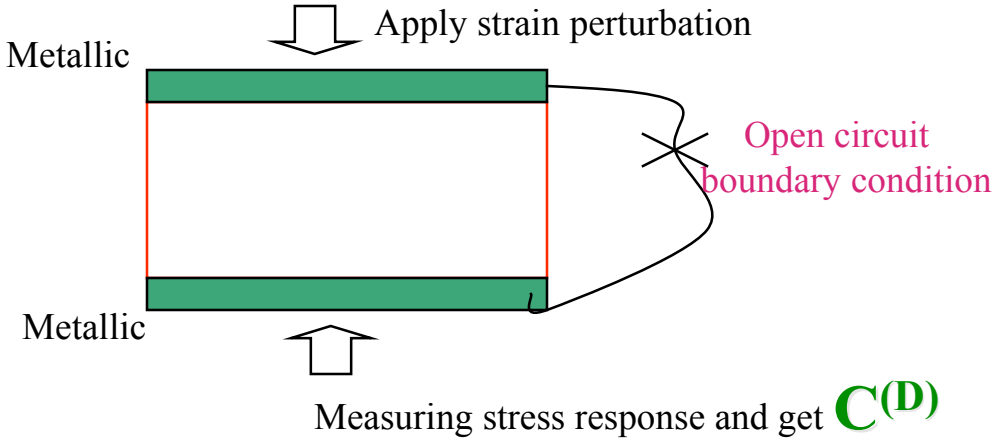
$C^{(\square)}$ (GPa)

226	139	123	0	0	0
139	226	123	0	0	0
123	123	242	0	0	0
0	0	0	40	0	0
0	0	0	0	40	0
0	0	0	0	0	44



$C^{(D)}$ (GPa)

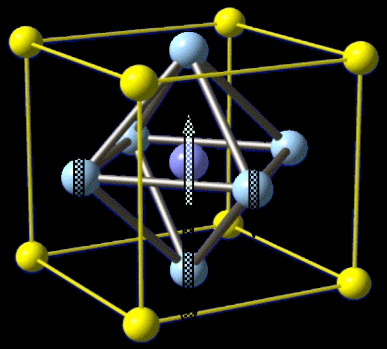
231	144	114	0	0	0
144	231	114	0	0	0
114	114	260	0	0	0
0	0	0	43	0	0
0	0	0	0	43	0
0	0	0	0	0	44

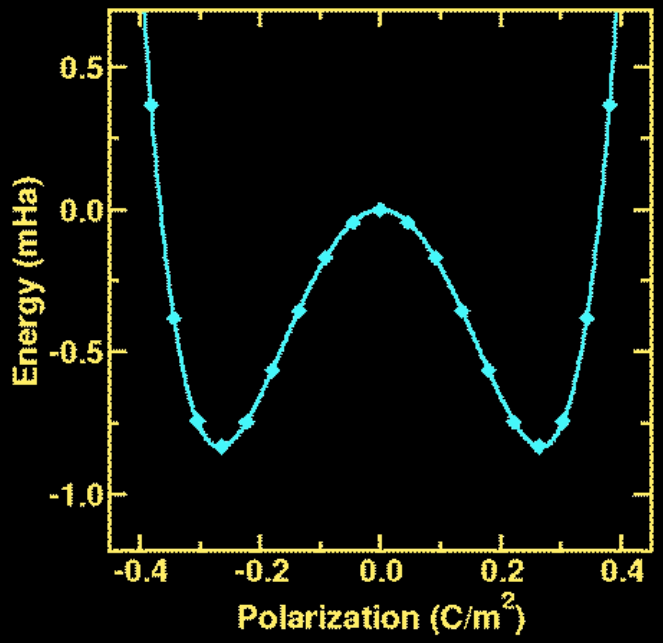


Outline

- Introduction
- Electric polarization
  - What is the problem?
  - What is the solution?
- Electric fields
  - What is the problem?
  - What is the solution?
- Localized description:
  - Wannier functions
- **Dielectric and piezoelectric properties**
  - Systematic treatment of E-fields and strains
  - **Mapping energy vs. polarization**
- Summary and prospects

Mapping Energy vs. Polarization





$$\min_{\substack{X,\psi \\ P(X,\psi)=P_t}} E(X,\psi) = \min_{\substack{X,\psi \\ \lambda \to P=P_t}} E(X,\psi) + \lambda[P_t - P(X,\psi)]$$

$$= \min_{\substack{X \\ \mathcal{E} \to P=P_t}} \min_{\psi} E(X,\psi) - \Omega \mathcal{E} P(X,\psi)$$

Oswaldo Dieguez (W26.7 3:42pm Thursday)

Status of Implementation in Code Packages

- Electric polarization
  - All major codes: ABINIT, PWSCF, VASP, CPMD, SIESTA, CRYSTAL, etc.
- Electric fields
  - ABINIT *(courtesy I. Souza, J. Iniguez, M. Veithen)*
- Maximally localized Wannier functions:
  - Package at www.wannier.org *(courtesy N. Marzari)*
- Systematic treatment of E-fields and strains
  - ABINIT *(courtesy X. Wu, D.R. Hamann, K. Rabe)*
- DFPT in finite electric field
  - Coming to ABINIT soon *(courtesy X. Wang)*
- Mapping energy vs. P
  - Coming to ABINIT soon *(courtesy O. Dieguez)*

Summary and Prospects

- Electric polarization
  - Problem and solution
- Electric fields
  - Problem and solution
- Localized description:
  - Wannier functions
- Dielectric and piezoelectric properties
  - Mapping energy vs. polarization
  - Systematic treatment of E-fields and strains
- New directions:
  - Dynamic generalizations of P_{berry}
    (I. Souza, Valley Prize Talk, B3.1 11:15am Monday)
  - DFPT in finite electric field
    (X. Wang, S32.3 2:30pm Wednesday)
- Many possible applications