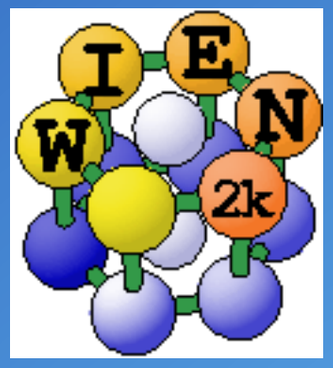
Wannier functions, macroscopic polarization (Berry phase) and related properties

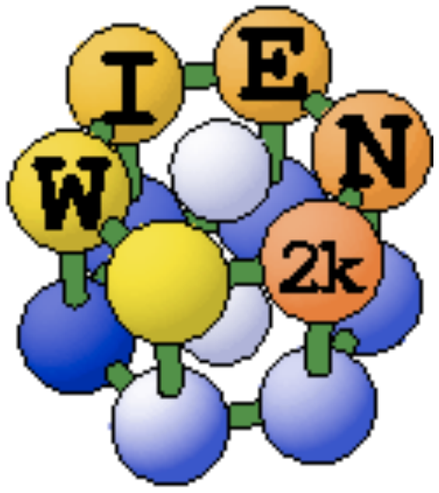
Oleg Rubel

Department of Materials Science and Engineering



@ McMaster University

Wannier functions



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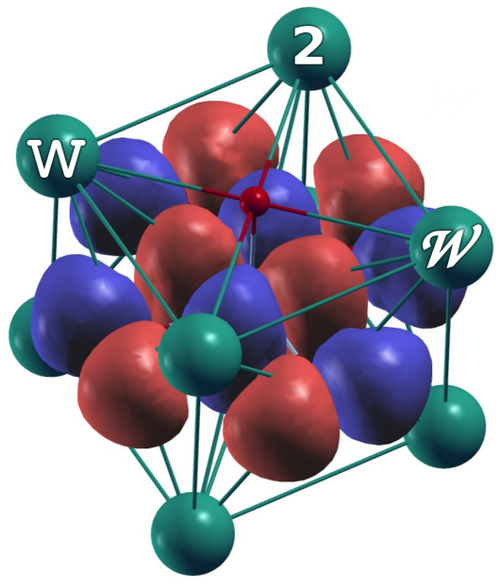


+

WANNIER90

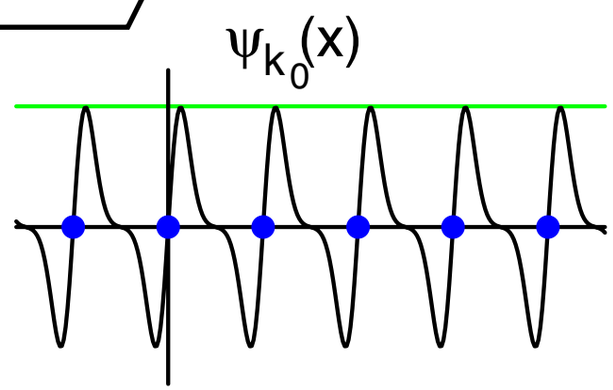
Bloch *vs* Wannier functions

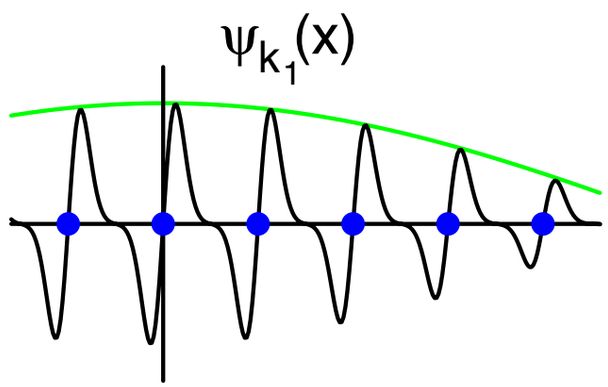
Bloch functions

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

Indexed by the wave vector

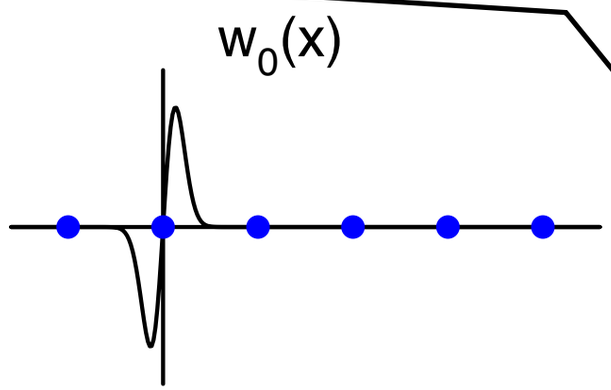
Γ-point

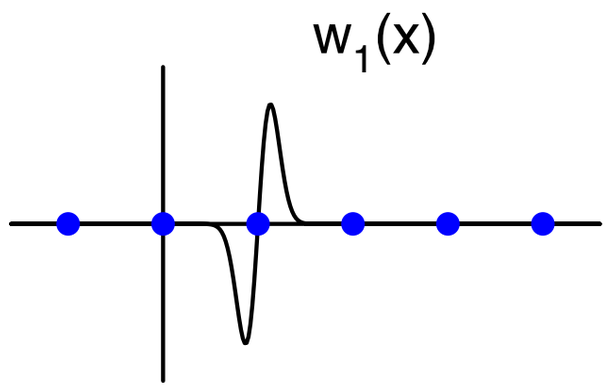




Wannier functions (localized orbitals)

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}}|\psi_{n\mathbf{k}}\rangle.$$





Indexed by the lattice vector in real space

Both sets: complete and orthonormal

Wannier:
PRB **52**, 191 (1937)
Marzari et al.:
PRB 56, 12847 (1997)
Rev. Mod. Phys. (2012)

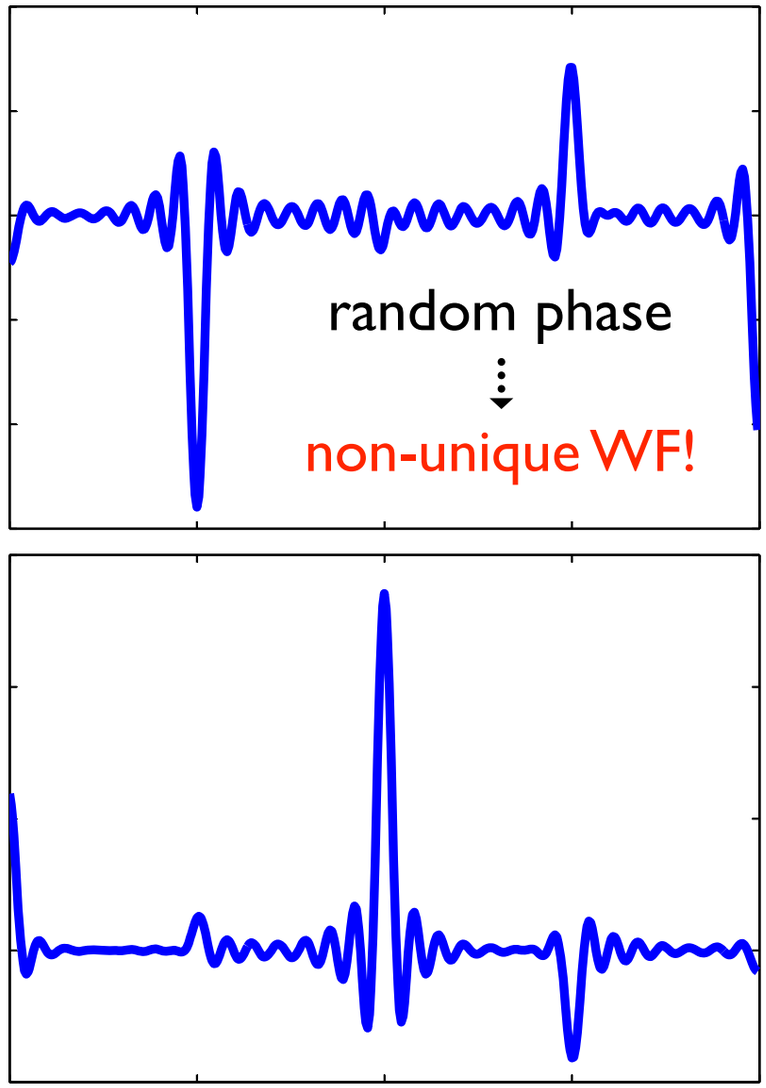
Ambiguity of Wannier functions

Bloch functions (more precisely):

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

gauge freedom

(does not change the physical description of the system)



General transformation of Bloch functions into Wannier functions:

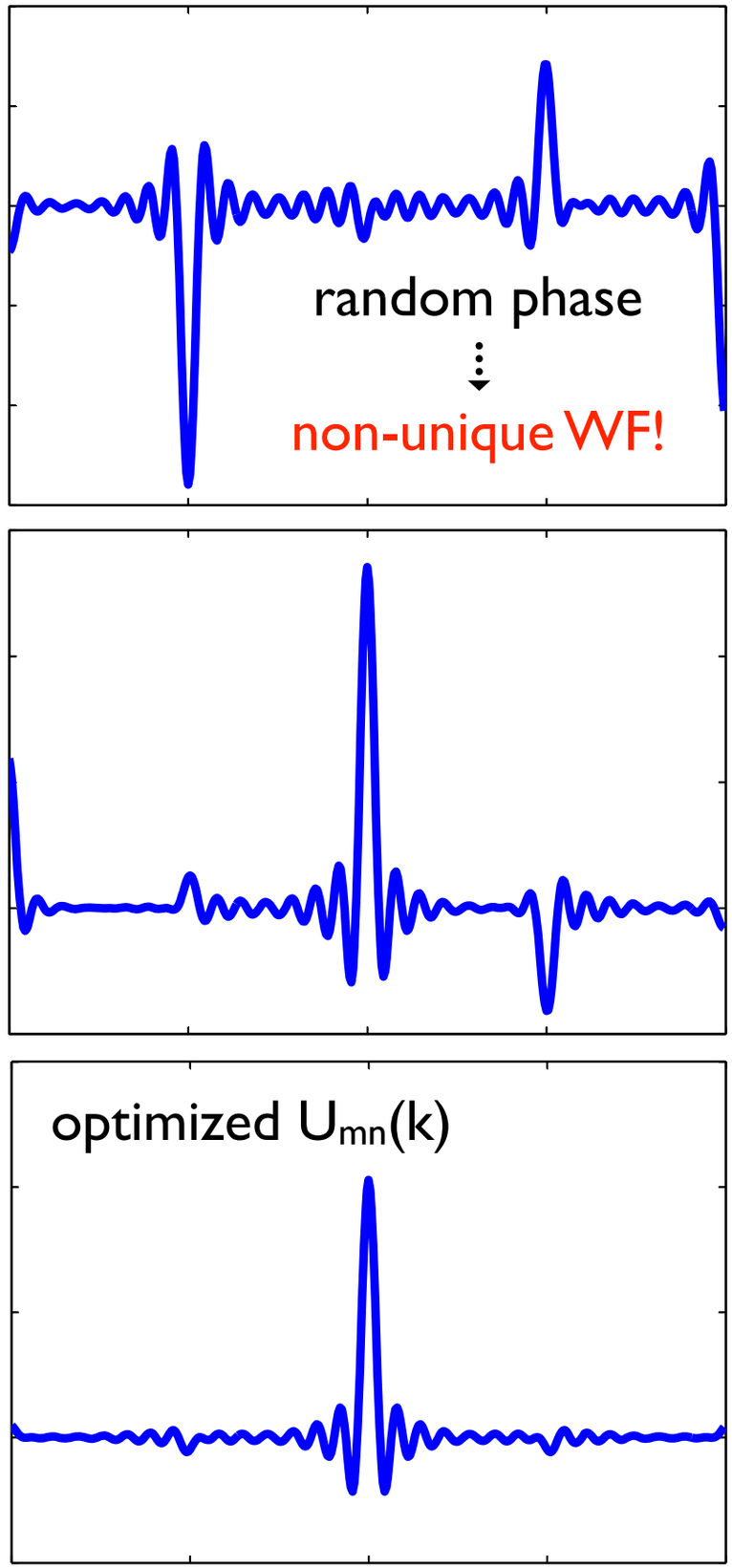
$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^{J} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}\rangle.$$

Bloch-like orbitals

The unitary matrix $U_{mn}(k)$ mixes bands (needed for degenerate bands)

Max. localized Wannier functions (MLWF)

Manipulations with coefficients of the unitary matrix $U_{mn}(k)$ allow to construct Bloch-like orbitals that are a localized in real space.



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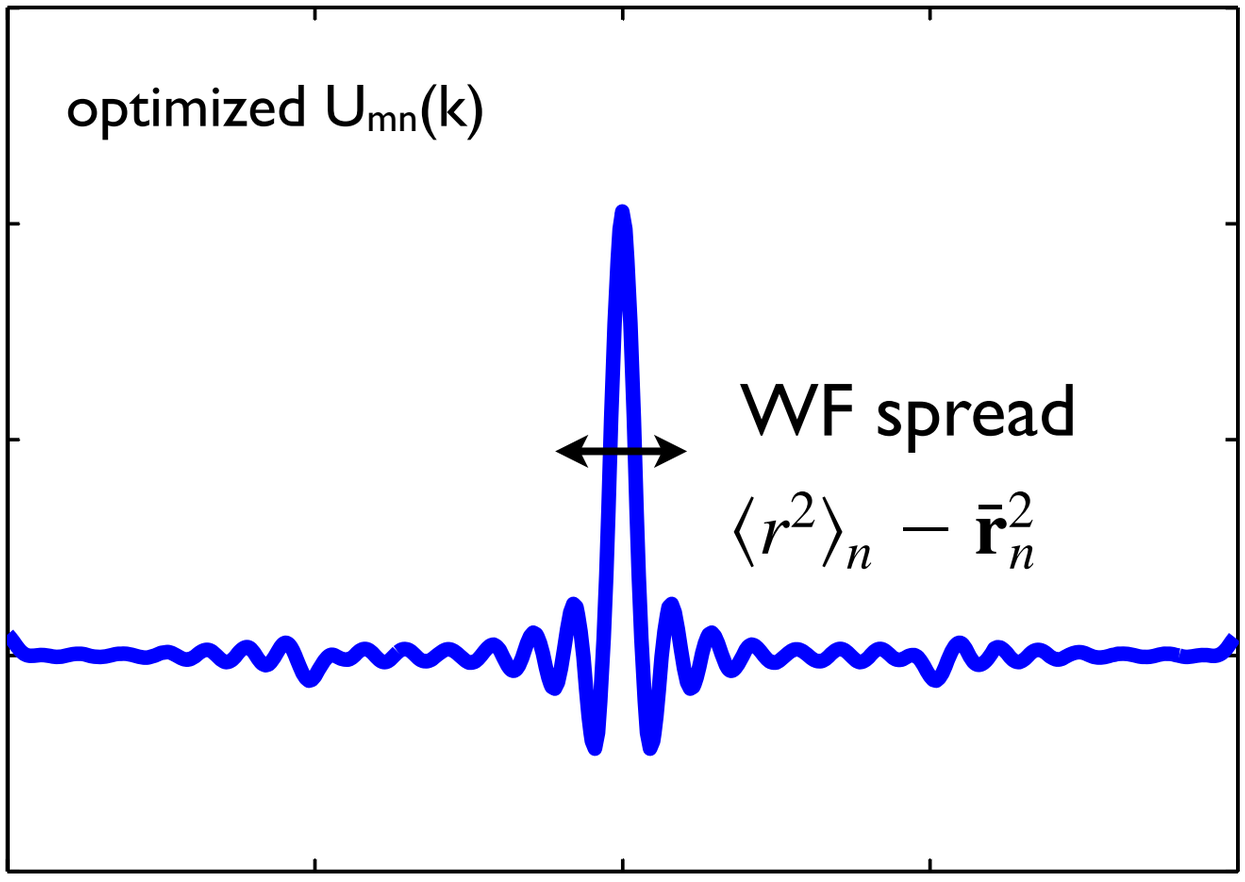
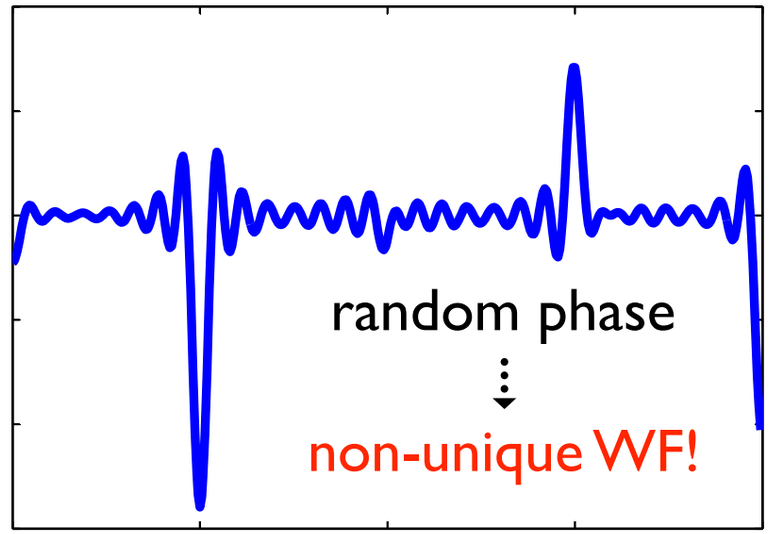
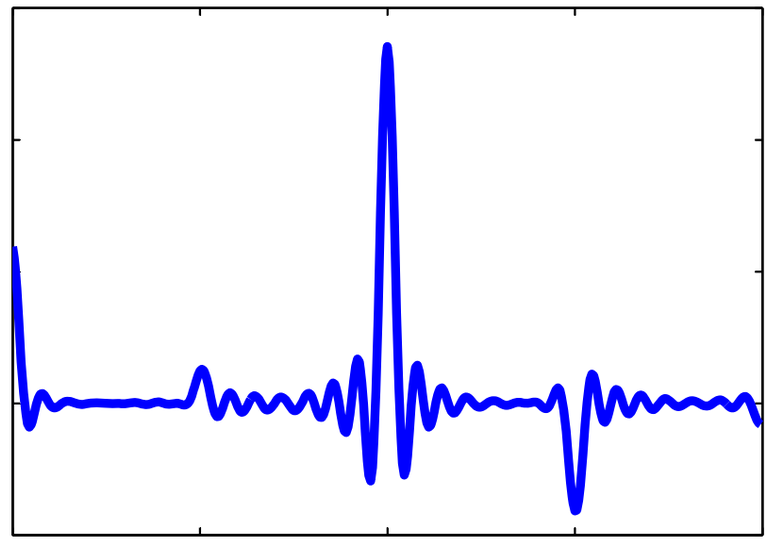
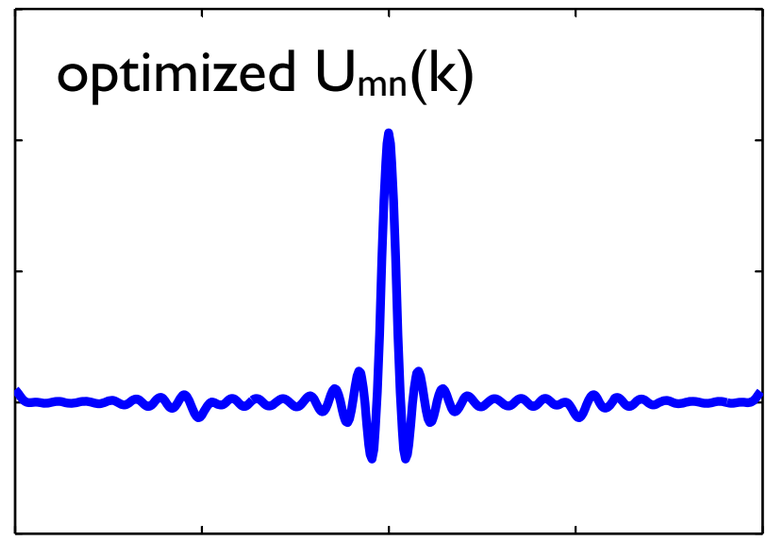








$$\Omega = \sum_n [\langle \mathbf{0}n|r^2|\mathbf{0}n\rangle - \langle \mathbf{0}n|\mathbf{r}|\mathbf{0}n\rangle^2] = \sum_n [\langle r^2 \rangle_n - \bar{\mathbf{r}}_n^2]$$

Wannier functions matrix elements

$\langle 0n|\mathbf{r}|0n\rangle$ – position of the Wannier center

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}}|\psi_{n\mathbf{k}}\rangle.$$

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

$\hat{\mathbf{r}} = i\nabla_{\mathbf{k}}$ -- position operator

$$\langle 0n|\mathbf{r}|0n\rangle = i\,\frac{V}{(2\pi)^3}\int d\mathbf{k}\,\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$$

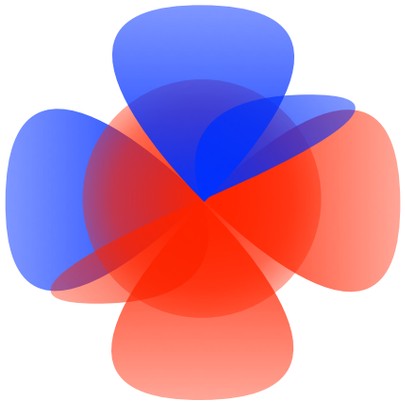
related to Berry phase, electronic polarization

Discretization:

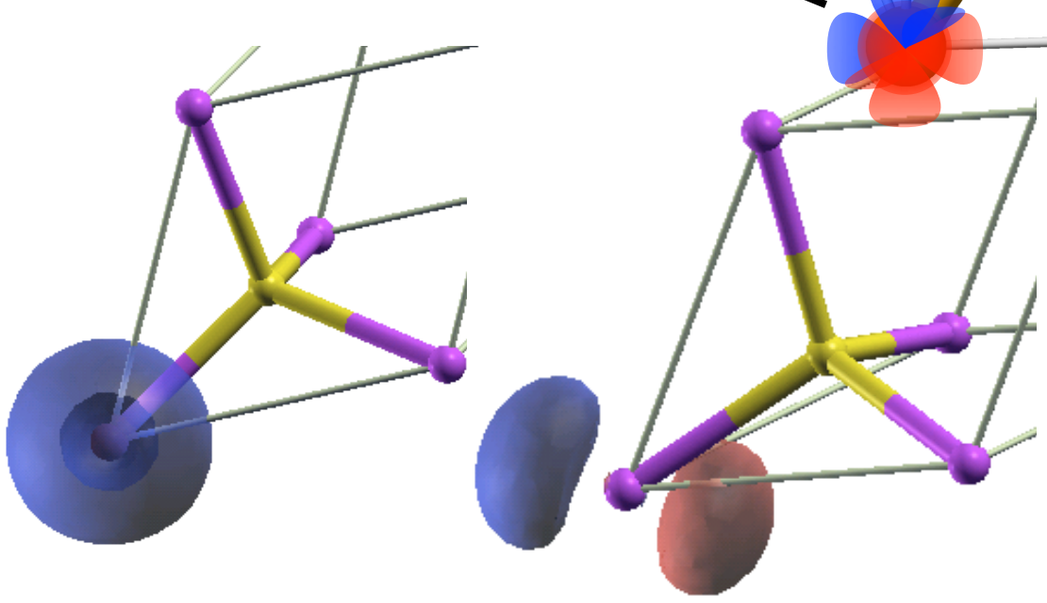
$$\mathrm{d}\varphi_n = -i\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle\cdot\mathrm{d}\mathbf{k} = -i\,\ln\langle u_{n\mathbf{k}}|u_{n(\mathbf{k}+\mathrm{d}\mathbf{k})}\rangle$$

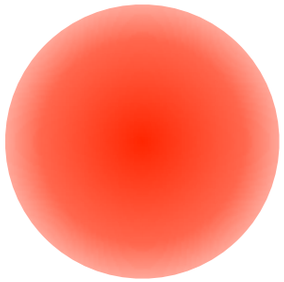
$\mathbb{S}_{mn}(\mathbf{k}_j,\mathbf{k}_{j+1}) = \langle u_{m\mathbf{k}_j}|u_{n\mathbf{k}_{j+1}}\rangle$ -- matrix elements

Initial projections

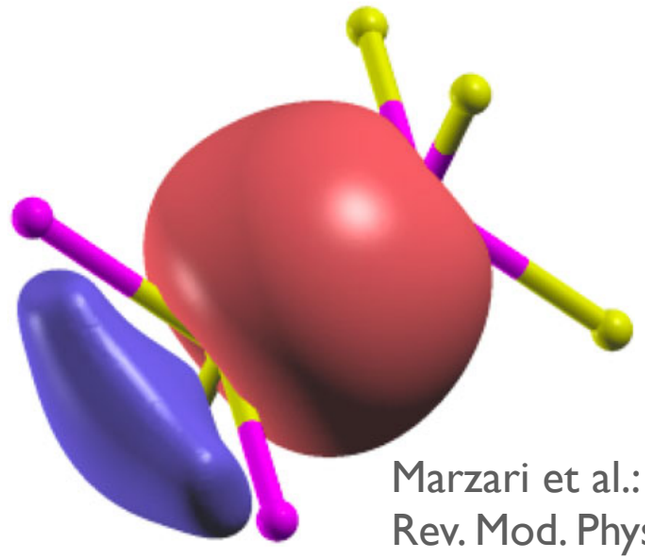


Atom centered sp^3-like





Bond centered s-like

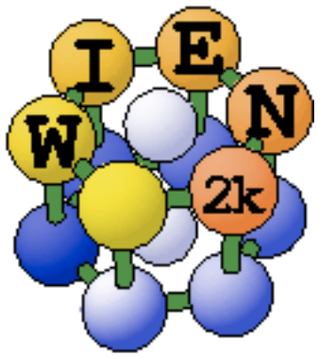


Marzari et al.:
Rev. Mod. Phys. (2012)

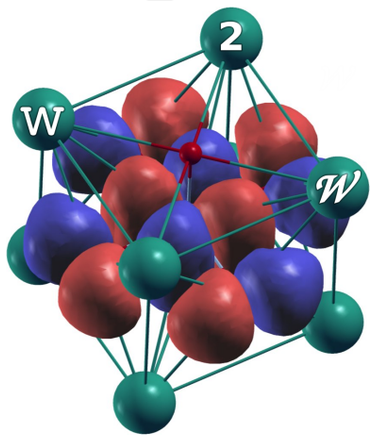
- includes *bonding* and *antibonding* states
- building effective hamiltonian

- includes *valence* states
- charge transfer and polarization

Workflow

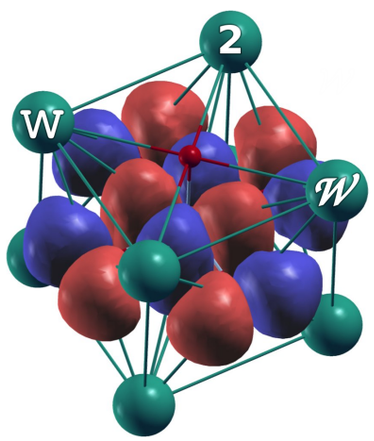


- Regular SCF calculation
- Band structure plot



- Initialize wien2wannier (`init_w2w`):
  - select **bands**, init. **projections**, **# of WF** (`case.inwf` file)
  - projected band structure "bands_plot_project" (`case.win` file)
  - additional options related to entanglement (`case.win` file)
- Compute overlap matrix element S_{mn} and projections M_{mn} (`x w2w`)

WANNIER90



- Perform Wannierization (`x wannier90`):
  - position of **Wannier centers** and spreads (`case.wout` file)
  - **Wannier hamiltonian** (`case_hr.dat` file)

- Initialize **plotting**, select plotting range, r-mesh (`write_inwplot`)
- Evaluate WF on the r-mesh selected (`x wplot`)
- Convert the output of `wplot` into `xcrysden` format for plotting (`wplot2xsf`)

XCrySDen

- Plot WF

Wannier functions as a tight-binding basis

(Atom-centered WF)

$ **less GaAs-WANN_hr.dat**

```
...
   0     0     0     1     1    -4.335108    0.000000
   0     0     0     2     1    -0.000001
   0     0     0     3     1     0.000000
   0     0     0     4     1    -0.000001
   0     0     0     5     1    -1.472358
   0     0     0     6     1    -1.157088
   0     0     0     7     1    -1.157088
   0     0     0     8     1    -1.157088
...
   0     0     1     1     1    -0.001219
...
```

⟨s1| |s1⟩

Matrix element (eV)
⟨s1|H|s1⟩ = E_{s1}

Im part = 0

Home unit cell

⟨s2|

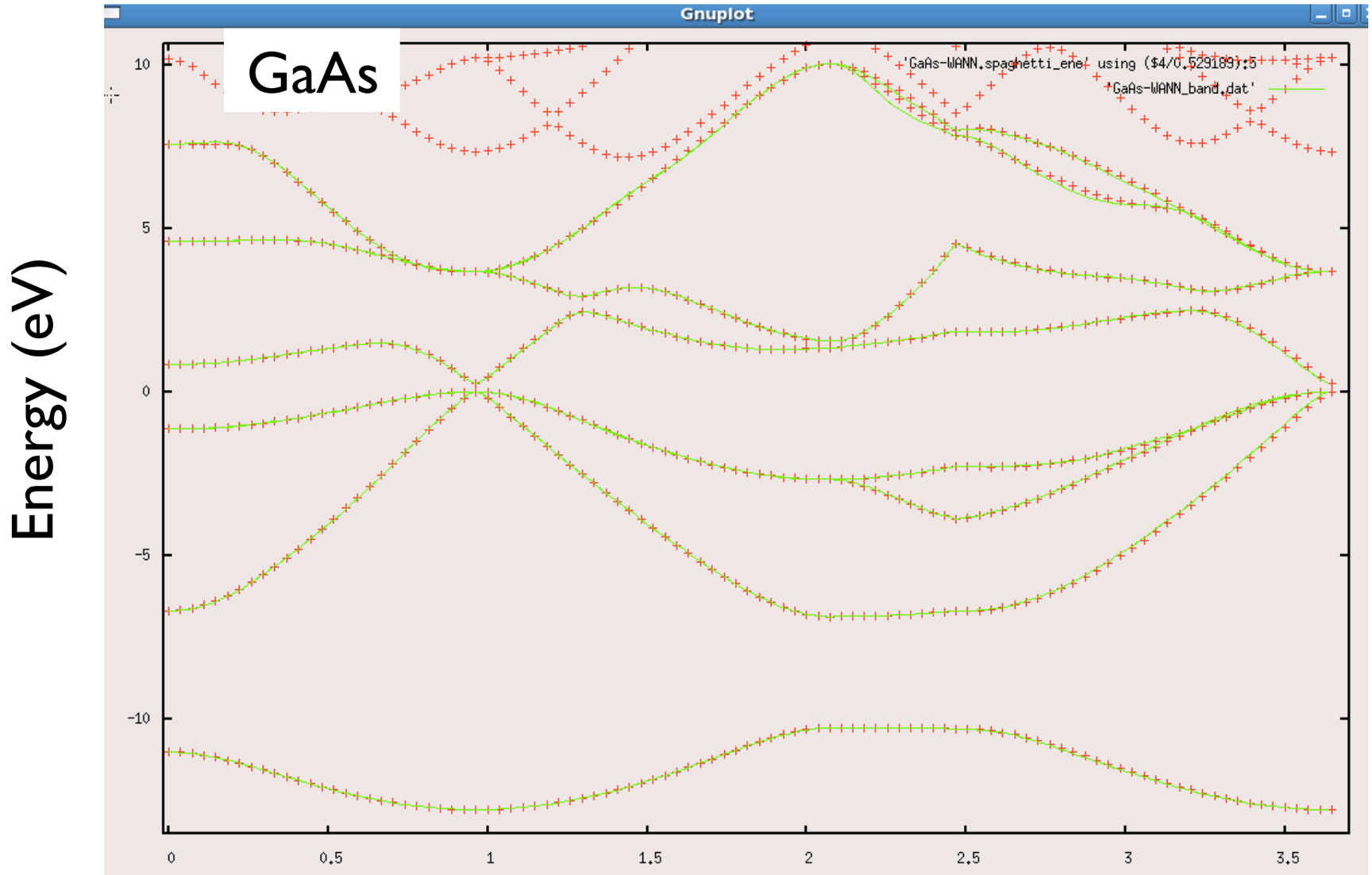
Matrix element (eV)
⟨s2|H|s1⟩ = $V_{ss\sigma}$

⟨p2|H|s1⟩ = V_{sp}

Neighbour unit cell

WF are well localized
⇒ nearest-neighbour suffice

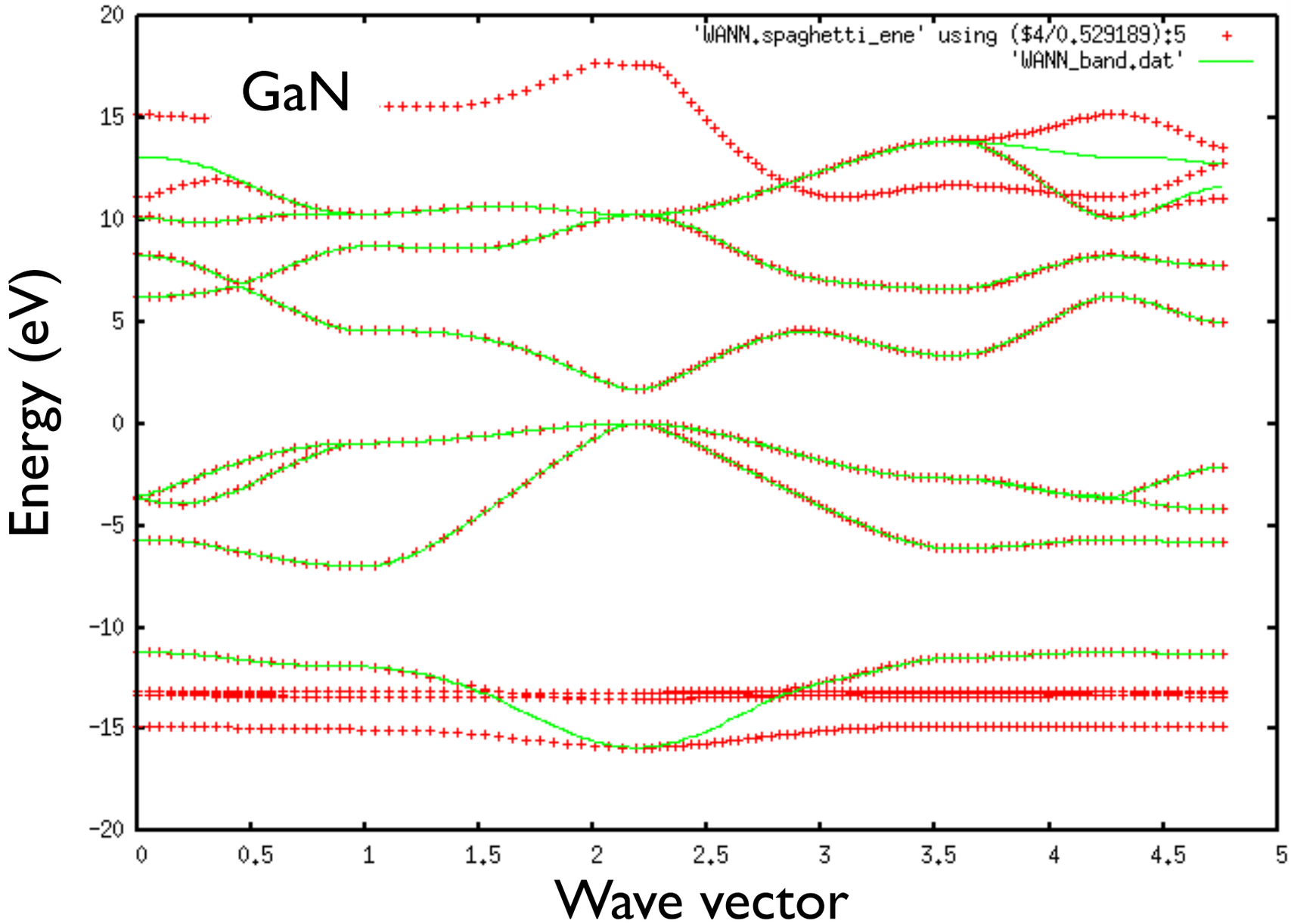
Band structure



E_F

+ original Wien2k band structure
– Band structure computed from Wannier hamiltonian

Disentanglement



E_F

} Ga-3d & N-2s

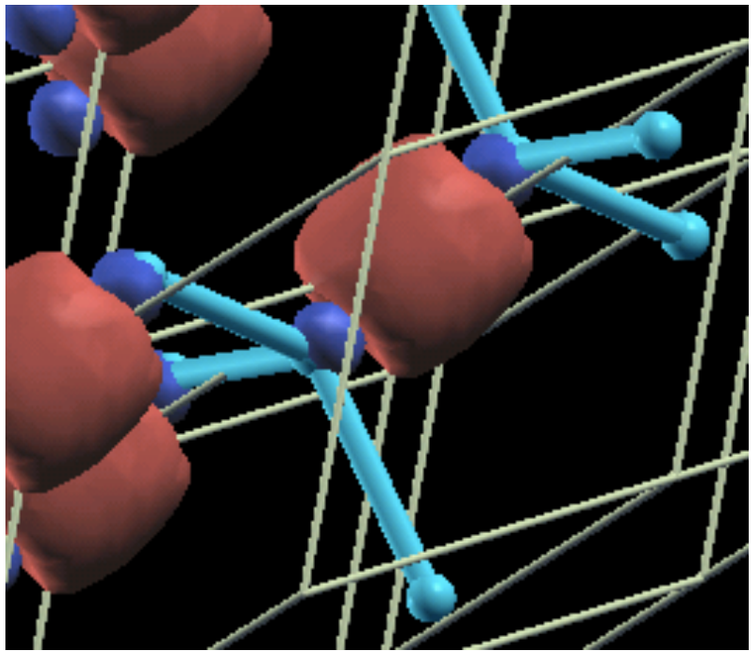
+ original Wien2k band structure
– Band structure computed from Wannier hamiltonian

Souza et al.:
PRB 65, 035109 (2001)

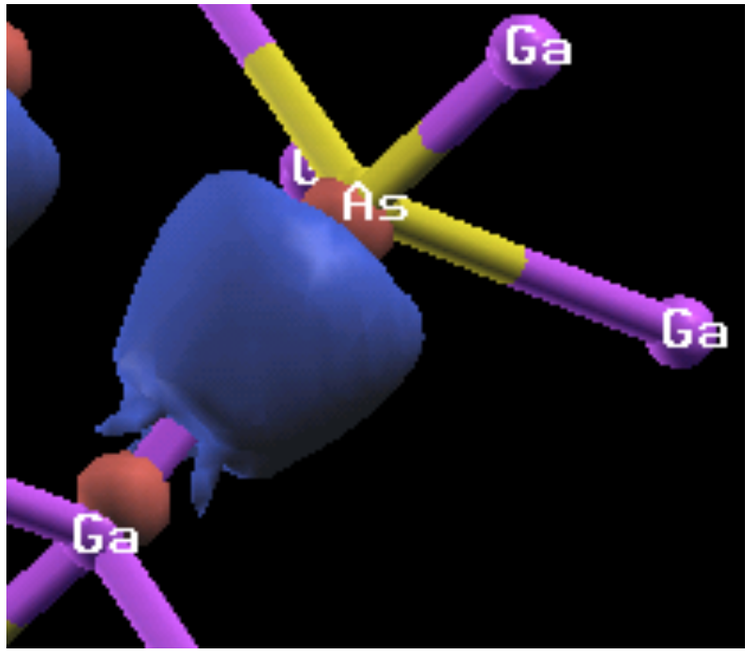
Relation to polarization

Bond-centered WF

Si



GaAs



+ Z_{As}

− Wannier center q_e

+ Z_{Ga}

symmetric (non-polar)

non-symmetric (polar)

$$\mathbf{P} = \frac{e}{V}\left(\sum_{\tau} Z_{\tau}\mathbf{r}_{\tau} - \sum_{n}\mathbf{r}_{n}\right)$$

Ionic part

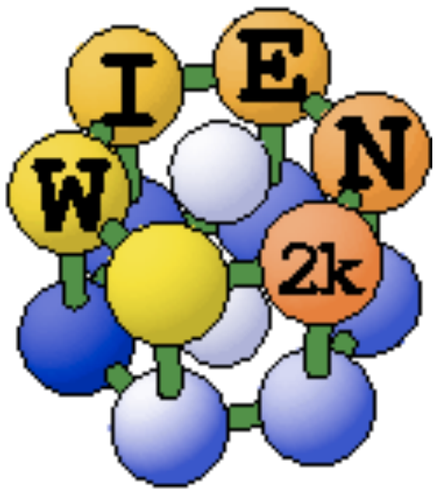
Electronic part

King-Smith & Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

Useful resources

- Jan Kuneš *et al.* "Wien2wannier: From linearized augmented plane waves to maximally localized Wannier functions", Comp. Phys. Commun. **181**, 1888 (2010).
- Wien2Wannier home and user guide: http://www.ifp.tuwien.ac.at/forschung/arbeitsgruppen/cms/software-download/wien2wannier/
- Wannier90 home and user guide: http://www.wannier.org/
- Nicola Marzari *et al.* "Maximally localized Wannier functions: Theory and applications", Rev. Mod. Phys. **84**, 1419 (2012)

Macroscopic polarization



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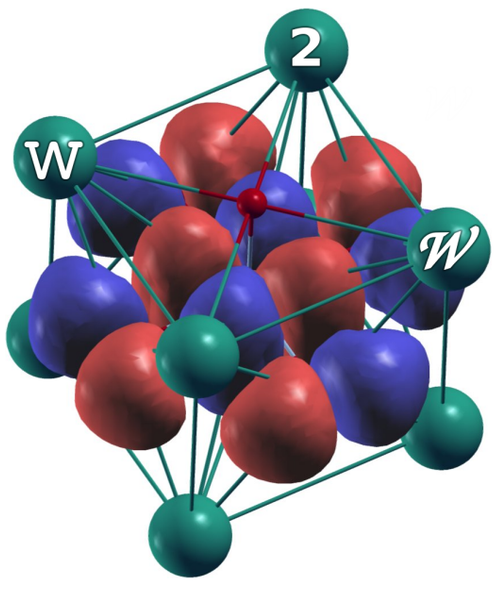
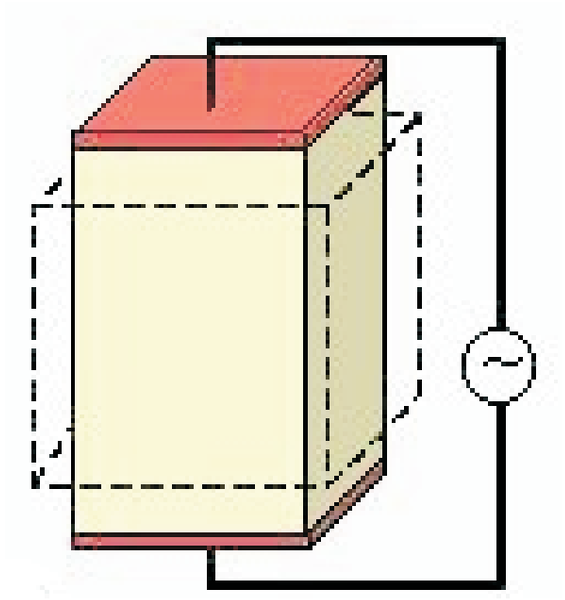


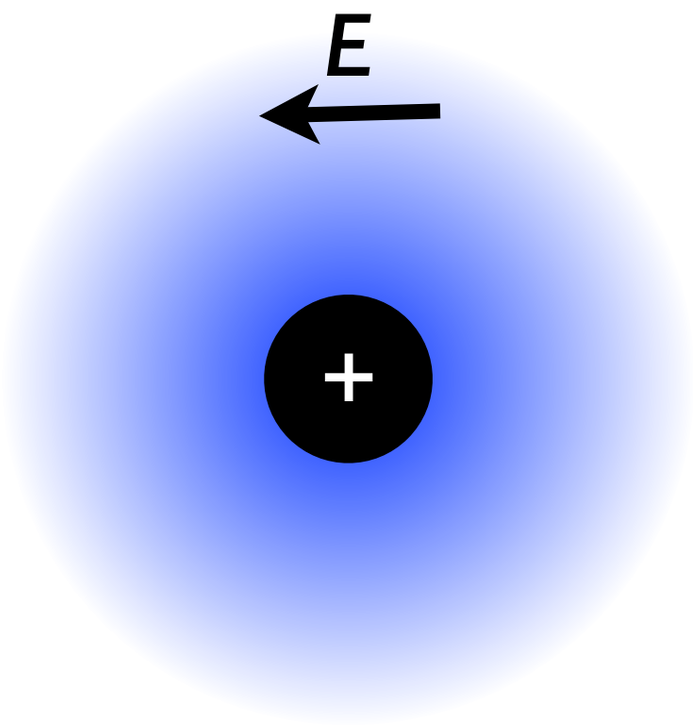
+ BerryPI

Material properties related to polarization

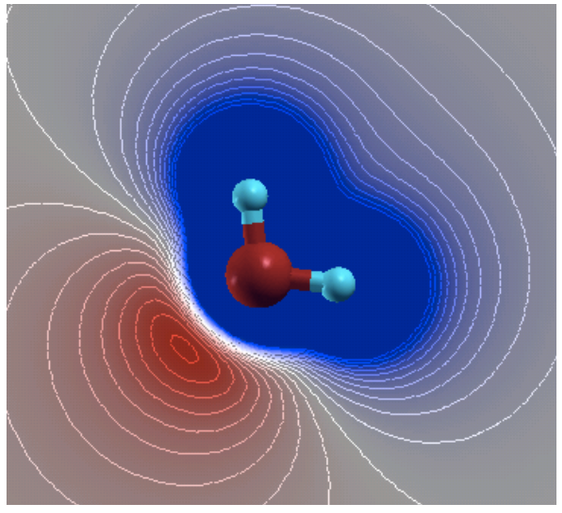
Piezo- and Ferroelectricity



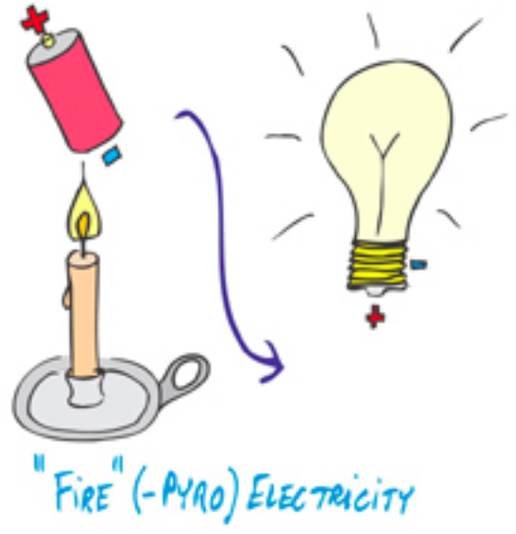
Dielectric screening



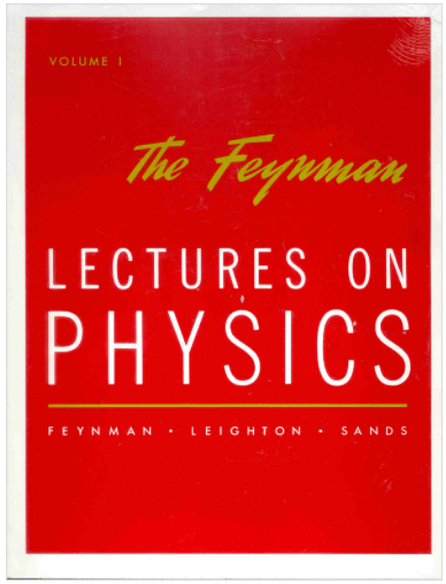
Effective charge



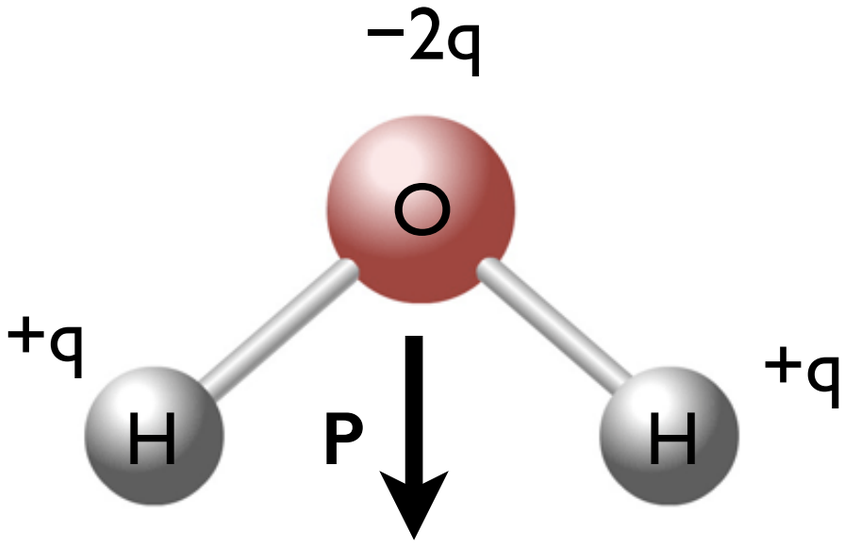
Pyroelectricity

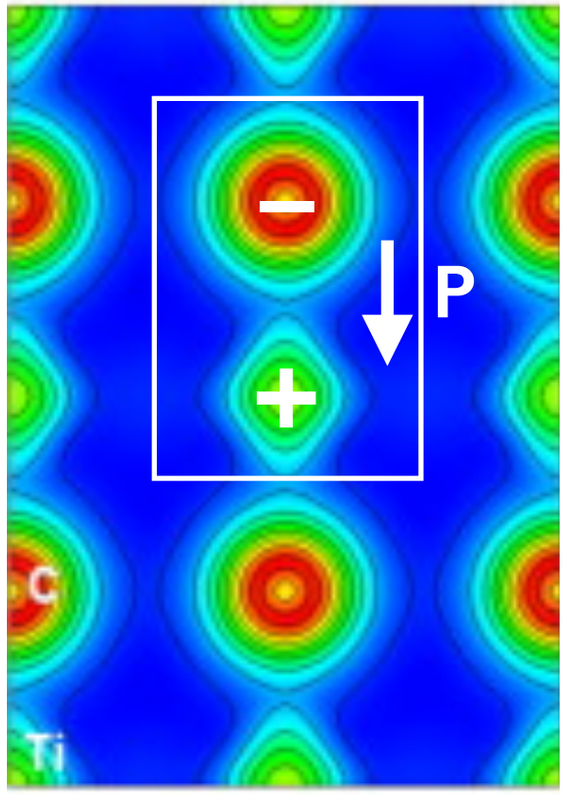


What is polarization?



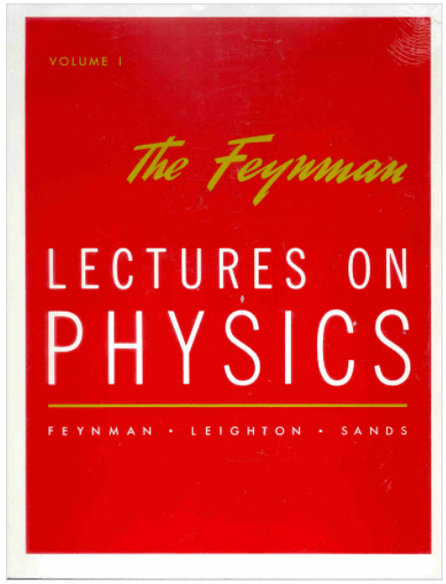
We will now assume that in each atom there are charges q separated by a distance δ, so that $q\delta$ is the dipole moment per atom. (We use δ because we are already using d for the plate separation.) If there are N atoms per unit volume, there will be a *dipole moment per unit volume* equal to $Nq\delta$. This dipole moment per unit volume will be represented by a vector, $\boldsymbol{P}$. Needless to say, it is in the direction of the individual dipole moments, i.e., in the direction of the charge





Polarization for periodic solids is undefined

What is polarization?



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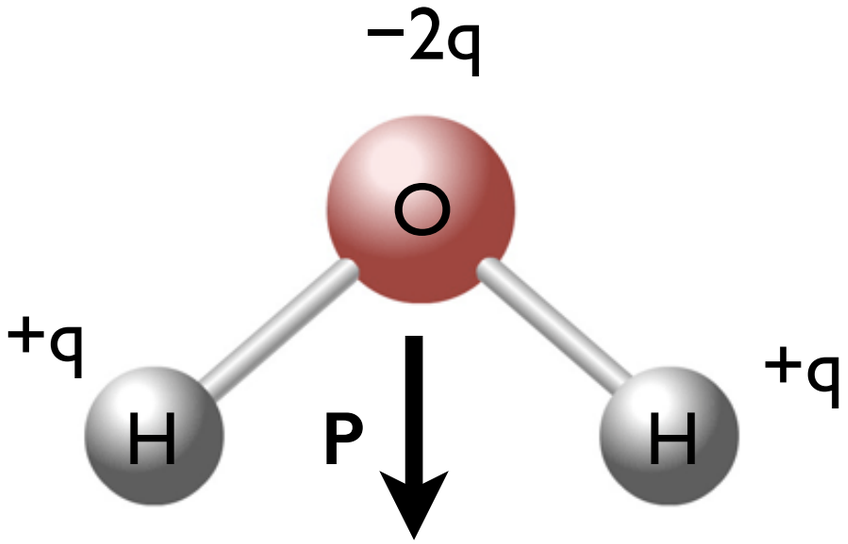
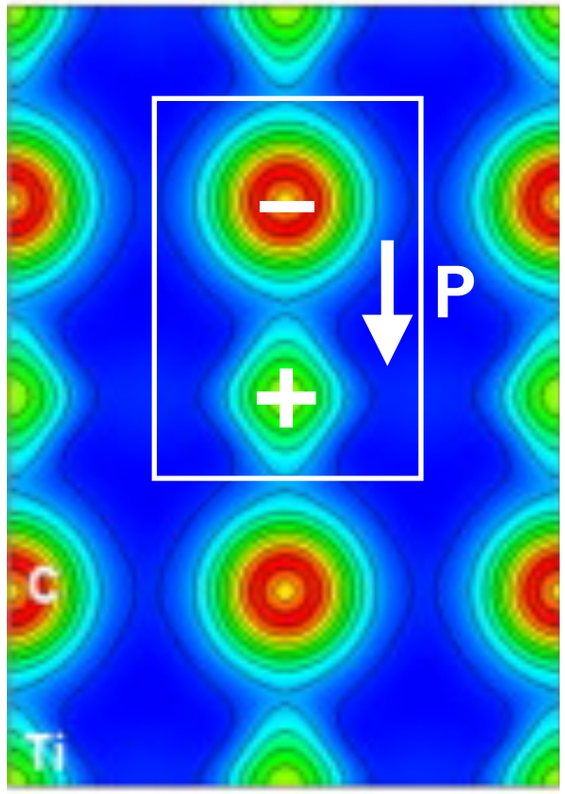
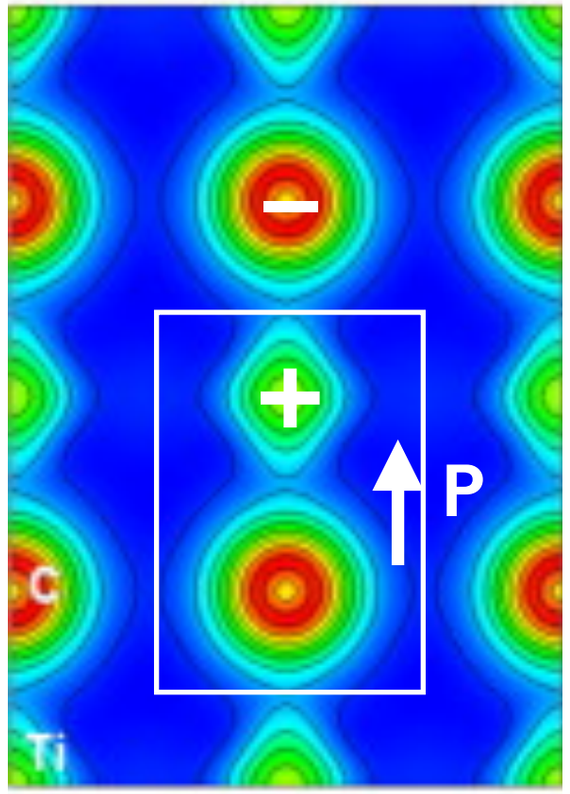






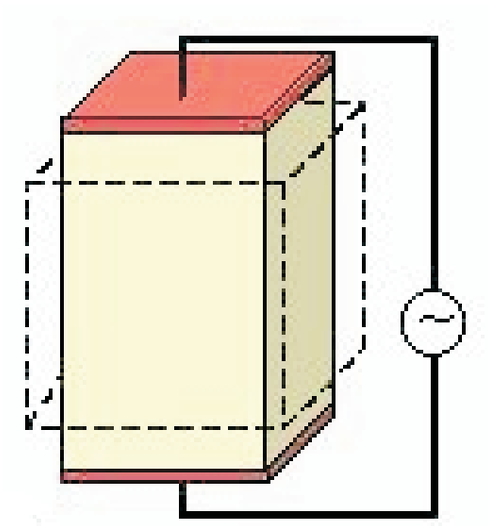
Polarization for periodic solids is undefined

Modern theory of polarization

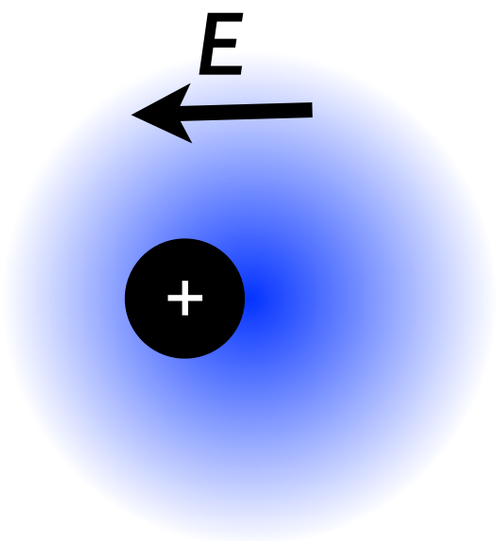
Pioneered by *King-Smith*, *David Vanderbilt* and *Raffaele Resta*

All measurable physical quantities are related to the **change** in polarization!

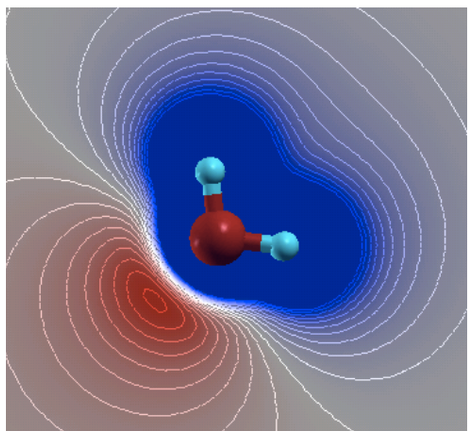
$$\Delta\mathbf{P} = \mathbf{P}^{(0)} - \mathbf{P}^{(1)}$$



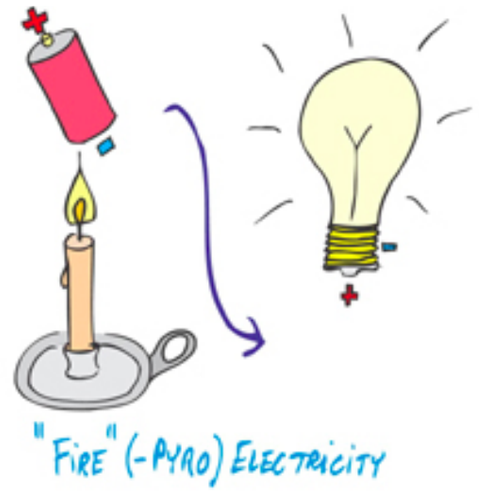
$$\frac{\Delta\mathbf{P}}{\Delta\text{strain}}$$



$$\frac{\Delta\mathbf{P}}{\Delta\mathbf{E}}$$

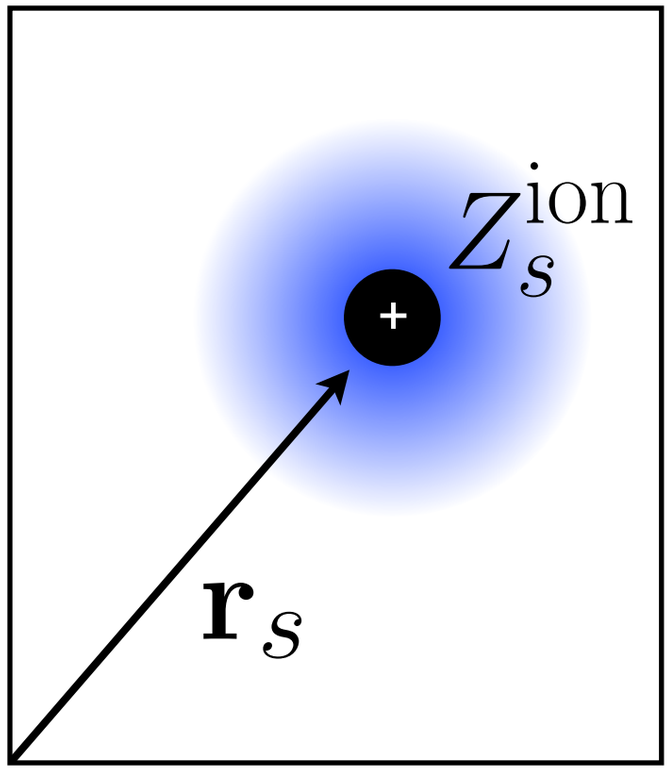


$$\frac{\Delta\mathbf{P}}{\text{displacement}}$$



$$\frac{\Delta\mathbf{P}}{\Delta T}$$

Components of polarization



$$\mathbf{P} = \mathbf{P}_{\text{ion}} + \mathbf{P}_{\text{el}}$$

ionic — electronic

$$\mathbf{P}_{\text{ion}} = \frac{e}{\Omega} \sum_{s}^{\text{atoms}} Z_s^{\text{ion}} \mathbf{r}_s$$

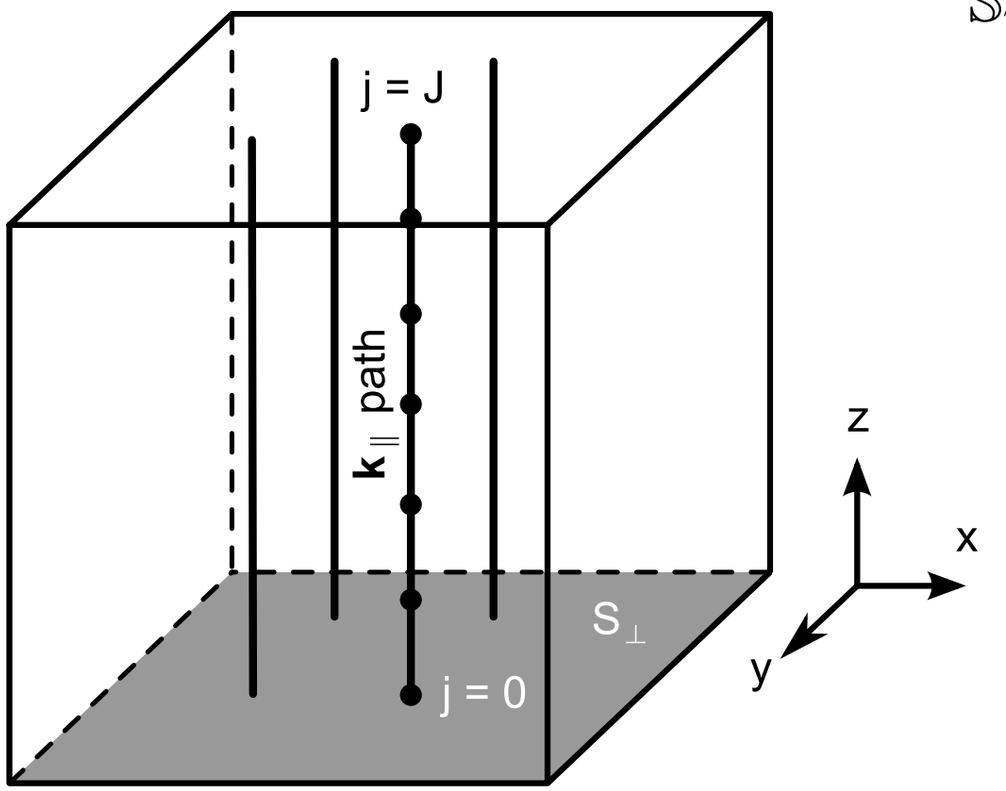
In Wien2k Z_s^{ion} is the core charge

$$-\mathbf{P}_{\text{el}} = \Omega^{-1} \int d\mathbf{r}\, \mathbf{r} \rho(\mathbf{r}) \;\; = \Omega^{-1} \sum_{n}^{\substack{\text{occ.} \\ \text{bands}}} \langle \psi_n | \mathbf{r} | \psi_n \rangle \;\; \equiv \frac{2ei}{(2\pi)^3} \sum_{n}^{\substack{\text{occ.} \\ \text{bands}}} \int_{\text{BZ}} \mathrm{d}\mathbf{k}\, \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$$

King-Smith and David Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

Berry phase

$$\mathrm{d}\varphi_n = -i\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle \cdot \mathrm{d}\mathbf{k} = -i\,\ln\langle u_{n\mathbf{k}}|u_{n(\mathbf{k}+\mathrm{d}\mathbf{k})}\rangle$$



$$\mathbb{S}_{mn}(\mathbf{k}_j, \mathbf{k}_{j+1}) = \langle u_{m\mathbf{k}_j}|u_{n\mathbf{k}_{j+1}}\rangle$$ WIEN2WANNIER

$$\varphi(\mathbf{k}_\parallel) = 2\,\mathrm{Im}\left[\ln\prod_{j=0}^{J-1}\det\mathbb{S}_{M\times M}(\mathbf{k}_j, \mathbf{k}_{j+1})\right]$$

$$\varphi_{\mathrm{el},\alpha} = S_\perp^{-1}\int_{S_\perp}\mathrm{d}S_\perp\;\varphi(\mathbf{k}_\parallel)$$

$$P_\alpha = \frac{e(\varphi_{\mathrm{el},\alpha}+\varphi_{\mathrm{ion},\alpha})}{2\pi\Omega}R_\alpha$$

King-Smith and David Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

BerryPI

Need `wien2k`, `wien2wannier`, `python` 2.7.x and `numpy`

```
[command line]$ berrypi -k 6:6:6 [-s] [-j] [-o]
```

- `[-s]` — Spin-polarized
- `[-j]` — Spin-orbit
- `[-o]` — Orbital potential (e.g., LDA+U)

completed SCF cycle

↓

generate k-mesh in the full BZ (`kgen`)

↓

prepare nearest-neighbour k-point list

↓

calculate wavefunctions (`lapw1`)

↓

calculate overlap matrix $\mathbf{S}_{mn}$ (`w2w`)

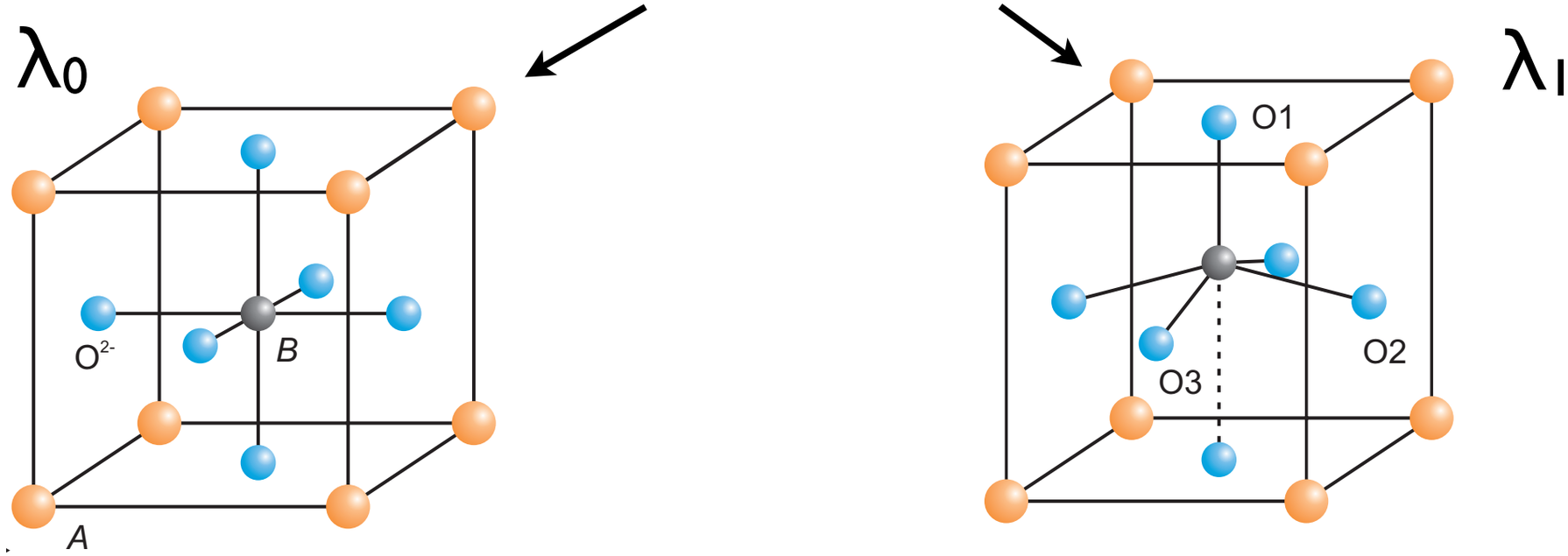
↓

determine electron. and ion. phases → **Polarization vector**

Comput. Phys. Commun. **184**, 647 (2013)

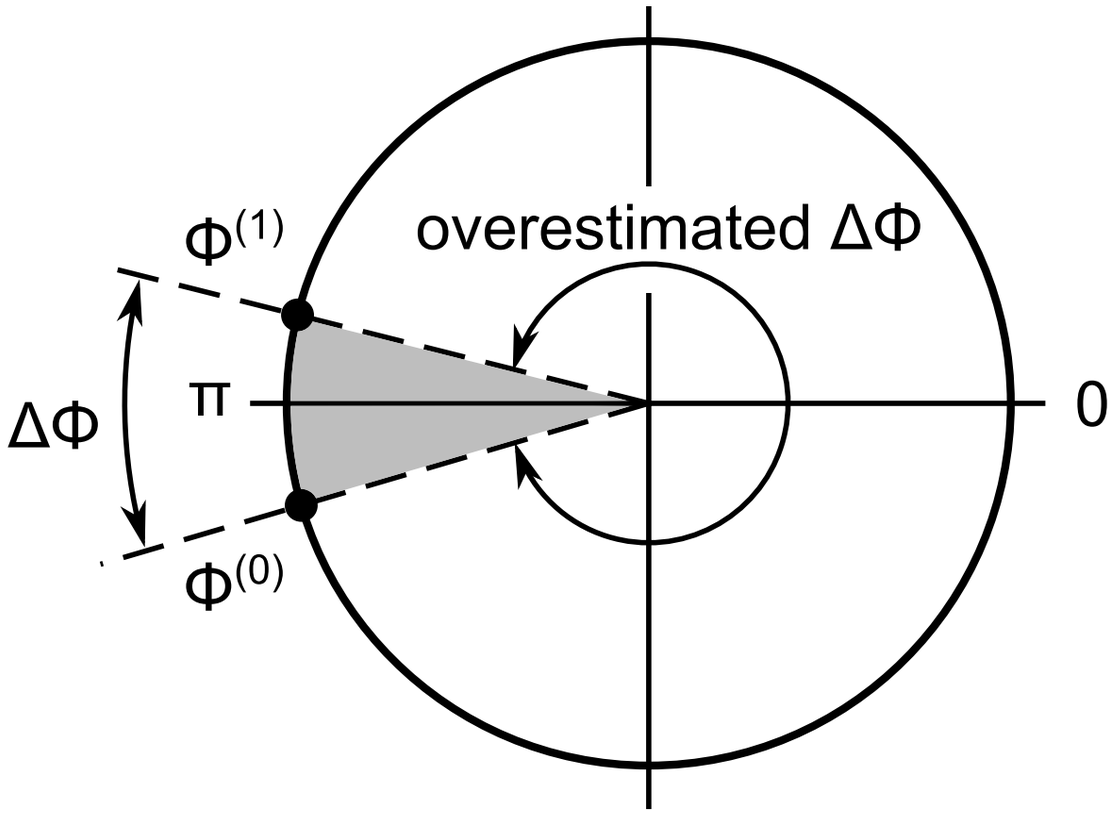
Typical workflow

$$\Delta \mathbf{P} = \mathbf{P}^{(0)} - \mathbf{P}^{(1)}$$



- structure file <u>must</u> preserve the symmetry
- begin with the lowest symmetry (λ_I) case
- copy case λ_I to case λ_0
- edit structure file for case λ_0
- do <u>not</u> initialize calculation (`init_lapw`)
- update density (`x dstart`)
- run SCF cycle (`run[sp]_lapw [-so -orb]`)
- run `BerryPI`

Uncertainties



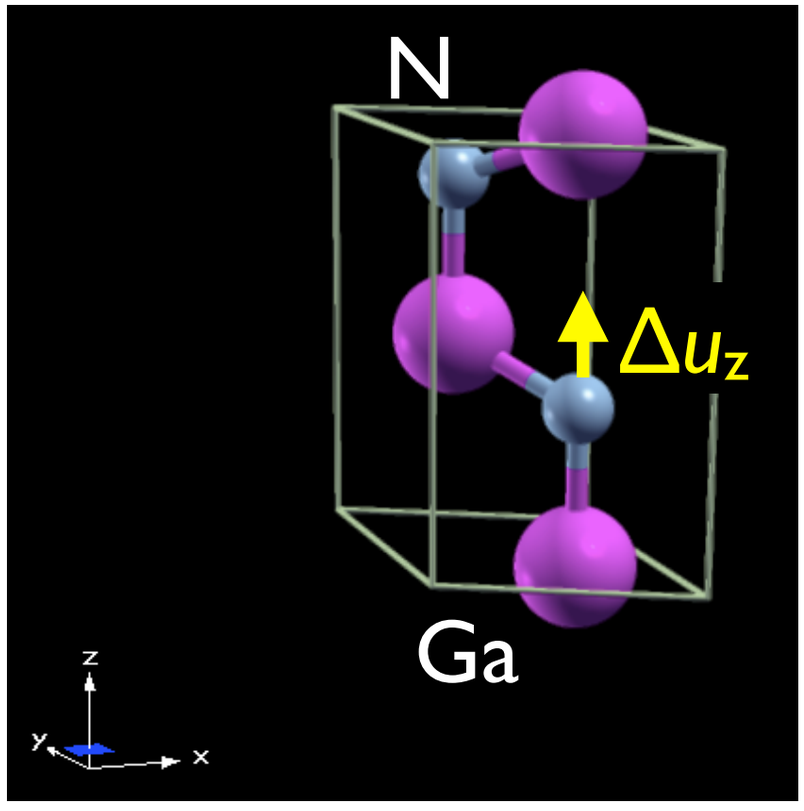
$$P_\alpha = \frac{e(\varphi_{\mathrm{el},\alpha} + \varphi_{\mathrm{ion},\alpha})}{2\pi\Omega} R_\alpha$$

$$\Delta\mathbf{P} = \mathbf{P}^{(0)} - \mathbf{P}^{(1)} \pm \frac{e}{\Omega}\mathbf{R}$$

- it is challenging to determine large polarization difference ~1 C/m^2

Solution: $\lambda_0 \Rightarrow \lambda_{1/2} \Rightarrow \lambda_1$

Demonstration: Effective charge of GaN



$$Z^*_{s,ij} = \frac{\Omega}{e}\frac{\Delta P_i}{\Delta r_{s,j}}$$

General definition

$$\varphi = \varphi_{\mathrm{el}} + \varphi_{\mathrm{ion}}$$

$$\Delta\varphi = \varphi(\mathrm{perturbed}) - \varphi(\mathrm{unperturbed})$$

$$Z^*_{s,ii} = \frac{\Delta\varphi_i}{2\pi\Delta u_{s,i}}$$

"Shortcut" (i=j, no volume change)

GaN z^* calculation

$\phi_{el}(0) = -0.1538$ $\phi_{ion}(0) = -1.5080$

$\phi_{el}(1) = -0.2509$ $\phi_{ion}(1) = -1.4451$

$\phi_{tot}(0) = -1.6618$

$\phi_{tot}(1) = -1.6960$

$\Delta\phi(0 \to 1) = -1.6960 + 1.6618$

$= -0.0342$

$\Delta u = 0.001 - 0 = 0.001$

$$z^* = \frac{\Delta\phi}{2\pi \cdot \Delta u \cdot \#\text{ of atoms moved}} =$$

$= -2.72$

Reality check

GaN: effective charge, dielectric constants - Springer
link.springer.com/content/pdf/10.1007%2F978-3-642-14148-5_230.pdf
by D Strauch - 2011 - Related articles
gallium nitride (**GaN**) property: **effective charge**, dielectric constants (lattice properties). Born **effective charge** (wurtzite structure). Physical. Property. Numerical.
You've visited this page 2 times. Last visit: 04/06/16

GaN: effective charge, dielectric constants

substance:	gallium nitride (GaN)
property:	effective charge, dielectric constants (lattice properties)

Born effective charge (wurtzite structure)

Physical Property	Numerical Values	Remarks	Ref.
Z^*	2.73(3)	from LO-TO splitting, Raman scattering from bulk GaN	01G
	2.51	ab initio DFT(LDA) calculation	01Z
	2.67	ab initio DFT(GGA) calculation	
Z_{xx}^*	2.60	ab initio DFT(LDA) calculation	02W
Z_{zz}^*	2.74		
$Z_{B,xx}^*$	1.14	$Z_{B,ij}^* = Z_{ii}^* / \sqrt{\varepsilon_{\infty,ii}}$	
$Z_{B,zz}^*$	1.18		
Z_{xx}^*	2.51	ab-initio DFT(LDA) calculation	06S
Z_{zz}^*	2.75		

Useful resources

- Sheikh J. Ahmed *et al.* "BerryPI: A software for studying polarization of crystalline solids with WIEN2k density functional all-electron package", Comp. Phys. Commun. **184**, 647 (2013).
- BerryPI home and tutorials: https://github.com/spichardo/BerryPI/wiki
- Raffaele Resta "Macroscopic polarization in crystalline dielectrics: the geometric phase approach" Rev. Mod. Phys. **66**, 899 (1994)
- Raffaele Resta and David Vanderbilt "Theory of Polarization: A Modern Approach" in *Physics of Ferroelectrics: a Modern Perspective* (Springer, 2007)

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