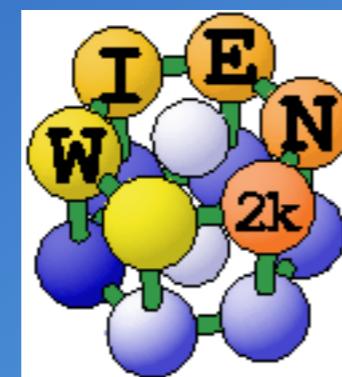


Wannier functions, macroscopic polarization (Berry phase) and related properties

Oleg Rubel

Department of Materials Science and Engineering

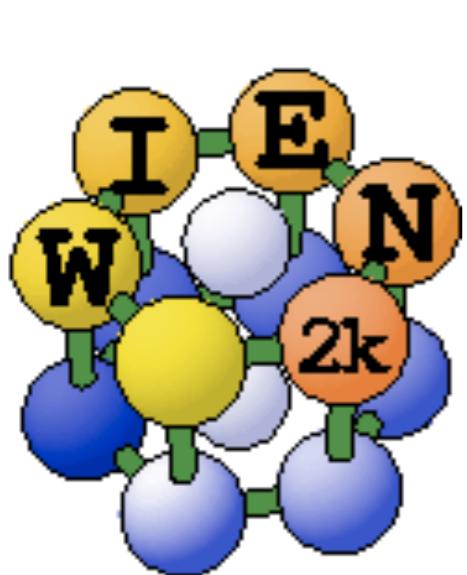


@

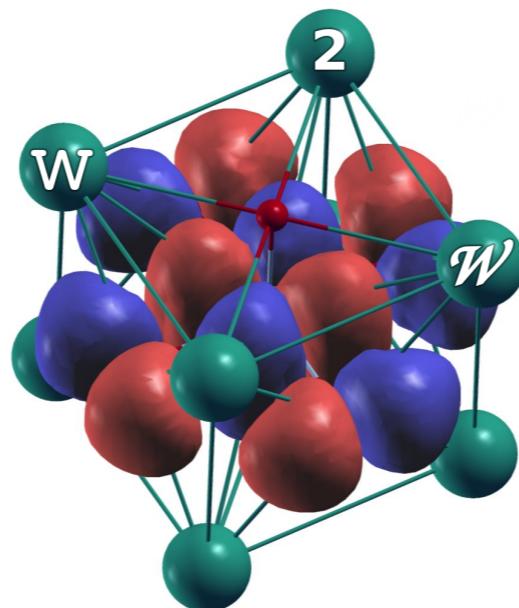
McMaster
University



Wannier functions



+



+



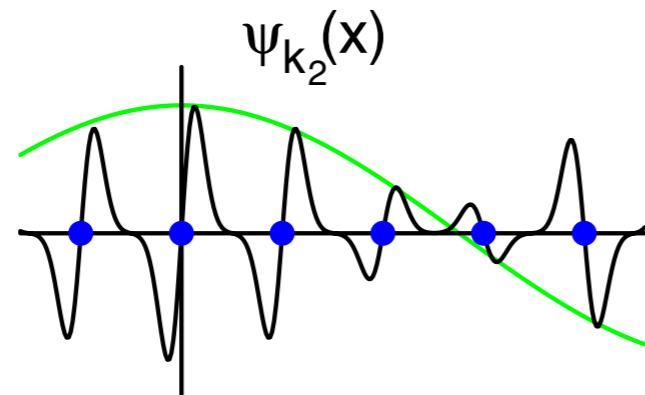
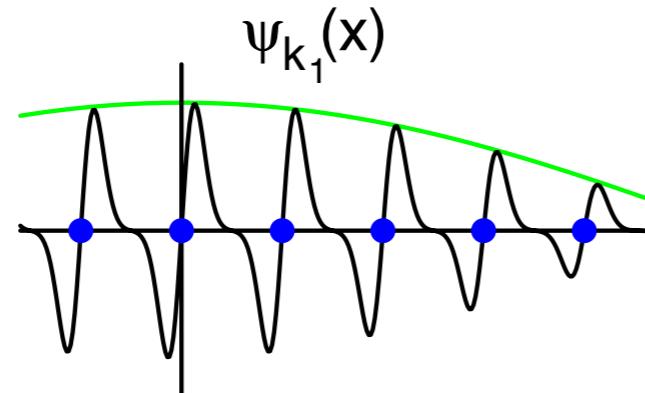
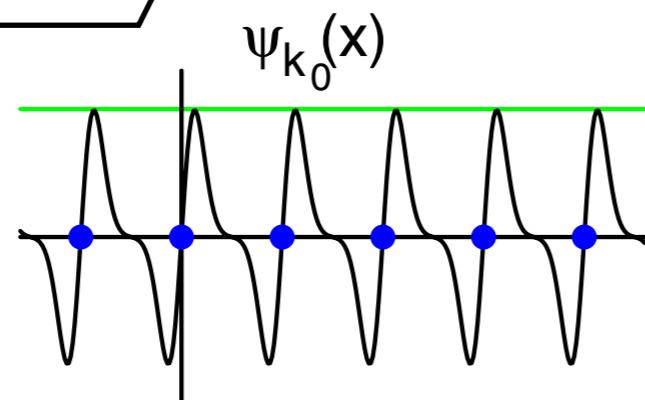
Bloch vs Wannier functions

Indexed by
the wave
vector

Γ -point

Bloch functions

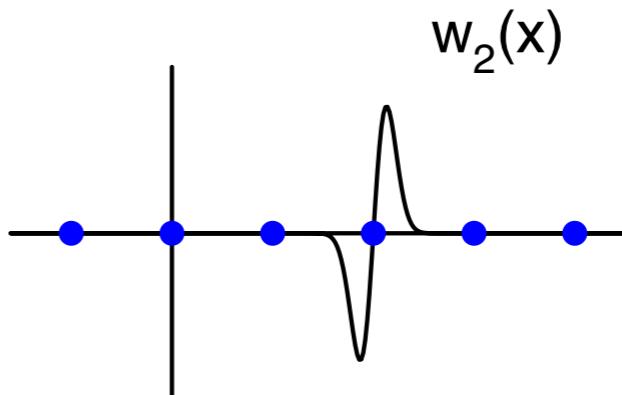
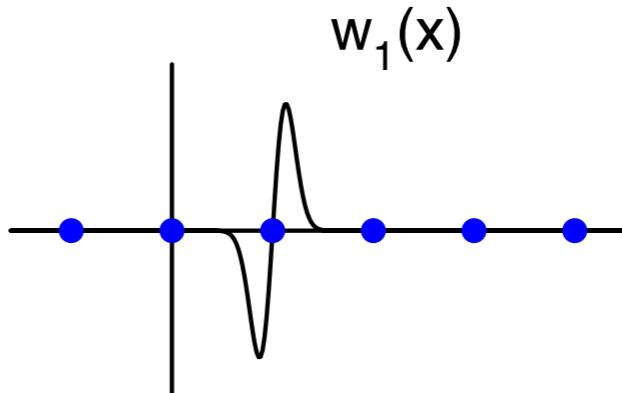
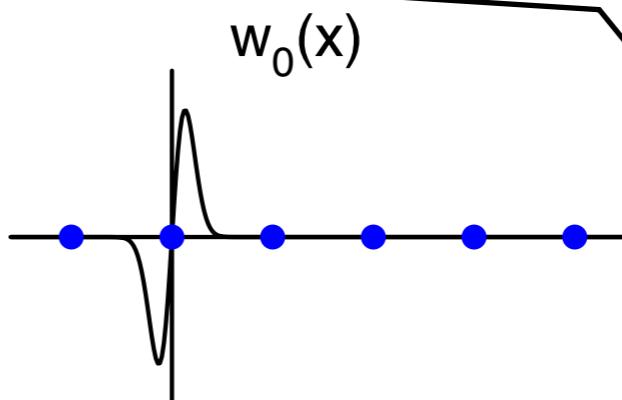
$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$



Both sets: complete and orthonormal

Wannier functions (localized orbitals)

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



Indexed by the
lattice vector
in real space

Wannier:
PRB 52, 191 (1997)
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

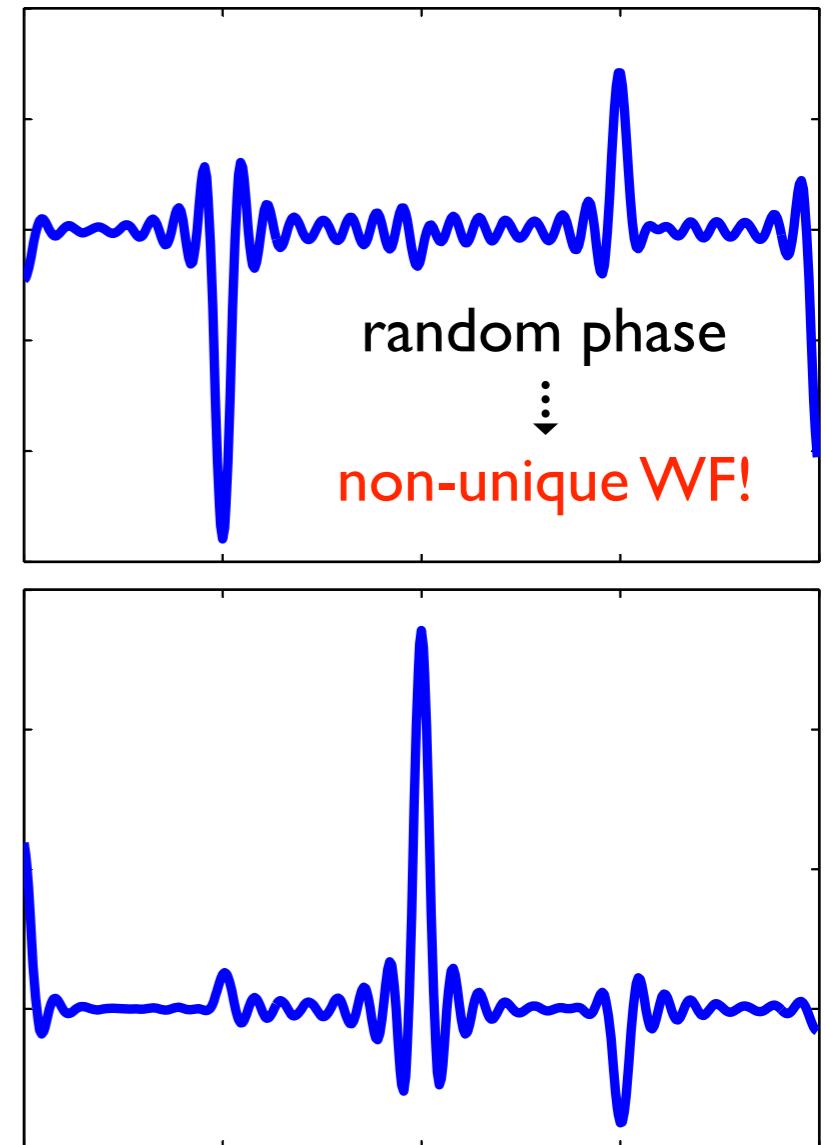
(does not change the physical description of the system)

General transformation of Bloch functions into Wannier functions:

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

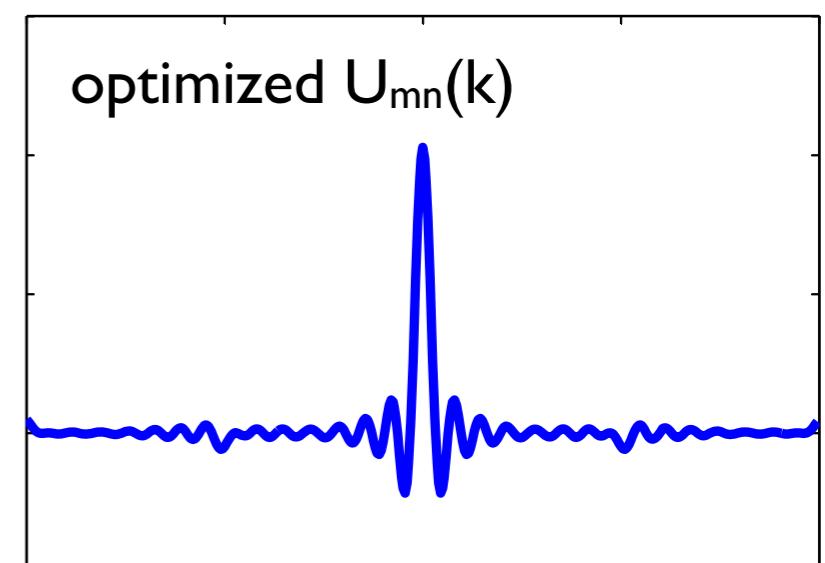
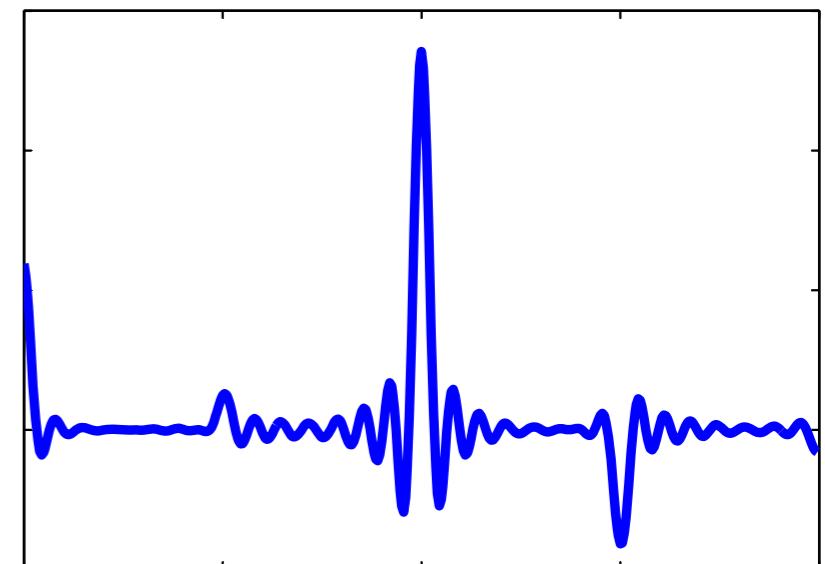
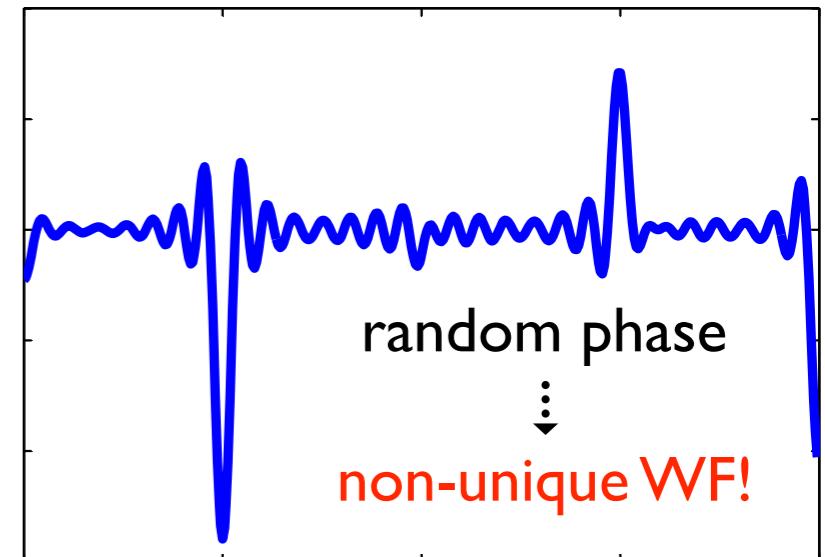
Bloch-like orbitals

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



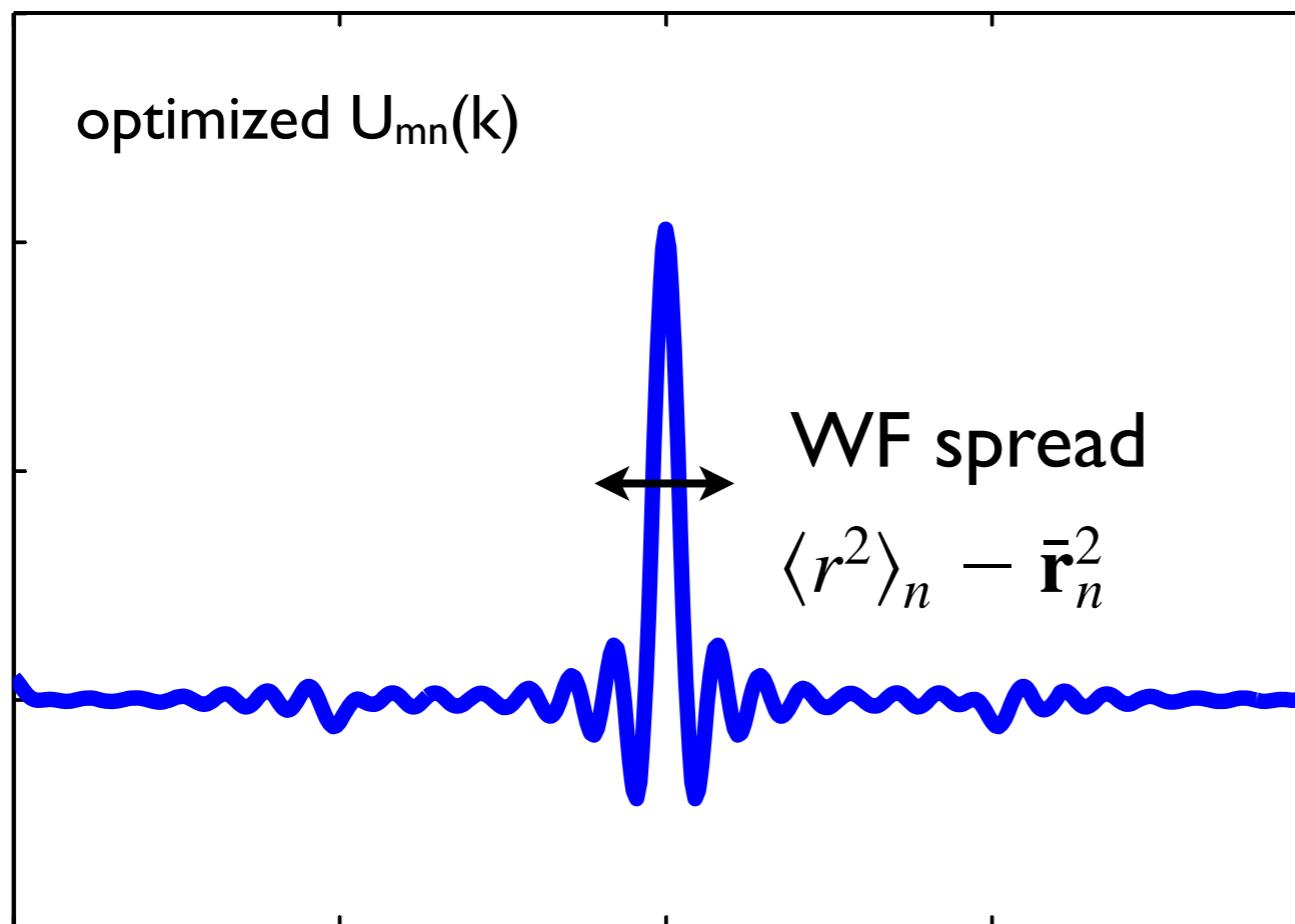
Max. localized Wannier functions (MLWF)

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

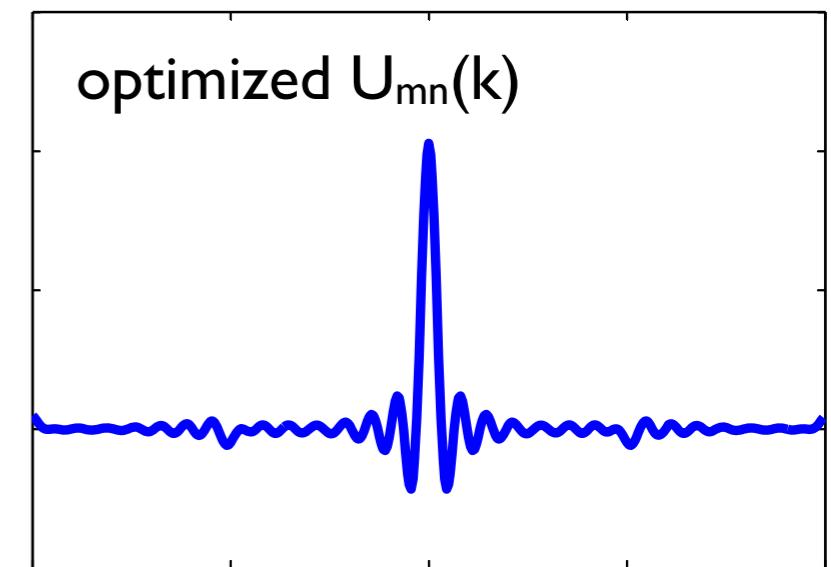
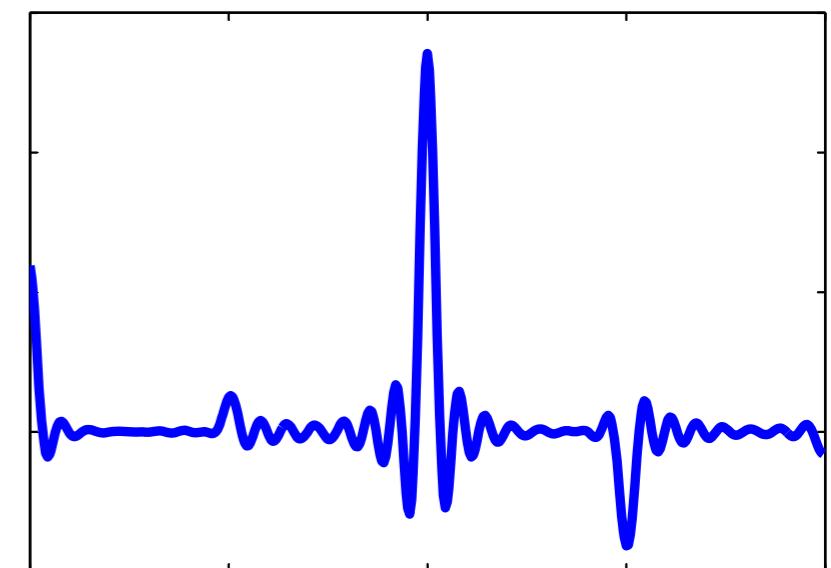
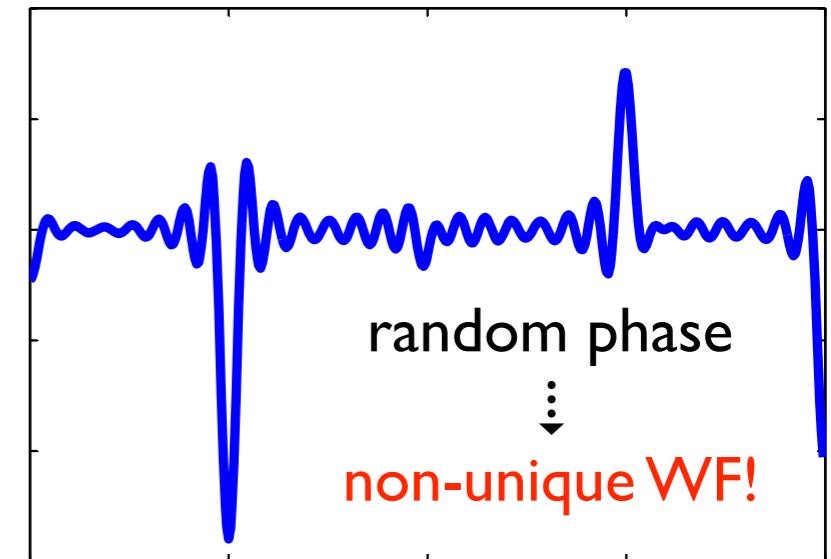


Max. localized Wannier functions (MLWF)

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



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



Wannier functions matrix elements

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

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

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

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

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

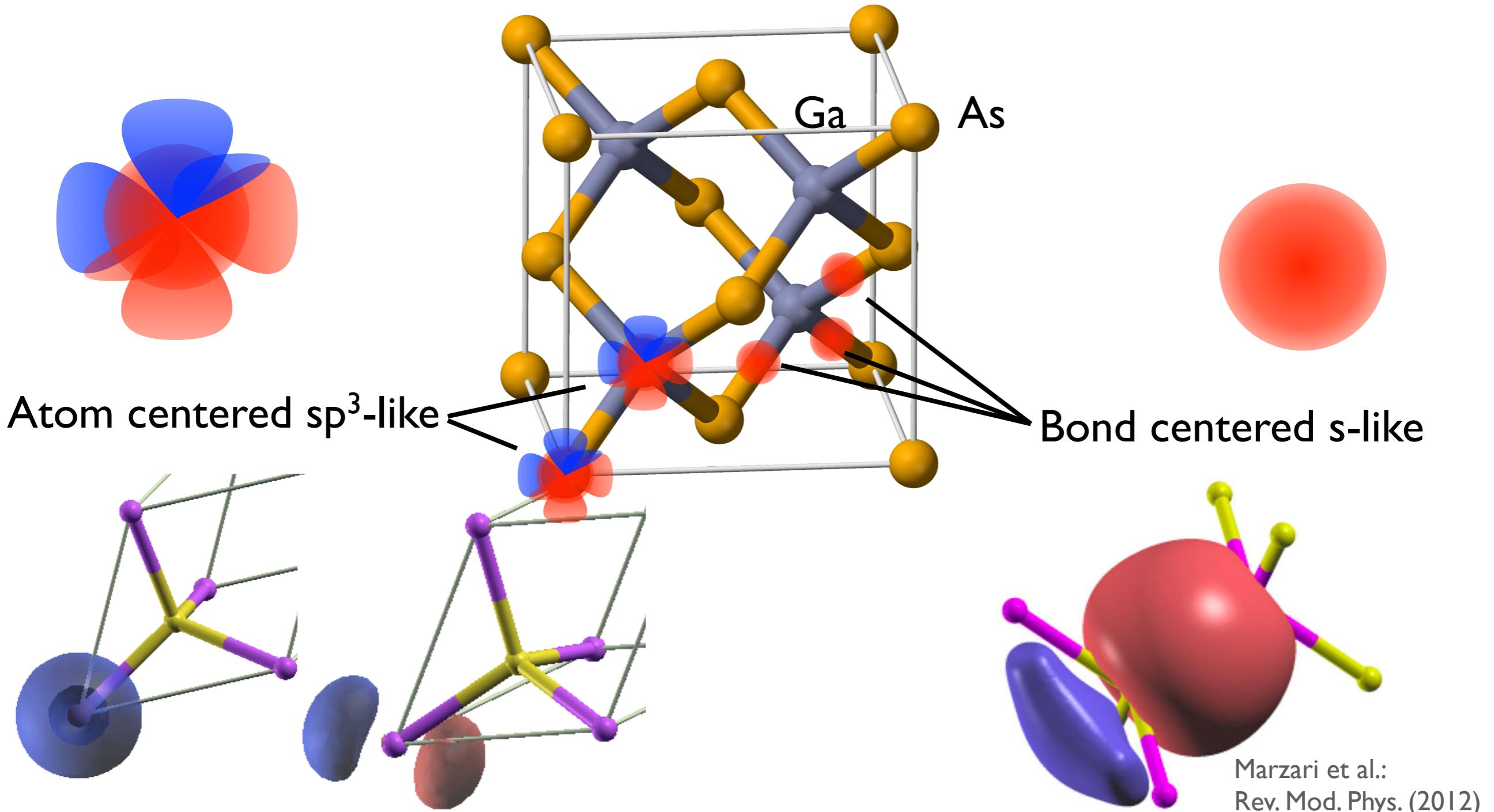
related to Berry phase,
electronic polarization

Discretization:

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

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

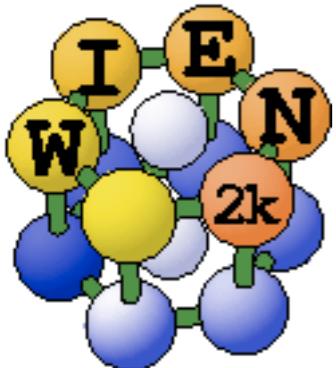
Initial projections



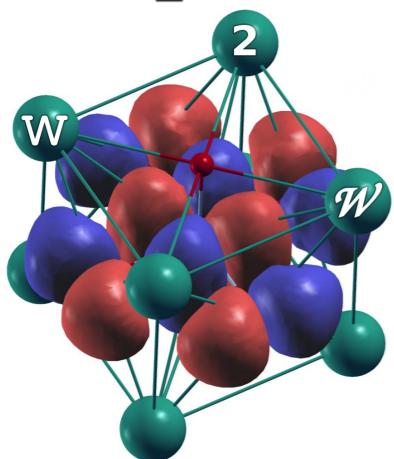
- includes *bonding* and *antibonding* states
- building effective hamiltonian

- includes *valence* states
- charge transfer and polarization

Workflow



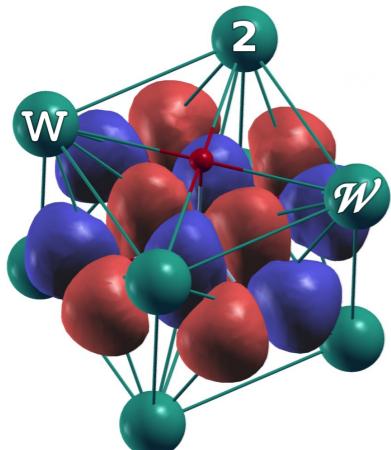
- Regular SCF calculation
- Band structure plot



- 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`)



- 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`)
- Plot WF



Wannier functions as a tight-binding basis

(Atom-centered WF)

\$ less GaAs-WANN_hr.dat

...

Home
unit cell

0	0	0
---	---	---

1	1	-4.335108
---	---	-----------

Matrix element (eV)

$$\langle s_1 | H | s_1 \rangle = E_{s1}$$

0.000000 Im part = 0

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	0
---	---	---

1	1	-0.001219
---	---	-----------

...

Neighbour
unit cell

$\langle s_1 |$ $| s_1 \rangle$

Matrix element (eV)

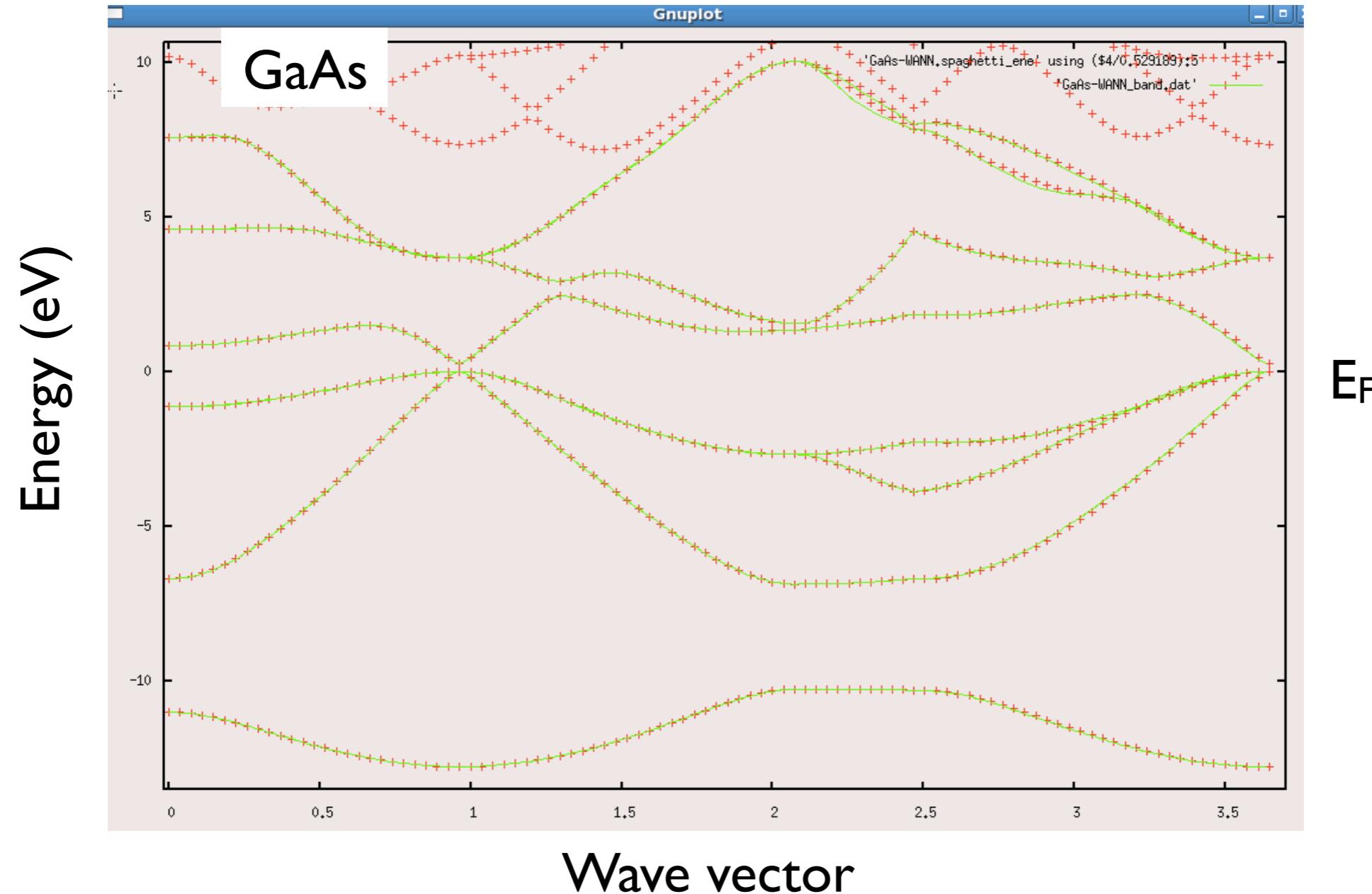
$$\langle s_2 | H | s_1 \rangle = V_{ss\sigma}$$

$$\langle p_2 | H | s_1 \rangle = V_{sp}$$

WF are well localized

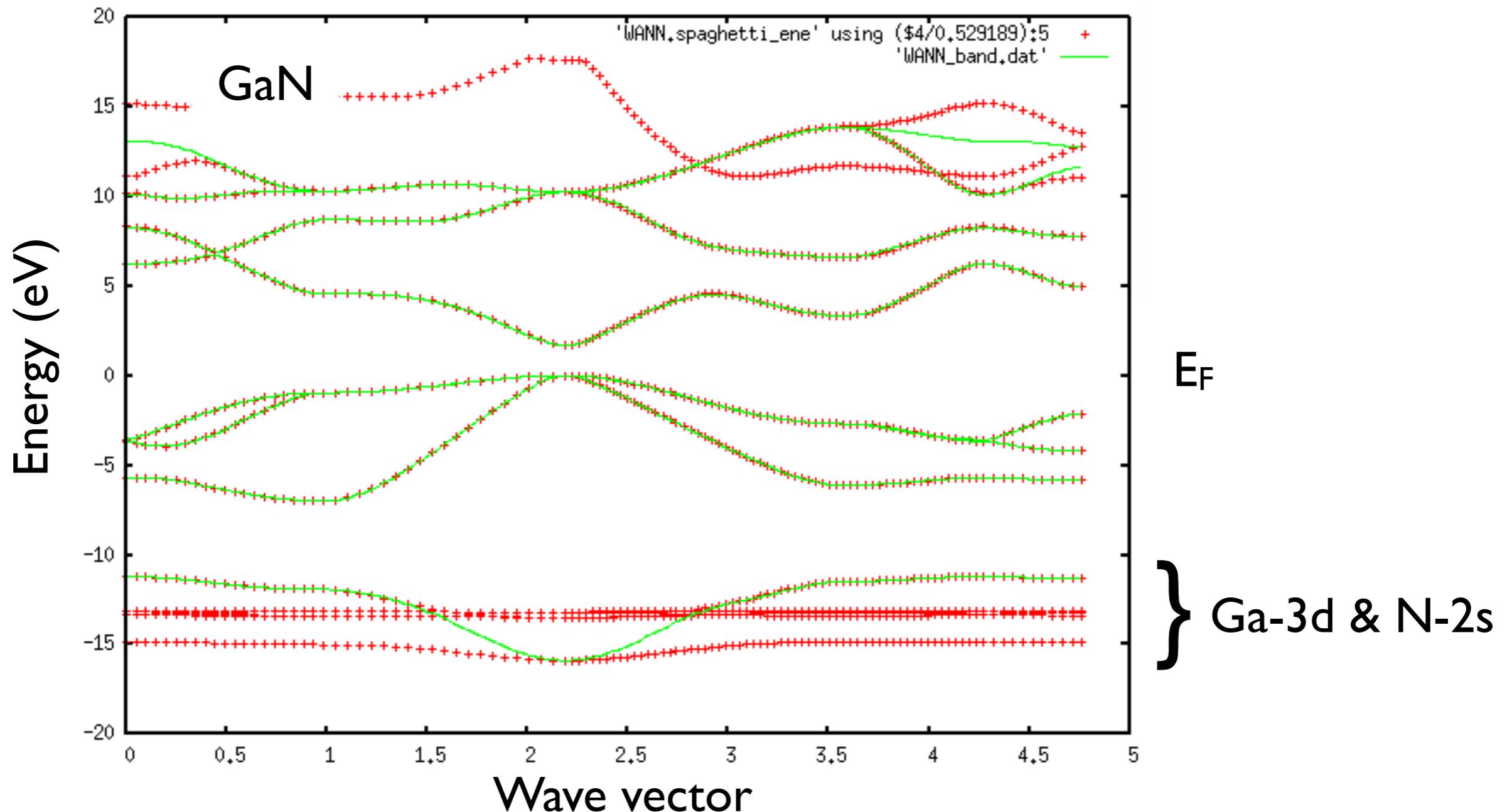
\Rightarrow nearest-neighbour suffice

Band structure



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

Disentanglement

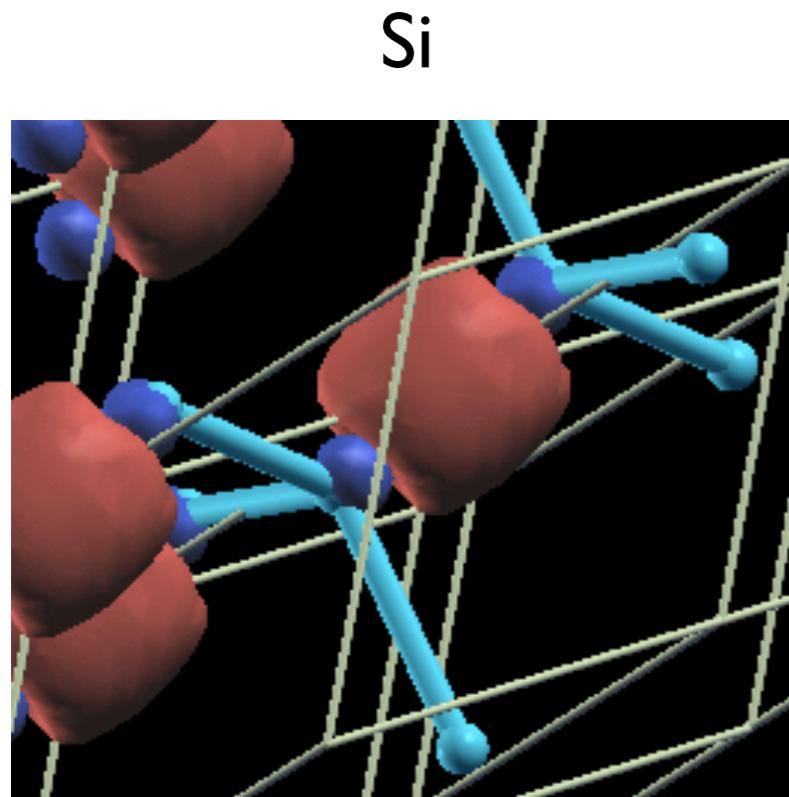


- + original Wien2k band structure
- Band structure computed from Wannier hamiltonian

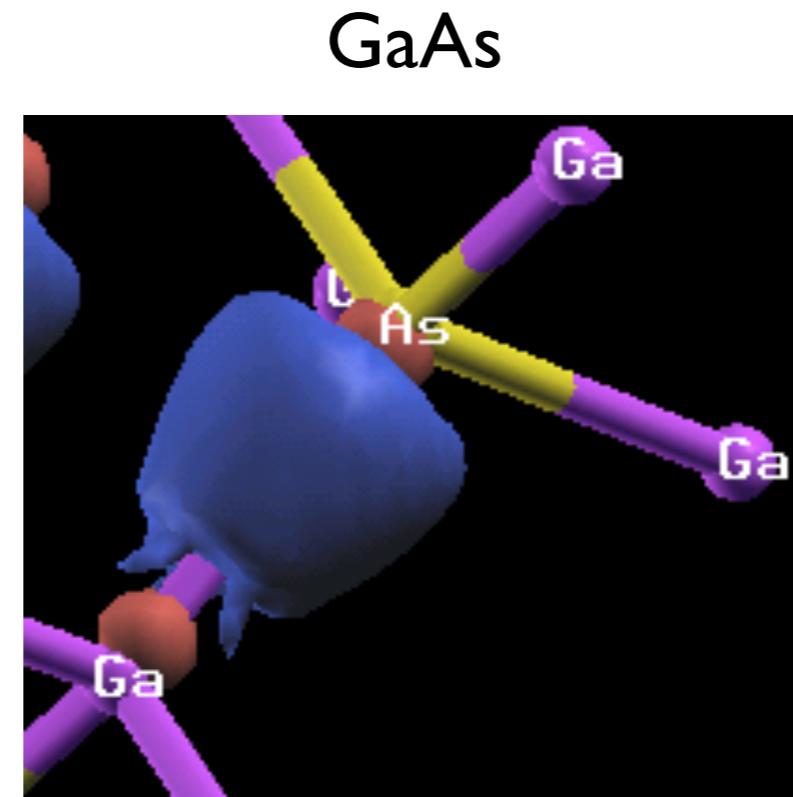
Souza et al.:
PRB 65, 035109 (2001)

Relation to polarization

Bond-centered WF



symmetric (non-polar)



non-symmetric (polar)

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

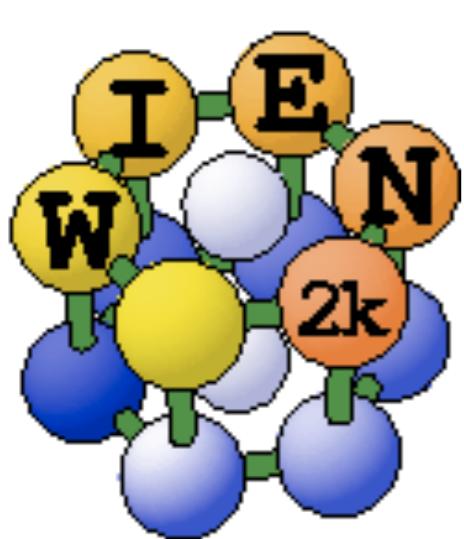
$$+ Z_{\text{As}} - \text{Wannier center } q_e$$

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

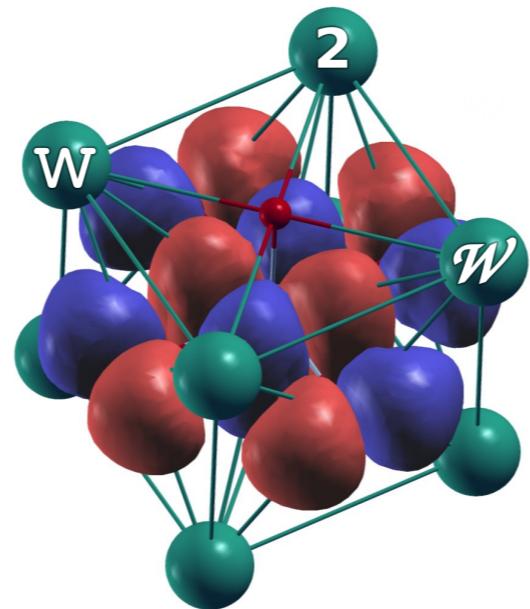
Useful resources

- 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/](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



+

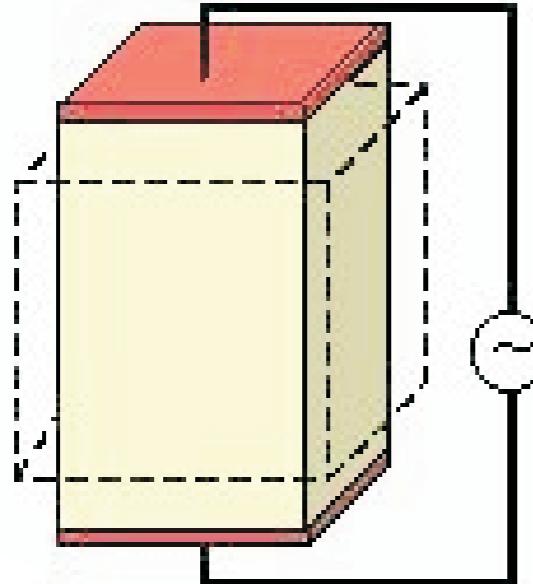


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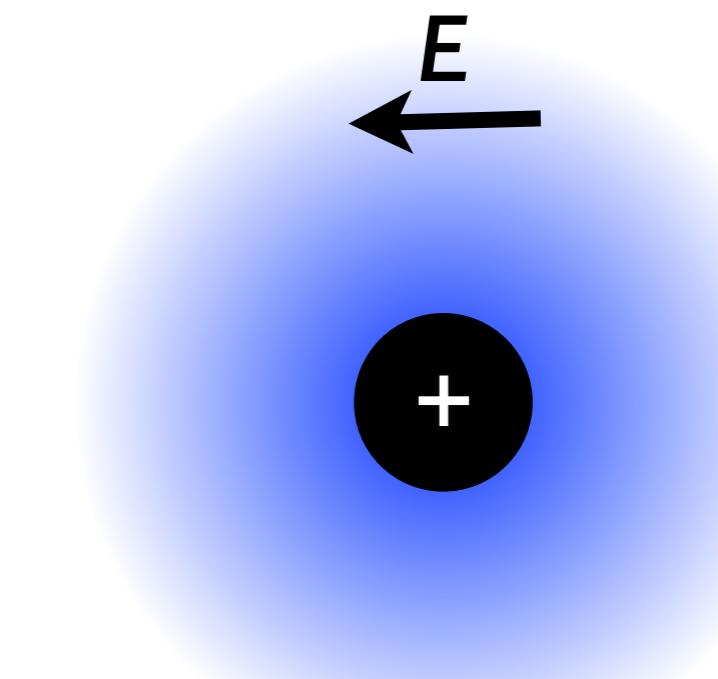
BerryPI

Material properties related to polarization

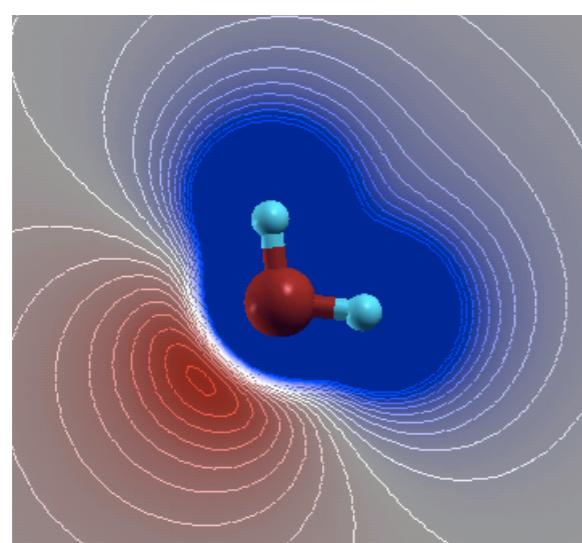
Piezo- and Ferroelectricity



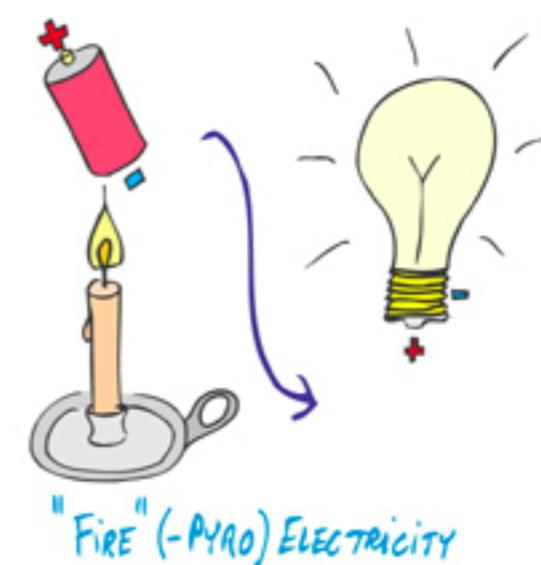
Dielectric screening



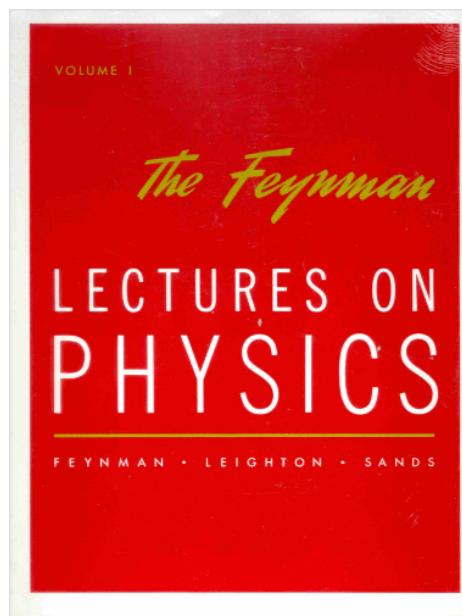
Effective charge



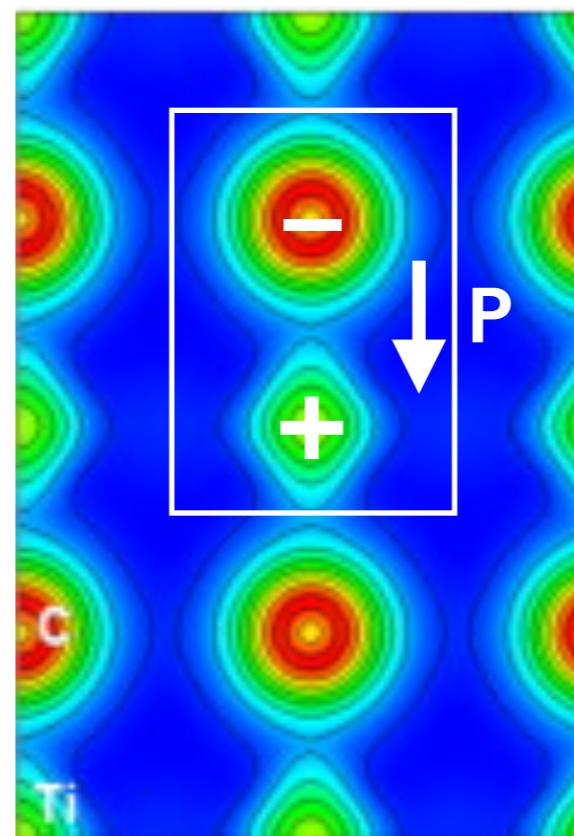
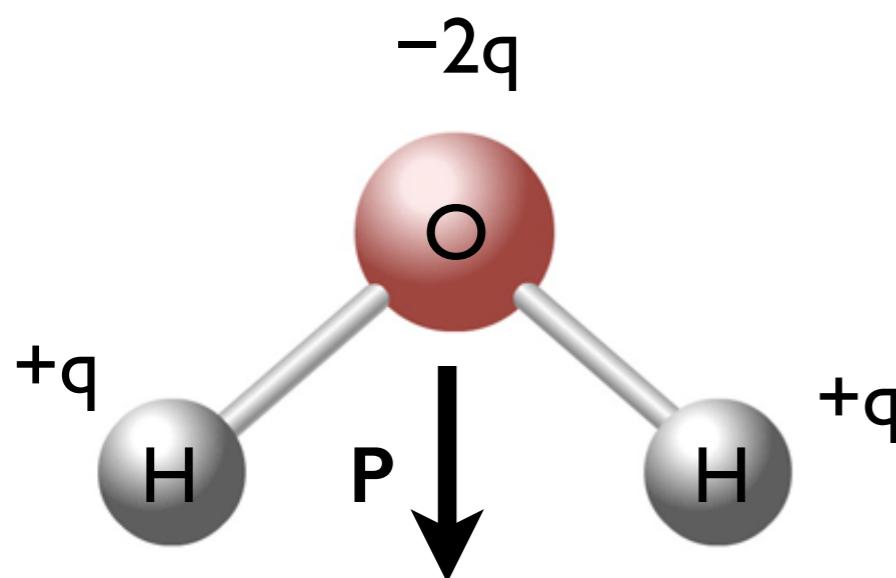
Pyroelectricity



What is polarization?

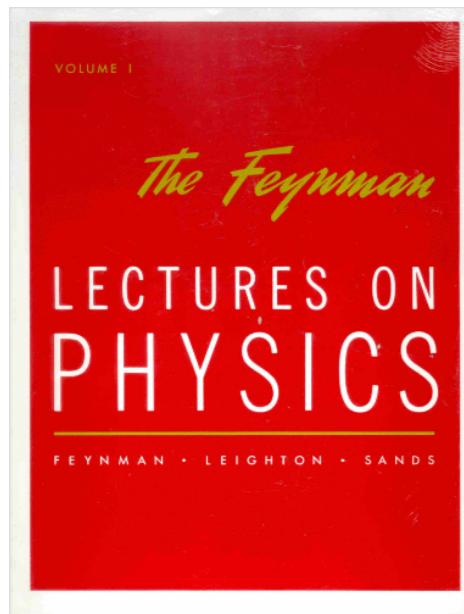


We will now assume that in each atom there are charges q separated by a distance δ , so that $q\delta$ is the dipole moment per atom. (We use δ because we are already using d for the plate separation.) If there are N atoms per unit volume, there will be a *dipole moment per unit volume* equal to $Nq\delta$.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

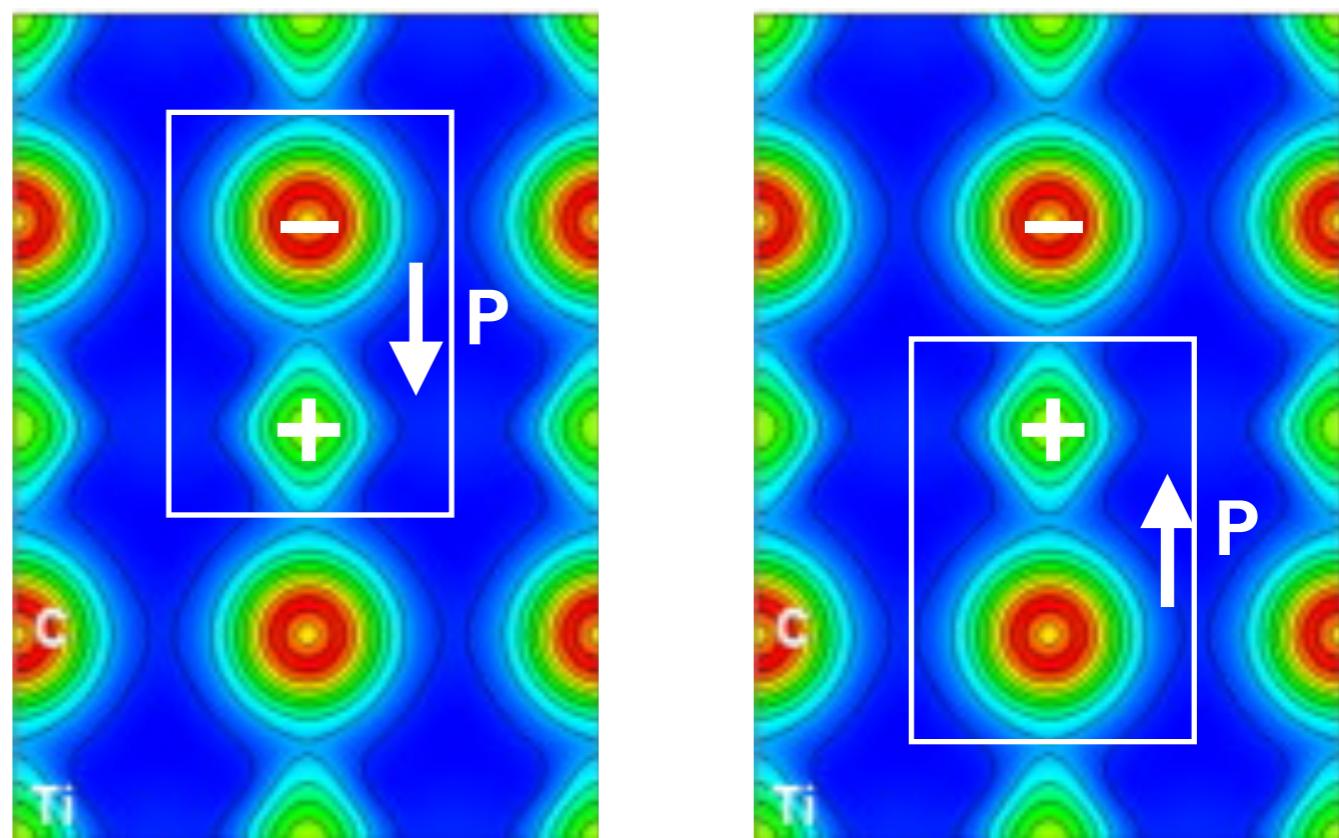
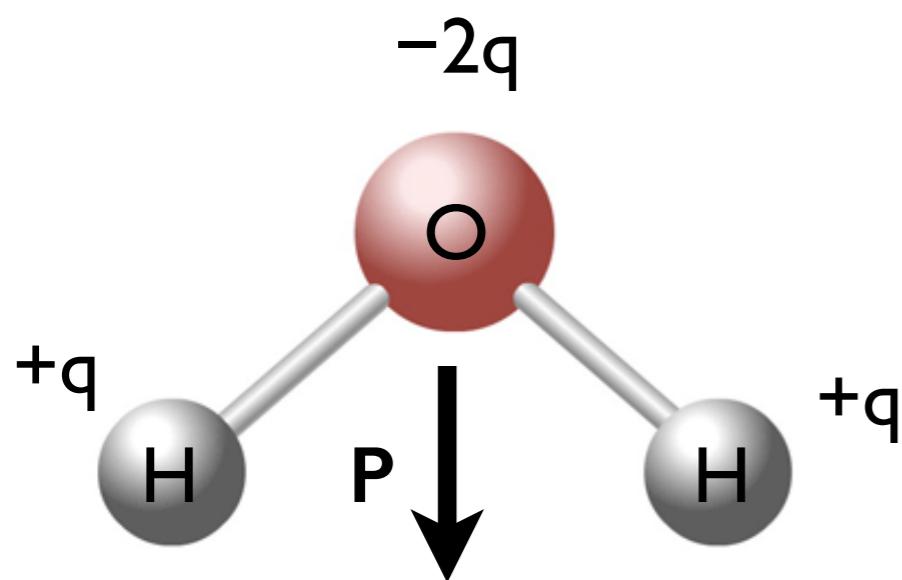


Polarization for periodic solids is undefined

What is polarization?



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, P . Needless to say, it is in the direction of the individual dipole moments, i.e., in the direction of the charge



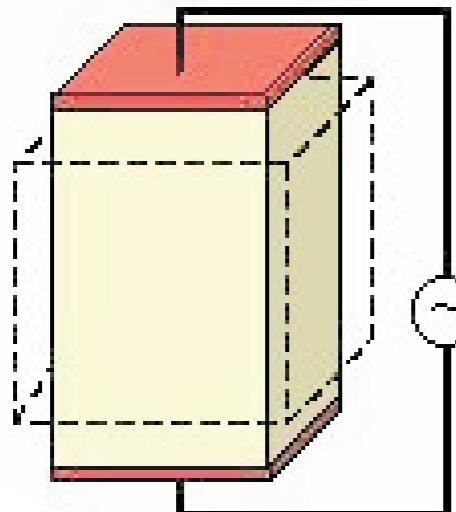
Polarization for periodic solids is undefined

Modern theory of polarization

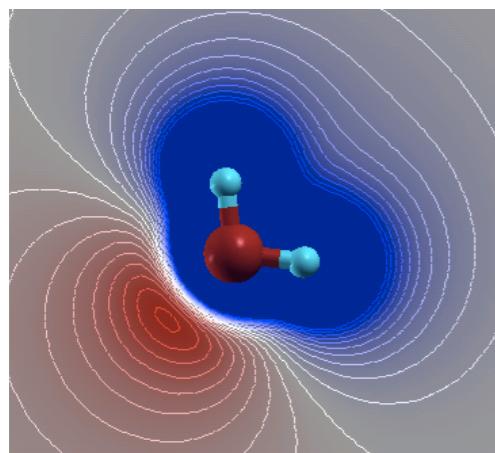
Pioneered by King-Smith, David Vanderbilt and Raffaele Resta

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

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



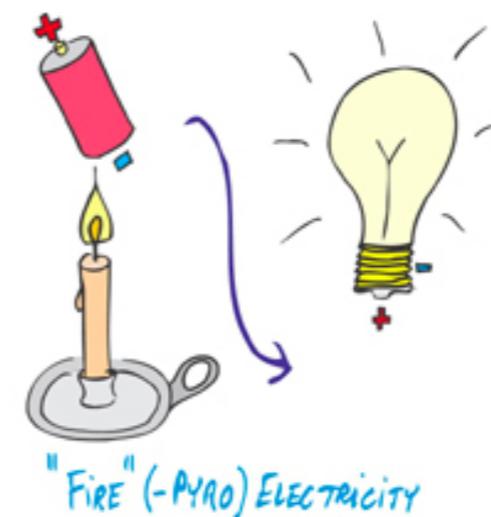
$$\frac{\Delta P}{\Delta \text{strain}}$$



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

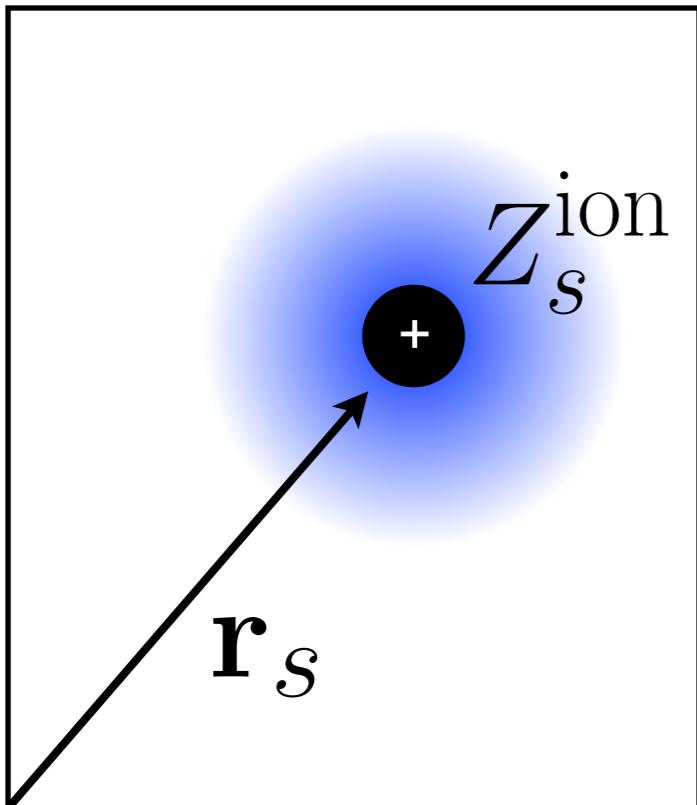


$$\frac{\Delta P}{\Delta E}$$



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

Components of polarization



0

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

ionic electronic

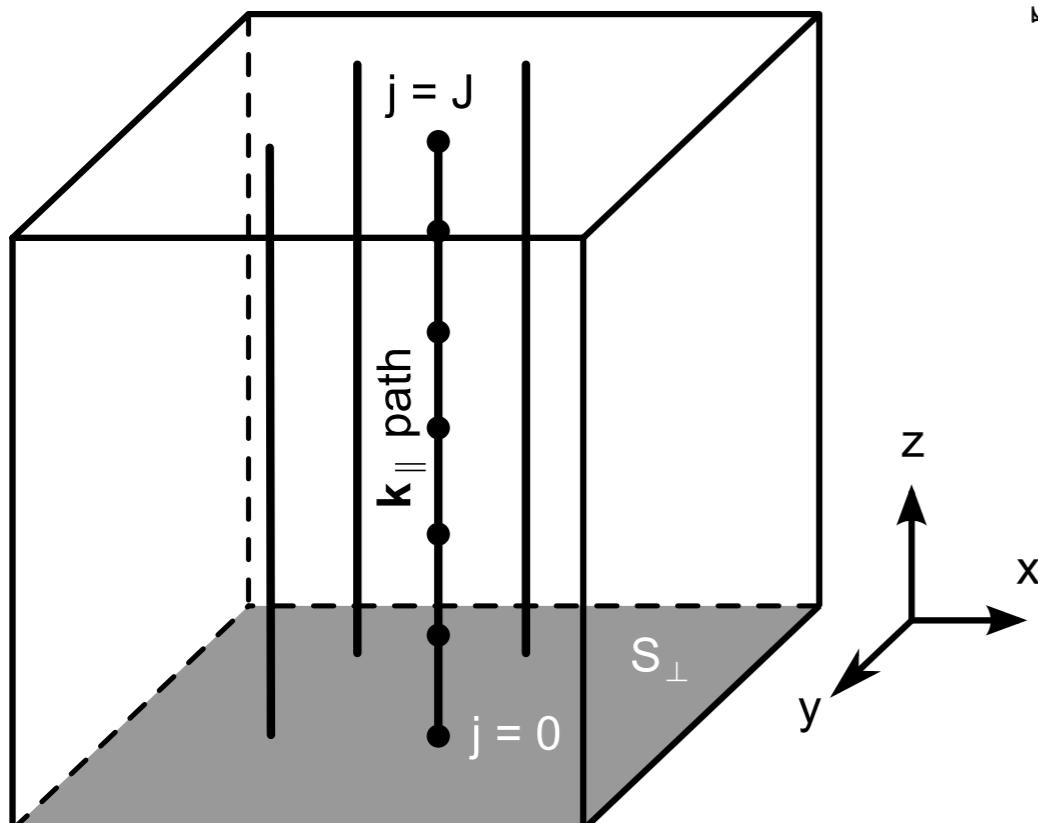
$$\mathbf{P}_{\text{ion}} = \frac{e}{\Omega} \sum_{\text{atoms}}^{\text{atoms}} Z_s^{\text{ion}} \mathbf{r}_s$$

In Wien2k Z_s^{ion} is the core charge

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

Berry phase

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



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

WIEN2WANNIER

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

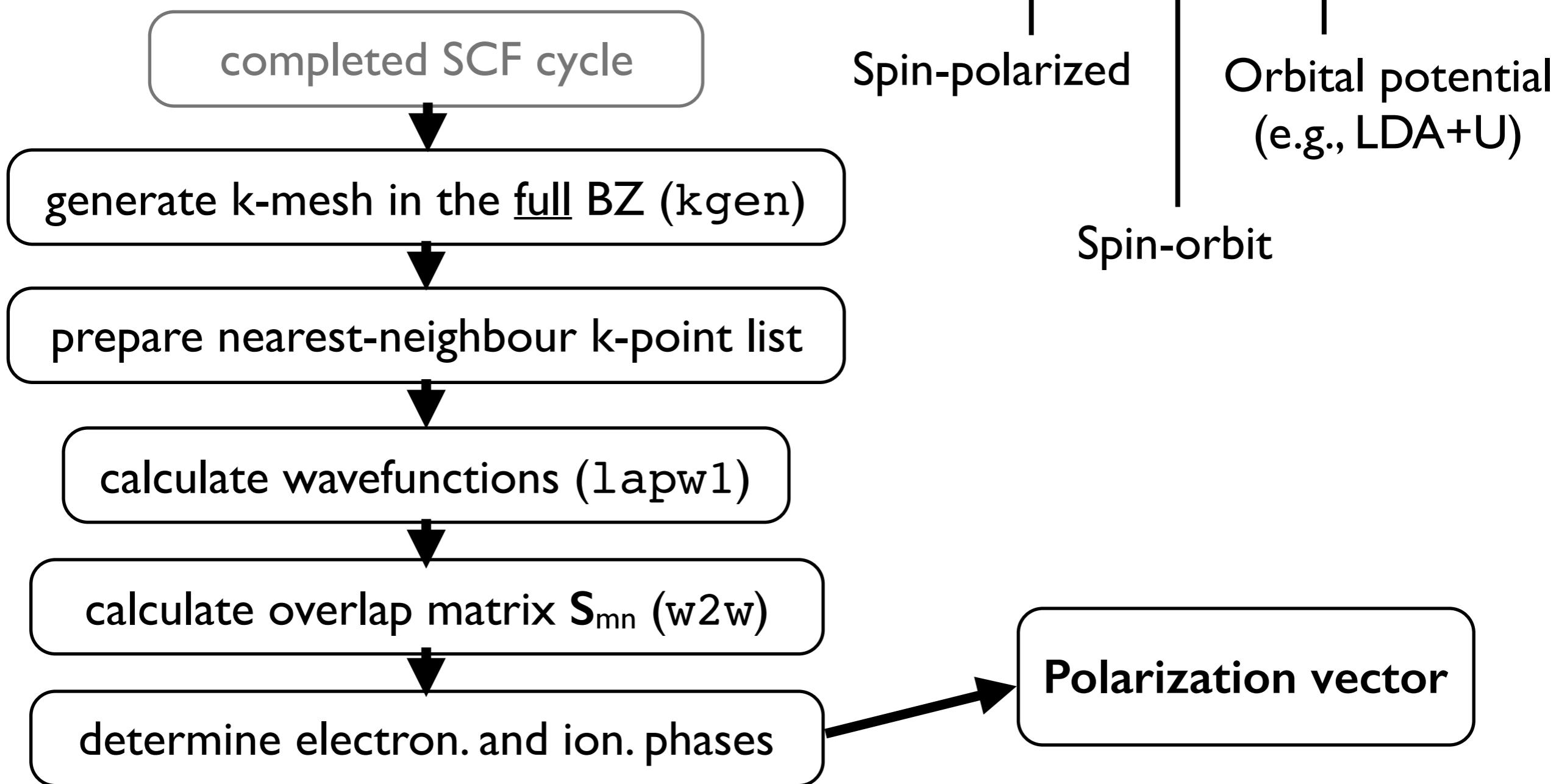
$$\varphi_{\text{el},\alpha} = S_{\perp}^{-1} \int_{S_{\perp}} dS_{\perp} \varphi(\mathbf{k}_{\parallel})$$

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

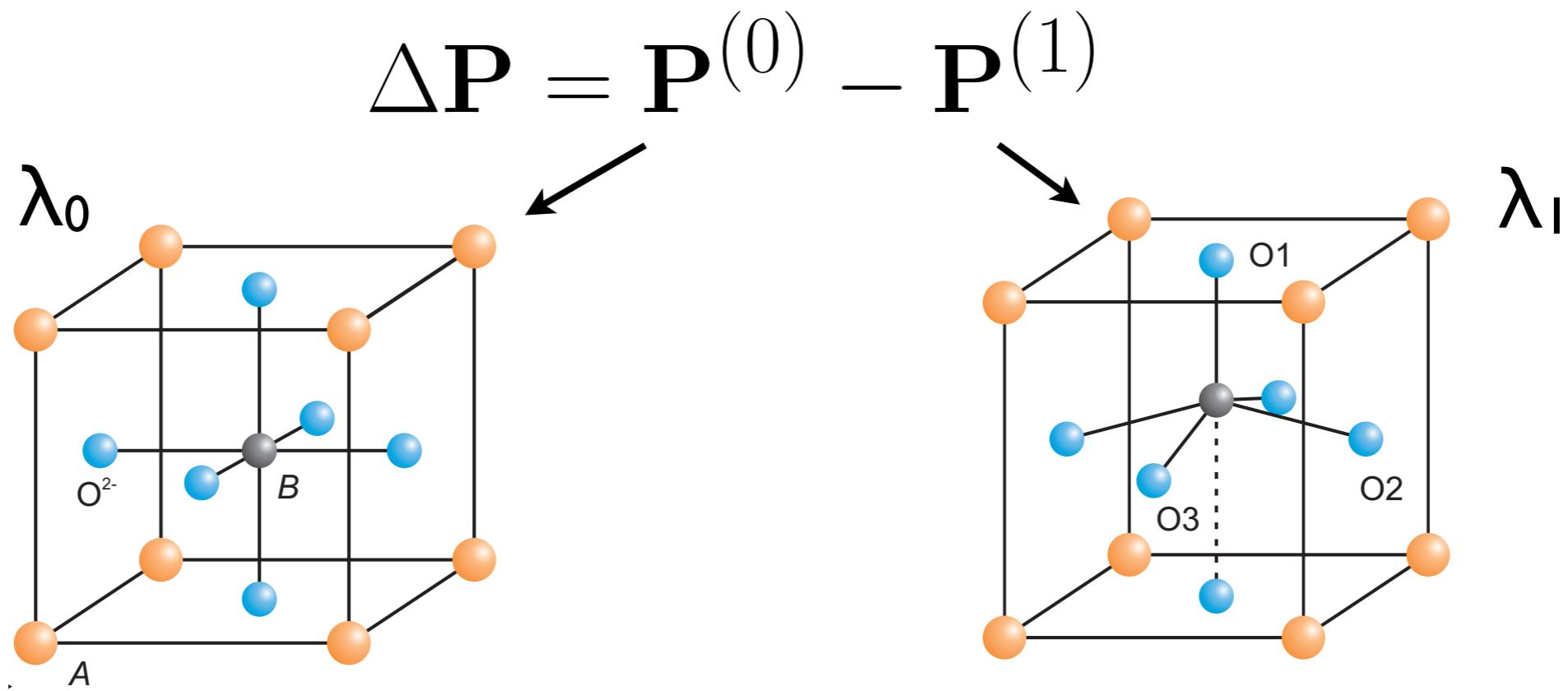
BerryPI

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

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

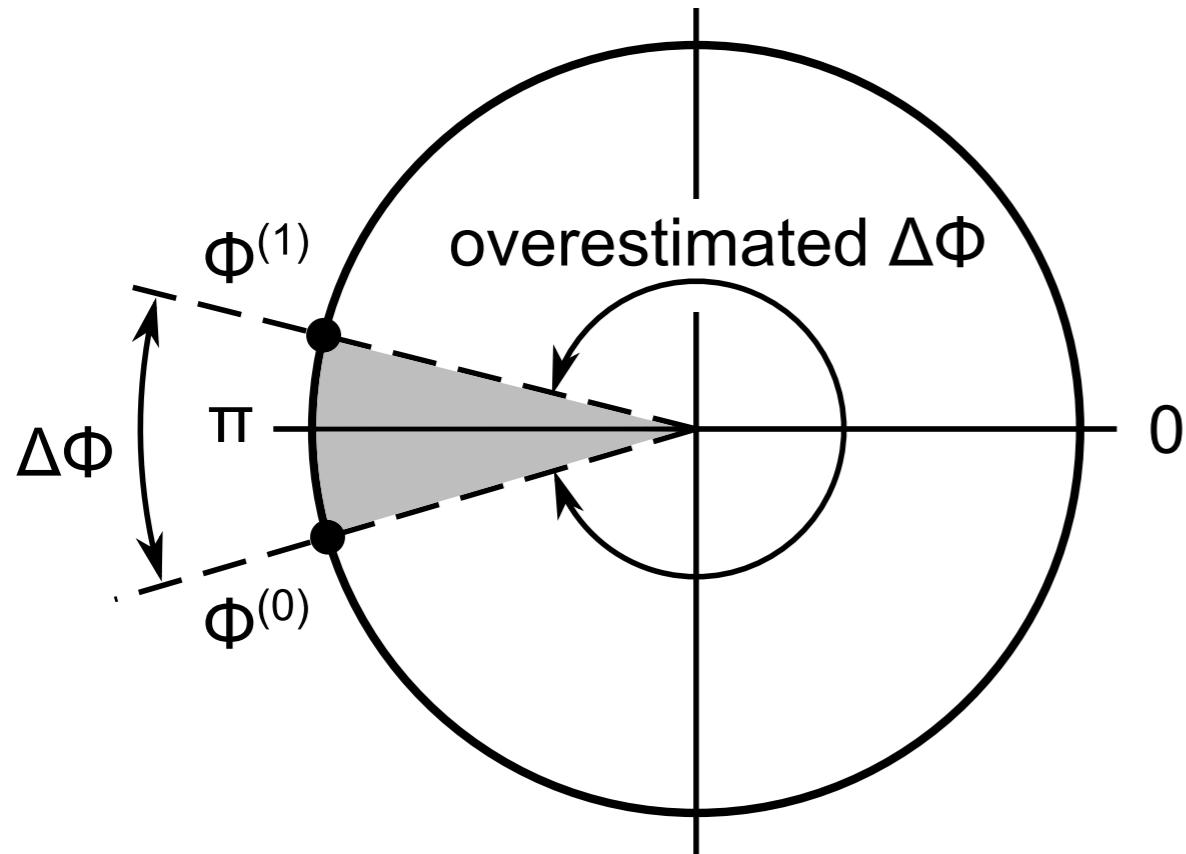


Typical workflow



- structure file must preserve the symmetry
- begin with the lowest symmetry (λ_1) case
- copy case λ_1 to case λ_0
- edit structure file for case λ_0
- do not initialize calculation (init_lapw)
- update density (x dstart)
- run SCF cycle (run[sp]_lapw [-so -orb])
- run BerryPI

Uncertainties



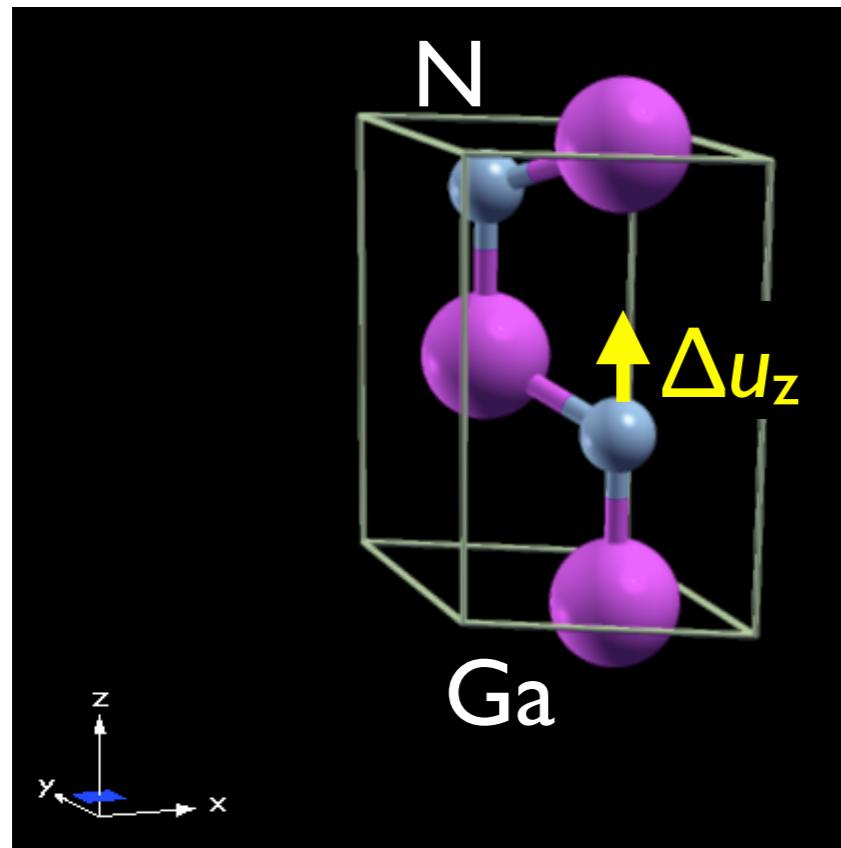
$$P_\alpha = \frac{e(\varphi_{\text{el},\alpha} + \varphi_{\text{ion},\alpha})}{2\pi\Omega} R_\alpha$$

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

- it is challenging to determine large polarization difference
 $\sim 1 \text{ C/m}^2$

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

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

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

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

“Shortcut” ($i=j$, no volume change)

GaN Z^* calculation

$$\Phi_{el}(0) = -0.1538 \quad \phi_{ion}(0) = -1.50\overset{80}{79}$$

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

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

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

$$\Delta \Phi(0 \rightarrow 1) = -1.6960 + 1.6618 \\ = -0.0342$$

$$\Delta U = 0.001 - 0 = 0.001$$

$$Z^* = \frac{\Delta \Phi}{2V \cdot \Delta U \cdot \# \text{ of. atoms moved}} =$$

$$= -2.72$$

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	$Z_{B,ij}^* = Z_{ii}^* / \sqrt{\epsilon_{x_i,ii}}$	
$Z_{B,zz}^*$	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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- Laura Curiel
- David Hassan
- Victor Xiao



WIEN2WANNIER:

- Elias Assmann
- Jan Kunes
- Philipp Wissgott

