

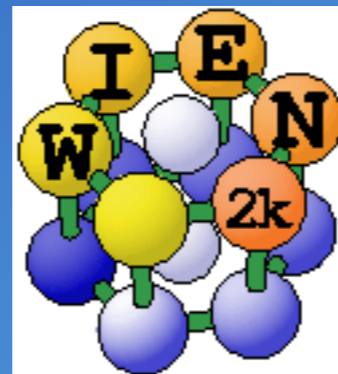
Wannier functions

Berry phase and related properties

Effective band structure of alloys

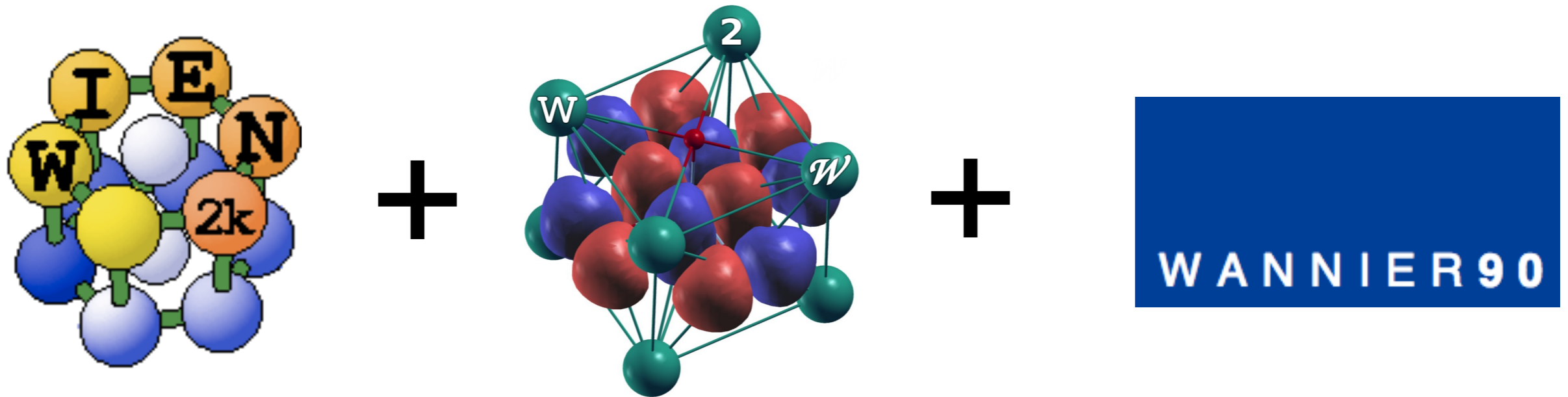
Oleg Rubel

Department of Materials Science and Engineering



McMaster
University 

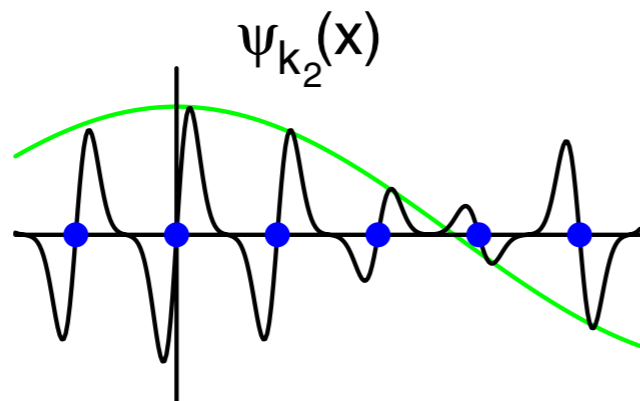
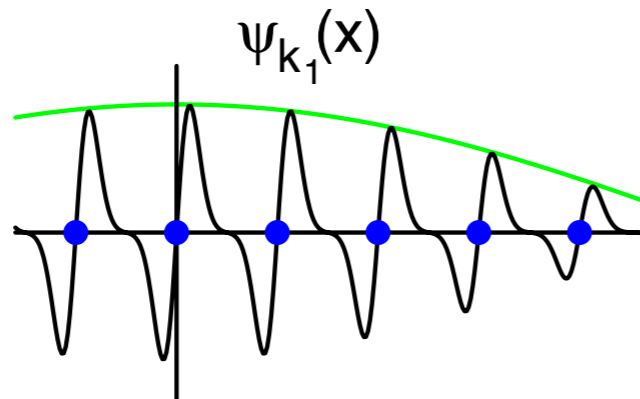
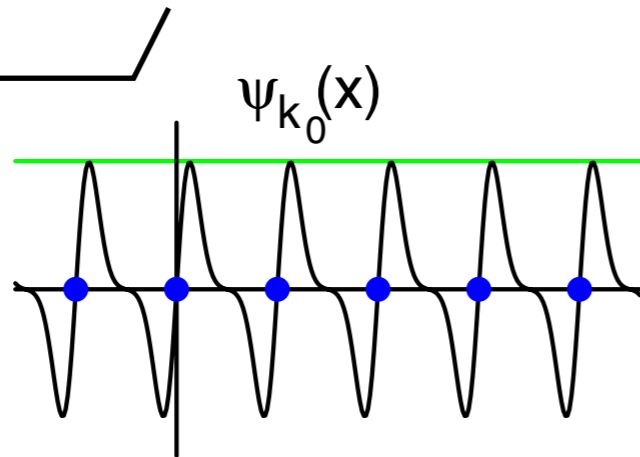
Wannier functions



Bloch vs Wannier functions

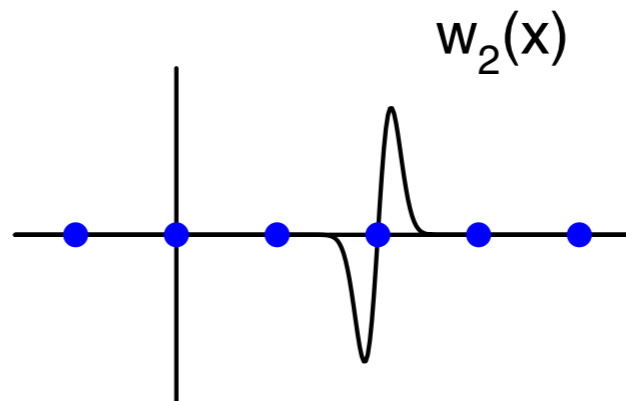
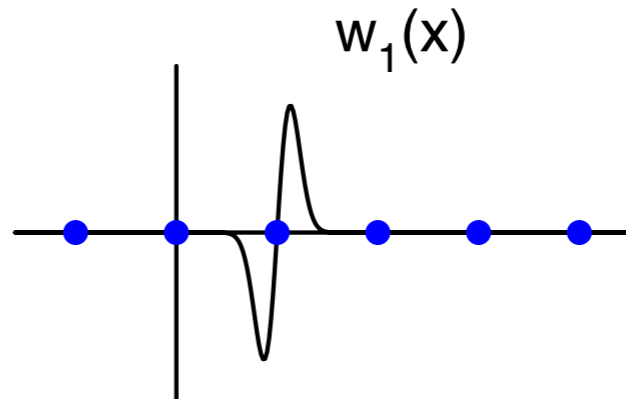
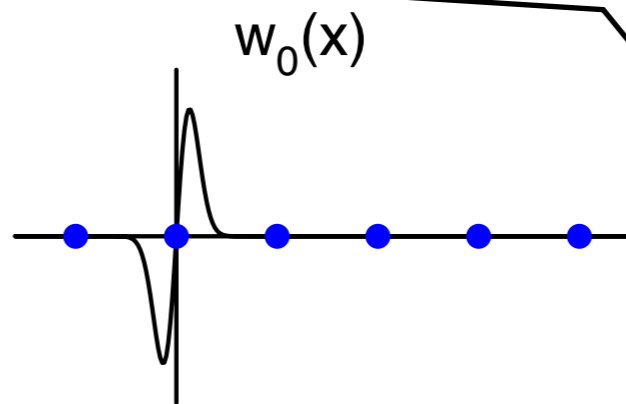
Bloch functions

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



Wannier functions (localized orbitals)

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



Indexed by
band number
(n) and wave
vector (**k**)
Γ-point

Indexed by the
lattice vector
in real space

Number of WF = number of bands!

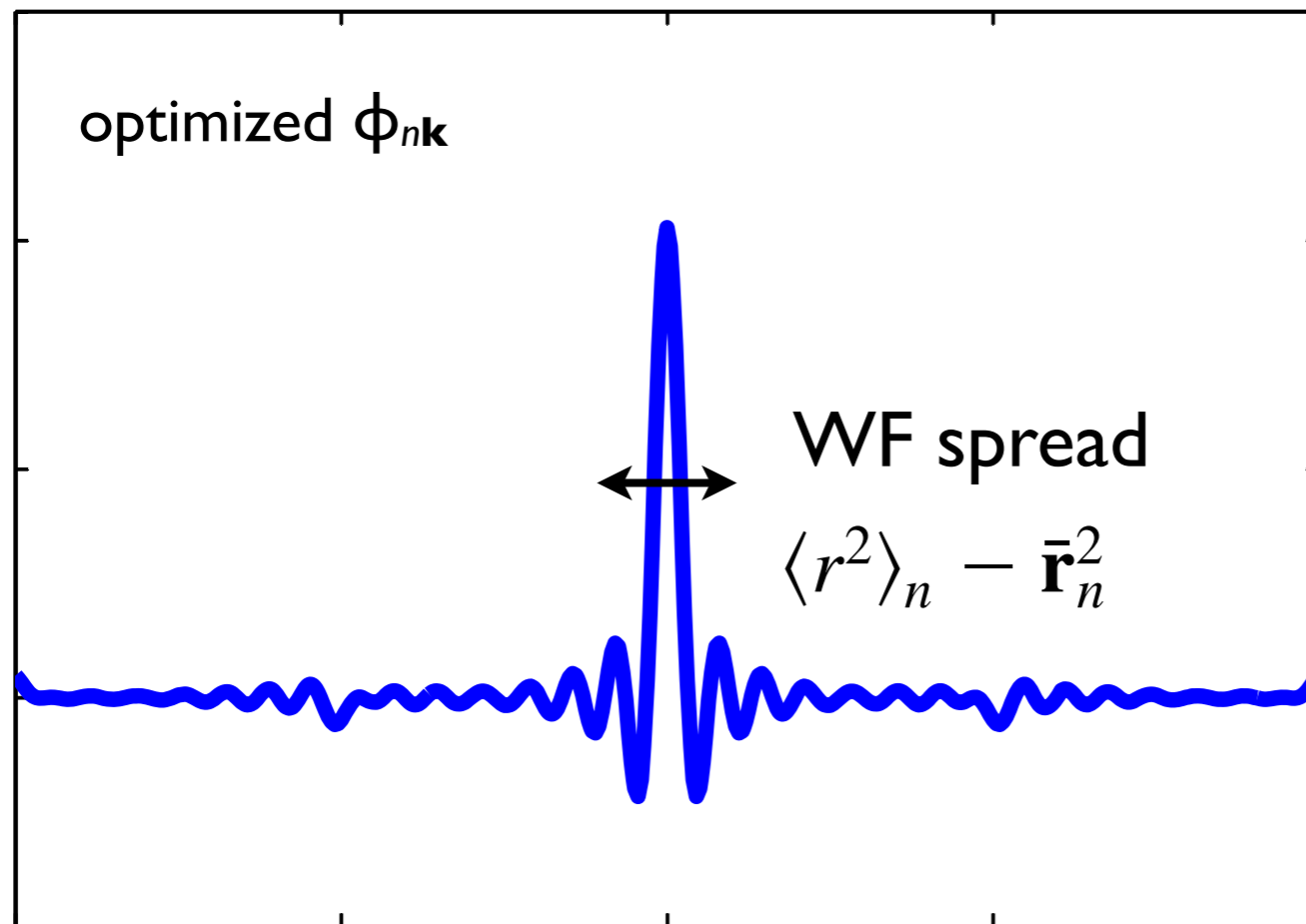
Wannier:
PRB **52**, 191 (1937)
Marzari et al.:
PRB **56**, 12847 (1997)
Rev. Mod. Phys. (2012)

Max. localized Wannier functions (MLWF)

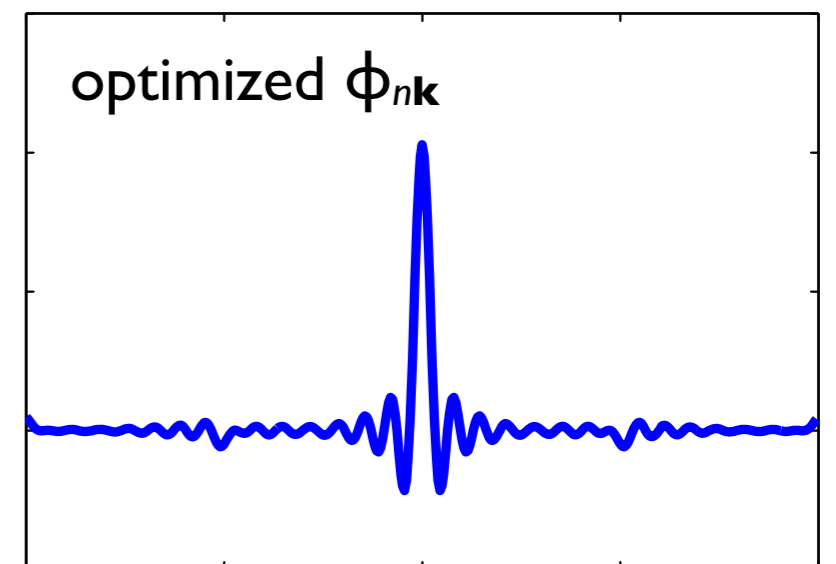
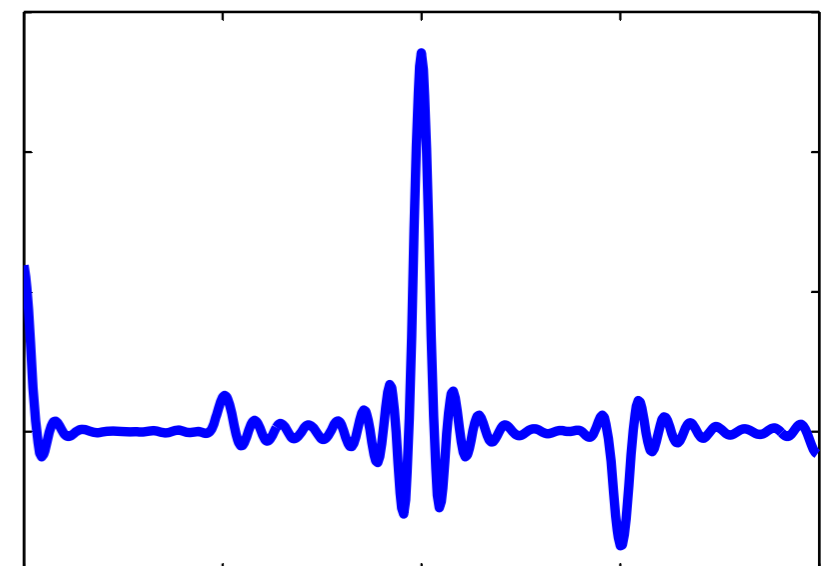
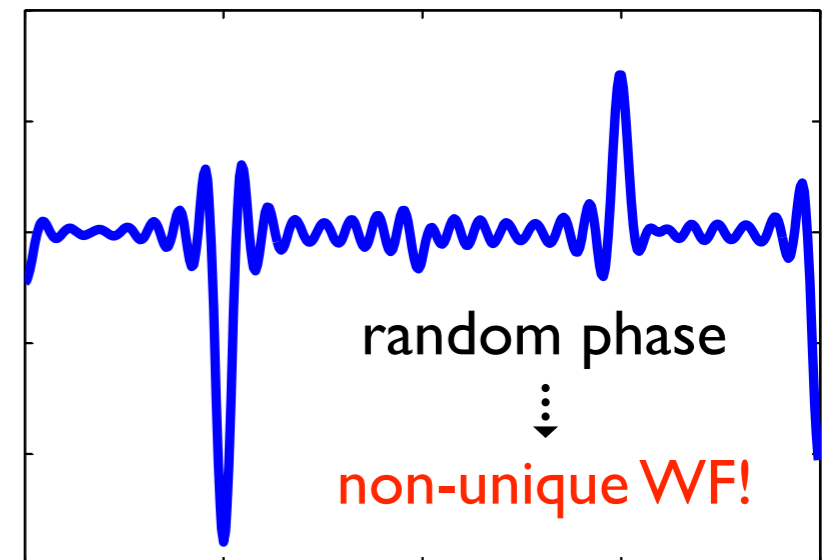
Bloch functions (more precisely):

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

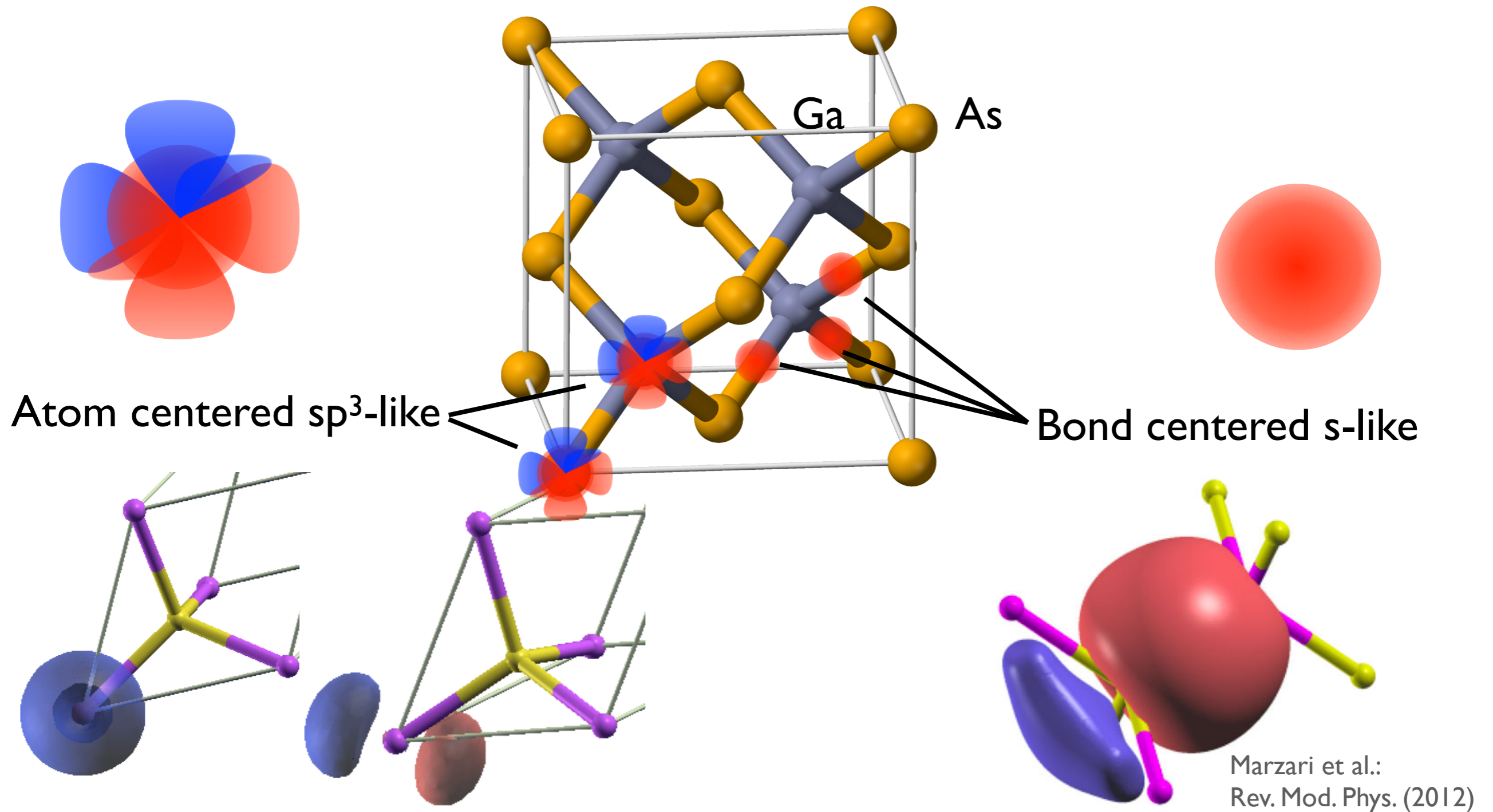
gauge freedom \rightarrow ambiguity



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



Two flavours of Wannier functions



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

- includes *valence* states
- charge transfer and polarization

Wannier functions as a tight-binding basis (atom centered FW)

\$ less GaAs-WANN_hr.dat

...

0	0	0	1	1	-4.335108	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	1	1	1	-0.001219		
...

Home unit cell

Neighbour unit cell

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

$\langle s_2 |$

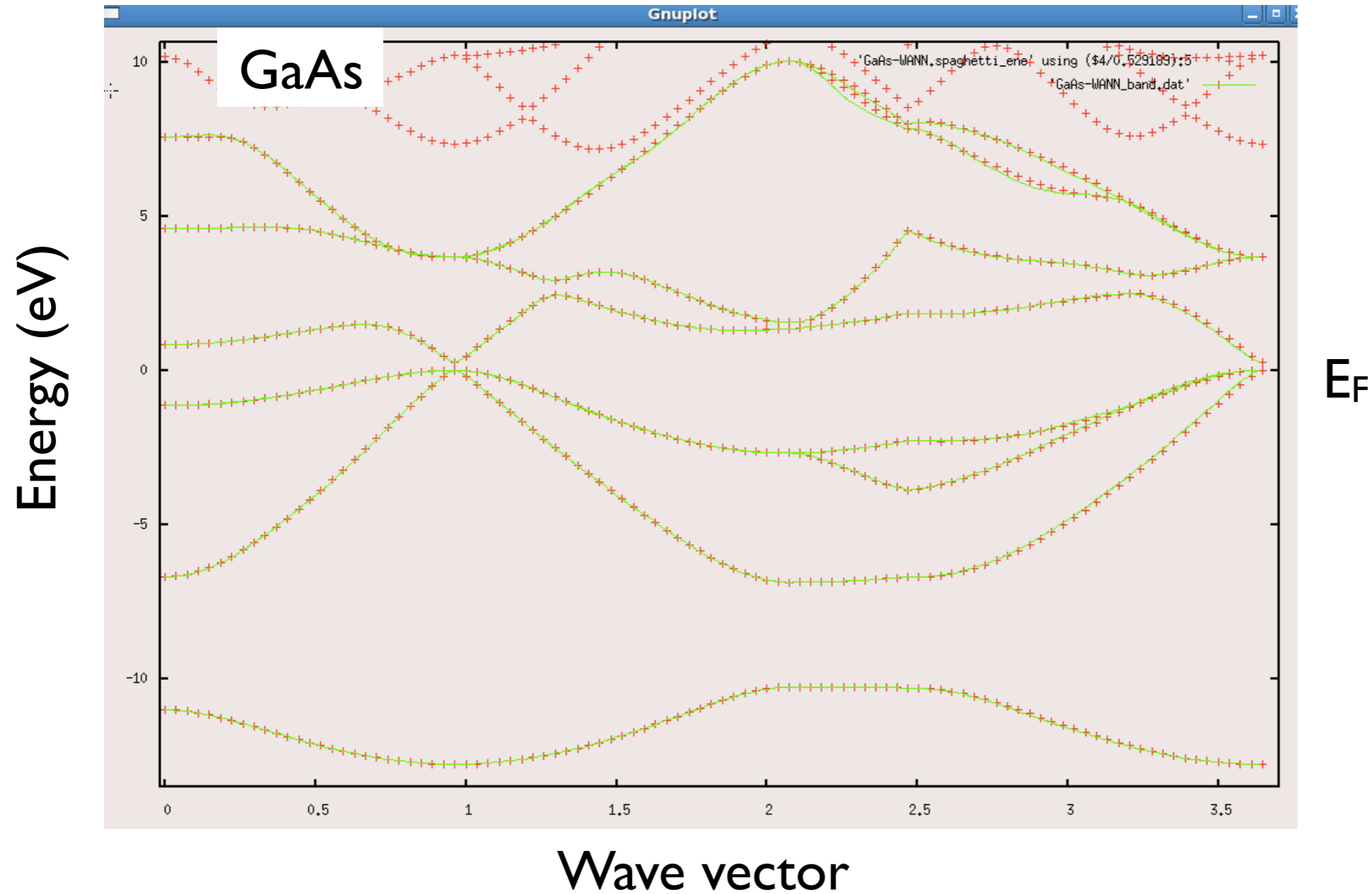
Matrix element (eV)
 $\langle s_1 | H | s_1 \rangle = E_{s_1}$

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

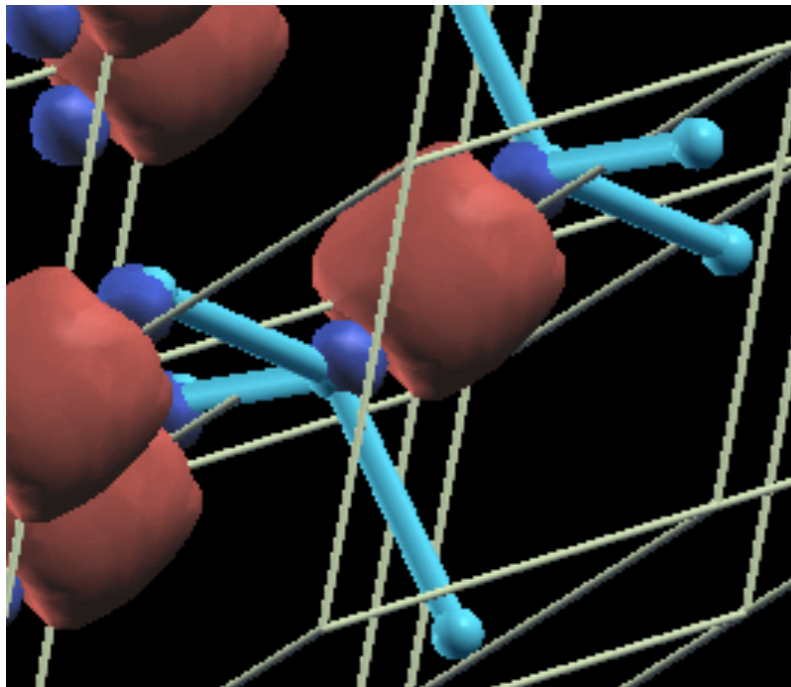


- + original Wien2k band structure
- Band structure computed from Wannier hamiltonian

Relation to polarization (bond centered WF)

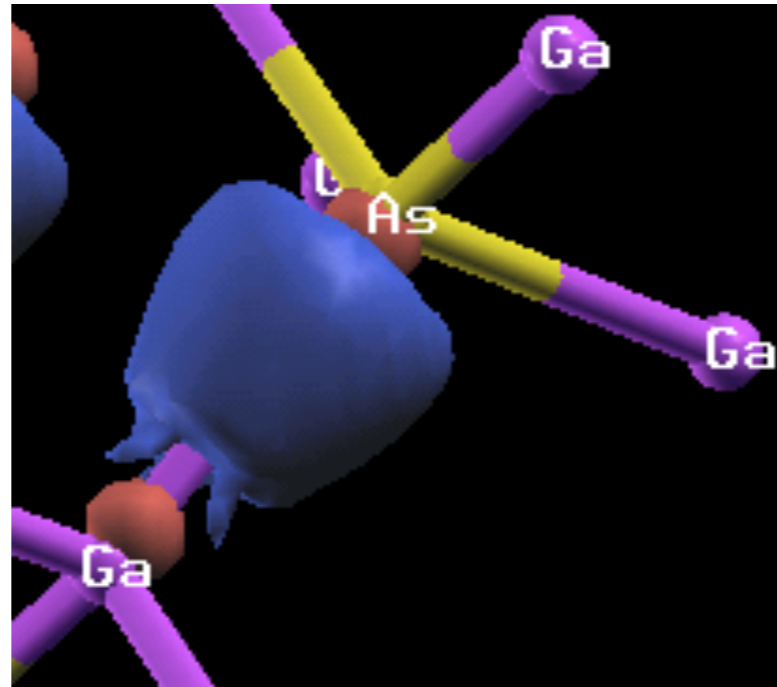
Bond-centered WF

Si



symmetric
(non-polar)

GaAs

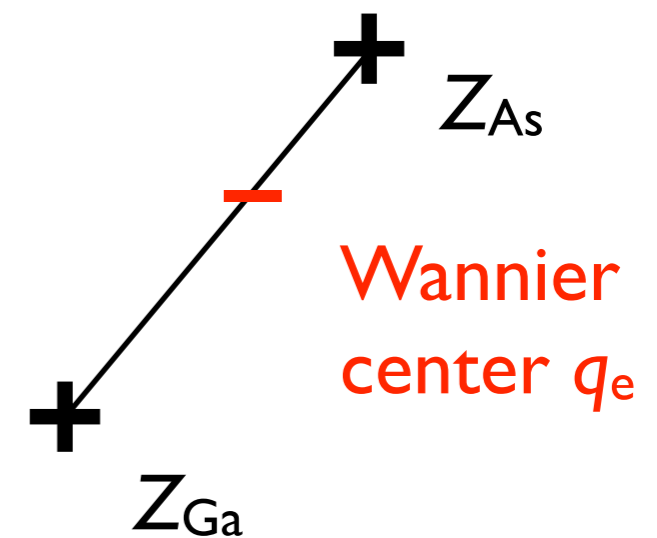


non-symmetric
(polar)

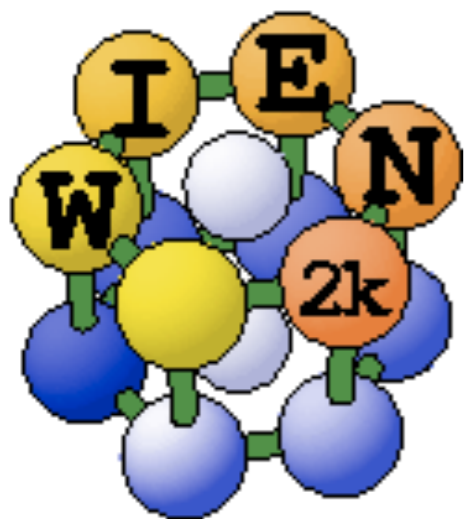
$$\mathbf{P} = \frac{e}{V} \left(\sum_{\tau} Z_{\tau} \mathbf{r}_{\tau} - \sum_n \mathbf{r}_n \right)$$

Ionic part

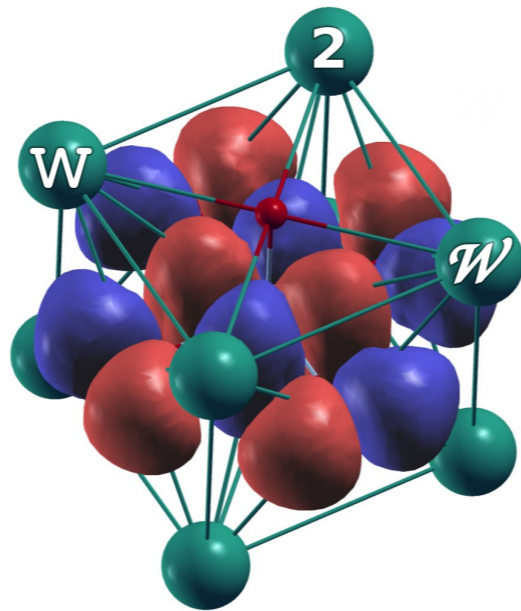
Electronic part



Berry phase



+

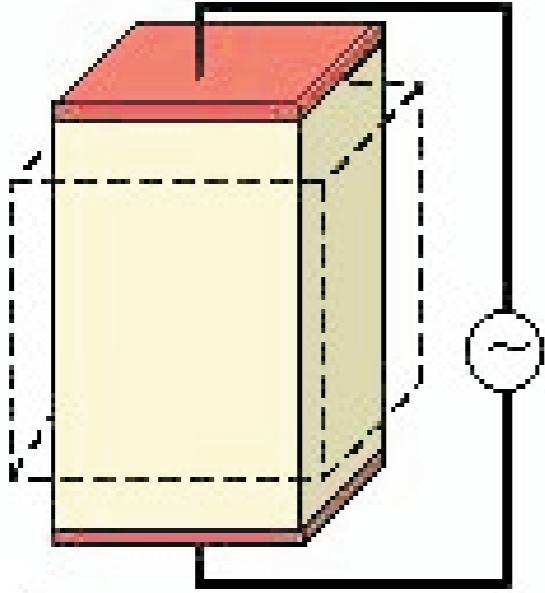


+

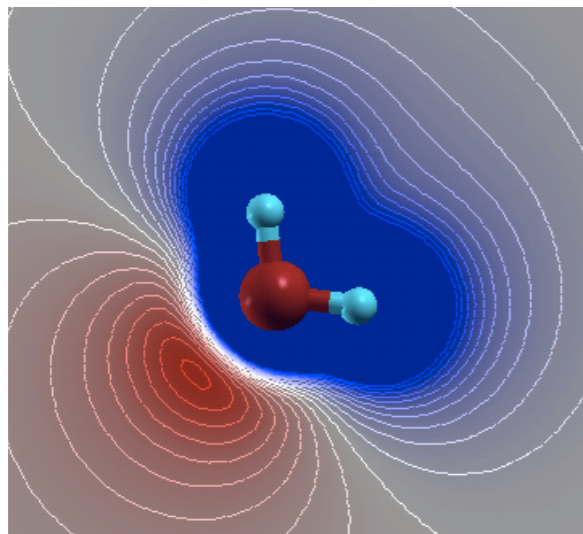
BerryPI

Material properties related to polarization

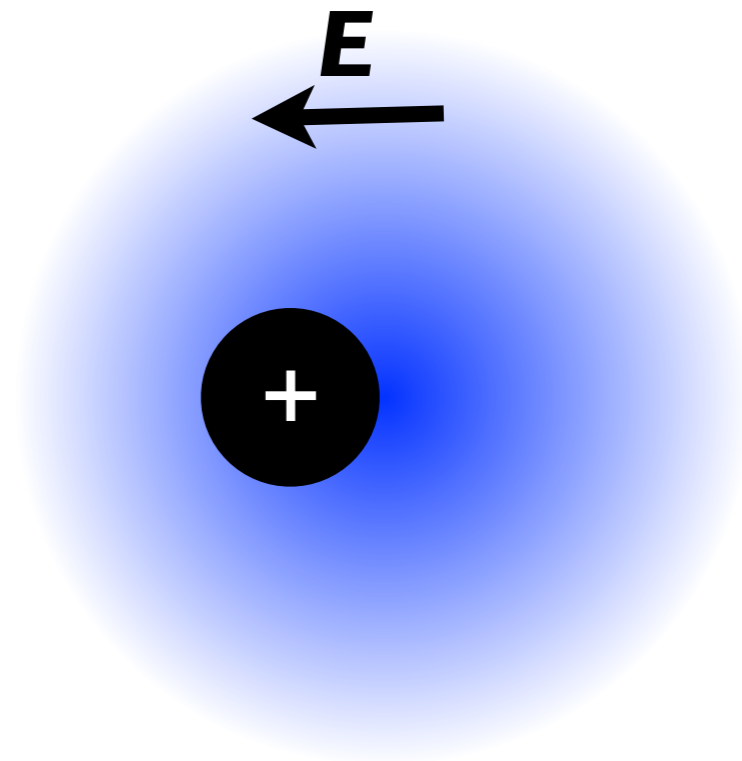
Piezo- and Ferroelectricity



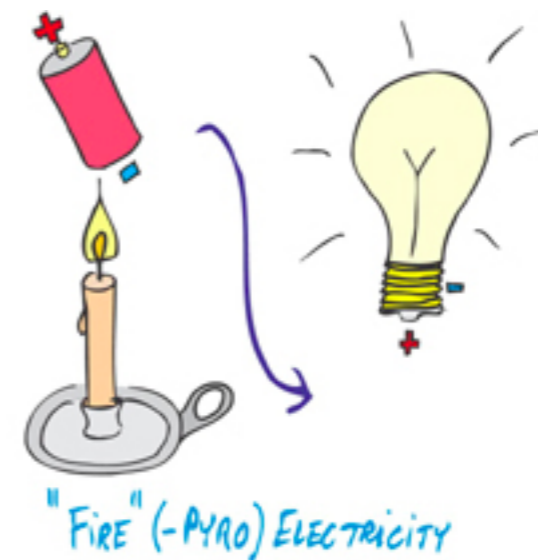
Effective charge



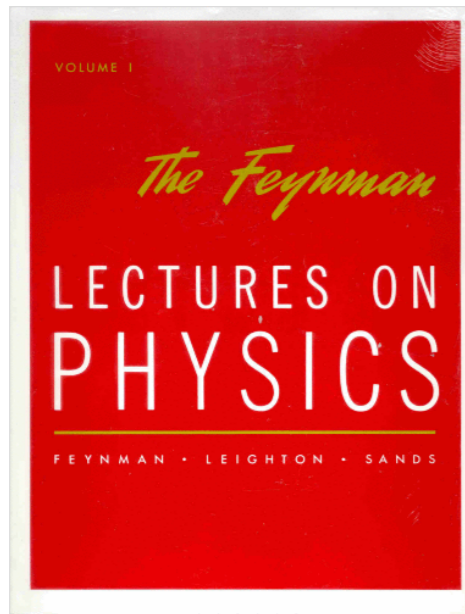
Dielectric screening



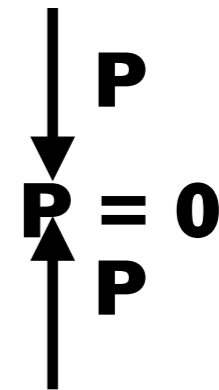
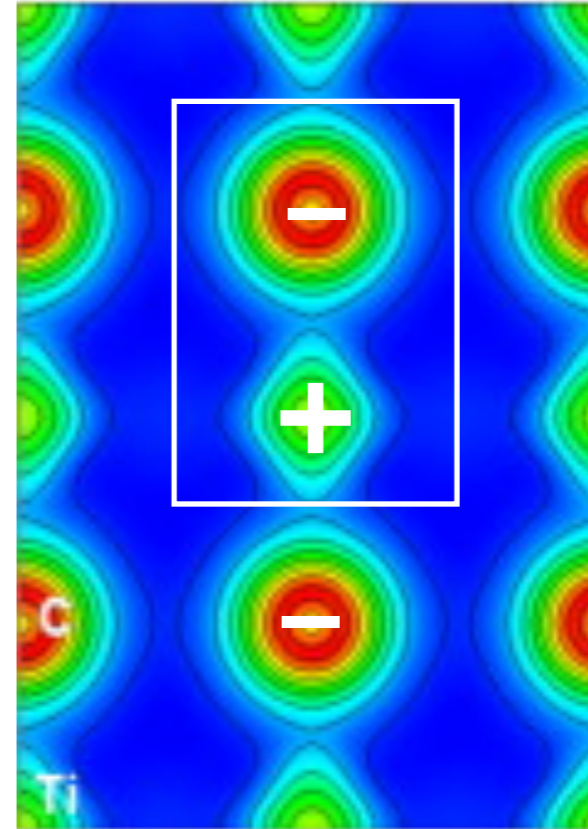
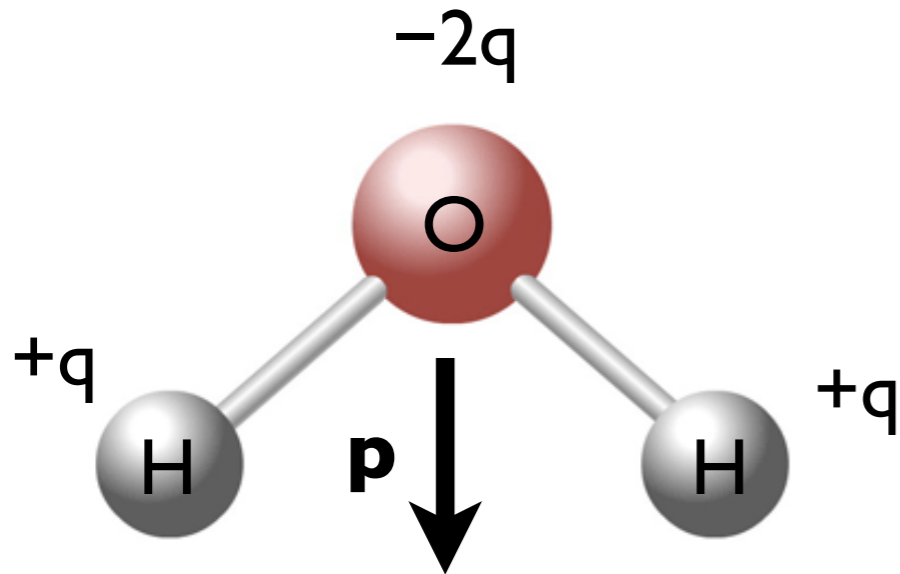
Pyroelectricity



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



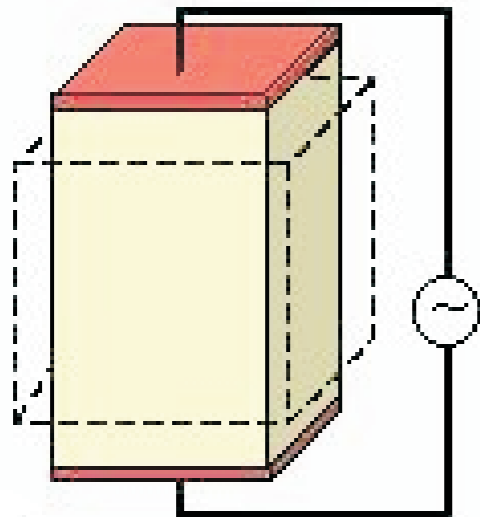
Polarization for periodic solids is undefined

Modern theory of polarization

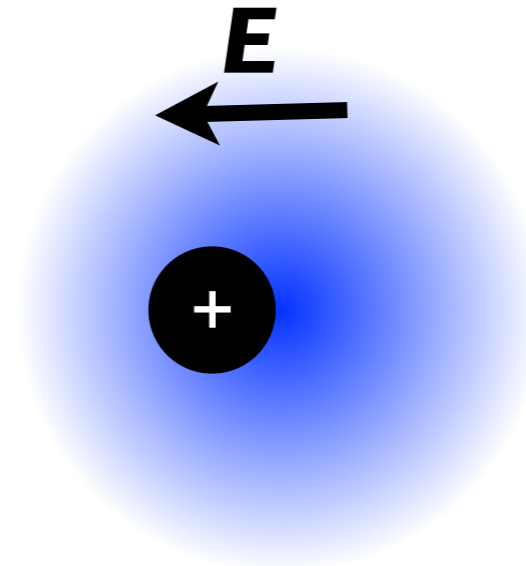
Pioneered by *King-Smith, David Vanderbilt and Raffaele Resta*

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

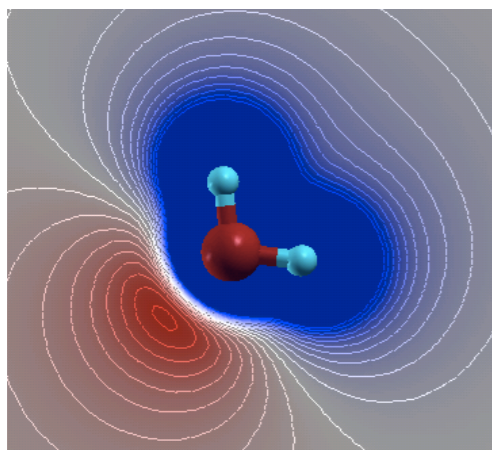
$$\Delta\mathbf{P} = \mathbf{P}^{(0)} - \mathbf{P}^{(1)}$$



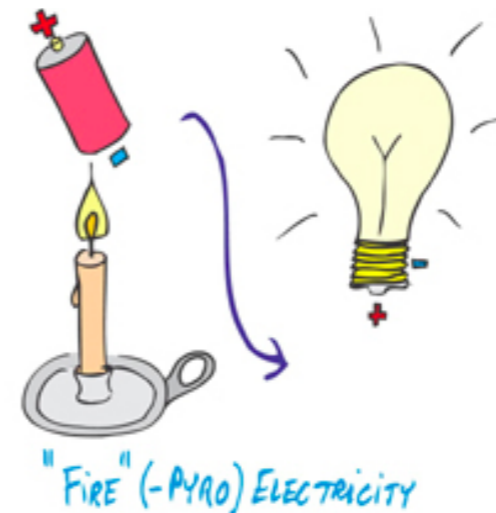
$$\frac{\Delta\mathbf{P}}{\Delta\text{strain}}$$



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

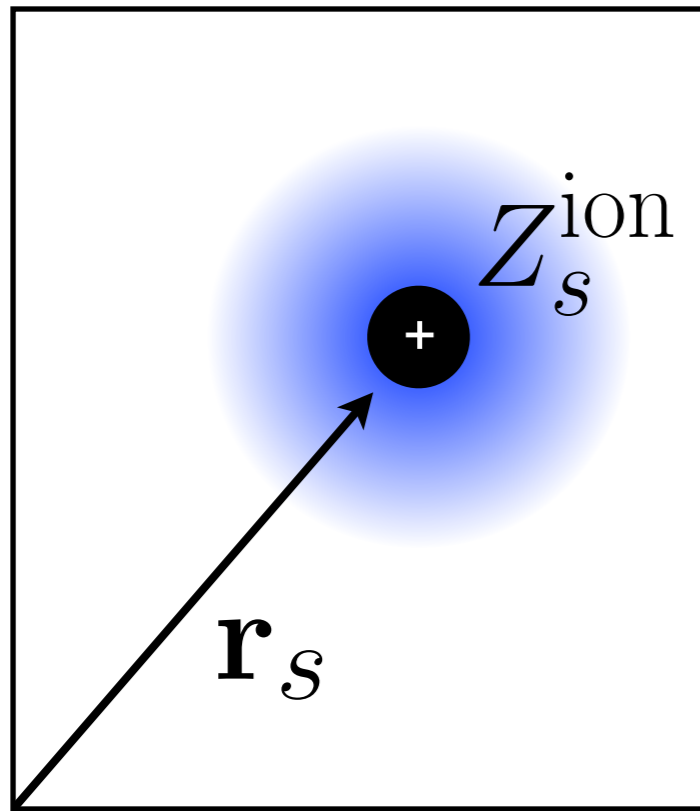


$$\frac{\Delta\mathbf{P}}{\text{displacement}}$$



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

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

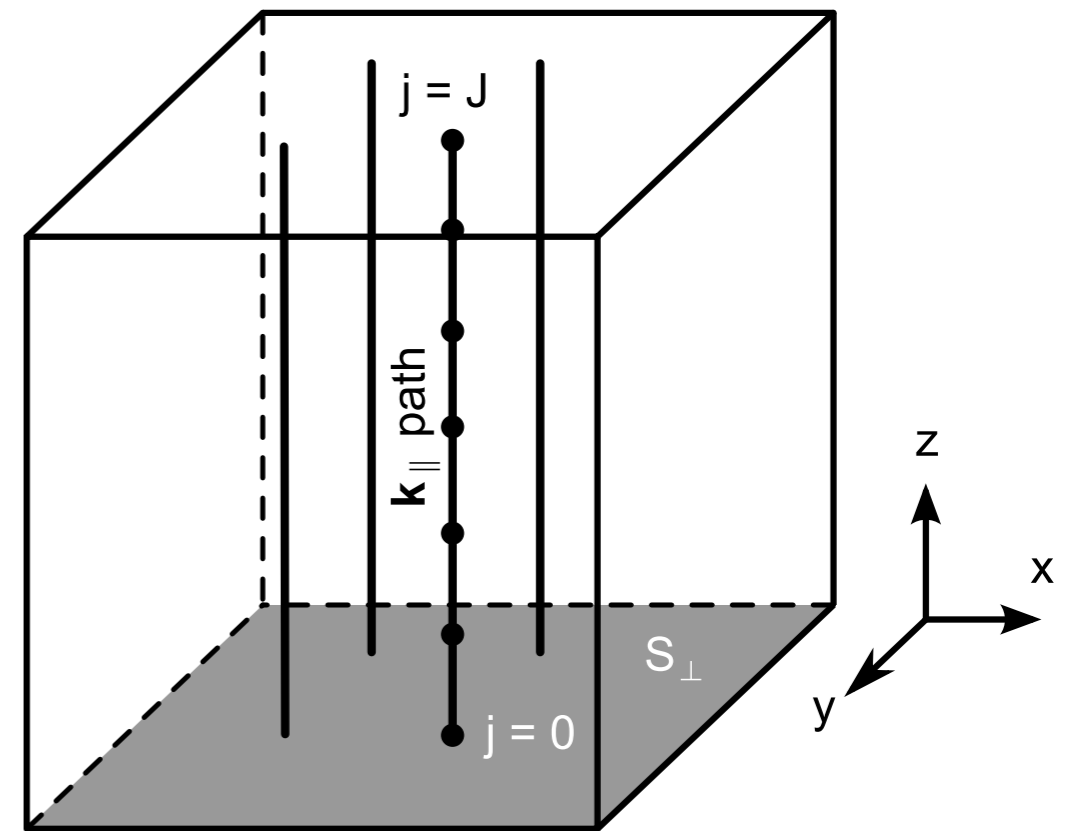
0

$$-\mathbf{P}_{\text{el}} = \Omega^{-1} \int d\mathbf{r} \mathbf{r} \rho(\mathbf{r}) = \Omega^{-1} \sum_n^{\text{occ. bands}} \langle \psi_n | \mathbf{r} | \psi_n \rangle$$

($\hat{\mathbf{r}} = i\nabla_{\mathbf{k}}$ position operator in k-space)

$$\equiv \frac{2ei}{(2\pi)^3} \sum_n^{\text{occ. bands}} \int_{\text{BZ}} d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$$

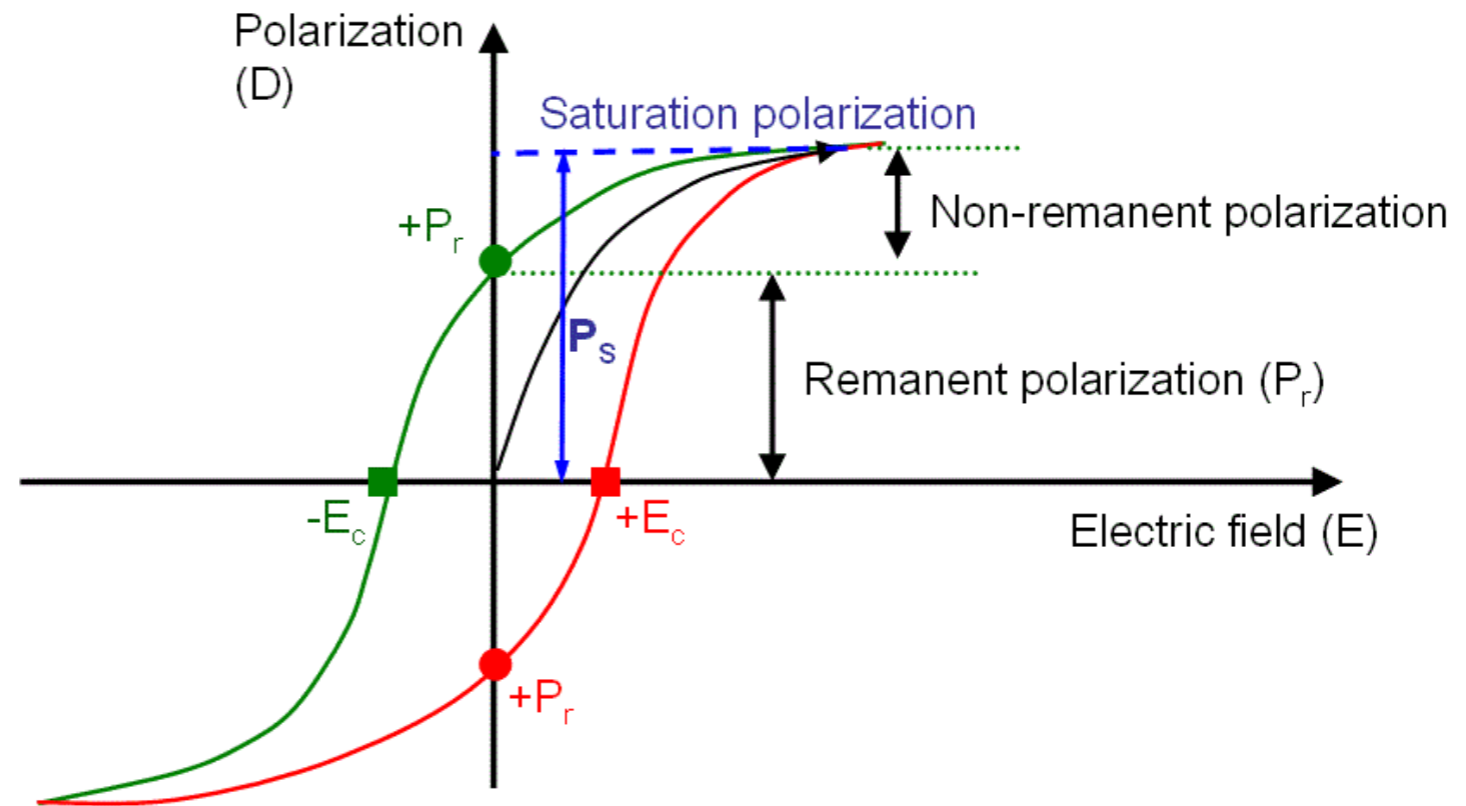
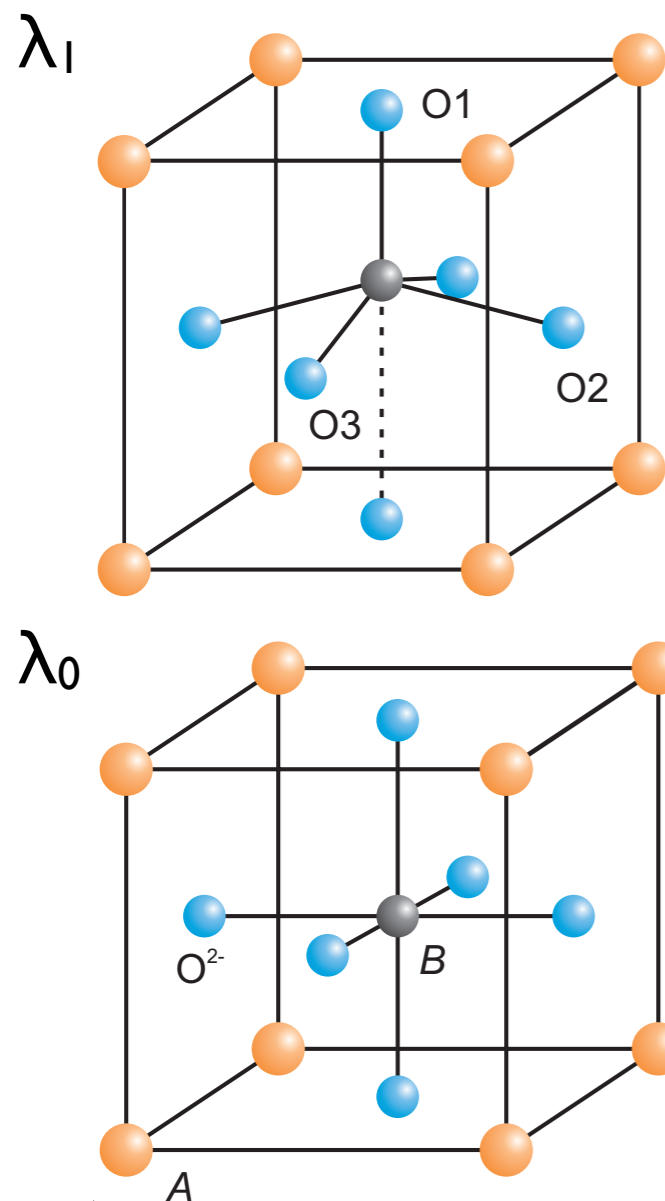
Berry connection



Choice of a reference structure

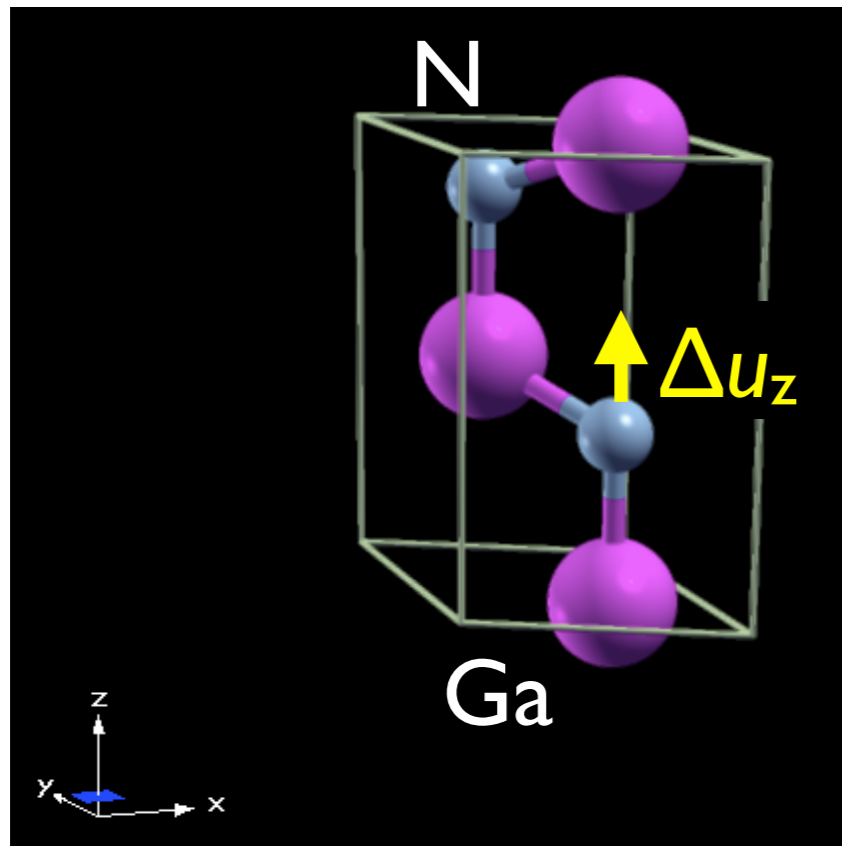
- calculation of macroscopic polarization always requires 2 structures
- begin with the lowest symmetry (λ_1) case

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



<http://www.globalsino.com/EM/page2380.html>

Demonstration: Born 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)

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

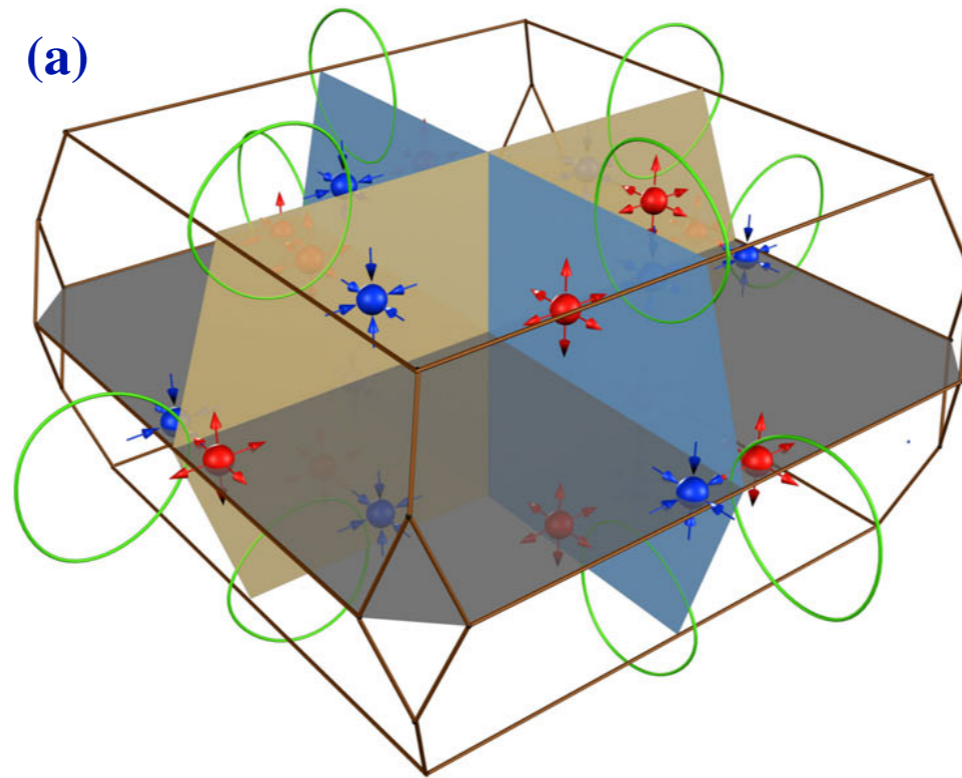
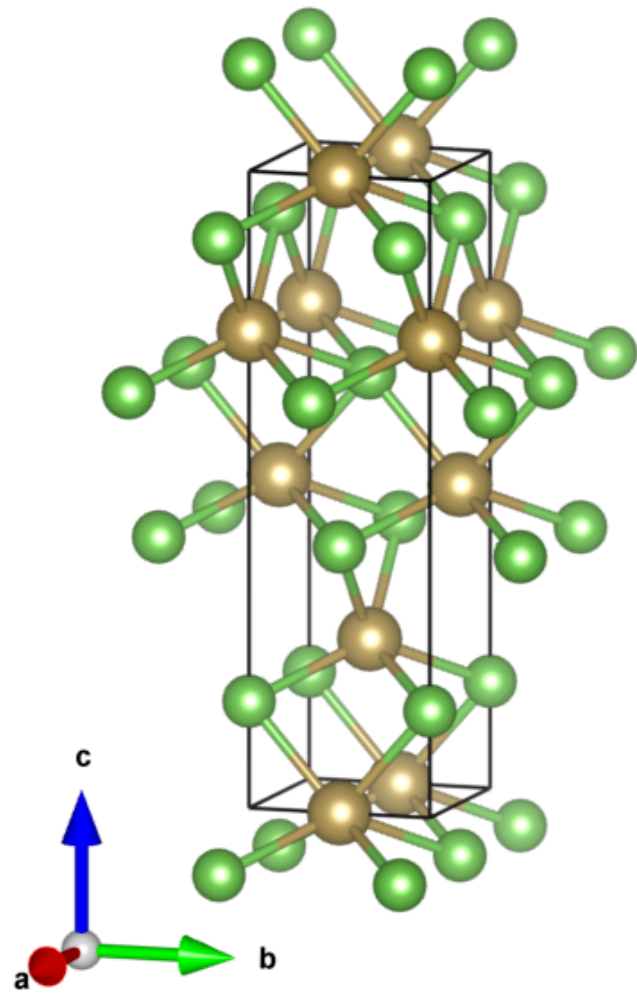
substance:	gallium nitride (GaN)
property:	effective charge, dielectric constants (lattice properties)

Born effective charge (wurtzite structure)

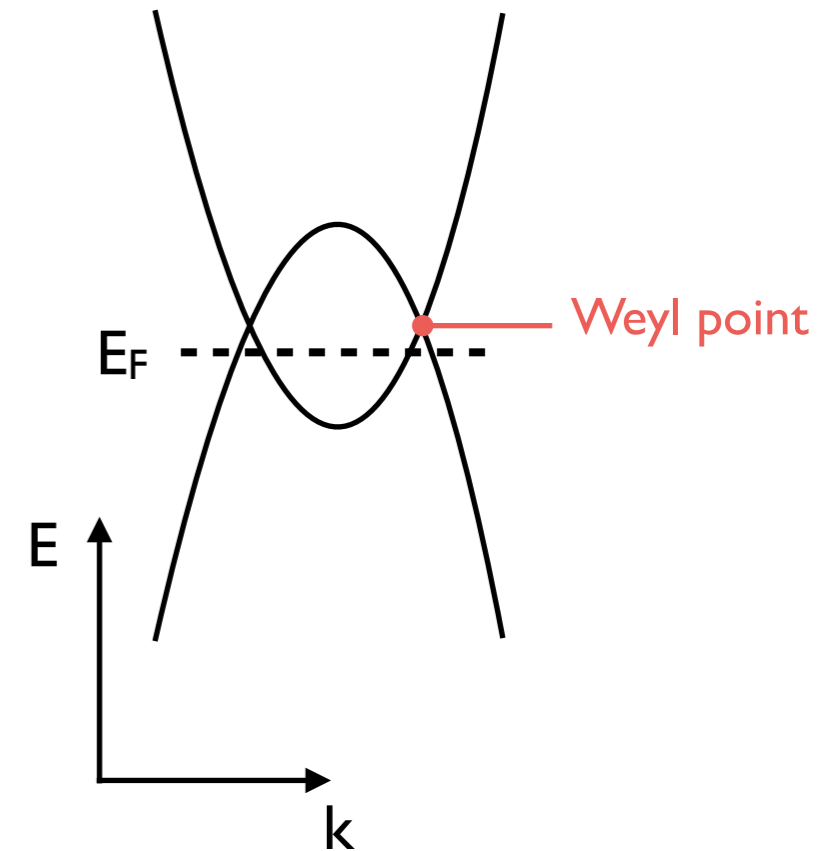
Physical Property	Numerical Values	Remarks	Ref.
Z^*	2.73(3)	from LO-TO splitting, Raman scattering from bulk GaN	01G
	2.51	ab initio DFT(LDA) calculation	01Z
	2.67	ab initio DFT(GGA) calculation	
Z_{xx}^*	2.60	ab initio DFT(LDA) calculation	02W
Z_{zz}^*	2.74		
$Z_{B,xx}^*$	1.14	$Z_{B,ij}^* = Z_{ij}^*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

Topological properties (new functionality 2019)

TaAs (Weyl semimetal)



Weng et al.,
Physical Review X 5, 011029 (2015)



Weyl point “charge”

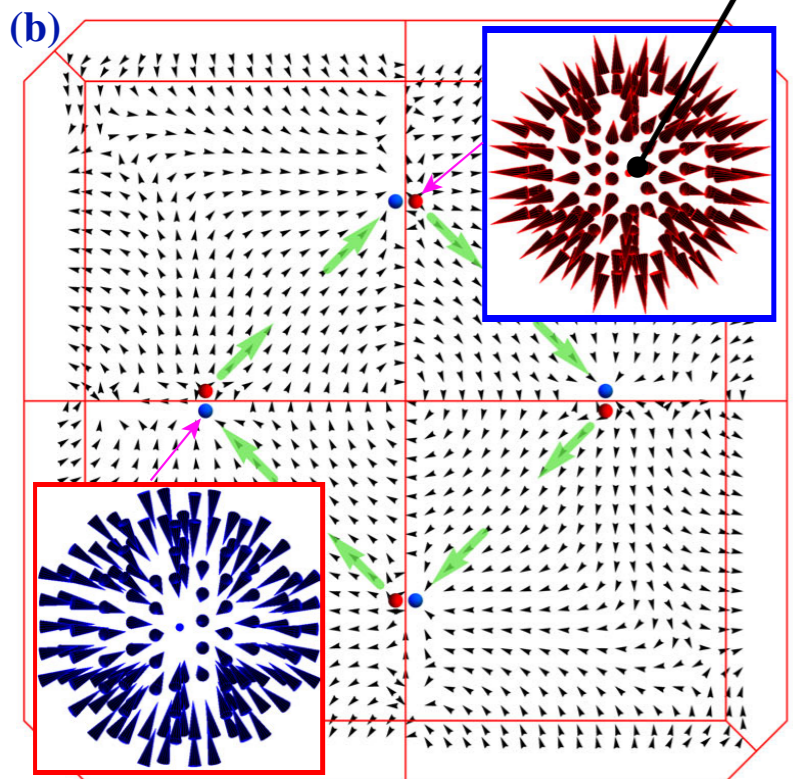
Berry connection

$$\vec{A} = i \langle u_{\vec{k}} | \nabla_{\vec{k}} | u_{\vec{k}} \rangle$$

Berry curvature

$$\vec{\nabla}_k \times \vec{A}$$

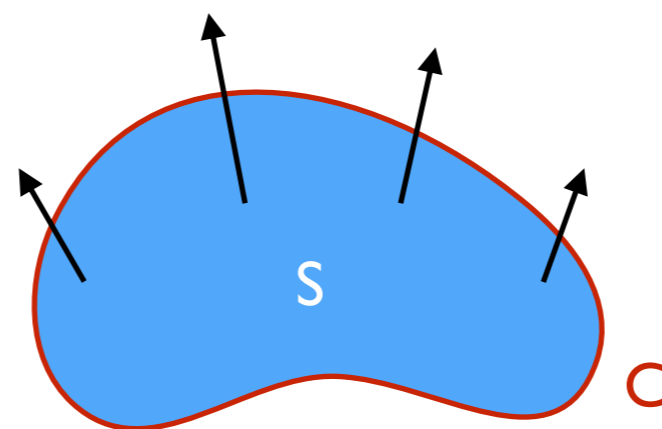
Analog of
monopole charge



Stokes' theorem

Vector field

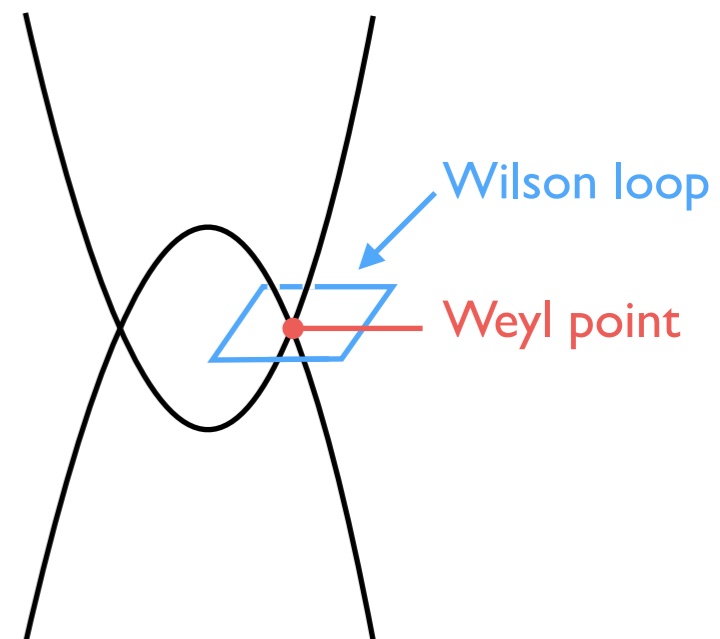
$$\vec{\nabla}_k \times \vec{A}$$



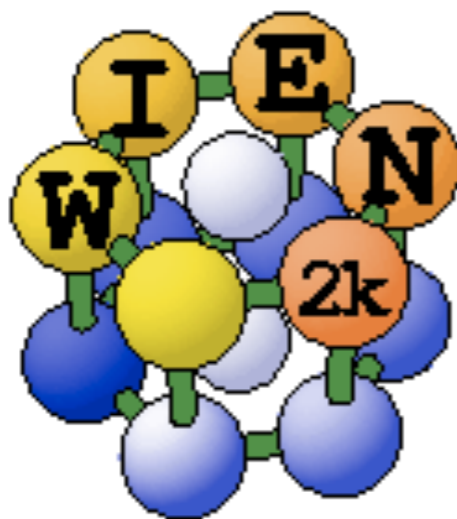
$$\iint_S (\vec{\nabla} \times \vec{A}) \cdot d\vec{S} = \oint_C \vec{A} \cdot d\vec{k}$$

Berry flux

Berry phase

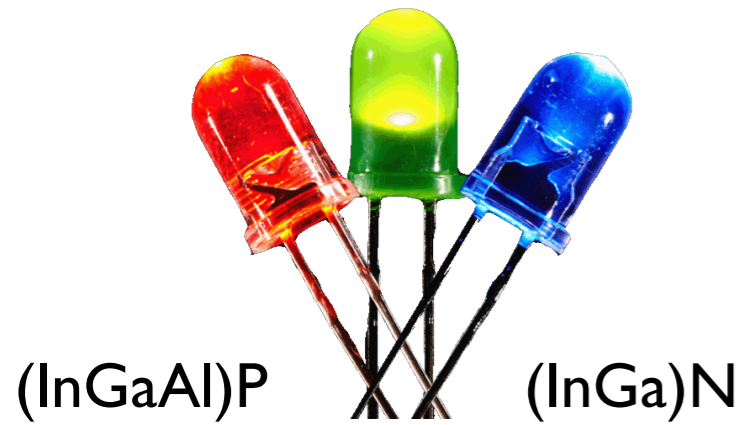


Effective band structure of alloys

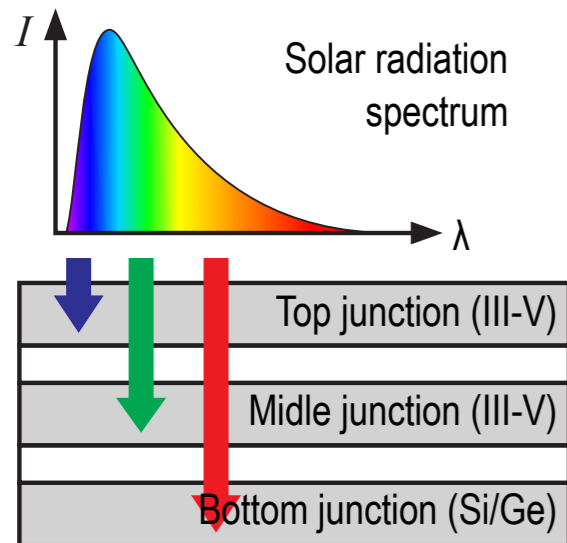
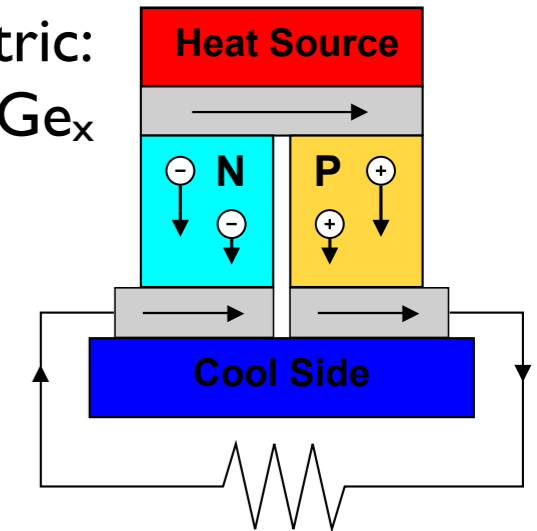


+ fold2Bloch

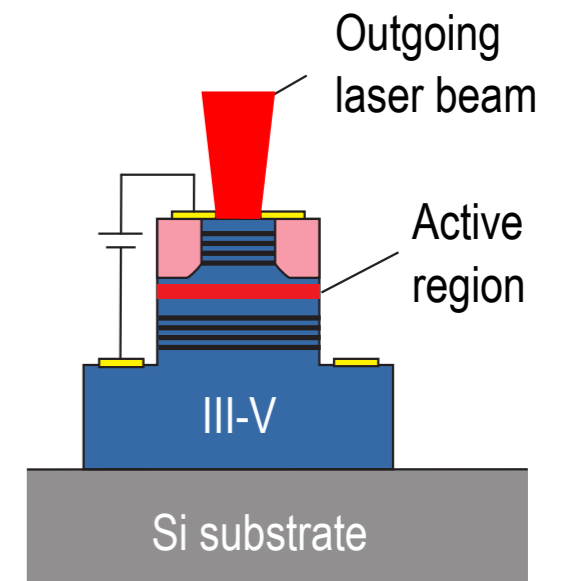
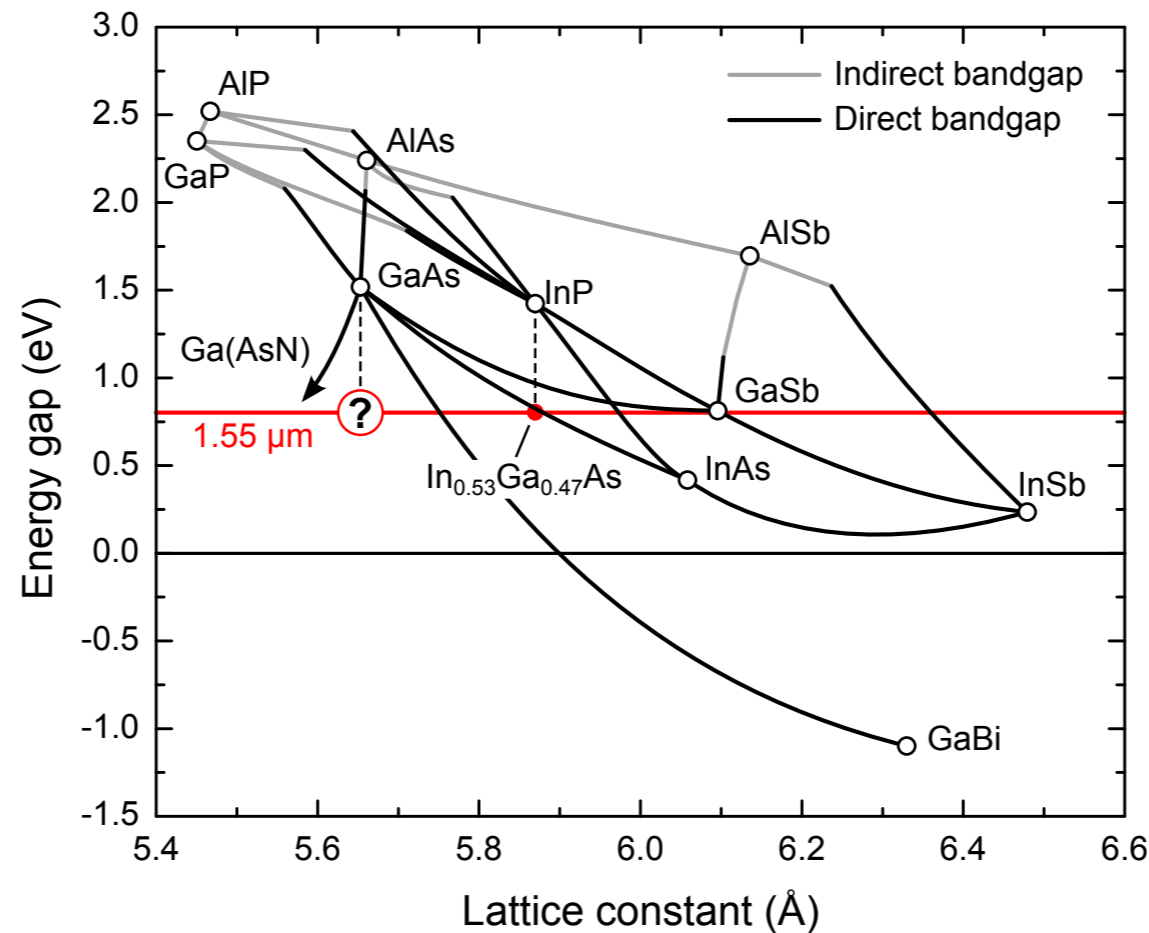
Semiconductor alloys



Thermoelectric:
 $\text{Si}_{1-x}\text{Ge}_x$

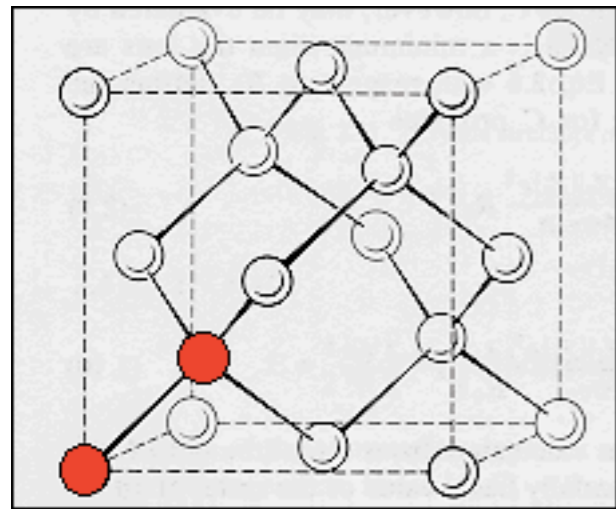


$E_g = 1 \text{ eV}$ junction:
(InGa)(NAs)



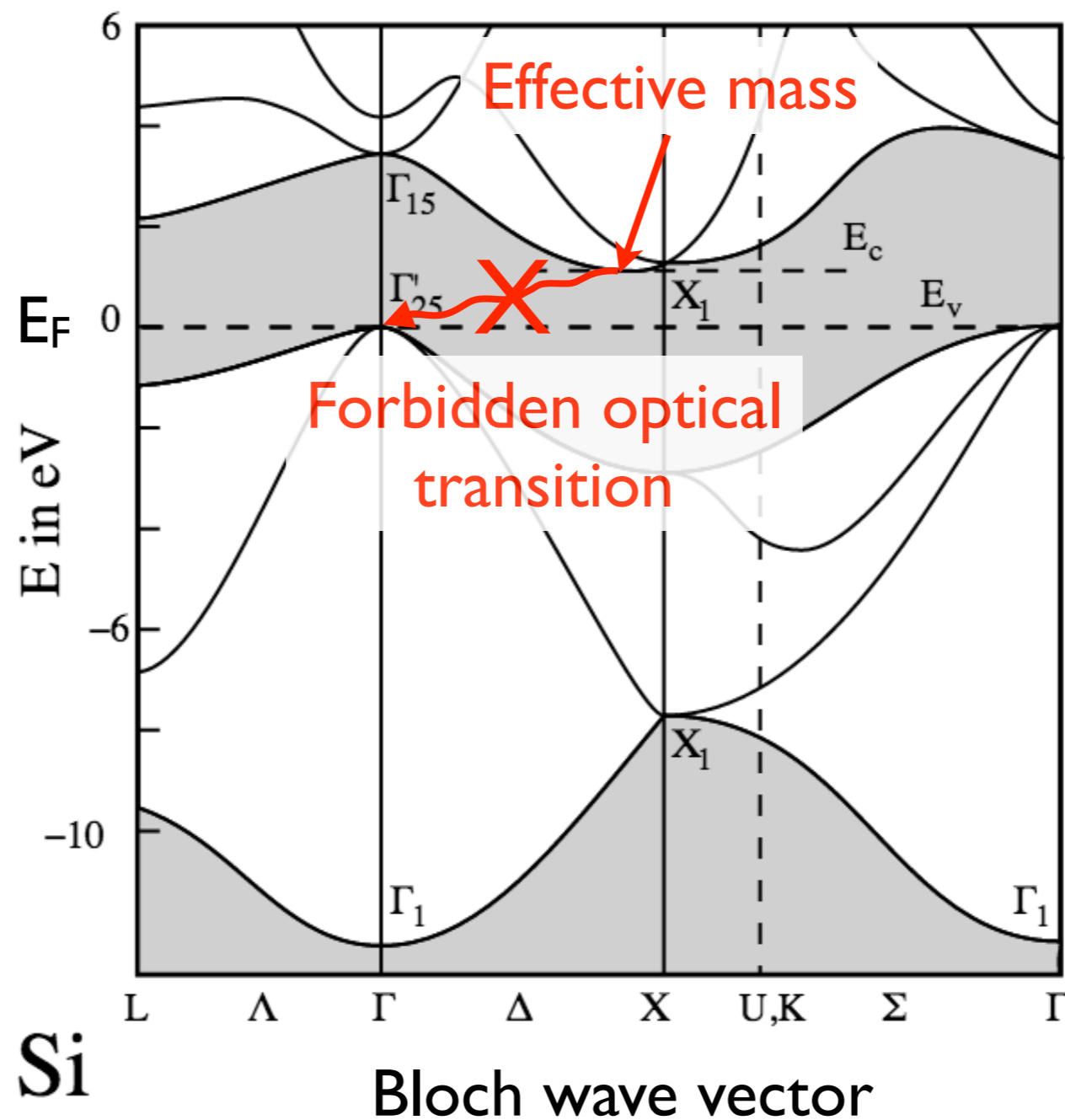
1.55 μm lasers:
(InGa)As
(InGa)(NAsSb)
Ga(AsBi)

Band structure

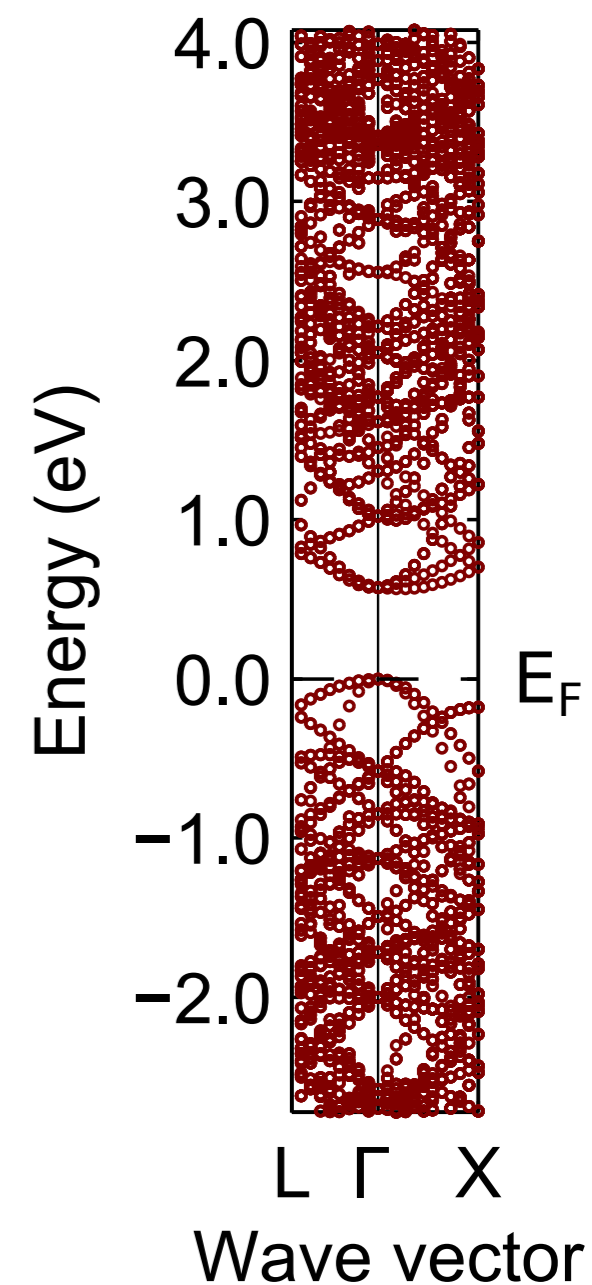


Energy gap \updownarrow

Silicon
2-atom basis



Silicon
250-atom supercell



Unfolding the first-principle band structure

Plane wave expansion

$$\Psi_{n,\mathbf{K}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{K}}(\mathbf{G}) e^{i(\mathbf{K}+\mathbf{G})\cdot\mathbf{r}}$$

Bloch spectral weight

$$w_n(\mathbf{k}) = \sum_{\mathbf{g}} |C_{n,\mathbf{K}}(\mathbf{k} + \mathbf{g})|^2$$

Popescu & Zunger:
Phys. Rev. Lett. **104**, 236403 (2010)

Rubel *et al.*
Phys. Rev. B **90**, 115202 (2014)

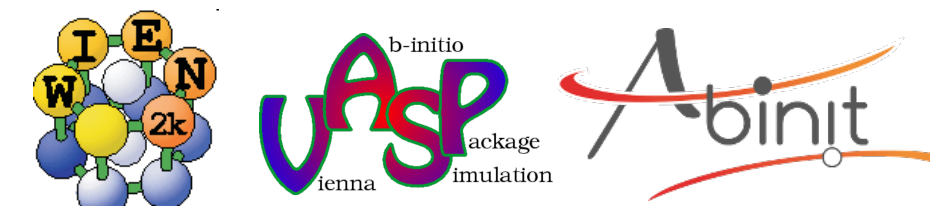
README.md

fold2Bloch

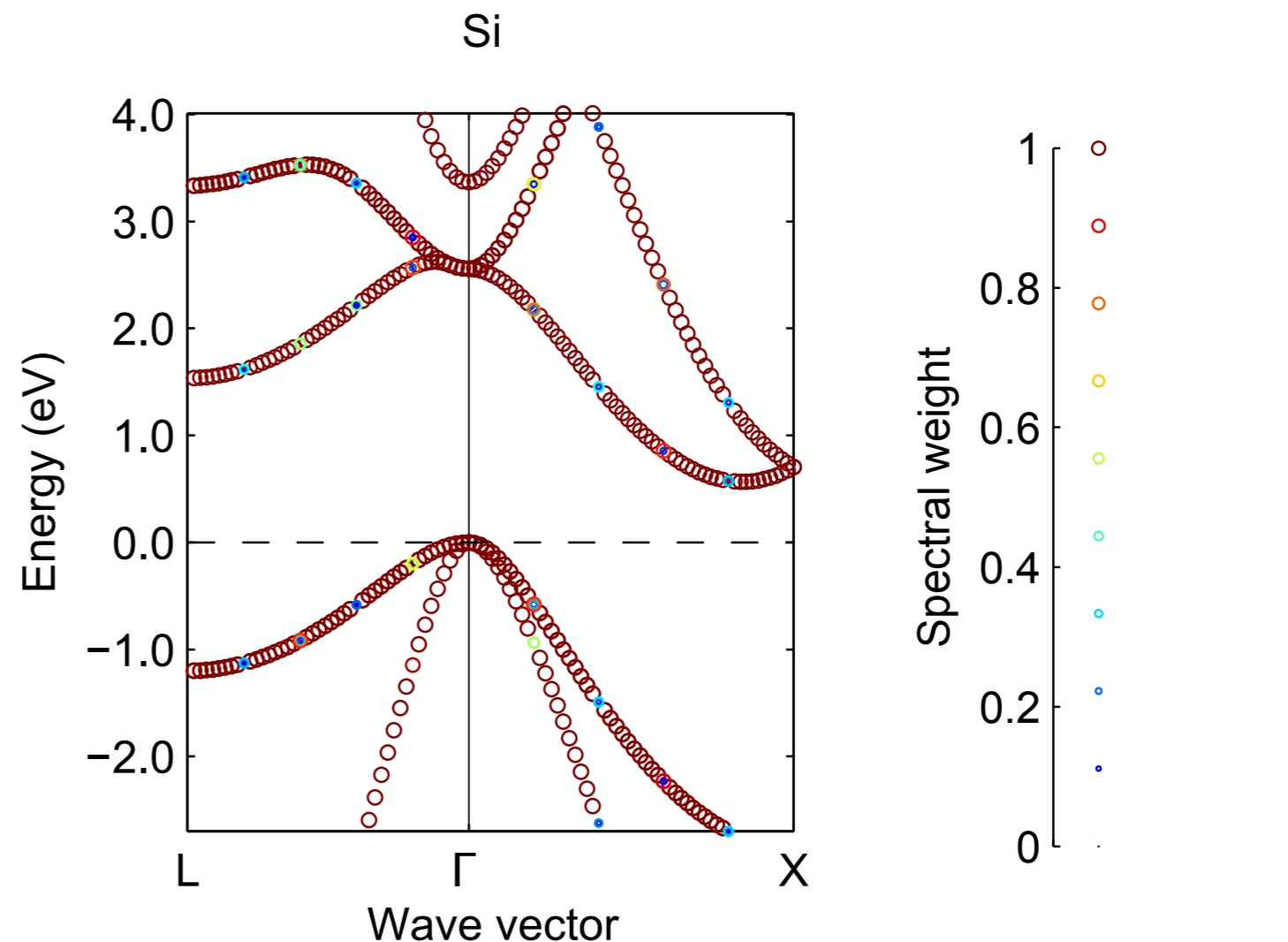
Unfolding of first-principle electronic band structure obtained with WIEN2k DFT-(L)APW code

Contributors:

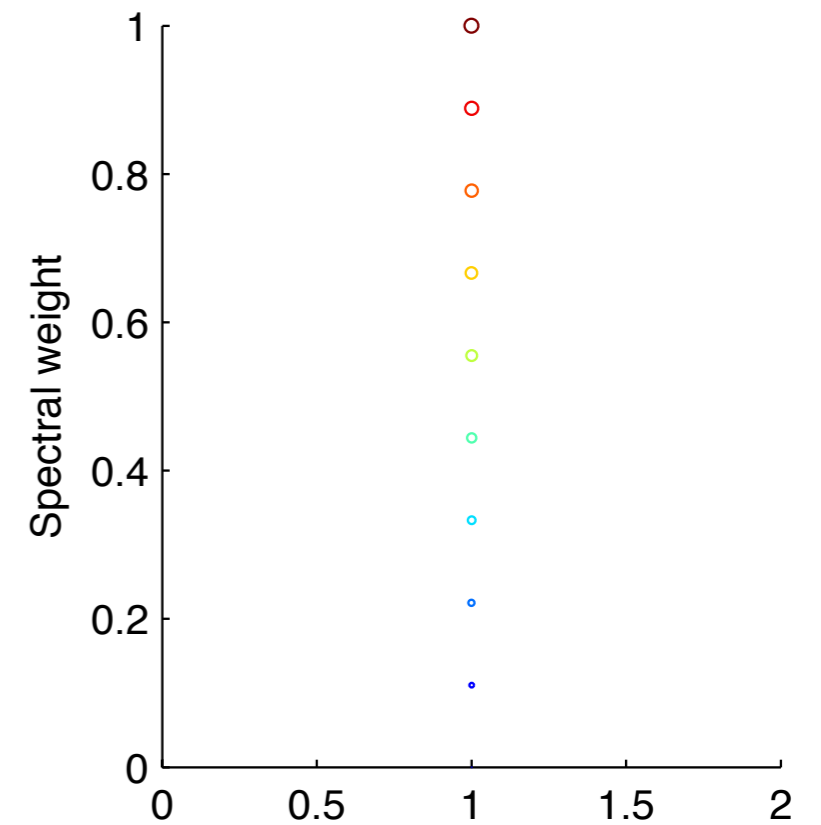
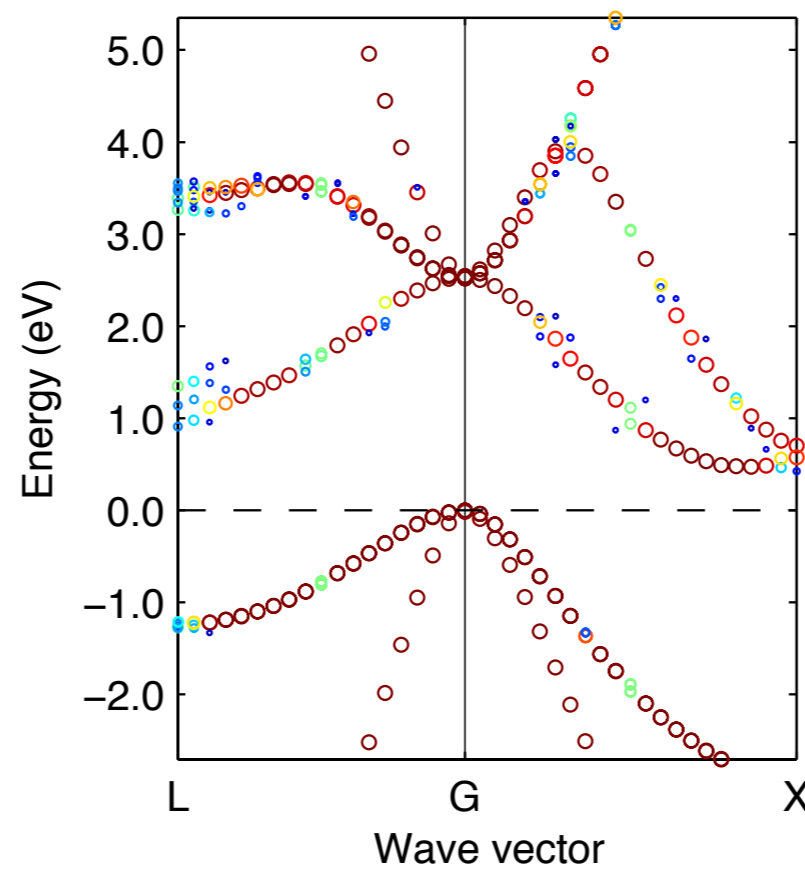
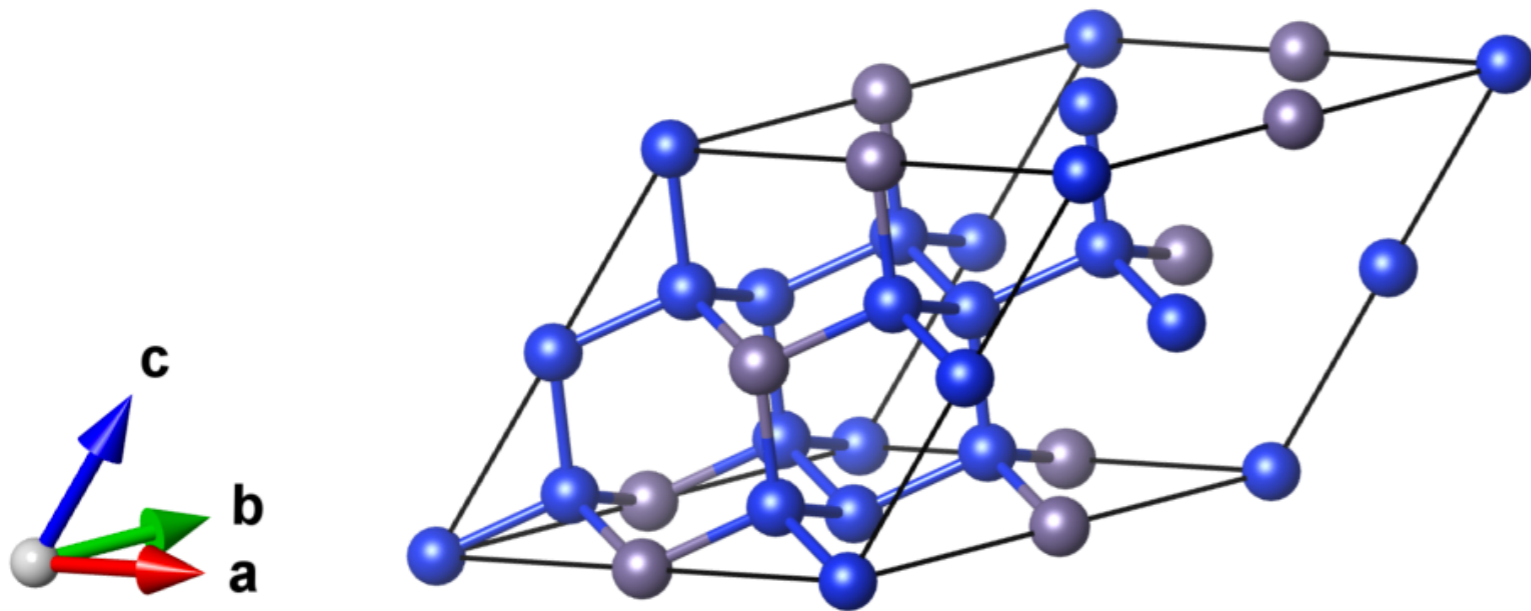
- Anton Bokhanchuk
- Elias Assmann
- Sheikh Jamil Ahmed
- Oleg Rubel



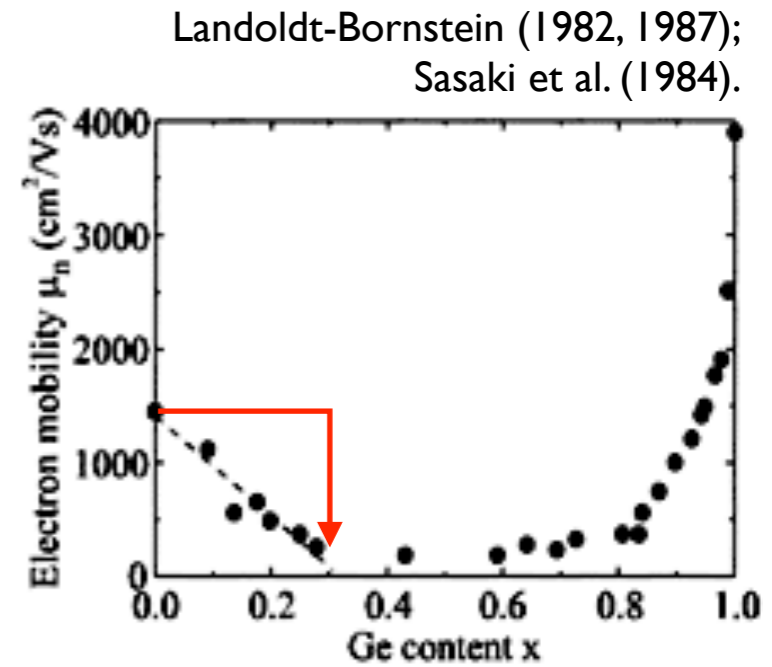
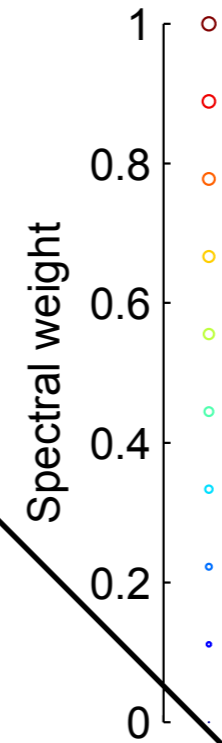
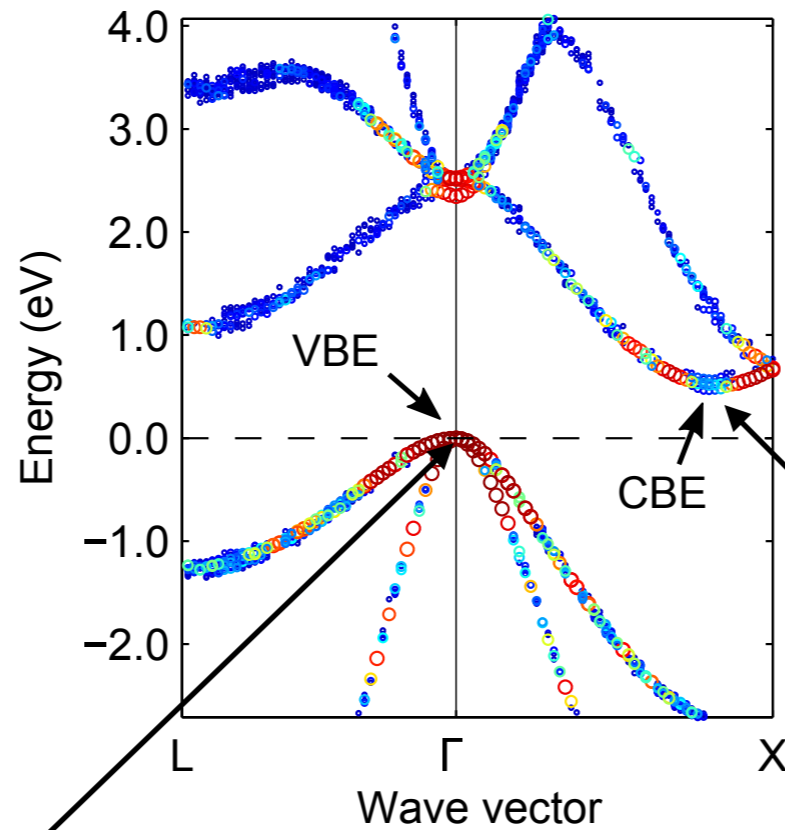
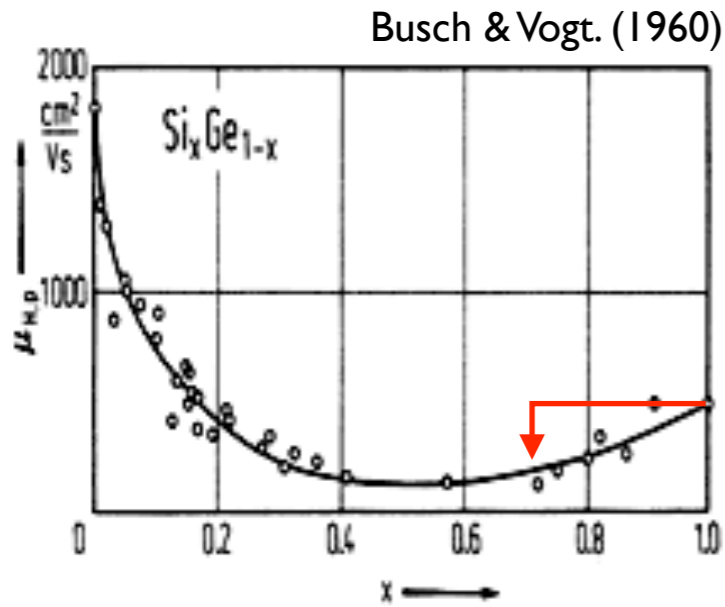
The image shows a screenshot of a README file for the 'fold2Bloch' software. It describes the software as a tool for unfolding first-principle electronic band structures obtained with WIEN2k DFT-(L)APW code. It lists four contributors: Anton Bokhanchuk, Elias Assmann, Sheikh Jamil Ahmed, and Oleg Rubel. To the right of the text are three logos: WIEN2k (a cluster of atoms with 'I', 'E', 'N', 'W', '2k' labels), VASP (Vienna Ab-initio Simulation Package) with 'b-initio' above it, and binit (a stylized 'A' logo).



Demonstration: Band structure of $\text{Si}_{1-x}\text{Ge}_x$ alloy ($x \sim 0.2$)

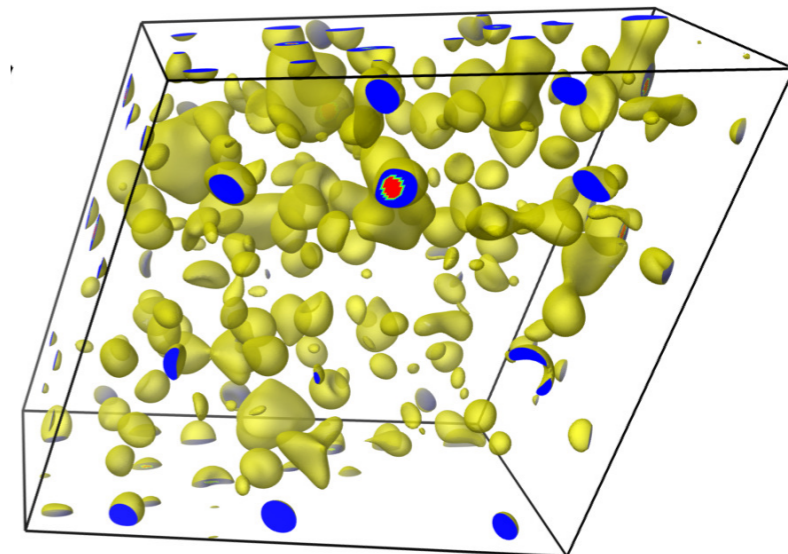
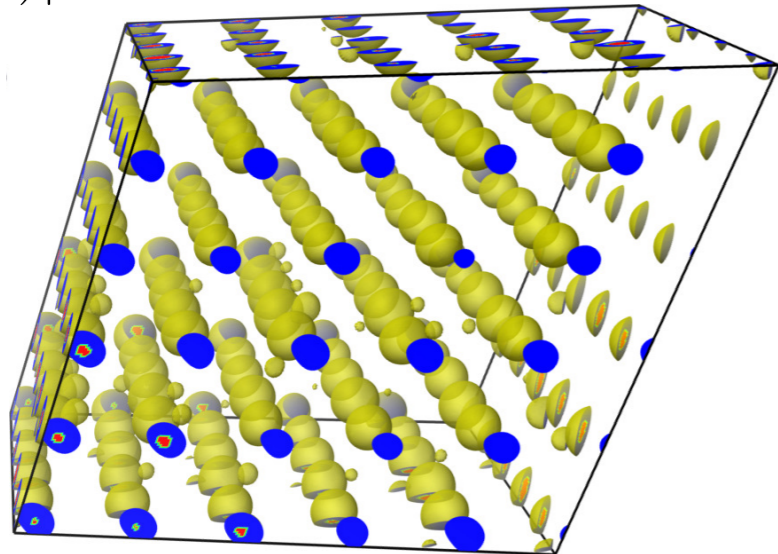


Thermoelectric material: Si_{0.7}Ge_{0.3}



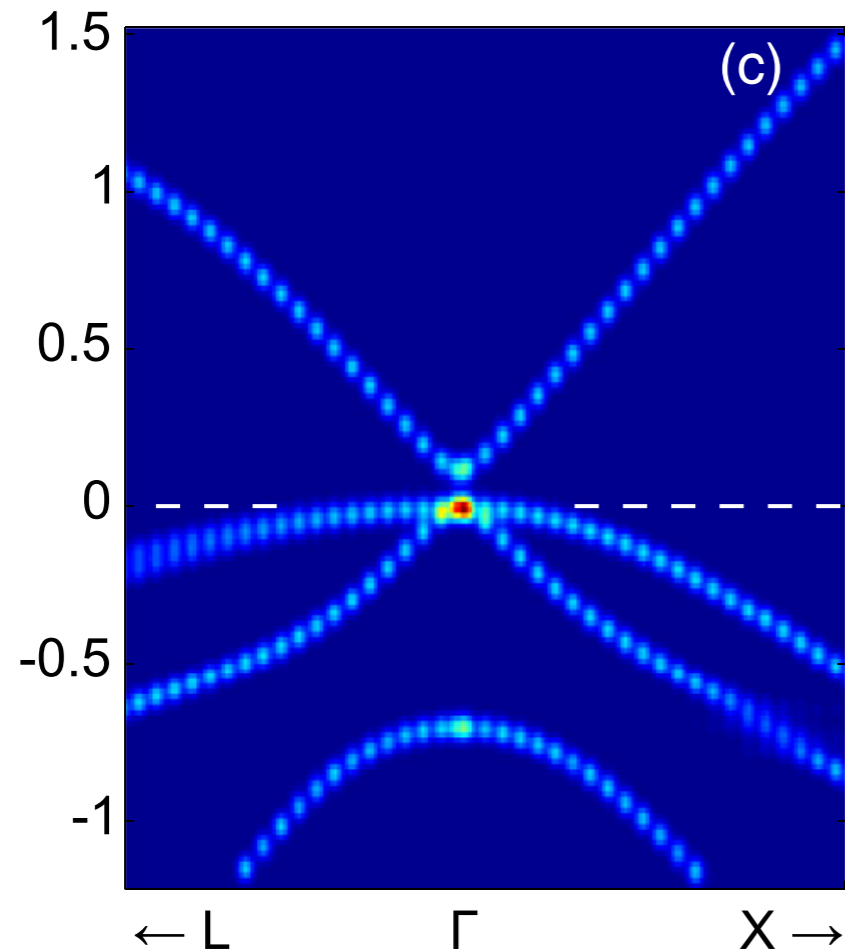
$$\Delta r \Delta k \sim 1$$

$$|\psi(\mathbf{r})|^2$$



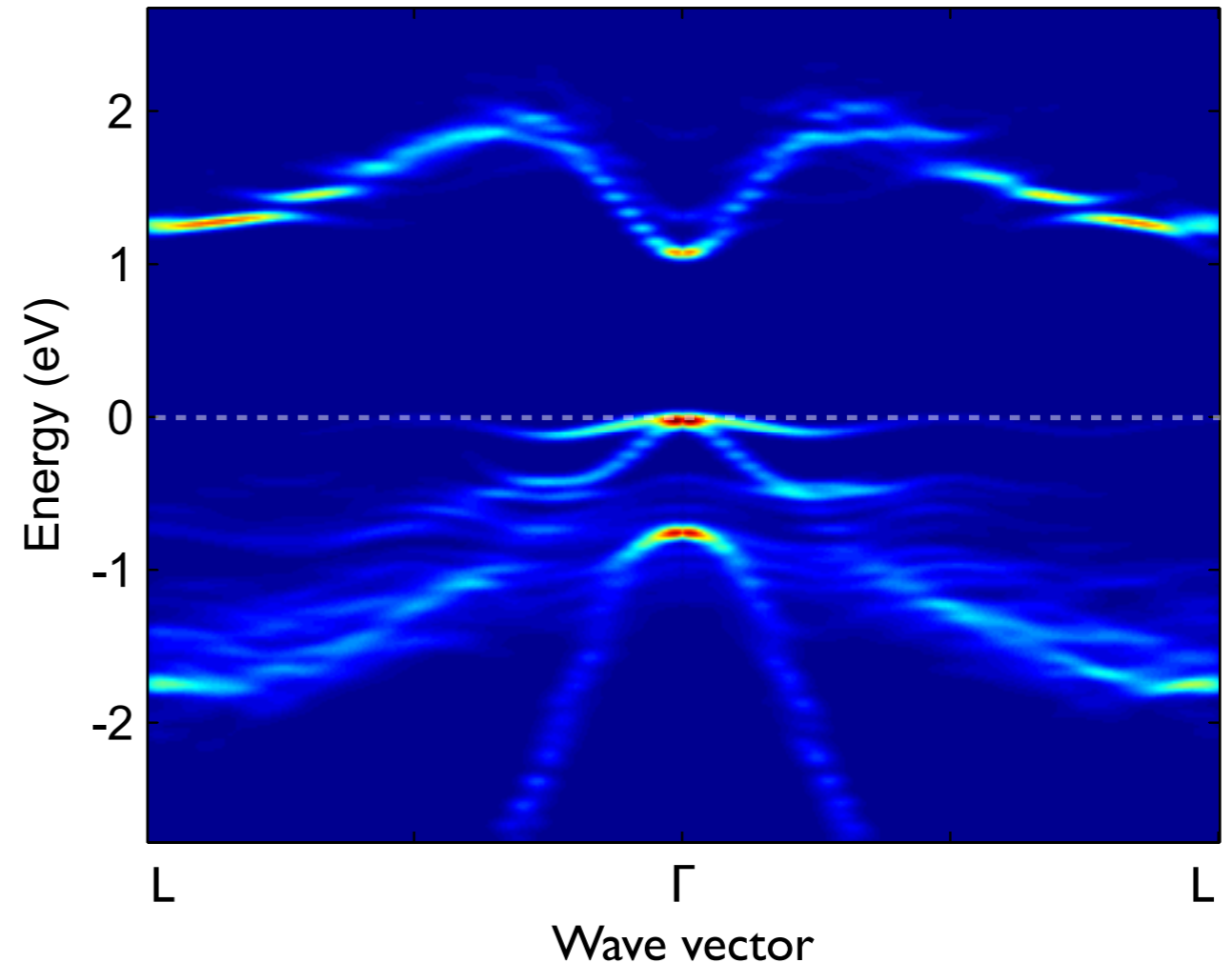
Impact of alloying disorder on charge transport

CdTe \rightarrow (HgCd)Te



$$\mu_e = 1,100 \rightarrow 1,000,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

GaAs \rightarrow Ga(AsBi)



$$\mu_h = 200 \rightarrow 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

$$\mu_e = 4,000 \rightarrow 2,500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

Acknowledgement

BerryPI contributors:

- Jon Kivinen
- Sheikh J.Ahmed
- Ben Zaporzhan
- Sam Pichardo
- Laura Curiel
- David Hassan
- Victor Xiao

WIEN2WANNIER:

- Elias Assmann
- Jan Kunes
- Philipp Wissgott

fold2Bloch:

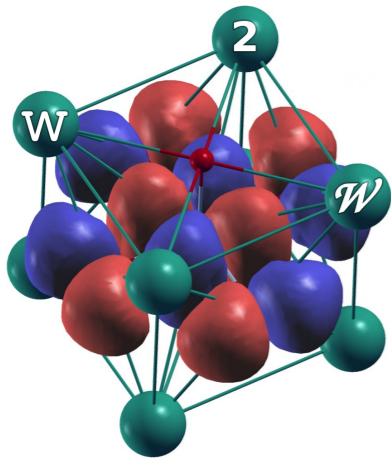
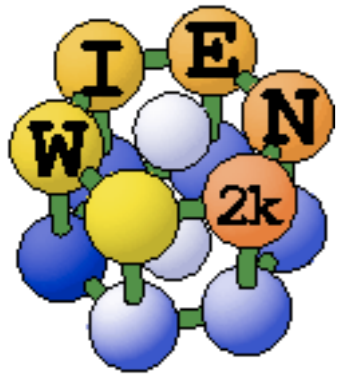
- Anton Bokhanchuk
- Derek Nievchas
- Elias Assmann
- Sheikh J.Ahmed



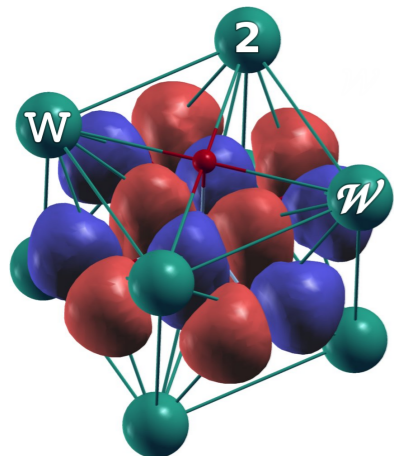


Spare slides

Wannier functions: 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: matrix elements

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

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

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

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

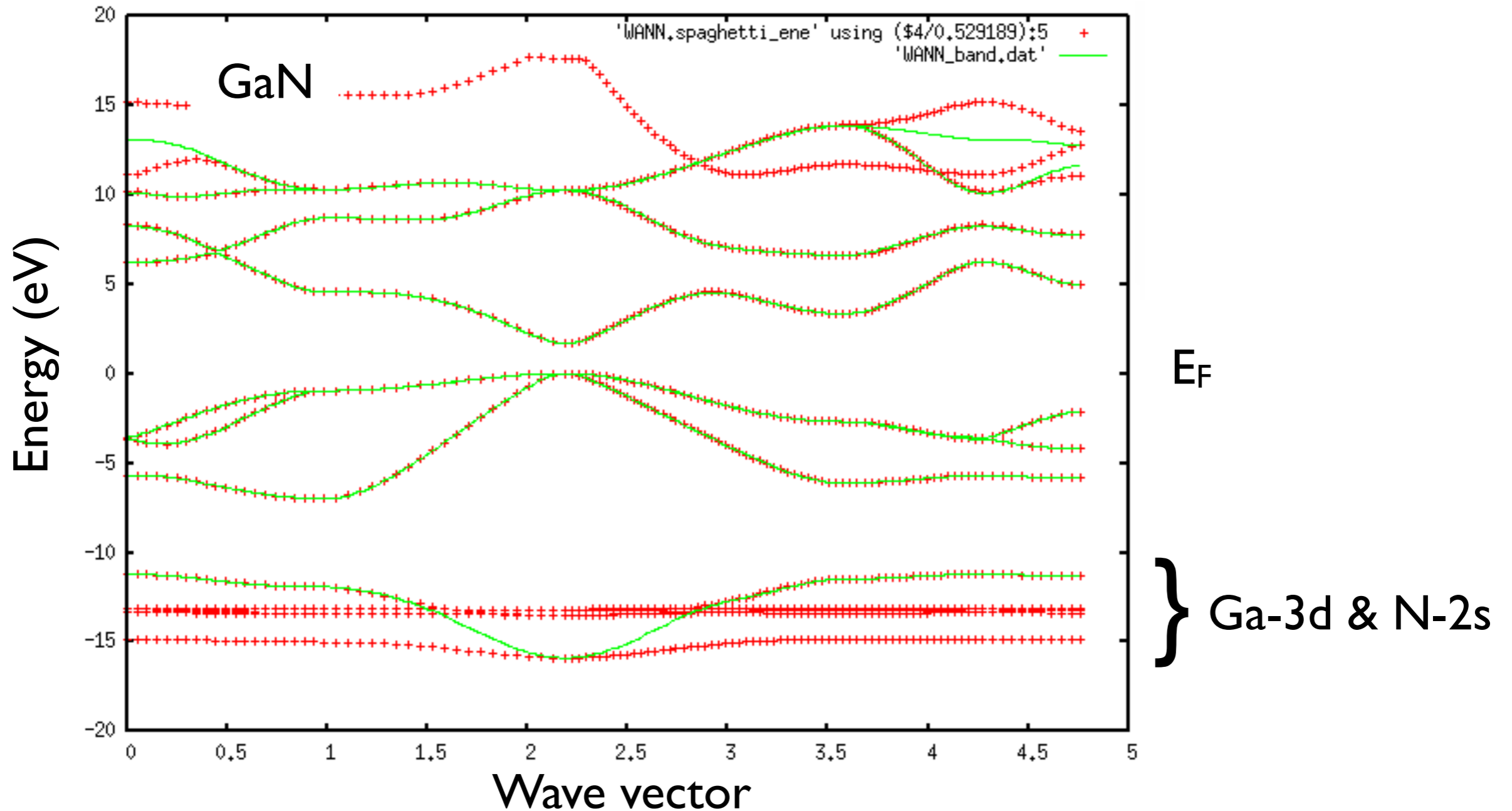
$$\langle 0n | \mathbf{r} | 0n \rangle = i \frac{V}{(2\pi)^3} \int d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle \quad \text{related to Berry phase, electronic polarization}$$

Discretization:

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

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

Wannier functions: disentanglement



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

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

Wannier functions: 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: Berry phase

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

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

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

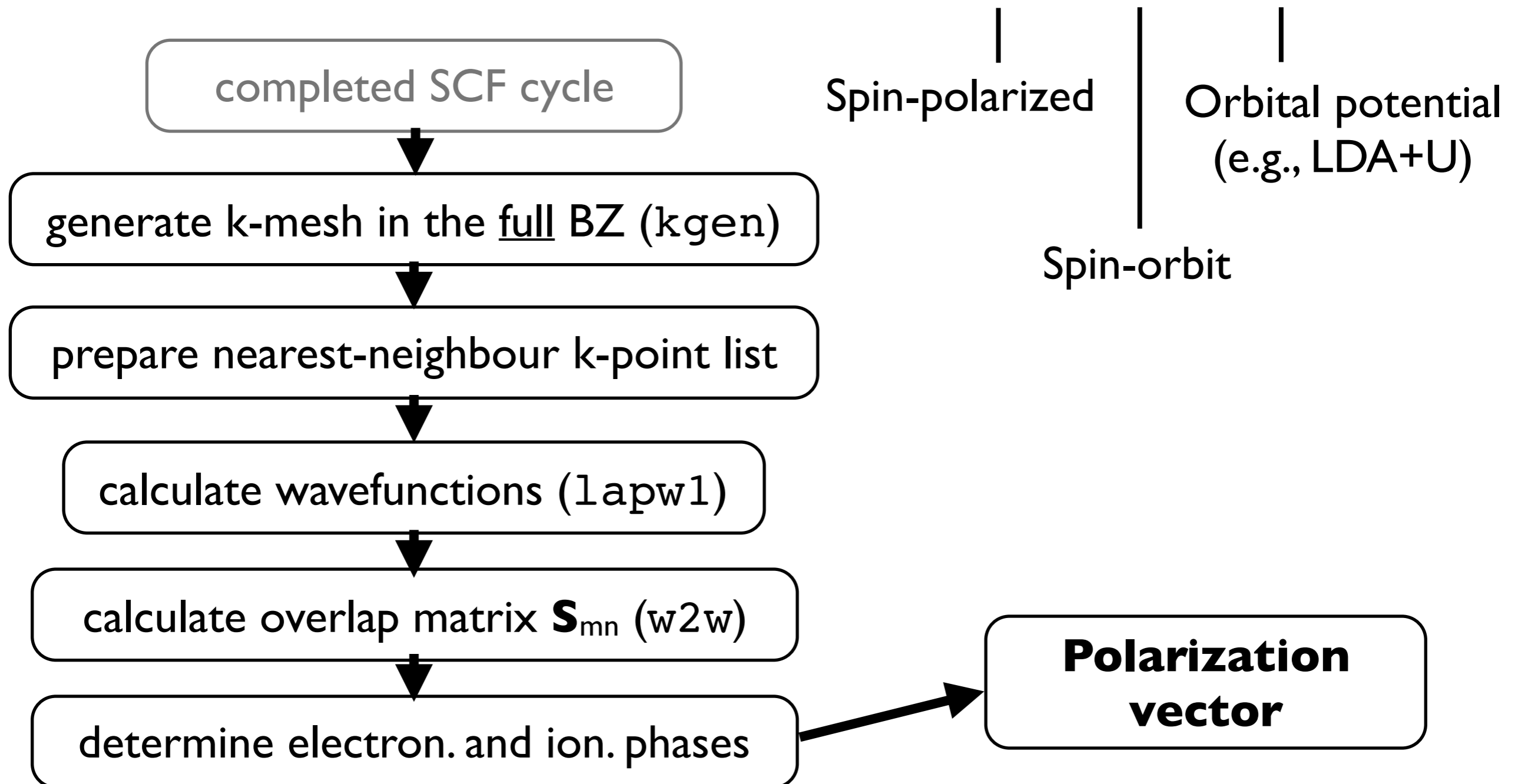
$$\varphi_{\text{el},\alpha} = S_{\perp}^{-1} \int_{S_{\perp}} dS_{\perp} \varphi(\mathbf{k}_{\parallel})$$

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

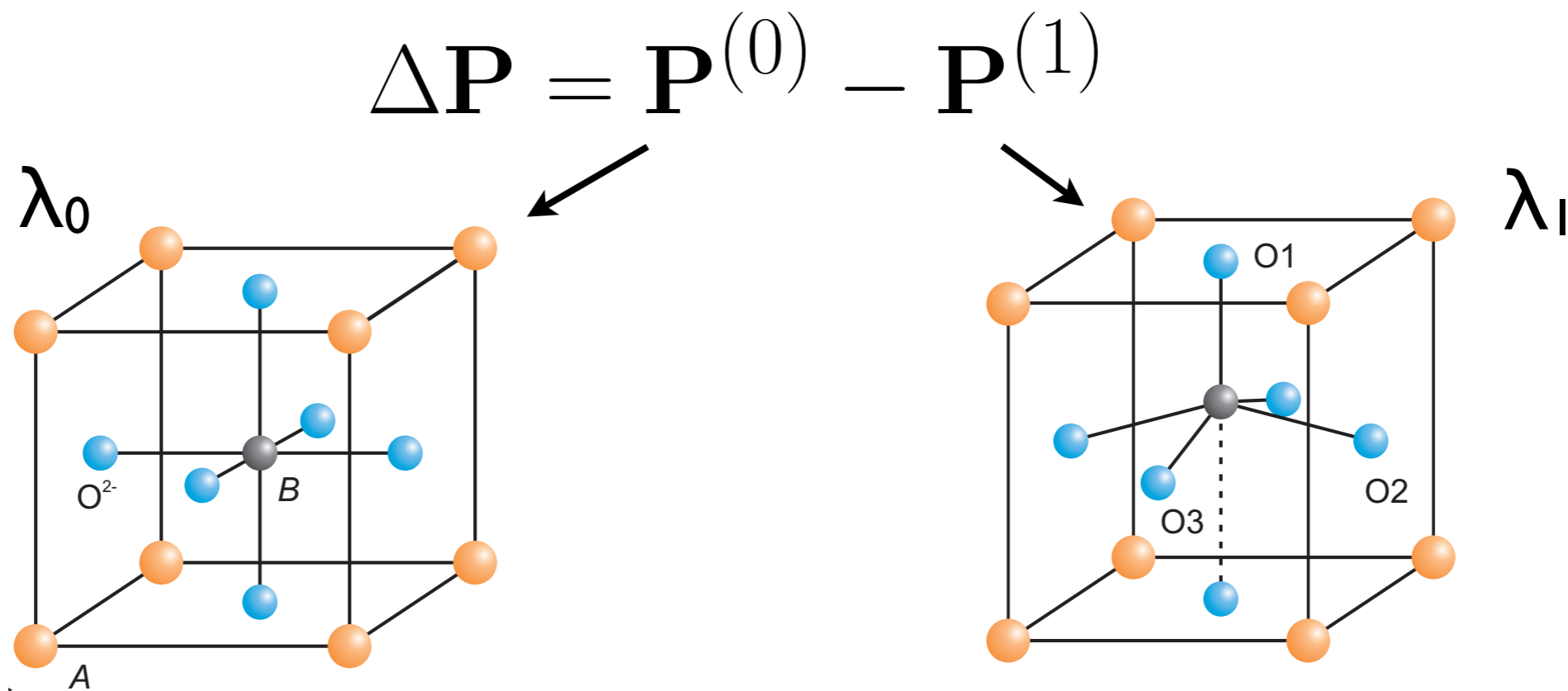
Macroscopic polarization: BerryPI workflow

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

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

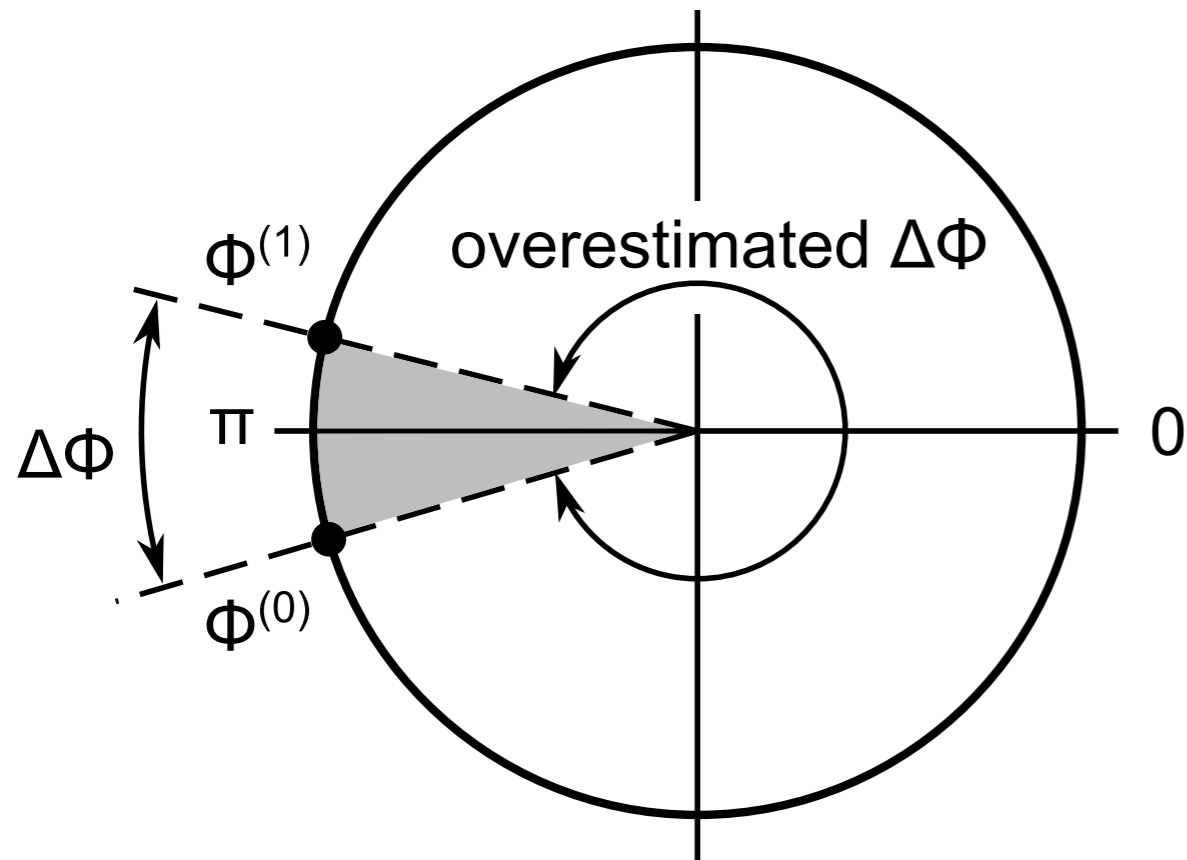


Macroscopic polarization: Choice of a reference structure



- 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

Macroscopic polarization: uncertainties



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

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

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

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

Macroscopic polarization: GaN Born eff. charge

GaN z^* calculation

$$\Phi_{el}(0) = -0.1538 \quad \phi_{ion}(0) = -1.5079$$

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

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

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

$$\begin{aligned} \Delta\Phi(0 \rightarrow 1) &= -1.6960 + 1.6618 \\ &= -0.0342 \end{aligned}$$

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

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

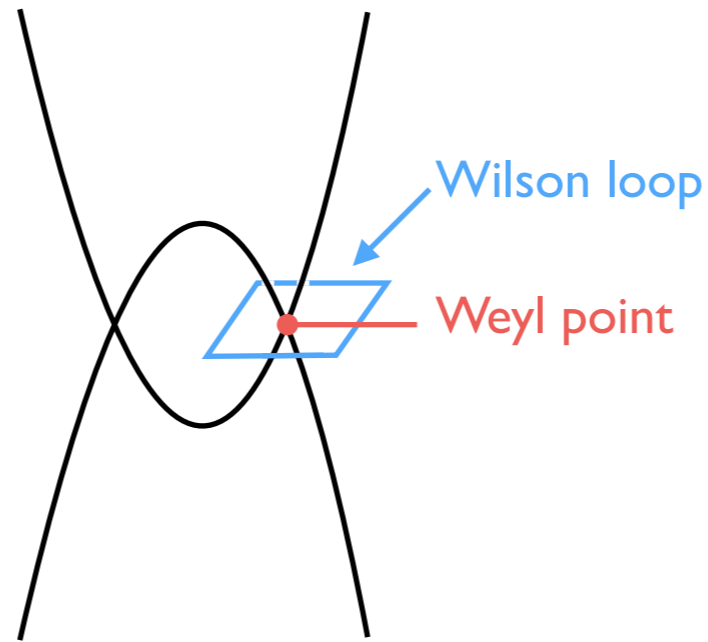
$$= -2.72$$

λ_1

Berry phase: 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)

Berry phase: Weyl point charge



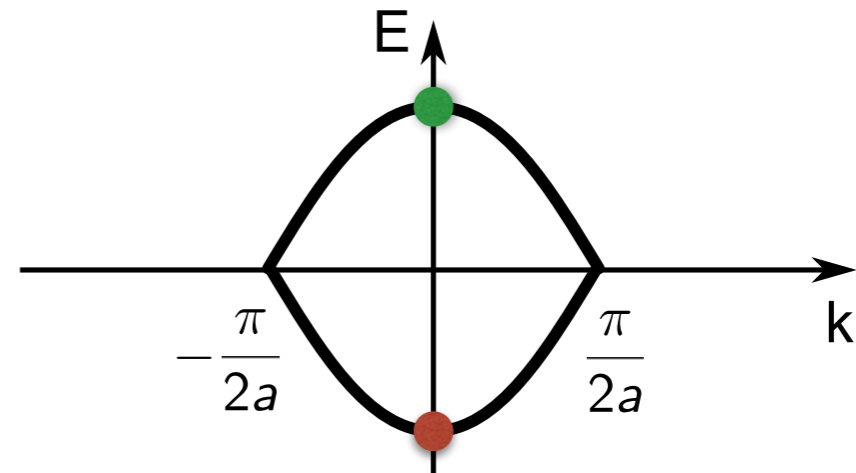
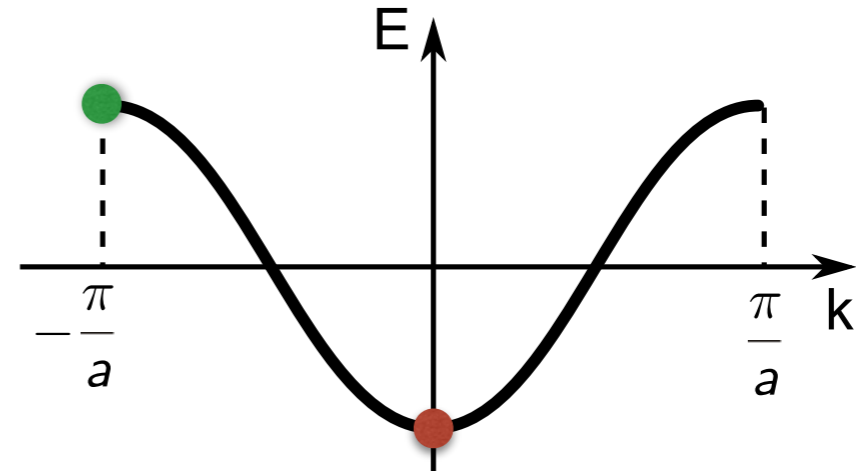
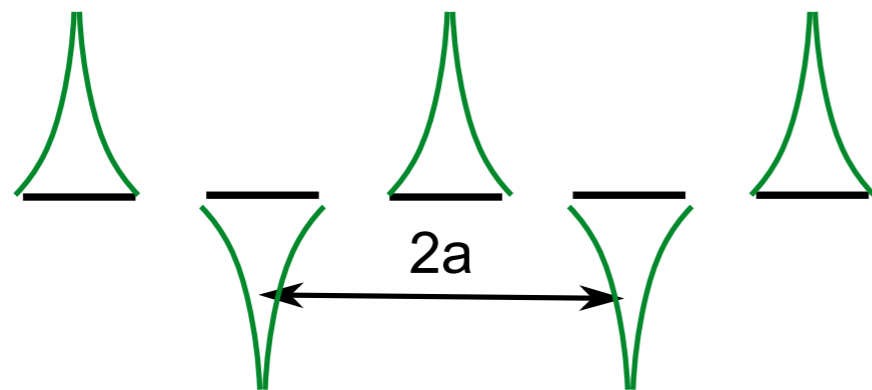
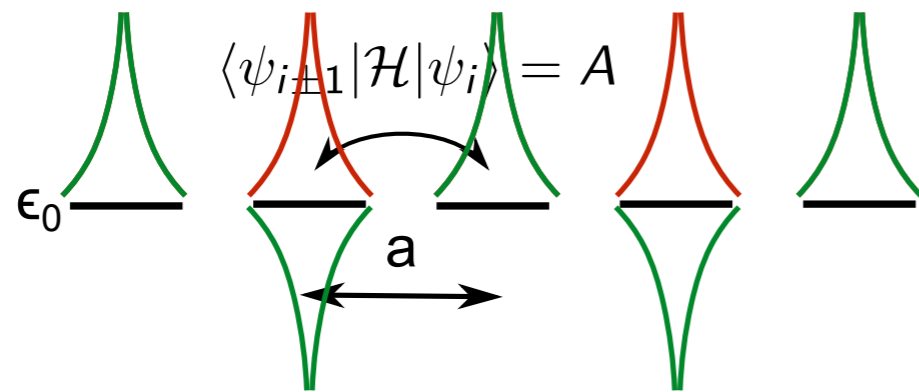
Need `case.klist` with k-points on the Wilson loop

```
[command line]$ berrypi -j -w -b 1:XX
```

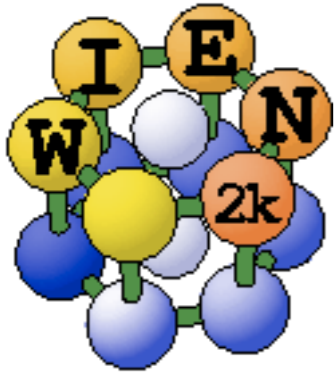


Band range (occupied only)

Effective band structure: Zone folding



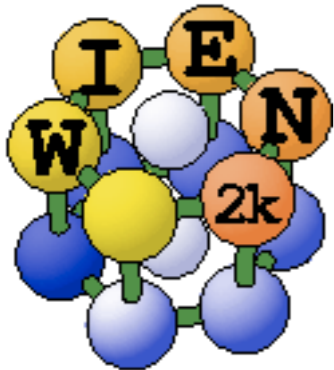
Effective band structure: Workflow



- Construct primitive unit cell
- Make supercell (`supercell`)
- Run SCF calculation

XCRYSDEN

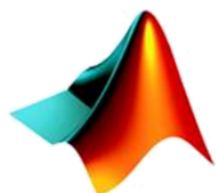
- Create k-path (`case.klist_band` file)



- Compute wave functions (`case.vector[so]` file) for the selected k-path:
 - `x lapw1 [-p]`
 - `x lapwso [-p]` (in the case of spin-orbit coupling)

fold2Bloch

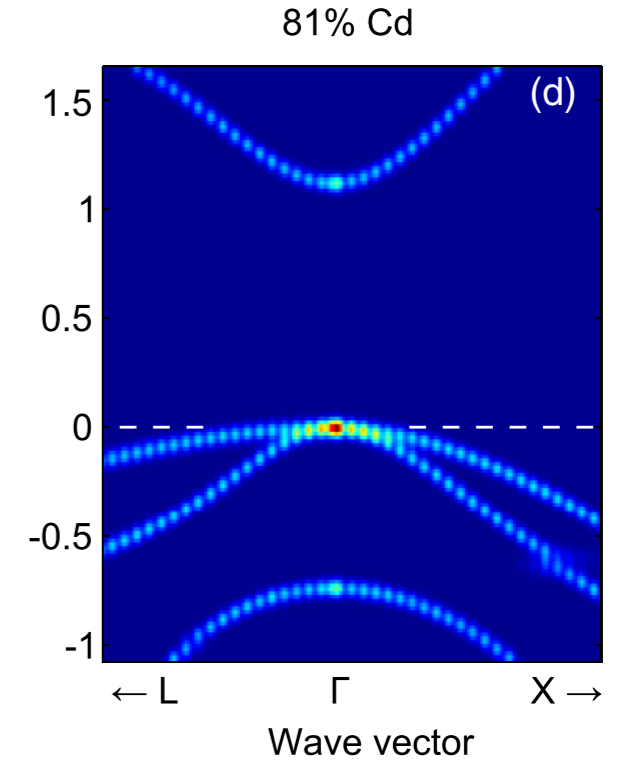
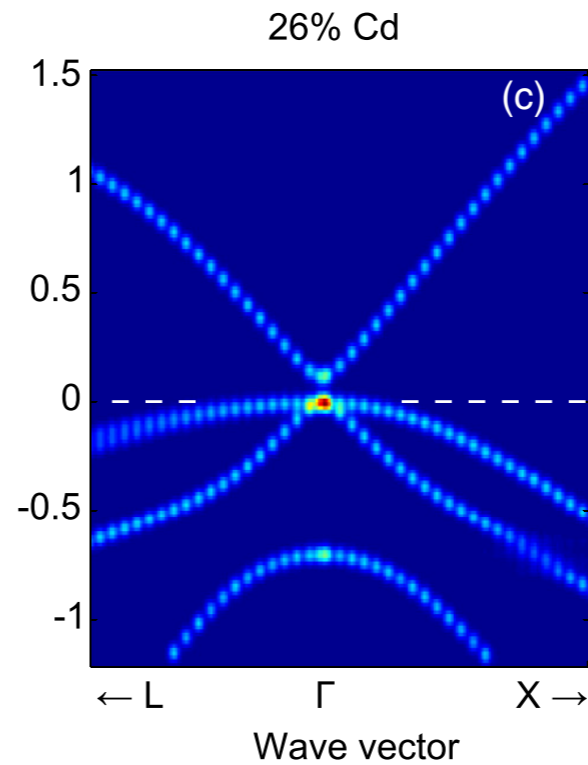
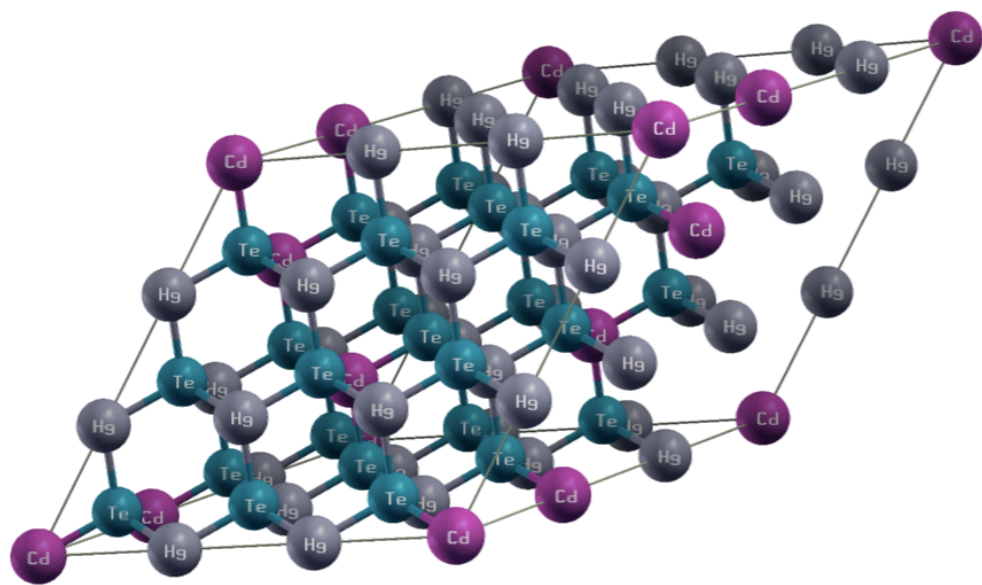
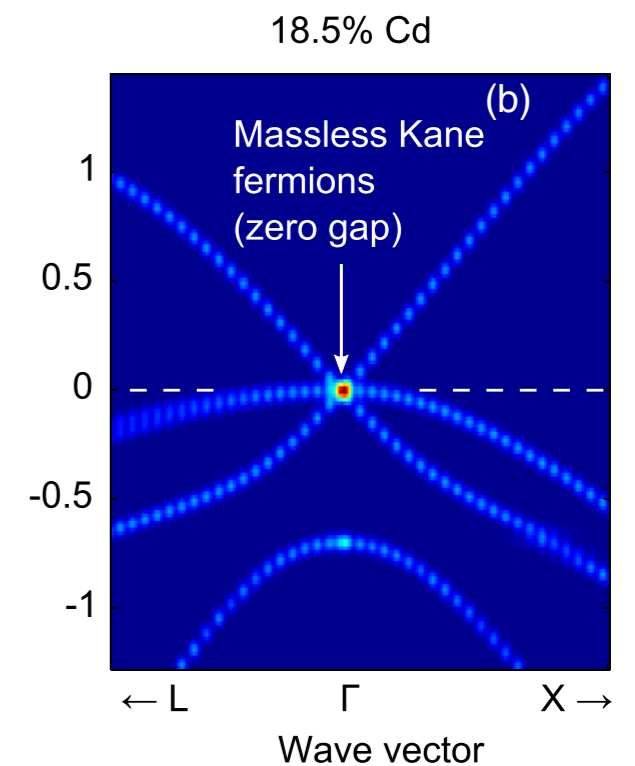
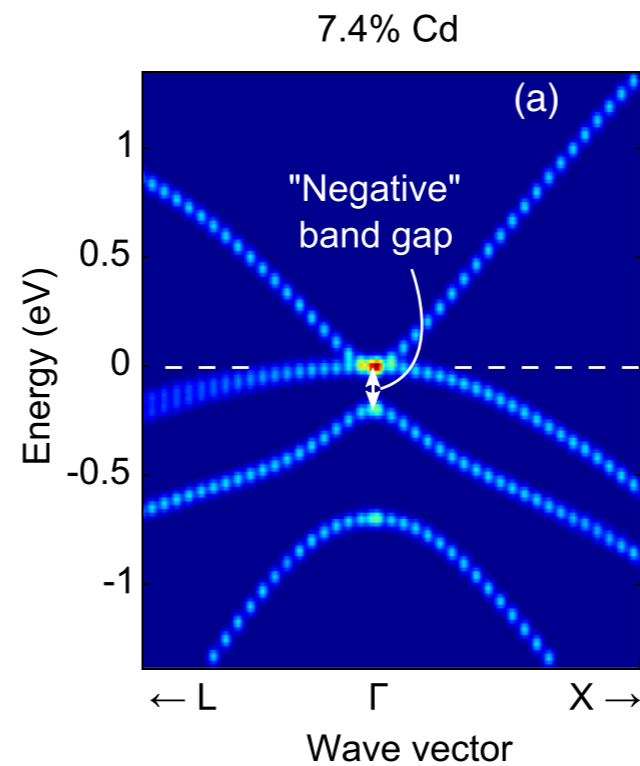
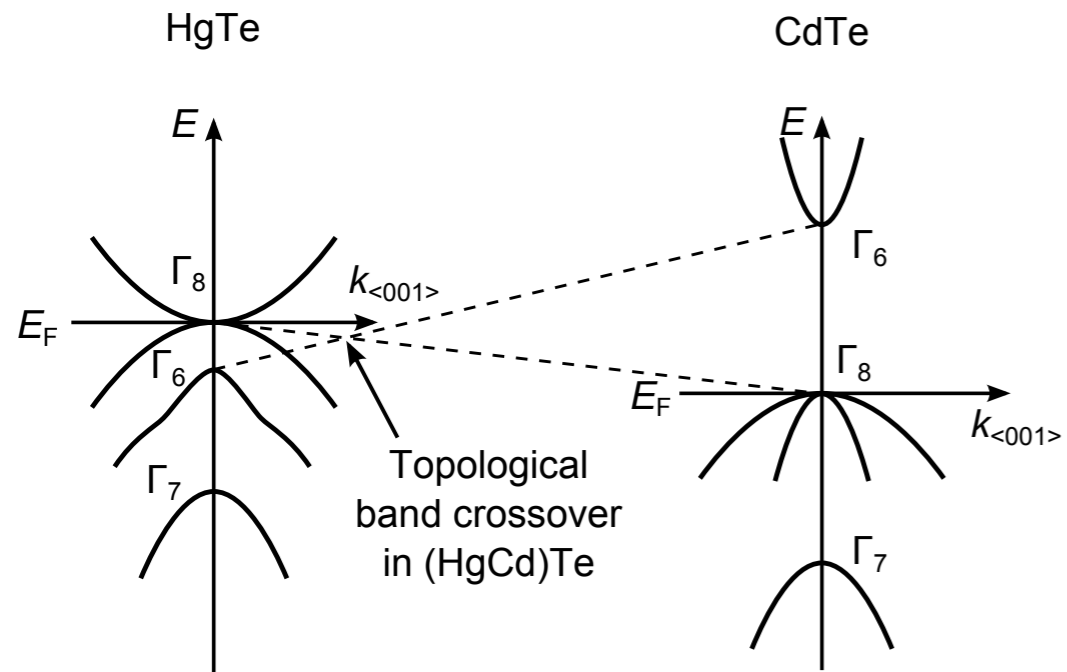
- Unfold band structure (`fold2Bloch`)



MATLAB

- Plot effective band structure (`ubs_dots*.m`)

Effective band structure: (Hg,Cd)Te band structure evolution



Effective band structure: Useful resources

- V. Popescu and A. Zunger, Phys. Rev. Lett. **104**, 236403 (2010).
- O. Rubel, A. Bokhanchuk, S. J. Ahmed, and E. Assmann
“Unfolding the band structure of disordered solids:
from bound states to high-mobility Kane fermions”
Phys. Rev. B **90**, 115202 (2014)
- fold2Bloch home and **tutorials**:
<https://github.com/rubel75/fold2Bloch>