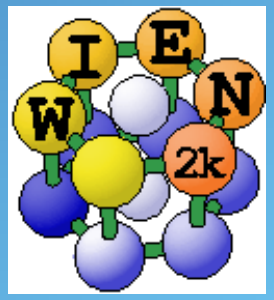
Wannier functions

Macroscopic polarization (Berry phase) and related properties

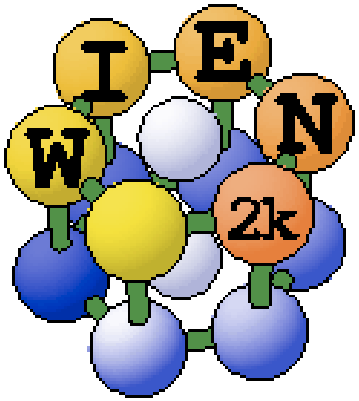
Effective band structure of alloys

P.Blaha
(from Oleg Rubel, McMaster Univ, Canada)



McMaster University

Wannier functions



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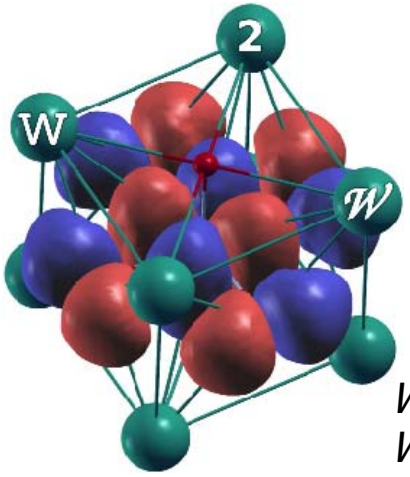


+

WANNIER90

Wannier90: A Tool for Obtaining Maximally-Localised Wannier Functions
A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt and N. Marzari
Comput. Phys. Commun. **178**, 685 (2008)
[http://wannier.org]

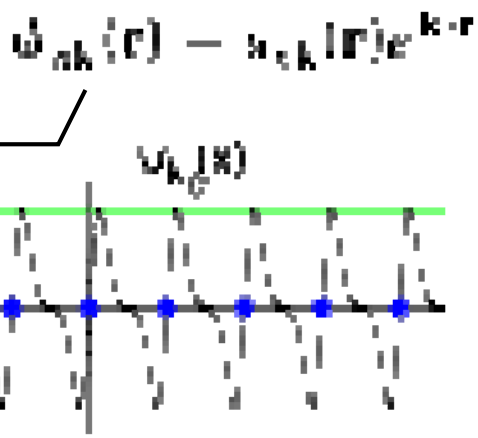
Bloch *vs* Wannier functions

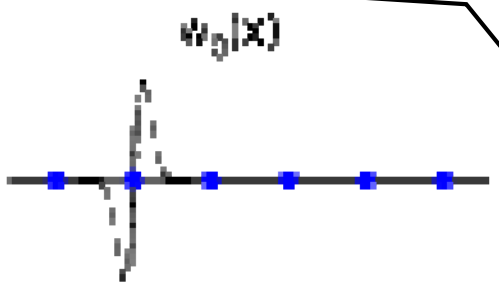
Bloch functions

Wannier functions (localized orbitals

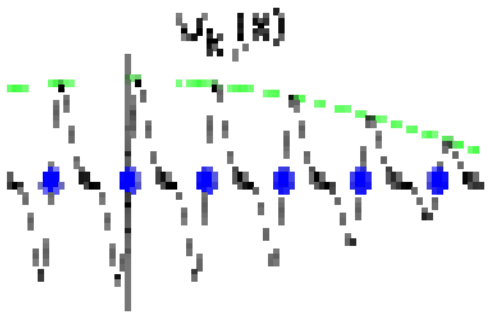
Indexed by the wave vector

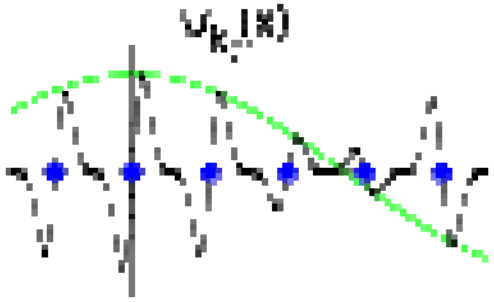
Γ-point

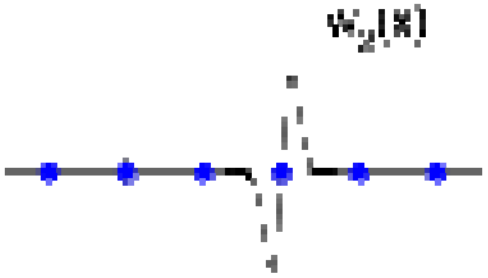




Indexed by the lattice vector in real space







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

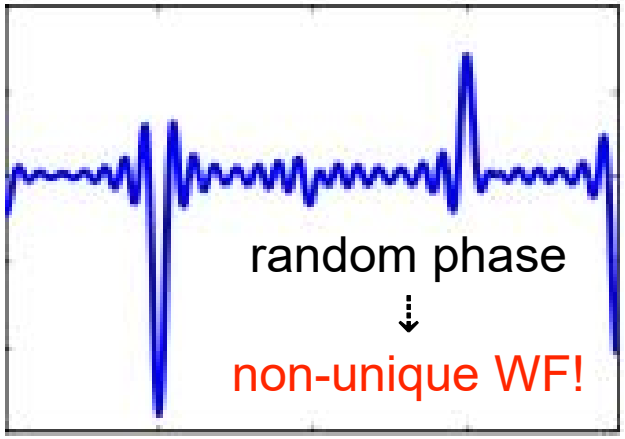
Both sets: complete and orthonormal

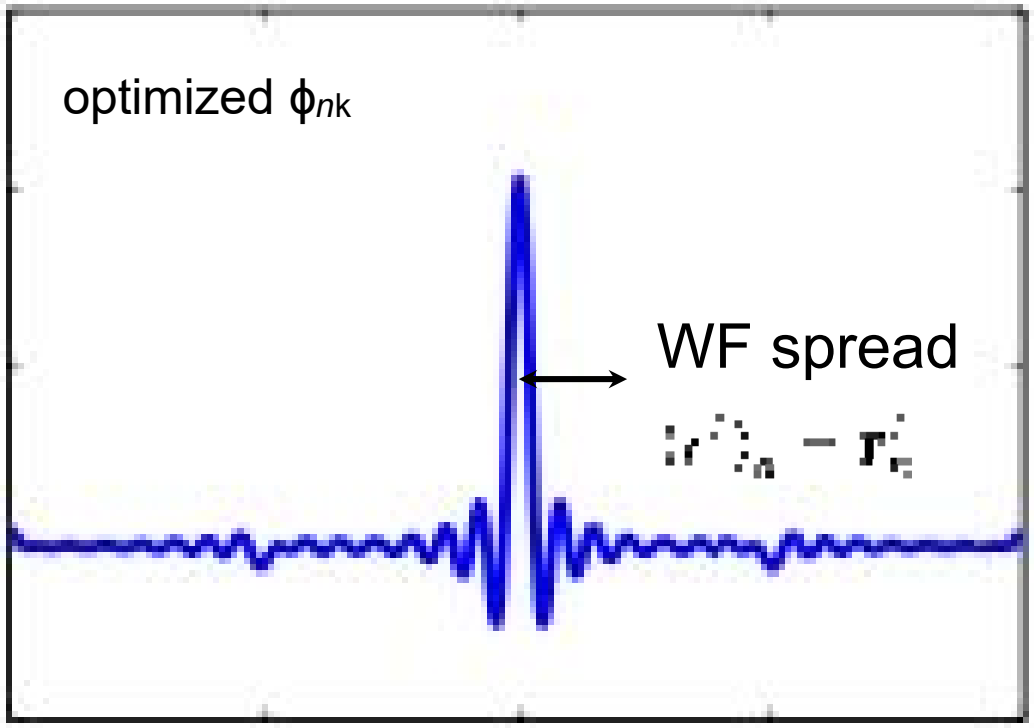
Max. localized Wannier functions (MLWF)

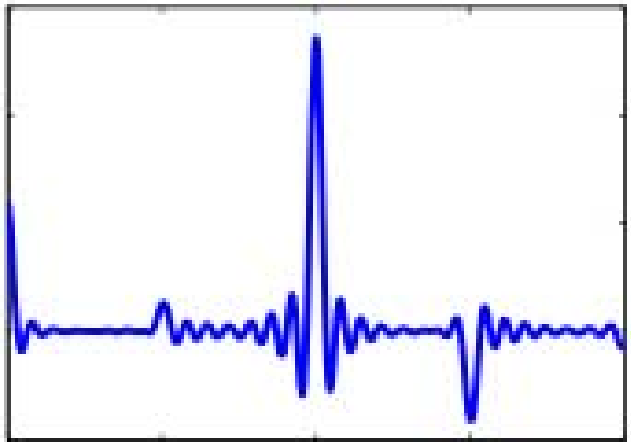
Bloch functions (more precisely):

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

gauge freedom → ambiguity





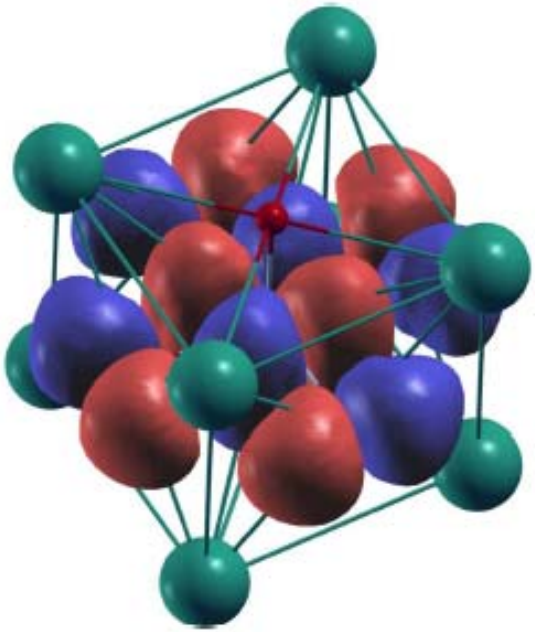


$$|w\,n\boldsymbol{R}\rangle = \frac{V}{(2\pi)} \int_{BZ} d\boldsymbol{k} \sum_m e^{i\boldsymbol{k}\boldsymbol{R}}\, U_{mn}(\boldsymbol{k})\, |\psi\, m\boldsymbol{k}\rangle$$

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

choose U(k) to minimize spread Ω

maximally localized wannier functions



- choose $U(\boldsymbol{k})$ to minimize spread $\rightsquigarrow$ MLWF
- total spread $\Omega = \Omega_I + \tilde{\Omega}$ can be split into gauge-invariant part and rest

$\rightsquigarrow$ minimize $\tilde{\Omega}$

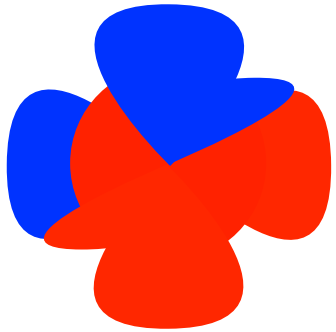
- `wannier90` computes $U(\boldsymbol{k})$ in this way

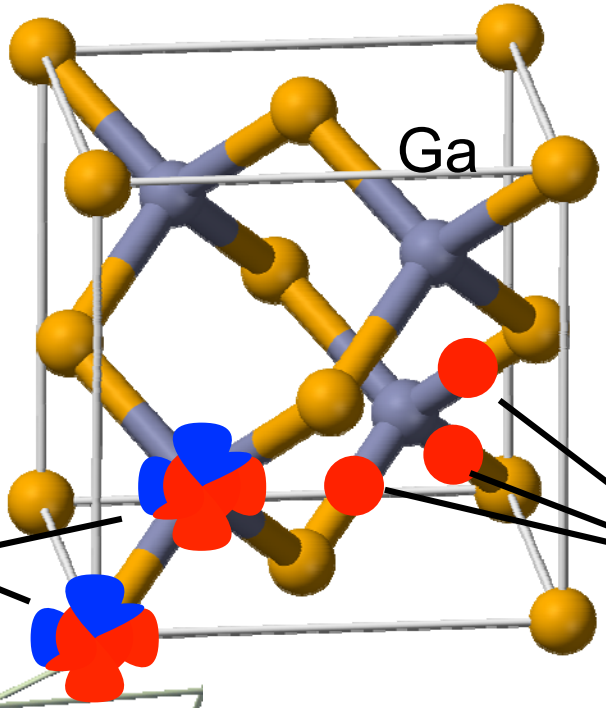
[Marzari *et al.*, Rev. Mod. Phys. 84, 1419 (2012)]
`http://wannier.org`

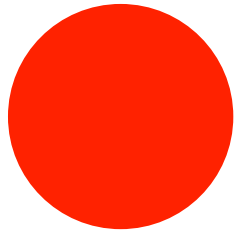
- `wien2wannier` provides interface to Wien2k

[Kuneš, Wissgott *et al.*, Comp. Phys. Commun. 181, 1888]

Two flavours of Wannier functions

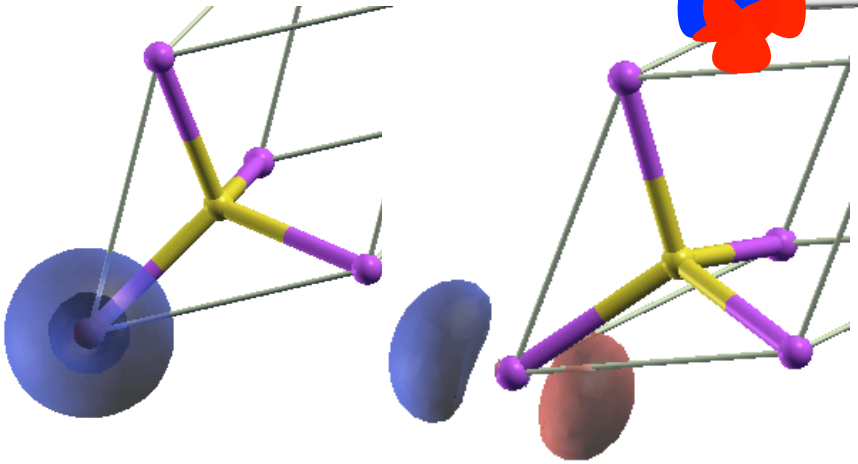






Atom centered sp^3-like

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

MLWF: applications

- analysis of chemical bonding

  bonding and *antibonding* states

- electric polarization and orbital magnetization

  BerryPi (O.Rubel et al.)

- Wannier interpolation (eg. Woptic, transport, ...)

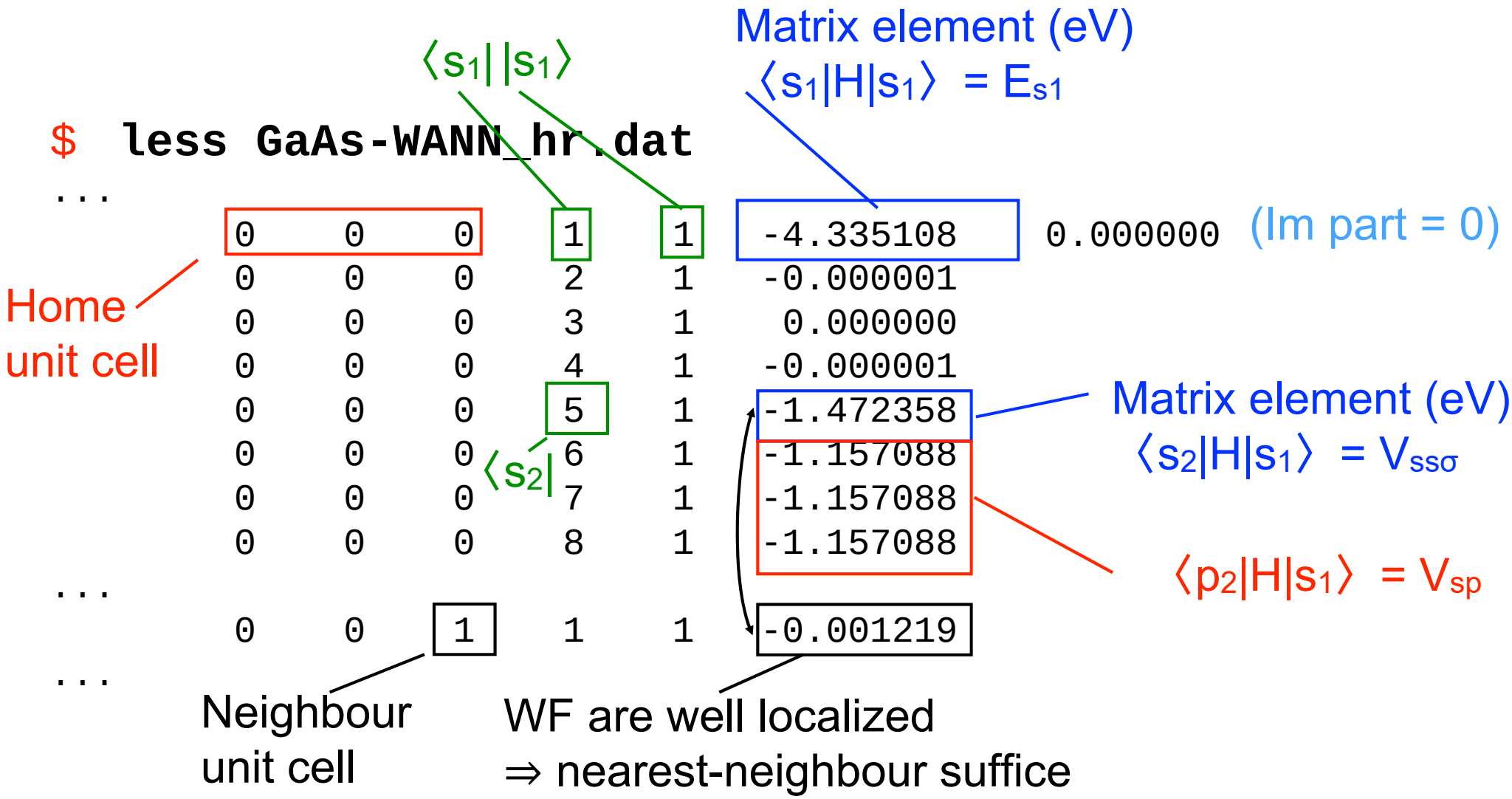
  $H(k)|_K \xrightarrow{F} H(R)|_{K^{-1}} \xrightarrow{F^{-1}} H(k)|_G$

- building effective hamiltonian

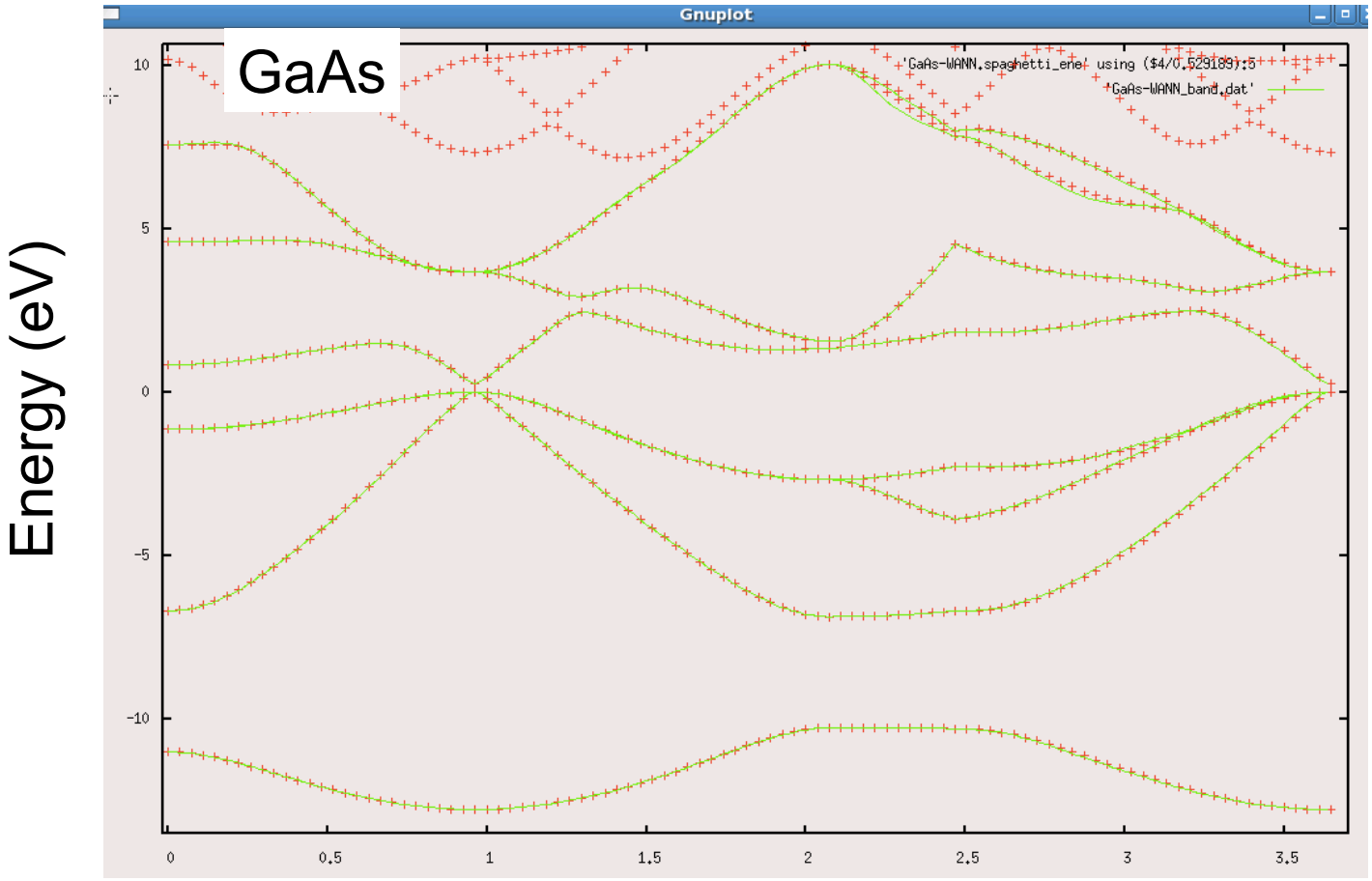
  tight binding parameters

  input for dynamical mean field theory

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



Band structure



Energy (eV)

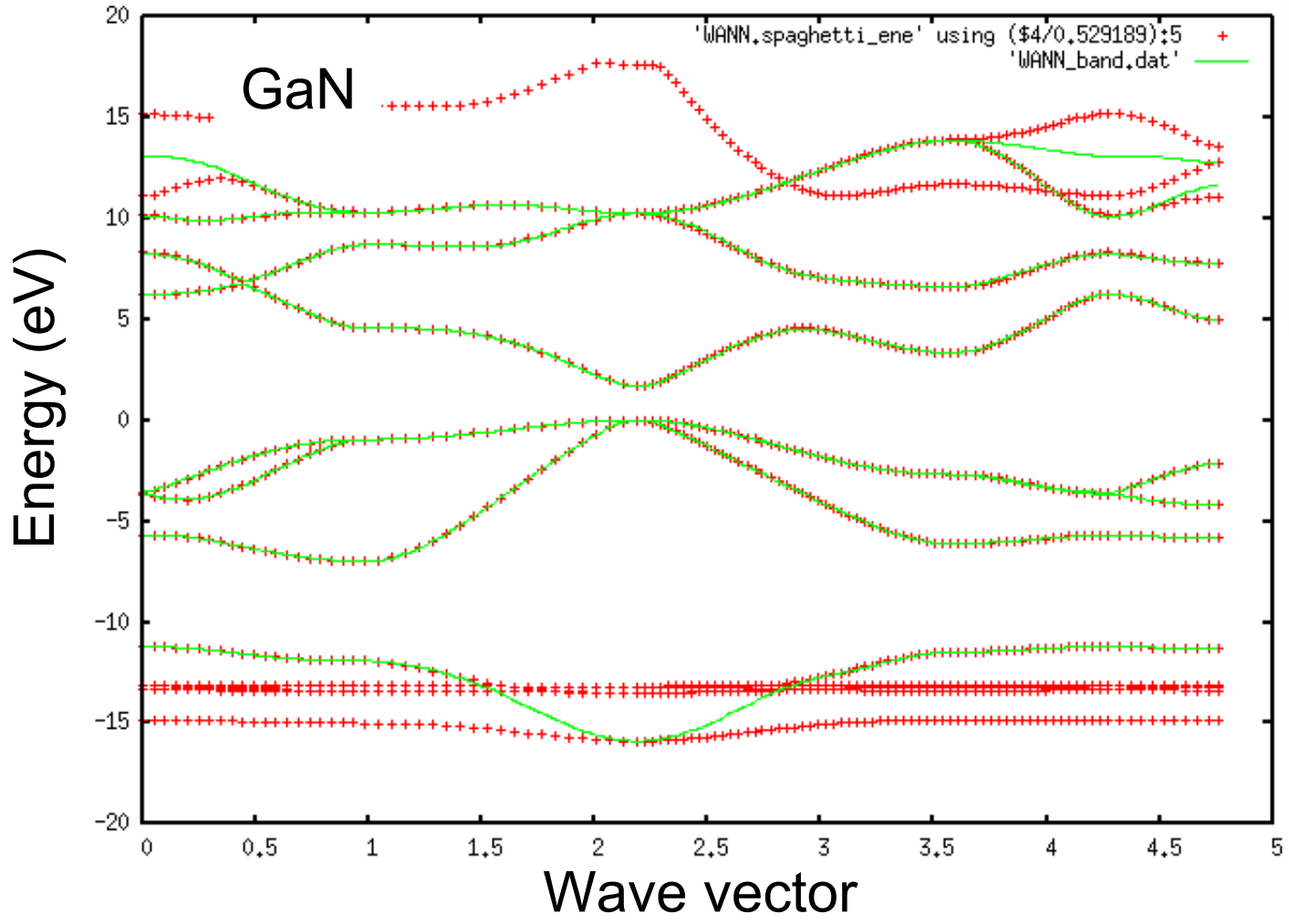
E_F

Wave vector

\+ original Wien2k band structure

\- Band structure computed from Wannier hamiltonian

Disentanglement



E_F

} Ga-3d & N-2s

Wannier functions without Ga-3d

\+ original Wien2k band structure

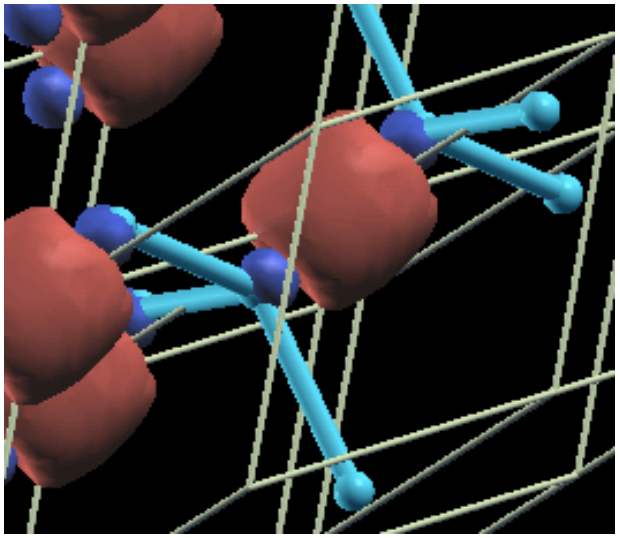
\- Band structure computed from Wannier hamiltonian

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

Relation to polarization (bond centered WF)

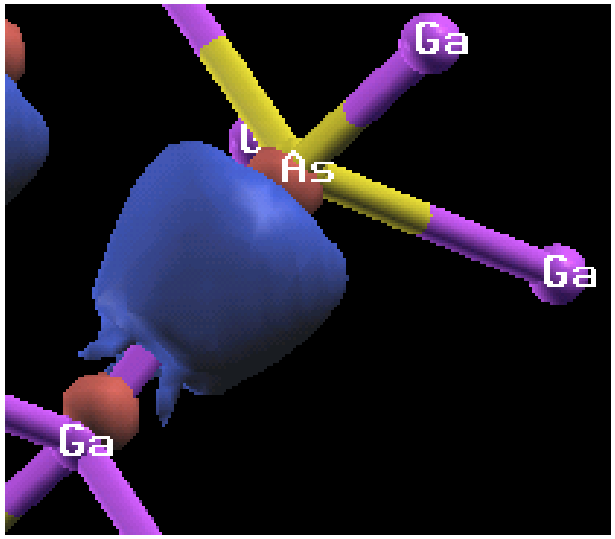
Bond-centered WF

Si



symmetric
(non-polar)

GaAs



non-symmetric
(polar)

$$\mathbf{P} = -\frac{e}{V}\left(\sum_i Z_i \mathbf{r}_i - \sum_n \mathbf{r}_n\right)$$

Ionic part

Electronic part

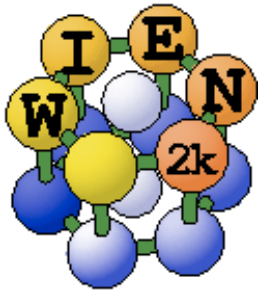
$+ Z_{As}$

$-$ Wannier center q_e

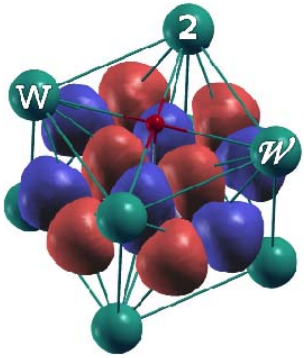
$+ Z_{Ga}$

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

Workflow

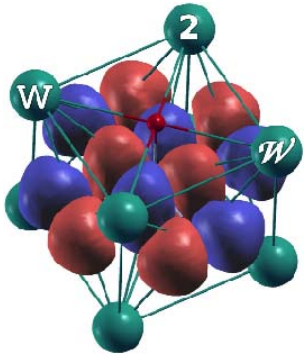


- Regular SCF calculation
- Band structure plot
- Initialize wien2wannier (`init_w2w`):
  - select bands, init. projections, # of WF (`case.inwf` file)
  - projected band structure “bands_plot_project” (`case.win` file)
  - additional options related to entanglement (`case.win` file)
- Compute overlap 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)



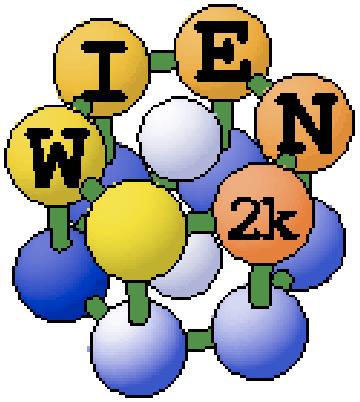
XCrySDen

- 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

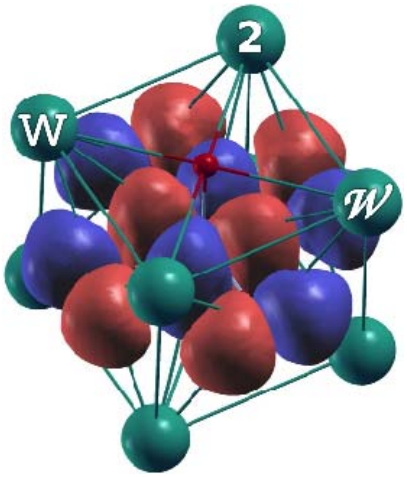
Useful resources

- 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



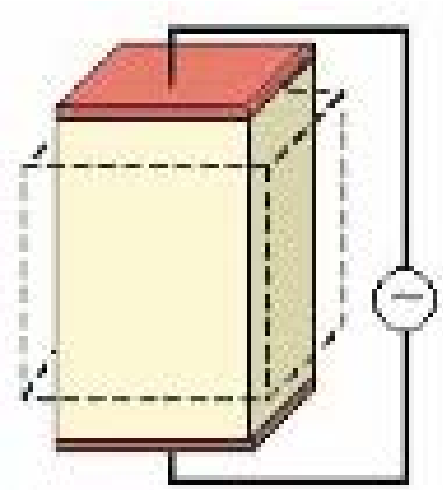
+



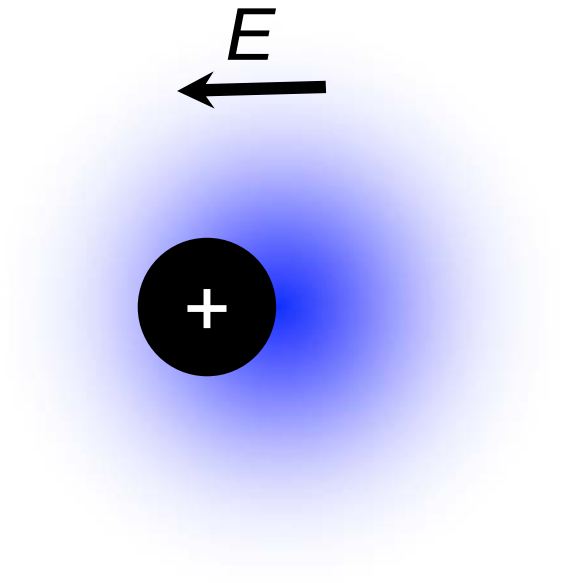
+ BerryPI

Material properties related to polarization

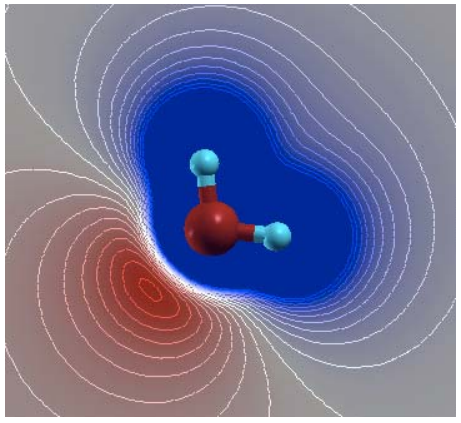
Piezo- and Ferroelectricity



Dielectric screening

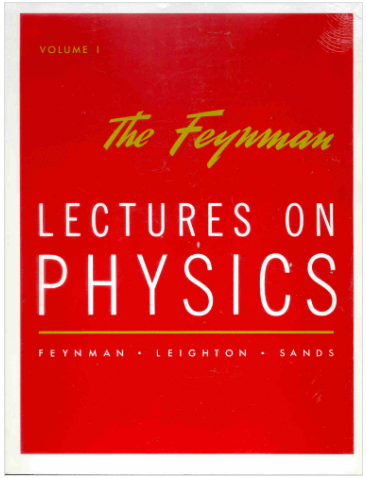


Effective charge

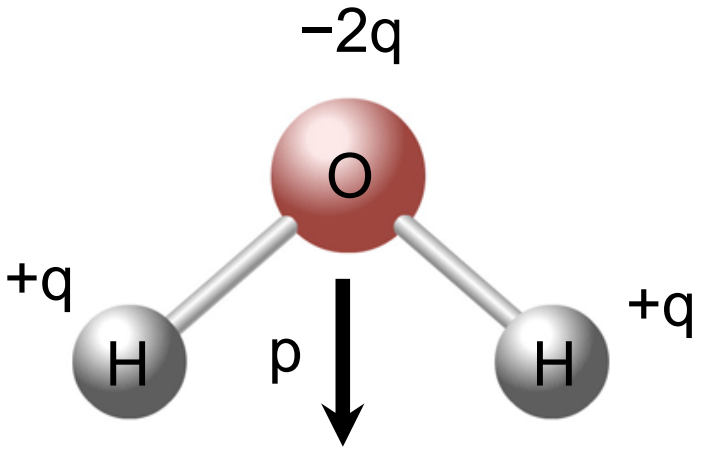


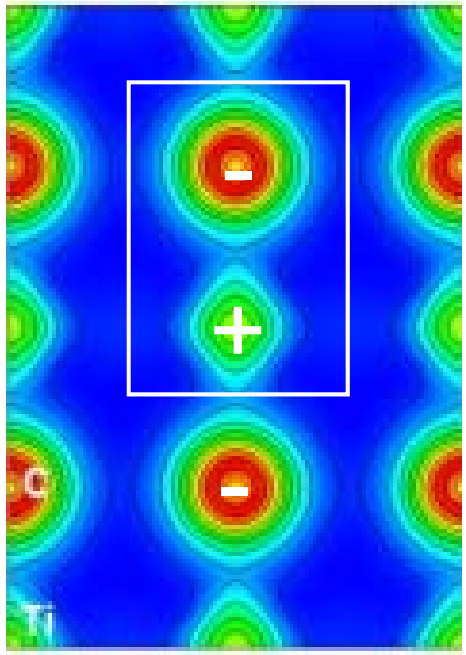
Pyroelectricity

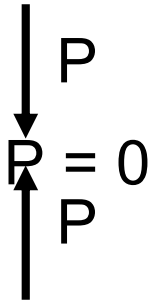
What is polarization?



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







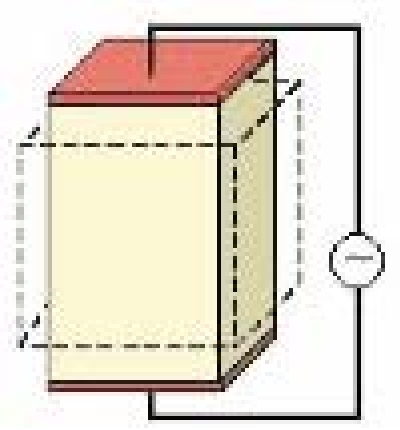
Polarization for periodic solids is undefined

Modern theory of polarization

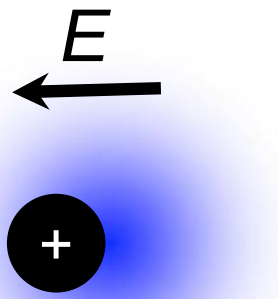
Pioneered by *King-Smith*, *David Vanderbilt* and *Raffaele Resta*

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

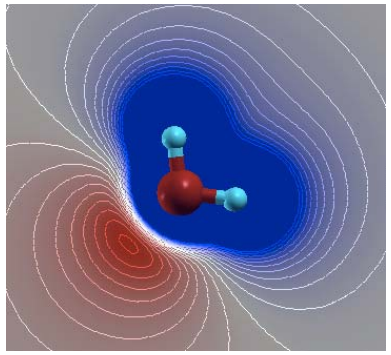
$$\Delta \mathbf{P} = \mathbf{P}^{(0)} \quad \mathbf{P}^{(1)}$$



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



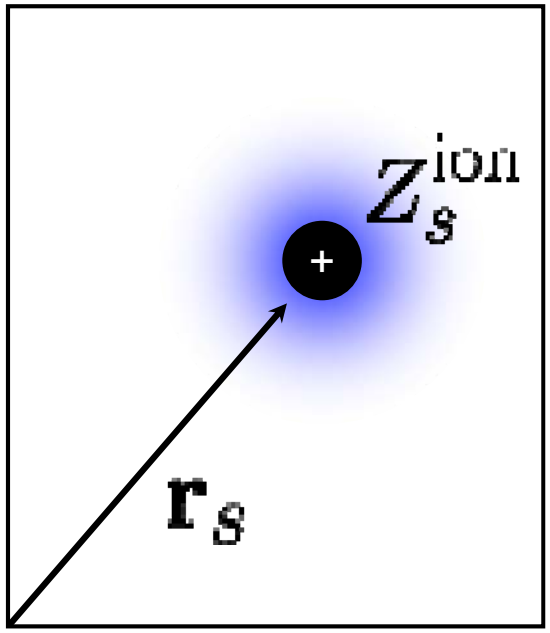
$$\frac{\Delta \mathbf{P}}{\Delta \mathbf{E}}$$



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

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

Components of polarization



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

ionic electronic

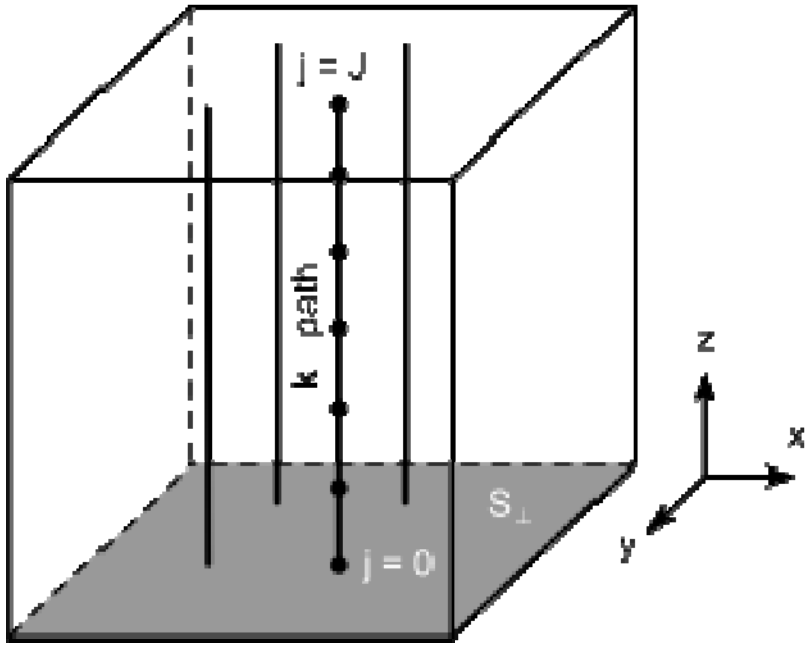
$$\mathbf{P}_{\text{ion}} = \frac{e}{\Omega} \sum_{s}^{\text{atoms}} Z_s^{\text{ion}} \mathbf{r}_s$$

In Wien2k Z_s^{ion} is the core charge

0

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

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



King-Smith and David Vanderbilt, Phys. Rev. B 47, 1651 (199

Berry phase

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

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

WIEN2WANNIER

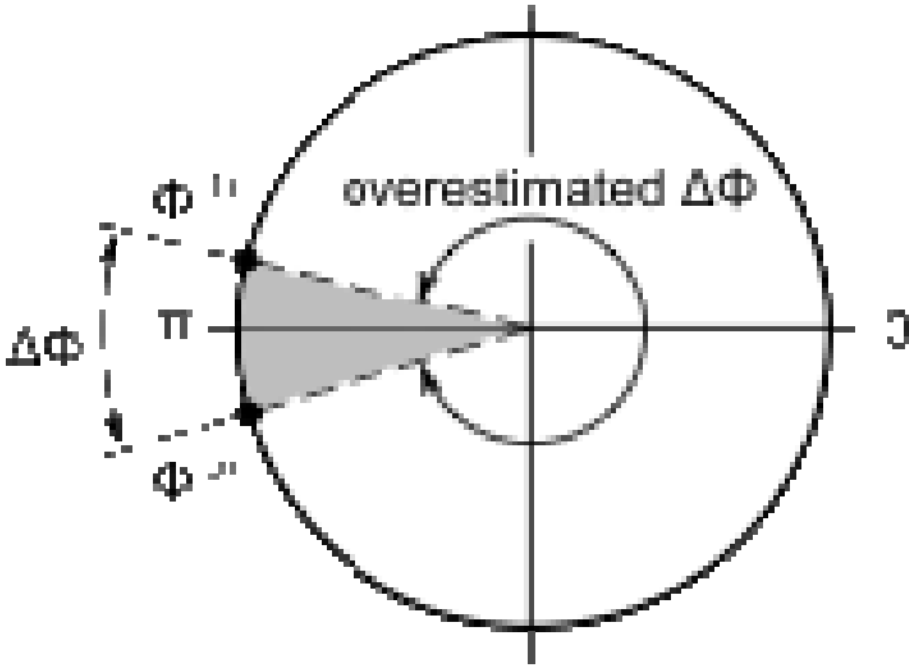
$$\varphi(\mathbf{k}_\parallel) = 2\,\mathrm{Im}\left[\ln \prod_{j=0}^{J-1} \det \mathbf{S}_{M\times M}(\mathbf{k}_j, \mathbf{k}_{j+1})\right]$$

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

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

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

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

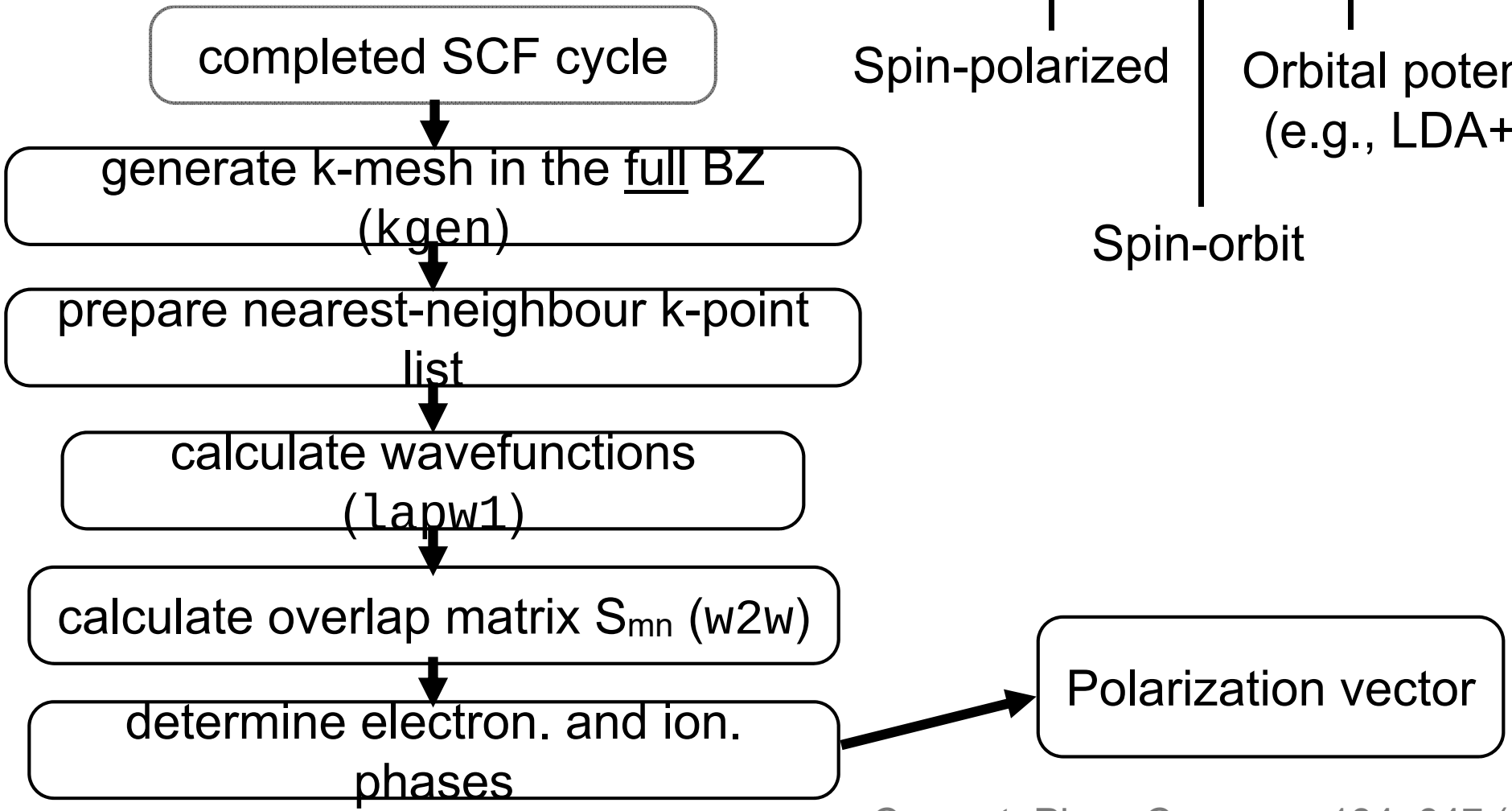
Solution: $\lambda_0 \Rightarrow \lambda_{1/2} \Rightarrow \lambda_1$

BerryPI workflow

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

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

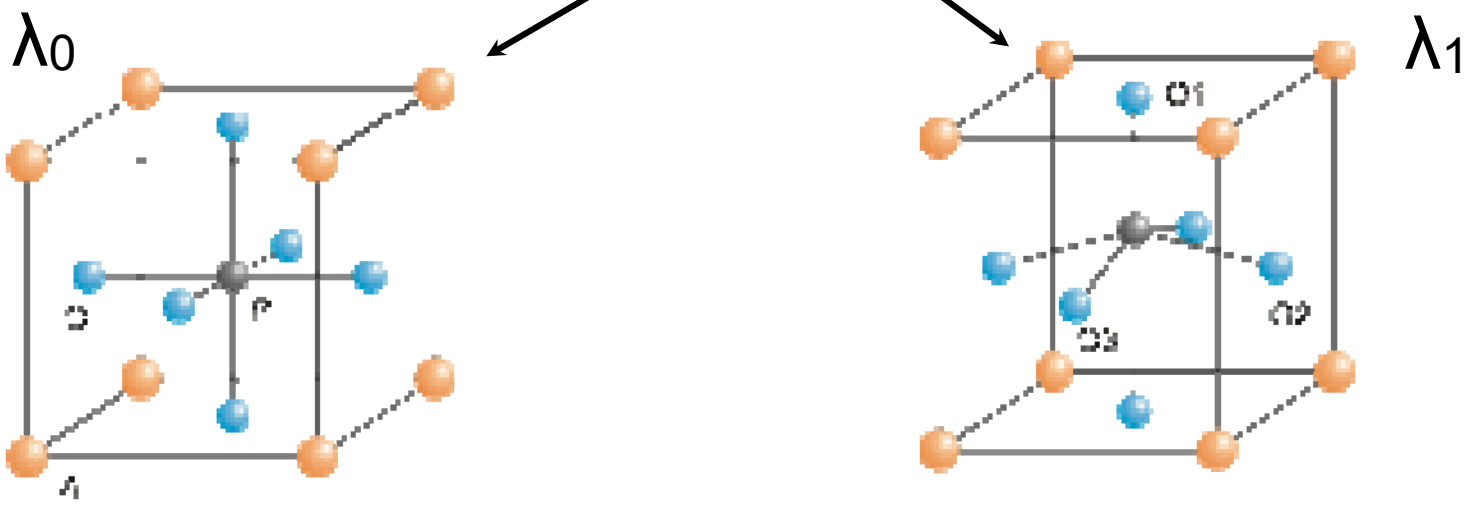
- `-s`: Spin-polarized
- `-j`: Spin-orbit
- `-o`: Orbital potential (e.g., LDA+U)



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

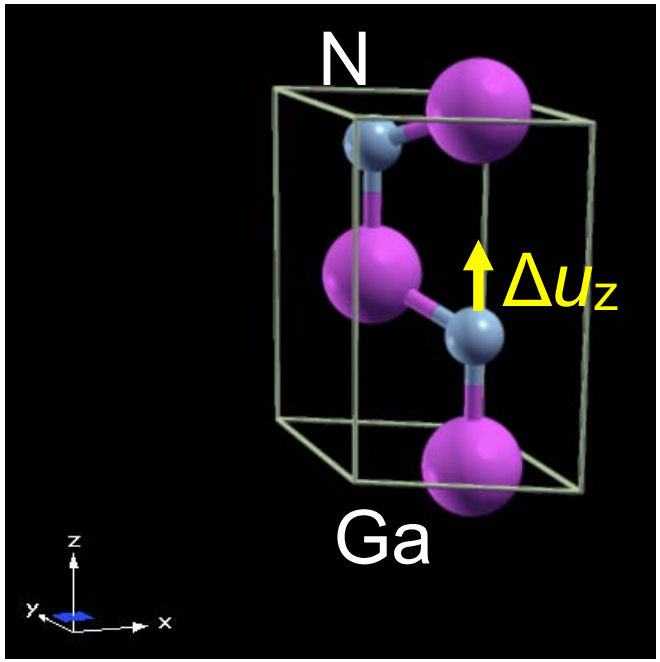
Choice of a reference structure

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



- 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`

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

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

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

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

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

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

$= -0.0342$

$\Delta u = 0.001 - 0 = 0.001$

$$Z^* = \frac{\Delta\Phi}{2\nabla \cdot \Delta u \cdot \#\text{ of atoms moved}} =$$

$= -2.72$

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)

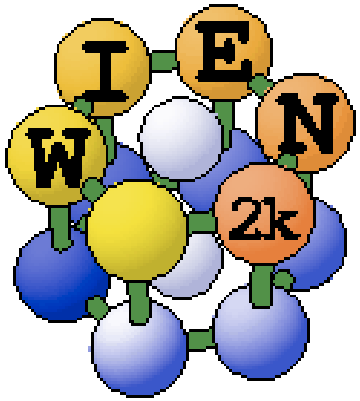
Born effective charge (wurtzite structure)

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

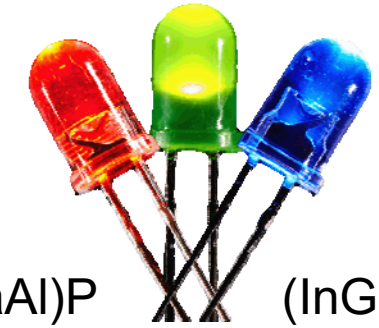
- Sheikh J. Ahmed *et al*. “BerryPI: A software for studying polarization of crystalline solids with WIEN2k density functional all-electron package”, Comp. Phys. Commun. 184, 647 (2013).
- BerryPI home and tutorials: https://github.com/spichardo/BerryPI/wiki
- Raffaele Resta “Macroscopic polarization 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)

Effective band structure of alloys



+ fold2Bloch

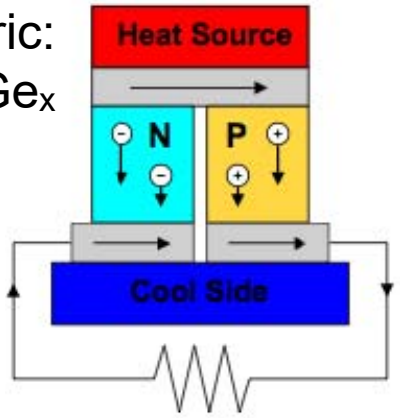
Semiconductor alloys

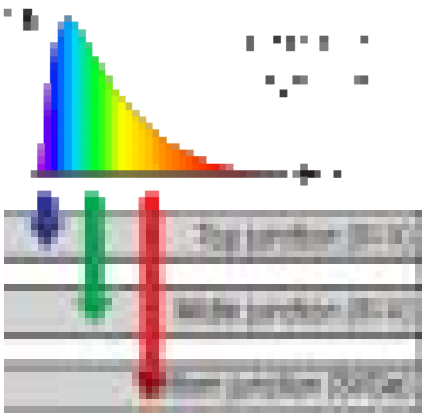


(InGaAl)P (InGa)N

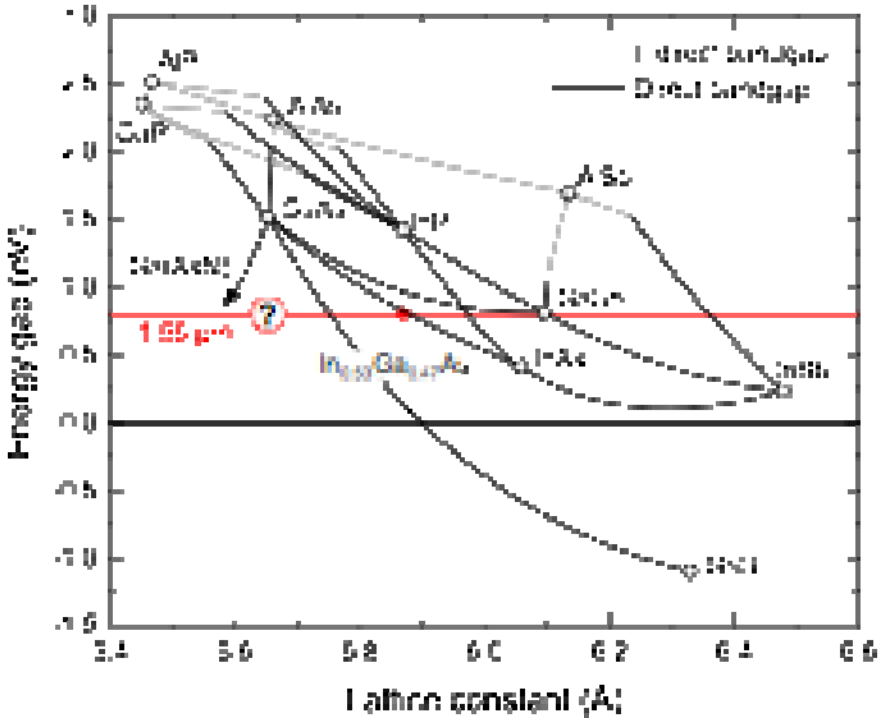
IR detector:
(HgCd)Te

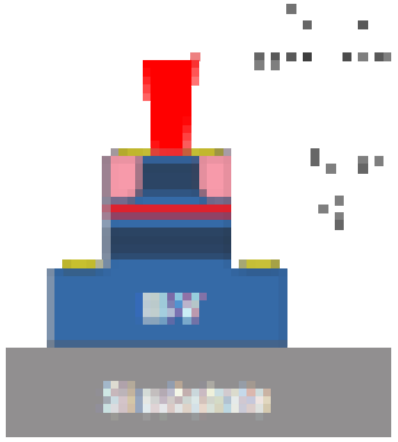
Thermoelectric:
$Si_{1-x}Ge_x$





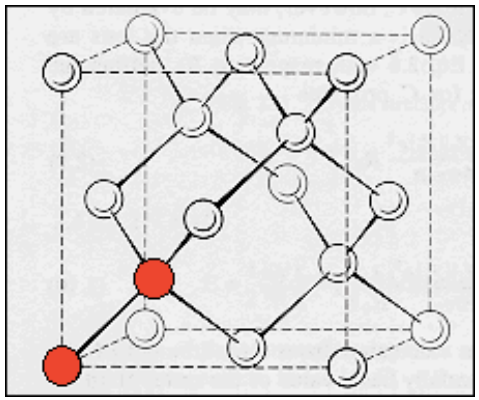
Eg = 1 eV junction:
(InGa)(NAs)





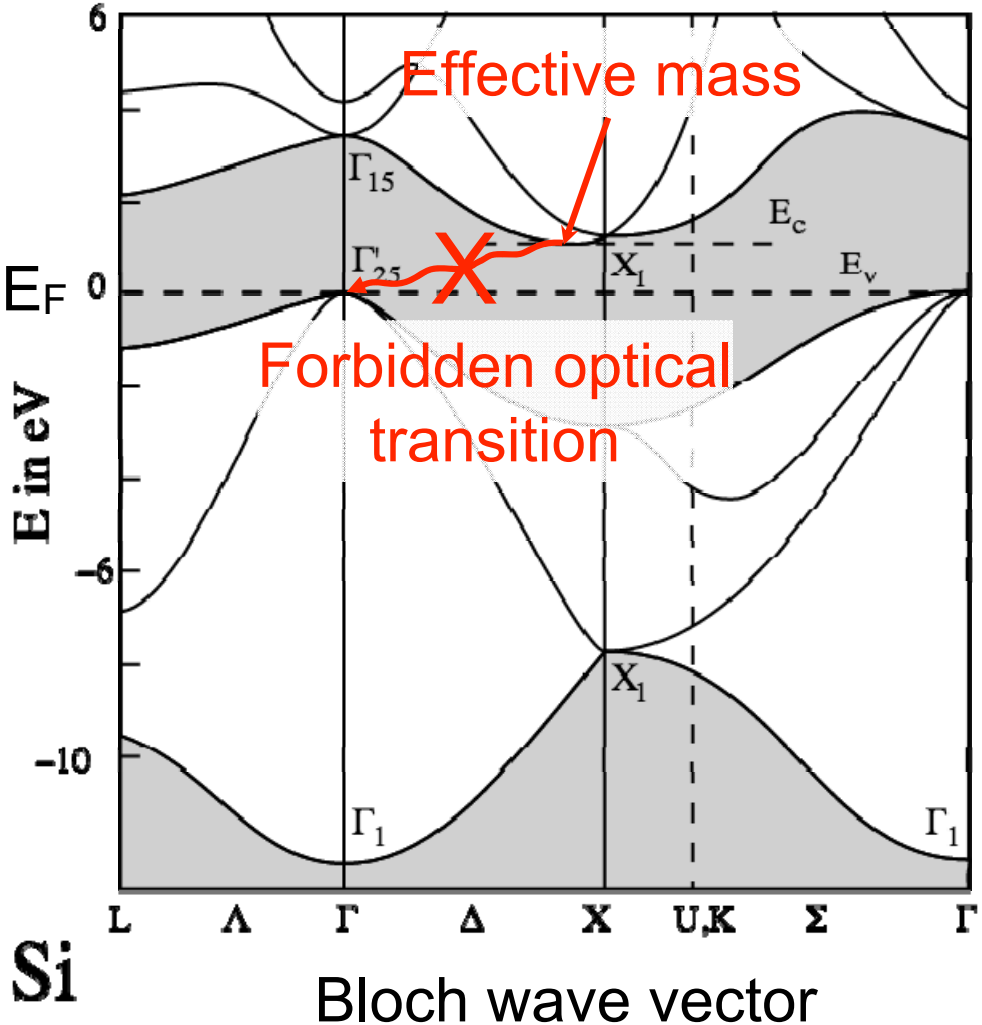
1.55 μm lasers:
(InGa)As
(InGa)(NAsSb)
Ga(AsBi)

Band structure

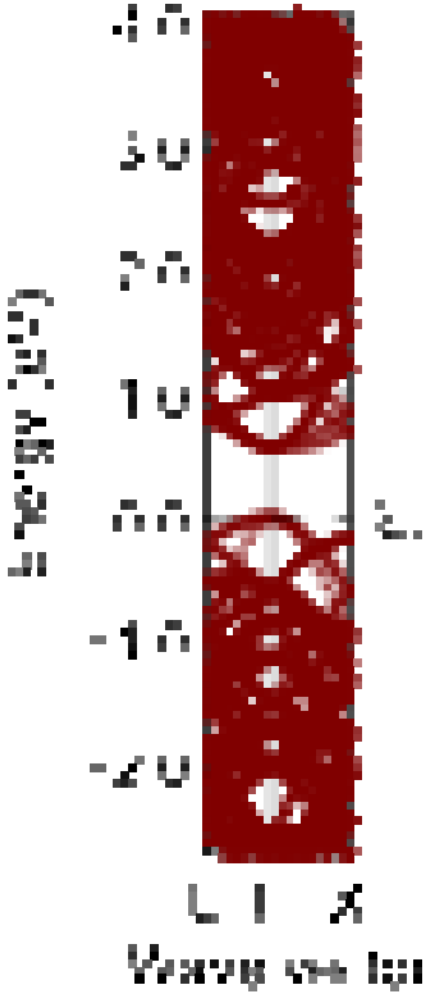


Energy gap ↕

Silicon
2-atom basis

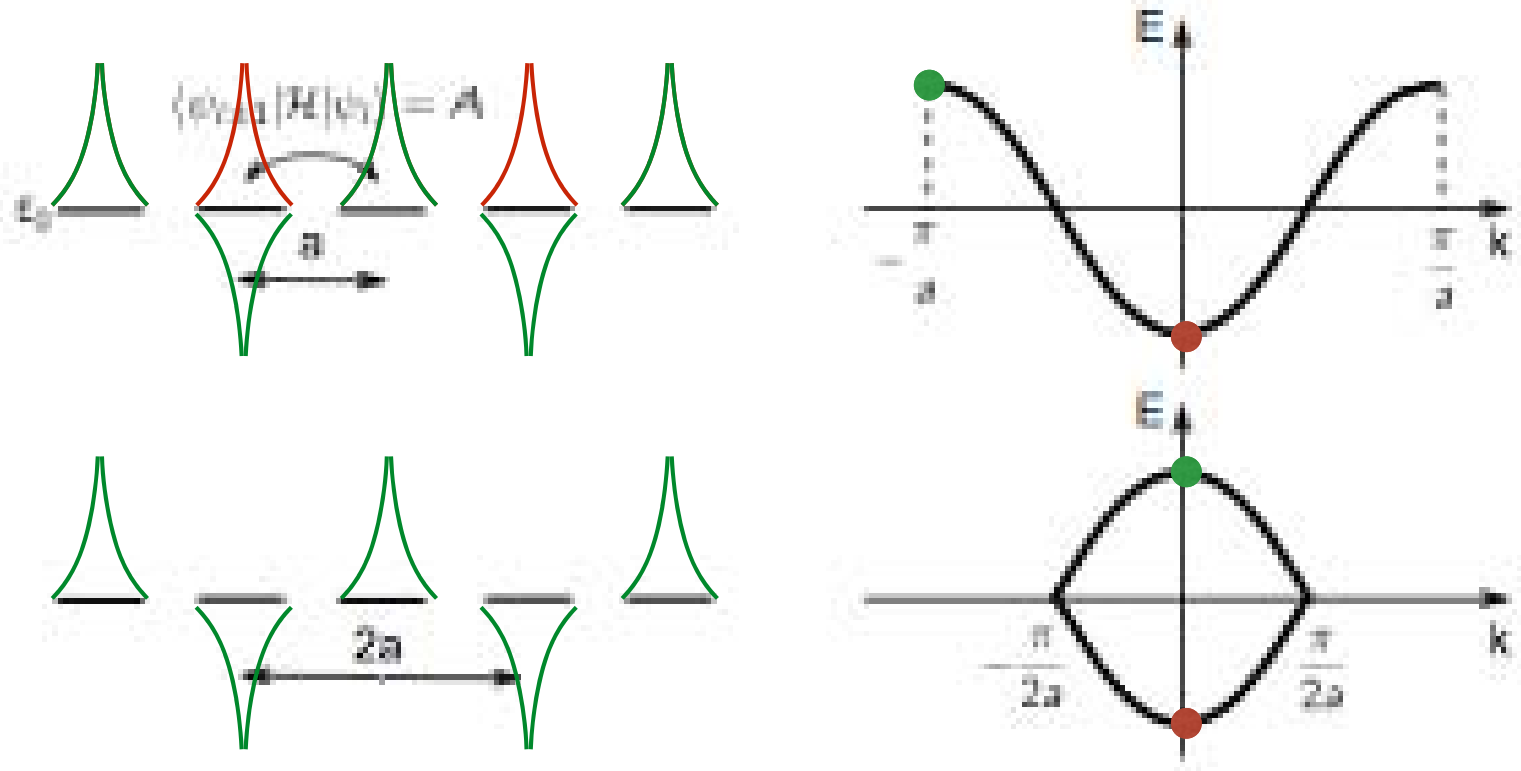


Silicon
250-atom supercell



Zone folding

The character of Φ changes between Γ – X
from bonding to anti-bonding



Doubling the unit cell → halfs the BZ
→ backfolding of X to Γ
the wavefunction can still tell you if an eigenvalue was Γ or X

Unfolding the first-principle band structure

Plane wave expansion

$$\Psi_{nk}(r) = \sum_{G} C_{nk}(G)\, e^{i(k+G)r}$$

Bloch spectral weight

$$A_n(k) = \sum_{g} C_{nk}(k-g)^2$$

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

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

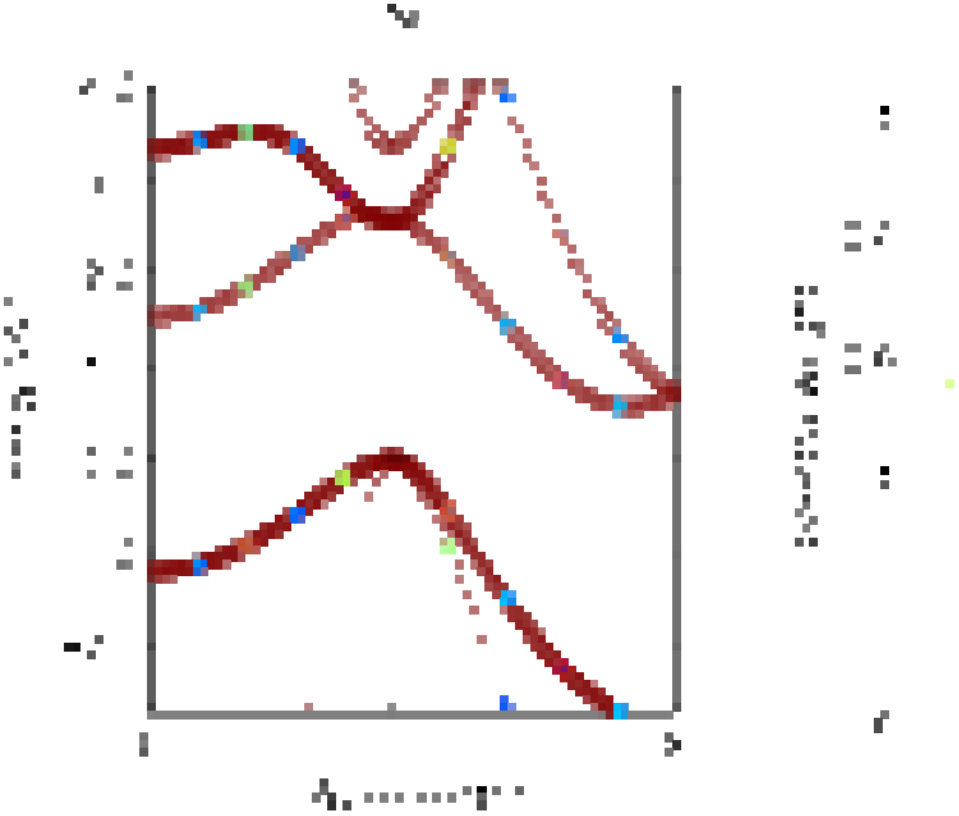
README.md

fold2Bloch

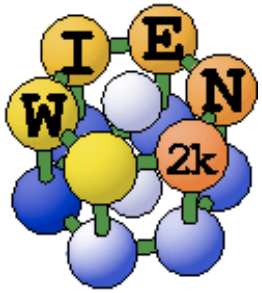
Unfolding of first-principle electronic band structure obtained with WIEN2k DFT-(L)APW code

Contributors:

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



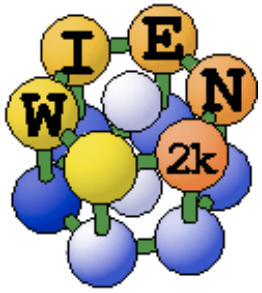
Workflow



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

XCrySDen

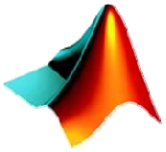
- Create k-path (`case.klist_band` file)



- 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

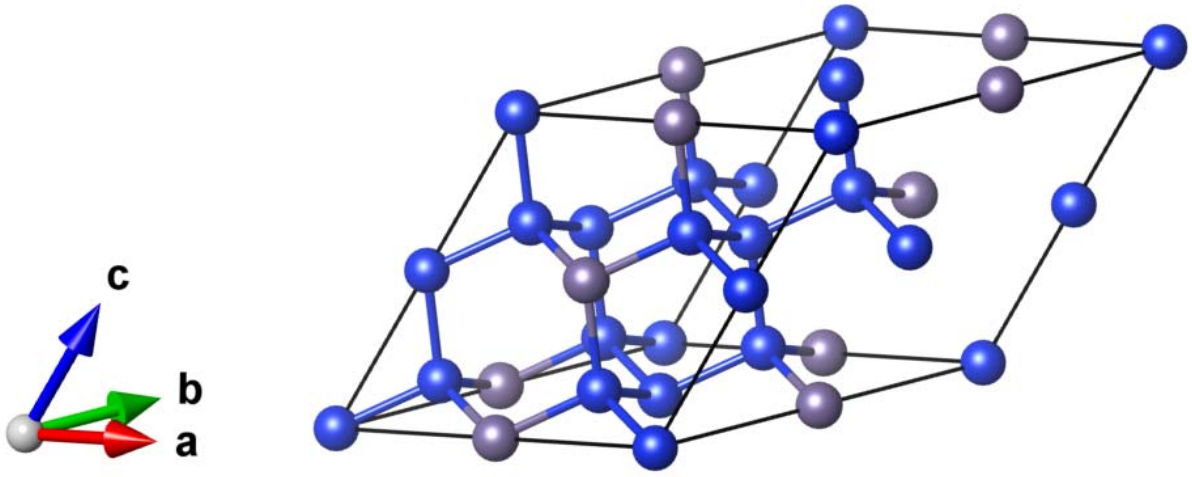
- Unfold band structure (`fold2Bloch`)

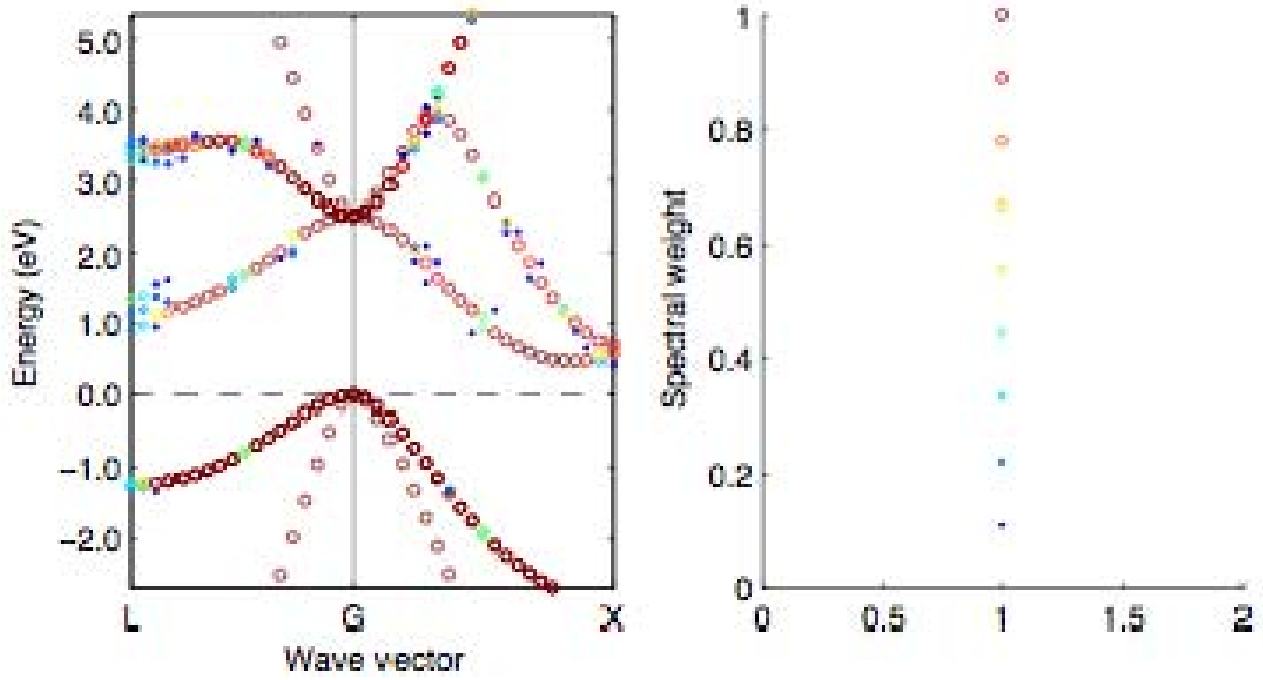


MATLAB

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

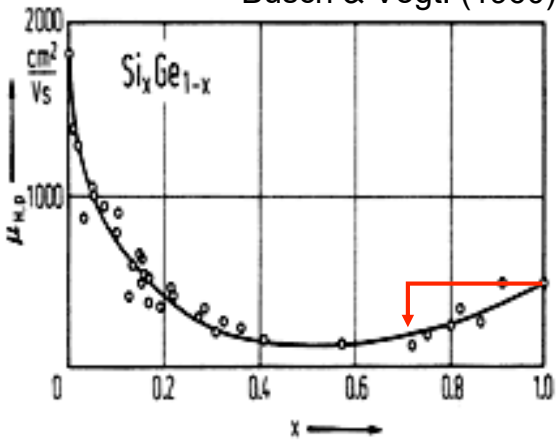
Demonstration: Band structure of $Si_{1-x}Ge_x$ alloy (x ~ 0.2)

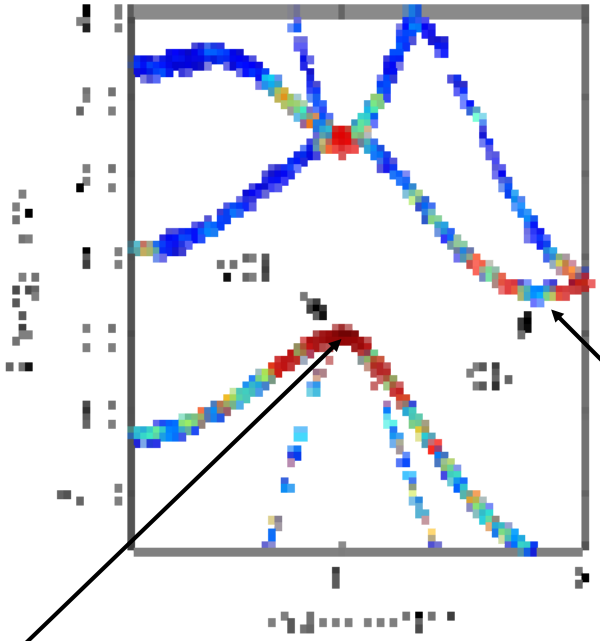




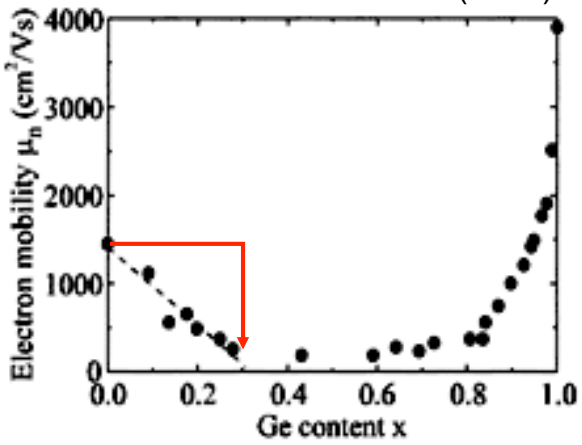
Thermoelectric material: $Si_{0.7}Ge_{0.3}$

Busch & Vogt. (1960)

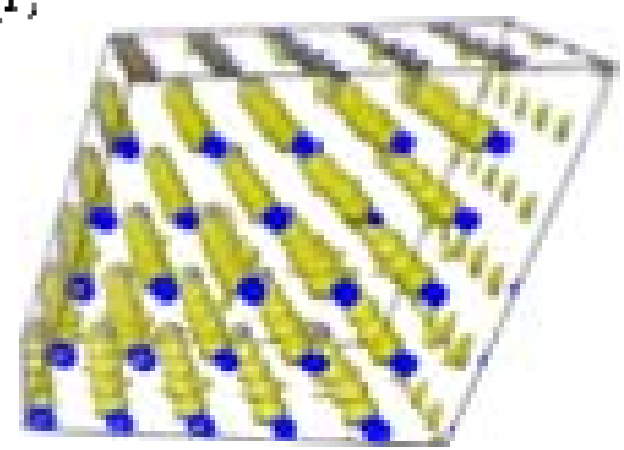


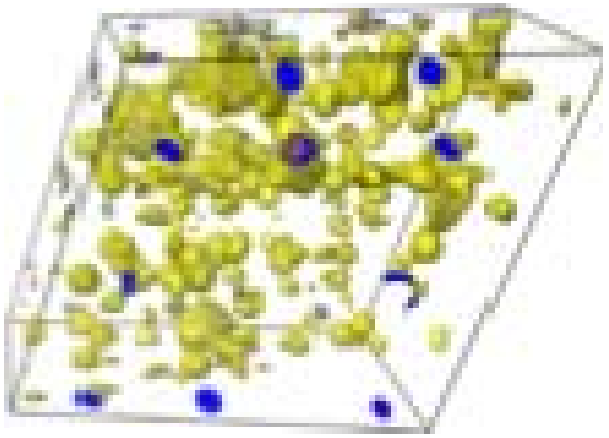


Landoldt-Bornstein (1982, 1987);
Sasaki et al. (1984).

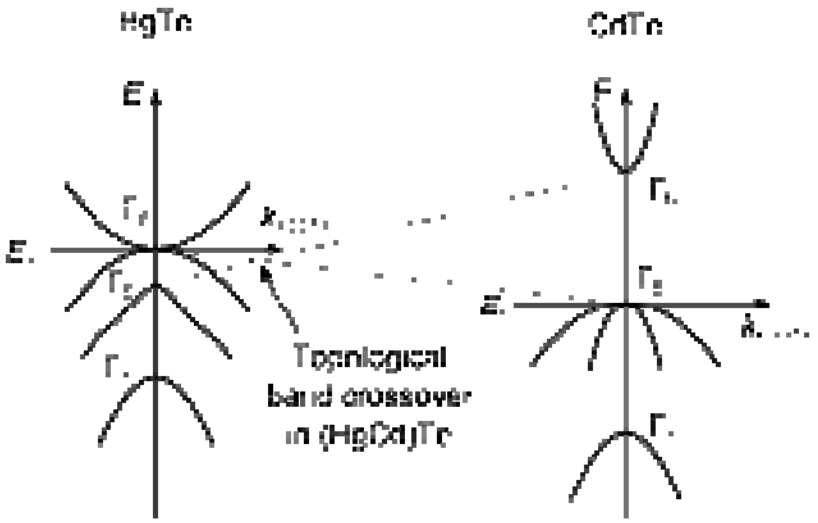


$\Delta r \Delta k \sim 1$

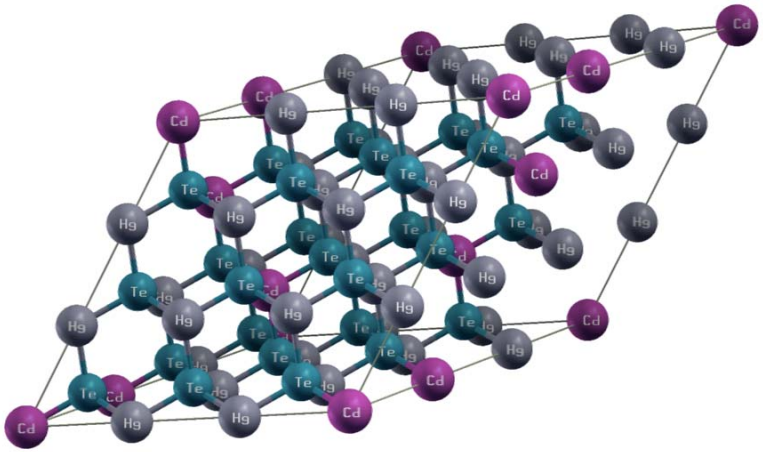


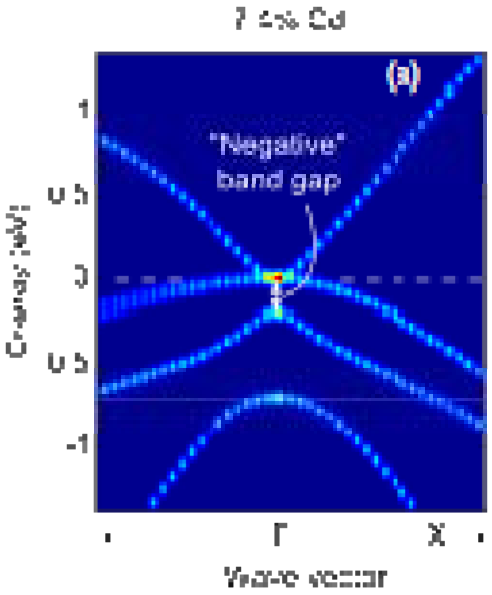


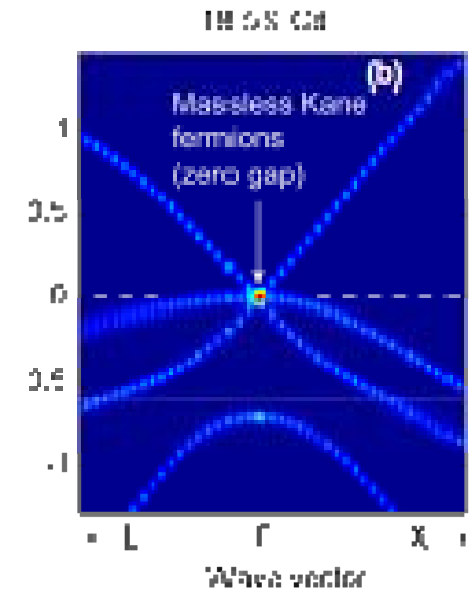
(Hg,Cd)Te band structure evolution

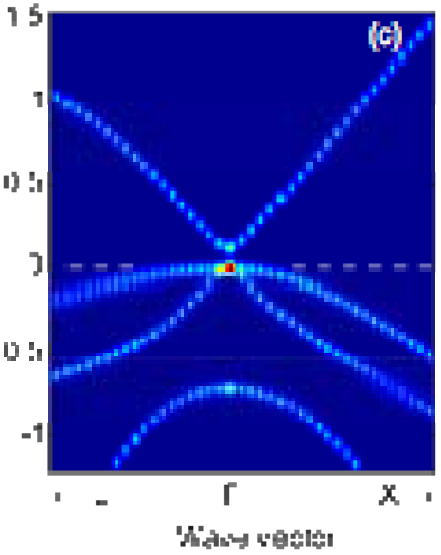


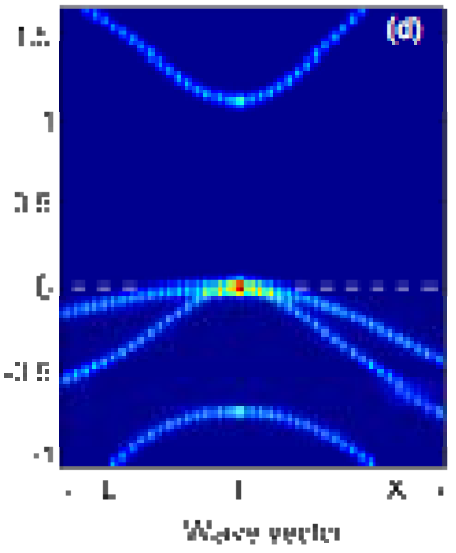
$Hg_{22}Cd_5Te_{27}$





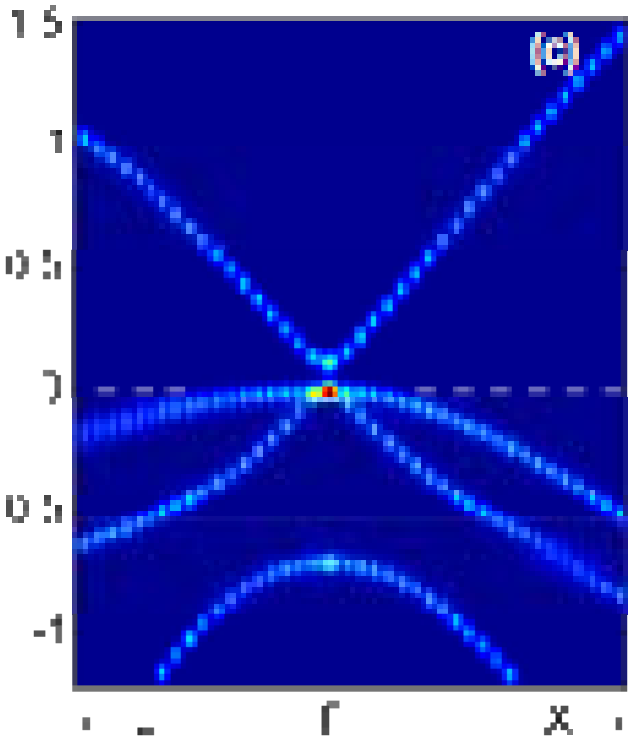




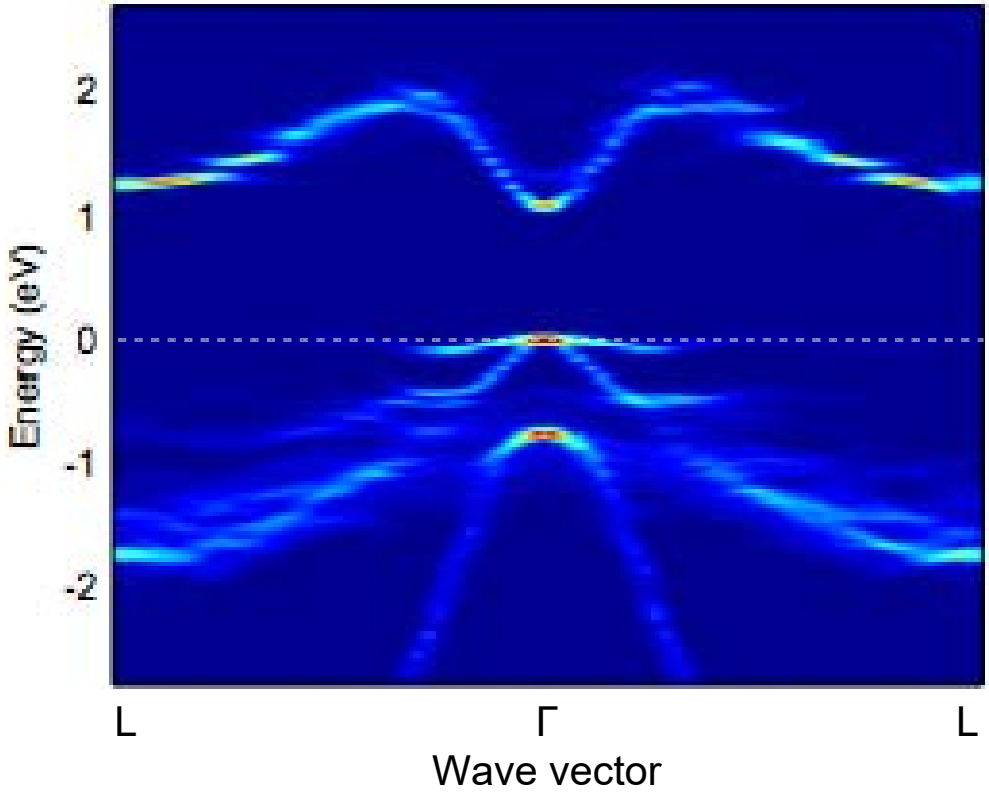


Impact of alloying disorder on charge transport

CdTe → (HgCd)Te



GaAs → Ga(AsBi)



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

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

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

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

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