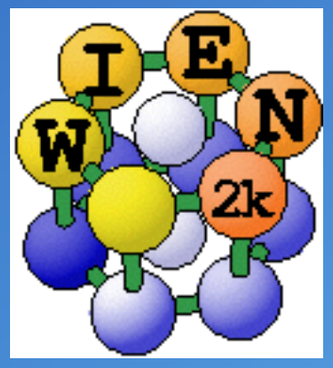
Wannier functions

Macroscopic polarization (Berry phase) and related properties

Effective band structure of alloys

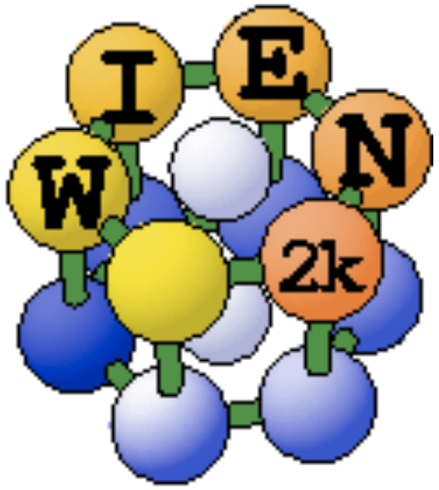
Oleg Rubel

Department of Materials Science and Engineering



McMaster University

Wannier functions



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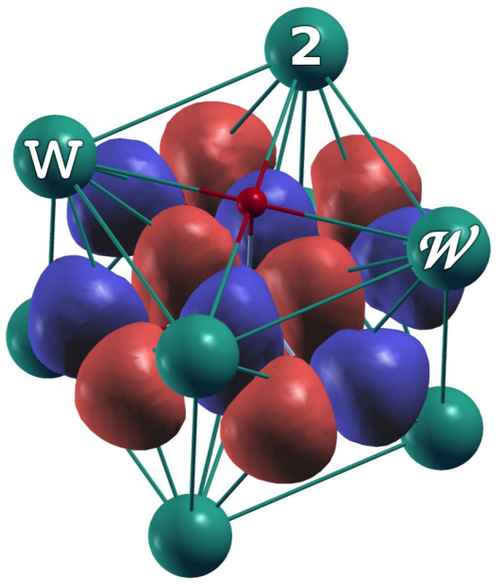


+

WANNIER90

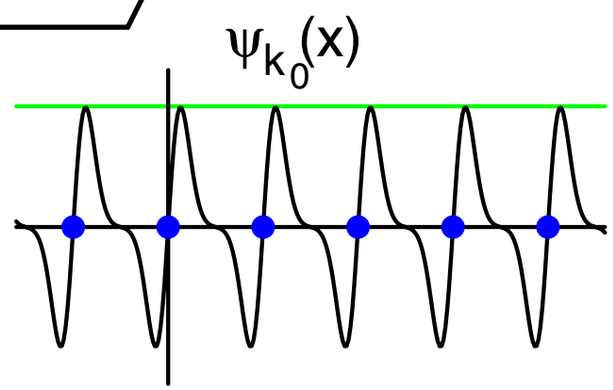
Bloch *vs* Wannier functions

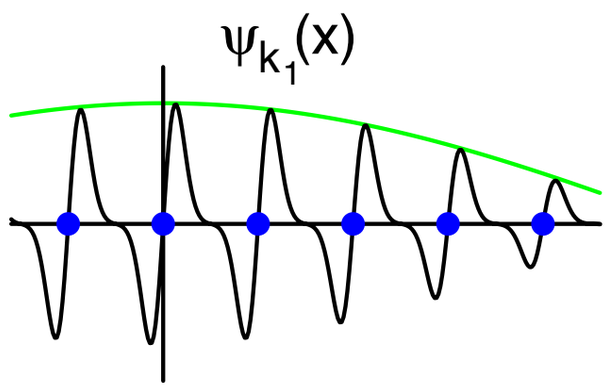
Bloch functions

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

Indexed by the wave vector

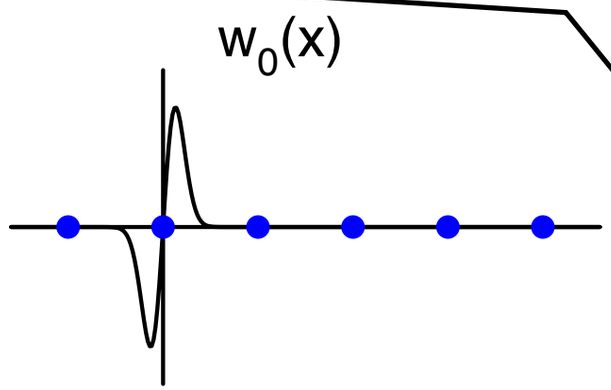
Γ-point

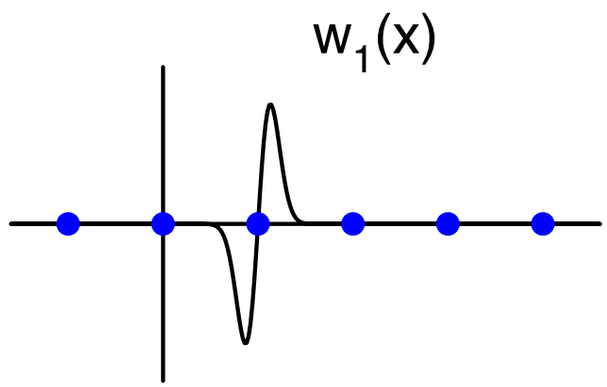




Wannier functions (localized orbitals)

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





Indexed by the lattice vector in real space

Both sets: complete and orthonormal

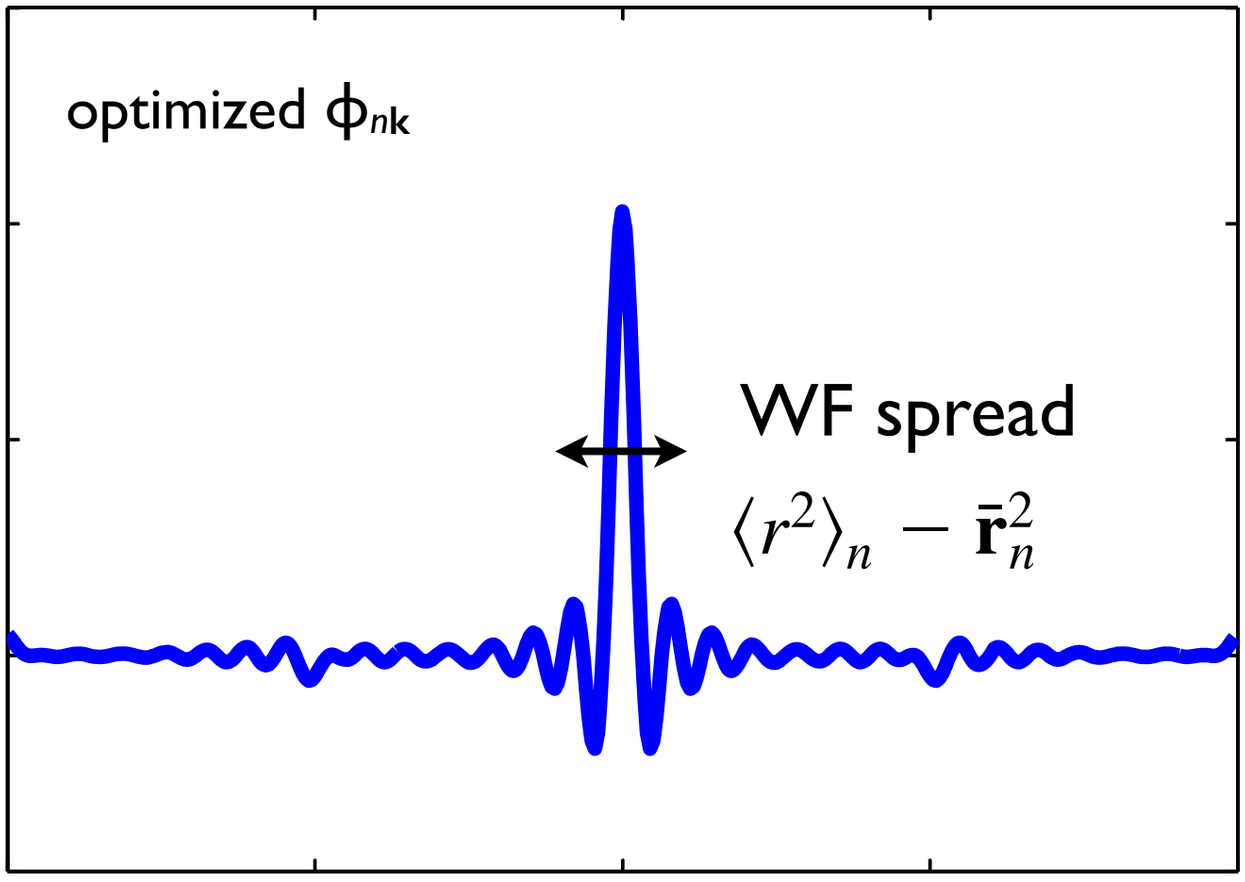
Wannier:
PRB **52**, 191 (1937)
Marzari et al.:
PRB 56, 12847 (1997)
Rev. Mod. Phys. (2012)

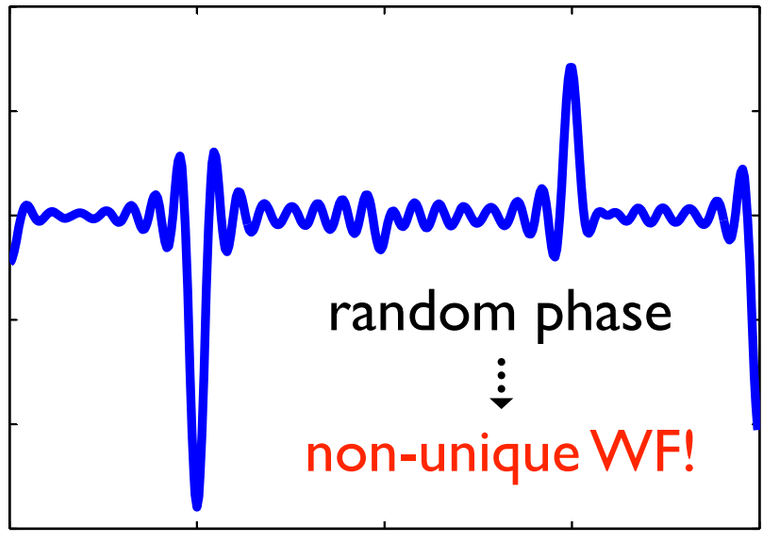
Max. localized Wannier functions (MLWF)

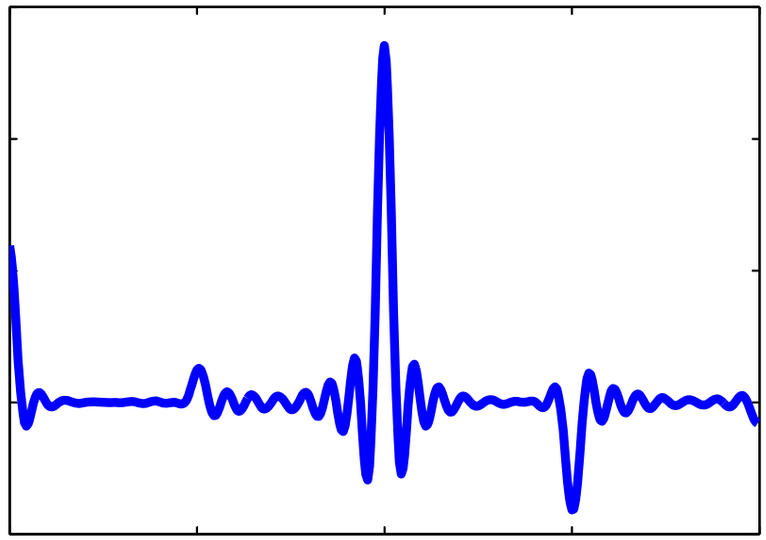
Bloch functions (more precisely):

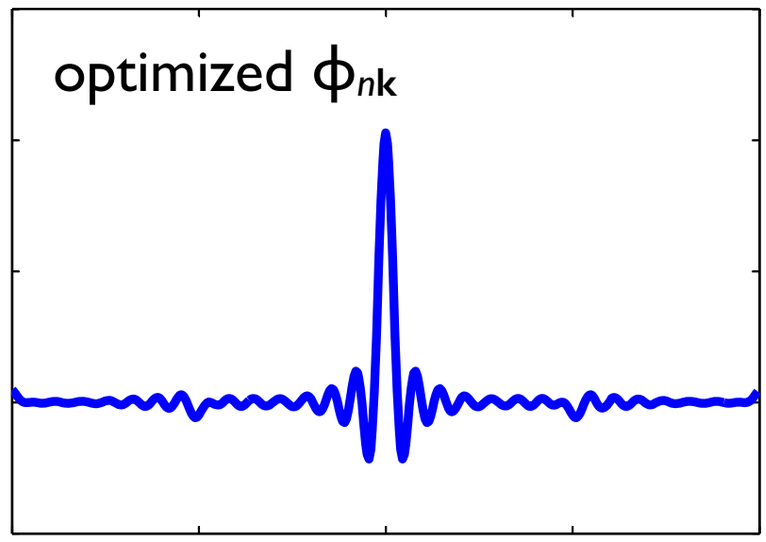
$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, e^{i\phi_{n\mathbf{k}}}$$

gauge freedom → ambiguity



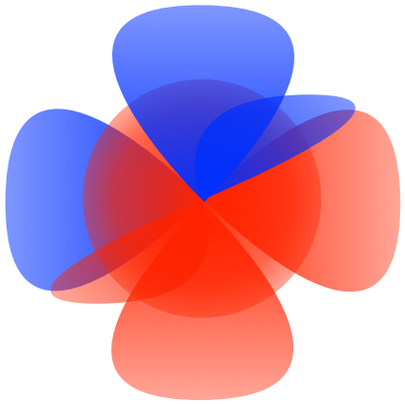


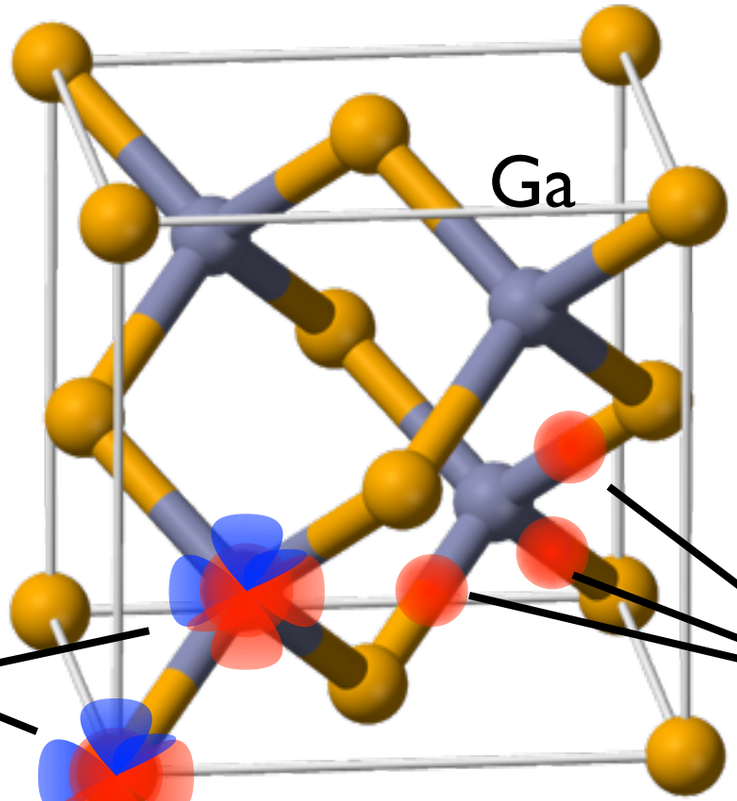


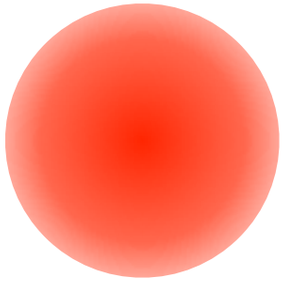


$$\Omega = \sum_n [\langle \mathbf{0}n|r^2|\mathbf{0}n\rangle - \langle \mathbf{0}n|\mathbf{r}|\mathbf{0}n\rangle^2] = \sum_n [\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2]$$

Two flavours of Wannier functions

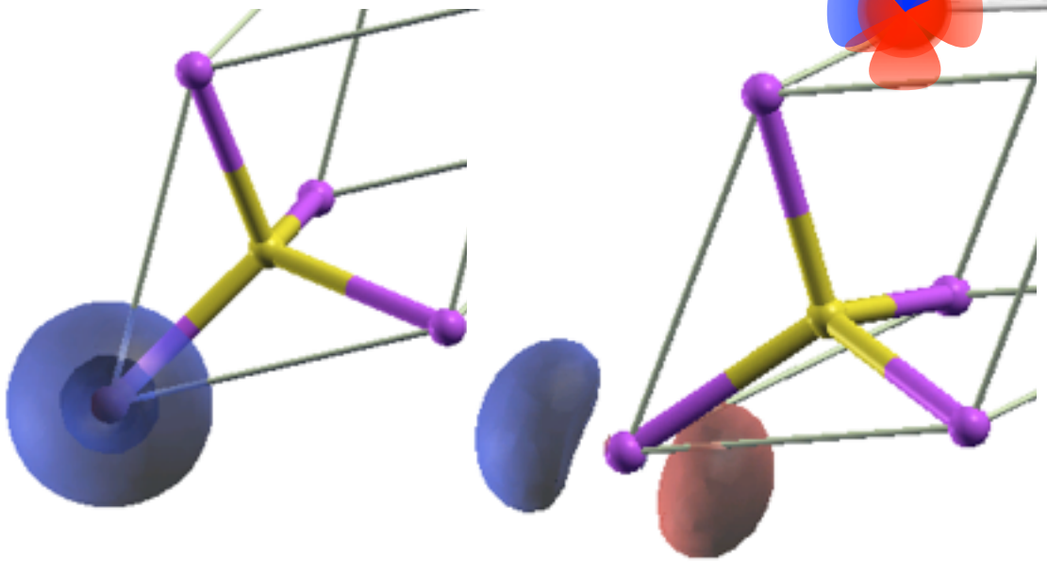


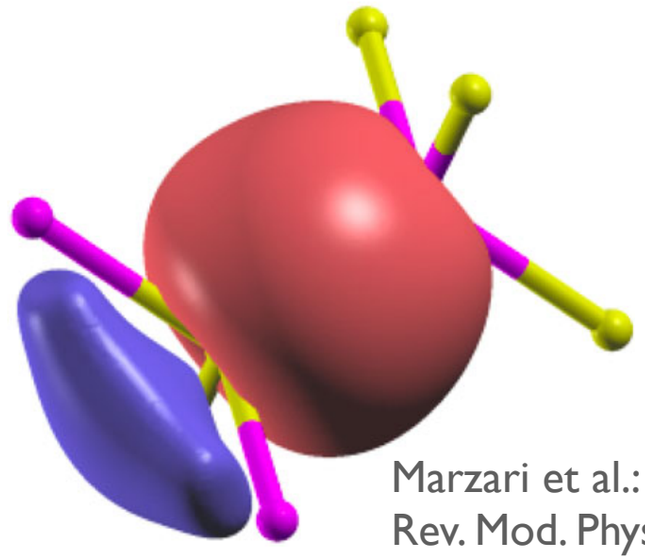




Atom centered sp^3-like

Bond centered s-like



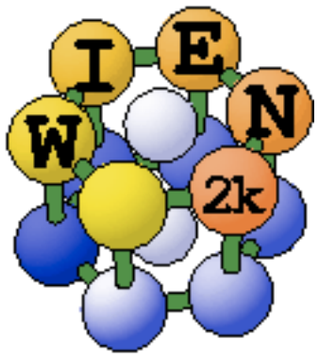


Marzari et al.:
Rev. Mod. Phys. (2012)

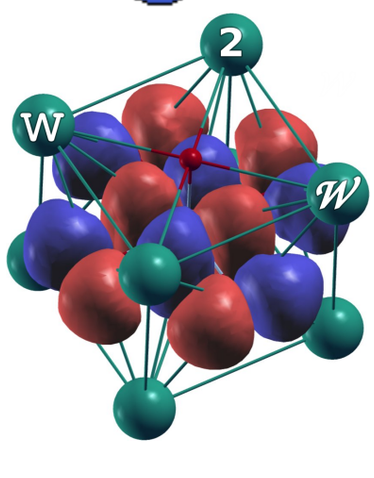
- includes *bonding* and *antibonding* states
- building effective hamiltonian

- includes *valence* states
- charge transfer and polarization

Workflow

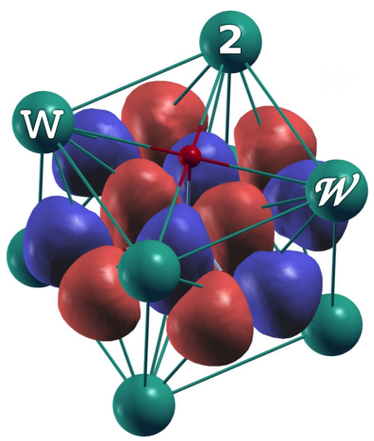


- Regular SCF calculation
- Band structure plot



- 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 FW)

(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
...
```

Home

unit cell

⟨s1| |s1⟩

⟨s2|

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

Im part = 0

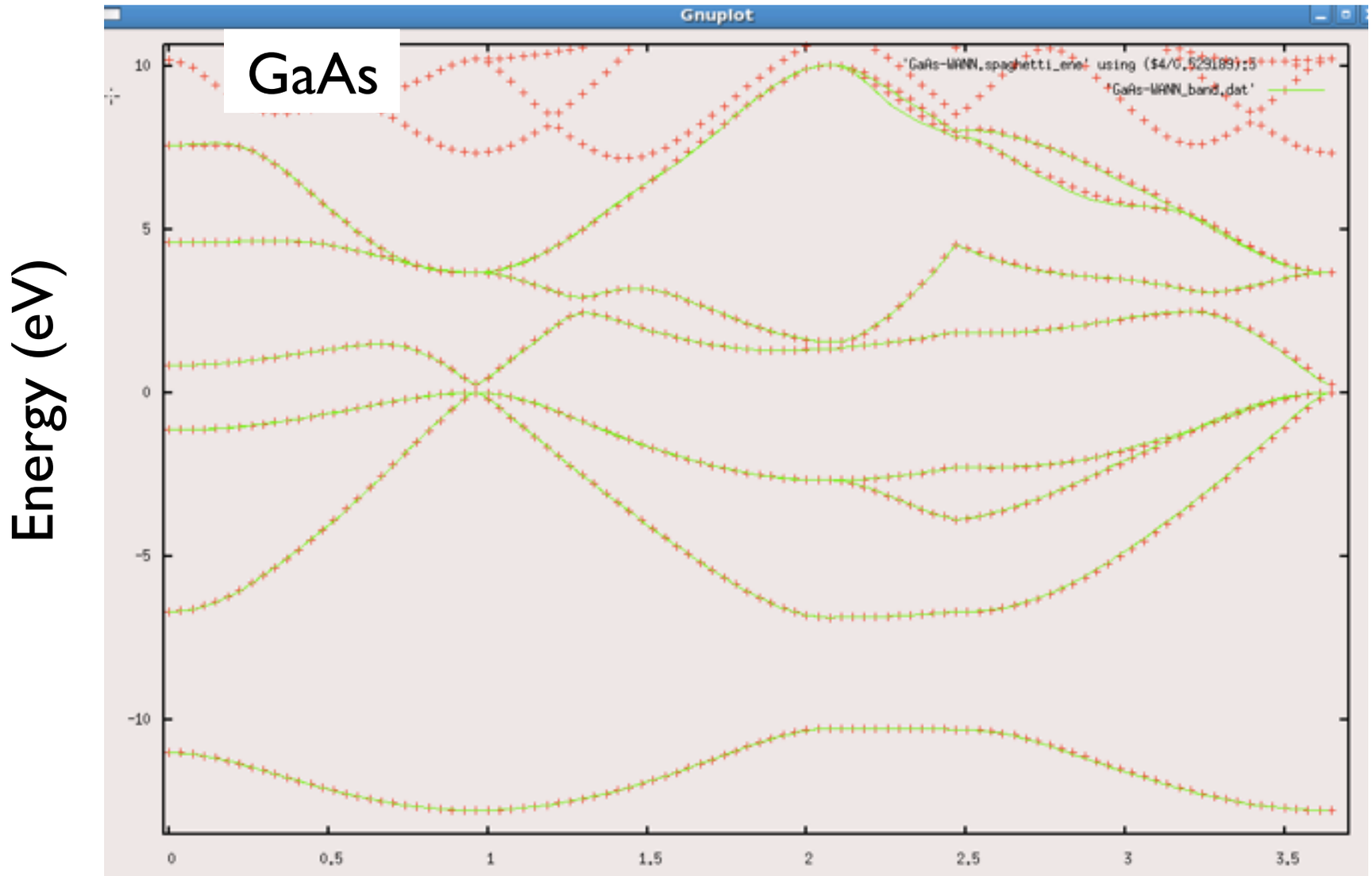
Matrix element (eV)
⟨s2|H|s1⟩ = $V_{ss\sigma}$

⟨p2|H|s1⟩ = V_{sp}

Neighbour unit cell

WF are well localized
⇒ nearest-neighbour suffice

Band structure



Energy (eV)

E_F

Wave vector

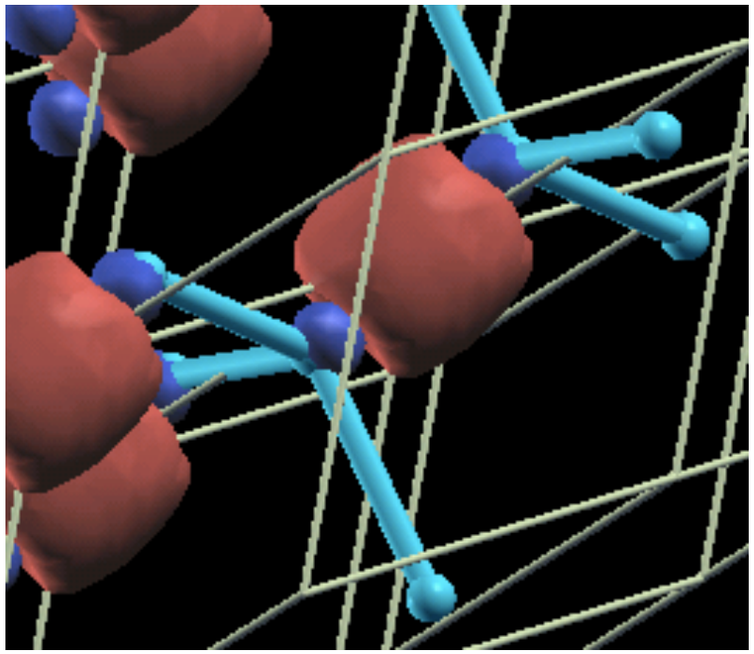
\+ original Wien2k band structure

– Band structure computed from Wannier hamiltonian

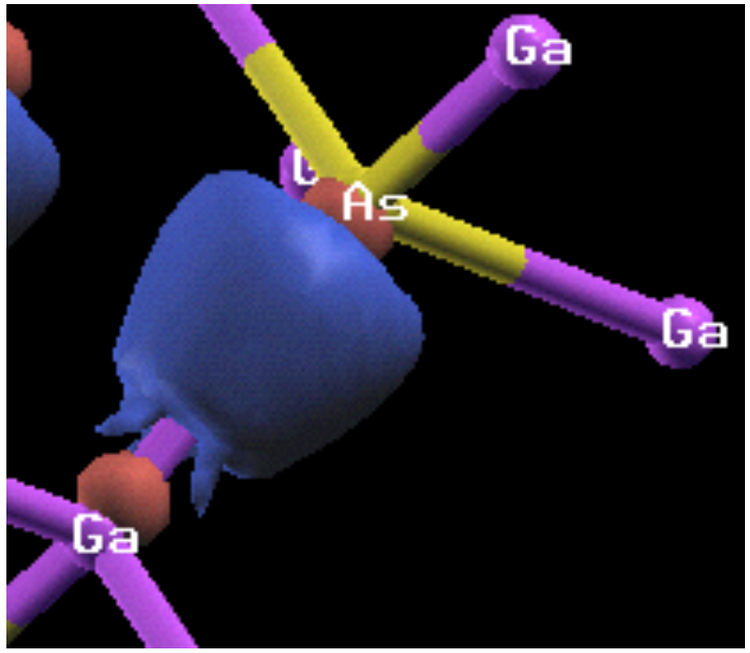
Relation to polarization (bond centered WF)

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

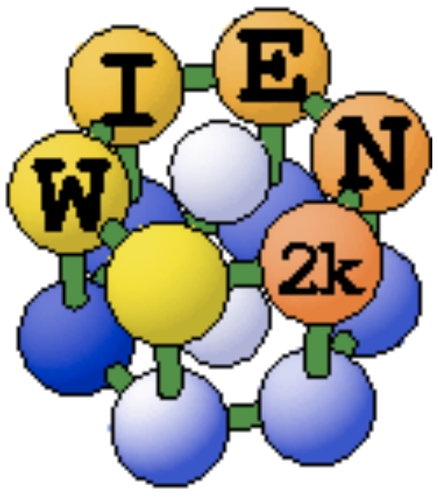
Electronic part

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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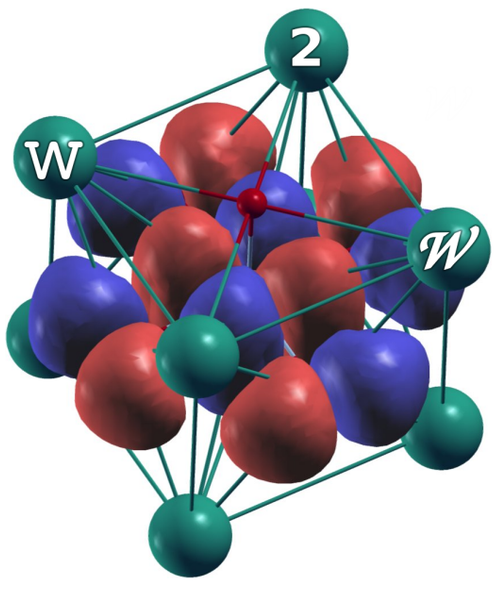
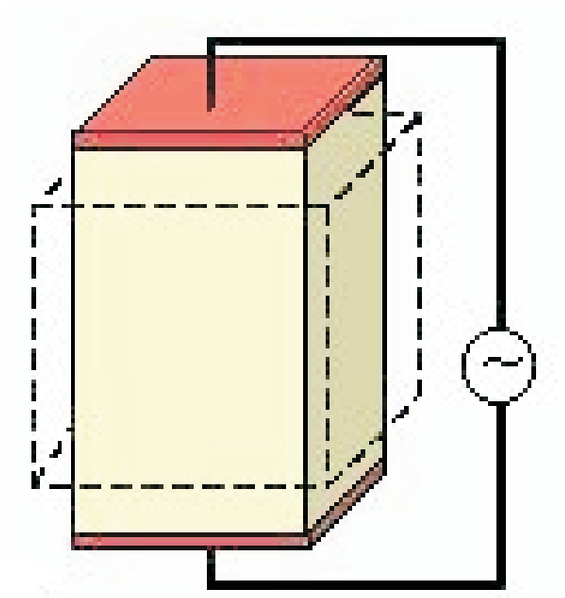


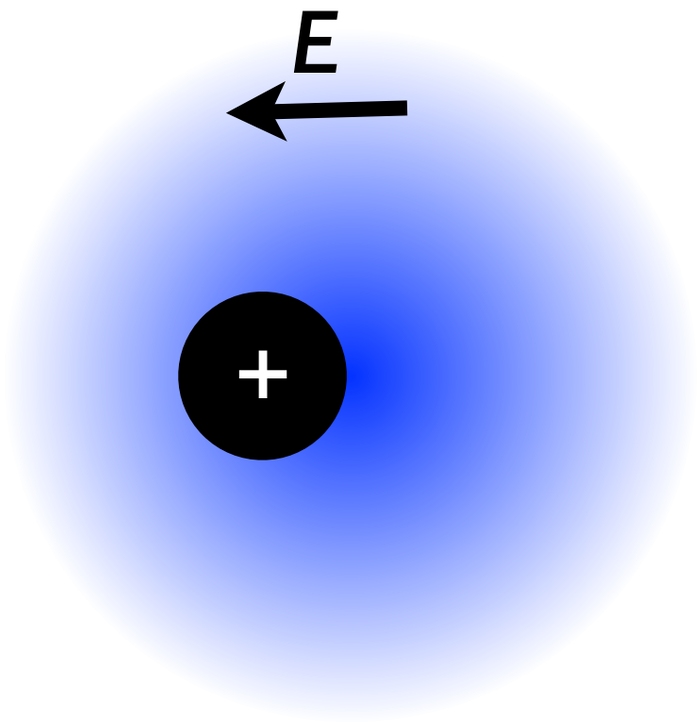
+ BerryPI

Material properties related to polarization

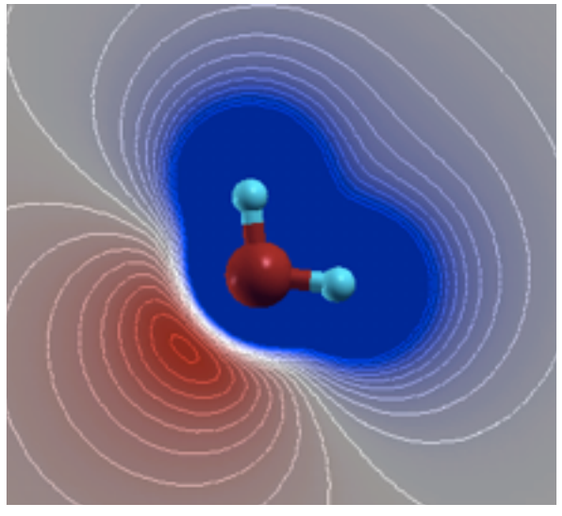
Piezo- and Ferroelectricity



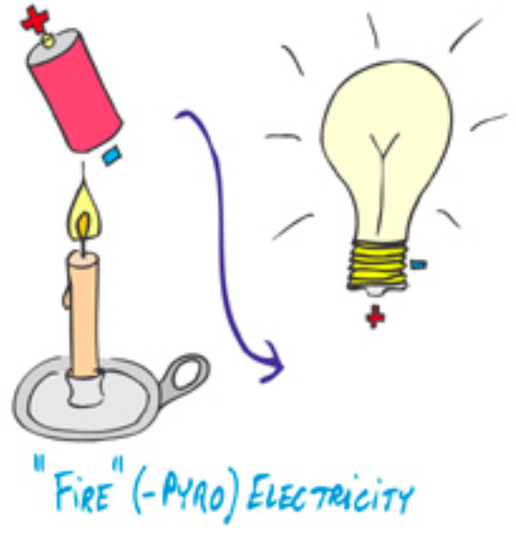
Dielectric screening



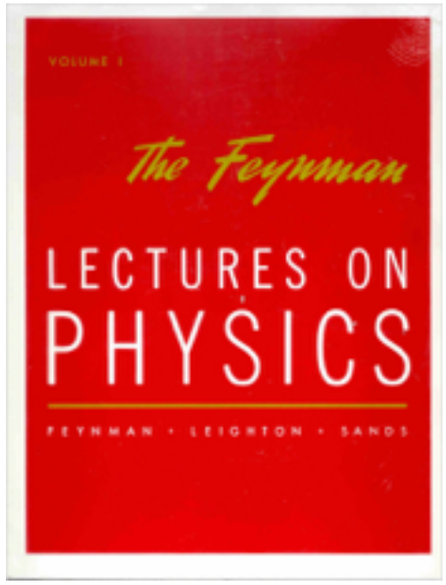
Effective charge



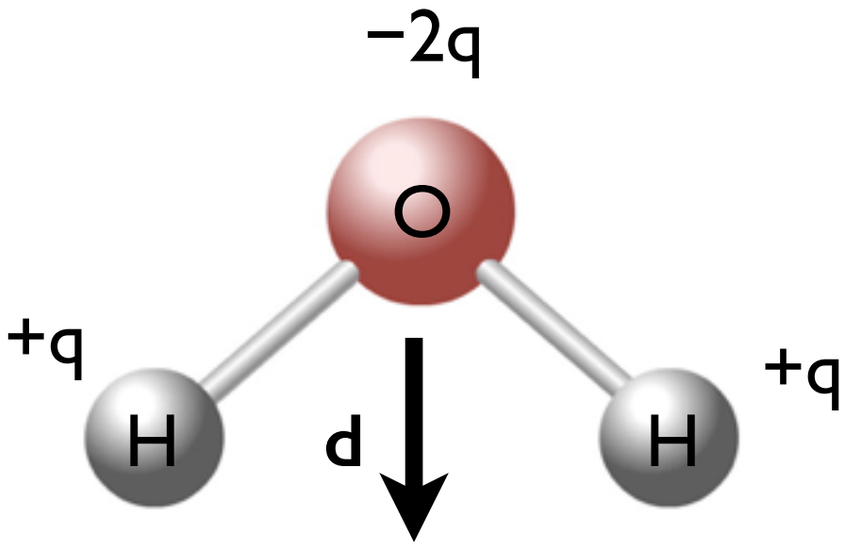
Pyroelectricity

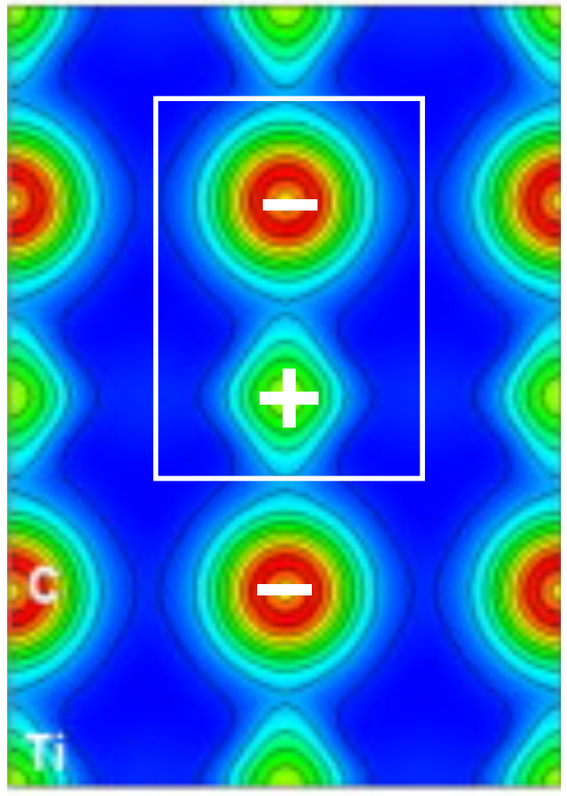


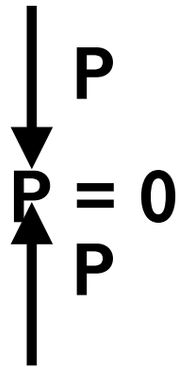
What is polarization?



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







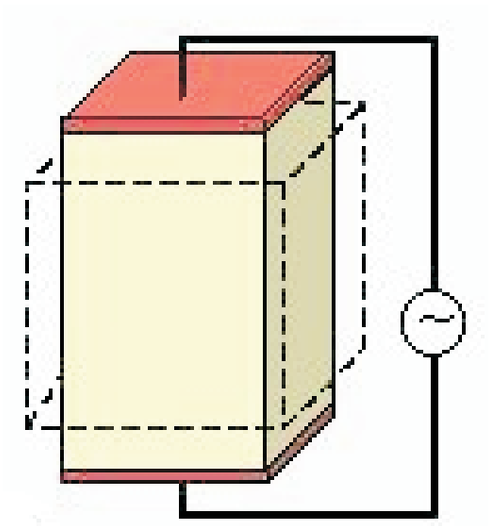
Polarization for periodic solids is undefined

Modern theory of polarization

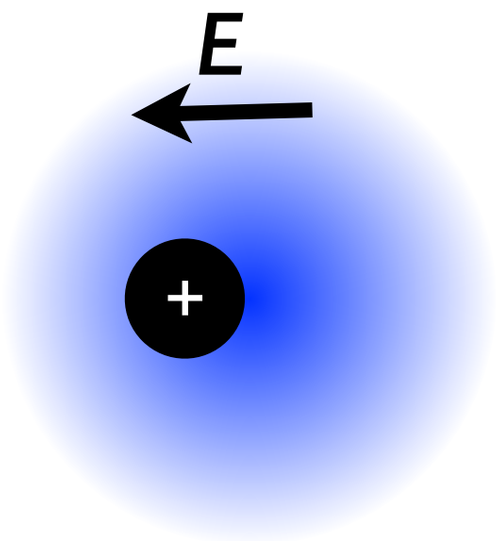
Pioneered by *King-Smith*, *David Vanderbilt* and *Raffaele Resta*

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

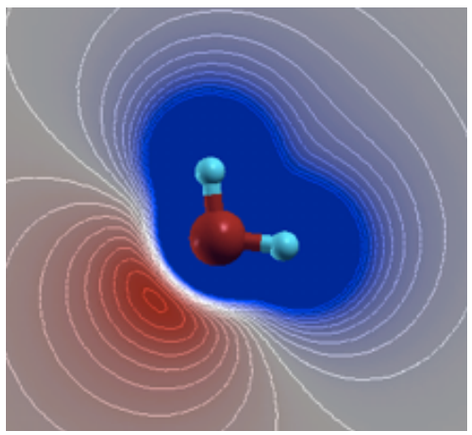
$$\Delta\mathbf{P} = \mathbf{P}^{(0)} - \mathbf{P}^{(1)}$$



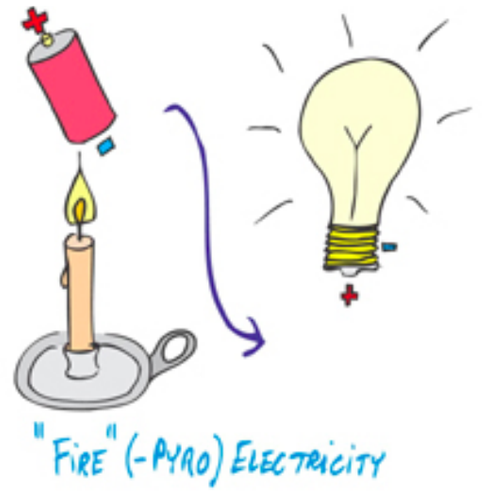
$$\frac{\Delta\mathbf{P}}{\Delta\text{strain}}$$



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

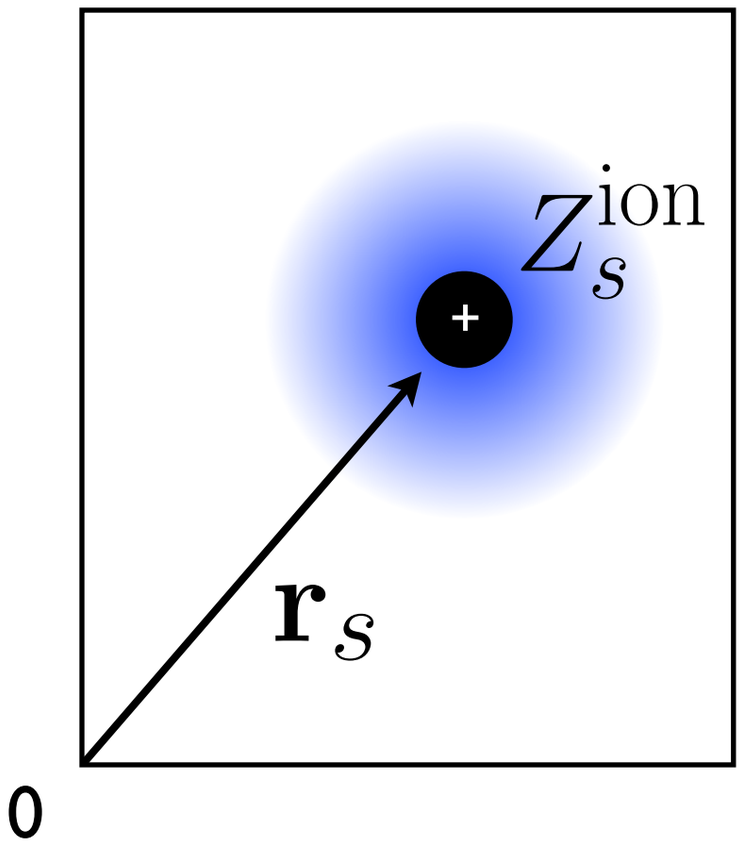


$$\frac{\Delta\mathbf{P}}{\text{displacement}}$$



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

Components of polarization



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

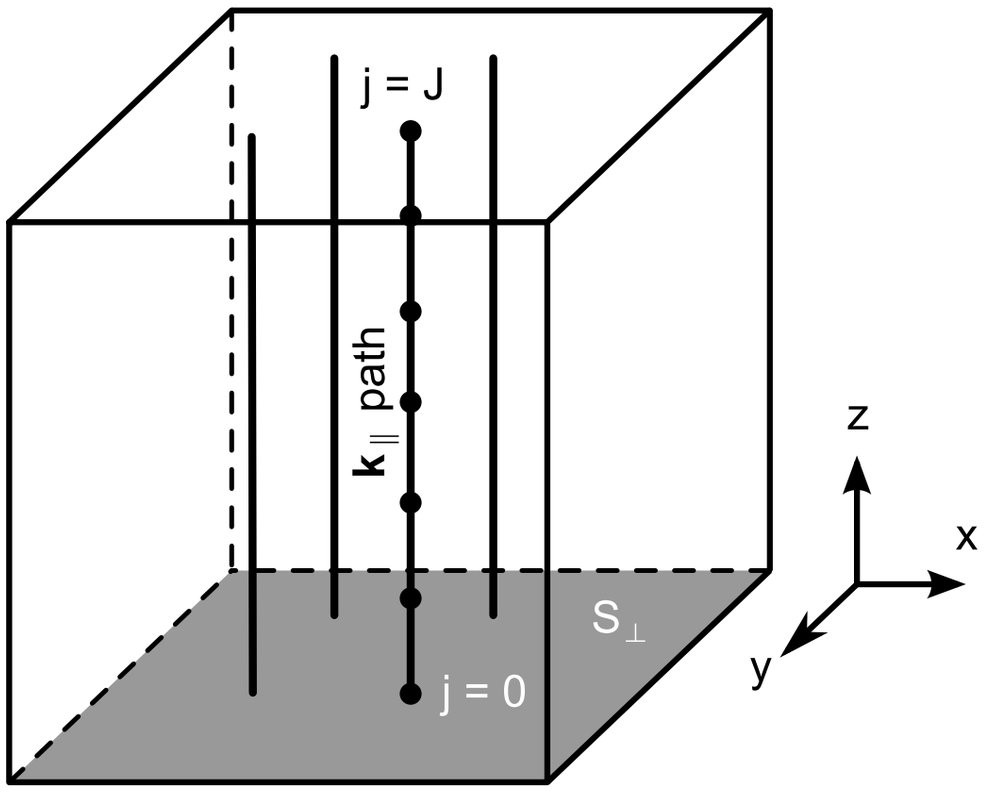
ionic — electronic

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

In Wien2k Z_s^{ion} is the core charge

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

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



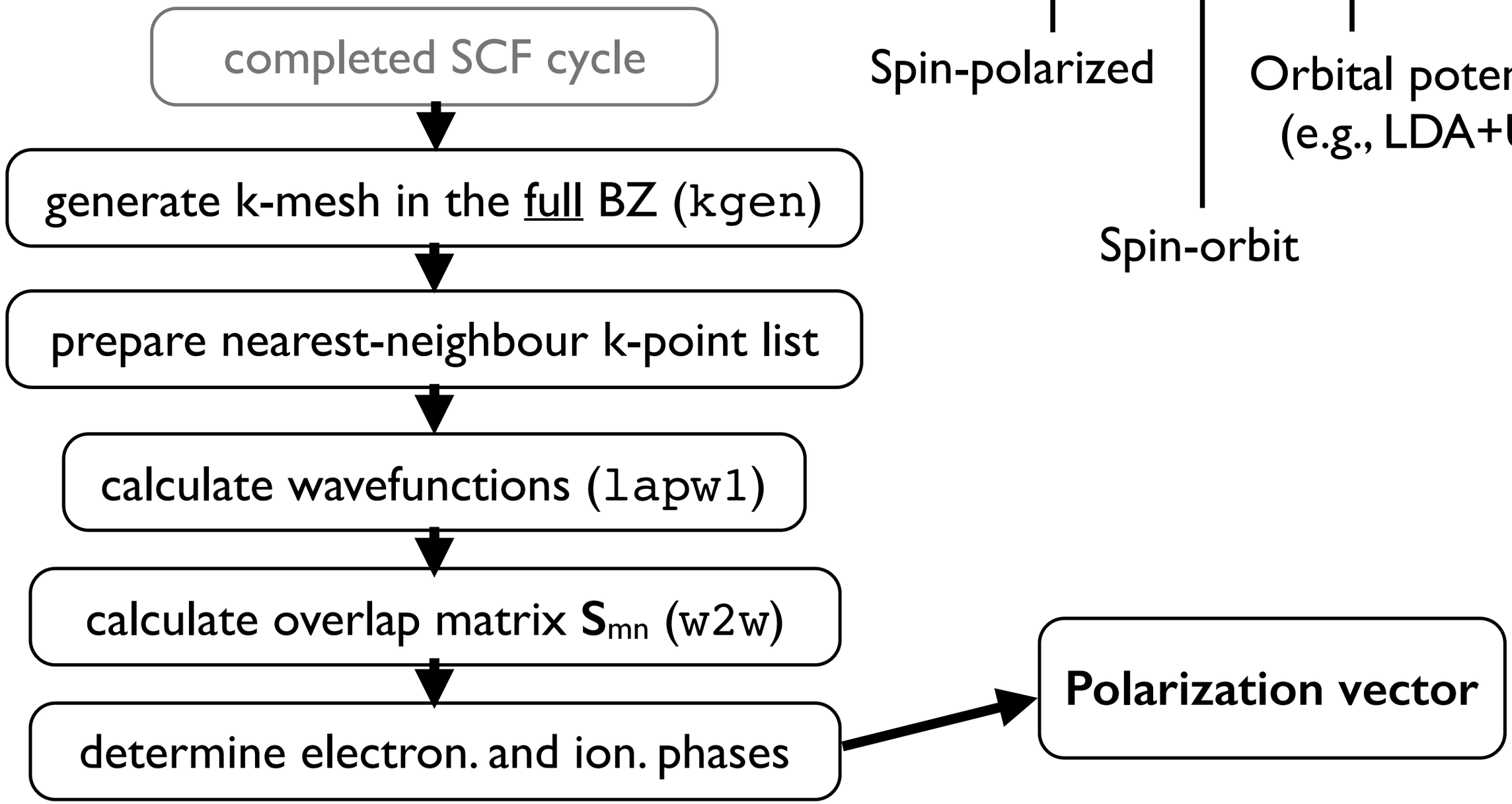
King-Smith and David Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

BerryPI workflow

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

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

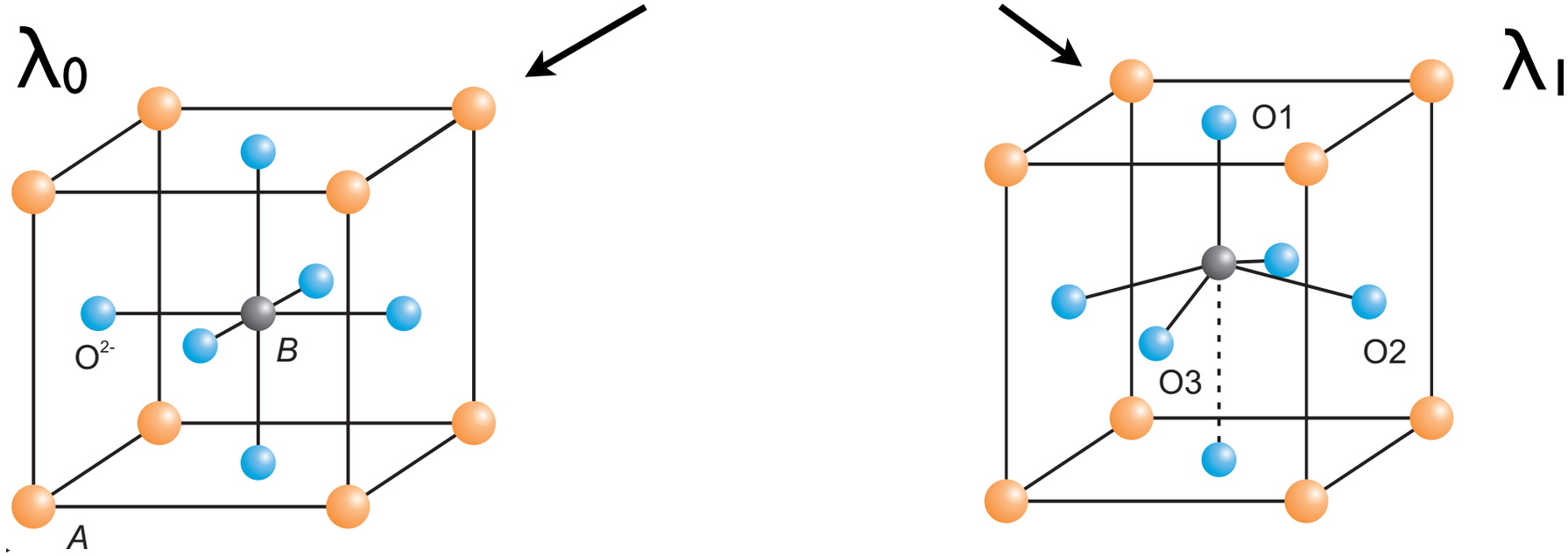
- `[-s]` — Spin-polarized
- `[-j]` — Spin-orbit
- `[-o]` — Orbital potential (e.g., LDA+U)



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

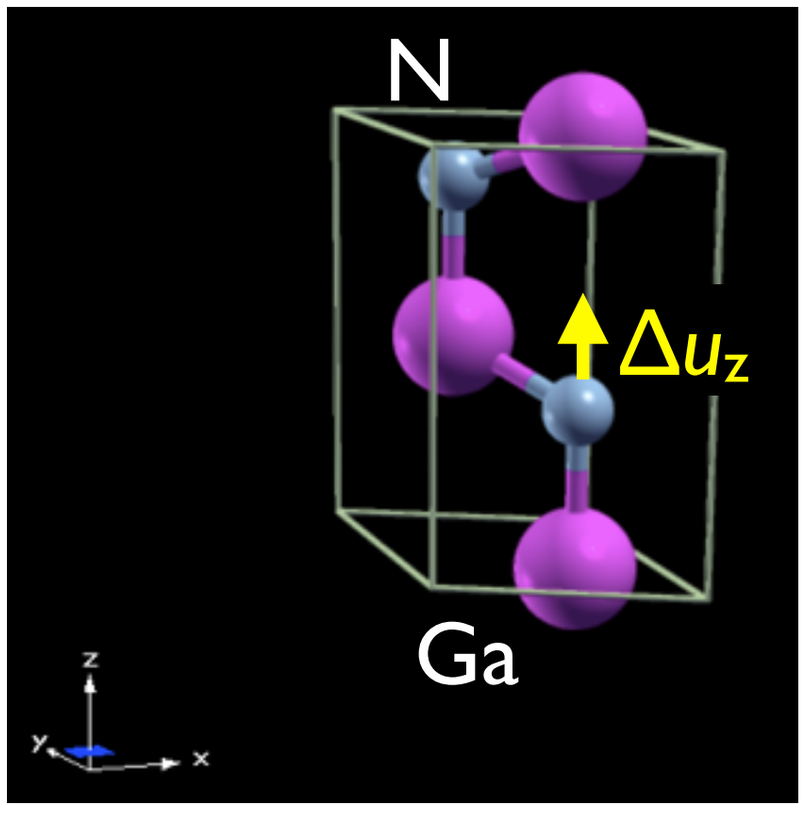
Choice of a reference structure

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



- structure file must preserve the symmetry
- begin with the lowest symmetry (λ_I) case
- copy case λ_I 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)

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)

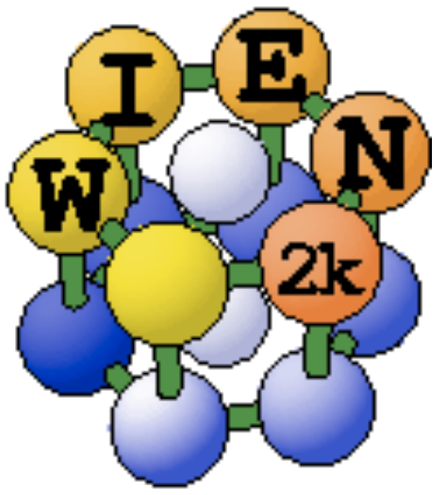
Born effective charge (wurtzite structure)

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

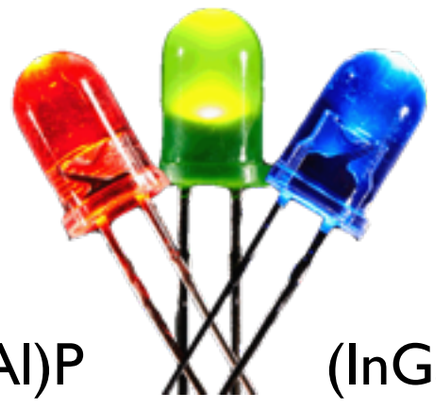
- Sheikh J. Ahmed *et al.* "BerryPI: A software for studying polarization of crystalline solids with WIEN2k density functional all-electron package", Comp. Phys. Commun. **184**, 647 (2013).
- BerryPI home and tutorials: https://github.com/spichardo/BerryPI/wiki
- Raffaele Resta "Macroscopic polarization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

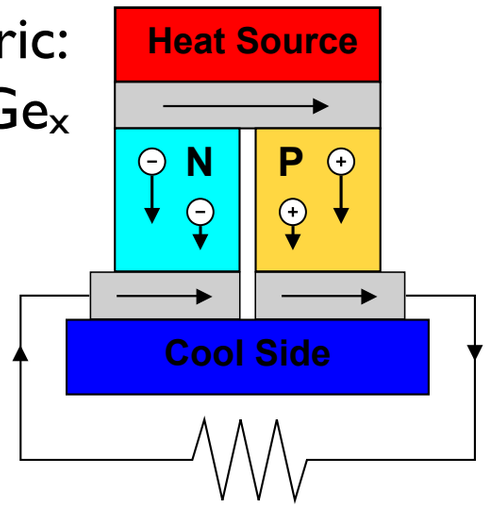
Semiconductor alloys

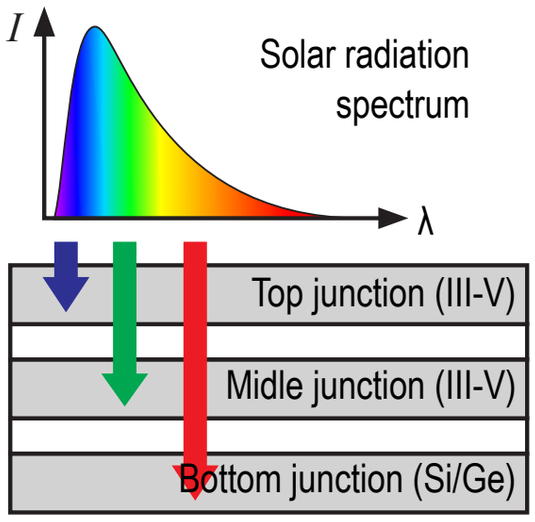


(InGaAl)P (InGa)N

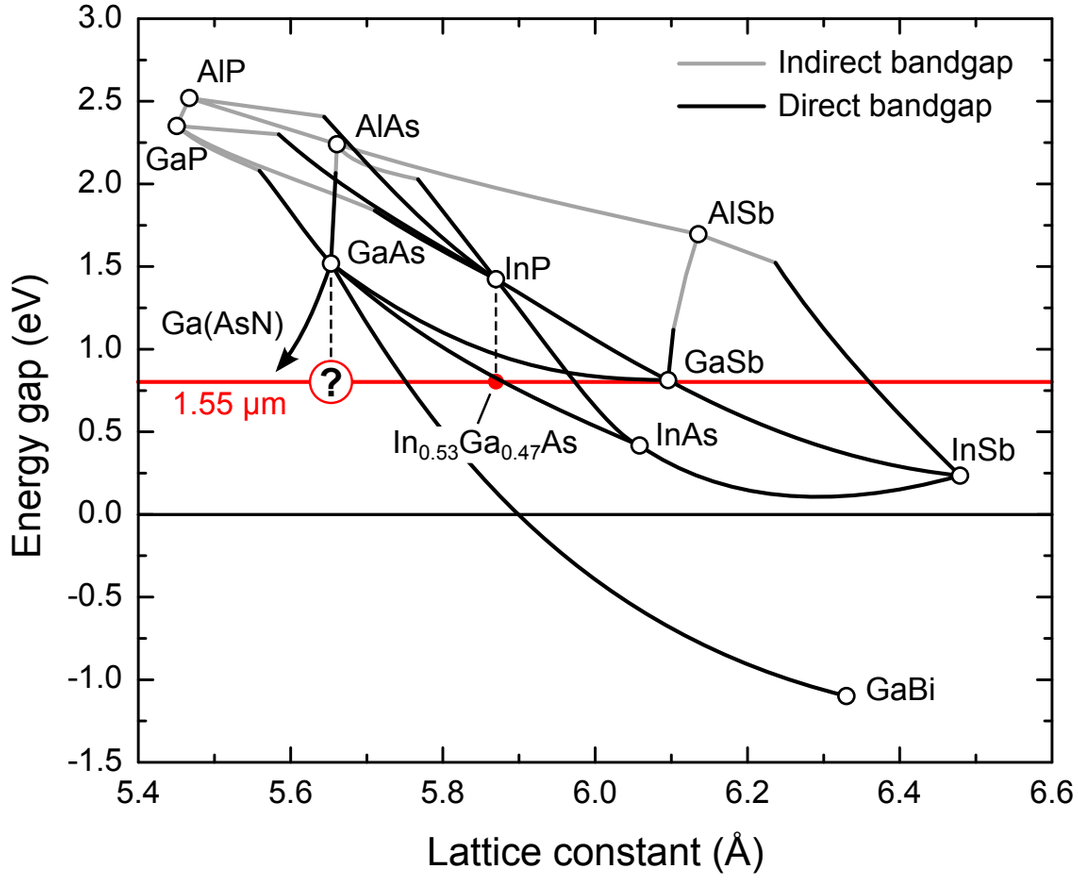
IR detector:
(HgCd)Te

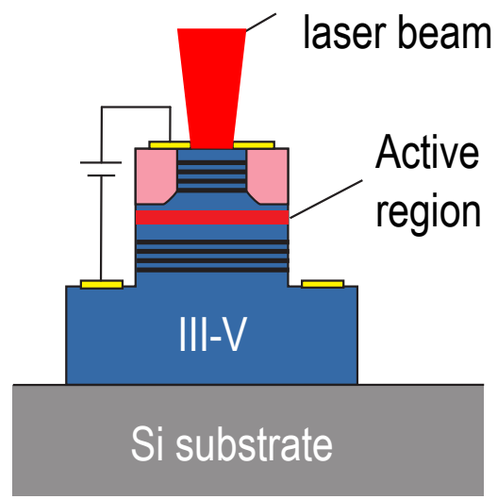
Thermoelectric:
$Si_{1-x}Ge_x$





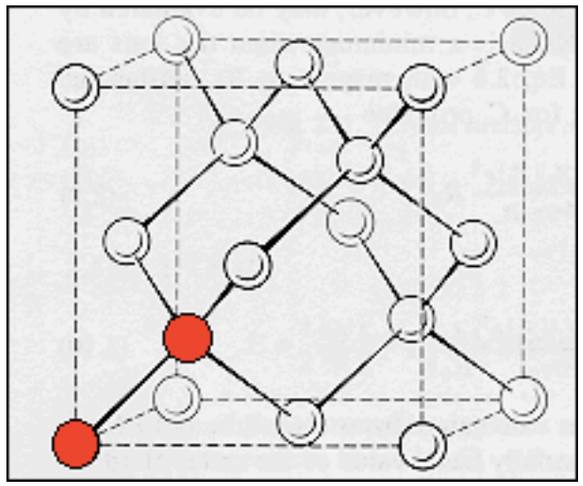
Eg = 1 eV junction:
(InGa)(NAs)





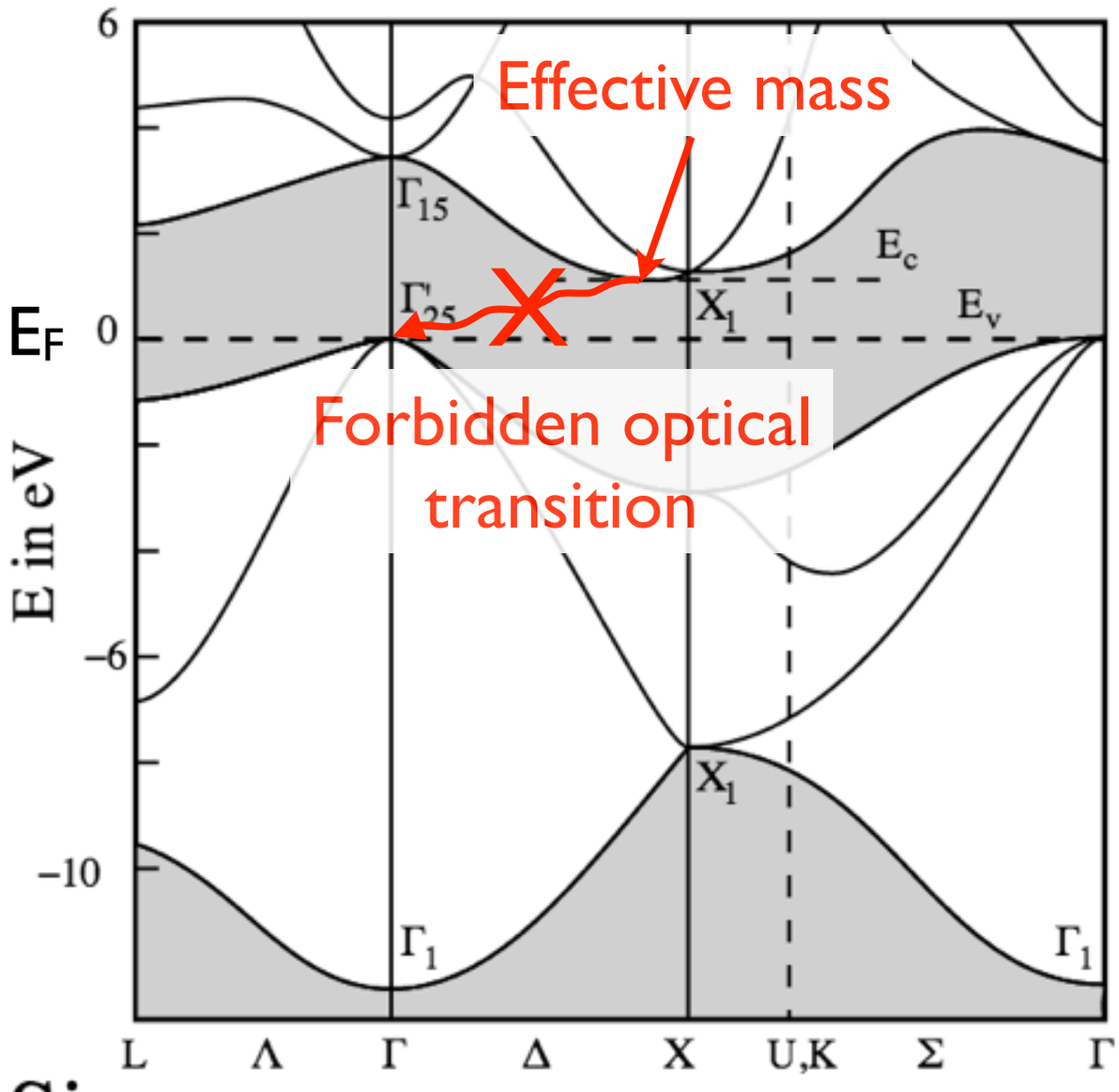
1.55 μm lasers:
(InGa)As
(InGa)(NAsSb)
Ga(AsBi)

Band structure

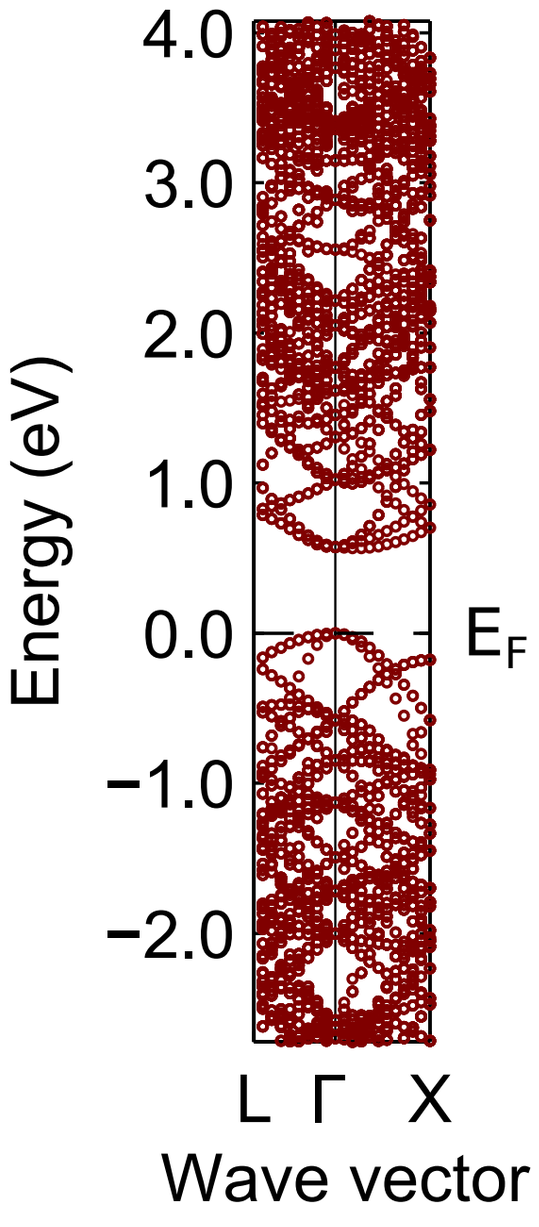


Energy gap ↕

Silicon
2-atom basis



Silicon
250-atom supercell



Unfolding the first-principle band structure

Plane wave expansion

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

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)

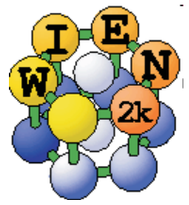
README.md

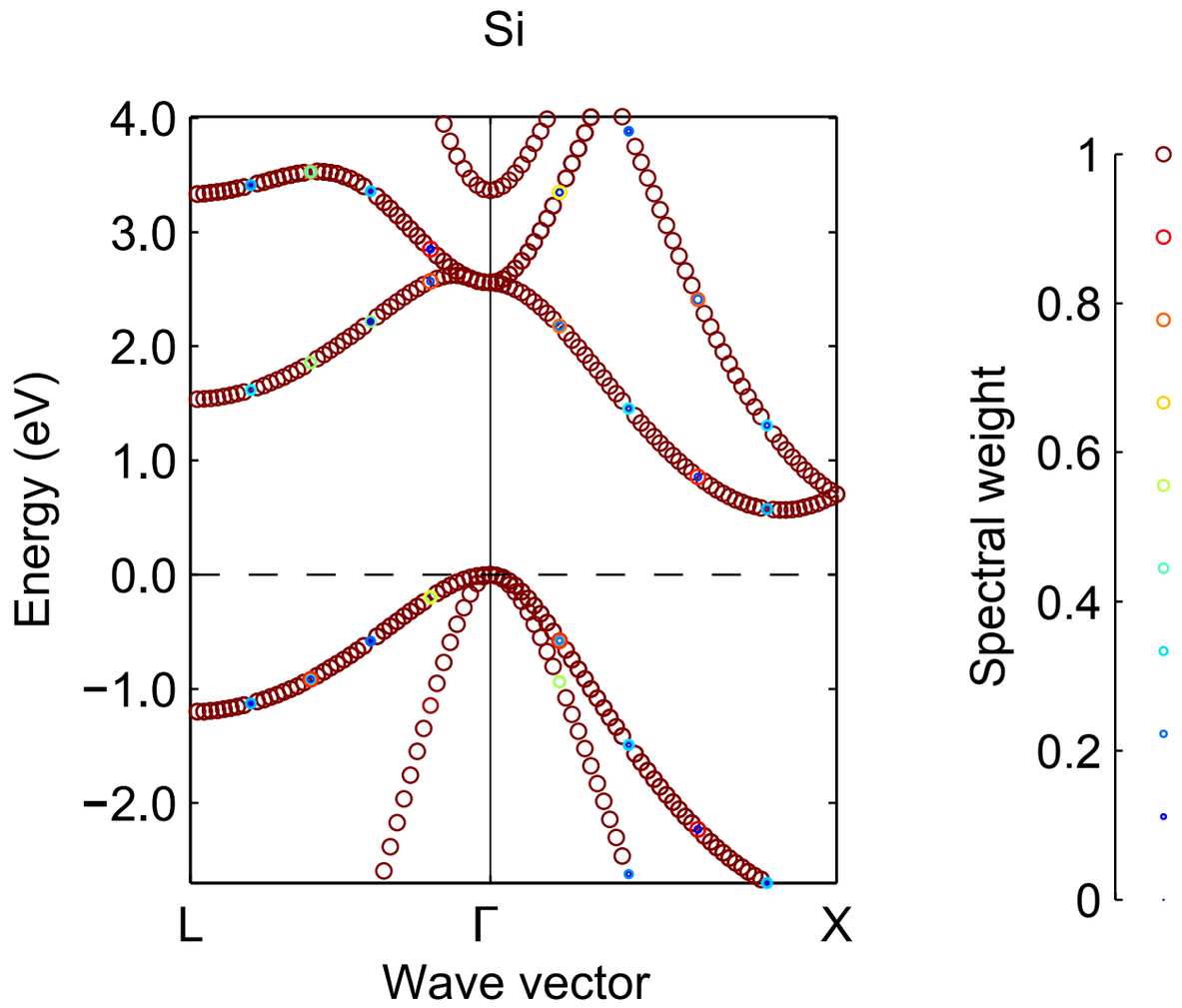
fold2Bloch

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

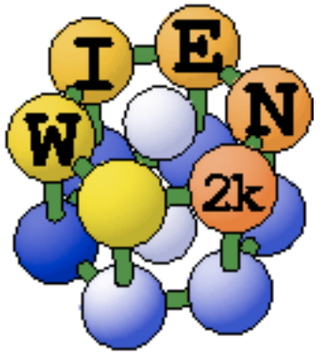
Contributors:

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





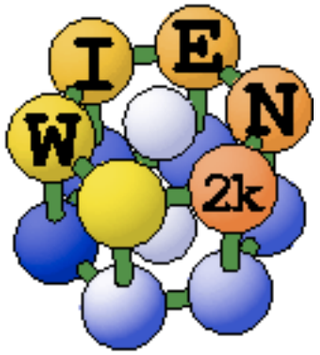
Workflow



- 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)

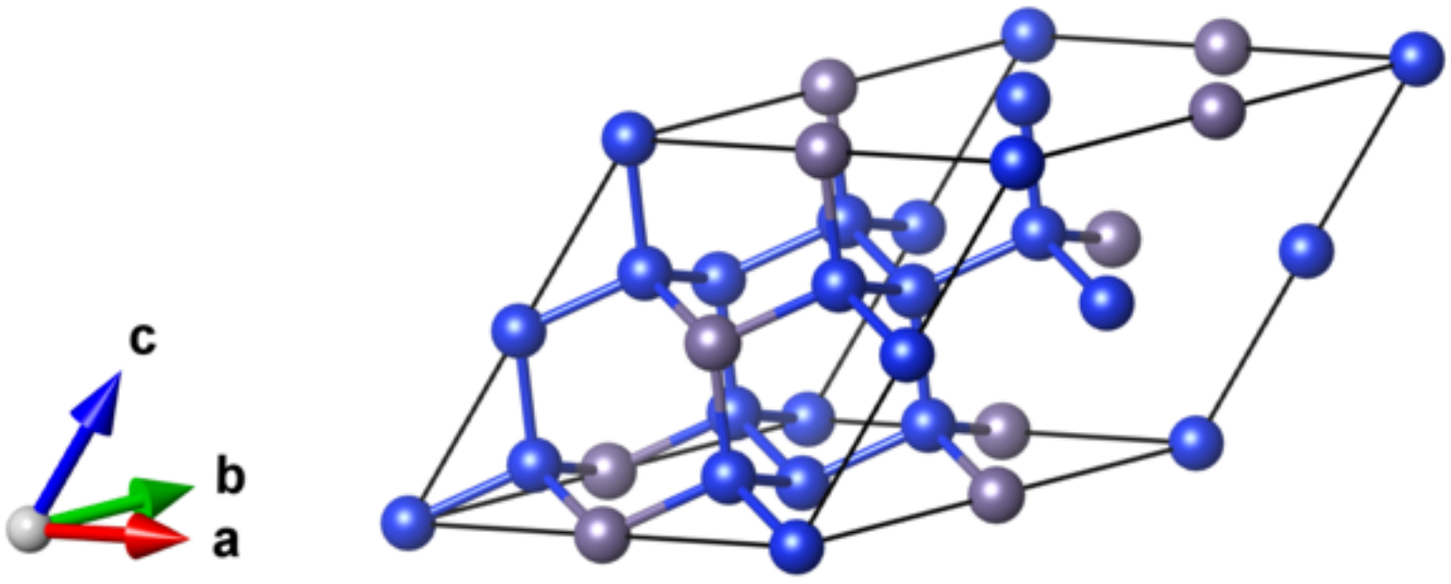
fold2Bloch

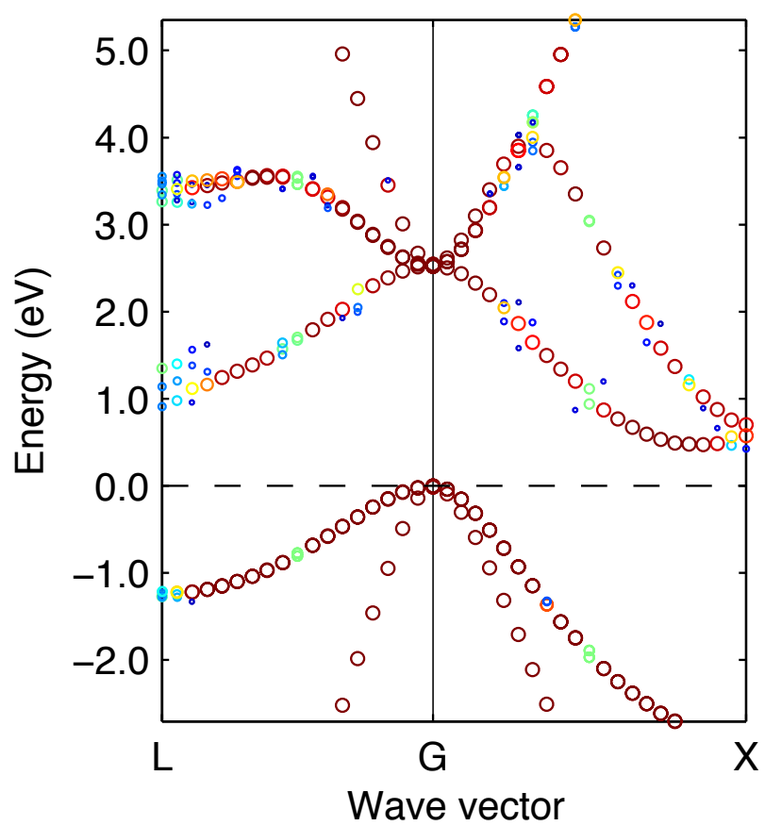
- Unfold band structure (`fold2Bloch`)

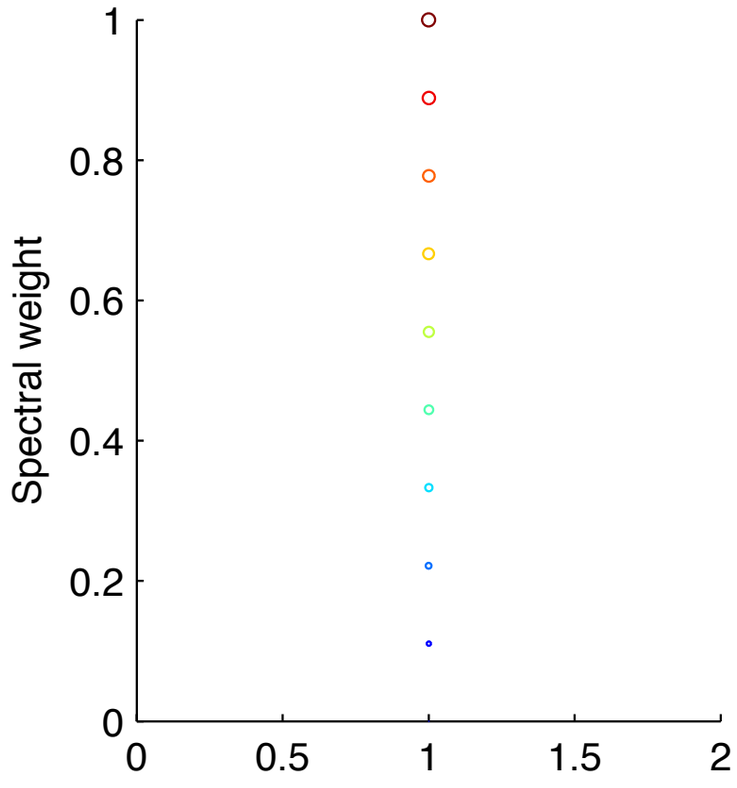

MATLAB

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

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

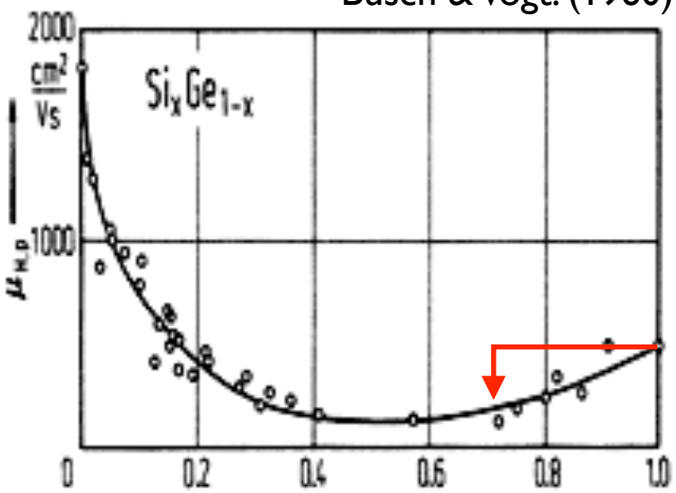


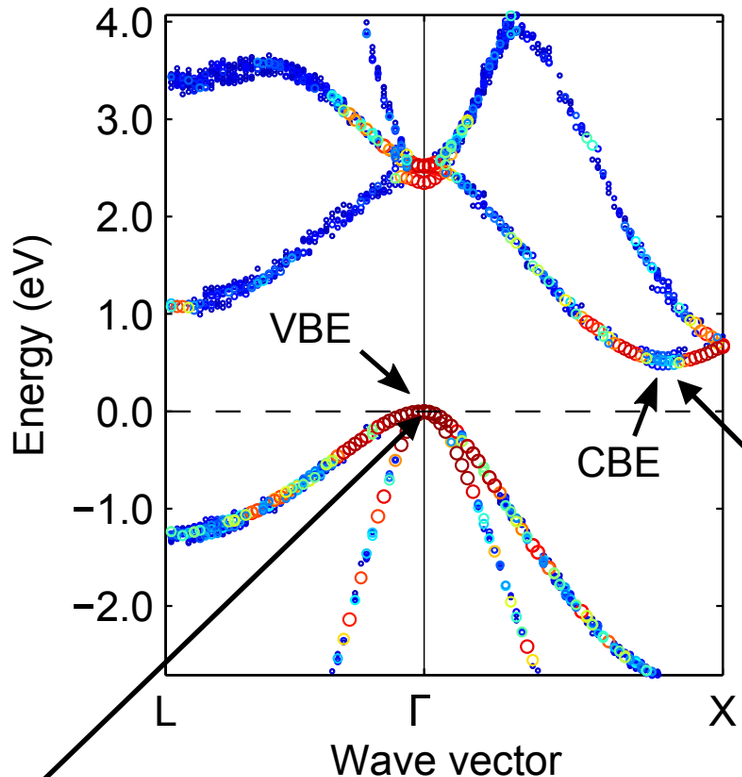


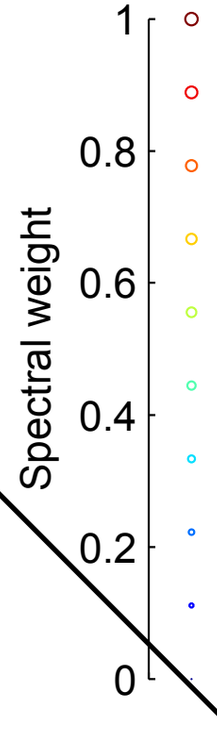


Thermoelectric material: $Si_{0.7}Ge_{0.3}$

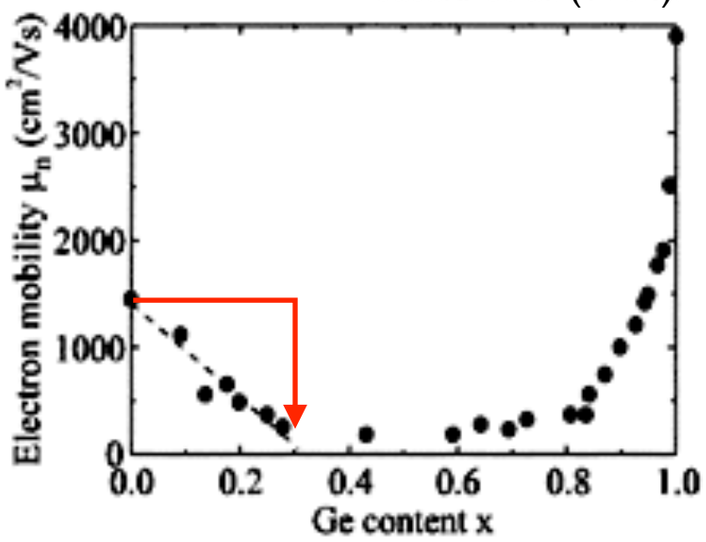
Busch & Vogt. (1960)







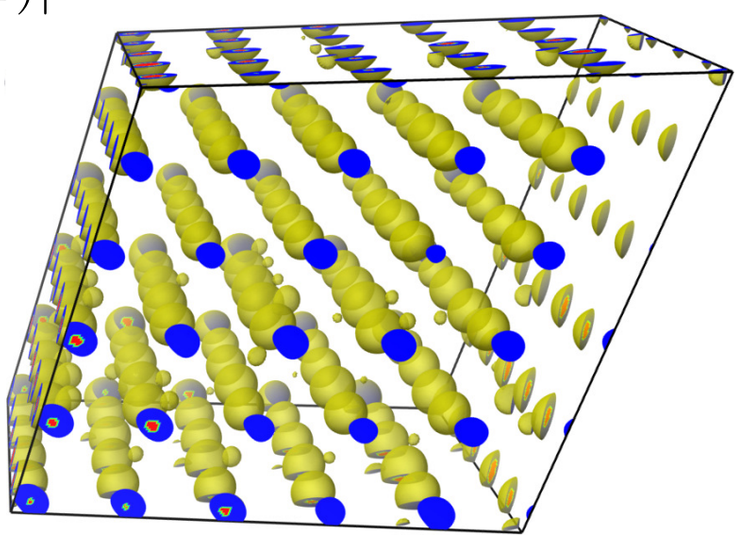
Landoldt-Bornstein (1982, 1987);
Sasaki et al. (1984).



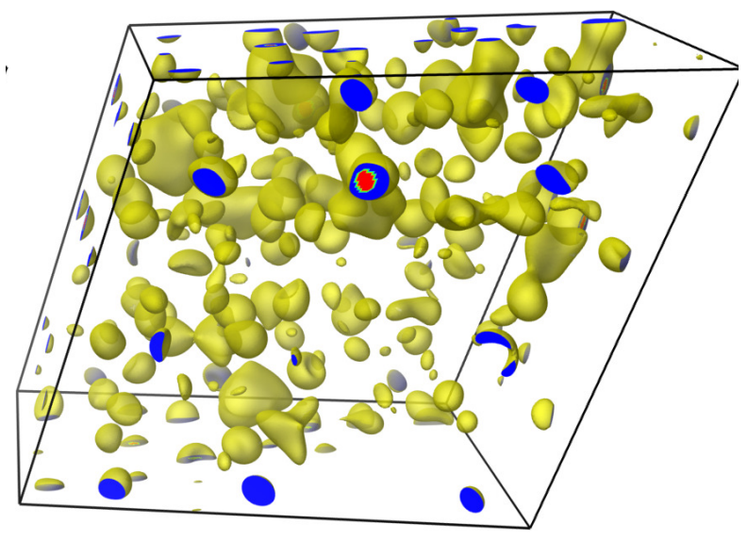
$\Delta r \Delta k \sim 1$

VBE

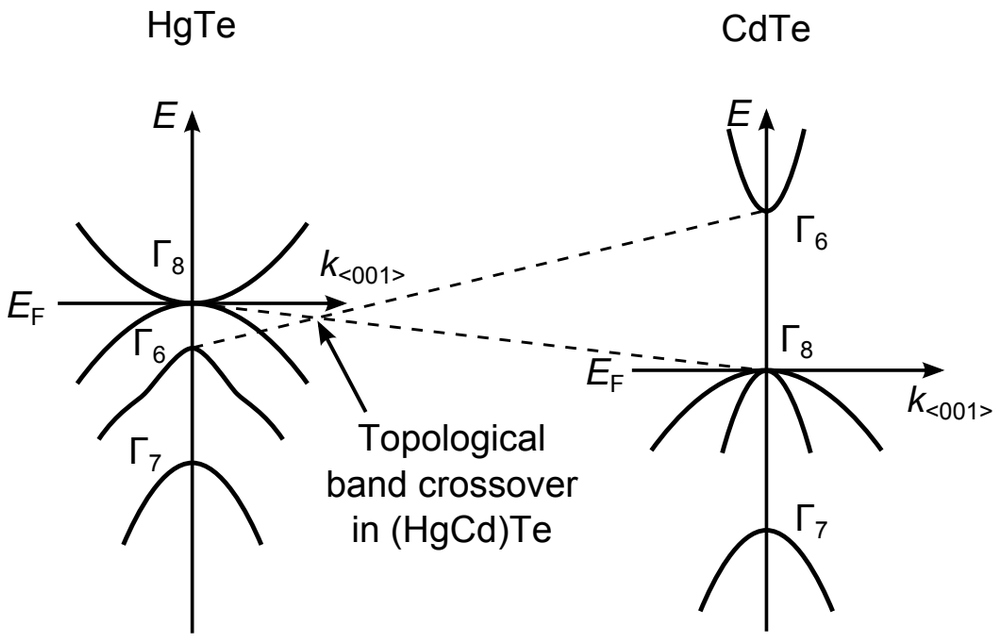
$|\psi(\mathbf{r})|^2$

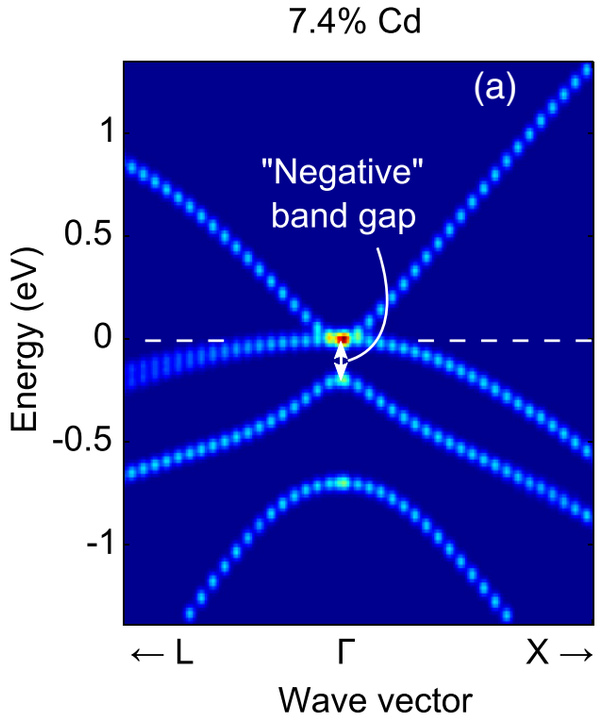


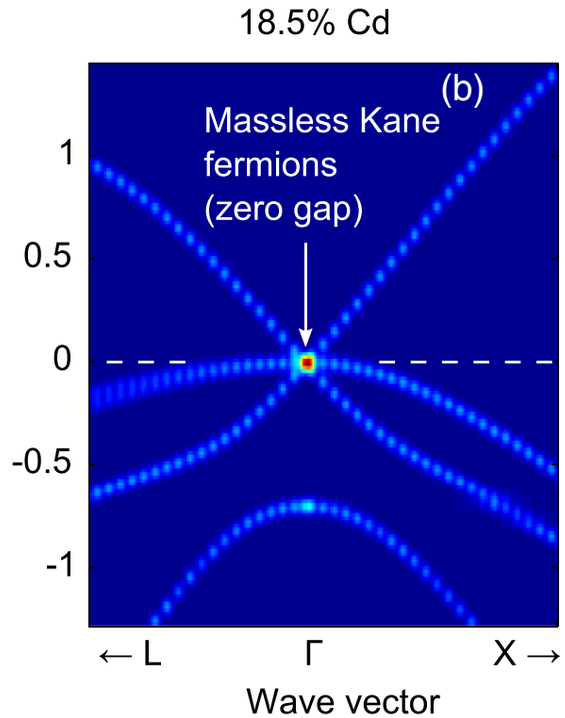
CBE



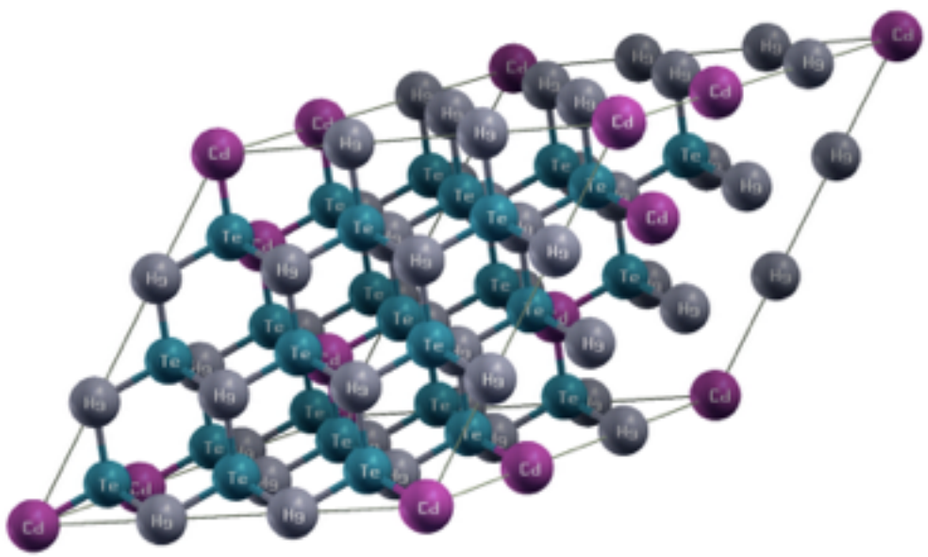
(Hg,Cd)Te band structure evolution

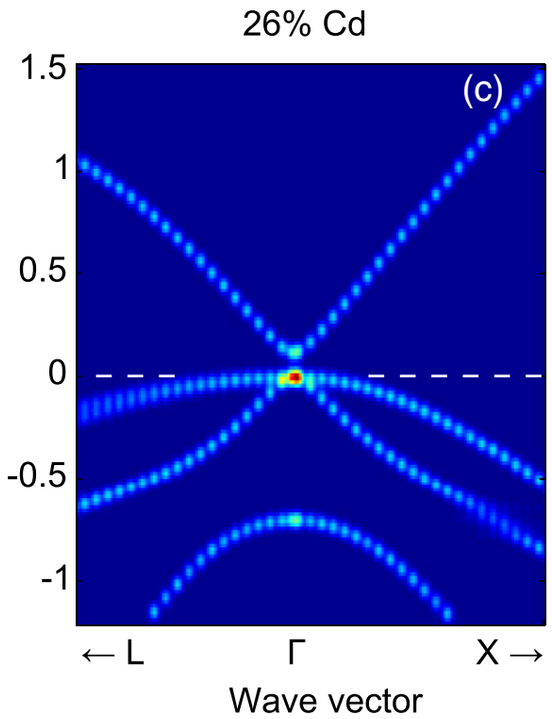


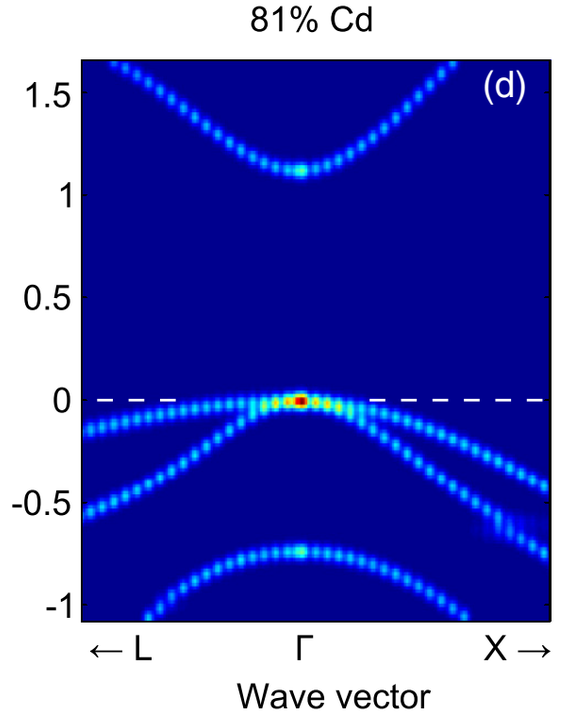




$Hg_{22}Cd_5Te_{27}$

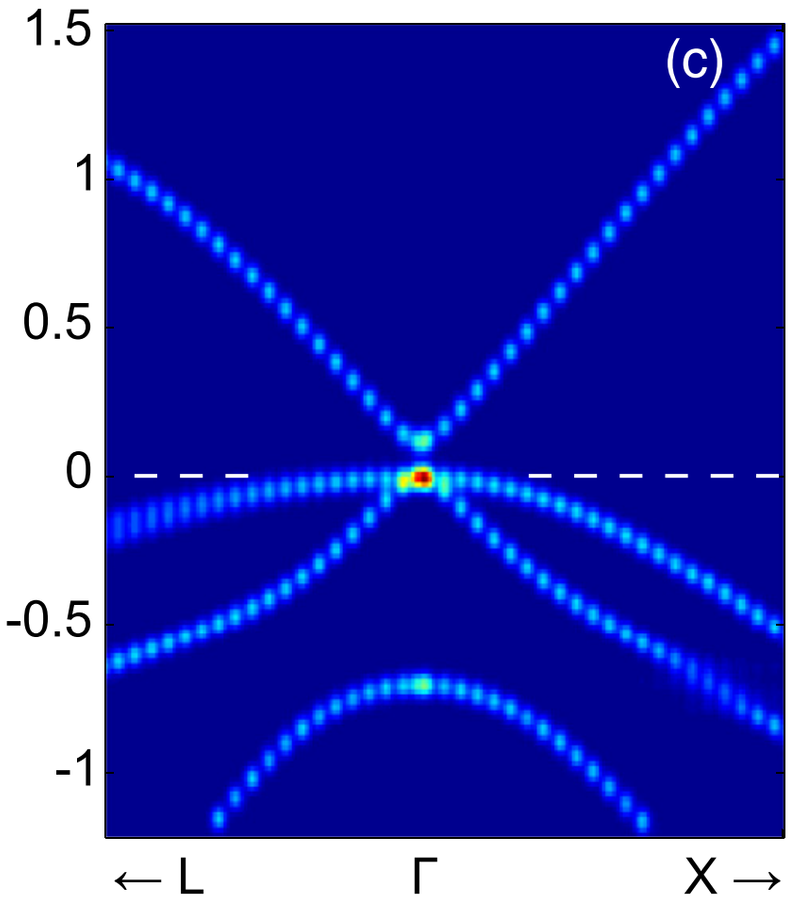






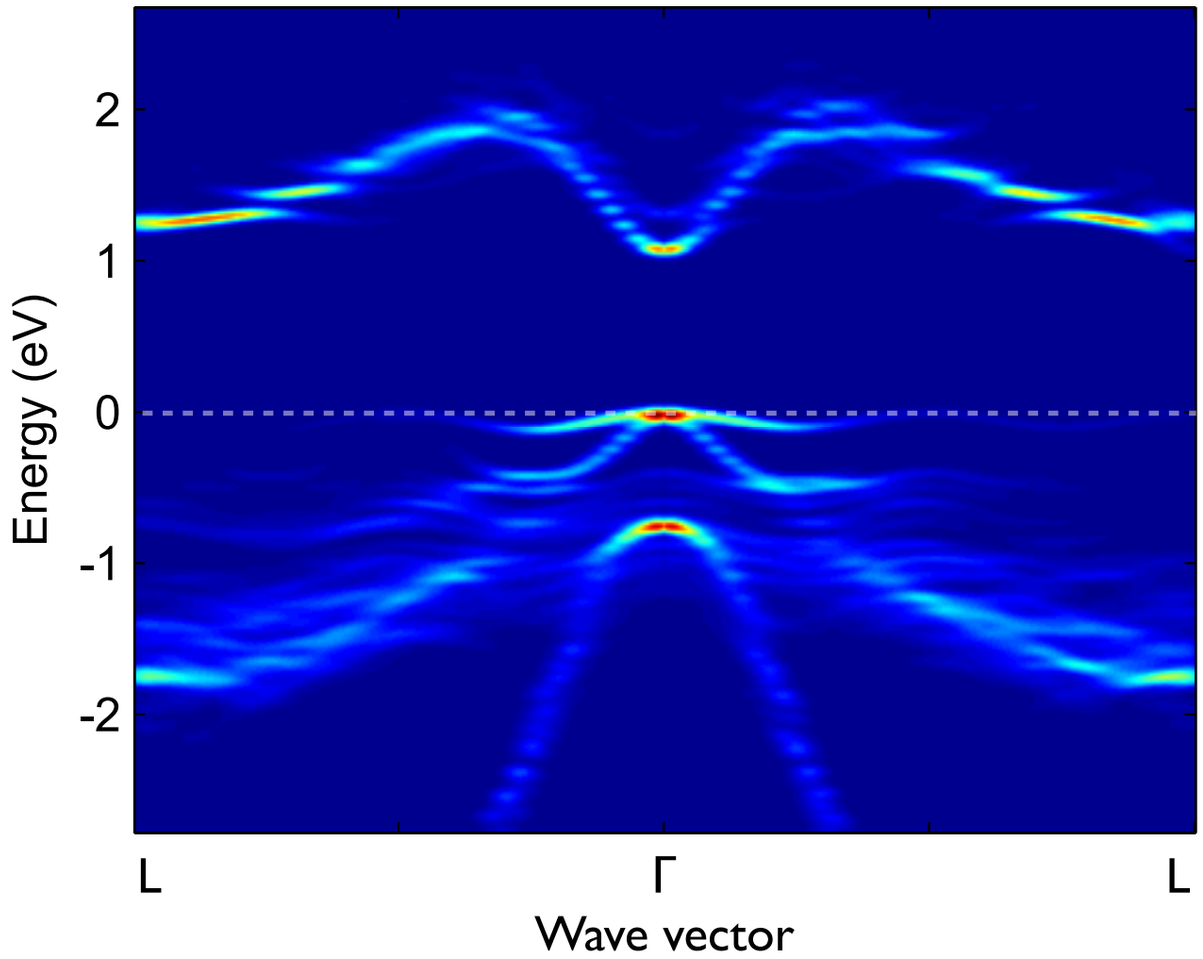
Impact of alloying disorder on charge transport

CdTe → (HgCd)Te



μ_e = 1,100 → 1,000,000 $cm^2V^{-1}s^{-1}$

GaAs → Ga(AsBi)



μ_h = 200 → 10 $cm^2V^{-1}s^{-1}$

μ_e = 4,000 → 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

NSERC CRSNG

Ontario Research Fund