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

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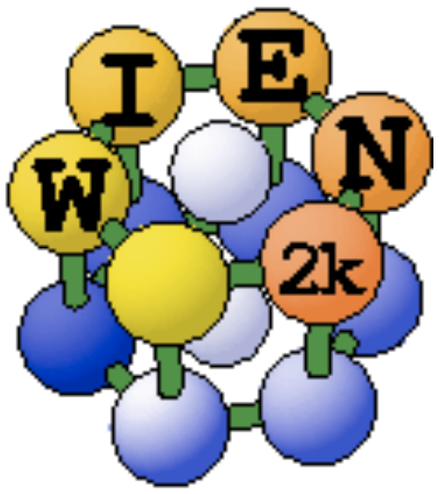
# Outline

- Wannier functions with Wien2k (wien2wannier)
- Modern theory of polarization (Berry phase)
- Tutorials overview

# Wannier functions

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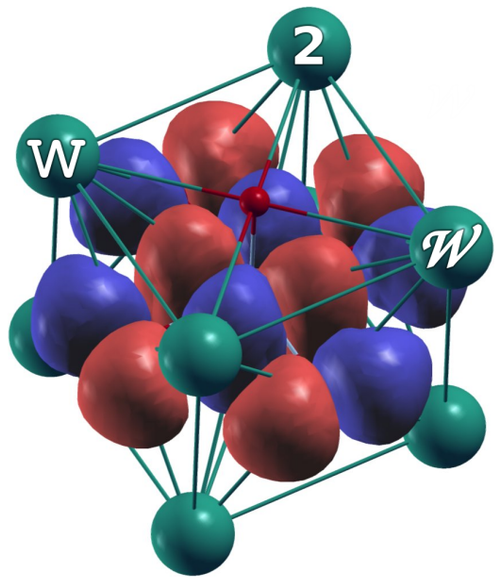



+

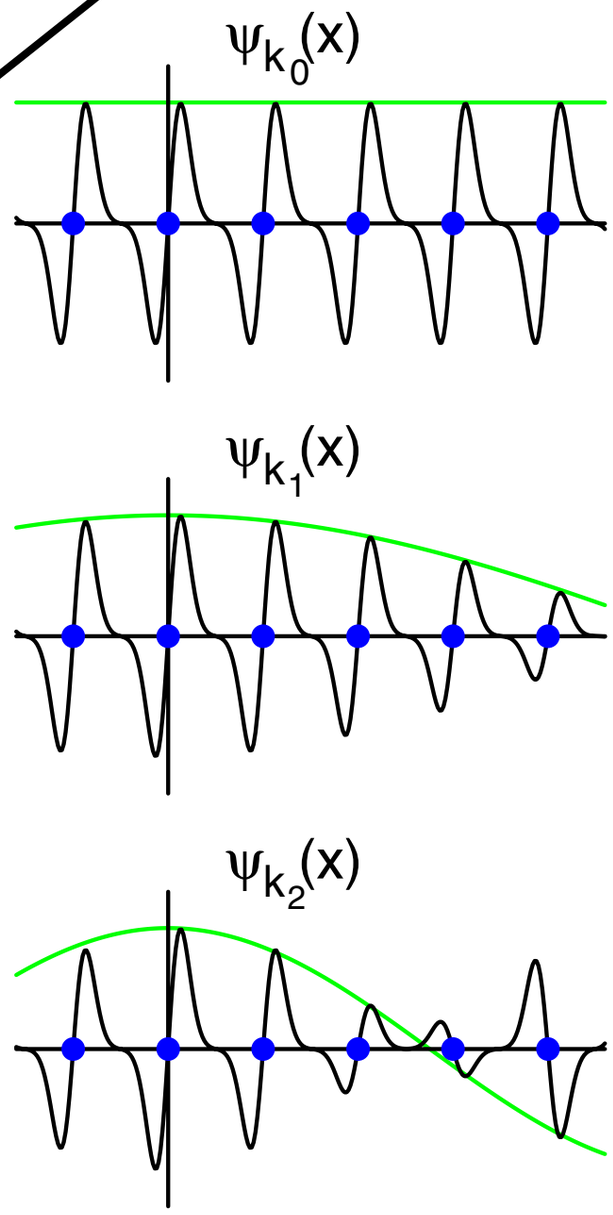
WANNIER90

# Bloch *vs* Wannier functions

## Bloch functions

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

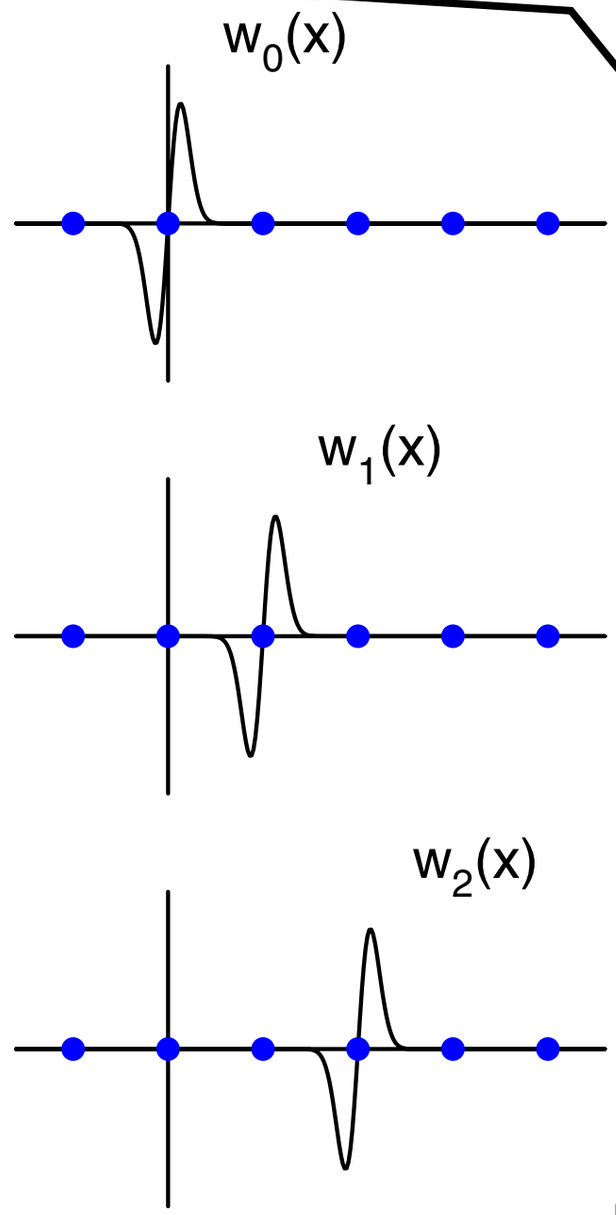
Indexed by the wave vector




## Wannier functions

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

Indexed by the lattice vector in real space




Both sets: complete and orthonormal

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

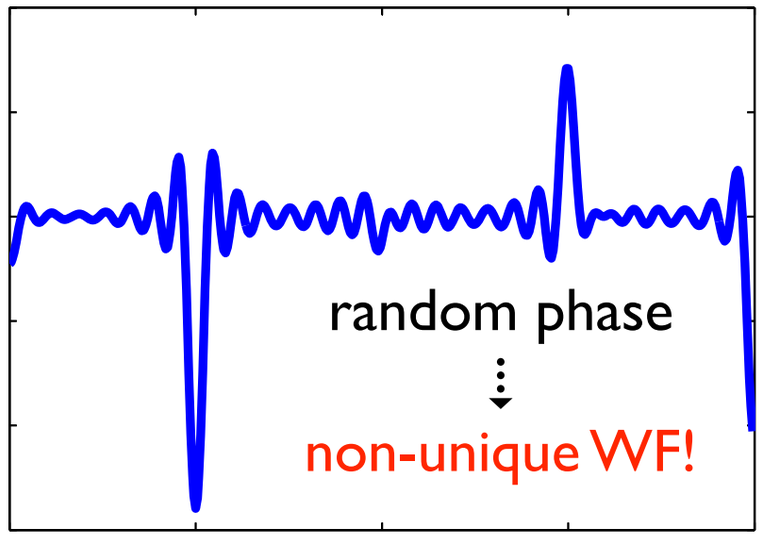
# Max. localized Wannier functions (MLWF)

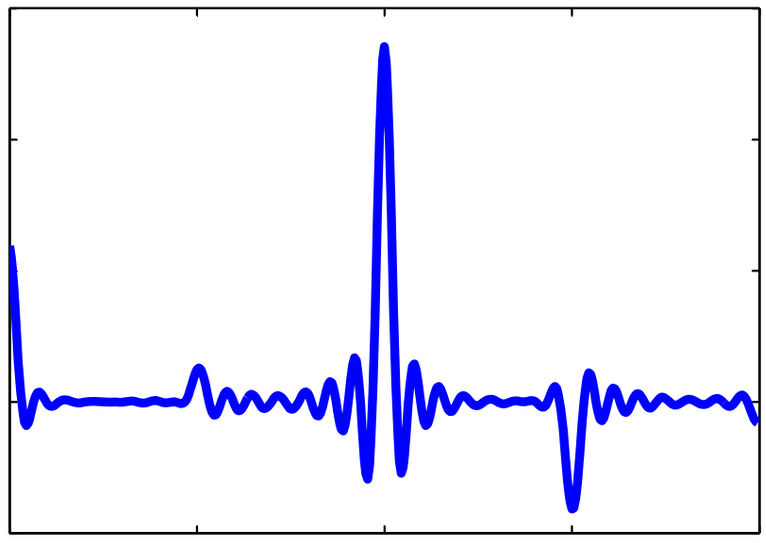
Bloch functions (more precisely):

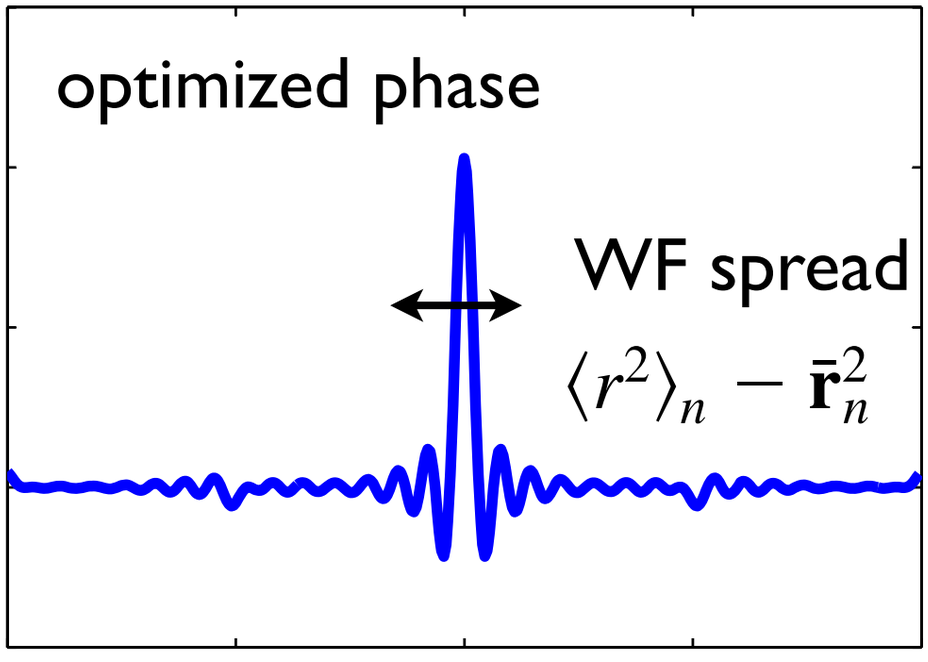
$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, e^{i\phi_{n\mathbf{k}}}$$

gauge freedom

(does not change the physical description of the system)






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

# Wannier functions matrix elements

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

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

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

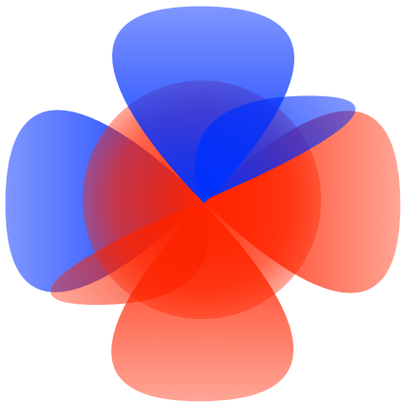
$\hat{\mathbf{r}} = i\nabla_{\mathbf{k}}$ -- position operator

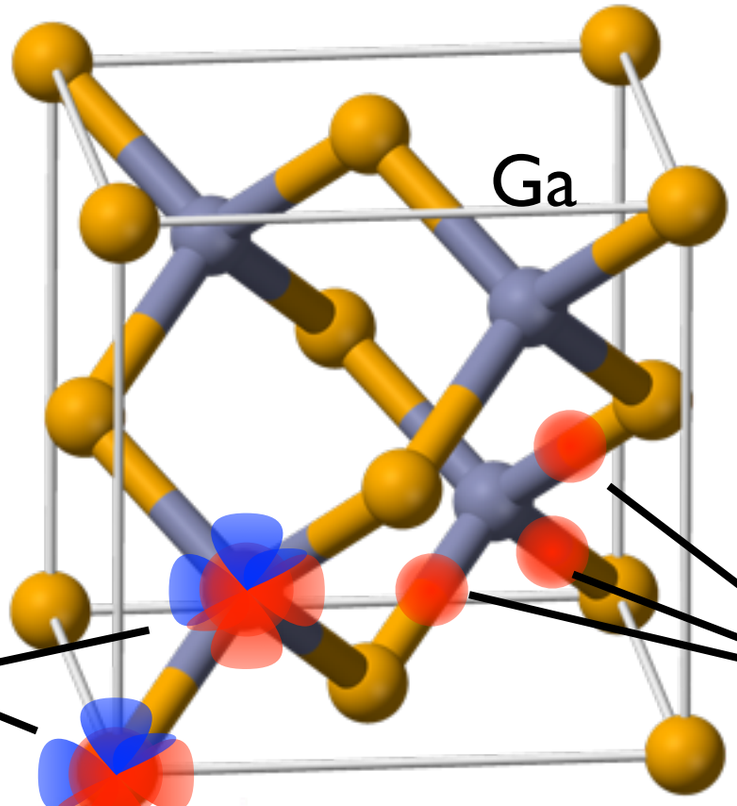
$$\langle 0n|\mathbf{r}|0n\rangle = i\,\frac{V}{(2\pi)^3}\int d\mathbf{k}\,\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$$

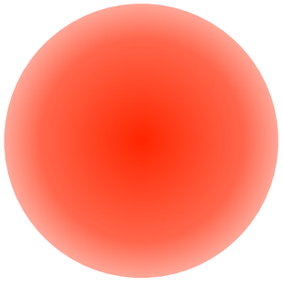
related to Berry phase, electronic polarization

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

# Initial projections

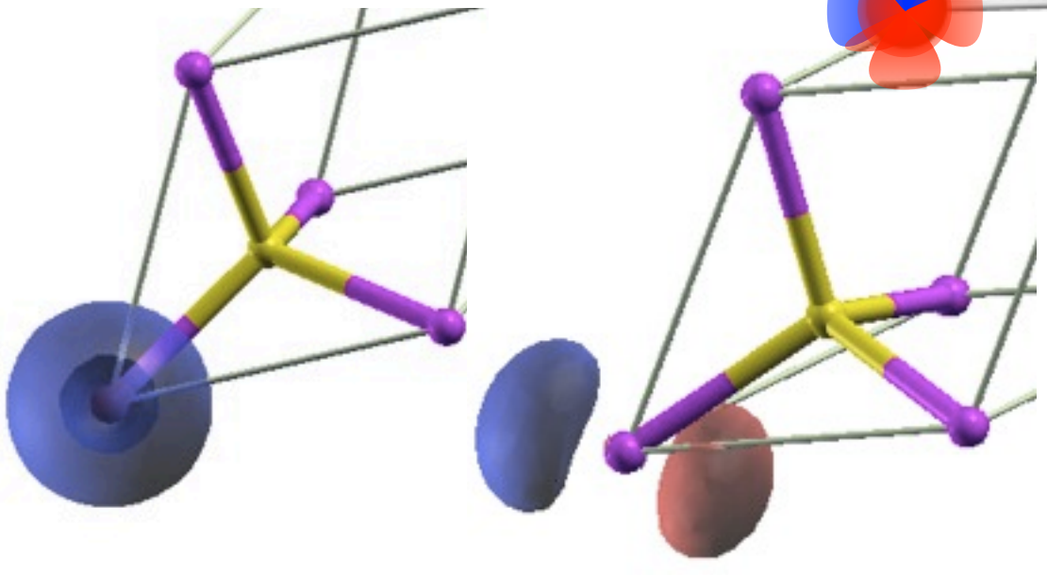


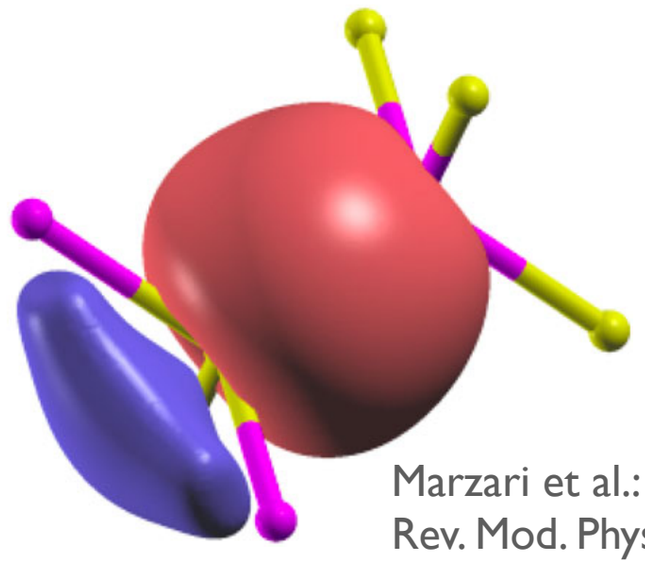


Atom centered $sp^3$-like

Bond centered s-like



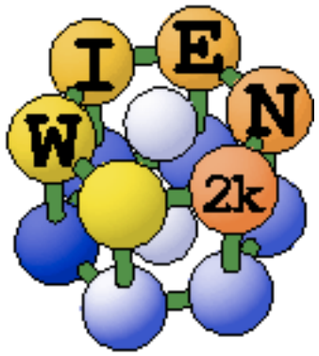


Marzari et al.:
Rev. Mod. Phys. (2012)

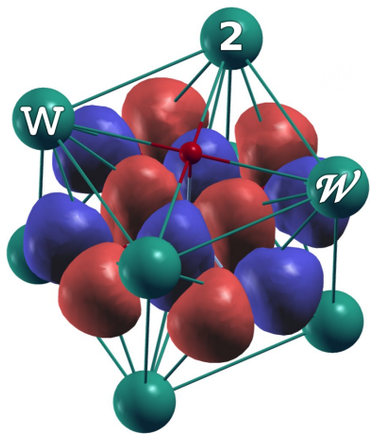
- includes *bonding* and *anibonding* states
- building effective hamiltonian

- includes *valence* states
- charge transfer and polarization

# Workflow



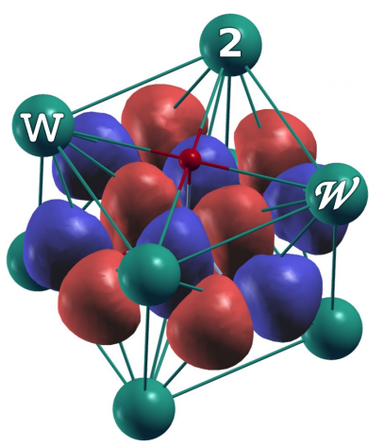

- Regular SCF calculation
- Band structure plot




- 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 $M_{mn}, A_{mn}$ (`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

# Wannier functions as a tight-binding basis

(Atom-centered WF)

$ less GaAs-WANN_hr.dat

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

Home unit cell

⟨s1|

|s1⟩

⟨s2|

Matrix element (eV)
⟨s1|H|s1⟩ = Es1

Im part = 0

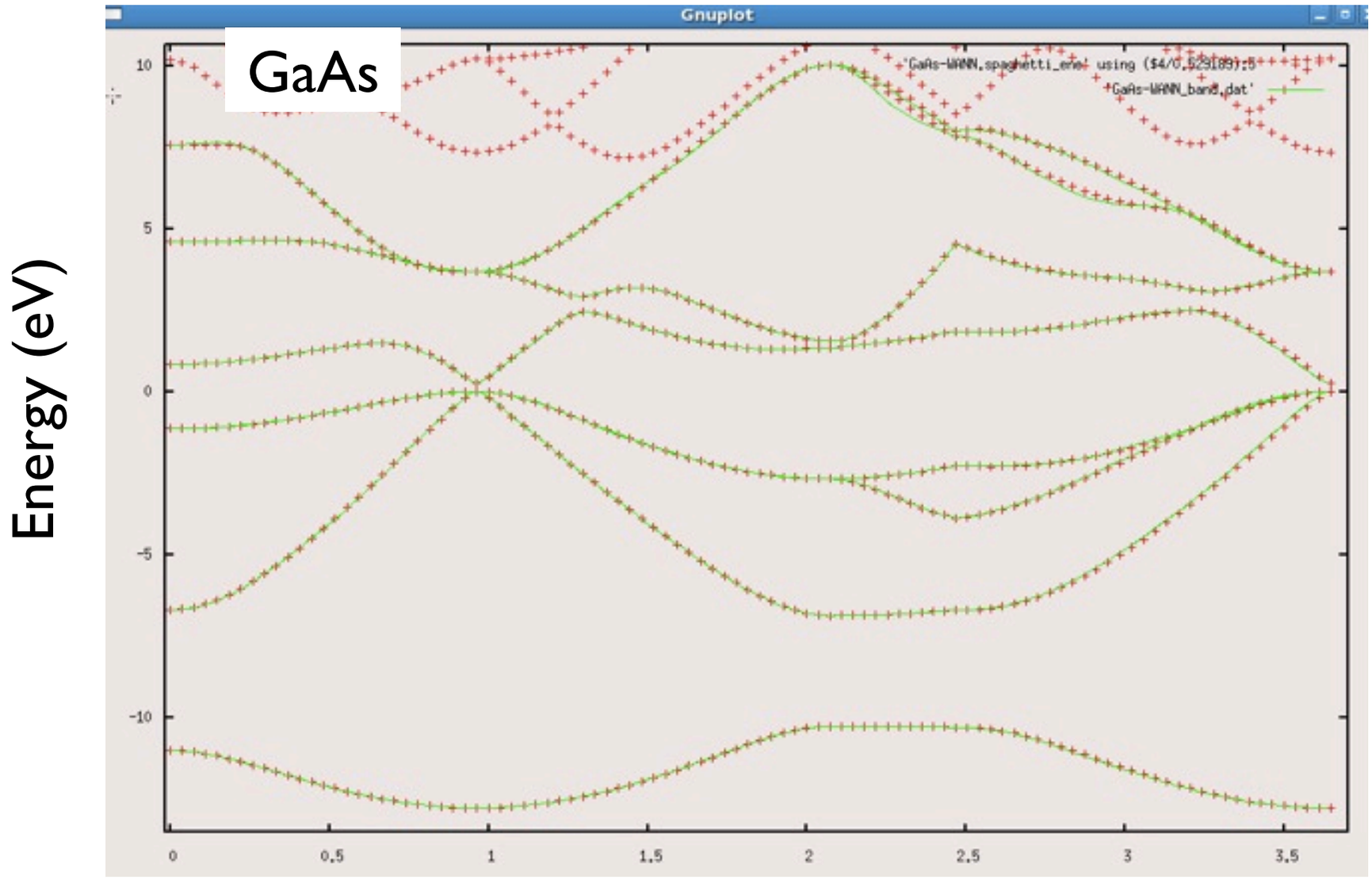
Matrix element (eV)
⟨s2|H|s1⟩ = Vssσ

⟨p2|H|s1⟩ = Vsp

Neighbour unit cell

WF are well localized
⇒ nearest-neighbour suffice

# Band structure, entanglement

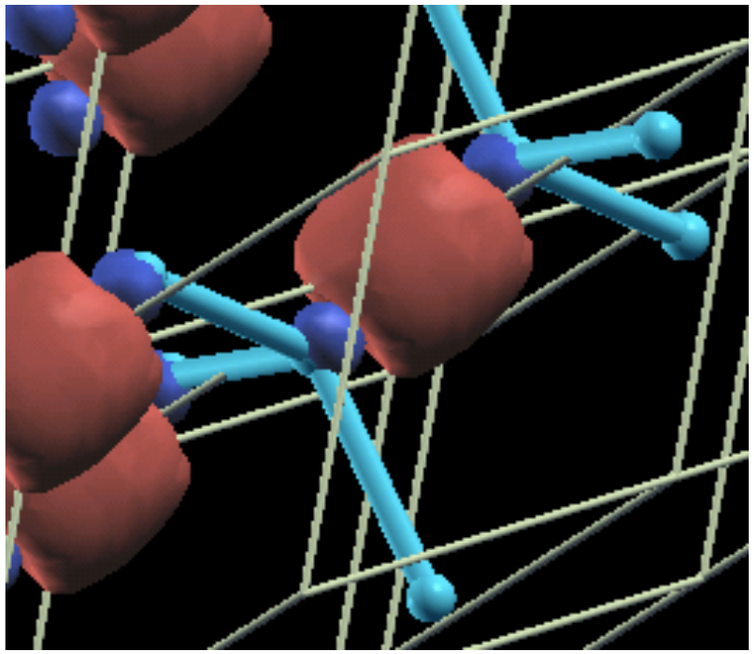



+ original Wien2k band structure
– Band structure computed from Wannier hamiltonian

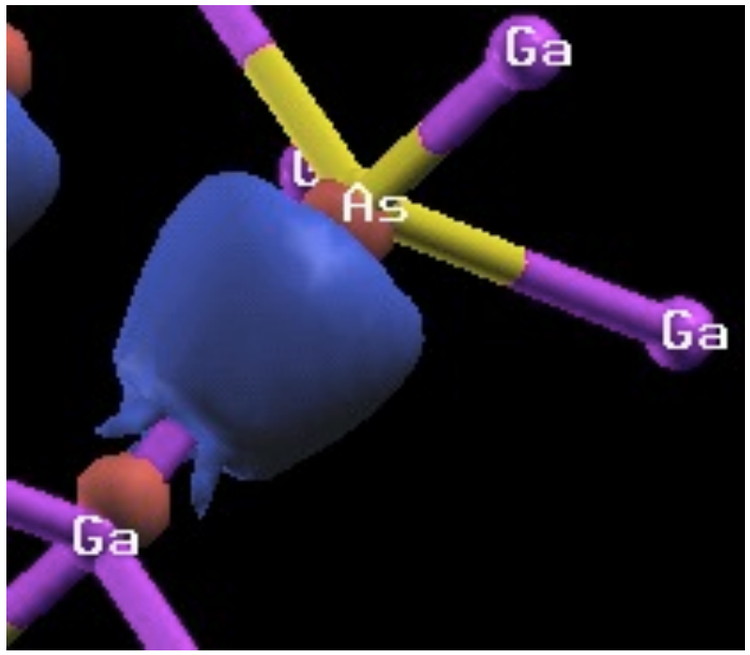
# Relation to polarization

Bond-centered WF

Si



GaAs




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

+ $Z_{As}$

− Wannier center $q_e$

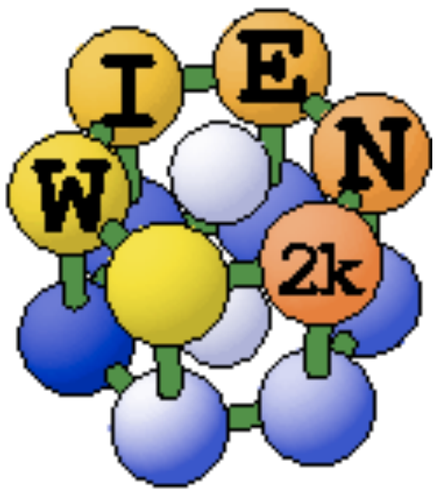
+ $Z_{Ga}$

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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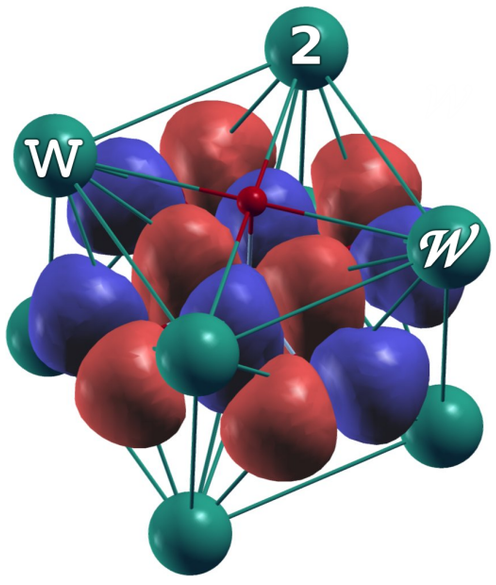
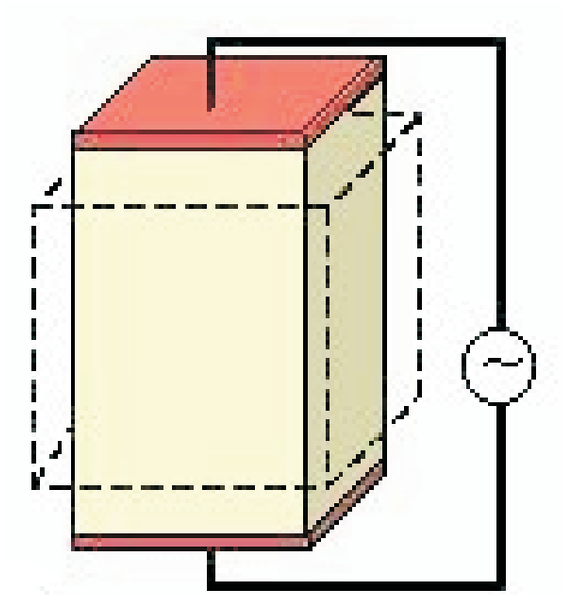


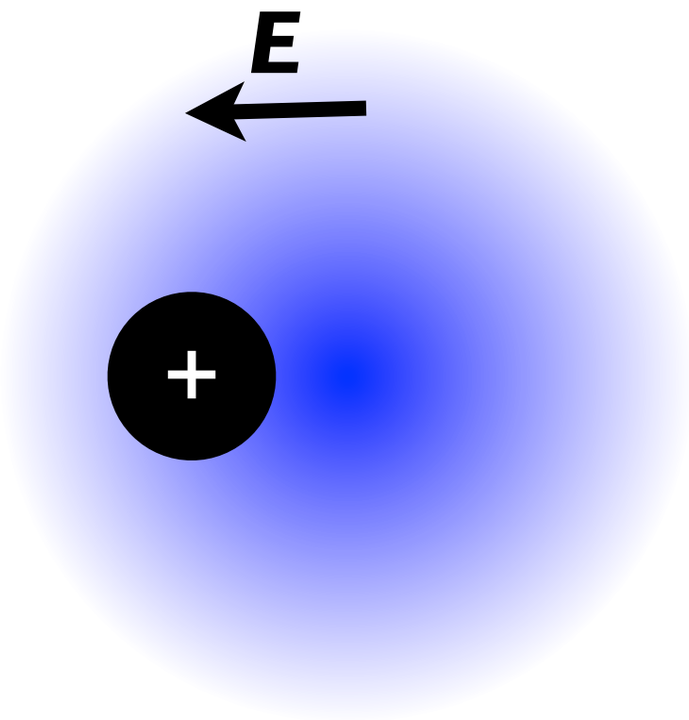

+ BerryPI

# Material properties related to polarization

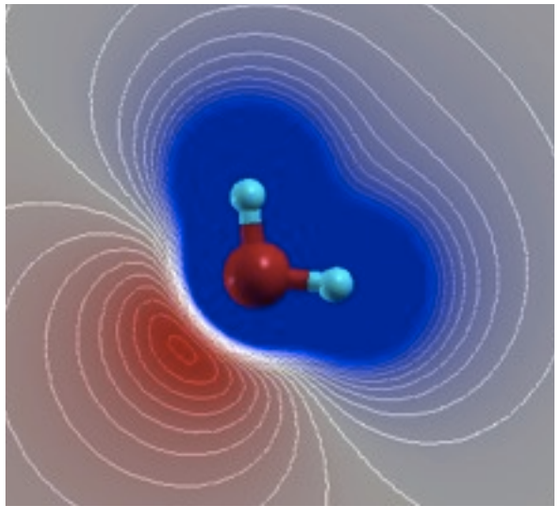
## Piezo- and Ferroelectricity



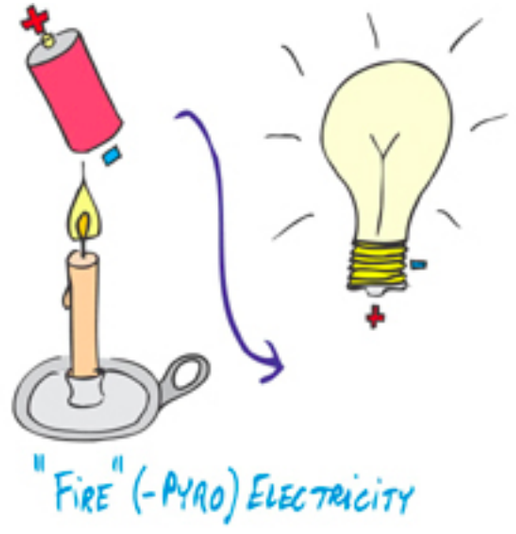
## Dielectric screening



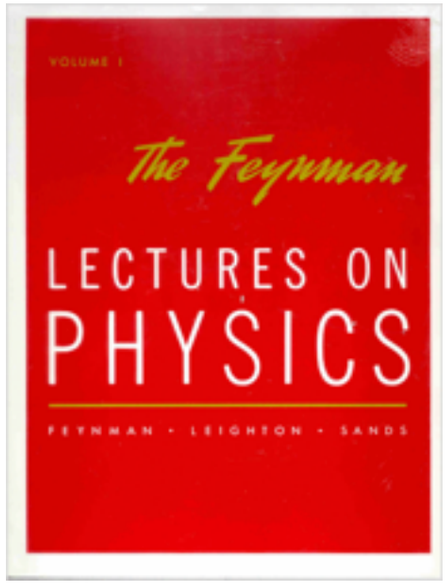

## Effective charge



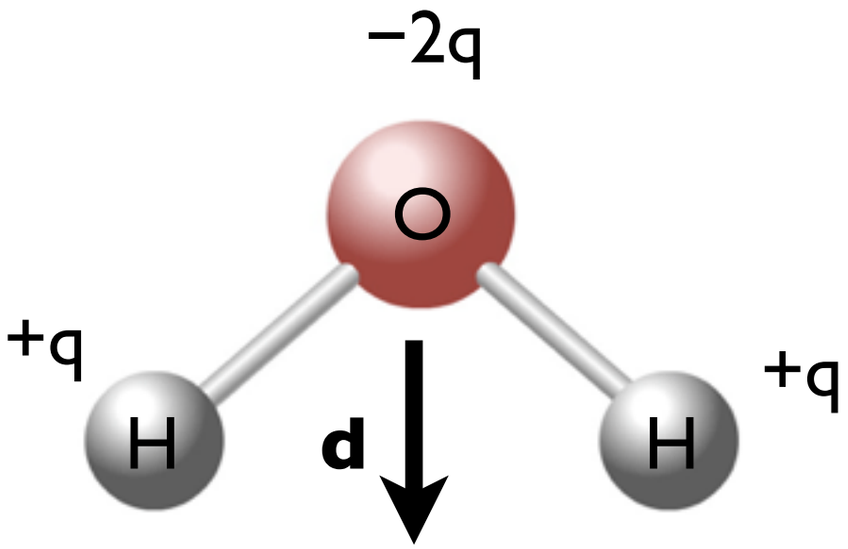
## Pyroelectricity

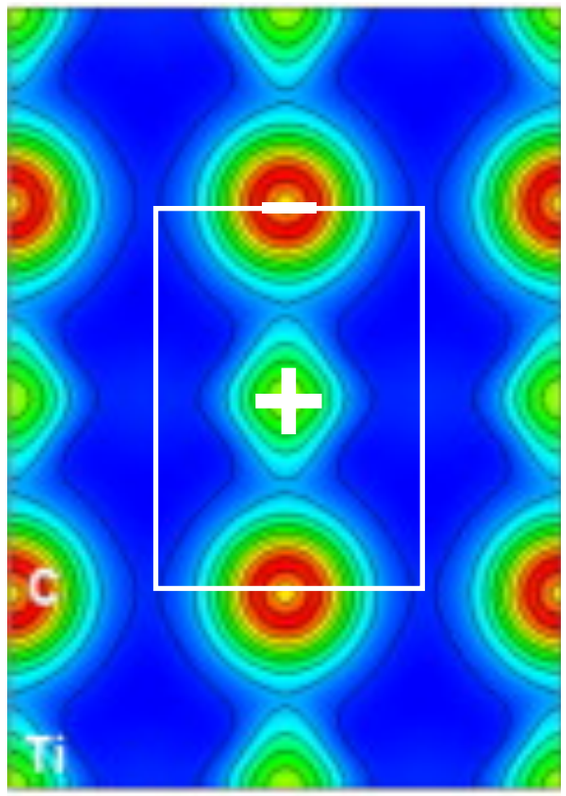


# What is polarization?




We will now assume that in each atom there are charges $q$ separated by a distance $\delta$, so that $q\delta$ is the dipole moment per atom. (We use $\delta$ 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



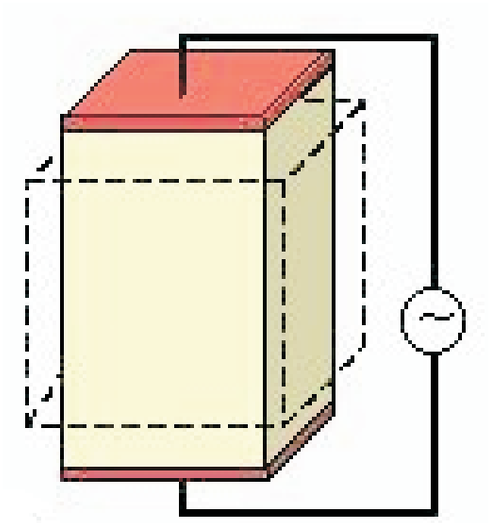

Polarization for periodic solids is undefined

# Modern theory of polarization

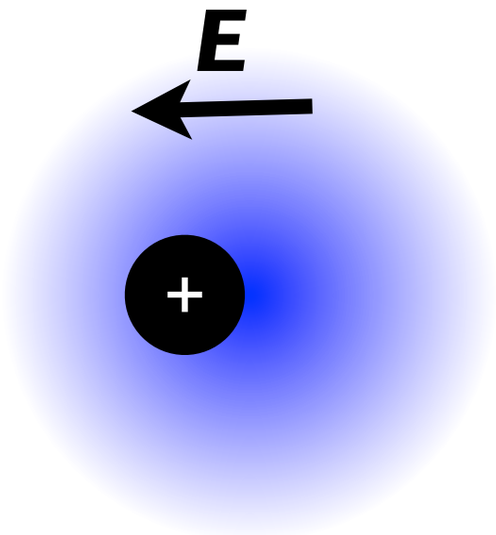
Pioneered by *King-Smith*, *David Vanderbilt* and *Raffaele Resta*

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

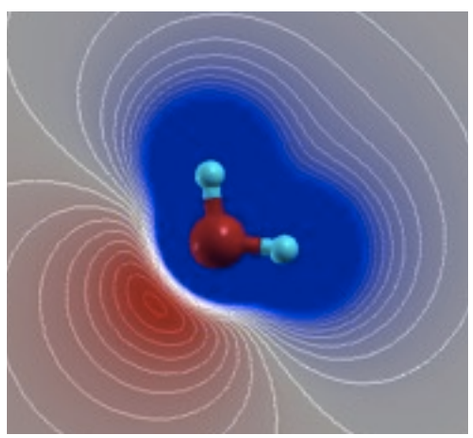
$$\Delta \mathbf{P} = \mathbf{P}^{(0)} - \mathbf{P}^{(1)}$$



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



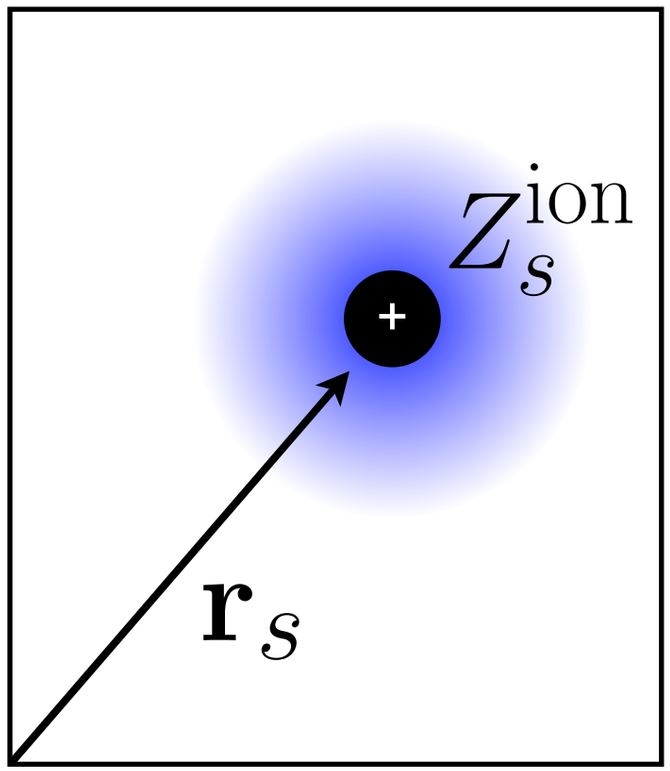

$$\frac{\Delta \mathbf{P}}{\Delta \mathbf{E}}$$



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


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

# Components of polarization




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

ionic — electronic

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

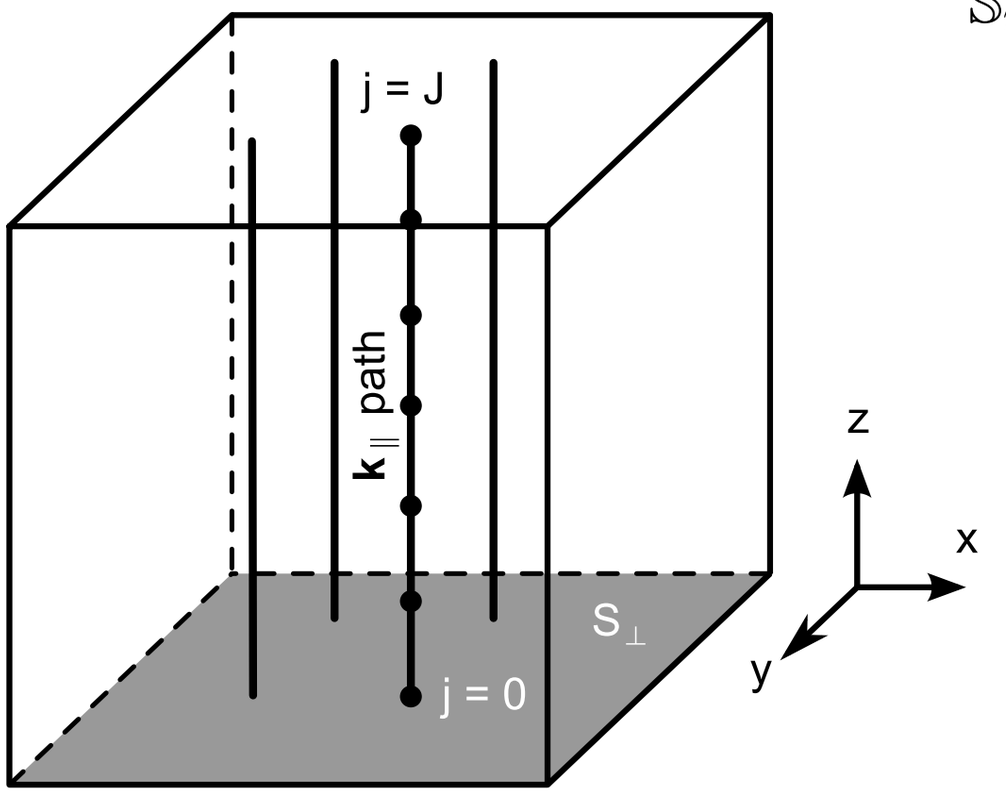
In Wien2k $Z_s^{\text{ion}}$ is the core charge

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

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

# Berry phase

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




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

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

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

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

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

# BerryPI

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

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

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

completed SCF cycle

↓

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

↓

prepare nearest-neighbour k-point list

↓

calculate wavefunctions (`lapw1`)

↓

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

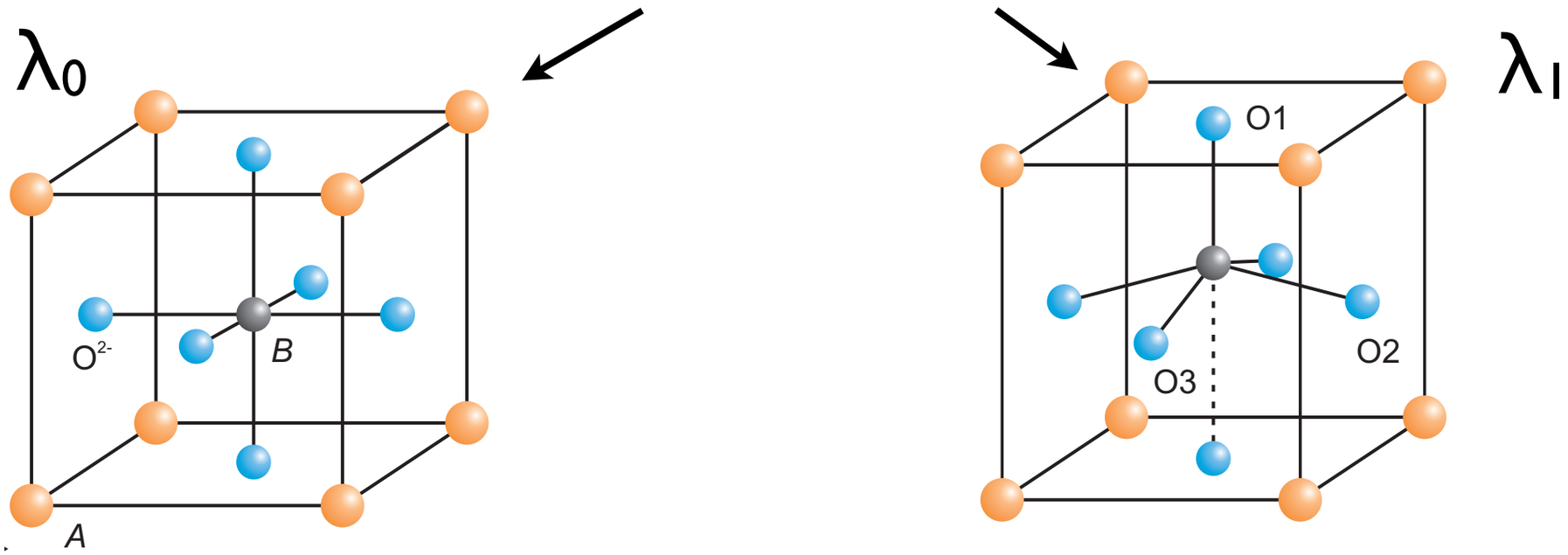
↓

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

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

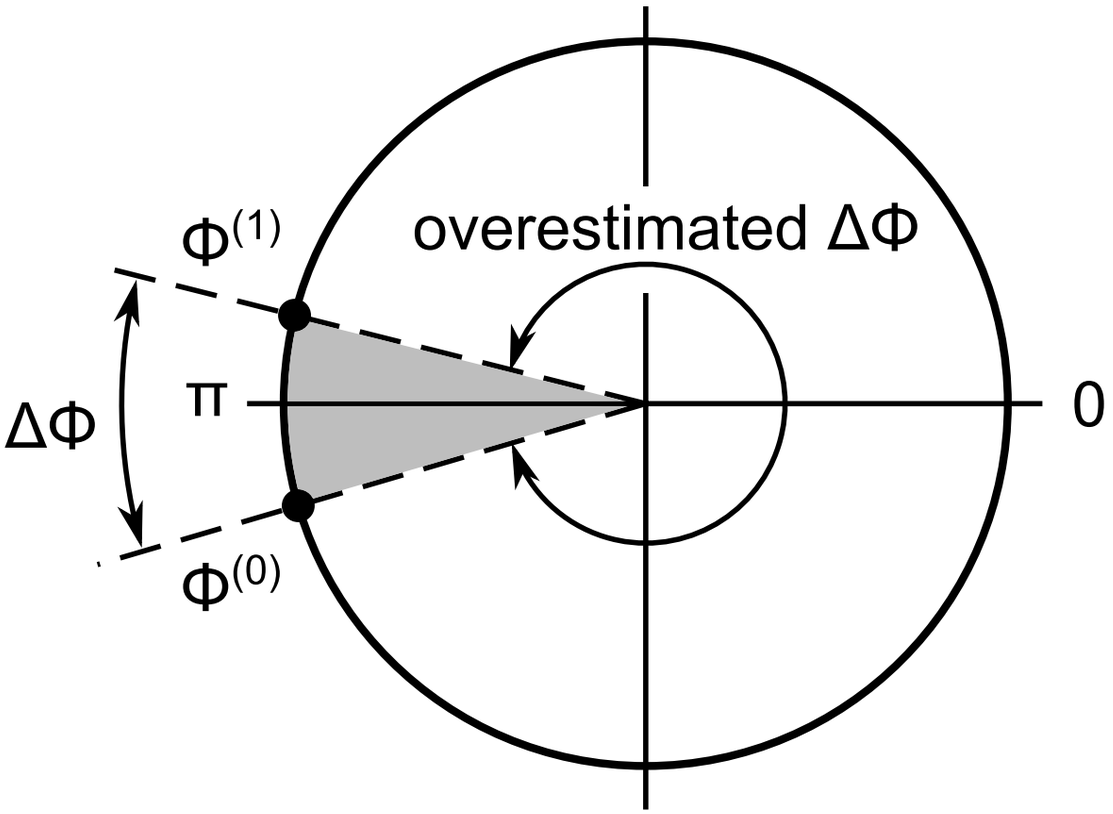
# Typical workflow

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




- structure file must preserve the symmetry
- begin with the lowest symmetry ($\lambda_I$) case
- copy case $\lambda_I$ to case $\lambda_0$
- edit structure file for case $\lambda_0$
- do not initialize calculation (`init_lapw`)
- update density (`x dstart`)
- run SCF cycle (`run[sp]_lapw [-so -orb]`)
- run `BerryPI`

# Uncertainties




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

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

- cannot determine large polarization difference ~1 C/m$^2$

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

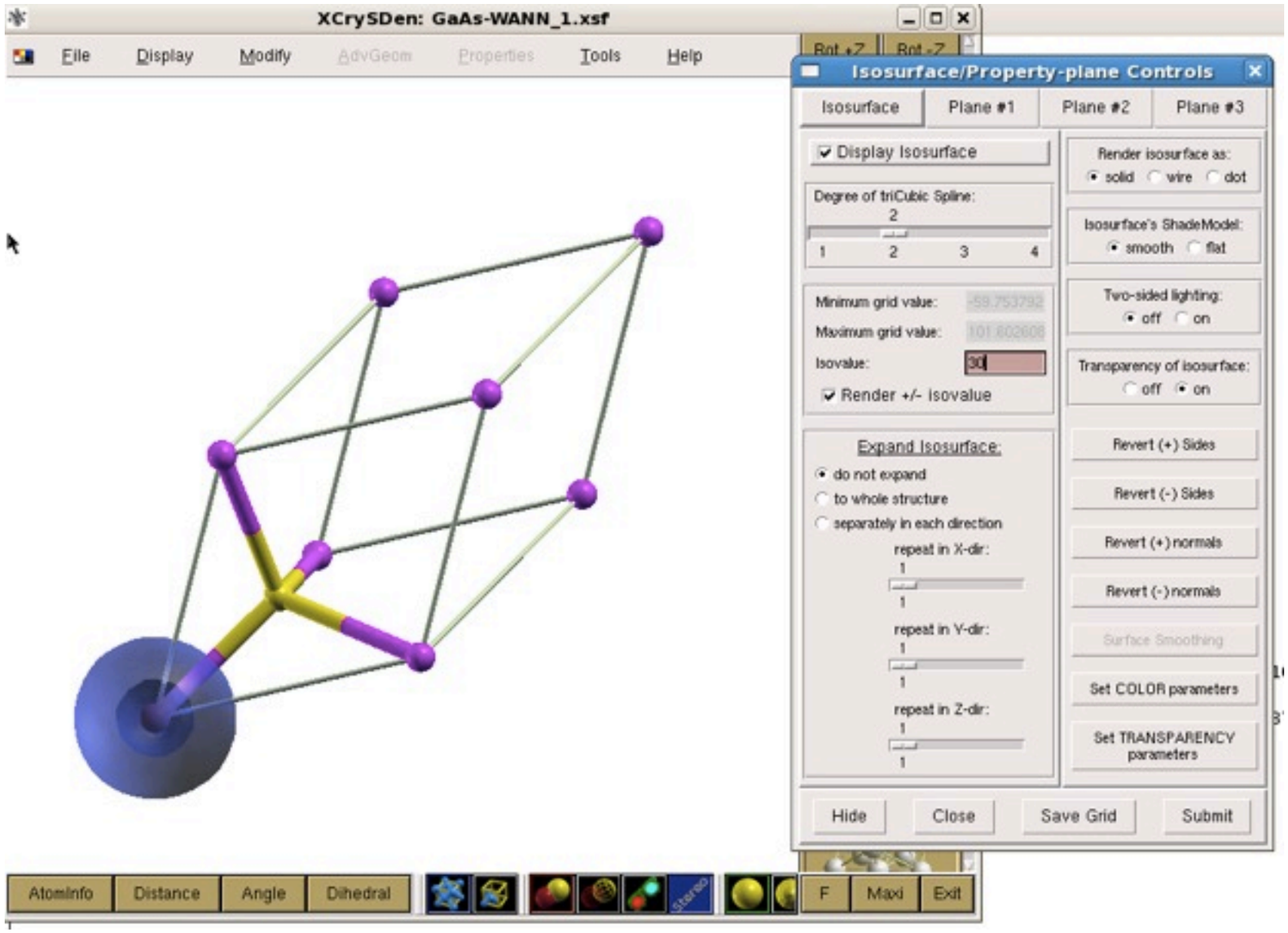
# Useful resources

- 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)

# Suggested exercises (Saturday, July 5)

# 1) GaAs — Max Localized Wannier Functions

- Build a set of atom-centered $sp^3$ Wannier functions
- Reproduce the band structure (VB and bottom of CB)
- Wannier hamiltonian
- Plotting of WFs



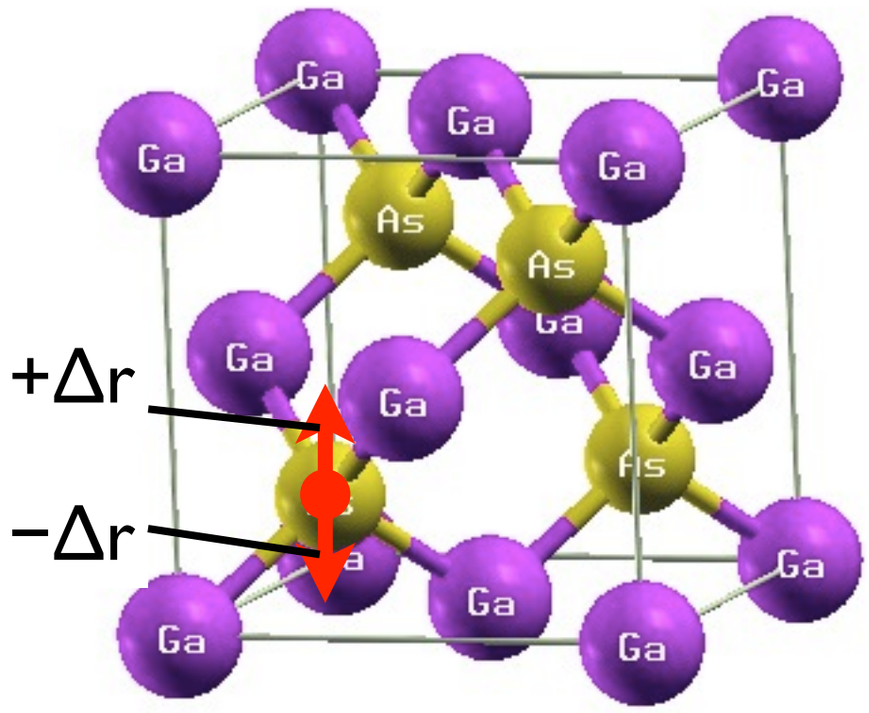
# 2) Born effective charge in GaAs

Born effective charge is related to polarization

$$Z^*_{s,\alpha\beta} = \frac{\Omega}{e}\frac{\partial P_\alpha}{\partial r_{s,\beta}}$$

P - Polarization
r - atom position
Ω - unit cell volume
e - elementary charge

Introduce small displacements
$\pm\Delta r \ll a_0$




Need to compute the polarization difference between 2 structures:
$dP = P(+\Delta r) - P(-\Delta r)$

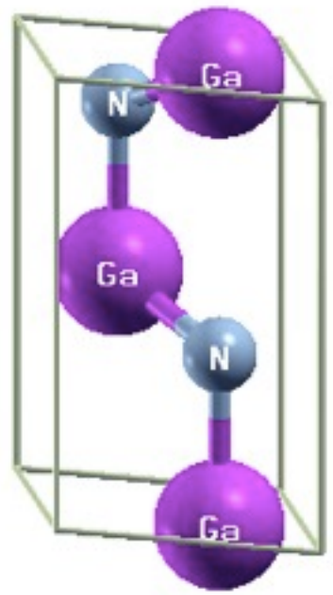
# 3) Polarization effects in GaN

## Wurtzite

A →

B →

A →




Has a finite polarization

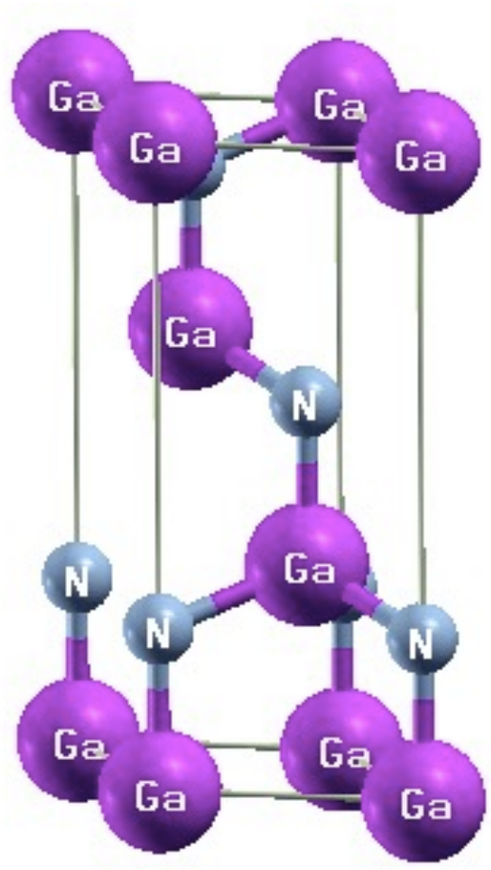
## Zinc-blende

A →

C →

B →

A →




Deemed to have *zero* polarization (reference structure)

$$P_s(GaN) = P(w\text{-}GaN) - P(zb\text{-}GaN)$$

# Acknowledgement


**BerryPI contributors:**

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

**WIEN2WANNIER:**

- Elias Assmann