(in no particular order)

- **GaAs -- MLWF (~40 mins)**

  Construction of maximally localized Wannier functions for the valence and conduction band

- **Born effective charge in GaAs (~30 mins)**

  Compute the Born effective charge in GaAs by calculating polarization induced by small atomic displacements

- **Polarization effects in GaN (~30 mins)**

  Determine polarization difference between wurtzite and zinc-blende structures of GaN

GaAs -- MLWF

 + +
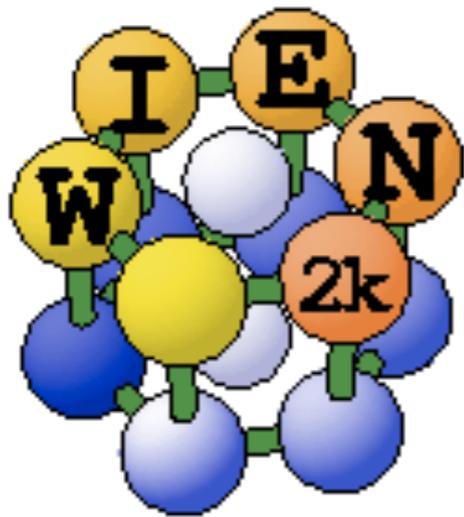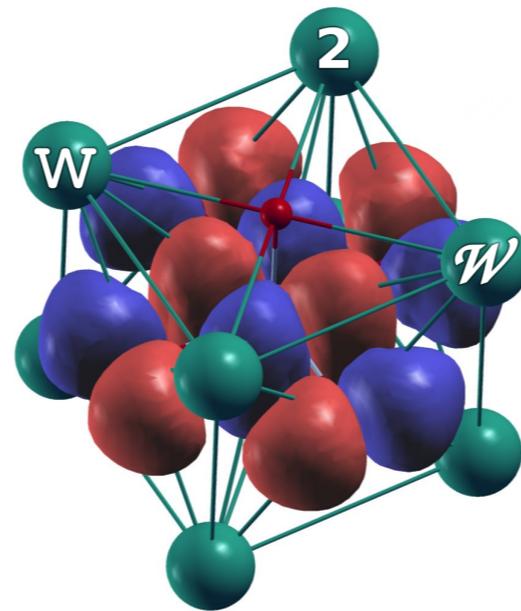
Special thanks to Elias Assmann (TU Vienna) for the generous help in preparation of this tutorial

1. Wien2k SCF

Create a tutorial directory, e.g.

$ `mkdir .../exerciseX/GaAs-MLWF`

Create the structure file using the following parameters:

2 atoms per primitive unit cell (Ga, As)

Lattice "F" = f.c.c.

Lattice parameters $a_0 = b_0 = c_0 = 10.683$ Bohr

Positions: "0 0 0" for Ga and "1/4 1/4 1/4" for As; RMT's - automatic

You can use `xcrysden` to view the structure

$ `xcrysden --wien_struct GaAs-MLWF.struct`

Initialize Wien2k calculation (LDA, ~600 k-points $\equiv$ 8x8x8 mesh)

$ `init_lapw -b -vxc 5 -numk 600`
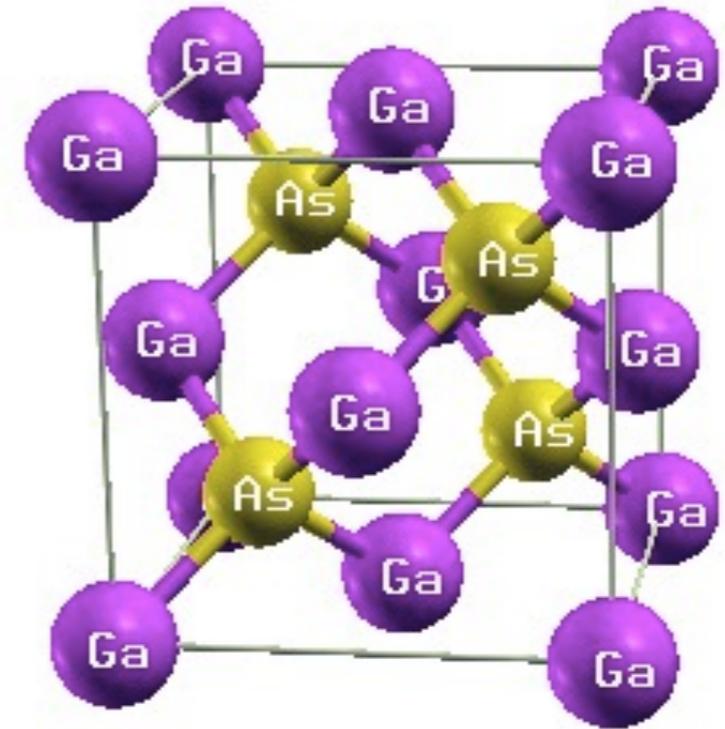
Run regular SCF calculation using default convergence criteria

$ `run_lapw`

After SCF cycle is completed (~7 iterations). We proceed with the band structure

Prepare the list of k-point to be used for the band structure plot (`GaAs-MLWF.klist_band` file) using `xcrysden`

`xcrysden` `File > Open Wien2k > Select k-path`

Select points L(1/2 0 0), Γ(0 0 0), X(1/2 1/2 0), U(5/8 5/8 1/4), Γ

Save the list as `GaAs-MLWF.klist_band`

Re-calculate eigenvalues for the k-point

$ `x lapw1 -band`
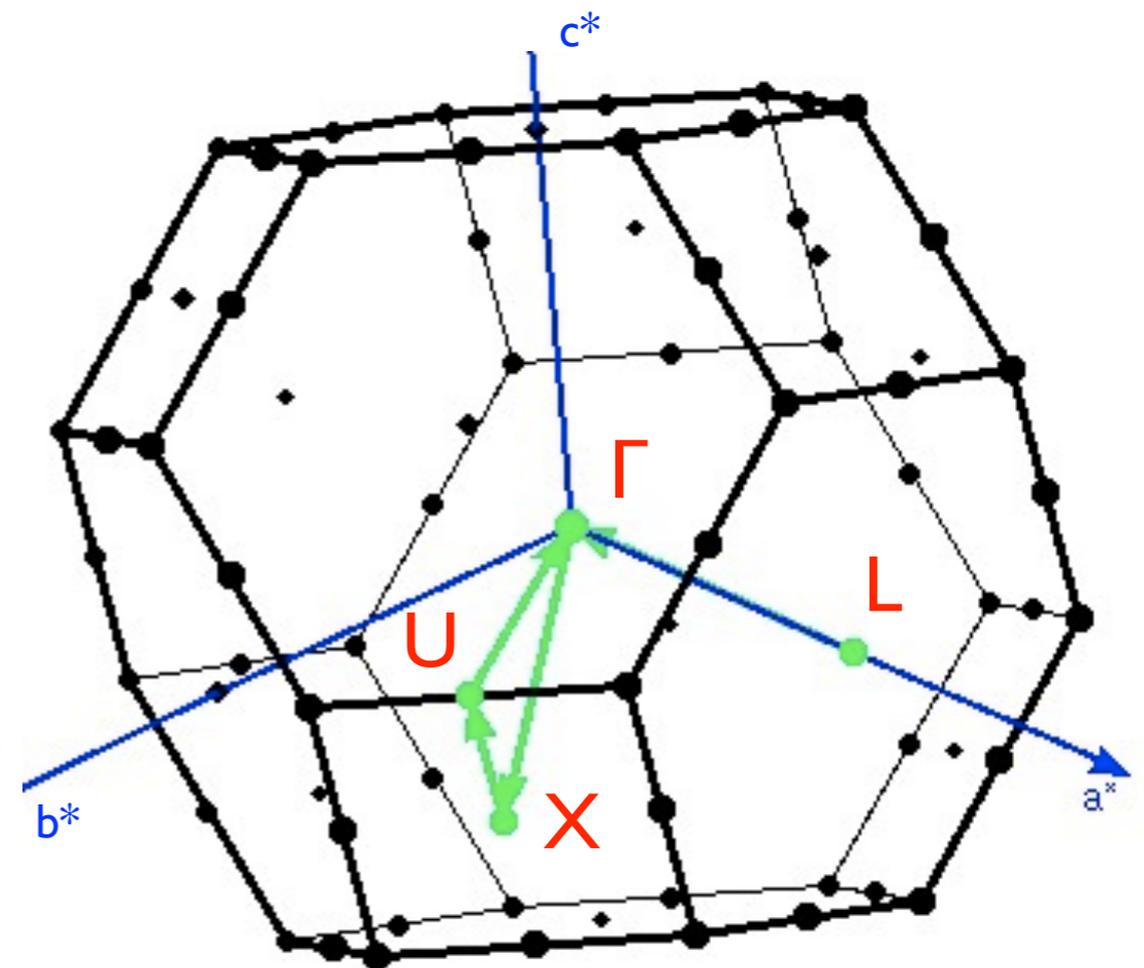
For the band structure plot we will use the web interface (w2web).
Create a new session and navigate to the current work directory.

w2web **Tasks > Bandstructure**

w2web **Select**
"Edit GaAs-MLWF.insp",
insert the Fermi energy,
save

w2web **x spaghetti**

w2web **plot band structure**

Your band structure will be similar
to the one shown on the right.
Our aim is to construct Wannier
functions that reproduce this band
structure including valence and some
conduction bands.

GaAs-MLWF atom O   size 0.20
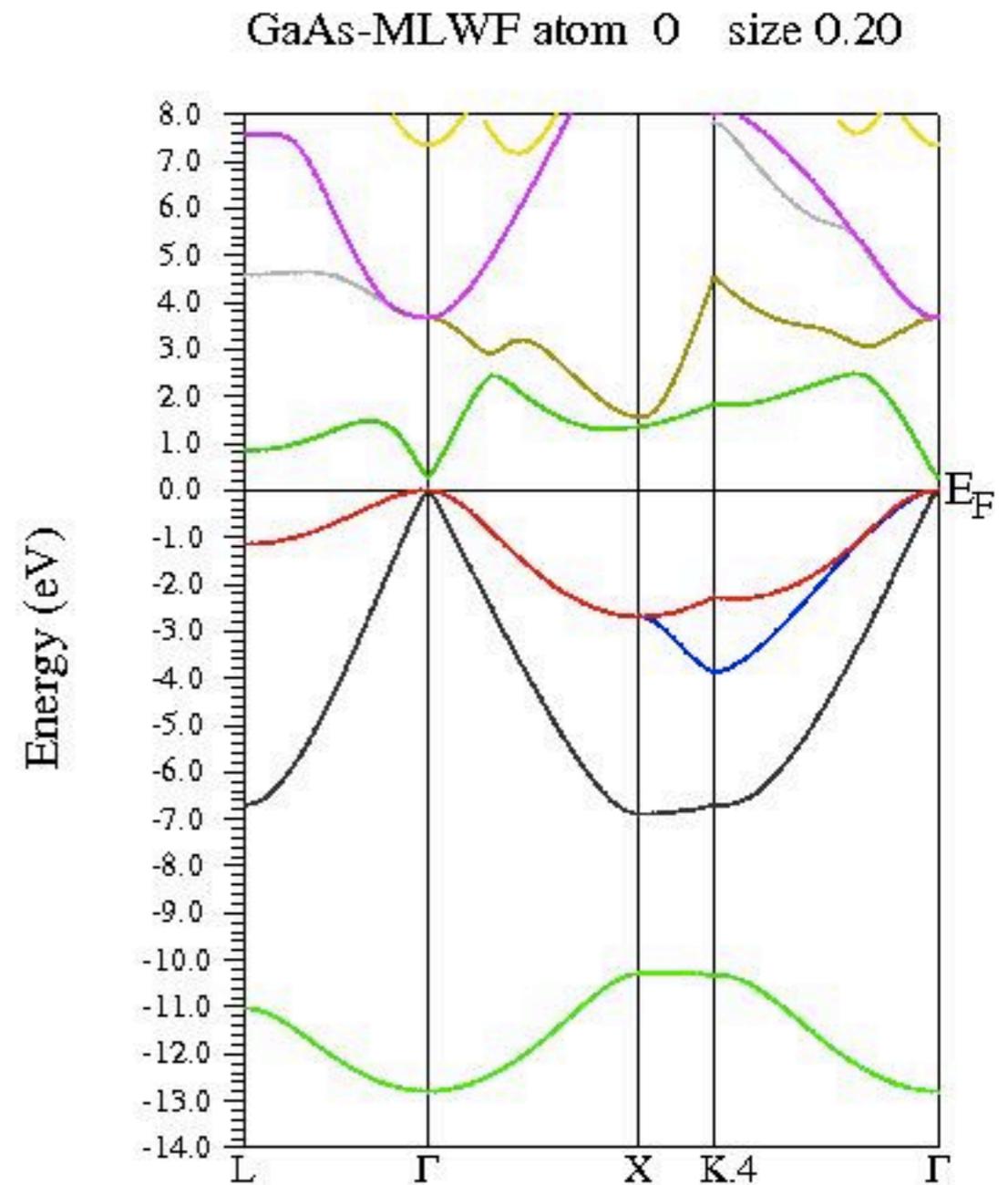
Before we proceed it is useful to determine the band indices for the region of interest

```
$ grep :BAN *scf2
```

		Emin (Ry)	Emax	occupancy	
:BAN00004:	4	−2.243815	−2.243263	2.00000000	d-orb. of
:BAN00005:	5	−2.243645	−2.243122	2.00000000	As and Ga
:BAN00006:	6	−0.757612	−0.748891	2.00000000	(do not
:BAN00007:	7	−0.748891	−0.745972	2.00000000	participate
:BAN00008:	8	−0.748891	−0.745814	2.00000000	in bonding)
:BAN00009:	9	−0.744948	−0.742764	2.00000000	
:BAN00010:	10	−0.743426	−0.742046	2.00000000	
:BAN00011:	11	−0.597475	−0.409554	2.00000000	
:BAN00012:	12	−0.163606	0.342616	2.00000000	
:BAN00013:	13	0.056810	0.342616	2.00000000	
:BAN00014:	14	0.094852	0.342616	2.00000000	
:BAN00015:	15	0.362856	0.675520	0.00000000	
:BAN00016:	16	0.456595	0.748030	0.00000000	
:BAN00017:	17	0.612912	1.080595	0.00000000	
:BAN00018:	18	0.612912	1.080595	0.00000000	
:BAN00019:	19	0.881735	1.145545	0.00000000	

⇧ Emin (Ry)   ⇧ Emax   ⇧ occupancy

2. Construction of Wannier functions

Prepare a separate directory

$ prepare_w2wdir GaAs-MLWF GaAs-WANN

$ cd GaAs-WANN

Initialize Wien2Wannier

$ init_w2w

Select 8x8x8 k-mesh (unshifted);

energy range (eV) -13 10 (this is not very critical);

band indices [Nmin Nmax] 11 18 (see the previous page);

for the projection we choose "1:s,p" and "2:s,p" (1 = Ga, 2 = As)

Get the vector file on the full Brillouin zone mesh

$ x lapw1

Compute matrix elements needed for Wannier90

$ `x w2w`

Run Wannier90

$ `x wannier90`

Verify the output
spread $\langle \Delta \mathbf{r}^2 \rangle$

$ `less GaAs-WANN.wout`
$\Downarrow$

```
...
Final State
  WF centre and spread    1  (   0.000000,   0.000000,   0.000000 )       1.91743858
  WF centre and spread    2  (   0.000000,   0.000000,   0.000000 )       5.85659132
  WF centre and spread    3  (   0.000000,   0.000000,   0.000000 )       5.85659132
  WF centre and spread    4  (   0.000000,   0.000000,   0.000000 )       5.85659105
  WF centre and spread    5  (   1.413312,   1.413312,   1.413312 )       1.61146495
  WF centre and spread    6  (   1.413313,   1.413312,   1.413312 )       3.82142578
  WF centre and spread    7  (   1.413312,   1.413312,   1.413312 )       3.82142578
  WF centre and spread    8  (   1.413312,   1.413312,   1.413313 )       3.82142553
...
```

There you can see the position and spread of the WF's, how they changed in the course of convergence. WF's 1-4 are all positioned at the origin (atom 1), WF's 5-8 are centred at the 2nd atom (please check the coordinates)

3. Post-processing

Plot the band structure

$ gnuplot

gnuplot> plot 'GaAs-WANN.spaghetti_ene' using ($4/0.529189):5, 'GaAs-WANN_band.dat' with lines
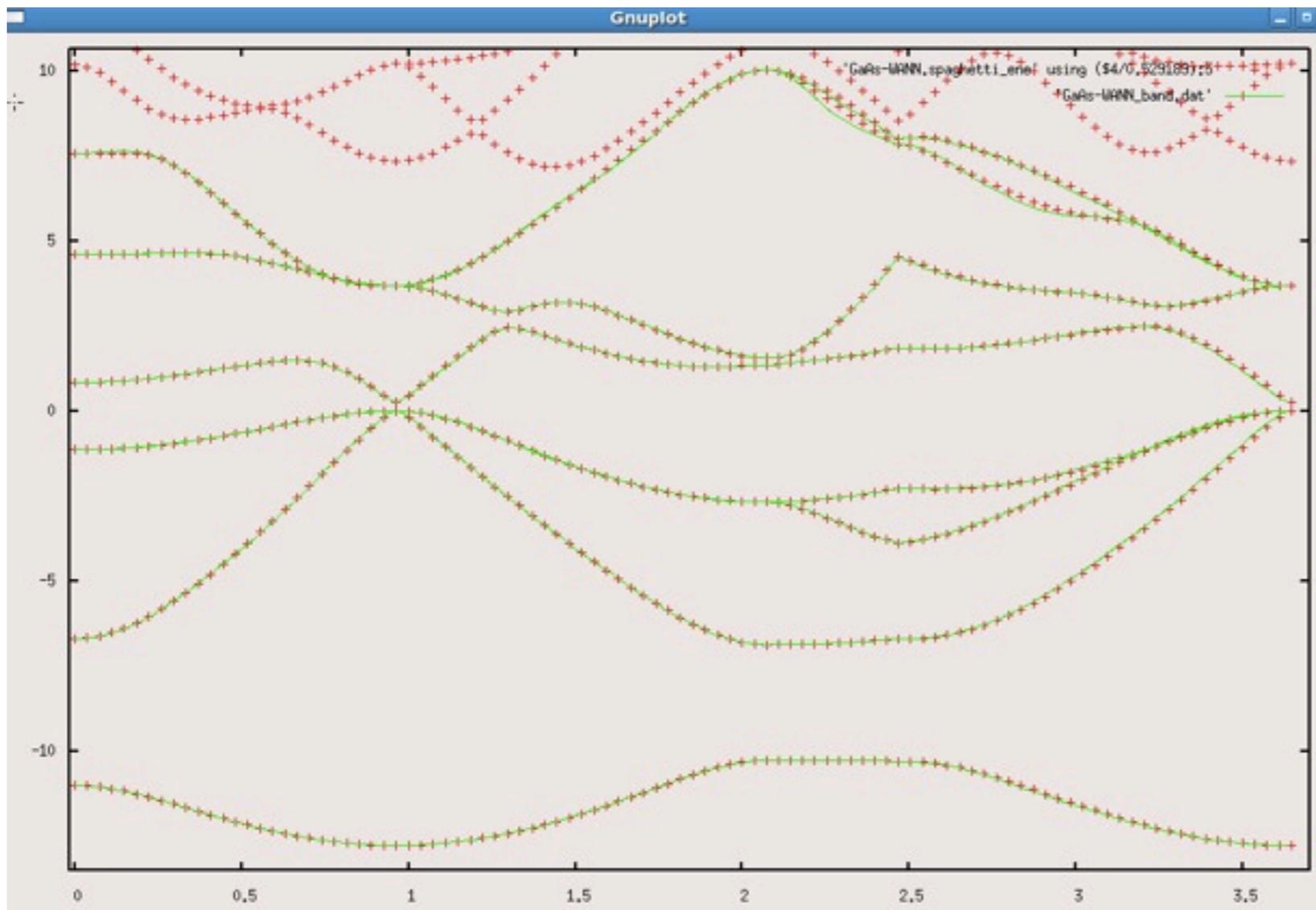
+ original Wien2k band structure

– Band structure computed from Wannier functions

Plotting WF's (can take a while)

$ `write_inwplot GaAs-WANN`

Select origin "`-1 -1 -1 1`" and axis x, y, z

"` 1 -1 -1 1`"

"`-1  1 -1 1`"

"`-1 -1  1 1`"

mesh: 30 30 30

(Sometimes it is necessary to extend the plotting region beyond the primitive lattice in order to capture WF's centred close to the edges)

Compute the 1st Wannier function on the mesh chosen

$ `x wplot -wf 1`

If you need to plot any other WF's (2, 3, etc), just edit the option.

Convert the output of `wplot` into `xcrysden` format for plotting.

$ `wplot2xsf`

Visualize with `xcrysden` (instructions on the next page)

$ `xcrysden --xsf GaAs-WANN_1.xsf`

`xcrysden` `Tools > Data Grid > OK`

Check "render +/- isovalue"

Play with the settings. You will get a spherical (s-like) WF centred at the origin.

The second WF resamples p-orbital (you can get it by editing "GaAs-WANN.inwplot", re-run "`x wplot`" and "`wplot2xsf`"). The new file should be called **`GaAs-WANN_2.xsf`**

WF #1

WF #2

Note different colours of the WF lobes
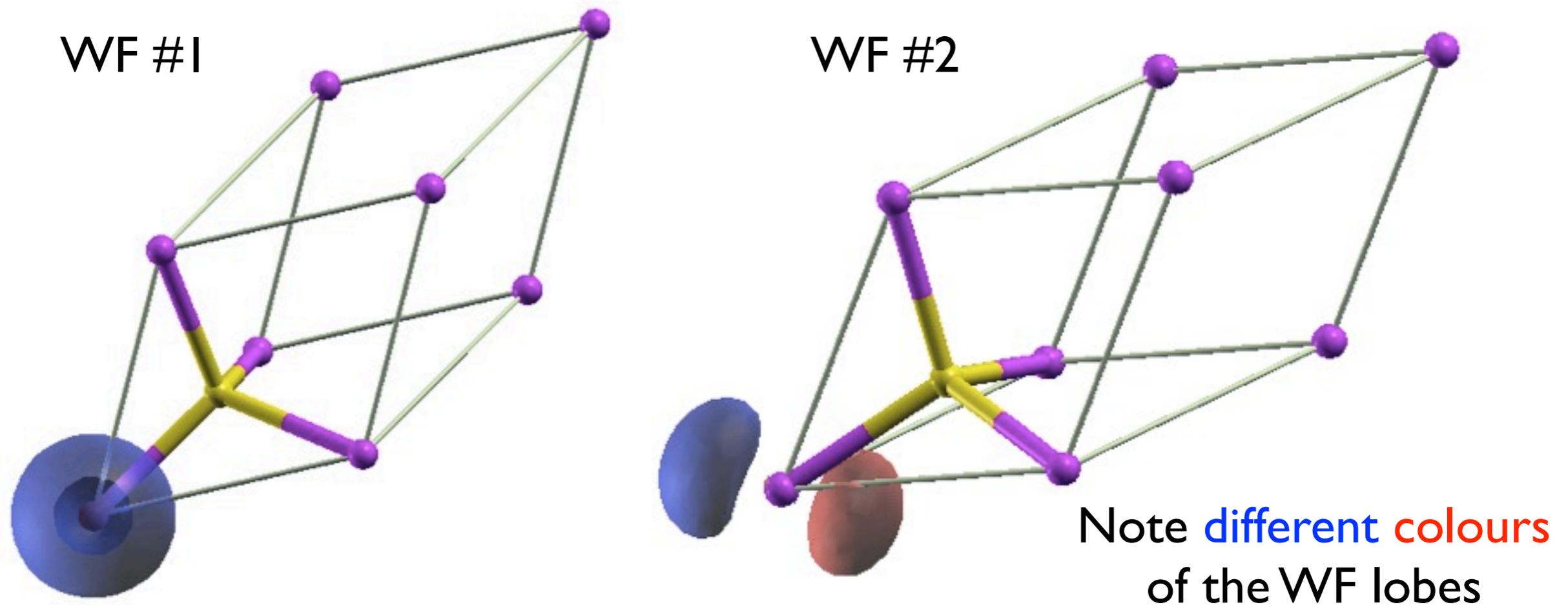
Wannier Hamiltonian (similar to LCAO)

Matrix element (eV)

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

$\$$ `less GaAs-WANN_hr.dat`

...

0	0	0	1	1	−4.335108	0.000000
0	0	0	2	1	−0.000001	0.000000
0	0	0	3	1	0.000000	0.000000
0	0	0	4	1	−0.000001	0.000000
0	0	0	5	1	−1.472358	0.000000
0	0	0	6	1	−1.157088	0.000000
0	0	0	7	1	−1.157088	
0	0	0	8	1	−1.157088	

Home unit cell

no imag. part of the matrix element

no on-site hopping between different orbitals

...

Determine on site energies E_s and E_p for Ga and As and compare them to those suggested by Harrison (note: only their relative differences are important)

From Harrison's solid state tables:

`Ep(Ga) - Es(Ga) = 5.9 eV`

`Ep(As) - Es(As) = 9.9 eV`

`Ep(Ga) - Ep(As) = 3.3 eV`

Wannier Hamiltonian (cont.)

...

```
0    0    0    1    1    -4.335108    0.000000
0    0    0    2    1    -0.000001    0.000000   ⟨s2|
0    0    0    3    1     0.000000    0.000000
0    0    0    4    1    -0.000001    0.000000
0    0    0    5    1    -1.472358    0.000000
0    0    0    6    1    -1.157088    0.000000
0    0    0    7    1    -1.157088    0.000000
0    0    0    8    1    -1.157088    0.000000

0    0    1    1    1    -0.001219    0.000000
```

$\langle s_2|$

$\langle s_2|H|s_1\rangle = V_{ss\sigma}$ (blue, −1.472358)

$\langle p_2|H|s_1\rangle = V_{sp}$ (red, −1.157088)

Neighbour unit cell

WF are well localized ⇒ nearest-neighbour suffice

Now you have all information required to build your *ab initio* TB sp3 Hamiltonian (Yu & Cardona)

Table 2.25. Matrix for the eight s and p bands in the diamond structure within the tight binding approximation

	S1	S2	X1	Y1	Z1	X2	Y2	Z2
S1	$E_s - E_k$	$V_{ss}g_1$	0	0	0	$V_{sp}g_2$	$V_{sp}g_3$	$V_{sp}g_4$
S2	$V_{ss}g_1^*$	$E_s - E_k$	$-V_{sp}g_2^*$	$-V_{sp}g_3^*$	$-V_{sp}g_4^*$	0	0	0
X1	0	$-V_{sp}g_2$	$E_p - E_k$	0	0	$V_{xx}g_1$	$V_{xy}g_4$	$V_{xy}g_3$
Y1	0	$-V_{sp}g_3$	0	$E_p - E_k$	0	$V_{xy}g_4$	$V_{xx}g_1$	$V_{xy}g_2$
Z1	0	$-V_{sp}g_4$	0	0	$E_p - E_k$	$V_{xy}g_3$	$V_{xy}g_2$	$V_{xx}g_1$
X2	$V_{sp}g_2^*$	0	$V_{xx}g_1^*$	$V_{xy}g_4^*$	$V_{xy}g_3^*$	$E_p - E_k$	0	0
Y2	$V_{sp}g_3^*$	0	$V_{xy}g_4^*$	$V_{xx}g_1^*$	$V_{xy}g_2^*$	0	$E_p - E_k$	0
Z2	$V_{sp}g_4^*$	0	$V_{xy}g_3^*$	$V_{xy}g_2^*$	$V_{xx}g_1^*$	0	0	$E_p - E_k$

Born effective charge
in GaAs

WIEN2k + + BerryPI

Background

Ionic bond

Covalent bond

$Z^* = +1$ $Z^* = -1$ $Z^* = 0$

Mixed

$Z^*?$

Effective charge

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
$\pm\Delta r \ll a_0$

$+\Delta r$

$-\Delta r$

Need to compute the polarization difference between 2 structures:
dP = P(+Δr) − P(−Δr)

Complications

Conventional cell
(8 atoms)

Primitive cell
(2 atoms)

We use this coordinate system when defining atomic positions in `*.struct`

Electronic structure is calculated in this coordinate system

⇩

⇩

P_{ionic} not additive $P_{electronic}$

need to convert P_{el} to Cartesian coordinates

Instructions

Construct a structure file (`../`GaAs1`/GaAs1.struct`) as described in the previous tutorial with one difference: slightly displace As-atom up along Z-axis by changing its coordinates to

`X=0.25000000 Y=0.25000000 Z=0.25100000`

Initialize calculation (LDA)

$ `init_lapw –b –vxc 5 –rkmax 7 –numk 800`

Run SCF cycle with default convergence criteria

$ `run_lapw`

Run `BerryPI` module that calculates polarization using Berry phase

$ `berrypi –k 6:6:6`

Save the results for ionic and electronic polarization as well as phases

Construct a structure file (`../`GaAs2`/GaAs2.struct`). This time we displace As-atom down along Z-axis by changing its coordinates to

`X=0.25000000 Y=0.25000000 Z=0.24900000`

Proceed with the calculation (all parameter must be identical to GaAs1)

$ `init_lapw -b -vxc 5 -rkmax 7 -numk 800`

$ `run_lapw`

$ `berrypi -k 6:6:6`

Save the results for ionic and electronic polarization as well as phases

Here we deal with a situation where the electronic phase is computed for the *primitive* lattice vectors, whereas the ionic phase is computed for the *conventional* lattice. Some additional work is required before the phases can be add up and the effective charge can be calculated.

Please refer to the link below for detailed instructions (steps 8+):

https://github.com/spichardo/BerryPI/wiki/Tutorial-3:-Non-orthogonal-lattice-vectors

Once calculations are done...

- What could be a maximum possible Z^* in group III-V semiconductors?

- Explain the sign of Z^*. Which element is *electropositive*, which is *electronegative*? What it has to do with the energy of valence electrons (`*.outputst` file)?

- Would you expect $|Z^*(Ga)|$ and $|Z^*(As)|$ be different? (check the acoustic sum rule)

- Which trend to expect in Z^* if we replace As → N? Which of the two elements is more electronegative? Why? Check if your guess is right (google: GaN effective charge)

Polarization effects
in GaN

WIEN2k + [structure] + BerryPI

Background: Polarization effects in group-III nitrides

Heterostructure
(InGa)N/GaN quantum well

P_{GaN} $P_{(InGa)N}$ P_{GaN}

Electric field profile

$\propto P_{GaN} - P_{(InGa)N}$

Note: it is the *difference* matters

Band diagram

Cond. band

e^-

Build-in electric field hinders recombination

Valence band

h^+

Structure

Wurtzite
(stable at ambient cond.)

A →
B →
A →

Has a finite polarization

Zinc-blende
(unstable)

A →
C →
B →
A →

Deemed to have *zero* polarization
(reference structure)

$$P_s(GaN) = P(\text{w-GaN}) - P(\text{zb-GaN})$$
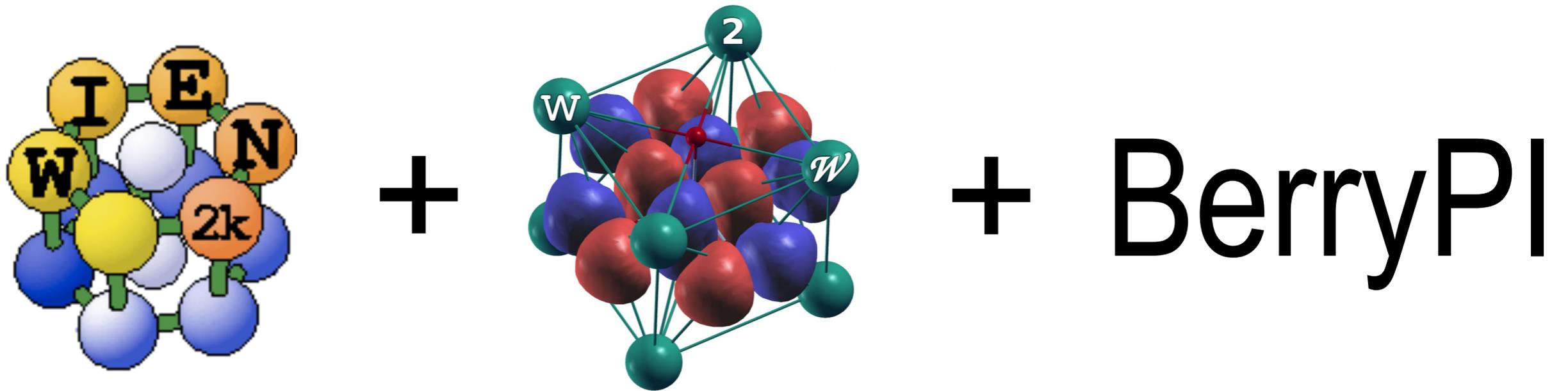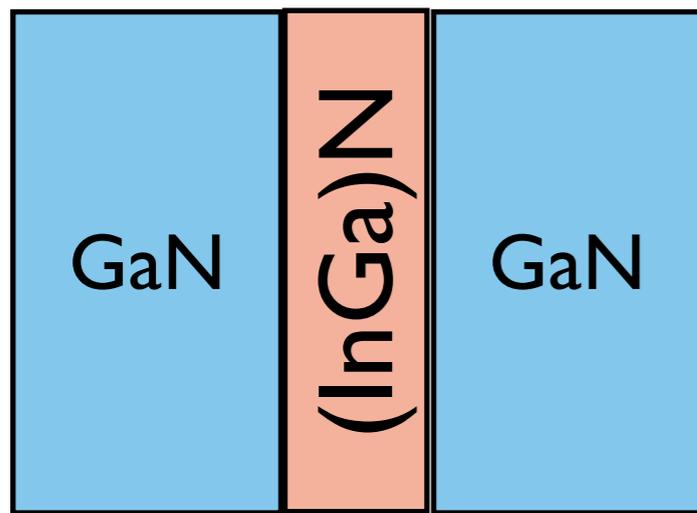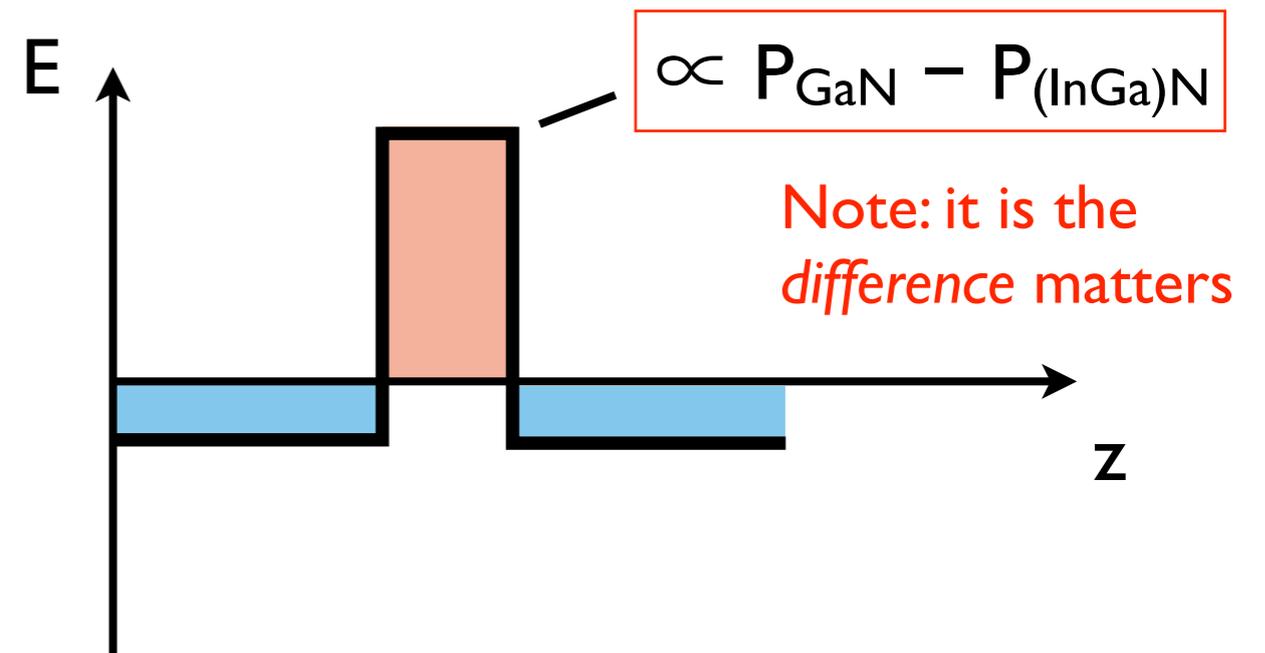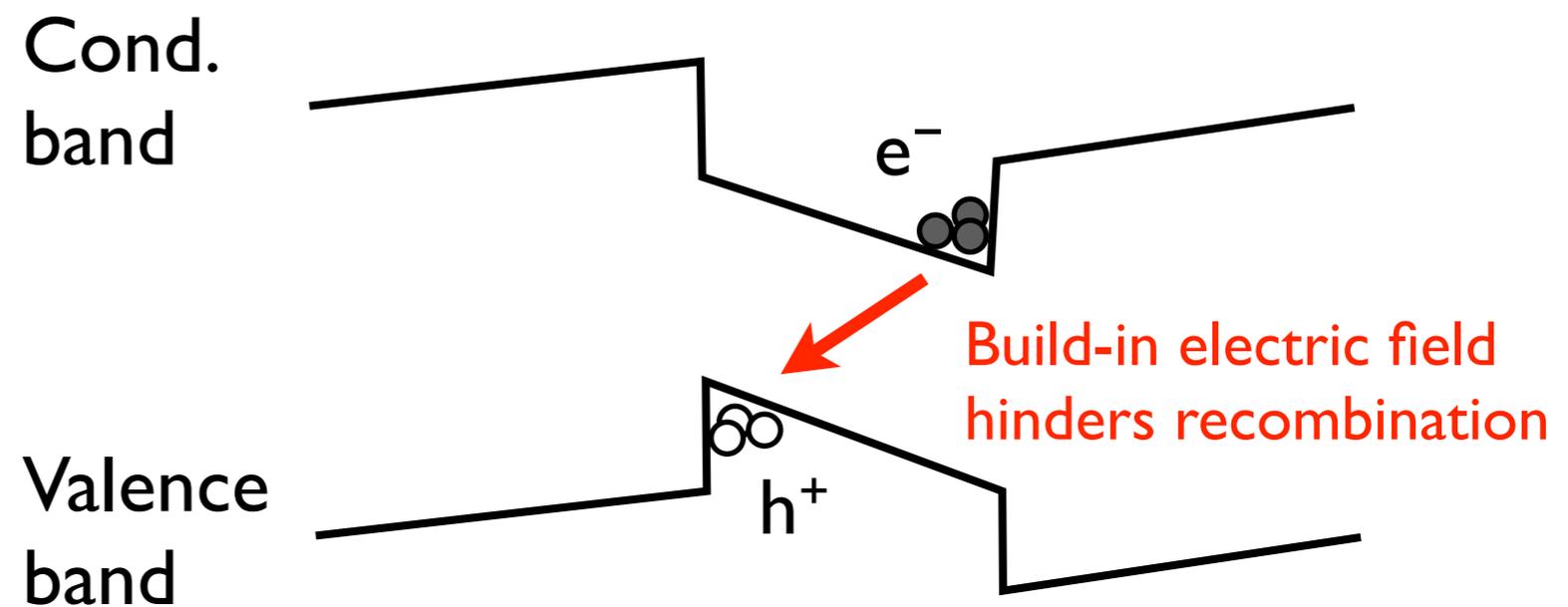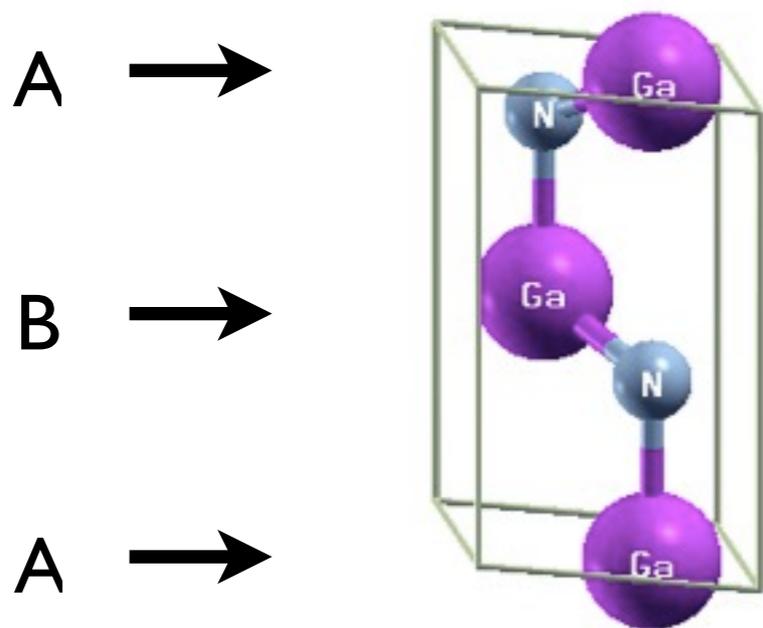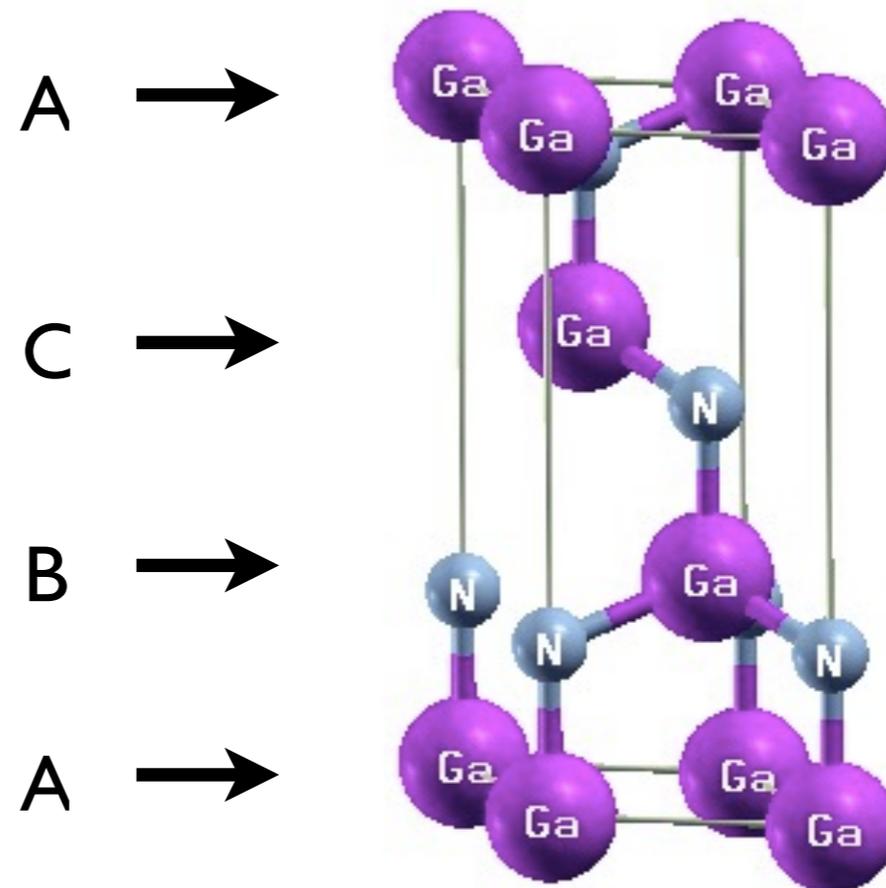
This is a "standard" definition of spontaneous polarization in wurtzite structures [PRL **64**, 1777 (1990), PRB **56**, R10024 (1997)], but some reservations exist [PRL **69**, 389 (1992)] that question its relevance to the heterostructures discussed above.

Instructions

w2web Construct a structure file (`../`GaN-W`/GaN-W.struct`)

4-atoms (2-Ga, 2-N) per unit cell

Hexagonal lattice "H", $\alpha = \beta = 90°$, $\gamma = 120°$

Cell size (Bohr): a = b = 5.963131; c = 9.722374

Coordinates:

Ga (2/3 1/3 0)

Ga (1/3 2/3 1/2)

N (2/3 1/3 0.376393)

N (1/3 2/3 0.876393)

> a, c, and Nintrogen z-position need to be fully optimized. Here we use LDA optimization results.

Initialize and run SCF calculation (LDA), then run Berry phase calc.

$ `init_lapw -b -vxc 5 -rkmax 7 -numk 300`

$ `run_lapw`

$ `berrypi -k 8:8:8`

> If you have time, you can test the convergence by choosing different k-mash for the Berry phase calculation

Save the results for total polarization

w2web Construct a structure file (`../``GaN-ZB``/GaN-ZB.struct`)

6-atoms (3-Ga, 3-N) per unit cell

Hexagonal lattice "H", $\alpha = \beta = 90°$, $\gamma = 120°$

Cell size (Bohr): a = b = 5.963131 (same as GaN-W); c = 14.606628

Coordinates:

Ga (0 0 0)

N (0 0 1/4)

Ga (1/3 2/3 1/3)

N (1/3 2/3 7/12)

Ga (2/3 1/3 2/3)

N (2/3 1/3 11/12)
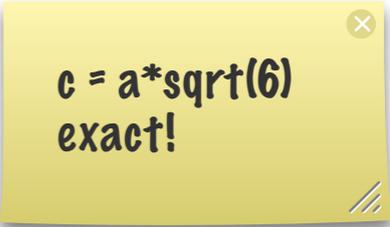
c = a*sqrt(6) exact!

Initialize and run SCF calculation (LDA), then run Berry phase calc.

$ `init_lapw -b -vxc 5 -rkmax 7 -numk 300`

$ `run_lapw`

$ `berrypi -k 8:8:8`

Compute the result for polarization difference between two structures and compare to Ps = -0.029 C/m2 reported by Bernardini et al., and also Ps = -0.022 C/m2 measured by Lähnemann et al.

Once calculations are done...

- Visualize the structure of wurtzite GaN, e.g. using `xcrysden`. By observing the symmetry, can you explain why the polarization is non-zero only in Z-direction?

- Repeat the same for the zinc-blende structure. What makes us to think the the z.b. structure has zero polarization? (hint: there should be other directions that look similar to Z)

- Estimate the electric field in the stack of w-GaN/zb-GaN using P_s found and assuming the dielectric constant of 5. What is the potential drop (eV) per unit cell? How thick can the heterostructure be before we get a metallic state (i.e., the Fermi energy touches the conduction band)?