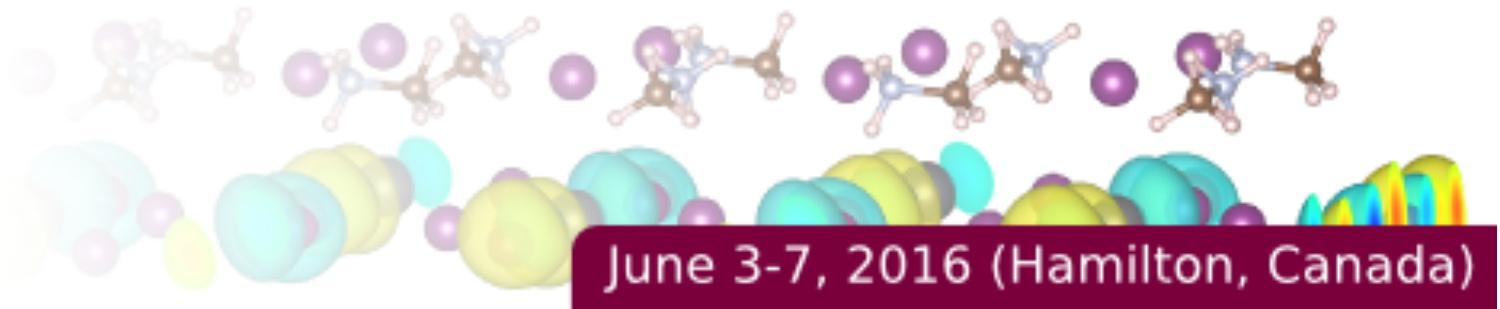


Exercise IX: Wannier functions and Berry phase

**23rd International
WIEN2k workshop**



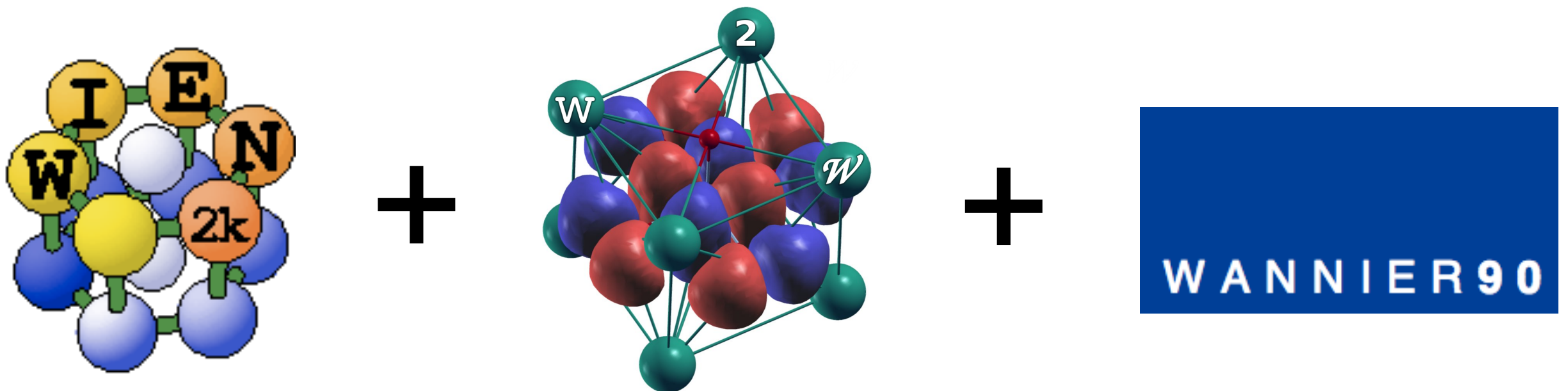
(can be completed in any order)

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

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

- **Born effective charge of GaN (~30 mins)**

GaAs -- MLWF



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



I. 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

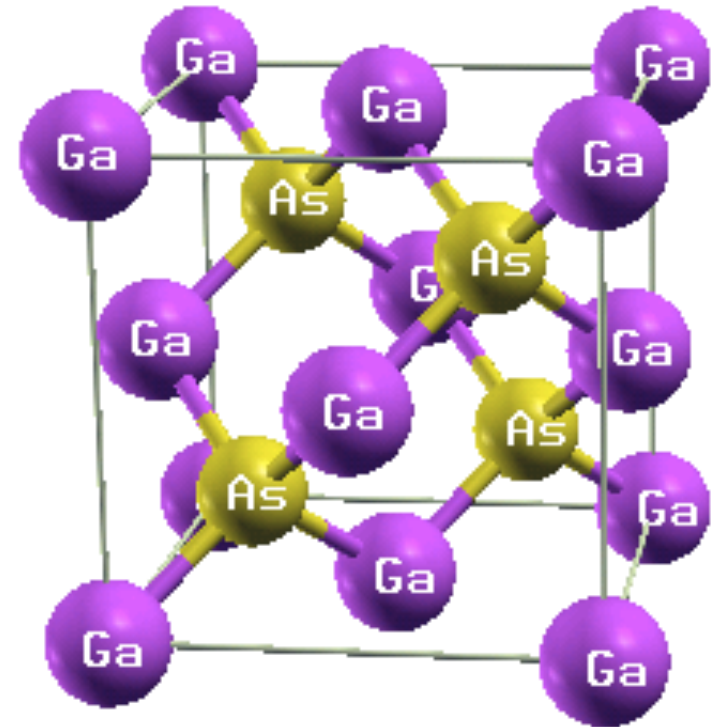
Positions: “0 0 0” for Ga and “1/4 1/4 1/4” for As; RMT’s - automatic

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

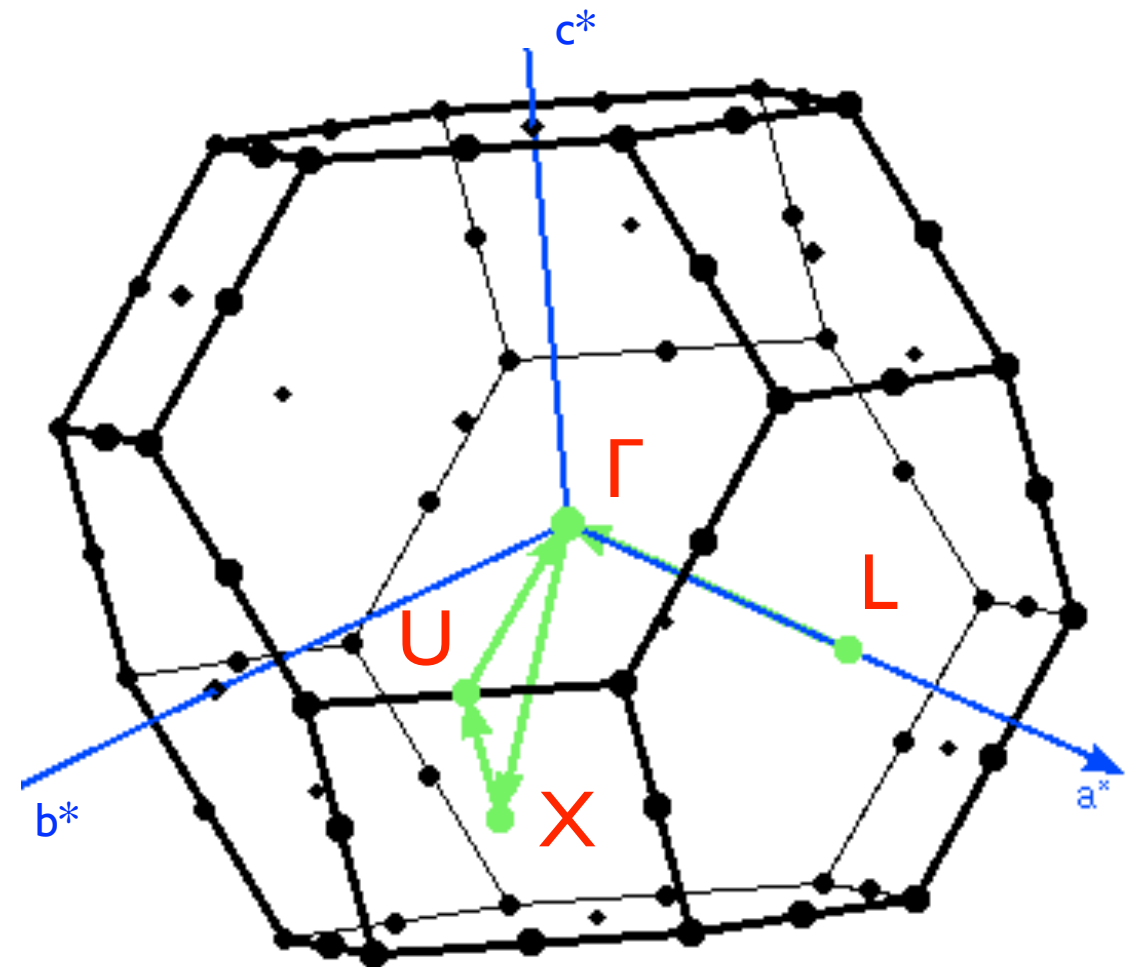
Select points L(1/2 0 0), Γ (0 0 0),
X(1/2 1/2 0), U(5/8 5/8 1/4), Γ

Save the list as

GaAs-MLWF.klist_band

Solve eigenproblem on the k-path

\$ 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**

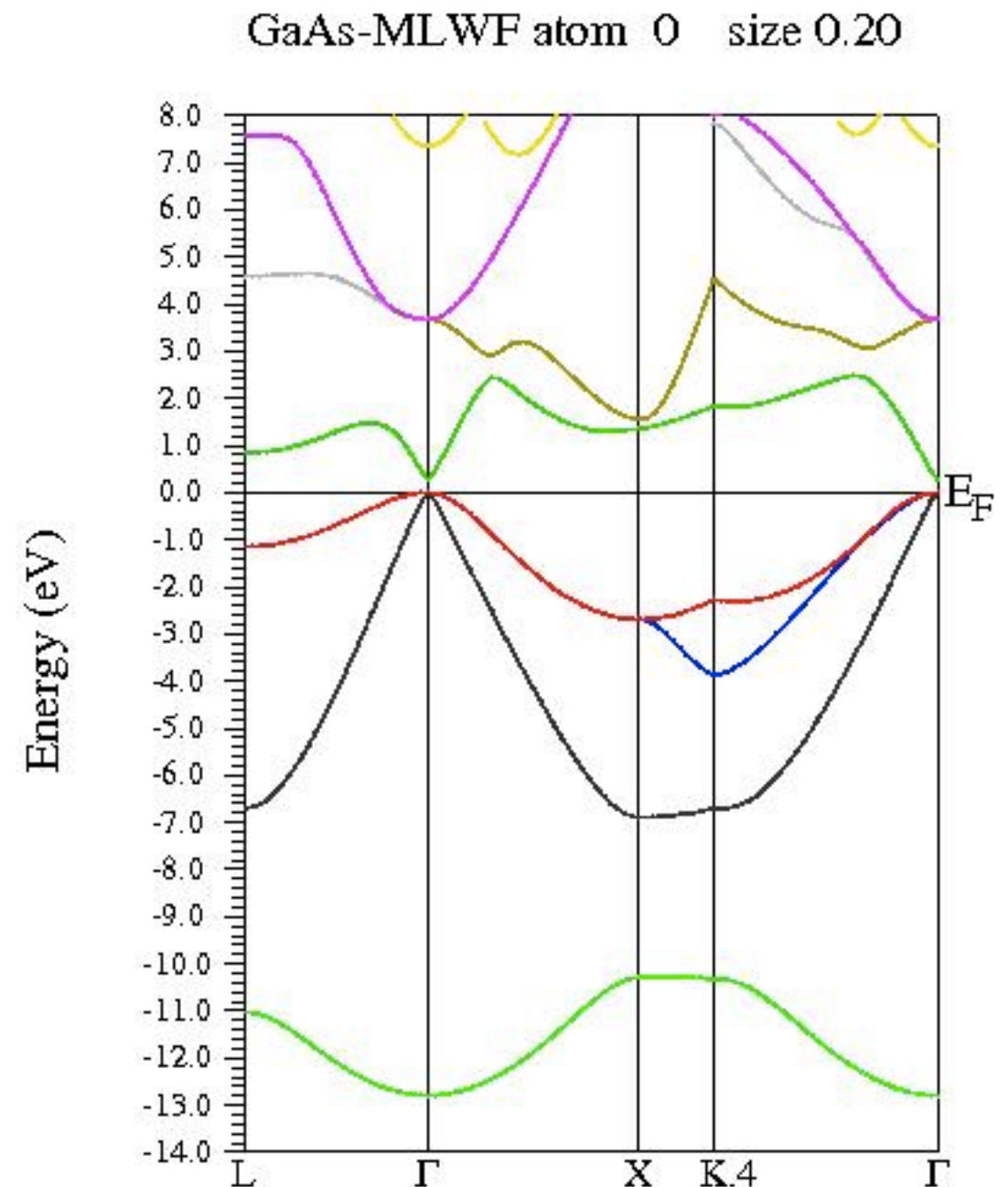
w2web **Select**

**"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.



Before we proceed it is useful to determine the band indices for the region of interest

\$ grep :BAN *scf2					
:BAN00004:	4	-2.243815	-2.243263	2.000000000	} d-orb. of As and Ga (do not participate in bonding)
:BAN00005:	5	-2.243645	-2.243122	2.000000000	
:BAN00006:	6	-0.757612	-0.748891	2.000000000	
:BAN00007:	7	-0.748891	-0.745972	2.000000000	
:BAN00008:	8	-0.748891	-0.745814	2.000000000	
:BAN00009:	9	-0.744948	-0.742764	2.000000000	
:BAN00010:	10	-0.743426	-0.742046	2.000000000	
:BAN00011:	11	-0.597475	-0.409554	2.000000000	
:BAN00012:	12	-0.163606	0.342616	2.000000000	
:BAN00013:	13	0.056810	0.342616	2.000000000	
:BAN00014:	14	0.094852	0.342616	2.000000000	
:BAN00015:	15	0.362856	0.675520	0.000000000	
:BAN00016:	16	0.456595	0.748030	0.000000000	
:BAN00017:	17	0.612912	1.080595	0.000000000	
:BAN00018:	18	0.612912	1.080595	0.000000000	
:BAN00019:	19	0.881735	1.145545	0.000000000	
		↑ 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

\$ less GaAs-WANN.wout

spread $\langle \Delta r^2 \rangle$



...

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

...

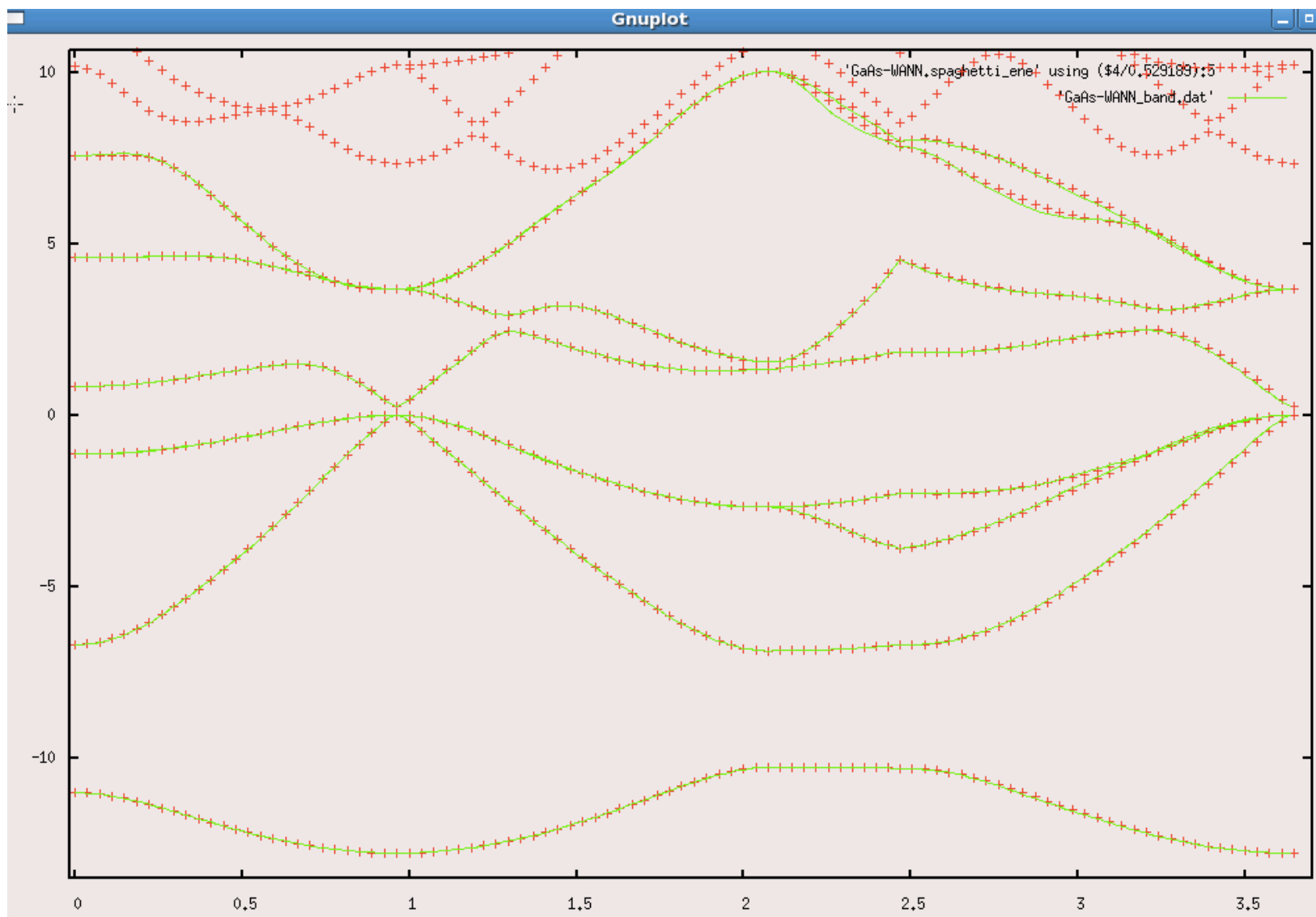
There you can see the position and spread of the WF's, how they changed in the course of convergence. WF's 1-4 are all positioned at the origin (atom 1), WF's 5-8 are centred at the 2nd atom (please check the coordinates)

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

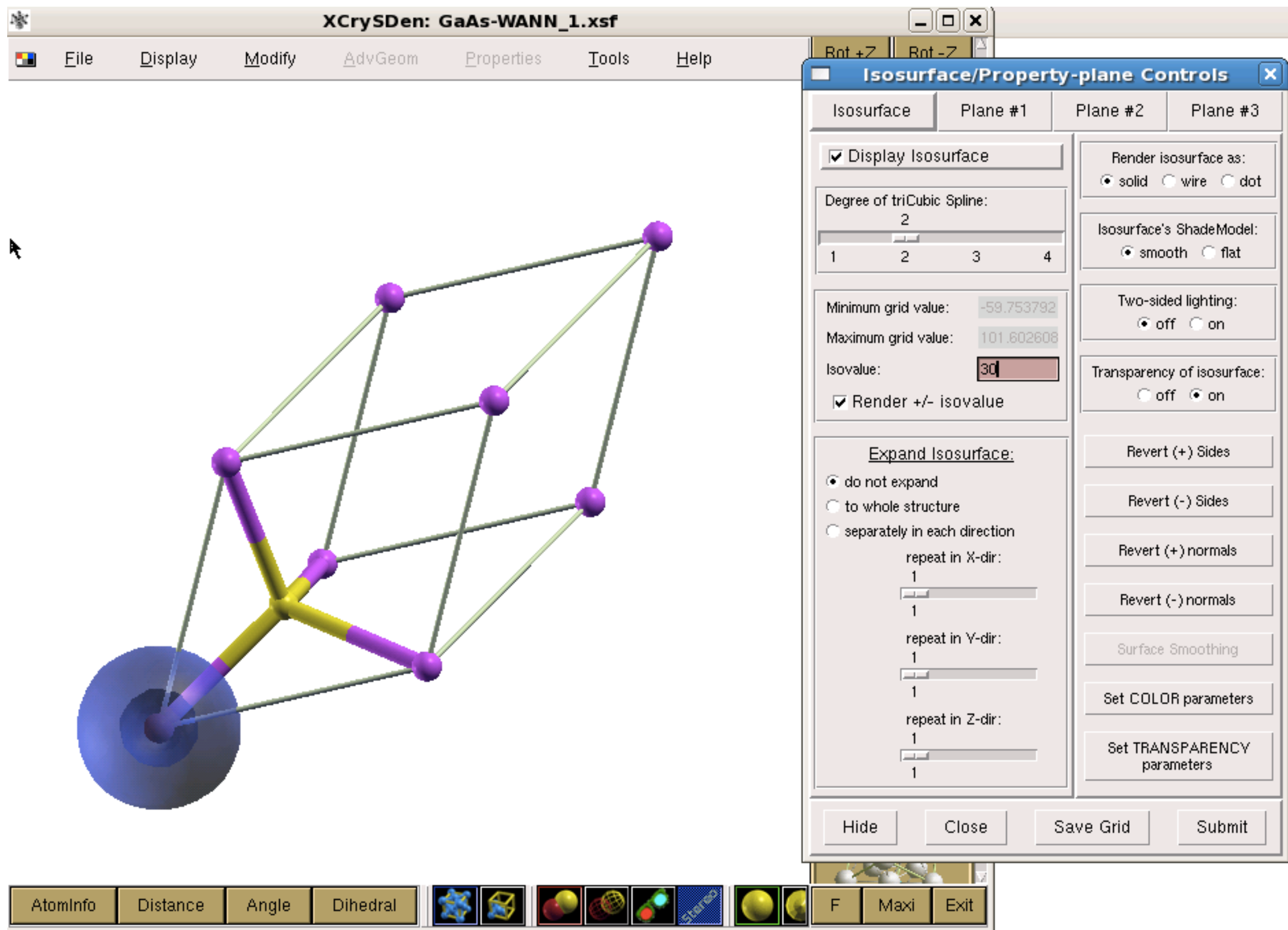
\$ x wplot -wf 1

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)



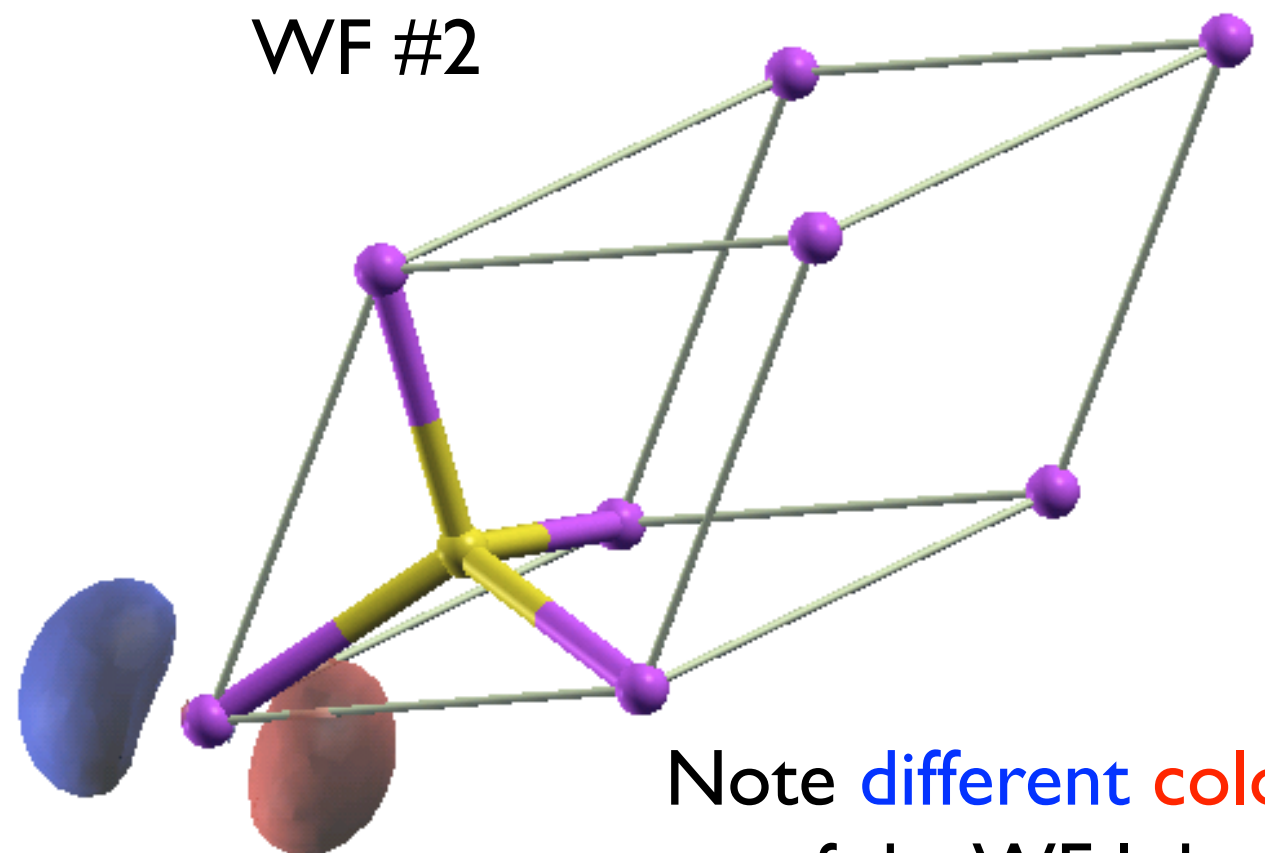
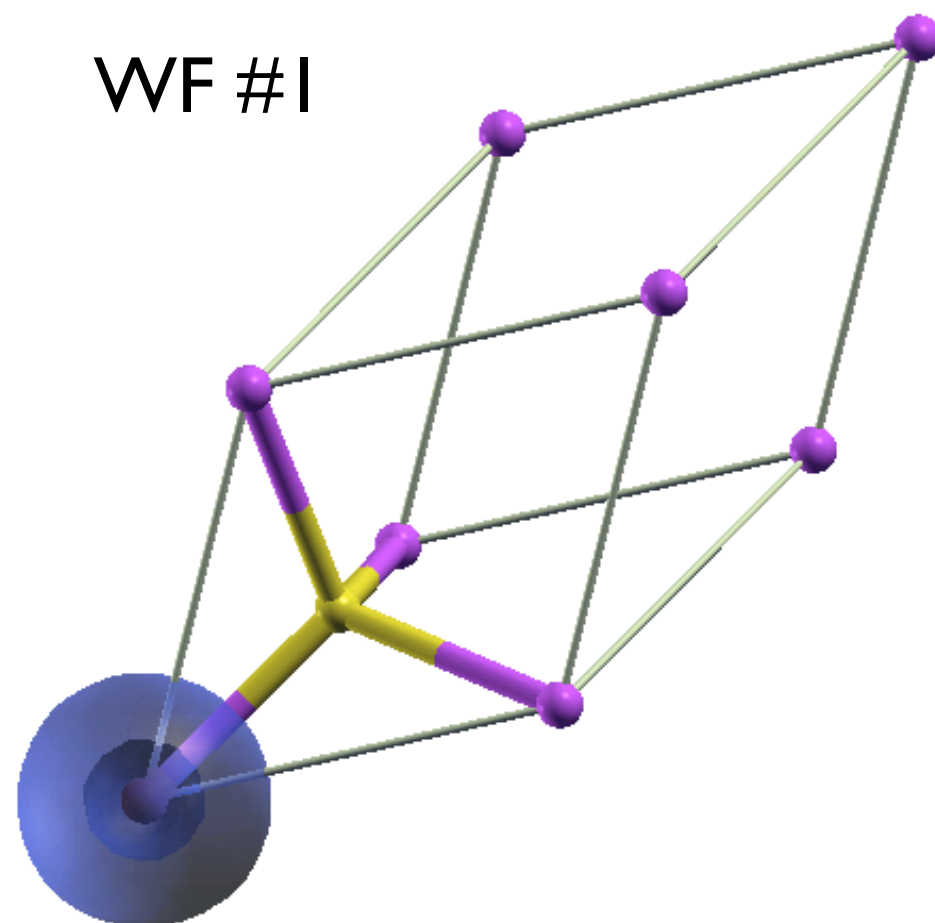
```
$ xcrysden --xsf GaAs-WANN_1.xsf
```

```
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**



Note different colours
of the WF lobes

Wannier Hamiltonian (similar to LCAO)

\$ less GaAs-WANN_hr.dat

...

Home unit cell

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	0.000000
0	0	0	8	1	-1.157088	0.000000

...

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

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:

$$E_p(\text{Ga}) - E_s(\text{Ga}) = 5.9 \text{ eV}$$

$$E_p(\text{As}) - E_s(\text{As}) = 9.9 \text{ eV}$$

$$E_p(\text{Ga}) - E_p(\text{As}) = 3.3 \text{ eV}$$

Wannier Hamiltonian (cont.)

...

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	0.000000
0	0	0	8	1	-1.157088	0.000000

...

0	0	1	1	1	-0.001219	0.000000
---	---	---	---	---	-----------	----------

Neighbour
unit cell

WF are well localized
⇒ nearest-neighbour suffice

Matrix element (eV)

$$\langle s_2 | H | s_1 \rangle = V_{ss\sigma}$$

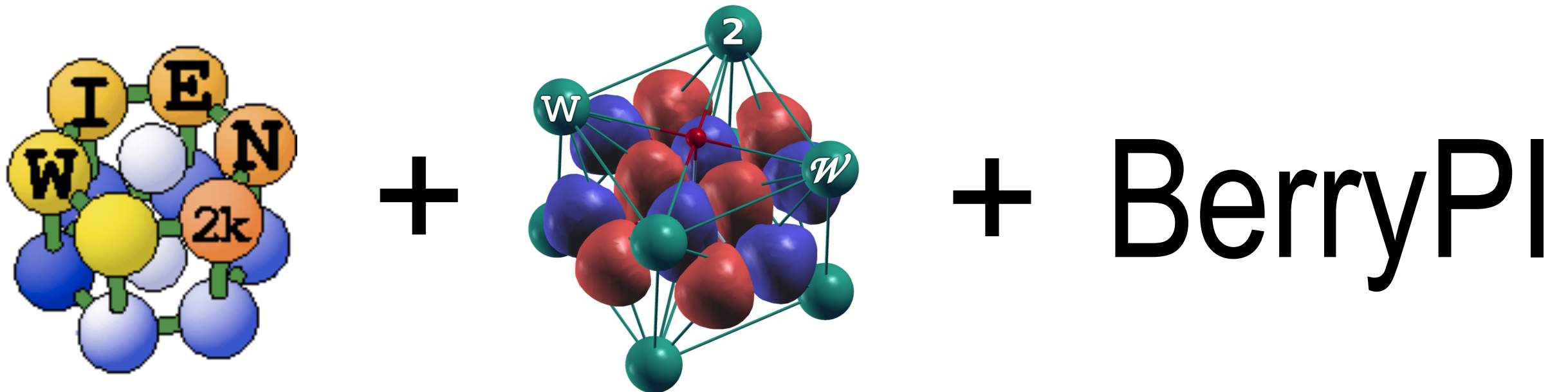
$$\langle p_2 | H | s_1 \rangle = V_{sp}$$

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	$E_p - E_k$

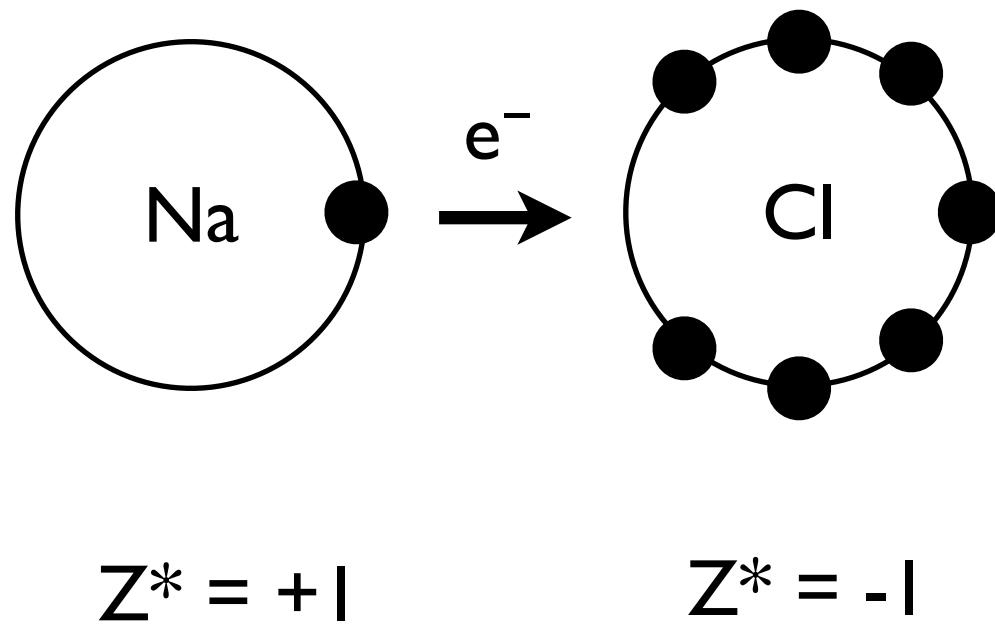
Now you have all
information
required to build
your *ab initio* TB
sp3 Hamiltonian
(Yu & Cardona)

Born effective charge of GaN

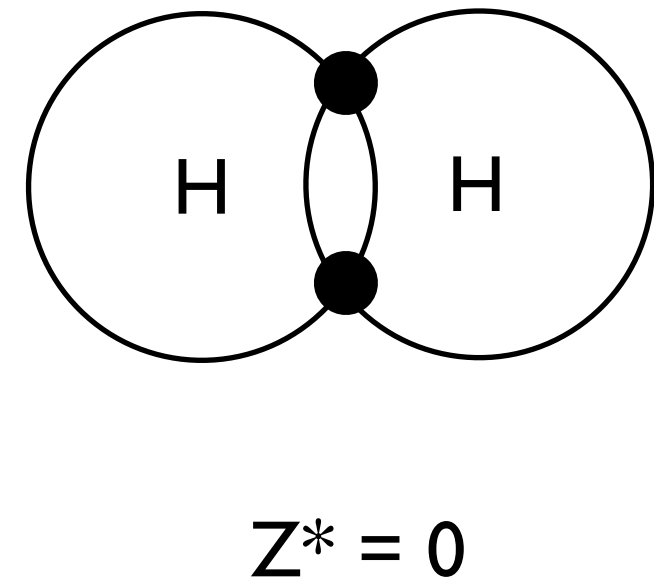


Background

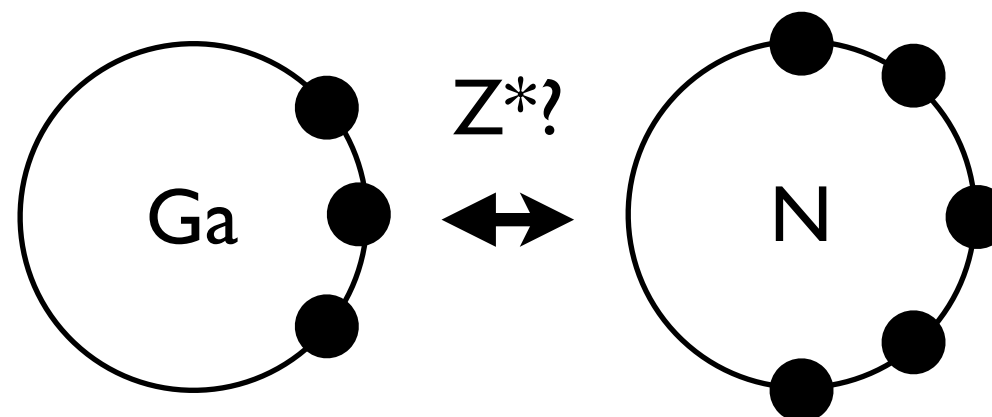
Ionic bond



Covalent bond



Mixed



Instructions

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

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

Hexagonal lattice “H”, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

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)

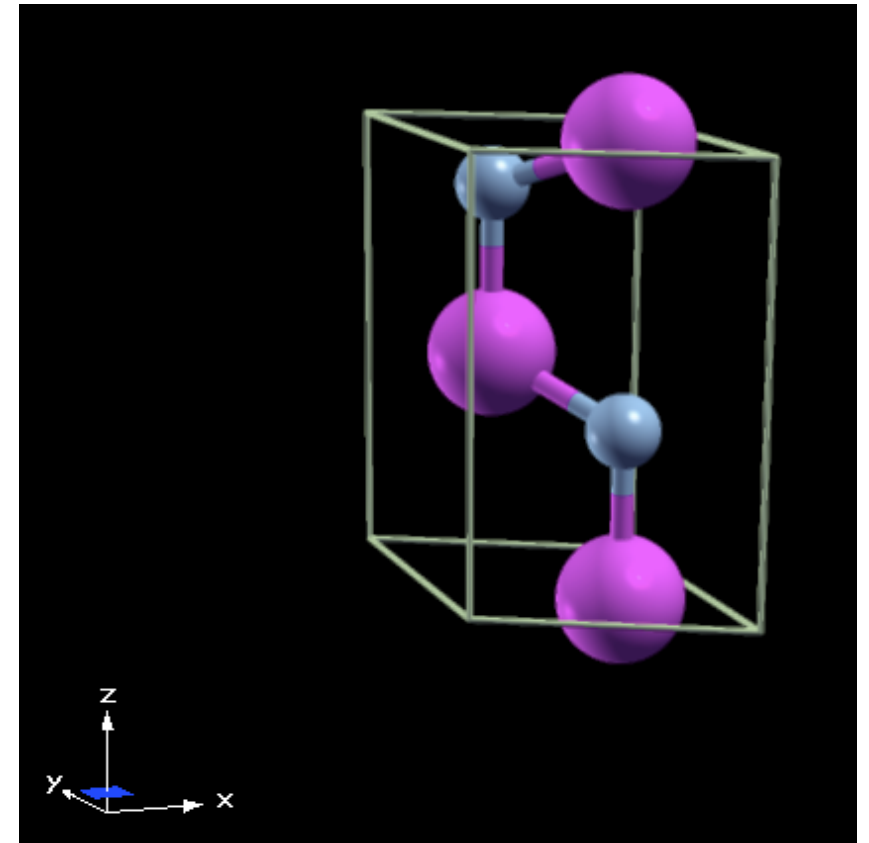
Initialize SCF calculation (LDA).

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

It is worth to verify the structure with XCrysDen

Perform regular SCF calculation

\$ run_lapw



Run Berry phase calculation

```
$ berrypi -k 8:8:4 | tee log
```

Note the ionic and electronic phases along Z-axis (wrapped $[-\pi \dots +\pi]$)

Save the calculation

```
$ save_lapw -d Lambda0
```

Introduce small displacement on N-atoms

w2web Edit Z-coordinate of N atoms by adding 0.001 to the equilibrium value of the fractional coordinate u_z . Since nitrogen has 2 equivalent positions, both need to be updated. Think what is the reason for the need to shift both atoms in this case.

Repeat initialization, SCF and Berry phase calculation steps (note “-a” option used in order to update the log file, not overwrite)

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

```
$ run_lapw
```

```
$ berrypi -k 8:8:4 | tee -a log
```

Evaluate the total Berry phase for each of two calculations performed

$$\phi = \phi_{\text{el}} + \phi_{\text{ion}}$$

and its change

$$\Delta\phi = \phi(\text{perturbed}) - \phi(\text{unperturbed})$$

Compute the effective charge Z^* of Nitrogen in GaN using a Berry phases and the “shortcut” expression

$$Z_{ii}^* = \frac{\Delta\phi_i}{2\pi\Delta u_i}$$

Here Δu is the displacement in fractional coordinates. The equation applies to the case of one atom displaced. In our case, we need to take into account that 2 N-atoms were shifted.

Compare computed Z^* with the literature value of -2.74 [Volume 44D of the series Landolt-Börnstein - Group III Condensed Matter pp 420-423, “GaN: effective charge, dielectric constants” by D. Strauch]

What is the effective charge of Ga in this structure?