VASP And Wannier90: A Quick Tutorial

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Wannier functions in two slides (simplified!)

- Wannier functions (WFs) are essentially an alternative basis for expanding the electronic states in periodic solids
- They are related to the more usual Bloch orbitals $\Psi_{n\mathbf{k}}$ by a unitary transformation:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} e^{i\varphi_n(\mathbf{k})} u_n(\mathbf{r}) \qquad w_{\mathbf{R}n}(\mathbf{r}) = \frac{V}{(2\pi)^3} \sum_{\mathbf{k}} \Psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k}.\mathbf{R}} e^{i\varphi_n(\mathbf{k})}$$

Arbitrary phase factor $e^{i\varphi_n(\mathbf{k})}$ not assigned by the Schrödinger equation

- The arbitrariness of $e^{i\varphi_n(\mathbf{k})}$ propagates to the WFs, but we can exploit this freedom to choose WFs which have the smallest "spread", i.e. "maximally locallised" WFs (MLWFs), which are the easiest to understand "chemically"

http://cfm.ehu.es/ivo/publications/marzari-psik03.pdf

Wannier functions in two slides (simplified!)

- The most general form of the WF <-> Bloch orbital transformation must take into account the fact that Bloch orbitals may be degenerate at some *k*-points:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow \sum_{n} U_{mn}^{(\mathbf{k})} \Psi_{\mathbf{mk}}(\mathbf{r}) \qquad w_{\mathbf{R}n}(\mathbf{r}) = \frac{V}{(2\pi)^3} \sum_{\mathbf{k}} \left[\sum_{n} U_{mn}^{(\mathbf{k})} \Psi_{\mathbf{mk}}(\mathbf{r}) \right] e^{-i\mathbf{k}.\mathbf{R}} e^{i\varphi_n(\mathbf{k})}$$

- The procedure for this is called “disentanglement”

- A few good links covering the mathematics in more detail:
  - http://journals.aps.org/rmp/abstract/10.1103/RevModPhys.84.1419
  - http://cfm.ehu.es/ivo/publications/marzari-psik03.pdf
  - http://www.tcm.phy.cam.ac.uk/~jry20/esdg2.pdf

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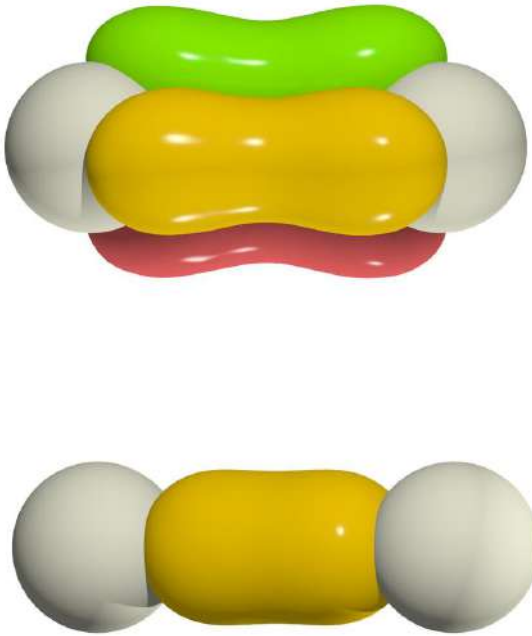
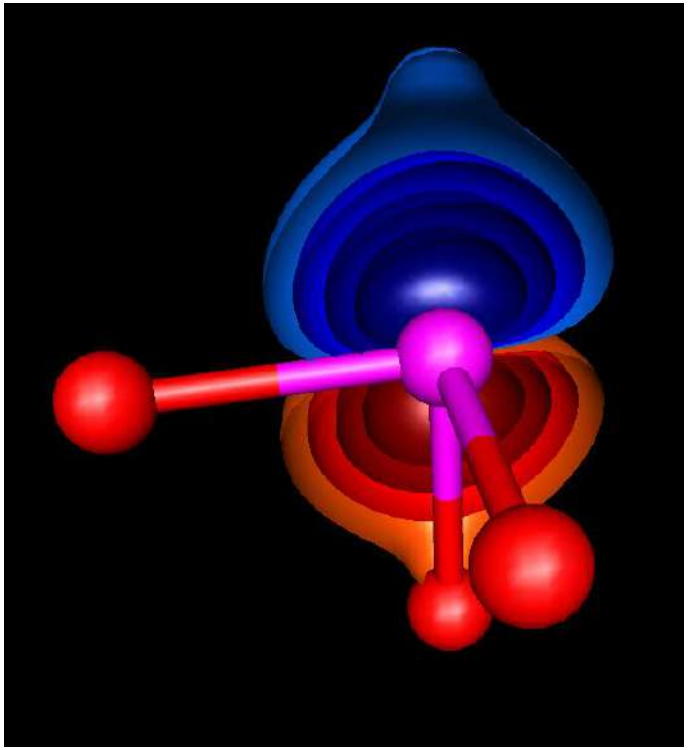
Wannier functions





Images from: https://en.wikipedia.org/wiki/Wannier_function

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Wannier functions: Why?

- MLWFs are the solid-state equivalent of molecular orbitals -> can be used to perform analyses which are difficult with Bloch orbitals:
    - More intuitive visualisation of orbitals
    - In an insulator, the charge centre of a MLWF provides a kind of classical definition for the location of an electron (pair) -> good for e.g. bonding analyses
    - The vector sum of the Wannier centres is directly related to the macroscopic polarisation
- Easy to obtain Bloch orbitals (and eigenvalues) at arbitrary *k*-points -> allows band dispersions to be computed from uniform *k*-point grids ("Wannier interpolation")
    - Potentially very useful for calculating effective masses

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http://cfm.ehu.es/ivo/publications/marzari-psik03.pdf

Building VASP with Wannier90 support

- Download Wannier90 1.2 from http://www.wannier.org/download.html [N.B. the interface from VASP 5.4.1 does *not* use the latest version]

- For more recent Intel compilers, copy `config/make.sys.ifort` to `make.sys` and edit as follows:

```
LIBDIR = /opt/intel/mkl721/lib/32
LIBS   =  -L$(LIBDIR) -lmkl_lapack  -lmkl_ia32 -lguide -lpthread

LIBDIR = ${MKLROOT}/lib/intel64
LIBS   =  -L$(LIBDIR) -mkl -lpthread
```

- Build the executable and library, run the tests, and check the report:

```
make wannier lib test
```

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Building VASP with Wannier90 support

- For VASP 5.4.1 and the Intel compilers, edit makefile.include as follows:

```
CPP_OPTIONS = ...
...
LLIBS = $(SCALAPACK) $(LAPACK) $(BLAS)

CPP_OPTIONS = -DVASP2WANNIER90 ...
...
LLIBS = install_path/libwannier.a $(SCALAPACK) $(LAPACK) $(BLAS)
```

- Recompile VASP:

```
make veryclean ; make gam std ncl
```

- N.B. The build was done from a copy of the source with all the latest patches applied - if you run into any strange build errors, try applying these to see if it fixes it

http://cms.mpi.univie.ac.at/wiki/index.php/LWANNIER90

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Tutorial: HSE 06 band structure

- First step:

```
ALGO = All
EDIFF = 1.0e-8
ENCUT = 500
ISIF = 2
ISMEAR = -5
KPAR = 2
NPAR = 1
LCHARG = .FALSE.
LREAL = .FALSE.
NBANDS = 16
NEDOS = 2000
PREC = Accurate
SYSTEM = Si

LHFCALC = .TRUE.
HFSCREEN = 0.2
```

Two-step job safer because typos in a `wannier90.win` file cause `VASP` to crash before writing out the `WAVECAR`; also, have to use `NPAR = N` with `LWANNIER90` set

- Second step (restart from `WAVECAR`):

```
ALGO = All
EDIFF = 1.0e-8
ENCUT = 500
ISIF = 2
ISMEAR = -5
KPAR = 2
!NPAR = 1
LCHARG = .FALSE.
LREAL = .FALSE.
NBANDS = 16
NEDOS = 2000
PREC = Accurate
SYSTEM = Si

LHFCALC = .TRUE.
HFSCREEN = 0.2

LWANNIER90 = .TRUE.
```

Appears to crash when `LWANNIER90` is set and `NPAR != N`

Switch on the `Wannier90` interface

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Tutorial: HSE 06 band structure

- `Wannier90` takes an input file `seedname.win` with control tags, plus a set of other input files containing information about the Bloch states
- The VASP interface uses a seedname of `wannier90`; VASP will look for `wannier90.win`, and create/update it if required
- Add the blocks in blue to the skeleton input file; these instruct `VASP`/`Wannier90` to use a random initial guess for the MLWFs, and to use them to guide the "Wannierisation"
- The remaining blocks are added by VASP *if they are not already there*

```
Begin Projections
  Random
End Projections

guiding_centres = true

num_wann = 16

begin unit_cell_cart
   2.7155  2.7155  0.000
   ...
end unit_cell_cart

begin atoms_cart
   Si  0.000  0.000  0.000
   ...
end atoms_cart

mp_grid = 8  8  8

begin kpoints
   ...
end kpoints
```

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Tutorial: HSE 06 band structure

- After the initial "Wannierisation", `Wannier90` can perform various post-processing - e.g. to compute a band structure:

```
restart = plot

bands_plot = true

begin kpoint_path
  L  0.50000  0.50000 0.50000  G  0.00000  0.00000 0.00000
  G  0.00000  0.00000 0.00000  X  0.50000  0.00000 0.50000
  X  0.50000  0.00000 0.50000  W  0.50000  0.25000 0.75000
  W  0.50000  0.25000 0.75000  G  0.00000  0.00000 0.00000
end kpoint_path

bands_num_points 50

bands_plot_format gnuplot xmgrace
```

Each line specifies a segment of the band structure

This sets the number of segments along the *first* path

If not specified, `gnuplot` is the default

http://www.wannier.org/doc/user_guide.pdf

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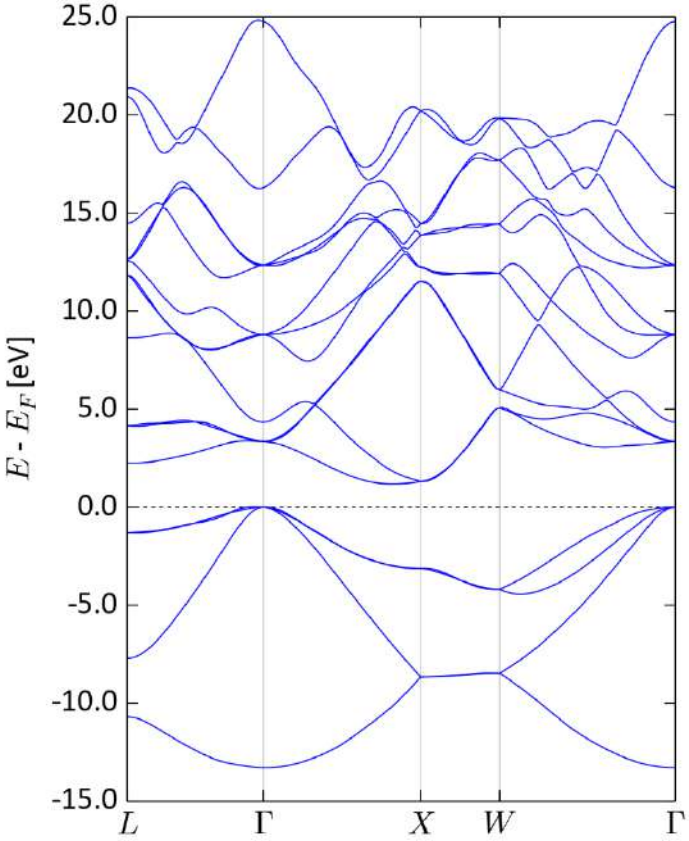
Tutorial: HSE 06 band structure



1. Run `VASP` with `LWANNIER90 = .TRUE.` and your skeleton input file in the working directory
2. Run:

   ```
   wannier90.x wannier90
   ```

   to minimise the MLWFs; the solutions are written to `wannier90.chk`
3. Add the band-structure (or other post-processing) commands and rerun `wannier90.x`
4. Raw data are written to `wannier90_band.dat`/`wannier90_kpt.dat`; scripts to plot using `gnuplot`/`grace` are also produced depending on `bands_plot_format`

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Wannier90 vs "fake self-consistency"

- The alternative technique for computing hybrid band structures in VASP is to introduce zero-weight *k*-points into the KPOINTS file
- The eigenvalues at these *k*-points are converged iteratively, but do not contribute to the total energy, and so are not part of the break criteria for the SCF loop

For hybrid functionals and Hartree-Fock, the band structure can be calculated by adding additional k-points with zero weight to the KPOINTS file. This is easily achieved, by performing first a standard hybrid functional calculation with a conventional KPOINTS file. After the run, copy the IBZKPT file to the KPOINTS file (this file stores explictly the list of k-points used in the previous calculation), and simply add the desired additional k-points with zero weight. Since VASP uses an iterative matrix diagonalization and since the added k-points do not influence the energy, one needs to force VASP to perform at least 5 iterations before inspecting the one-electron energies at k-points with zero weight (NELMIN = 5).

http://cms.mpi.univie.ac.at/vasp/vasp/Accurate_DOS_Band_structure_calculations.html

Wannier90 vs “fake self-consistency”

- How many iterative steps (NELMIN) are needed to converge the eigenvalues at the zero-weight *k*-points? We can check by comparing the “mesh” and “band” Γ-point eigenvalues…

k-point 1 : 0.0000 0.0000 0.0000

band No.	band energies	occupation
1	-7.8357	2.00000
2	5.4647	2.00000
3	5.4647	2.00000
4	5.4647	2.00000
5	8.8034	0.00000
6	8.8034	0.00000
7	8.8034	0.00000
8	9.7959	0.00000
9	14.2683	0.00000
10	14.2683	0.00000
11	14.2739	0.00000
12	17.8122	0.00000
13	17.8122	0.00000
14	17.8122	0.00000
15	21.7603	0.00000
16	30.2363	0.00000

k-point 39 : 0.0000 0.0000 0.0000

band No.	band energies	occupation
1	-7.2102	0.00000
2	7.0956	0.00000
3	7.4845	0.00000
4	9.1114	0.00000
5	8.8483	0.00000
6	12.7657	0.00000
7	11.5932	0.00000
8	8.3881	0.00000
9	11.7581	0.00000
10	25.6173	0.00000
11	16.9587	0.00000
12	22.9149	0.00000
13	29.8875	0.00000
14	27.4218	0.00000
15	27.8106	0.00000
16	35.8819	0.00000

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Wannier90 vs “fake self-consistency”

- Restart from WAVECAR w/ NELMIN = 5

```
 k-point     1 :       0.0000    0.0000    0.0000     k-point    39 :       0.0000    0.0000    0.0000
  band No.  band energies     occupation                 band No.  band energies     occupation
      1      -7.8357       2.00000                         1      -7.2102       0.00000
      2       5.4647       2.00000                         2       7.0956       0.00000
      3       5.4647       2.00000                         3       7.4845       0.00000
      4       5.4647       2.00000                         4       9.1114       0.00000
      5       8.8034       0.00000                         5       8.8483       0.00000
      6       8.8034       0.00000                         6      12.7657       0.00000
```

- Restart from WAVECAR w/ NELMIN = 10

```
 k-point     1 :       0.0000    0.0000    0.0000     k-point    39 :       0.0000    0.0000    0.0000
  band No.  band energies     occupation                 band No.  band energies     occupation
      1      -7.8357       2.00000                         1      -7.5815       0.00000
      2       5.4647       2.00000                         2       6.7979       0.00000
      3       5.4647       2.00000                         3       7.3720       0.00000
      4       5.4647       2.00000                         4       7.7883       0.00000
      5       8.8034       0.00000                         5       8.7538       0.00000
      6       8.8034       0.00000                         6      10.9143       0.00000
```

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Wannier90 vs “fake self-consistency”

- In practice, the best solution is to run a “clean” SCF (i.e. restart from fresh, or from a standard DFT WAVECAR) with the zero-weight *k*-points present…
- This is how it’s done in the Si tutorial on the VASP Wiki

k-point 1 : 0.0000 0.0000 0.0000			k-point 39 : 0.0000 0.0000 0.0000		
band No.	band energies	occupation	band No.	band energies	occupation
1	-7.8357	2.00000	1	-7.8219	0.00000
2	5.4647	2.00000	2	5.4785	0.00000
3	5.4647	2.00000	3	5.4785	0.00000
4	5.4647	2.00000	4	5.4788	0.00000
5	8.8034	0.00000	5	8.8034	0.00000
6	8.8034	0.00000	6	8.8034	0.00000
7	8.8034	0.00000	7	8.8050	0.00000
8	9.7959	0.00000	8	9.7953	0.00000
9	14.2683	0.00000	9	14.2742	0.00000
10	14.2683	0.00000	10	14.2705	0.00000
11	14.2739	0.00000	11	14.2706	0.00000
12	17.8122	0.00000	12	17.8126	0.00000

- The “clean” SCF does 10 steps in this particular case (i.e. the same as NELMIN = 10), but gives much better convergence - presumably an implementation detail…?

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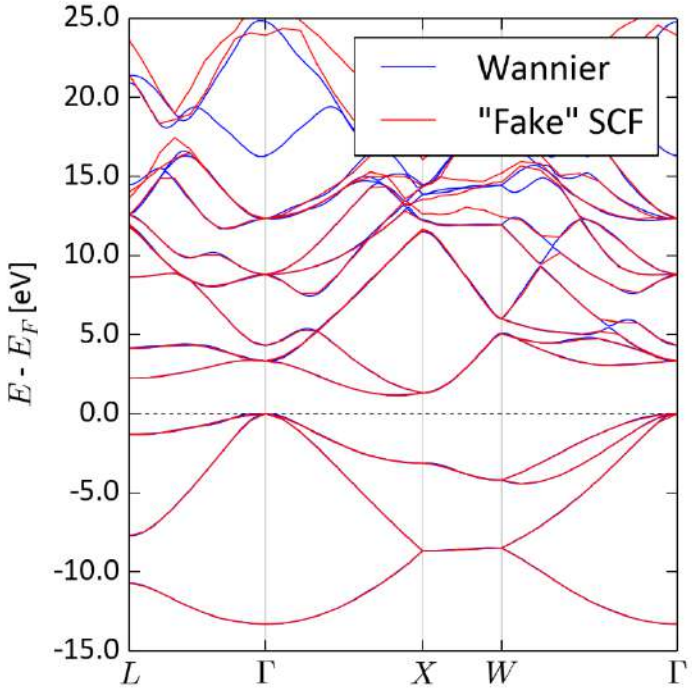
Wannier90 vs “fake self-consistency”

- The main issue with the “fake SCF” method is that the eigenvalues at the zero-weight *k*-points still need to be explicitly calculated, which increases the calculation time



Calculation	SCF time [s]
8x8x8 Γ-centred mesh	1063.904
+ 40 zero-weight *k*-points	2511.258
10x10x10 Γ-centred mesh	3349.650

Using Wannier90 is *much* cheaper - if you have computing time to burn, use a larger *k*-point sampling mesh and/or more bands instead!

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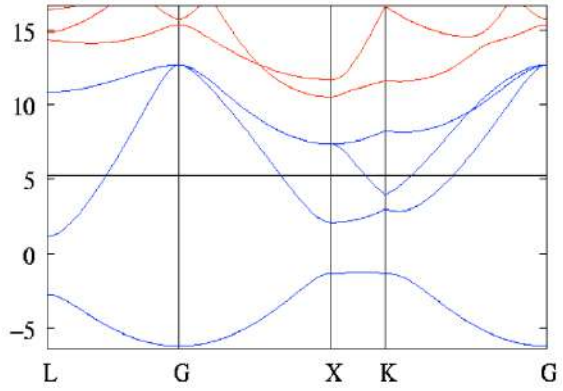
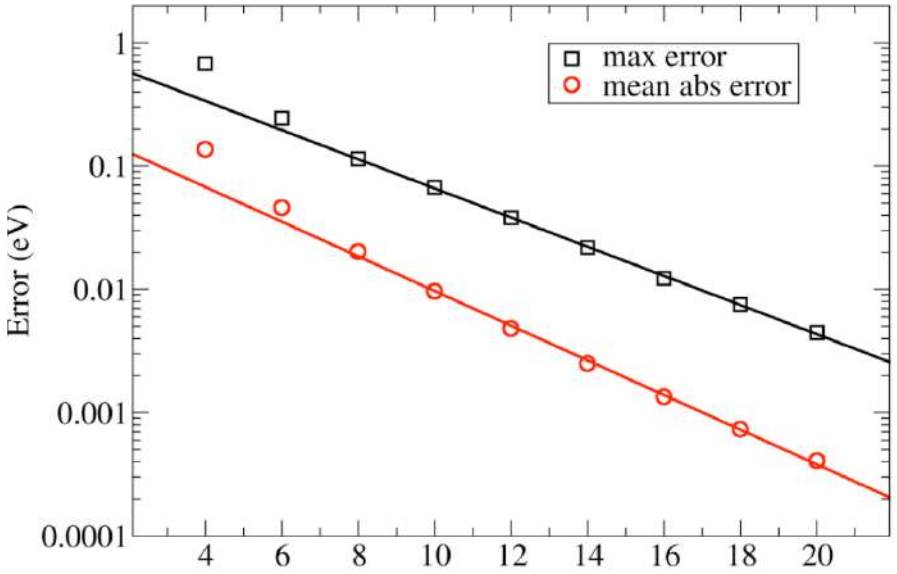
Wannier90 vs “fake self-consistency”

- The Wannier-interpolated eigenvalues converge exponentially to the exact ones as a function of the size of the uniform *k*-point sampling mesh





Figures from: http://www.tcm.phy.cam.ac.uk/~jry20/esdg2.pdf

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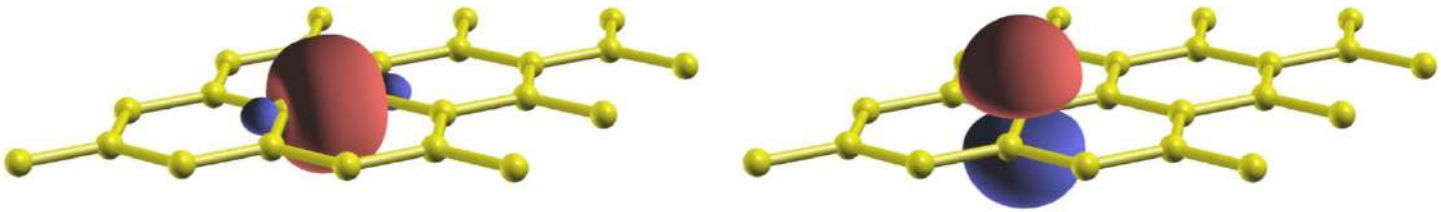
Tutorial: Some other post processing

- Plot the MLWFs for visualisation
  1. Re-run VASP (restart from `WAVECAR`) with `LWRITE_UNK = .TRUE.` in the `INCAR` file; this writes the cell-periodic part of the wavefunctions at each *k*-point, which are needed by `Wannier90` for plotting
  2. Run `Wannier90` to generate the MLWFs, then restart with the following post-processing tags:

```
wannier_plot = true
wannier_plot_supercell = 2
wannier_plot_format = xcrysden
```

Technically, the Wannier functions exist in a supercell compatible with the *k*-point mesh used to generate them



Images from: http://www.tcm.phy.cam.ac.uk/~jry20/esdg2.pdf

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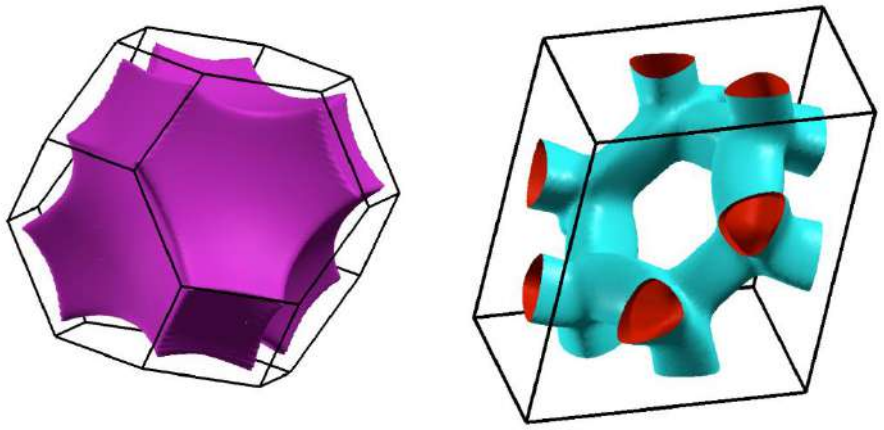
Tutorial: Some other post processing

- Calculate and plot the Fermi surface (when E_F cuts across bands):
  - Restart `Wannier90` with the following post-processing tags:

```
restart = plot
fermi_energy = 5.465085
fermi_surface_plot = true
```

Get from `OUTCAR`



Images from: http://www.tcm.phy.cam.ac.uk/~jry20/esdg2.pdf

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Tutorial: Some other post processing

- To output the coordinates of the Wannier centres:
  - Just add `write_xyz = true` to the input file
  - Can also add `translate_home_cell = true` to translate centres to the first unit cell

```
 16
 Wannier centres, written by Wannier90 on14Feb2016 at 13:33:04
X          4.73106304       3.08479106       3.22307628
X          0.58670091       2.37932699       1.81687824
X          1.84763232       2.03487825       1.28324033
X          3.35644008       4.04048840       4.09626106
X          2.24955146       2.58038861       4.71003077
X          1.29288053       3.20634223       3.14141564
X          2.49404870       0.75778886       3.04055439
X          3.16416139       2.89011223       0.91641396
...
Si         0.00000000       0.00000000       0.00000000
Si         1.35775000       1.35775000       1.35775000
```

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Summary (and a caveat)

- `Wannier90` is easy to use with `VASP` (when you know how!), and is a great post-processing tool
- Particularly good for band structures
  - The "correct" way to do hybrid band structures
  - The only way to do *GW* band structures
  - Recalculating band structures (e.g. with different *k*-point paths) is trivial once the initial calculation has been done
- Potentially useful for a lot of other things (e.g. visualisation, calculating effective masses)
- Unfortunately, the `VASP`/`Wannier90` interface does not yet support spin-orbit coupling - newer versions of `Wannier90` support SoC, but the `VASP` interface needs to be updated to pass it the necessary information

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Some useful links

- Covering the mathematics in detail (again):
  - http://journals.aps.org/rmp/abstract/10.1103/RevModPhys.84.1419
  - http://cfm.ehu.es/ivo/publications/marzari-psik03.pdf
  - http://www.tcm.phy.cam.ac.uk/~jry20/esdg2.pdf

- `Wannier90` manual: http://www.wannier.org/doc/user_guide.pdf

- `VASP` manual page on the `LWANNIER90` tag and Si band structure tutorials:
  - http://cms.mpi.univie.ac.at/wiki/index.php/Si_bandstructure
  - http://cms.mpi.univie.ac.at/wiki/index.php/Bandstructure_of_Si_in_GW_(VASP2WANNIER90)

- Tutorial (explains the features; easily adaptable): http://wannier.org/doc/tutorial.pdf

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