Localizing wave functions

Maximally localized Wannier functions

02/18/2022
Downfolding school, discussion 2

Install Wannier90, pyWannier90 on campuscluster

The compilation does not work for my local Mac M1 machine. It is only tested on campus cluster.

Wannier90: http://www.wannier.org/download/

pyWannier90: https://github.com/hungpham2017/pyWannier90

Lucas' instructions for setting up conda environment on campus cluster: http://wagner.physics.illinois.edu/resources/campus_cluster/

Support:

- User guide and tutorials for Wannier90: http://www.wannier.org/support/

Compilation: get Wannier90 and pyWannier90

Once on campuscluster, you may follow these steps:

```
module load anaconda/3
module load openmpi/4.1.0-gcc-7.2.0
. /usr/local/anaconda/5.2.0/python3/etc/profile.d/conda.sh
conda activate
conda create --name pywannier python=3.10.0
module load intel/18.0
```

Load the environment: `conda activate pywannier`. Then clone pyWannier90:

```
git clone https://github.com/hungpham2017/pyWannier90.git
```

Download Wannier90, unzip it, replace wannier_lib.F90:

```
wget https://github.com/wannier-developers/wannier90/archive/v3.1.0.tar.gz
tar -xf v3.1.0.tar.gz
cd wannier90-3.1.0
cp ../pyWannier90/src/wannier_lib.F90 ./src/wannier_lib.F90
cp /projects/wagner/yueqing2/downfolding/wannier90-3.1.0/make.inc ./
make
make lib
```

```
cd ../pyWannier90/src
cp /projects/wagner/yueqing2/downfolding/pyWannier90/src/Makefile ./
```

- modify the W90DIR in the Makefile to: `W90DIR = the_path_to_your_compiled_wannier90-3.1.0` . Then,

```
pip install pybind11
make
```

Compilation: let PySCF know you have pyWannier now

- After you get the compiled libwannier90.cpython-39-x86_64-linux-gnu.so ,
  test by typing `python3 -c "import libwannier90”.` If there is no output, the compilation is successful.

You can re-install pyscf, remember to replace the pywannier90.py with the one in pyWannier90:

```
cd ../../
git clone https://github.com/pyscf/pyscf.git
cp ./pyWannier90/src/pywannier90.py ./pyscf/pyscf/pbc/tools/
cd pyscf
```

- Modify the file: `pyscf/pbc/tools/pywannier90.py` such that it knows where your compiled libwannier90 is.

  For example, I edited the following line

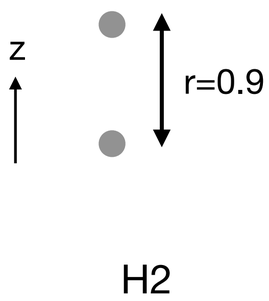
```
W90DIR = '/projects/wagner/yueqing2/downfolding/pyWannier90/src/'
```

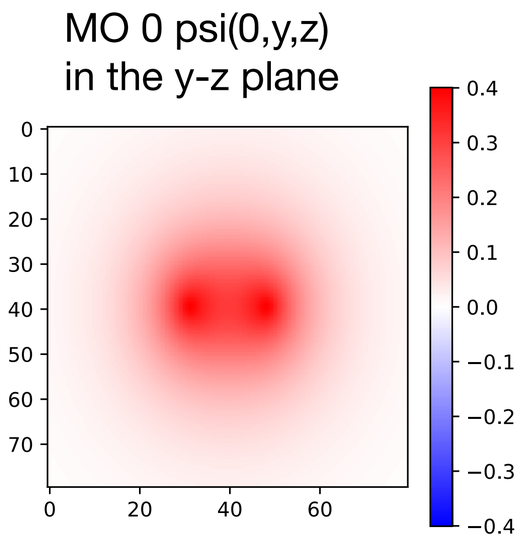
```
cd ../../../
module unload intel/18.0
module load cmake
pip install ./
```

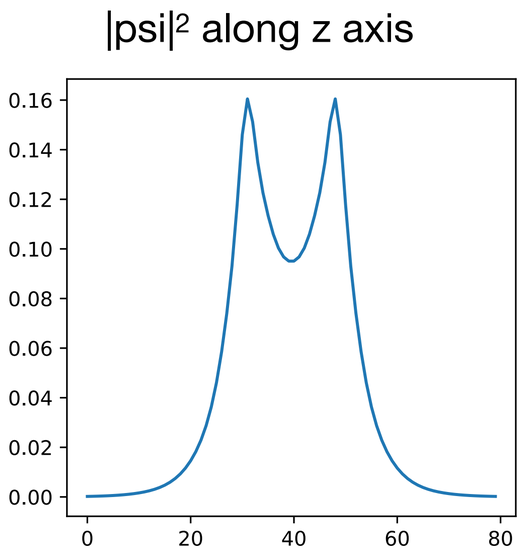
Remember to run these to activate the environment:

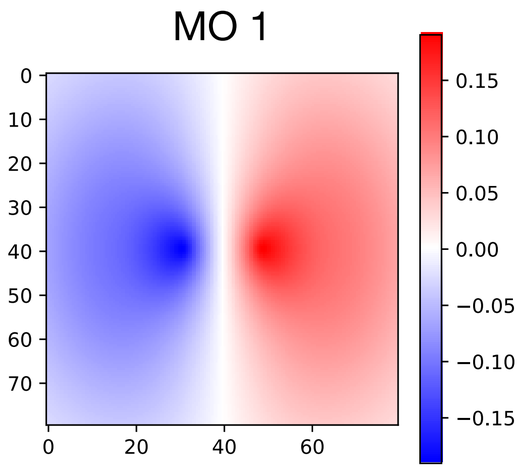
```
module load anaconda/3
module load openmpi/4.1.0-gcc-7.2.0
. /usr/local/anaconda/5.2.0/python3/etc/profile.d/conda.sh
conda activate pywannier
module load intel/18.0
```

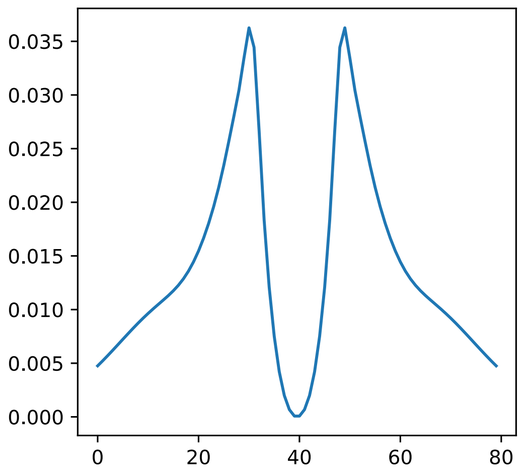
Example: H2 molecule











Effective Hamiltonian in MO basis:

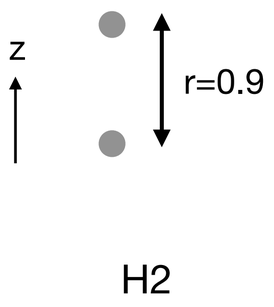
$$H_{\text{eff}} = |\Phi_0\rangle\, \epsilon_0\, \langle\Phi_0| + |\Phi_1\rangle\, \epsilon_1\, \langle\Phi_1|$$

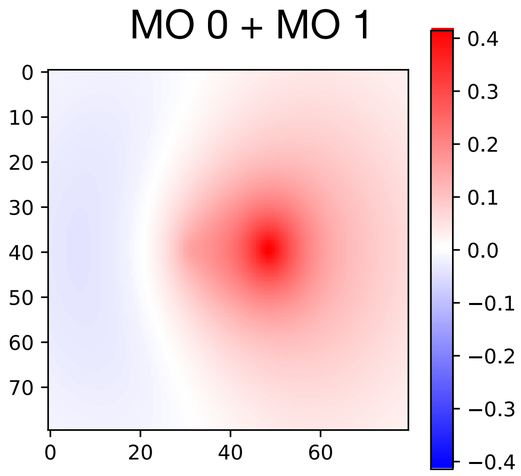
Or in matrix form:

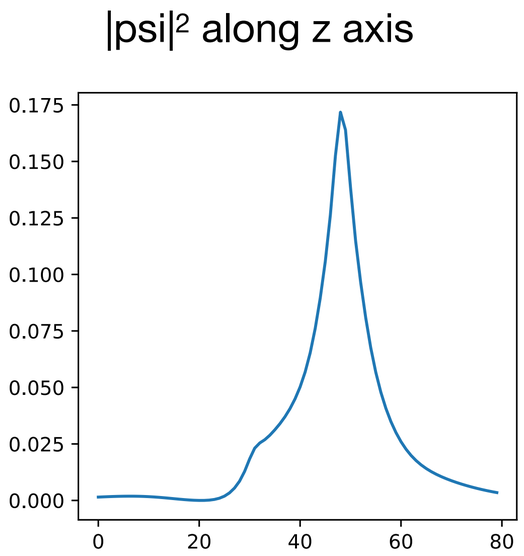
$$H_{\text{eff}} = \begin{bmatrix} \epsilon_0 & 0 \\ 0 & \epsilon_1 \end{bmatrix}$$

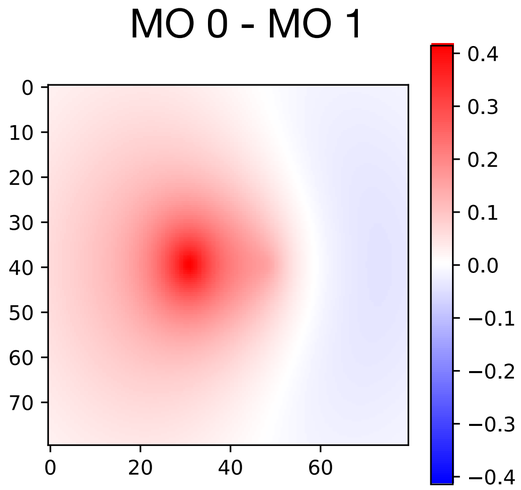
Example: H2 molecule

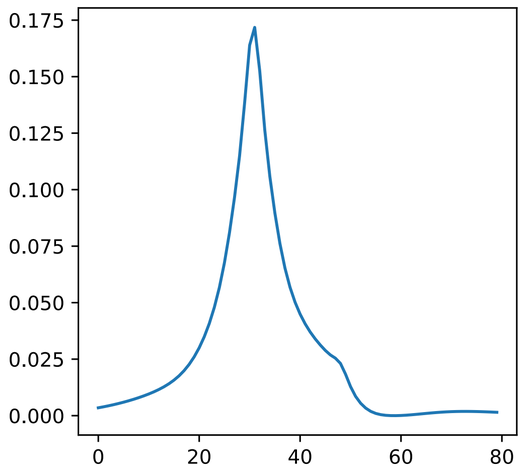
Rotate within these two MOs





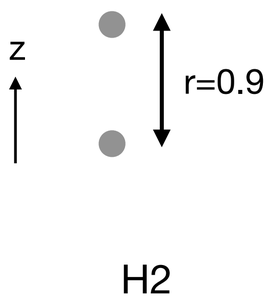


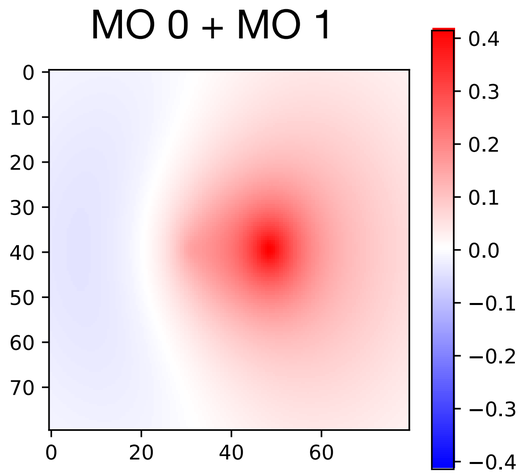


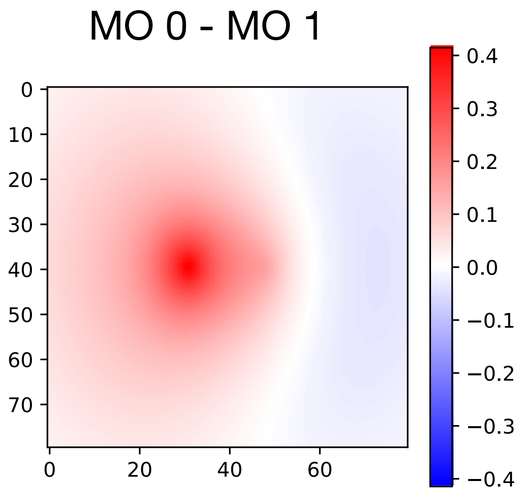


Example: H2 molecule

Rotate within these two MOs







Transformation matrix

$$U = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$$

The transformed effective Hamiltonian in localized basis:

$$UHU^{\dagger} = \frac{1}{2} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} \epsilon_0 & 0 \\ 0 & \epsilon_1 \end{bmatrix} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$$

The Hamiltonian before the transformation:

$$\begin{bmatrix} -0.55005221 & 0 \\ 0 & -0.1422164 \end{bmatrix}$$

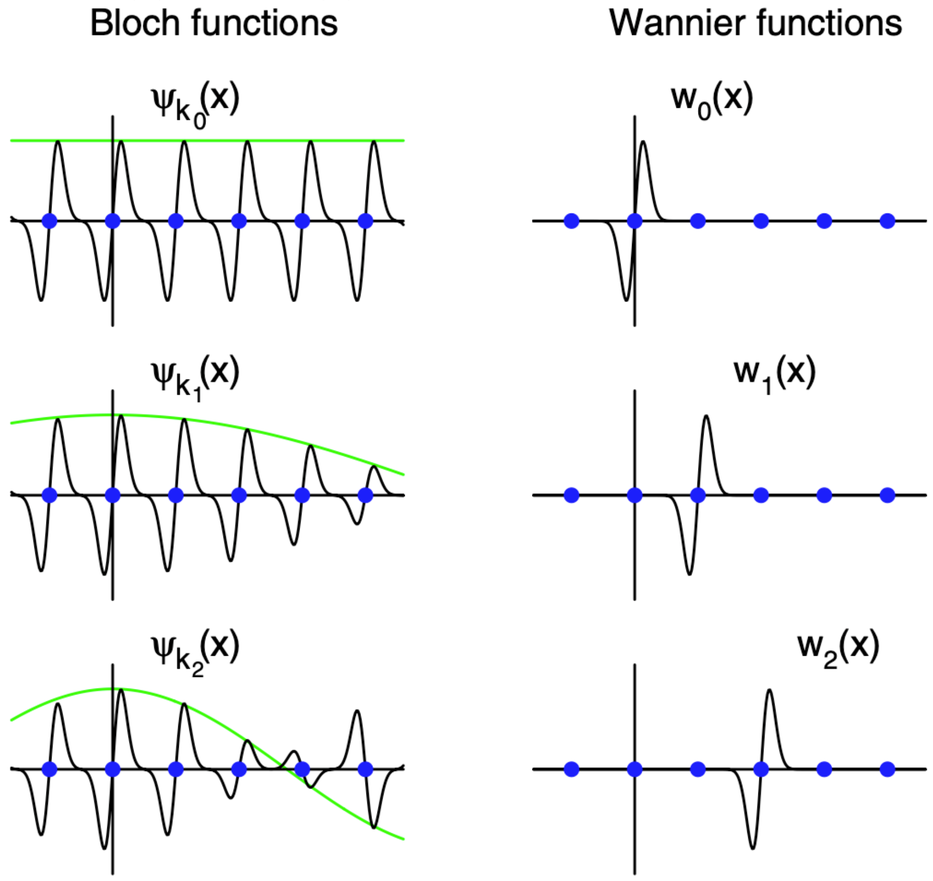
After:

$$\begin{bmatrix} -5.54889167 & -9.41879897 \\ -9.41879897 & -5.54889167 \end{bmatrix}$$

Wannier functions as a linear superposition of the Bloch functions

General formalism: (Single band in a 1D chain)

$$\psi_k(x) = e^{ikx} u_k(x)$$



Constructing the Wannier functions is like doing Fourier transformation on the Bloch orbitals

$$w_0(x) = \frac{a}{2\pi} \int_{\mathrm{BZ}} dk \psi_k(x)$$

Generalize to multiple bands in 3D:

$$w_0(\mathbf{r}) = \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \psi_{n\mathbf{k}}(\mathbf{r})$$

Translate the real space Wannier function by a lattice vector **R**:

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

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\mathbf{R}n\rangle$$

N. Marzari et al. Rev. Mod. Phys., 84.1419 (2012)

The “gauge freedom” in the definition of the Bloch functions

There exists a “gauge freedom” in the definition of the Bloch functions:

$$|\tilde{\psi}_{n\mathbf{k}}\rangle = e^{i\varphi_n(\mathbf{k})}|\psi_{n\mathbf{k}}\rangle$$

or equivalently for Bloch orbitals:

$$|\tilde{u}_{n\mathbf{k}}\rangle = e^{i\varphi_n(\mathbf{k})}\,|u_{n\mathbf{k}}\rangle$$

Smoothness criterion:

$\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$ is well defined at every ***k***.

Generalize to the multi band case:

For *J* bands, one can define a “gauge transformation” (or basis rotation) that conserves the trace over this band manifold

$$\left|\tilde{\psi}_{n\mathbf{k}}\right\rangle = \sum_{m=1}^{J} U_{mn}^{(\mathbf{k})}\,|\psi_{m\mathbf{k}}\rangle$$

Here $U_{mn}^{(\mathbf{k})}$ is a unitary matrix of dimension *J*, and is periodic in **k**.

One can verify that the projection operator is invariant under the gauge transformation:

$$P_{\mathbf{k}} = \sum_{n=1}^{J} |\psi_{n\mathbf{k}}\rangle\,\langle\psi_{n\mathbf{k}}| = \sum_{n=1}^{J} \left|\tilde{\psi}_{n\mathbf{k}}\right\rangle\left\langle\tilde{\psi}_{n\mathbf{k}}\right|$$

Comments:

1. Wannier functions are non-unique.
2. Smoothness criterion is usually incompatible with the localization of the Wannier functions. Directly taking the Bloch functions to compute the Wannier orbitals, you usually would not get very localized orbitals.
3. In the case when there is band degeneracy, $\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$ is not well defined.

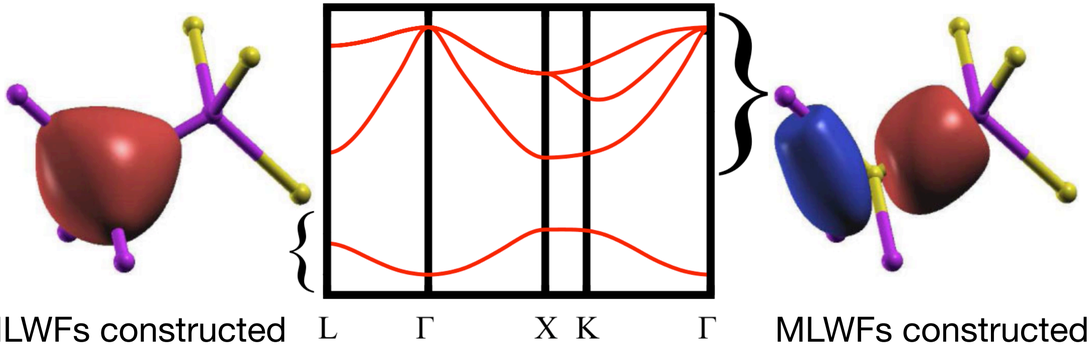
N. Marzari et al. Rev. Mod. Phys., 84.1419 (2012)

The chosen active space can be isolated or attached.

1. Isolated bands

- The desired bands lie within a limited energy range are isolated from other bands

Example: GaAs



MLWFs constructed from n=1, As s band

MLWFs constructed from n=2-4, As p bands

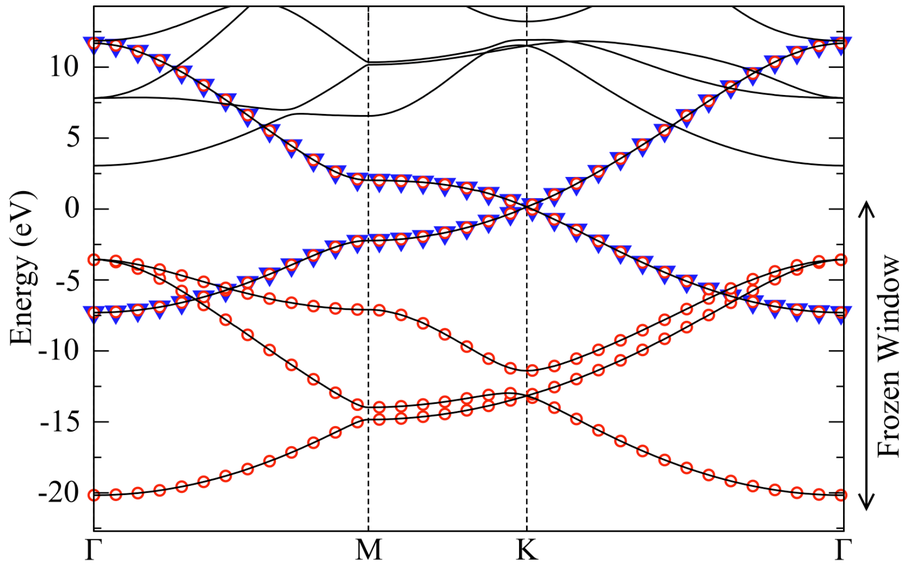
It is important to know what is the active space we want to ‘downfold’ to.

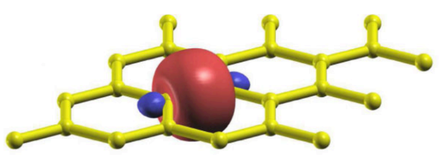
N. Marzari et al. Rev. Mod. Phys., 84.1419 (2012)

2. Entangled bands

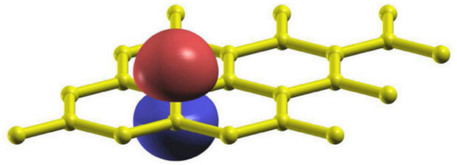
- The desired bands lie within a limited energy range but overlap and hybridize with other bands which extend further out in energy

Example: graphene





MLWFs constructed from bands denoted by red circles



MLWFs constructed from bands denoted by blue triangles

Isolated bands: starting from projecting onto some trial orbitals

Wannier functions via projection

One starts from a set of *J* localized trial localized orbitals $g_n(\mathbf{r})$

These $g_n(\mathbf{r})$ are projected on to the Bloch manifold

$$|\phi_{n\mathbf{k}}\rangle = \sum_{m=1}^{J} |\psi_{m\mathbf{k}}\rangle \langle \psi_{m\mathbf{k}} \mid g_n\rangle$$

Then orthonormalize these states.

In practice, one computes the matrix of inner products

$$(A_{\mathbf{k}})_{mn} = \langle \psi_{m\mathbf{k}} \mid g_n\rangle$$

Then construct

$$|\phi_{n\mathbf{k}}\rangle = \sum_{m=1}^{J} (A_{\mathbf{k}})_{mn} |\psi_{m\mathbf{k}}\rangle$$

And the overlap matrix

$$(S_{\mathbf{k}})_{mn} = \langle \phi_{m\mathbf{k}} \mid \phi_{n\mathbf{k}}\rangle_V = \left(A_{\mathbf{k}}^{\dagger} A_{\mathbf{k}}\right)_{mn}$$

Then construct the Löwdin-orthonormalized Bloch-like states:

$$\boxed{\left|\tilde{\psi}_{n\mathbf{k}}\right\rangle} = \sum_{m=1}^{J} |\phi_{m\mathbf{k}}\rangle \left(S_{\mathbf{k}}^{-1/2}\right)_{mn}$$

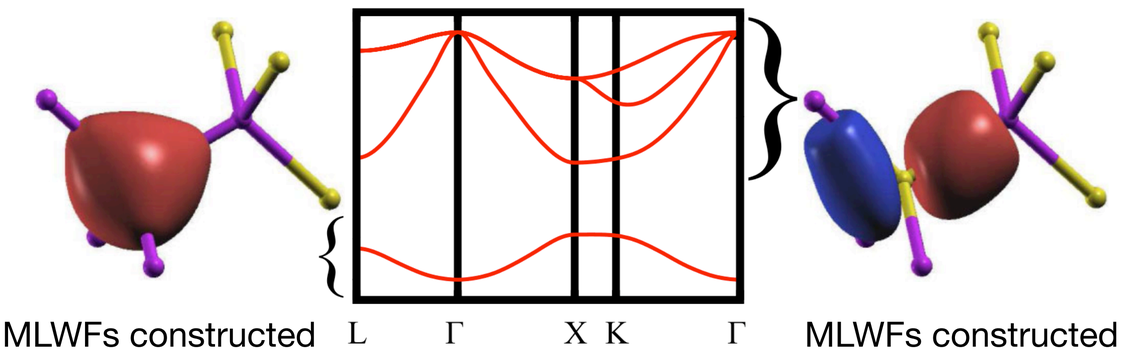
These are good starting point for constructing localized Wannier functions.

(One can prove that $|\tilde{\psi}_{n\mathbf{k}}\rangle$ are related to $|\psi_{n\mathbf{k}}\rangle$ by the unitary transformation $A(A^{\dagger}A)^{-1/2}$.)

N. Marzari et al. Rev. Mod. Phys., 84.1419 (2012)

Maximally localized Wannier functions (MLWFs)

The reference orbitals are good starting point for refining the unitary transformation $U_{mn}^{(\mathbf{k})}$ in order to get <u>the maximally localized Wannier functions (MLWFs).</u>



MLWFs constructed from n=1, As s band

MLWFs constructed from n=2-4, As p bands

To obtain the MLWFs, the localization functional is defined.

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

It measures the sum of the quadratic spreads of all the Wannier functions in the home unit cell around their centers.

By minimizing it self-consistently, one can obtain the best unitary transformation that gives MLWFs.

N. Marzari et al. Rev. Mod. Phys., 84.1419 (2012)

The localization functional

A general and now widely used approach to construct maximally localized Wannier functions:

Def. The localization functional: $\Omega = \Omega_{\mathrm{I}} + \tilde{\Omega}$

gauge-invariant

$$\Omega_{\mathrm{I}} = \sum_n \left[\langle \mathbf{0}n | r^2 | \mathbf{0}n \rangle - \sum_{\mathbf{R}m} |\langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle|^2 \right]$$

gauge-dependent

$$\tilde{\Omega} = \sum_n \sum_{\mathbf{R}m \neq 0n} |\langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle|^2$$

Reciprocal space representation:

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

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

Ω_{I} measures the "change of character " of states across the BZ.

The gradient for any smooth function *f*(**k**) (finite difference)

$$\nabla f(\mathbf{k}) = \sum_{\mathbf{b}} w_b \mathbf{b} [f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k})] + \mathcal{O}\left(b^2\right)$$

$$|\nabla f(\mathbf{k})|^2 = \sum_{\mathbf{b}} w_b [f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k})]^2 + \mathcal{O}\left(b^3\right)$$

Define the **overlap matrix** between Bloch orbitals at neighboring k points:

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} \mid u_{n,\mathbf{k}+\mathbf{b}} \rangle$$

Localization functional written in terms of overlap matrices:

$$\Omega_{\mathrm{I}} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \left(J - \sum_{mn} \left| M_{mn}^{(\mathbf{k},\mathbf{b})} \right|^2 \right)$$

$$\tilde{\Omega} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_{m \neq n} \left| M_{mn}^{(\mathbf{k},\mathbf{b})} \right|^2 + \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_n \left(-\operatorname{Im} \ln M_{nn}^{(\mathbf{k},\mathbf{b})} - \mathbf{b} \cdot \bar{\mathbf{r}}_n \right)^2$$

N. Marzari et al. Rev. Mod. Phys., 84.1419 (2012)

Localization procedure

From last slide:

Define the **overlap matrix** between Bloch orbitals at neighboring k points:

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} \mid u_{n,\mathbf{k}+\mathbf{b}} \rangle$$

Localization functional written in terms of overlap matrices:

$$\Omega_{\mathrm{I}} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \left(J - \sum_{mn} \left| M_{mn}^{(\mathbf{k},\mathbf{b})} \right|^2 \right)$$

$$\begin{aligned} \tilde{\Omega} = & \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_{m \neq n} \left| M_{mn}^{(\mathbf{k},\mathbf{b})} \right|^2 \\ & + \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_{n} \left(-\operatorname{Im} \ln M_{nn}^{(\mathbf{k},\mathbf{b})} - \mathbf{b} \cdot \bar{\mathbf{r}}_n \right)^2 \end{aligned}$$

Using gradient descent to minimize $\tilde{\Omega}$

Starting from constructing the initial overlap matrix, and taking *U* to be δ_{mn}

$$M_{mn}^{(0)(\mathbf{k},\mathbf{b})} = \left\langle u_{m\mathbf{k}}^{(0)} \mid u_{n,\mathbf{k}+\mathbf{b}}^{(0)} \right\rangle$$

$$|u_{n\mathbf{k}}\rangle = \sum_{m} U_{mn}^{(\mathbf{k})} \left| u_{m\mathbf{k}}^{(0)} \right\rangle$$

Compute the change in localization functional due to an infinitesimal change in *U,*

$$U_{mn}^{(\mathbf{k})} = \delta_{mn} + dW_{mn}^{(\mathbf{k})}$$

$$\frac{\Delta\Omega}{\Delta W^{(\mathbf{k})}} = \ldots$$

Update *U* and compute the new overlap matrix

$$M^{(\mathbf{k},\mathbf{b})} = U^{(\mathbf{k})\dagger} M^{(0)(\mathbf{k},\mathbf{b})} U^{(\mathbf{k}+\mathbf{b})}$$

…… until the localization functional does not decrease.

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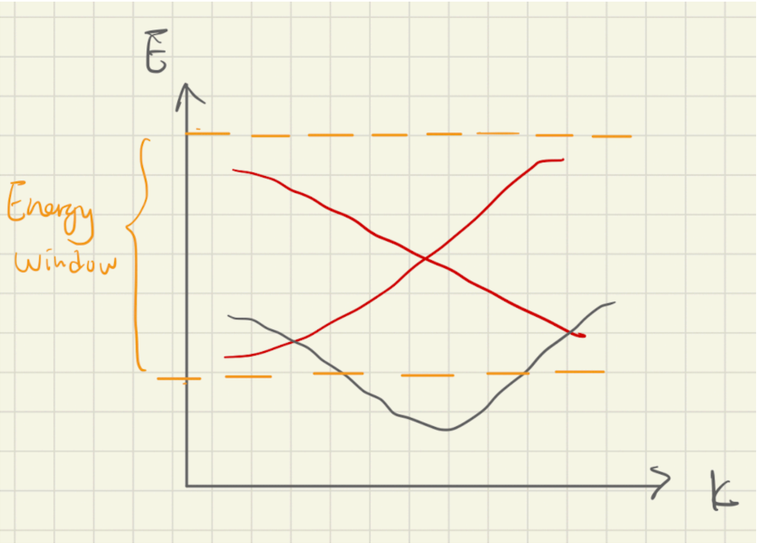
Entangled bands

- **The bands of interest are not isolated:**
  - The desired bands lie within a limited energy window but overlap and hybridize with other bands which extend further out in energy



1. Choose an energy window that encompasses the *N* bands of interest.
   At each *k*,
   the number of bands N_k within the window >= *N*

   If $N_k = N$, we don't need to do anything.
   If $N_k > N$, we need to find an *N*-dim space *S*(*N*) at this *k* such that Ω_{I} is minimized.

2. Minimizing Ω_{I}

   Ω_{I} measures the "spillage" or mismatch between states at nearby *k*-points.

$$\Omega_{\mathrm{I}} = \frac{1}{N_{\mathrm{kp}}} \sum_{\mathbf{k},\mathbf{b}} w_b \left[N - \sum_{m,n} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2 \right]$$

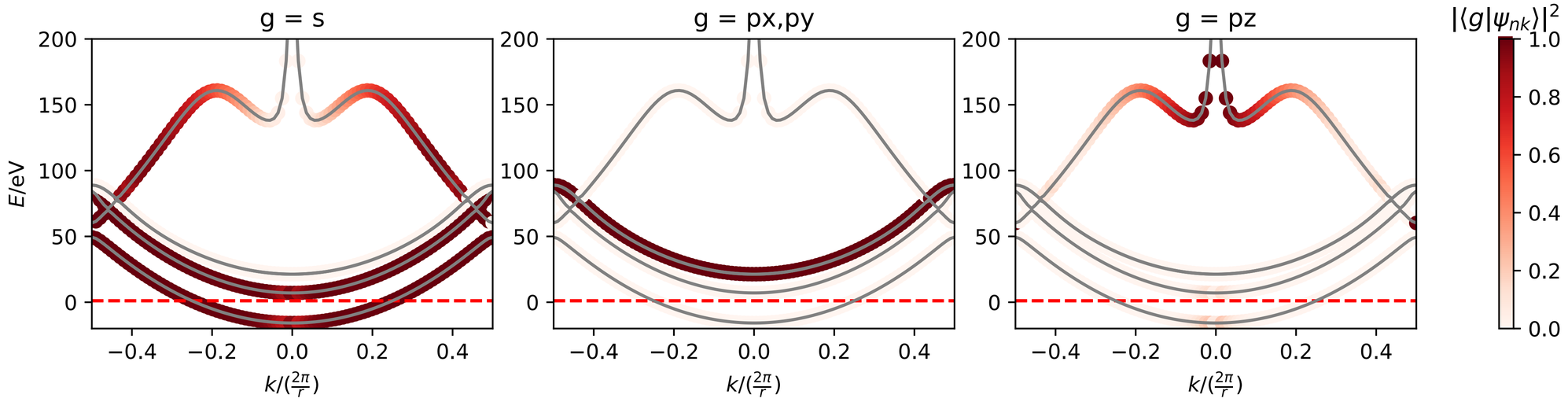
   This is done self-consistently throughout the BZ.
   On the i-th iteration, find *N* states $u_{n\mathbf{k}}^{(i)}$

   such that the "spillage" over the neighboring subspace from last iteration is as small as possible.

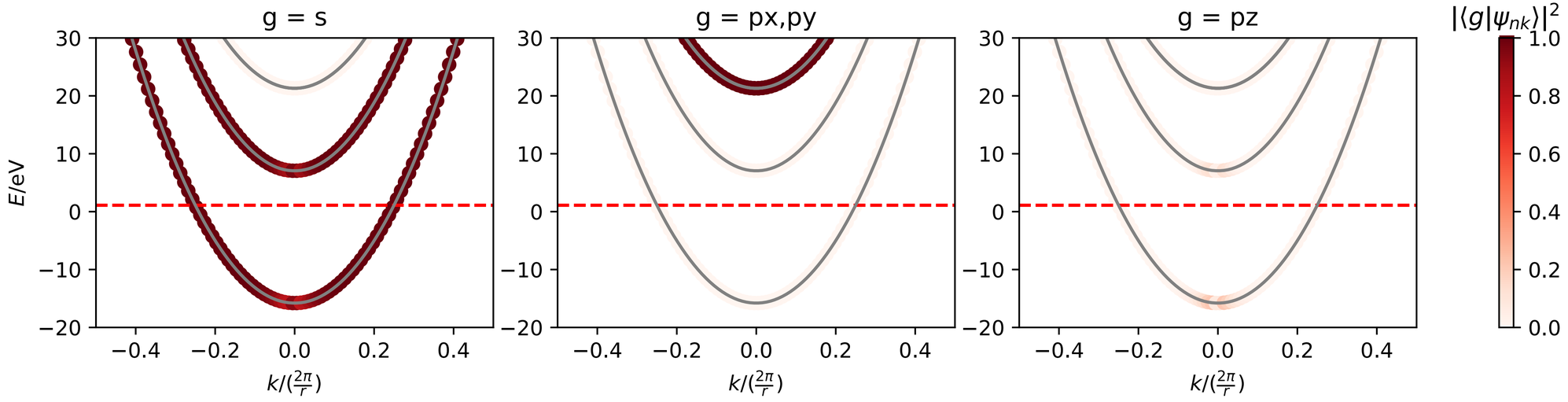
3. Find a unitary transformation at each *k* such that $\tilde{\Omega}$ is minimized (same with the isolated bands case).

I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).

Recall the H1 with PBC: Fat bands



Zoom in to the low energy bands



Example: H1 with PBC

r=1.4, start with *s*, only 1 Wannier function

.win file

```
num_bands        = 5
num_wann        = 1

Begin Unit_Cell_Cart
 5.2917721   0.0000000   0.0000000
 0.0000000   5.2917721   0.0000000
 0.0000000   0.0000000   0.7408481
End Unit_Cell_Cart

Begin atoms_cart
H  0.0000000  0.0000000  0.3704240
End atoms_cart

!Additional keywords

exclude_bands: 3,4,5
begin projections
H:s
end projections
write_xyz = True
write_hr = True
```

How many bands to include, and downfold to how many Wannier functions?
Here we are using vdz basis to represent Bloch functions, thus total number of bands = 5

What bands to exclude when computing overlap matrices *M*

Define your starting trial orbitals

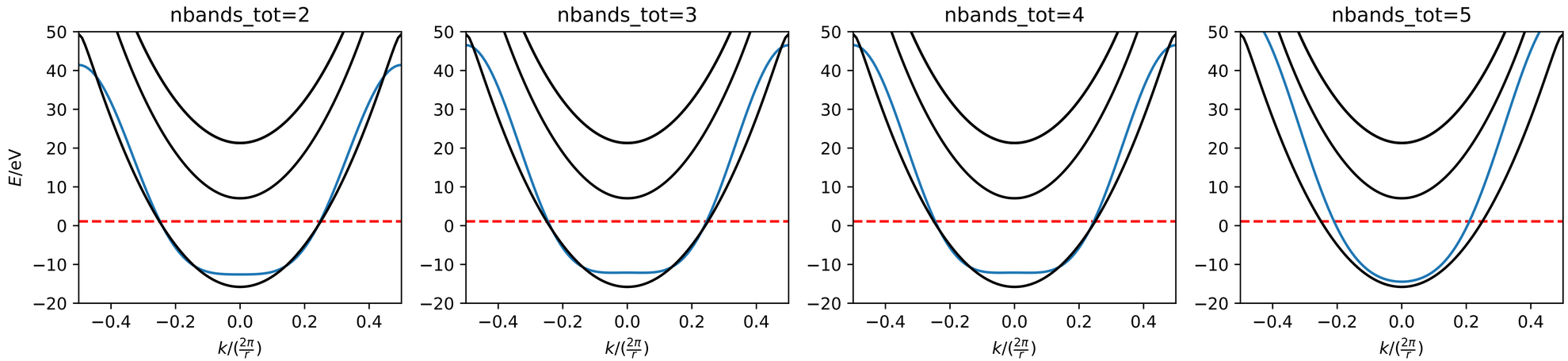
Print out the center coordinates of the Wannier functions, and the Hamiltonian in real space

You can also have other keywords such as dis_win_min/max, dis_froz_min/max in order to specify what active space to disentangle

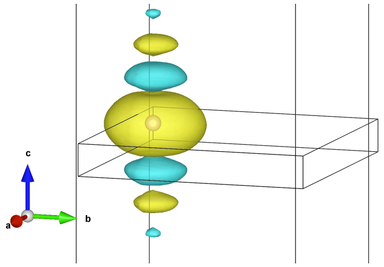
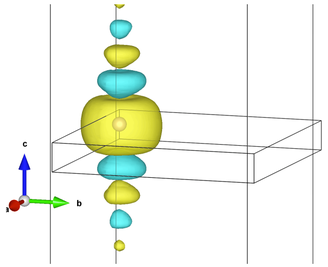
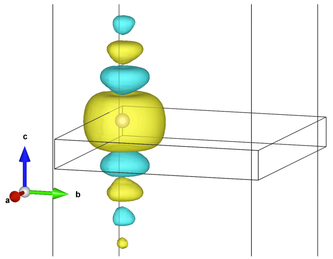
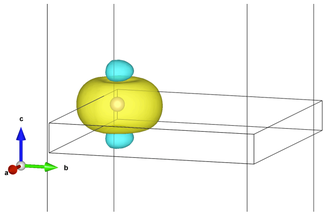
Example: H1 with PBC

r=1.4, start with *s*, only 1 Wannier function

Include different number of bands into the active space:



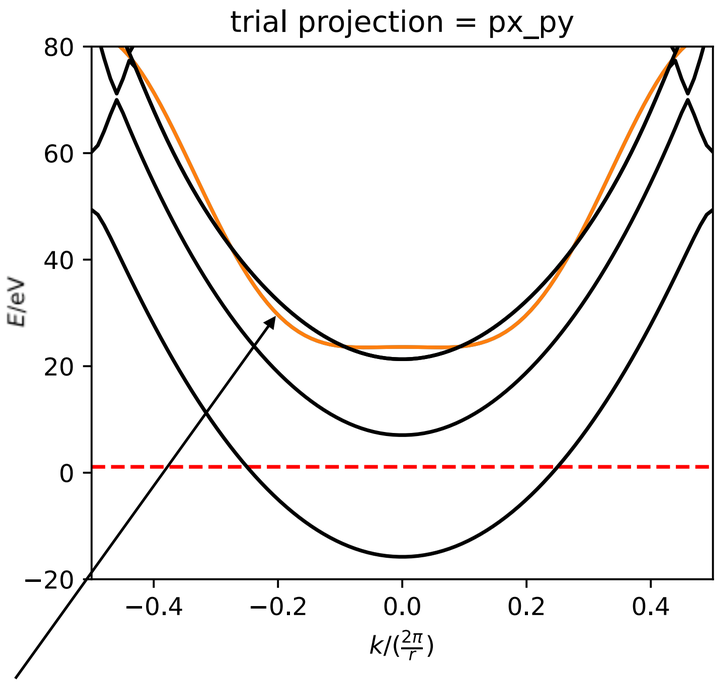
Spread of the Wannier function (Angstrom^2):

	0.515	0.362	0.362	0.213
Plots (value)				

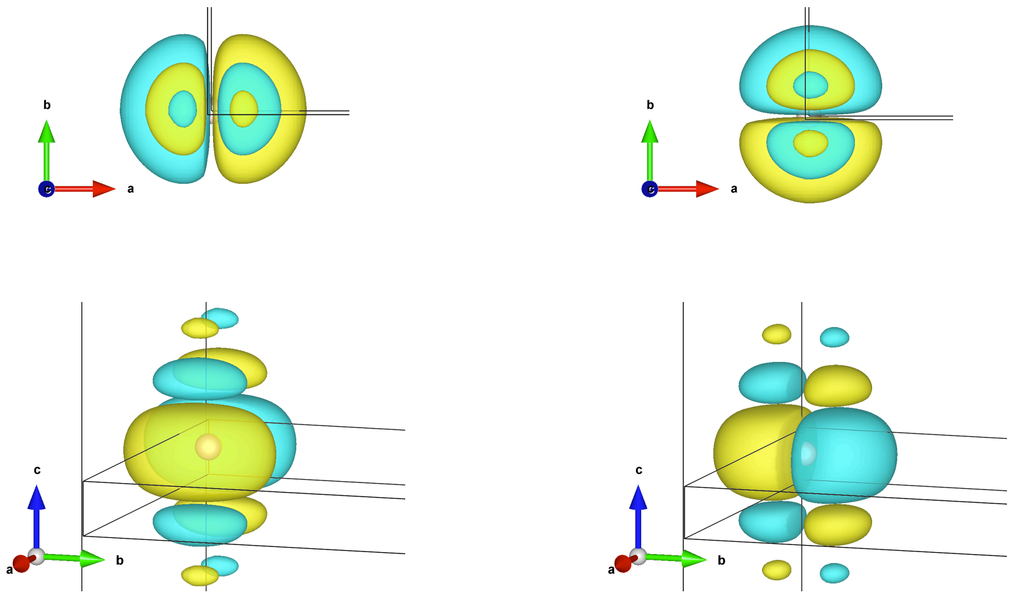
More bands included -> more localized Wannier functions

Example: H1 with PBC

r=1.4, start with *px, py* (all 5 bands included)



The 2 Wannier functions:

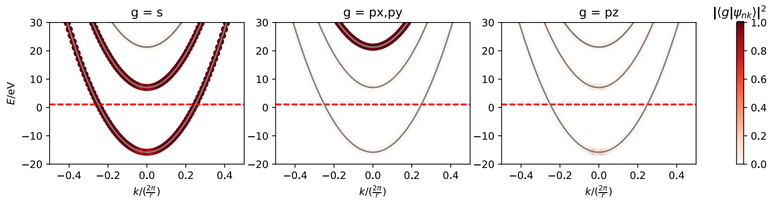


There are 2 bands… they are doubly degenerate

General rule of thumb

1. **Always first figure out which active space you want to downfold to, and roughly the 'contents' of the bands within the active space**

   You can do this by looking at the projections of the KS states onto atomic orbitals, or even get the 'fat band' plot



   This will also help you find a better trial localized orbitals.

2. **When you can not cleanly get an energy window such that all the bands you want to include in the active space are isolated, try to get an energy window where there are more bands than the bands you want to downfold from.**

   Make sure that at each k,
   the number of bands N_k within the window >= N

Next week:

1. How to use QE+Wannier90?
2. More examples in realistic systems on how to choose an active space, and what is a better starting point
3. Obtain the Hamiltonian at different k points. How to get the band structure from Wannier interpolation?
4. Convergence with kmesh in scf calculation.