

# Wannier functions in band structure codes

## 1 Wannier functions definition

The Wannier functions are constructed in three steps. First, the non-orthogonal Bloch-functions are obtained by projecting the localized atomic-like trial orbitals  $g_n(\mathbf{r})$  onto the chosen eigen-function subspace of the Hamiltonian:

$$|\tilde{u}_{n\mathbf{k}}\rangle = \sum_i |\psi_{i\mathbf{k}}\rangle \langle \psi_{i\mathbf{k}} | g_n \rangle = \sum_i \tilde{a}_{ni}^{\mathbf{k}} |\psi_{i\mathbf{k}}\rangle, \quad (1)$$

where the summation over bands is limited by low and top band numbers  $N_1 \leq i \leq N_2$  or by energy window  $i : E_1 \leq \epsilon_{i\mathbf{k}} \leq E_2$ . Second, the Bloch functions (1) are orthonormalized using the inverse square root of the overlap matrix  $S_{mn}^{\mathbf{k}} = \langle \tilde{u}_{m\mathbf{k}} | \tilde{u}_{n\mathbf{k}} \rangle$  (this procedure is often referred as "symmetric" or "Löwdin" orthonormalization):

$$|u_{n\mathbf{k}}\rangle = \sum_m (S^{\mathbf{k}})^{-1/2}_{mn} |\tilde{u}_{m\mathbf{k}}\rangle = \sum_i a_{ni}^{\mathbf{k}} |\psi_{i\mathbf{k}}\rangle, \quad (2)$$

where

$$a_{ni}^{\mathbf{k}} = \sum_m (S^{\mathbf{k}})^{-1/2}_{mn} \tilde{a}_{mi}^{\mathbf{k}} \quad (3)$$

Finally, WFs are constructed from (2) by  $\mathbf{k}$ -point summation:

$$|W_{n\mathbf{T}}\rangle = \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{T}} \sum_i a_{ni}^{\mathbf{k}} |\psi_{i\mathbf{k}}\rangle \quad (4)$$

The choice of the trial orbitals in (1) is not unique. Usually,  $g_n(\mathbf{r})$ 's are picked as "natural localized orbitals for a given method". In LMTO or any other atomic-orbital basis method  $g_n(\mathbf{r})$ 's are atomic orbitals themselves. In pseudopotential plane wave methods  $g_n(\mathbf{r})$ 's are pseudo-atomic orbitals. In LAPW and related methods  $g_n(\mathbf{r})$ 's are localized orbitals vanishing outside the muffin-tin spheres.

## 2 Wannier function application

### 2.1 Hopping parameters and downfolded Hamiltonian

Using the “bra-ket” representation of the one-particle Hamiltonian  $\hat{H} = \sum_{i\mathbf{k}} |\psi_{i\mathbf{k}}\rangle \epsilon_{i\mathbf{k}} \langle \psi_{i\mathbf{k}}|$  the hopping parameters in WF basis (4) are easily computed:

$$t_{mn}(\mathbf{T}) = \langle W_{m\mathbf{0}} | \hat{H} | W_{n\mathbf{T}} \rangle = \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{T}} h_{mn}(\mathbf{k}), \quad (5)$$

where

$$h_{mn}(\mathbf{k}) = \sum_i a_{mi}^{\mathbf{k}*} a_{ni}^{\mathbf{k}} \epsilon_{i\mathbf{k}} \quad (6)$$

is the Hamiltonian in WF basis written in the reciprocal space (so-called downfolded Hamiltonian).

### 2.2 Matrix elements of operators written in WF basis

Using the expansion of Wannier functions (4) it is straightforward to compute the matrix elements of any single-particle operator, written in WF basis. If  $\hat{V}_{WF}$  is an operator in WF basis:

$$\hat{V}_{WF} = \sum_{nn', \mathbf{T}} |W_{n\mathbf{0}}\rangle V_{nn'}(\mathbf{T}) \langle W_{n'\mathbf{T}}| \quad (7)$$

then it's matrix elements in  $\{\psi_{i\mathbf{k}}\}$  basis are:

$$\langle \psi_{i\mathbf{k}} | \hat{V}_{WF} | \psi_{j\mathbf{k}} \rangle = \sum_{nn'} a_{ni}^{\mathbf{k}} a_{n'j}^{\mathbf{k}*} \sum_{\mathbf{T}} e^{i\mathbf{k}\mathbf{T}} V_{nn'}(\mathbf{T}) \quad (8)$$

Using the same algebra, one can go from WF basis to the basis, over which  $\psi_{i\mathbf{k}}$ 's are expanded (LMTO, plane waves, LAPW etc.)

### 2.3 Calculation of Hubbard U in WF basis

One of the efficient ways of calculating the Hubbard U parameter is to use “constrained” LDA calculation for the total energy variation with respect to the occupation number of the localized orbitals. Numerically it is done by taking the first derivative of the orbital's energy over its occupancy:

$$U = \frac{\partial E_n}{\partial Q_n} \approx \frac{\Delta E_n}{\Delta Q_n} \quad (9)$$

The energies and occupancies of Wannier states are defined as:

$$\begin{aligned} E_n &= \langle W_{n0} | \left( \sum_{i\mathbf{k}} |\psi_{i\mathbf{k}}\rangle \epsilon_{i\mathbf{k}} \langle \psi_{i\mathbf{k}}| \right) | W_{n0} \rangle = \sum_{i\mathbf{k}} a_{ni}^{\mathbf{k}*} a_{ni}^{\mathbf{k}} \epsilon_{i\mathbf{k}} \\ Q_n &= \langle W_{n0} | \left( \sum_{i\mathbf{k}} |\psi_{i\mathbf{k}}\rangle f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}}| \right) | W_{n0} \rangle = \sum_{i\mathbf{k}} a_{ni}^{\mathbf{k}*} a_{ni}^{\mathbf{k}} f_{i\mathbf{k}}, \end{aligned} \quad (10)$$

where  $f_{i\mathbf{k}}$  – band occupation numbers. The disbalance of WF's energies and occupancies is done by introducing different potential correction (for example, positive and negative) to WF states via diagonal operator:

$$\hat{V}^{poco} = \sum_{n,\mathbf{T}} |W_{n\mathbf{T}}\rangle \delta V_n \langle W_{n\mathbf{T}}| \quad (11)$$

## 2.4 "Shifting" bands

Using the operator (11) it is possible to shift bands of particular character. One could sketch an algorithm to do this:

- Define Wannier states of desired symmetry (character) (Eq. 4)
- Apply significant negative (or positive) correction to Wannier states that are going to be "shifted" (Eq. 8,11)
- Do it in DFT self-consistent loop to allow WF relaxation and change of hybridization

## 3 Examples

### 3.1 NiO: downfolded Hamiltonian

The downfolded Hamiltonian was calculated using Eq. (6) in the basis of i) WFs of Ni-3d and O-2p symmetry (8 WFs) using bands in [-9,2] eV region (Fig. 1) and ii) WFs of Ni-3d symmetry only (5 WFs) using bands in [-3,2] eV region (Fig. 2).

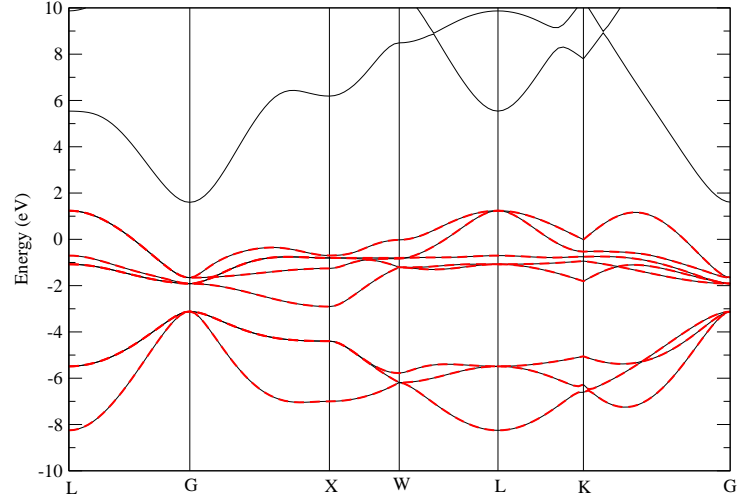


Figure 1: Eigenvalues of "full" Hamiltonian (black) and downfolded  $2p - 3d$  Hamiltonian (dashed red) for NiO

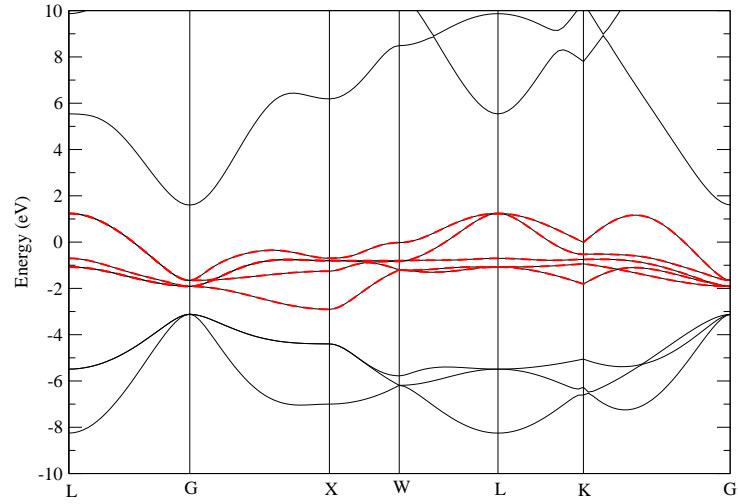


Figure 2: Eigenvalues of "full" Hamiltonian (black) and downfolded  $3d$  Hamiltonian (dashed red) for NiO

### 3.2 NiO: 2p-3d Hamiltonian properties

The energies and occupancies of basis Wannier functions for the p-d Hamiltonian were calculated using Eq. (10) and are listed in the Table 1. The occupation numbers of  $t_{2g}$ ,  $e_g$  and  $2p$  Wannier functions reflect the fact that  $e_g$  states hybridize more with  $2p$  states whereas  $t_{2g}$  states remain almost unhybridized due to the cubical symmetry. Using matrix Green's function it is possible to construct partial densities of states for each WF:

$$N_n(\omega) = -\frac{1}{\pi} \text{Im} \sum_{\mathbf{k}} \left[ \frac{1}{\omega + i\eta - h(\mathbf{k})} \right]_{nn} \quad (12)$$

The total and partial densities of states obtained by (12) are shown on Fig. (3).

Table 1: Energies (E) relative to  $E_f$  and occupancies (Q) of basis WFs for p-d Hamiltonian

WF	E (eV)	Q
$t_{2g}$	-1.4349	1.980013
$e_g$	-1.0709	1.314901
$2p$	-4.6788	1.810053

### 3.3 NiO: 3D shape of WF

Wannier functions on a real-space 3D grid were computed in Exciting FP-LAPW code using the definition (4). The post-processing of the grid data was done using IBM's OpenDX package. On the Fig. (4) shape of WFs with  $3z^2 - y^2$ ,  $x^2 - y^2$  and  $xy$  symmetry is shown.

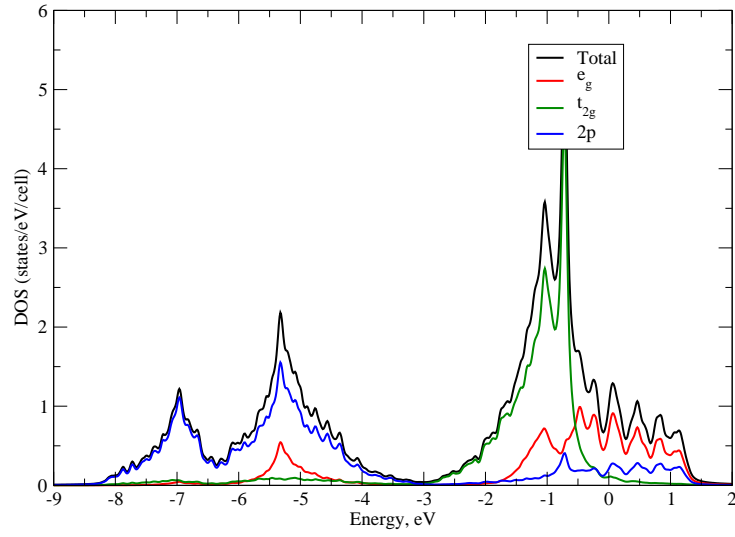


Figure 3: Total and partial density of states for NiO. Partial density of states is computed for WFs with given symmetry.

# NiO Wannier functions

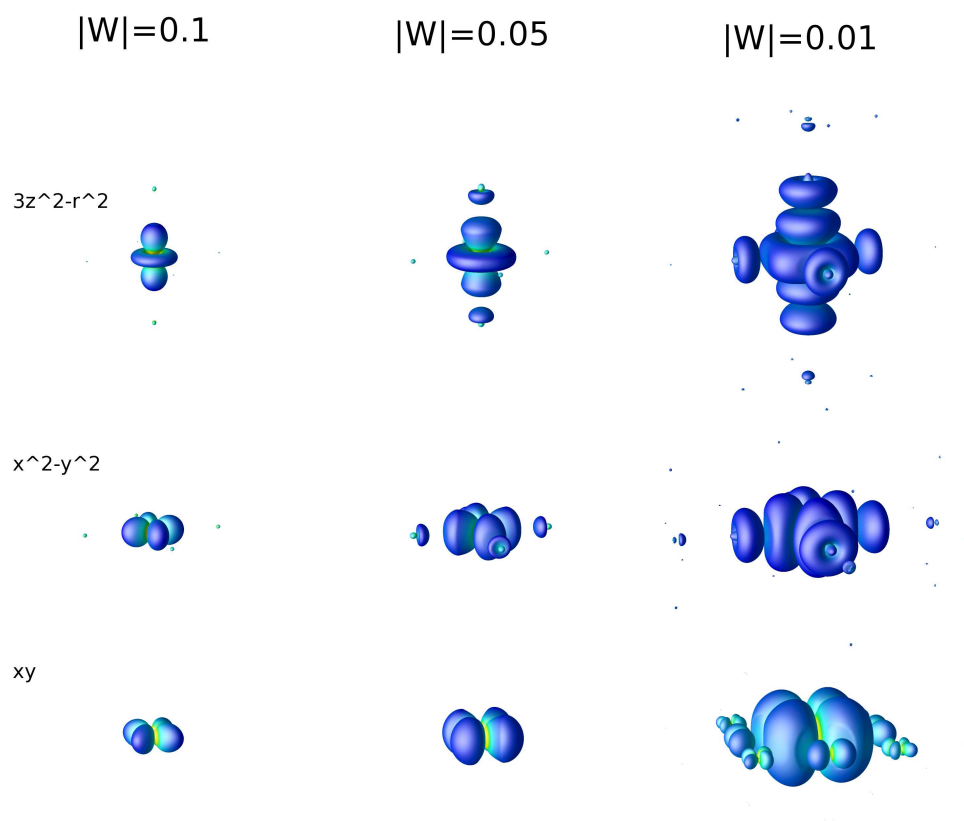


Figure 4: 3D shape of modulus of WF with given symmetry for different isovalues. WFs are normalized to 1.