Computational Physics Course

Learn to use software packages

Suppose a crystalline solid. The one-particle effective Hamiltonian $\hat{H}$ then commutes with the lattice-translation operator $\hat{T}_{\mathbf{R}}$, allowing one to choose as common eigenstates the Bloch orbitals $|\,\psi_{n\mathbf{k}}\,\rangle$,

$$[\,\hat{H},\,\hat{T}_{\mathbf{R}}\,] \;=\; 0 \;\;\Rightarrow\;\; \psi_{n\mathbf{k}}(\mathbf{r}) \;=\; e^{i\phi_n(\mathbf{k})}\,u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}} \;\;, \tag{1}$$

where $u_{n\mathbf{k}}(\mathbf{r})$ has the periodicity of the Hamiltonian. There is an arbitrary phase $\phi_n(\mathbf{k})$, periodic in reciprocal space.

We obtain a (non-unique) Wannier representation using any unitary transformation of the form $\langle\, n\mathbf{k}\,|\,\mathbf{R}n\,\rangle = e^{i\varphi_n(\mathbf{k})\,-\,i\mathbf{k}\cdot\mathbf{R}}$:

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

Here V is the real-space primitive cell volume, and $\varphi_n(\mathbf{k}+\mathbf{G}) = \varphi_n(\mathbf{k})$, for any reciprocal-lattice translation $\mathbf{G}$.

It is easily shown that the $|\,\mathbf{R}n\,\rangle$ form an orthonormal set, and that two Wannier functions $|\,\mathbf{R}n\,\rangle$ and $|\,\mathbf{R}'n\,\rangle$ transform into each other with a translation of a lattice vector $\mathbf{R}-\mathbf{R}'$. The arbitrariness that is present in $\varphi_n(\mathbf{k})$ [or $\phi_n(\mathbf{k})$] propagates to the resulting Wannier functions, making the Wannier representation non-unique.

Since the electronic energy functional in an insulator is also invariant with respect to a unitary transformation of its N occupied Bloch orbitals, there is additional freedom associated with the choice of a full unitary matrix (and not just a diagonal one) transforming the orbitals between themselves at every wavevector $\mathbf{k}$. Thus, the most general operation that transforms the Bloch orbitals into Wannier functions is given by

$$|\,\mathbf{R}n\,\rangle \;=\; \frac{V}{(2\pi)^3}\int_{BZ} \sum_{m=1}^{N} U_{mn}^{(\mathbf{k})}\,|\,\psi_{m\mathbf{k}}\,\rangle\, e^{-i\mathbf{k}\cdot\mathbf{R}}\,d\mathbf{k} \;\;, \tag{3}$$

where $U_{mn}^{(\mathbf{k})}$ is a unitary matrix of dimension N.

Alternatively, we can regard this as a two-step process in which one first constructs Bloch-like orbitals

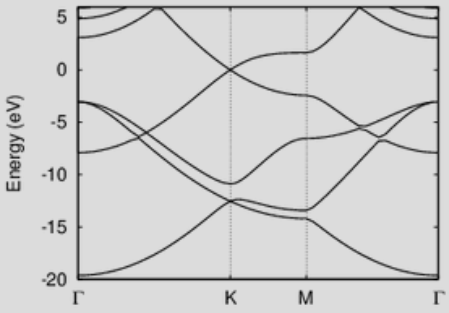
$$|\,\widetilde{\psi}_{n\mathbf{k}}\,\rangle = \sum_{m=1}^{N} U_{mn}^{(\mathbf{k})}\,|\,\psi_{m\mathbf{k}}\,\rangle \tag{4}$$

and then constructs Wannier function $|\,w_n\,\rangle$ from the manifold of states $|\,\widetilde{\psi}_{n\mathbf{k}}\,\rangle$.

Theory of Wannier orbital

Let us read the article written by Marzari, who developed the theory of the most localized Wannier orbital.

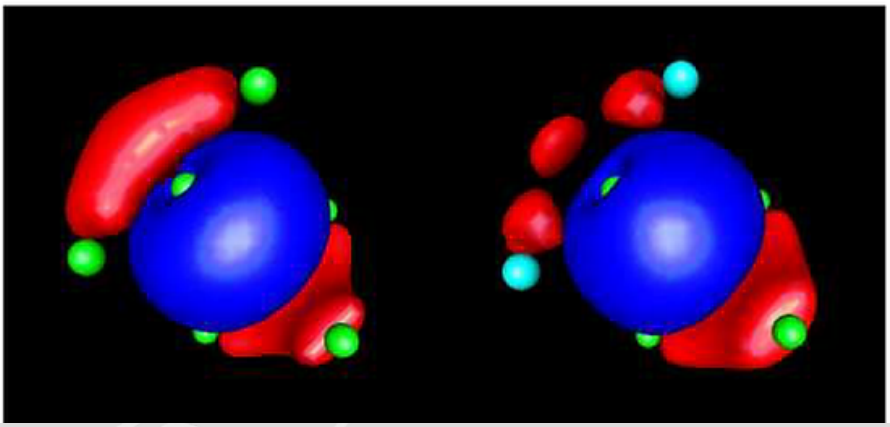
Wannier orbitals was introduced many years ago as a method to interpret a band in terms of a bond. Originally this was done by Fourtier transforming the Bloch orbitals with respect to the reciprocal vector. The degree of localization is not sufficient in many cases, requiring thereby more stronger localization method. In this context, Prof. Marzari invented an effective procedure.



Function

An attempt to construct a single Wannier function from the single lowest-energy or highest-energy band would be doomed in this case, because of non-analyticity of the Bloch functions in the neighborhood of the degeneracy points. Instead, the introduction of the unitary matrices $U_{mn}^{(\mathbf{k})}$ allows for the construction of states $|\tilde{\psi}_{n\mathbf{k}}\rangle$ that are everywhere smooth functions of $\mathbf{k}$.

In this case, the Wannier functions $w_n(\mathbf{r}-\mathbf{R}) = |\mathbf{R}n\rangle$, can be shown to be well localized: for a $\mathbf{R}_i$ far away from $\mathbf{R}$, $w_n(\mathbf{R}_i-\mathbf{R})$ is a combination of terms like $\int_{BZ} u_{m\mathbf{k}}(0)e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R})}\,d\mathbf{k}$, which are small due to the rapidly varying character of the exponential factor . By way of illustration, the MLWFs that result from our procedure for the cases of Si and GaAs are shown in Fig. 1.



How to construct the Wannier orbital in practice.

It can be shown that each of these quantities is *positive-definite* (in particular $\Omega_{\rm I}$); moreover, $\Omega_{\rm I}$ is also *gauge-invariant*, i.e., it is invariant under any arbitrary unitary transformation (3) of the Bloch orbitals. The minimization procedure thus corresponds to the minimization of $\widetilde{\Omega} = \Omega_{\rm D} + \Omega_{\rm OD}$. At the minimum, the elements $\left|\langle \mathbf{R}m|\mathbf{r}|\mathbf{0}n\rangle\right|^2$ are as small as possible, realizing the best compromise in the simultaneous diagonalization, within the space of the Bloch bands considered, of the three position operators x, y and z (which do not in general commute when projected within this space).

Matrix elements of the position operator between Wannier functions take the form

$$\langle \mathbf{R}n|\mathbf{r}|\mathbf{0}m\rangle = i\frac{V}{(2\pi)^3}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{m\mathbf{k}}\rangle \tag{10}$$

and

$$\langle \mathbf{R}n|r^2|\mathbf{0}m\rangle = -\frac{V}{(2\pi)^3}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|\nabla^2_{\mathbf{k}}|u_{m\mathbf{k}}\rangle \ . \tag{11}$$

These expressions provide the needed connection with our underlying Bloch formalism, since they allow us to express the localization functional Ω in terms of the matrix elements of $\nabla_{\mathbf{k}}$ and $\nabla^2_{\mathbf{k}}$.

To proceed further, we make the assumption throughout this work that the Brillouin zone has been discretized into a uniform Monkhorst-Pack mesh, and the Bloch orbitals determined on that mesh. Let $\mathbf{b}$ be a vector connecting a k-point to one of its near neighbors, and let Z be the number of such neighbors to be included in the finite-difference formulas. We use the simplest possible finite-difference formula for $\nabla_{\mathbf{k}}$, i.e., the one involving the smallest possible Z. When the Bravais lattice point group is cubic, it will only be necessary to include the first shell of $Z = 6$, 8, or 12 k-neighbors for simple cubic, bcc, or fcc k-space meshes, respectively.

It is possible to satisfy the condition

$$\sum_{\mathbf{b}} w_b b_\alpha b_\beta = \delta_{\alpha\beta} \tag{12}$$

by an appropriate choice of a weight w_b associated with each shell $|\mathbf{b}| = b$. (For the three kinds of cubic mesh, Eq. (12) is satisfied with $w_b = 3/Zb^2$

$$\rho(\boldsymbol{r}) = \sum_i \int_{BZ} d\boldsymbol{k}|\psi_{i\boldsymbol{k}}(\boldsymbol{r})|^2$$

How to compute gradients wrt k

These useful expressions allow us to compute the parameters required for the variational localization function (5).

Now, if $f(\mathbf{k})$ is a smooth function of $\mathbf{k}$, its gradient can be expressed as

$$\nabla f(\mathbf{k}) = \sum_{\mathbf{b}} w_b \mathbf{b} \left[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k}) \right] . \tag{13}$$

In a similar way,

$$|\nabla f(\mathbf{k})|^2 = \sum w_b \left[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k}) \right]^2 . \tag{14}$$

[17] N. Marzari and D. Vanderbilt, "Maximally localized generalized Wannier functions for composite energy bands," *Physical Review B*, vol. 56, no. 20, pp. 12847–12865, 1997.

TABLE I. Hopping amplitudes in eV implied by four different **k**-point sampling densities. Intersublattice and intrasublattice amplitudes are grouped separately. The two models on the left, with 5 and 15 parameters, respectively, provide good compromises between accuracy and simplicity.

AB	n	m	N^0	d_n/a	$t_{n,3\times3}$	$t_{n,6\times6}$	$t_{n,12\times12}$	$t_{n,30\times30}$
	1	1	3	$\frac{1}{\sqrt{3}}$	−3.00236	−2.94015	−2.92774	−2.92181
	2	3	3	$\frac{2}{\sqrt{3}}$	−0.22464	−0.26199	−0.27586	−0.27897
	3	4	6	$\sqrt{\frac{7}{3}}$	0.05205	0.03172	0.02807	0.02669
	4	7	6	$\sqrt{\frac{13}{3}}$		−0.00830	−0.00727	−0.00885
	5	8	3	$\frac{4}{\sqrt{3}}$		−0.02463	−0.01812	−0.01772
	6	9	6	$\sqrt{\frac{19}{3}}$		0.00096	0.00463	0.00675
	7	11	3	$\frac{5}{\sqrt{3}}$		0.00467	−0.00227	−0.00262
	8	13	6	$\sqrt{\frac{28}{3}}$		−0.00724	−0.00088	0.00019
	9	14	6	$\sqrt{\frac{31}{3}}$		0.00562	0.00044	−0.00068
	10	16	6	$\sqrt{\frac{37}{3}}$			−0.00230	−0.00237
AA	n	m	N^0	d_n/a	$t'_{n,3\times3}$	$t'_{n,6\times6}$	$t'_{n,12\times12}$	$t'_{n,30\times30}$
	0	0	1	0	0.4770	0.3590	0.3307	0.3208
	1	2	6	1	0.20509	0.21813	0.22377	0.22378
	2	5	6	$\sqrt{3}$	0.06912	0.04357	0.04555	0.04813
	3	6	6	2		−0.02379	−0.02406	−0.02402
	4	10	12	$\sqrt{7}$		0.00538	0.00313	0.00263
	5	12	6	3		0.00783	0.00296	0.00111
	6	15	6	$\frac{6}{\sqrt{3}}$		−0.01429	−0.00110	0.00018
	7	17	12	$\sqrt{\frac{39}{3}}$			−0.00066	−0.00008

For the tight-binding model, please read excellent documents in the web, e.g. the note written by Prof. Fujimori (in Japanese).

Having learned DFT, let us move to learning program packages. We begin by learning Quantum Espresso