



Computational Physics Course

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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 $|\psi_{\mathbf{nk}}\rangle$,

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

where $u_{\mathbf{nk}}(\mathbf{r})$ 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 $|\mathbf{nk}\rangle \rightarrow |\mathbf{Rn}\rangle = e^{i\varphi_n(\mathbf{k}) - i\mathbf{k}\cdot\mathbf{R}}$:

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

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 $|\mathbf{Rn}\rangle$ form an orthonormal set, and that two Wannier functions $|\mathbf{Rn}\rangle$ 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

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

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

$$|\tilde{\psi}_{\mathbf{nk}}\rangle = \sum_{m=1}^N U_{mn}^{(\mathbf{k})} |\psi_{\mathbf{mk}}\rangle \quad (4)$$

and then constructs Wannier function $|w_n\rangle$ from the manifold of states $|\tilde{\psi}_{\mathbf{nk}}\rangle$.

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 $|\tilde{\psi}_{\mathbf{nk}}\rangle$ that are everywhere smooth functions of \mathbf{k} .

In this case, the Wannier functions $w_n(\mathbf{r} - \mathbf{R}) = |\mathbf{Rn}\rangle$, 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 $\int_{BZ} u_{\mathbf{nk}}(0) e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R})} d\mathbf{k}$, 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.

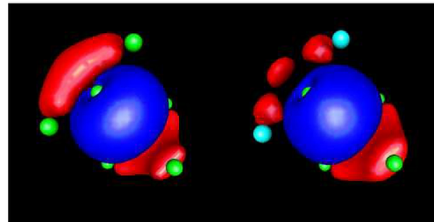


Figure 1: Amplitude isosurface contours for maximally-localized Wannier functions in Si (left panel) and GaAs (right panel). Red and blue contours are for isosurfaces of identical absolute value but opposite signs; Si and As atoms are in green, Ga in cyan. Each unit cell displays four (spin-unpolarized) equivalent WFs, localized around the centers of the four covalent bonds; breaking of inversion symmetry in GaAs polarizes the WFs towards the more electronegative As anion.

We introduce a well-defined *localization criterion*, choosing the functional

$$\Omega = \sum_n [\langle 0n | r^2 | 0n \rangle - \langle 0n | \mathbf{r} | 0n \rangle^2] = \sum_n [(\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2)] \quad (5)$$

as the measure of the spread of the Wannier functions. The sum runs over the n functions $|0n\rangle$; $\langle r^2 \rangle_n$ and $\langle \mathbf{r} \rangle_n$ are the expectation values $\langle 0n | r^2 | 0n \rangle$ and $\langle 0n | \mathbf{r} | 0n \rangle$. Given a set of Bloch orbitals $|\psi_{\mathbf{nk}}\rangle$, the goal is to find the choice of $U_{mn}^{(\mathbf{k})}$ in (3) that minimizes the values of the localization functional (5).

We are able to express the gradient $G = \frac{\partial \Omega}{\partial U_{mn}^{(\mathbf{k})}}$ of the localization functional with respect to an infinitesimal unitary rotation of our set of Bloch orbitals

$$|u_{\mathbf{nk}}\rangle \rightarrow |u_{\mathbf{nk}}\rangle + \sum_m dW_{mn}^{(\mathbf{k})} |u_{\mathbf{mk}}\rangle, \quad (6)$$

where dW an infinitesimal antiunitary matrix $dW^\dagger = -dW$ such that

$$U_{mn}^{(\mathbf{k})} = \delta_{mn} + dW_{mn}^{(\mathbf{k})}. \quad (7)$$

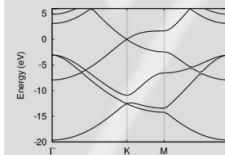
This provides an “equation of motion” for the evolution of the $U_{mn}^{(\mathbf{k})}$, and of the $|\mathbf{Rn}\rangle$ derived in (3), towards the minimum of Ω ; e.g., in the steepest-descent approach small finite steps in the direction opposite to the gradient decrease the value of Ω , until a minimum is reached. The unitary matrices are then used to construct the Wannier functions via Eq. (3).

There are several interesting consequences stemming from the choice of (5) as the localization functional, that we briefly summarize here. Adding and subtracting the off-diagonal

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 Fourier 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.



MLWF=Maximally Localized Wannier Function

How to construct the Wannier orbital in practice.

components $\tilde{\Omega} = \sum_n \sum_{\mathbf{R}m|0n} |\langle \mathbf{R}m | \mathbf{r} | 0n \rangle|^2$, we obtain the decomposition

$$\Omega = \Omega_1 + \tilde{\Omega} = \Omega_1 + \Omega_D + \Omega_{OD} \quad (8)$$

where Ω_1 , $\tilde{\Omega}$, Ω_D and Ω_{OD} are respectively

$$\begin{aligned} \Omega_1 &= \sum_n \left[\langle 0n | r^2 | 0n \rangle - \sum_{\mathbf{R}m} |\langle \mathbf{R}m | \mathbf{r} | 0n \rangle|^2 \right], \\ \tilde{\Omega} &= \sum_n \sum_{\mathbf{R}m \neq 0n} |\langle \mathbf{R}m | \mathbf{r} | 0n \rangle|^2, \\ \Omega_D &= \sum_n \sum_{\mathbf{R} \neq 0} |\langle \mathbf{R}n | \mathbf{r} | 0n \rangle|^2, \\ \Omega_{OD} &= \sum_{m \neq n} \sum_{\mathbf{R}} |\langle \mathbf{R}m | \mathbf{r} | 0n \rangle|^2. \end{aligned} \quad (9)$$

It can be shown that each of these quantities is *positive-definite* (in particular Ω_1); moreover, Ω_1 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 $\tilde{\Omega} = \Omega_D + \Omega_{OD}$. At the minimum, the elements $|\langle \mathbf{R}m | \mathbf{r} | 0n \rangle|^2$ 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

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

and

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

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 $\nabla_{\mathbf{k}}^2$.

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 \mathbf{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 \mathbf{k} -neighbors for simple cubic, bcc, or fcc \mathbf{k} -space meshes, respectively.

It is possible to satisfy the condition

$$\sum_{\mathbf{b}} w_{\mathbf{b}} b_{\alpha} b_{\beta} = \delta_{\alpha\beta} \quad (12)$$

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

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

$$\nabla f(\mathbf{k}) = \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})]. \quad (13)$$

In a similar way,

$$|\nabla f(\mathbf{k})|^2 = \sum_{\mathbf{b}} w_{\mathbf{b}} [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})]^2. \quad (14)$$

It now becomes straightforward to calculate the scalar products involving the reciprocal-space derivatives of Eqs. (10) and (11), since the only elements needed will be the matrix elements between Bloch orbitals at neighboring \mathbf{k} -points

$$M_{mn}^{(\mathbf{k}, \mathbf{b})} = \langle u_{n\mathbf{k}} | u_{m, \mathbf{k} + \mathbf{b}} \rangle \quad (15)$$

After some algebra [17] we can obtain the relevant quantities needed to compute the spread functional, that we report here starting from the center of n th orbital

$$\bar{\mathbf{r}}_n = -\frac{1}{N} \sum_{\mathbf{k}, \mathbf{b}} w_{\mathbf{b}} \mathbf{b} \operatorname{Im} \ln M_{nn}^{(\mathbf{k}, \mathbf{b})}, \quad (16)$$

to its second moment

$$\langle r^2 \rangle_n = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{b}} w_{\mathbf{b}} \left\{ [1 - |M_{nn}^{(\mathbf{k}, \mathbf{b})}|^2] + [\operatorname{Im} \ln M_{nn}^{(\mathbf{k}, \mathbf{b})}]^2 \right\} \quad (17)$$

and the different terms in the localization functional

$$\Omega_1 = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{b}} w_{\mathbf{b}} \left(N_{nnnn} - \sum_{m \neq n} |M_{mn}^{(\mathbf{k}, \mathbf{b})}|^2 \right), \quad (18)$$

$$\Omega_{OD} = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{b}} w_{\mathbf{b}} \sum_{m \neq n} |M_{mn}^{(\mathbf{k}, \mathbf{b})}|^2, \quad (19)$$

$$\Omega_D = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{b}} w_{\mathbf{b}} \sum_n (-\operatorname{Im} \ln M_{nn}^{(\mathbf{k}, \mathbf{b})} - \mathbf{b} \cdot \bar{\mathbf{r}}_n)^2. \quad (20)$$

From these, we can calculate the change in the localization functional in response to an infinitesimal unitary transformation of the Bloch orbitals as a function of the $M_{mn}^{(\mathbf{k}, \mathbf{b})}$; once these gradients are available, it is straightforward to construct a procedure that updates the $U_{mn}^{(\mathbf{k})}$ (and consequently the $M_{mn}^{(\mathbf{k}, \mathbf{b})}$) towards the minimum localization.

[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.

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

How to compute gradients wrt \mathbf{k}

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

TABLE I. Hopping amplitudes in eV implied by four different \mathbf{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	$t_{n,3 \times 3}$	$t'_{n,6 \times 6}$	$t''_{n,12 \times 12}$	$t'''_{n,30 \times 30}$
	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	$\sqrt{\frac{4}{3}}$		-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	$t'_{n,3 \times 3}$	$t'_{n,6 \times 6}$	$t'_{n,12 \times 12}$	$t'_{n,30 \times 30}$
	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	$\frac{6}{\sqrt{2}}$		-0.01429	-0.00110	0.00018

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



The University of Tokyo

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

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