Wannier Function Localization

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1 Periodic systems and Wannier functions

Firstly we establish the formulation of periodic systems following [LL19]. Consider some Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\Delta + U(\boldsymbol{r}), \tag{1}$$

where $U(\boldsymbol{r})$ admits

$$U(\boldsymbol{r}) = U(\boldsymbol{R} + \boldsymbol{r}) \tag{2}$$

for any $\boldsymbol{R} \in \{\boldsymbol{R} = n_1\boldsymbol{a_1} + n_2\boldsymbol{a_2} + n_3\boldsymbol{a_3} : n_1, n_2, n_3 \in \mathbb{Z}\} =: \mathbb{L}$, and $\boldsymbol{a_1}, \boldsymbol{a_2}, \boldsymbol{a_3}$ are vectors in $\mathbb{R}^3$. The lattice $\mathbb{L}$ is called the Bravais lattice. $\Omega := \{\boldsymbol{R} = c_1\boldsymbol{a_1} + c_2\boldsymbol{a_2} + c_3\boldsymbol{a_3} : -1/2 \le c_1, c_2, c_3 < 1/2\}$ is called a unit cell.

Consider the translation operator $T_{\boldsymbol{R}}$ for some $\boldsymbol{R} \in \mathbb{L}$, it is clear that

$$[T_{\boldsymbol{R}}, H] = 0 \tag{3}$$

thus they can be diagonalized in the same basis (and this holds true for any $\boldsymbol{R} \in \mathbb{L}$!), say $\{\psi_i\}$. Denote the associated eigenvalues of $T_{\boldsymbol{R}}$ as $C_{\boldsymbol{R},i}$. Obviously, $T_{\boldsymbol{R}}$ is a unitary operator in $L_2(\mathbb{R}^3)$, and $C_{\boldsymbol{R},i}C_{\boldsymbol{R'},i} = C_{\boldsymbol{R+R'},i}$, indicating

$$C_{\boldsymbol{R},i} = e^{\imath \boldsymbol{k}\cdot\boldsymbol{R}}. \tag{4}$$

[Notice that i is used for indices and $\imath$ is the imaginary number.] Thus

$$\psi_i(\boldsymbol{r} + \boldsymbol{R}) = e^{\imath \boldsymbol{k}\cdot\boldsymbol{R}}\psi_i(\boldsymbol{r}). \tag{5}$$

Now we replace the index i as a pair $(n, \boldsymbol{k})$ and consider $u_{(n,\boldsymbol{k})}(\boldsymbol{r}) := \psi_{(n,\boldsymbol{k})}(\boldsymbol{r})/e^{\imath \boldsymbol{k}\cdot\boldsymbol{r}}$, one may immediately find out that $u_{(n,\boldsymbol{k})}(\boldsymbol{r})$ admits a period as $\boldsymbol{R}$, i.e. $u_{(n,\boldsymbol{k})}(\boldsymbol{r} + \boldsymbol{R}) = u_{(n,\boldsymbol{k})}(\boldsymbol{r})$.

Now we are ready to define the reciprocal space. For

$$\mathbb{L}^* = \{G = n_1\boldsymbol{b_1} + n_2\boldsymbol{b_2} + n_3\boldsymbol{b_3}, n_1, n_2, n_3 \in \mathbb{Z}\}, \tag{6}$$

where

$$\boldsymbol{b_\alpha} \cdot \boldsymbol{a_\beta} = 2\pi\delta_{\alpha,\beta}, \tag{7}$$

Because of the periodicity of u, it admits a Fourier expansion as

$$u_{(n,\boldsymbol{k})}(\boldsymbol{r}) = \sum_{\boldsymbol{G}\in\mathbb{L}^*} c_{\boldsymbol{G}+\boldsymbol{k},n} e^{\imath \boldsymbol{G}\cdot\boldsymbol{r}}. \tag{8}$$

Also, $\psi_{(n,\boldsymbol{k})}(\boldsymbol{r}) = \psi_{(n,\boldsymbol{k}+\boldsymbol{G})}(\boldsymbol{r})$. So if we view $\psi_{(n,\boldsymbol{k})}$ as a function depending on $\boldsymbol{k}$, it also leads to a Fourier expansion:

$$\psi_{(n,\boldsymbol{k})}(\boldsymbol{r}) = \sum_{\boldsymbol{R}\in\mathbb{L}} W_{(n,\boldsymbol{R})}(\boldsymbol{r}) e^{\imath \boldsymbol{k}\cdot\boldsymbol{R}}. \tag{9}$$

The coefficient functions $W_{(n,\boldsymbol{R})}$ are called Wannier functions.

Remark 1. *There may be some constant in the definition of Wannier functions, depending on the definition of Fourier transformation.*

Now we turn to consider

$$\Omega^* := \{n_1\boldsymbol{b_1} + n_2\boldsymbol{b_2} + n_3\boldsymbol{b_3}, -1/2 \le c_1, c_2, c_3 < 1/2\}. \tag{10}$$

Remark 2. *One can show that for $\boldsymbol{k_1}, \boldsymbol{k_2} \in \Omega^*$,*

$$\langle \psi_{(m,\boldsymbol{k_1})} | H | \psi_{(n,\boldsymbol{k_2})} \rangle = 0 \tag{11}$$

if $\boldsymbol{k_1} \neq \boldsymbol{k_2}$, thus the Periodic Hamiltonian is block-diagonalized in terms of $\boldsymbol{k}$.

The inverse Fourier transformation leads to a more formal definition of $W_{(n,\boldsymbol{R})}$, i.e.

$$W_{(n,\boldsymbol{R})} = \frac{1}{|\Omega^*|} \int_{\Omega^*} \psi_{(n,\boldsymbol{k})}(\boldsymbol{r}) e^{-\imath \boldsymbol{k}\cdot\boldsymbol{R}} \mathrm{d}\boldsymbol{k}. \tag{12}$$

By definition, it is clear that $W_{(n,\boldsymbol{R})}$ admits

$$W_{(n,\boldsymbol{R})}(\boldsymbol{r}) = W_{(n,\boldsymbol{0})}(\boldsymbol{r} - \boldsymbol{R}). \tag{13}$$

Thus we can focus on making $W_{(n,\boldsymbol{0})}$ localized around $\boldsymbol{0}$, which makes all Wannier functions $W_{(n,\boldsymbol{R})}$ localized around $\boldsymbol{R}$. Notice that

$$W_{(n,\boldsymbol{0})}(\boldsymbol{r}) = \frac{1}{|\Omega^*|} \int_{\Omega^*} \psi_{(n,\boldsymbol{k})}(\boldsymbol{r}) \mathrm{d}\boldsymbol{k} = \frac{1}{|\Omega^*|} \int_{\Omega^*} u_{(n,\boldsymbol{k})}(\boldsymbol{r}) e^{\imath \boldsymbol{k}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{k}. \tag{14}$$

This in turn requires that $u_{(n,\boldsymbol{k})}(\boldsymbol{r})$ is smooth in terms of $\boldsymbol{k}$, thus $\psi_{(n,\boldsymbol{k})}$ is smooth in terms of $\boldsymbol{k}$.

Remark 3. *If one needs the Wannier function being real, the restriction $\psi_{(n,\boldsymbol{k})} = \psi^\dagger_{(n,-\boldsymbol{k})}$ can be imposed.*

2 Super Cell Formulation and Brillouin Zone Sampling

We are interested in the thermodynamic limit (TDL) of the system. Two equivalent ways are provided, i.e. the super cell formulation and the Brillouin zone sampling.

The super cell formulation can be considered as introducing $N_1^\ell \times N_2^\ell \times N_3^\ell$ unit cells along $\boldsymbol{a_1}, \boldsymbol{a_2}$ and $\boldsymbol{a_3}$. Then the system can be treated as a giant molecule and then solved. An additional boundary condition (Born-von Karman boundary condition) is enforced for the orbitals, say

$$\psi(\boldsymbol{r} + N_\alpha^\ell \boldsymbol{a}_\alpha) = \psi(\boldsymbol{r}). \tag{15}$$

Now we restrict our attention (i.e. the integration) on this supercell, since the functions cannot be $L_2(\mathbb{R}^3)$ due to the periodicity.

Recall that $\psi_{(n,\boldsymbol{k})} = e^{\imath \boldsymbol{k}\cdot\boldsymbol{R}} u_{(n,\boldsymbol{k})}(\boldsymbol{r})$. The new boundary condition implies

$$e^{\imath \boldsymbol{k}\cdot(N_\alpha^\ell \boldsymbol{a}_\alpha)} = 1, \tag{16}$$

meaning

$$\boldsymbol{k}\cdot\boldsymbol{a}_\alpha = 2m\pi/N_\alpha^\ell, \quad \text{for } m\in\mathbb{Z}. \tag{17}$$

Now reciprocal space Ω^* is discretized. The possible $\boldsymbol{k}$'s are now

$$\mathcal{K}^\ell := \{c_1\boldsymbol{b}_1 + c_2\boldsymbol{b}_2 + c_3\boldsymbol{b}_3 \mid c_\alpha \in \{-1/2, -1/2+1/N_\alpha^\ell, \cdots, 1/2-1/N_\alpha^\ell\}\}. \tag{18}$$

One then could try to get the ground energy in terms of finding a set of periodic functions $\{u_{n,\boldsymbol{k}}\}$, which is an eigenvalue problem for separate $\boldsymbol{k}$'s, according to Remark 2.

3 Linear Combination of Atomic Orbitals

Here we briefly discuss the framework of Linear Combination of Atomic Orbitals (LCAO). Consider a supercell $\mathbb{L}_s$, for a given set of basis functions $\{\mu_{\boldsymbol{R}}\}$ that is defined on a unit cell centered at $\boldsymbol{R}\in\mathbb{L}_s\subset\mathbb{L}$ (and the μ here should also be considered as some index), apply Fourier transformation on $\{\mu_{\boldsymbol{R}}\}$,

$$\mu_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} e^{\imath\boldsymbol{k}\cdot\boldsymbol{R}}\mu_{\boldsymbol{R}}(\boldsymbol{r}), \tag{19}$$

and $\mu_{\boldsymbol{k}}$ admits that $\mu_{\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{T}) = e^{\imath\boldsymbol{k}\cdot\boldsymbol{T}}\mu_{\boldsymbol{k}}(\boldsymbol{r})$ for $\boldsymbol{T}\in\mathbb{L}_s$. We may also consider its periodic extension $\{\tilde{\mu}_{\boldsymbol{R}}\}$ where $\tilde{\mu}_{\boldsymbol{R}} := \sum_{\boldsymbol{L}}\mu_{\boldsymbol{R}+\boldsymbol{L}}$ and $\boldsymbol{L}$ is the labels the Bravais lattice vectors of the supercell.

These orbitals $\{\mu_{\boldsymbol{k}}\}$ are called Bloch AOs. Now we can try to construct $\psi_{(n,\boldsymbol{k})}$ as a linear combination of $\{\mu_{\boldsymbol{k}}\}$, say

$$\psi_{(n,\boldsymbol{k})} = \sum_\mu C_{n,\mu}\mu_{\boldsymbol{k}}. \tag{20}$$

Then $\psi_{(n,\boldsymbol{k})}$ must admit the property defined in Equation 5.

Remark 4. *The atomic orbitals $\{\mu_{\boldsymbol{R}}\}$ are chosen to satisfy*

$$\mu_{\boldsymbol{R}}(\boldsymbol{r}-\boldsymbol{R}) = \mu_{\boldsymbol{0}}(\boldsymbol{r}), \tag{21}$$

meaning we choose the atomic orbitals for each unit-cell and then translate them throughout the supercell. It is easy to see that the Wannier functions defined in Equation 14 satisfy this.

4 Boys Localization, Wannier Localization and the Pipek-Mezey Metric

Suppose that we have already solved the Schrödinger equation and the orbitals are $\{\psi_i\}$, we are interested in finding a unitary transformation U, which transform the orbitals into

$$\tilde{\psi}_k = \sum_i U_{ki}\psi_i. \tag{22}$$

Remark 5. *Note that any unitary transformation could possibly break the lattice translational symmetry, and the new functions are not the eigenstate of the periodic Hamiltonian anymore. However, the density remains the same. Then what is the benefit of localization?*

The goal of the transformation is to look for localization. A direct transformation one can choose is

$$\tilde{\psi}_{(n,\boldsymbol{k})} = e^{\imath\theta_{(n,\boldsymbol{k})}}\psi_{(n,\boldsymbol{k})}, \tag{23}$$

where $e^{\imath\theta_{(n,\boldsymbol{k})}}$ is chosen to make sure $\langle\tilde{\psi}_{(m,\boldsymbol{k})}|\tilde{\psi}_{(m,\boldsymbol{0})}\rangle$ is real. This "increases" the smoothness of $\{\tilde{\psi}_{(n,\boldsymbol{k})}\}$.

Another choice is to define a functional

$$\Omega(\{\tilde{\psi}_i\}) := \sum_i\left[\langle\tilde{\psi}_i|\boldsymbol{r}^2|\tilde{\psi}_i\rangle - \langle\tilde{\psi}_i|\boldsymbol{r}|\tilde{\psi}_i\rangle^2\right] \tag{24}$$

and consider its minimization. This procedure is called the Boys localization. According to the discussion before, this is equivalent to minimizing $\Omega(\{W_{(i,\boldsymbol{0})}\})$.

Remark 6. *Here* $\boldsymbol{r}^2 := \boldsymbol{r}\cdot\boldsymbol{r}$ *and* $\langle\tilde{\psi}_i|\boldsymbol{r}|\tilde{\psi}_i\rangle^2 := \langle\tilde{\psi}_i|\boldsymbol{r}|\tilde{\psi}_i\rangle \cdot \langle\tilde{\psi}_i|\boldsymbol{r}|\tilde{\psi}_i\rangle$.

Instead of considering the variance of the estimator $\boldsymbol{r}$, another objective metric is proposed. Recall the definition of $\{\tilde{\mu}_{\boldsymbol{R}}\}$, we know that if $\{\mu_{\boldsymbol{R}}\}$ is localized, $\{\tilde{\mu}_{\boldsymbol{R}}\}$ is localized, in the sense of at each unit cell.

First of all let us assume that $\{\tilde{\mu}_{\boldsymbol{R}}\}$ is an orthonormal set. The Pipek-Mezey (PM) metric is then defined as

$$\langle O\rangle_{\mathrm{PM}} = \sum_{\mu,i} \left(\langle W_{(i,\mathbf{0})}(\boldsymbol{r})|\ |\tilde{\mu}_{\boldsymbol{R}}\rangle\langle\tilde{\mu}_{\boldsymbol{R}}|\ |W_{(i,\mathbf{0})}(\boldsymbol{r})\rangle\right)^p, \tag{25}$$

here $p = 2$ or 4. The metric is not obvious at first glance, but we can discuss its property in a qlitative way. Suppose $W_{(i,\mathbf{0})}(\boldsymbol{r})$ is localized around $\mathbf{0}$, and it is close to some $\mu_{\boldsymbol{R}}$, $\langle O\rangle_{\mathrm{PM}}$ should be close to 1 for each term. Otherwise, assume $W_{(i,\mathbf{0})}$ is uniformly spread out, each term will be small, thus the power p will lead to a smaller value.

In practice, the basis $\{\tilde{\mu}_{\boldsymbol{R}}\}$ does not form a orthonormal basis, and the metric is revised as

$$\langle O\rangle_{\mathrm{PM}} = \sum_{\mu,i}\left(\left\langle W_{(i,\mathbf{0})}(\boldsymbol{r})\middle|\ |\tilde{\mu}_{\boldsymbol{R}}\rangle \sum_{\nu,\boldsymbol{R'}} (S^{-1})^{\boldsymbol{R},\boldsymbol{R'}}_{\mu,\nu}\langle\tilde{\nu}_{\boldsymbol{R'}}|\ \middle| W_{(i,\mathbf{0})}(\boldsymbol{r})\right\rangle\right)^p. \tag{26}$$

Here S is a matrix defined as

$$S = [\langle\tilde{\mu}_{\boldsymbol{R}}|\tilde{\nu}_{\boldsymbol{R'}}\rangle]^{\boldsymbol{R},\boldsymbol{R'}}_{\mu,\nu}. \tag{27}$$

An important property here is that

$$\left[\sum_{\nu,\boldsymbol{R'}}(S^{-1})^{\boldsymbol{R},\boldsymbol{R'}}_{\mu,\nu}\langle\tilde{\nu}_{\boldsymbol{R'}}|\right]|\tilde{\gamma}_{\boldsymbol{R''}}\rangle = \sum_{\mu,\boldsymbol{R'}}(S^{-1})^{\boldsymbol{R},\boldsymbol{R'}}_{\mu,\nu}(S)^{\boldsymbol{R'},\boldsymbol{R''}}_{\nu,\gamma} = \delta^{\boldsymbol{R},\boldsymbol{R''}}_{\mu,\gamma} := \delta_{\mu,\gamma}\delta_{\boldsymbol{R},\boldsymbol{R''}}. \tag{28}$$

Even though the form has changed, the orbital

$$\sum_{\nu,\boldsymbol{R'}}(S^{-1})^{\boldsymbol{R},\boldsymbol{R'}}_{\mu,\nu}\langle\tilde{\nu}_{\boldsymbol{R'}}| \tag{29}$$

serves as $\langle\tilde{\mu}_{\boldsymbol{R}}|$ because of the property in Equation 28.

Remark 7. *It is clear that the PM-metric highly depends on the choice of atomic orbitals. Generally, the PM metric is ill-defined [LJ14].*

5 Intrinsic Atomic Orbitals

Introduced in [Kni13], the Intrinsic Atomiz Orbitals (IAO) are introduced to better adjust the orbitals. Consider two basis functions, namely B_1 and B_2, and we have solved the system of interest with B_1, where it leads to occupied orbitals $|i\rangle$.

Define two projectors as

$$P_{12} = \sum_{\mu,\nu\in B_1}|\mu\rangle(S^{-1})_{\mu,\nu}\langle\nu|,\quad P_{21} = \sum_{\rho,\sigma\in B_2}|\rho\rangle(S^{-1})_{\rho,\sigma}\langle\sigma|, \tag{30}$$

we can obtain an orthonormal function set that sets in the space spanned by B_2, i.e.

$$\{|\tilde{i}\rangle\} = \mathrm{orth}(P_{21}P_{12}|i\rangle), \tag{31}$$

where orth represents an orthogonalization process. Another two projectors

$$O := \sum_i |i\rangle\langle i|,\quad \widetilde{O} := \sum_i|\tilde{i}\rangle\langle\tilde{i}|, \tag{32}$$

and the IAOs are defined as

$$|\rho_{\mathrm{IAO}}\rangle = [O\widetilde{O} + (1-O)(1-\widetilde{O})]|\rho\rangle, \tag{33}$$

where $|\rho\rangle\in B_2$.

Remark 8. *An intuitive way of understanding the Equation 33 is that, an atomic orbital is projected into two spaces: the first part is* $O\widetilde{O}$*, occupied subspace both in* B_1 *and* B_2*; similarly, the second part represents the virtual subspace generated by both* B_1 *and* B_2*.*

As suggested in [ZT24], instead of directly adopting the atomic orbitals that are used to solve the periodic system, one may construct a new basis by the IAO procedure, where B_1 and B_2 should be used to generate Bloch AOs, as outlined in Section 3. As suggested by Remark 7, this could provide further advantage in optimizing the PM metric thus solving the localization problem.

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