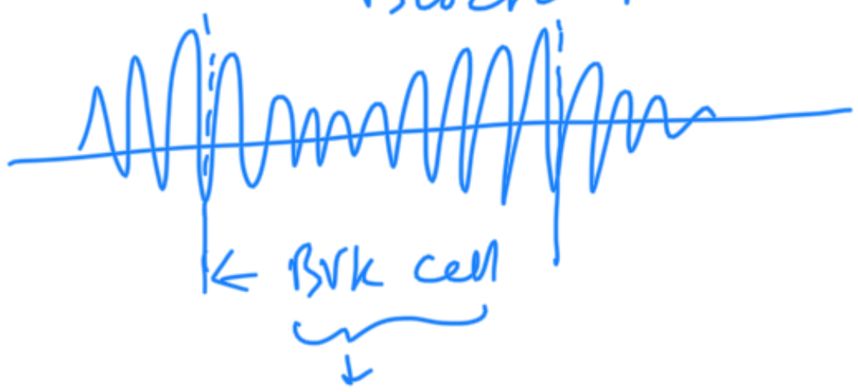
Wannier fn as tight binding basis:

Recall, for an electron in a periodic potential:

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{n_k}} \sum_{R}^{n_k} e^{i\vec{k}\cdot\vec{R}} w_{nR}(\vec{r}) \quad , \quad n_k = \text{number of allowed values of } \vec{k} \text{ in the BVK super cell.}$$

$\psi_{n\vec{k}}(\vec{r})$ → Bloch state

$w_{nR}(\vec{r})$ → Wannier fn.



n_k number of unit cells.

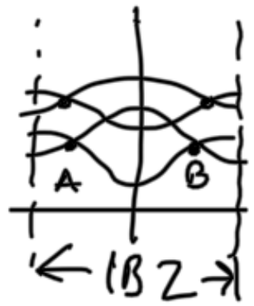
Conversely, $$w_{nR}(\vec{r}) = \frac{1}{\sqrt{n_k}} \sum_{k}^{n_k} e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) \quad \text{—— (2)}$$

However in the above we are simply assuming that we can associate a WF for each band.

This is possible only when bands are "completely" isolated

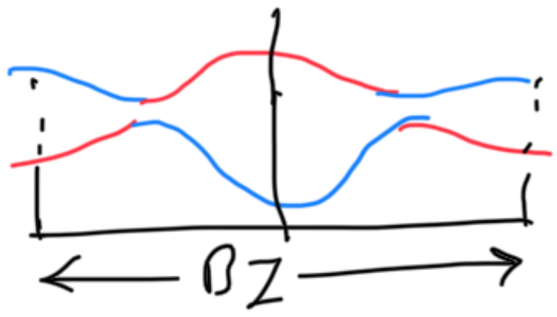
like:

However in general we have bands crossing:



So across the points A and B how do we assign the band index?

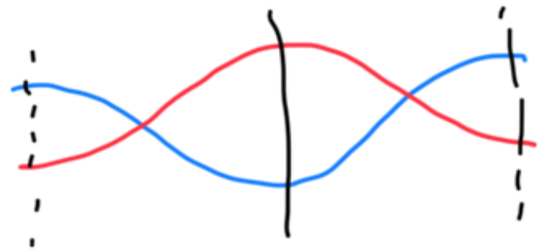
Even if they do not cross they may have mixed orbital character:



$-\phi_1$

$-\phi_2$

We want to separate out two bands as:



so that even if they cross we can follow their orbital character unambiguously.

So we take linear combination of Bloch states at each $\vec{k}$ so that the energies of the resultant states form bands which can be associated with specific orbitals. The orbitals can be a bonding orbital, an antibonding orbital, or an atomic orbital,

depending on the subspace of Bloch states considered and the nature of chemical bonds present in the system.

If $\{\phi\}$ be such orbitals then we have from ②:

$$\phi_{nR}(\vec{r}) = \frac{1}{\sqrt{n_k}} \sum_{k}^{n_k} e^{-i\vec{k}\cdot\vec{R}} \sum_{l} U_{nl}(\vec{k})\, \psi_{l\vec{k}}(\vec{r})$$

of Bloch states

where $\sum_{l} U_{nl}(\vec{k})\, \psi_{l\vec{k}}(\vec{r})$ implies the linear combination at each $\vec{k}$.

$$\Rightarrow \sum_{mn} U^{\dagger}_{mn}(k')\, \phi_{nR}(\vec{r}) = \frac{1}{\sqrt{n_k}} \sum_{k} e^{-i\vec{k}\cdot\vec{R}} \sum_{l} U^{\dagger}_{mn}(k)\, U_{nl}(k)\, \psi_{lk}(\vec{r})$$

$$\Rightarrow = \frac{1}{\sqrt{n_k}} \sum_{k} e^{-i\vec{k}\cdot\vec{R}} \sum_{n} \sum_{l} U^{\dagger}_{mn}(k')\, U_{nl}(k)\, \psi_{lk}(\vec{r})$$

$$\Rightarrow \sum_{R} e^{i\vec{k}'\cdot R} \sum_{n} U^{\dagger}_{mn}(k')\, \phi_{nR}(\vec{r}) = \frac{1}{\sqrt{n_k}} \sum_{k} \left[\sum_{R} e^{i\vec{R}\cdot(\vec{k}'-\vec{k})} \right] \sum_{n} \sum_{l} U^{\dagger}_{mn}(k')\, U_{nl}(k)\, \psi_{lk}(\vec{r})$$

$$\Rightarrow = \sqrt{n_k} \sum_{k} \delta_{k'k} \sum_{n} \sum_{l} U^{\dagger}_{mn}(k')\, U_{nl}(k)\, \psi_{lk}(\vec{r})$$

$$\Rightarrow \frac{1}{\sqrt{n_k}} \sum_R e^{ik\cdot R} \sum_n U^{\dagger}(k)_{mn} \phi_{nR}(r) = \Psi_{mk}(\vec{r})$$

$\{\phi\}$ in our case are the HAWOs and so we know the $U(k)$ matrices. We get $U(\vec{k})$ through Lowdin Symm orthogonalization or Singular Value decomposition of overlap matrices. We still went to construct H in the HAWO basis to extract a minimal description of only the relevant orbitals/electrons.

But in general we do not have access to $\{\phi\}$ apriori and $\{\phi\}$ are chosen as some reasonable set of localized orbitals in the basis of which we want to calculate $\Psi_{nk}(\vec{r})$.

So we propose $\Psi_{mk}(\vec{r}) = \frac{1}{\sqrt{n_k}} \sum_R e^{i\vec{k}\cdot\vec{R}} \sum_n C_{nm}(\vec{k}) \phi_{nR}(\vec{r})$

and our goal is to find $\{C_{nm}^{(k)}\}$

Start with H: $H|\psi_{n\vec{k}}\rangle = E_{n\vec{k}}|\psi_{n\vec{k}}\rangle$

$$\Rightarrow \quad H \sum_{k}^{n_k} e^{i\vec{k}\cdot\vec{R}} \sum_{\ell}^{N} C_{n\ell}^{(k)} |\phi_{\ell R}\rangle = E_{n\vec{k}} \sum_{R'}^{n_k} e^{i\vec{k}\cdot\vec{R}'} \sum_{m}^{N} C_{nm}^{(k)} |\phi_{mR'}\rangle$$

Taking $\langle \phi_{j0}|$ on both sides:

$$\sum_{R}^{n_k} e^{i\vec{k}\cdot\vec{R}} \sum_{\ell}^{N} C_{n\ell}^{(k)} \langle \phi_{j0}|H|\phi_{\ell R}\rangle = E_{n\vec{k}} \sum_{R'}^{n_k} e^{i\vec{k}\cdot\vec{R}'} \sum_{m}^{N} C_{nm}^{(k)} \langle \phi_{j0}|\phi_{mR'}\rangle$$

$j0 \equiv R$

for orthonormal basis $\langle \phi_{j0}|\phi_{mR'}\rangle = \delta_{jm}\delta_{0R'}$

$$\Rightarrow \sum_{R}^{n_k} e^{i\vec{k}\cdot\vec{R}} \sum_{\ell}^{N} C_{n\ell}^{(k)} H_{j0,\ell R} = E_{n\vec{k}} C_{nm}^{(k)} \; ; \; H_{j0,\ell R} = \langle \phi_{j0}|\hat{H}|\phi_{\ell R}\rangle$$

$$\Rightarrow \sum_{\ell} \left(\sum_{R} e^{i\vec{k}\cdot\vec{R}} H_{j0,\ell R} \right) C_{n\ell}^{(k)} = E_{n\vec{k}} C_{nm}^{(k)}$$

Recall: Bloch formalism: One electron theory of periodic system.

$$\hat{H} = \sum_{i} V_i(r) + \Delta V + \hat{T} \; ; \quad V_i(\vec{r}) \rightarrow \text{ith atomic potential.}$$

$\Delta V \rightarrow$ all other electrons.

ΔV : accounts for average effect of