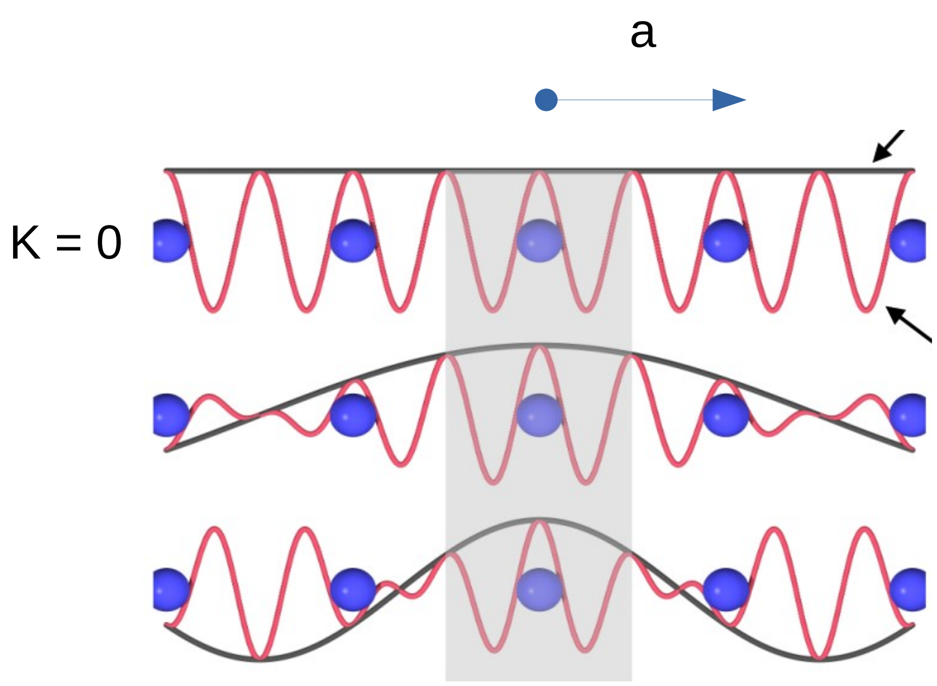
Bloch‘s Theorem → Using symmetry



$$|\psi(x)|^2 = |\psi(x + a)|^2$$

$$\psi(x + a) = C \cdot \psi(x)$$

$$|C| = 1$$

$$C^N \cdot \psi(x) = \psi(x) \longrightarrow C^N = 1 \longrightarrow C = \exp\frac{i \cdot 2\pi s}{N}$$

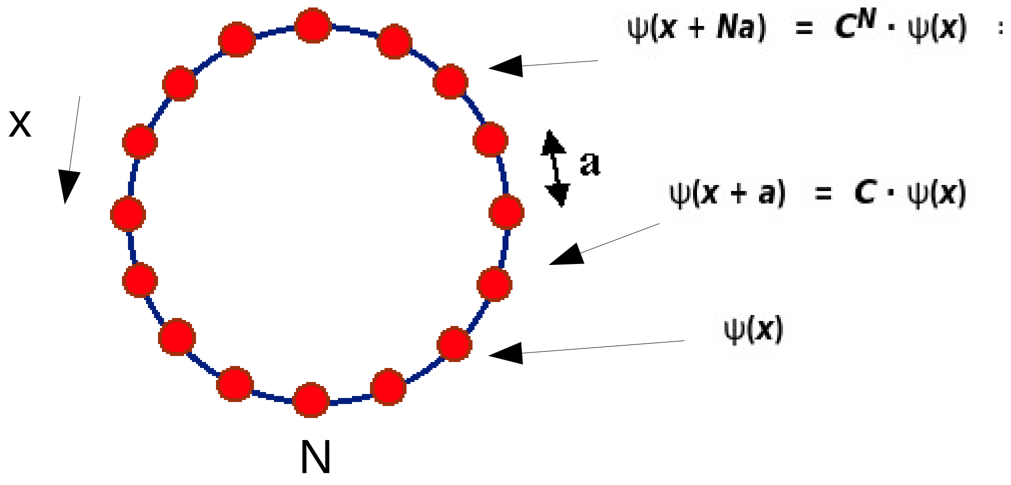
$$\psi(x + a) = C \cdot \psi(x)$$

$$\psi(x + a) = \psi(x) \exp\frac{i \cdot 2\pi s}{N}$$

$$u_k(x) = u_k(x + a),$$

$$\psi(x) = u_k(x) \cdot \exp\frac{i \cdot 2\pi \cdot s \cdot x}{N \cdot a}$$

pbc



$$k \cdot = \frac{\cdot\, 2\pi s}{N \ a}$$

$$\psi(x) = u(x) \cdot \exp(ikx)$$

Bloch's theorem states that solutions to the Schrödinger equation in a periodic potential take the form of a plane wave modulated by a periodic function

$\psi(x + a) = \exp(ika) \cdot \psi(x)$

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r} + \boldsymbol{R}_m) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}_m}\psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

$\psi(x) = u(x) \cdot \exp(ikx)$

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{\boldsymbol{k}n}(\boldsymbol{r})$$

While Bloch functions are the eigenstates of the Hamiltonian for a given band and a given crystal momentum, they are oscillating and delocalized in real space.

Often, orbitals that are localized in real space offer more microscopic insights into the underlying chemical and physical processes.

Maximally localized generalized Wannier functions for composite energy bands

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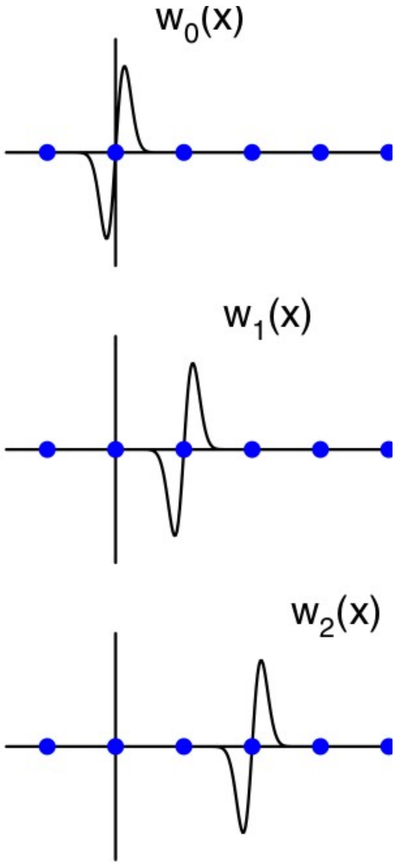


As the Bloch states are periodic in momentum space, we may express them in terms of a **Fourier series**:

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} W_{\boldsymbol{R}n}(\boldsymbol{r})$$

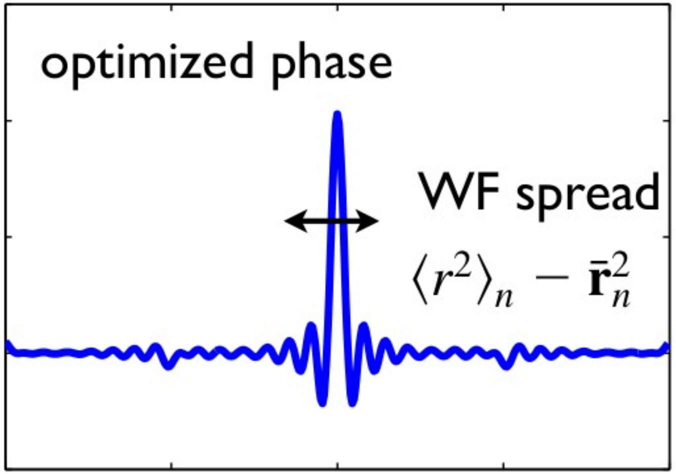
The inverse of this series leads to so-called **Wannier functions** (WFs) that are Fourier transformations of the original Bloch states:

$$W_{\boldsymbol{R}n}(\boldsymbol{r}) = \frac{1}{N} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

Bloch functions (more precisely):

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\ e^{i\mathbf{k}\cdot\mathbf{r}}\ e^{i\phi_{n\mathbf{k}}}$$

gauge freedom
(does not change the physical description of the system)



$$\Omega = \sum_n [\langle \mathbf{0}n|r^2|\mathbf{0}n\rangle - \langle \mathbf{0}n|\mathbf{r}|\mathbf{0}n\rangle^2] = \sum_n [\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2]$$

$$\bar{\boldsymbol{r}}_n = \langle W_{\mathbf{0}n}|\boldsymbol{r}|W_{\mathbf{0}n}\rangle \qquad \langle r^2\rangle_n = \langle W_{\mathbf{0}n}|r^2|W_{\mathbf{0}n}\rangle$$

$$W_{\boldsymbol{R}n}(\boldsymbol{r}) = \frac{1}{N}\sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

$\langle 0n|\mathbf{r}|0n\rangle$ – position of the Wannier center

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

$$\Omega = \sum_n [\langle \mathbf{0}n|r^2|\mathbf{0}n\rangle - \langle \mathbf{0}n|\mathbf{r}|\mathbf{0}n\rangle^2] = \sum_n [\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2]$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

$\hat{\mathbf{r}} = i\nabla_{\mathbf{k}}$ -- position operator

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\ e^{i\mathbf{k}\cdot\mathbf{r}}\ e^{i\phi_{n\mathbf{k}}}$$

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

$$\langle 0n|\mathbf{r}^2|0n\rangle = -\,\frac{V}{(2\pi)^3}\int d\mathbf{k}\,\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}^2|u_{n\mathbf{k}}\rangle$$

$$\psi(x + a) = u_k(x + a) \cdot \exp \frac{i \cdot 2\pi \cdot s \cdot (x + a)}{N \cdot a}$$

$$\psi(x + a) = u_k(x) \cdot \exp \frac{i \cdot 2\pi \cdot s \cdot x}{N \cdot a} \cdot \exp \frac{i \cdot 2\pi \cdot s}{N} = \psi(x) \cdot \exp \frac{i\, 2\pi \cdot s}{N}$$