TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

SFB 1143

Solid State Theory (SS2020)

Lecture 11: Wannier functions & LCAO

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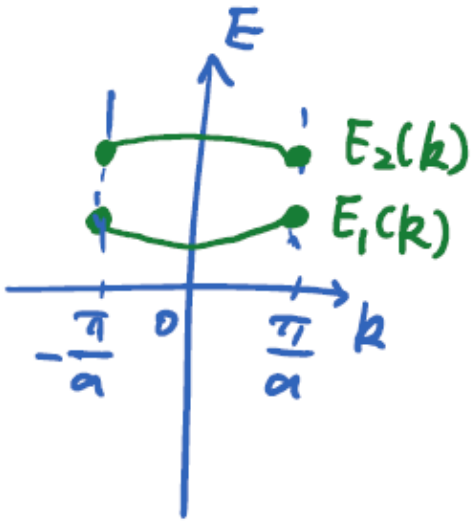
§ 3.4 Wannier function

- Electron in a periodic potential:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \qquad V(x) = V(x+na), \quad n \in \mathbb{Z}$$

  - $V(x)$ weak: nearly free electrons
  - $V(x)$ strong: tight-binding model



Single-electron energies form energy bands!

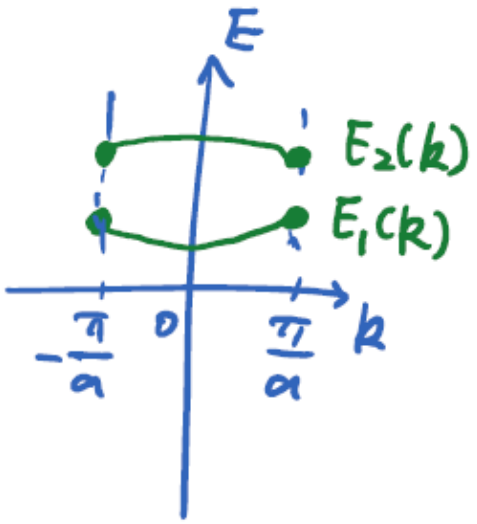
§ 3.4 Wannier function

- General consideration:

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}_r^2 + V(\vec{r})\right]\psi_n(\vec{k},\vec{r}) = E_n(\vec{k})\,\psi_n(\vec{k},\vec{r})$$

$$\psi_n(\vec{k},\vec{r}) = u_{\vec{k},n}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}} \qquad k \in \text{FBZ}$$

n: band index



- We need to develop methods to calculate energy bands and (single-electron) wave functions.

§ 3.4 Wannier function

- Define Wannier function:

Expand $\psi_n(\vec{k}, \vec{r})$ in terms of Fourier components:

$$\psi_n(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\mu} a_n(\vec{R}_\mu, \vec{r})\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

$a_n(\vec{R}_\mu, \vec{r})$: Wannier function

§ 3.4 Wannier function

Wannier function :

$$a_n(\vec{R}_\mu, \vec{r}) \equiv \frac{1}{\sqrt{N}} \sum_{\vec{k}\in FBZ} e^{-i\vec{k}\cdot\vec{R}_\mu} \psi_n(\vec{k}, \vec{r})$$

$$= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_\mu} u_{\vec{k},n}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$$

$$= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}-\vec{R}_\mu)} u_{\vec{k},n}(\vec{r})$$

$$\equiv a_n(\vec{r}-\vec{R}_\mu)$$

$u_{\vec{k},n}(\vec{r}) = u_{\vec{k},n}(\vec{r}-\vec{R}_\mu)$

↓

"localized" close to $\vec{R}_\mu$

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- Orthogonality:

$$\int d\vec{r}\; a_n^*(\vec{r}-\vec{R}_\mu)\, a_m(\vec{r}-\vec{R}_\nu)$$

$$= \int d\vec{r}\; \frac{1}{N}\sum_{\vec{k},\vec{k}'} e^{i\vec{k}\cdot\vec{R}_\mu - i\vec{k}'\cdot\vec{R}_\nu}\, \psi_n^*(\vec{k},\vec{r})\, \psi_m(\vec{k}',\vec{r})$$

$$= \delta_{nm}\; \frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}_\mu-\vec{R}_\nu)}$$

$$= \delta_{nm}\delta_{\mu\nu}$$

$\psi_n^*(\vec{k},\vec{r})\,\psi_m(\vec{k}',\vec{r}) = \delta_{nm}\,\delta_{\vec{k},\vec{k}'}$

$\frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}_\mu-\vec{R}_\nu)} = \delta_{\mu\nu}$ (discrete orthogonality)

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- Phase freedom:

$$a_n(\vec{r}-\vec{R}_\mu) = \frac{1}{\sqrt{N}} \sum_{\vec{k}\in FBZ} e^{-i\vec{k}\cdot(\vec{r}-\vec{R}_\mu)} u_{\vec{k},n}(\vec{r})$$

$$u_{\vec{k},n}(\vec{r}) \longrightarrow e^{i\theta_{\vec{k},n}} u_{\vec{k},n}(\vec{r})$$

Single-electron wave function "unchanged", but this leads to a different set of Wannier functions!

Thus, we are allowed to choose $\theta_{\vec{k},n}$ to make Wannier function maximally localized.

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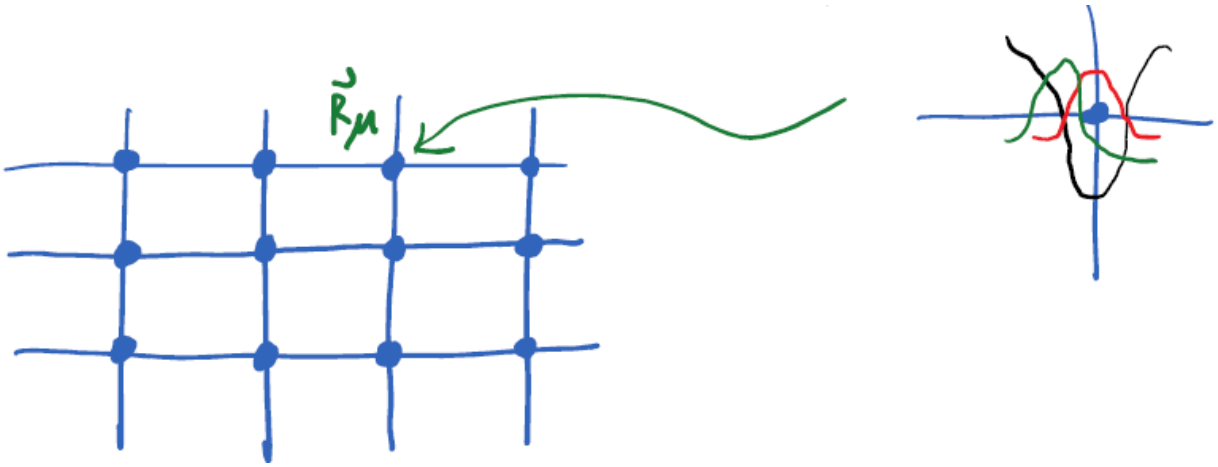
- Phase freedom:

$$a_n(\vec{r}-\vec{R}_\mu) = \frac{1}{\sqrt{N}} \sum_{\vec{k}\in FBZ} e^{-i\vec{k}\cdot(\vec{r}-\vec{R}_\mu)} u_{\vec{k},n}(\vec{r})$$

$$u_{\vec{k},n}(\vec{r}) \rightarrow e^{i\theta_{\vec{k},n}} u_{\vec{k},n}(\vec{r})$$



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- Wannier function:

Wannier function: real-space description of bands

Bloch function: momentum-space description of bands

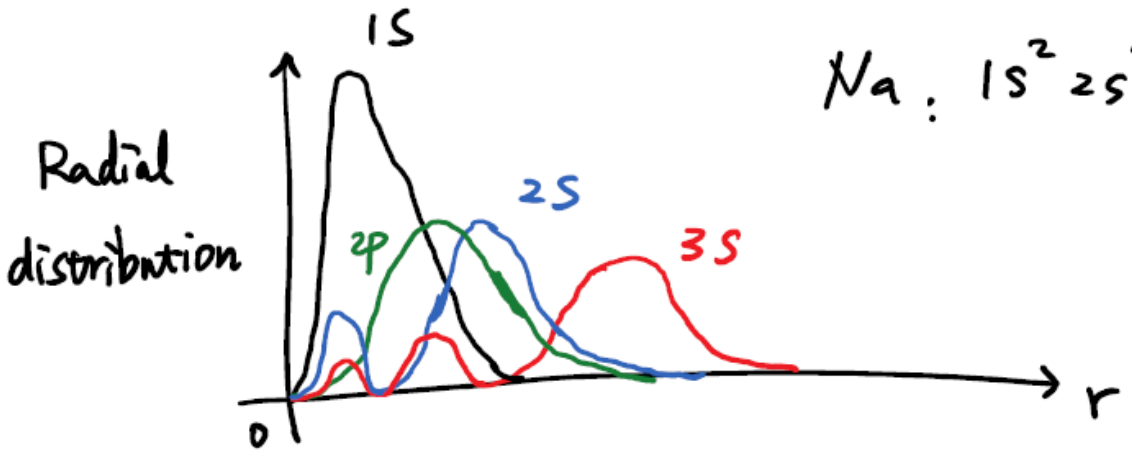
Next important question:

How to build reasonable "Wannier ansatz" for determining energy bands ?

§ 3.4 Wannier function

- Tight-binding model:

Choose atomic wave functions as Wannier functions!



Na: $1s^2 2s^2 2p^6 3s^1$

$$a_n(\vec{r}-\vec{R}_\mu) \simeq \varphi_n^{at}(\vec{r}-\vec{R}_\mu)$$

("at" means atomic)

§ 3.4 Wannier function

- Tight-binding model:

$$a_n(\vec{r}-\vec{R}_\mu) \simeq \varphi_n^{at}(\vec{r}-\vec{R}_\mu)$$ ("at" means atomic)

(drawback: orthogonality is lost!)

➢ Nevertheless we may build a trial wave function to calculate energy bands.

$$\psi_n(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} a_n(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

$$\simeq \frac{1}{\sqrt{N}} \sum_\mu \varphi^{at}(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

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$$H\psi_n(\vec{k},\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(\vec{r})\right]\psi_n(\vec{k},\vec{r})$$

$$= \frac{1}{\sqrt{N}}\sum_{\mu}\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(\vec{r})\right]a_n(\vec{r}-\vec{R}_\mu)\,e^{i\vec{k}\cdot\vec{R}_\mu}$$

$$V(\vec{r}) = V^{at}(\vec{r}-\vec{R}_\mu) + \left[V(\vec{r}) - V^{at}(\vec{r}-\vec{R}_\mu)\right]$$

$$\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V^{at}(\vec{r}-\vec{R}_\mu)\right]a_n(\vec{r}-\vec{R}_\mu) = E_n^{at}\,a_n(\vec{r}-\vec{R}_\mu)$$

E_n^{at}: atomic energy levels

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$$H\psi_n(\vec{k},\vec{r}) = E_n^{at} \underbrace{\frac{1}{\sqrt{N}}\sum_{\mu} a_n(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}}_{=\psi_n(\vec{k},\vec{r})} + \frac{1}{\sqrt{N}}\sum_{\mu}\left[V(\vec{r}) - V^{at}(\vec{r}-\vec{R}_\mu)\right] a_n(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

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$$\langle \psi_n | H | \psi_n \rangle$$

$$= \int d\vec{r}\, [\psi_n(\vec{k},\vec{r})]^* H\, \psi_n(\vec{k},\vec{r})$$

$$= E_n^{at} + \sum_{\mu\nu} \frac{1}{N} \int d\vec{r}\; a_n^*(\vec{r}-\vec{R}_\nu)\left[V(\vec{r}) - V^{at}(\vec{r}-\vec{R}_\mu)\right] a_n(\vec{r}-\vec{R}_\mu) \times e^{i\vec{k}\cdot(\vec{R}_\mu - \vec{R}_\nu)}$$

dominant contributions:

1) $\mu = \nu$

2) μ and ν are nearest neighbors.

($a_n(\vec{r}-\vec{R}_\mu)$ localized !)

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$\mu = \nu$ term :

$$C_n = \frac{1}{N} \int d\vec{r} \sum_{\mu} a_n^*(\vec{r} - \vec{R}_\mu) \left[V(\vec{r}) - V^{at}(\vec{r} - \vec{R}_\mu) \right] a_n(\vec{r} - \vec{R}_\mu)$$

constant correction !

$$\vec{\delta} = \vec{R}_\nu - \vec{R}_\mu$$

$\langle \mu\nu \rangle$ term (μ and ν are nearest neighbors) :

$$t_n = \frac{1}{N} \int d\vec{r}\; a_n^*(\vec{r} - \vec{R}_\mu - \vec{\delta}) \left[V(\vec{r}) - V(\vec{r} - \vec{R}_\mu) \right] a_n(\vec{r} - \vec{R}_\mu)$$

↑ exchange integral (assumed to be the same for all neighbors)

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$$\langle \psi_n | H | \psi_n \rangle = E_n^{at} + C_n + t_n \sum_{\vec{\delta}} e^{-i\vec{k}\cdot\vec{\delta}}$$

↑ sum over all nearest neighbors of μ

Example: cubic lattice

nearest neighbors: $\vec{\delta} = \vec{R}_\nu - \vec{R}_\mu = \pm a\hat{x}, \pm a\hat{y}, \pm a\hat{z}$

$$E_n(\vec{k}) = E_n^{at} + C_n + 2t_n\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right]$$

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- A few remarks:

1) n-th energy level of an isolated atom becomes the n-th band.

2) band width $\sim t_n$ (exchange integral)

3) Straightforward extension to longer-range neighbors, spatially anisotropic exchange integrals ...

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- A few remarks:

Drawback: possible mixings/hybridizations of different atomic orbitals were NOT considered!

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- LCAO (linear combination of atomic orbitals):

$$a_n(\vec{r}-\vec{R}_\mu) = \sum_{n'} C_{nn'}\, \psi^{at}_{n'}(\vec{r}-\vec{R}_\mu)$$

superposition coefficients

(variational parameters, to be determined)

➢ $a_n(\vec{r}-\vec{R}_\mu)$ can be made orthogonal by adjusting $C_{nn'}$!

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$$\psi_n(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\mu} a_n(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

$$= \frac{1}{\sqrt{N}} \sum_{n',\mu} C_{nn'} \psi^{at}_{n'}(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

$$= \sum_{n'} C_{nn'}\, \phi_{\vec{R},n'}(\vec{r})$$

$$\phi_{\vec{R},n'}(\vec{r}) \equiv \frac{1}{\sqrt{N}} \sum_{\mu} \psi^{at}_{n'}(\vec{r}-\vec{R}_\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}$$

$\langle \phi_{\vec{R},n} | \phi_{\vec{R},n'} \rangle \neq 0$ (non-orthogonal basis)

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$$H\psi_n(\vec{k},\vec{r}) = E\psi_n(\vec{k},\vec{r})$$

$$\Rightarrow \quad \sum_{n'} C_{nn'} H\phi_{\vec{k},n'}(\vec{r}) = E\sum_{n'} C_{nn'}\phi_{\vec{k},n'}(\vec{r})$$

$$\Rightarrow \quad \sum_{n'} C_{nn'} \int d\vec{r}\ \phi^*_{\vec{k},n''}(\vec{r}) H\phi_{\vec{k},n'}(\vec{r})$$

$$\langle \phi_{\vec{k},n''}|H|\phi_{\vec{k},n'}\rangle = \mathcal{H}_{n'',n'}(\vec{k})$$

$$= E\sum_{n'} C_{nn'} \int d\vec{r}\ \phi^*_{\vec{k},n''}(\vec{r})\phi_{\vec{k},n'}(\vec{r})$$

$$\langle \phi_{\vec{k},n''}|\phi_{\vec{k},n'}\rangle = S_{n'',n'}(\vec{k})$$

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- LCAO becomes a generalized eigenvalue problem:

$$\sum_{n'} \left[H_{n'',n'}(\vec{k}) - E\, S_{n'',n'}(\vec{k}) \right] C_{nn'} = 0$$

$$\det\left(H(\vec{k}) - E\, S(\vec{k}) \right) = 0$$

This determines $E_n(\vec{k})$ and $C_{nn'}$!