

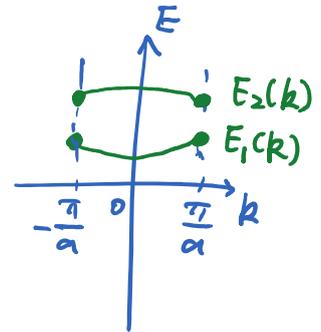
## §3. Band electrons

\*) Wannier functions

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

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

$n$ : band index



Single-electron wave functions are defined within  $\vec{k} \in \text{FBZ}$ , but it can be extended to be a "periodic" function in  $\vec{k}$ -space:

$$\psi_n(\vec{k} + \underbrace{\vec{G}_m}_{\text{reciprocal vector}}, \vec{r}) = \psi_n(\vec{k}, \vec{r})$$

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

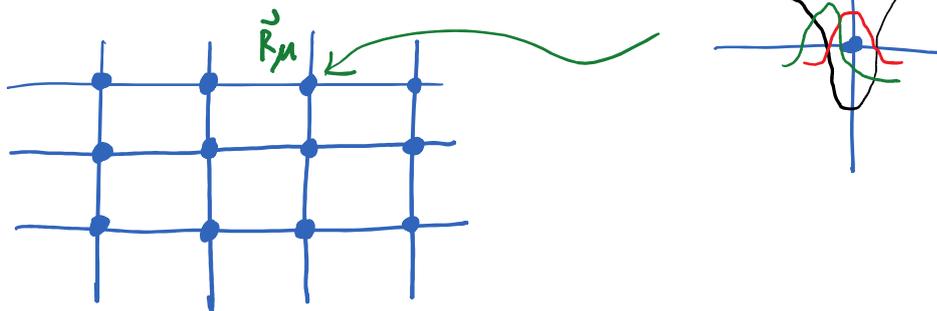
$$\psi_n(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\mu} \underbrace{a_n(\vec{R}_{\mu}, \vec{r})}_{\text{Wannier function}} e^{i\vec{k} \cdot \vec{R}_{\mu}}$$

Wannier function

Wannier function:

$$\begin{aligned}
 a_n(\vec{R}_\mu, \vec{r}) &\equiv \frac{1}{\sqrt{N}} \sum_{\vec{k} \in \text{FBZ}} e^{-i\vec{k} \cdot \vec{R}_\mu} \psi_n(\vec{k}, \vec{r}) \\
 &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k} \cdot \vec{R}_\mu} u_{\vec{k}, n}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \\
 &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{r} - \vec{R}_\mu)} \underbrace{u_{\vec{k}, n}(\vec{r})}_{\parallel} \\
 &\equiv a_n(\vec{r} - \vec{R}_\mu) \quad \underbrace{u_{\vec{k}, n}(\vec{r} - \vec{R}_\mu)}_{\parallel}
 \end{aligned}$$

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



1) Orthogonality:

$$\begin{aligned}
 &\int d\vec{r} a_n^*(\vec{r} - \vec{R}_\mu) a_m(\vec{r} - \vec{R}_\nu) \\
 &= \int d\vec{r} \frac{1}{N} \sum_{\vec{k}, \vec{k}'} e^{i\vec{k} \cdot \vec{R}_\mu - i\vec{k}' \cdot \vec{R}_\nu} \underbrace{\psi_n^*(\vec{k}, \vec{r}) \psi_m(\vec{k}', \vec{r})}_{\parallel} \\
 &= \delta_{nm} \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{R}_\mu - \vec{R}_\nu)} \underbrace{\delta_{nm} \delta_{\vec{k}, \vec{k}'}}_{\parallel} \\
 &= \delta_{nm} \delta_{\mu\nu} \quad \parallel \quad \delta_{\mu\nu} \quad (\text{discrete orthogonality})
 \end{aligned}$$

2) Phase freedom:

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

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

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

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

{ 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?

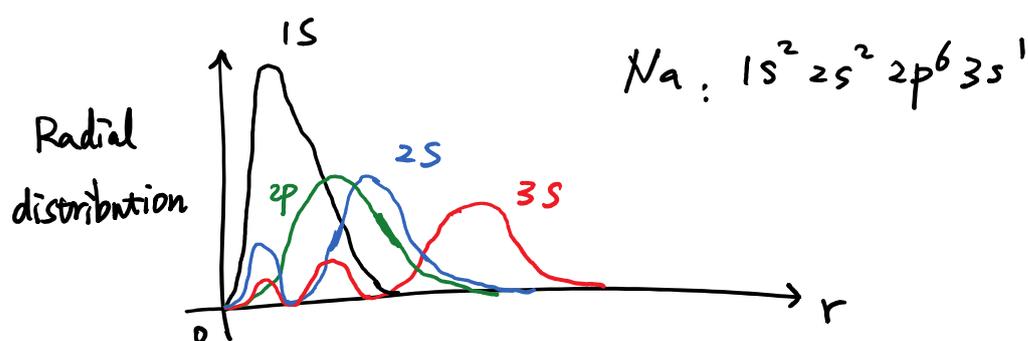
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– Tight-binding model

Choose atomic wave functions as Wannier functions!

When the electron is close to an ion, it is mostly affected by THIS ion, and thus the electron wave functions are close to atomic wave functions.



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

(drawback: orthogonality is lost!)

$$\begin{aligned} \psi_n(\vec{k}, \vec{r}) &= \frac{1}{\sqrt{N}} a_n(\vec{r} - \vec{R}_\mu) e^{i\vec{k} \cdot \vec{R}_\mu} \\ &\simeq \frac{1}{\sqrt{N}} \sum_{\mu} \psi_n^{\text{at}}(\vec{r} - \vec{R}_\mu) e^{i\vec{k} \cdot \vec{R}_\mu} \end{aligned}$$

Below we use  $\psi_n(\vec{k}, \vec{r})$  as a trial wave function.

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

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

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

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

atomic energy levels

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

$$\underbrace{\hspace{10em}}_{= \psi_n(\vec{k}, \vec{r})}$$

$$+ \frac{1}{\sqrt{N}} \sum_{\mu} [V(\vec{r}) - V^{\text{at}}(\vec{r} - \vec{R}_{\mu})] a_n(\vec{r} - \vec{R}_{\mu}) e^{i\vec{k} \cdot \vec{R}_{\mu}}$$

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

$$= \int d\vec{r} [\psi_n(\vec{k}, \vec{r})]^* \underbrace{H \psi_n(\vec{k}, \vec{r})}_{\text{from above}}$$

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

dominant contributions:

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

1)  $\mu = \nu$

2)  $\mu$  and  $\nu$  are nearest neighbors.

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 $\mu = \nu$  term:

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

constant correction!

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

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

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

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

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

↑  
sum over all nearest neighbors of  $\mu$

Example: cubic lattice

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

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

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Several remarks on the tight-binding model:

- 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 ...

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

Improved method:

LCAO (linear combination of atomic orbitals)

$$\psi_n(\vec{r} - \vec{R}_\mu) = \sum_{n'} c_{nn'} \psi_{n'}^{\text{at}}(\vec{r} - \vec{R}_\mu)$$

superposition coefficients

(variational parameters, to be determined)

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$$\begin{aligned}
 \psi_n(\vec{k}, \vec{r}) &= \frac{1}{\sqrt{N}} \sum_{\mu} a_n(\vec{r} - \vec{R}_{\mu}) e^{i\vec{k} \cdot \vec{R}_{\mu}} \\
 &= \frac{1}{\sqrt{N}} \sum_{n', \mu} C_{nn'} \psi_{n'}^{\text{at}}(\vec{r} - \vec{R}_{\mu}) e^{i\vec{k} \cdot \vec{R}_{\mu}} \\
 &= \sum_{n'} C_{nn'} \phi_{\vec{k}, n'}(\vec{r})
 \end{aligned}$$

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

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

Determination of  $C_{nn'}$  and  $E_n(\vec{k})$ :

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

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

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

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

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

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

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

To have nontrivial solutions, we have the secular equation :

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

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

(You may formulate LCAO as a variational problem of minimizing  $\langle \psi_n | H | \psi_n \rangle$  with respect to  $C_{n,n'}$  and  $C_{n,n'}^*$ , which also leads to the above secular equation.)