

## Lecture 12

Continuing tight-binding picture of the bands...

Calculate the band dispersion, corresponding to the Bloch function  $\Psi_k(\vec{r})$ .

$$E_k = \langle \Psi_k | H | \Psi_k \rangle =$$
$$= \frac{1}{NV(\vec{k})} \sum_{\vec{R}, \vec{R}'} e^{-i\vec{k} \cdot (\vec{R} - \vec{R}')} \int d\vec{r} \Psi^*(\vec{r} - \vec{R}) \cdot H \cdot \Psi(\vec{r} - \vec{R}')$$

$$H = H_{\text{at}} + \delta U(\vec{r})$$

Here  $H_{\text{at}}$  is a purely atomic part of the Hamiltonian in a given unit cell,  $\delta U(\vec{r})$  is a correction due to the presence of other atoms.

$$\int d\vec{r} \Psi^*(\vec{r} - \vec{R}) H_{\text{at}} \Psi(\vec{r} - \vec{R}') = \epsilon \delta_{\vec{R}, \vec{R}'}, \text{ where}$$

$\epsilon$  is the energy of the atomic orbital  $\Psi(\vec{r} - \vec{R})$

(same for every atom since they are all equivalent).

$$\int d\vec{r} \Psi^*(\vec{r} - \vec{R}) H \Psi(\vec{r} - \vec{R}') =$$
$$= \epsilon \delta_{\vec{R}, \vec{R}'} + \int d\vec{r} \Psi^*(\vec{r} - \vec{R}) \delta U(\vec{r}) \Psi(\vec{r} - \vec{R}')$$

Then we obtain:

$$\begin{aligned}
 E_{\vec{k}} &= \frac{1}{N V(\vec{k})} \sum_{\vec{R}, \vec{R}'} \left[ \varepsilon \delta_{\vec{R}, \vec{R}'} + \int d\vec{r}^+ \psi^*(\vec{r}^+ - \vec{R}) \delta U(\vec{r}^+) \psi(\vec{r}^+ - \vec{R}') \right] \\
 &= \frac{\varepsilon}{V(\vec{k})} + \frac{1}{N V(\vec{k})} \sum_{\vec{R}'} |\psi(\vec{r}^+ - \vec{R})|^2 \delta U(\vec{r}^+) + \\
 &+ \frac{1}{N V(\vec{k})} \sum_{\vec{R}, \vec{R}'} \int d\vec{r}^+ \psi^*(\vec{r}^+ - \vec{R}) \delta U(\vec{r}^+) \psi(\vec{r}^+ - \vec{R}') \\
 &\cdot e^{i\vec{k} \cdot \vec{R}'}
 \end{aligned}$$

Here we have again assumed that overlap between atomic orbitals is only negligible for nearest-neighbor sites of the lattice.

$$\text{let } \beta = \int d\vec{r}^+ |\psi(\vec{r}^+ - \vec{R})|^2 \delta U(\vec{r}^+)$$

$$\gamma = - \int d\vec{r}^+ \psi^*(\vec{r}^+ - \vec{R}) \delta U(\vec{r}^+) \psi(\vec{r}^+ - \vec{R}') e^{i\vec{k} \cdot \vec{R}'}$$

$\alpha$ ,  $\beta$  and  $\gamma$  are constants, which depend on the atomic and crystal structure.

Then we obtain:

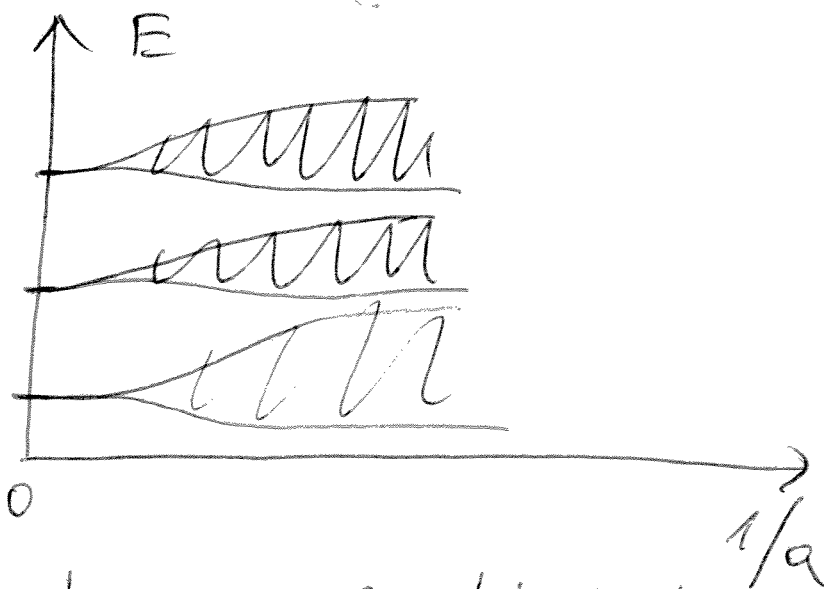
$$E_k = \frac{\epsilon + \beta - \gamma \sum_{\lambda} \cos(\vec{k} \cdot \vec{r}_{\lambda})}{v(\vec{k})} =$$

$$= \frac{\epsilon + \beta - \gamma \sum_{\lambda} \cos(\vec{k} \cdot \vec{r}_{\lambda})}{1 + \alpha \sum_{\lambda} \cos(\vec{k} \cdot \vec{r}_{\lambda})}$$

Thus the general form of the ~~the~~ band dispersion, corresponding to  $\psi_k(\vec{r})$ , is:

$$E_k = \epsilon - \gamma \sum_{\lambda} \cos(\vec{k} \cdot \vec{r}_{\lambda})$$

Here I have neglected the constant energy shift  $\beta$  and redetermined  $\gamma$ .



When atoms are brought together to form a crystal, atomic ~~the~~ levels broaden into bands, and the atomic wavefunctions start overlapping significantly.

The bandwidth is proportional to the overlap integral  $J$ .  
 Introduce another very important concept - Wannier functions.

Wannier functions are defined as:

$$\Phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \Psi_{\vec{k}}(\vec{r}) e^{-i\vec{k} \cdot \vec{R}}$$

Here  $\Psi_{\vec{k}}(\vec{r})$  is a Bloch function of a particular band.

Substitute the expression for  $\Psi_{\vec{k}}(\vec{r})$  in terms of atomic orbitals:

$$\begin{aligned} \Phi_{\vec{k}}(\vec{r}) &= \frac{1}{N} \sum_{\vec{k}', \vec{R}'} \frac{e^{-i\vec{k} \cdot (\vec{R} - \vec{R}')}}{\sqrt{V(\vec{k})}} \Psi(\vec{r} - \vec{R}') = \\ &= \sum_{\vec{R}'} K(\vec{R} - \vec{R}') \Psi(\vec{r} - \vec{R}') \\ K(\vec{R}) &= \frac{1}{N} \sum_{\vec{k}} \frac{e^{-i\vec{k} \cdot \vec{R}}}{\sqrt{V(\vec{k})}} \end{aligned}$$

$$V(\vec{k}) = 1 + \alpha \sum_{\vec{\lambda}} \cos(\vec{k} \cdot \vec{\lambda})$$

Assume vanishing overlap between the atomic wavefunctions:  
 $\alpha \rightarrow 0$ ,  $V(\vec{k}) \rightarrow 1$ .

$$\therefore \text{Then } K(\vec{R}-\vec{R}') = \frac{1}{N} \sum_{\vec{k}} e^{-i\vec{k} \cdot (\vec{R}-\vec{R}')} = \delta_{\vec{R}, \vec{R}'} \quad 5$$

$$\Phi_{\vec{R}}(\vec{r}) = \psi(\vec{r}-\vec{R})$$

Thus when there is no overlap between the atomic orbitals, Wannier function is the same as the atomic orbital wavefunction.

When the overlap is nonzero but small,

$\Phi_{\vec{R}}(\vec{r})$  is very close to  $\psi(\vec{r}-\vec{R})$ .

The important difference is the following.

$\psi(\vec{r}-\vec{R})$  at different  $\vec{R}$  are not orthogonal:  
 $\int d\vec{r} \psi^*(\vec{r}-\vec{R}) \psi(\vec{r}-\vec{R}') \neq 0$ .

But Wannier functions, corresponding to different  $\vec{R}$ , are orthogonal:

$$\int d\vec{r} \Phi_{\vec{R}}^*(\vec{r}) \Phi_{\vec{R}'}(\vec{r}) = \int d\vec{r} \frac{1}{N} \sum_{\vec{k}} \psi_{\vec{k}}^*(\vec{r})$$

$$\cdot \psi_{\vec{k}'}(\vec{r}) e^{i\vec{k} \cdot \vec{R}} e^{-i\vec{k}' \cdot \vec{R}'} = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{R}-\vec{R}')} = \delta_{\vec{R}, \vec{R}'}$$

Thus Wannier functions form a complete orthonormal set of single-particle states, that is sometimes more convenient to use than the Bloch states.

Let us now derive the Hamiltonian for electrons in a crystal in the Wannier representation. We will still be considering only a single band, ~~corresponding to Bloch functions~~ corresponding to Bloch functions:

$$\psi_{\mathbf{k}}(\mathbf{r}^+) = \frac{1}{\sqrt{N V(\mathbf{k})}} \sum_{\mathbf{R}} \psi(\mathbf{r}^+ - \mathbf{R}) e^{i\mathbf{k}^+ \cdot \mathbf{R}}$$

constructed out of atomic orbitals  $\psi(\mathbf{r}^+ - \mathbf{R})$ .

The Hamiltonian in the Bloch representation is given by:

$$H = \sum_{\mathbf{k}^+ \sigma} E_{\mathbf{k}} C_{\mathbf{k}\sigma}^{\dagger} C_{\mathbf{k}\sigma}$$

Here  $\mathbf{k}^+$  is the first BZ momentum and  $\sigma$  is the spin.

~~$$C_{\mathbf{k}\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} C_{\mathbf{R}\sigma}$$~~

Use Dirac notation:  $|\mathbf{k}^+\rangle$  will denote Bloch state at momentum  $\mathbf{k}^+$  and

$|\mathbf{R}^+\rangle$  - Wannier state corresponding to lattice site  $\mathbf{R}$ .

$$|\mathbf{k}^+\rangle = \sum_{\mathbf{R}} |\mathbf{R}^+\rangle \langle \mathbf{R}^+ | \mathbf{k}^+ \rangle$$

This implies that:

$$C_{\mathbf{k}\sigma}^{\dagger} = \sum_{\mathbf{R}^+} \langle \mathbf{R}^+ | \mathbf{k}^+ \rangle C_{\mathbf{R}\sigma}^{\dagger}$$

$$\Phi_{\vec{R}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \psi_{\vec{k}}(\vec{r}) e^{-i\vec{k} \cdot \vec{R}}$$

$$\langle \vec{r} | \vec{R} \rangle = \sum_{\vec{k}} \langle \vec{r} | \vec{k} \rangle \langle \vec{k} | \vec{R} \rangle$$

$$\text{Thus } \langle \vec{r} | \vec{R} \rangle = \frac{1}{\sqrt{N}} e^{-i\vec{k} \cdot \vec{R}}$$

Thus we obtain:

$$C_{\vec{R}\sigma}^{\dagger} = \sum_{\vec{k}} \frac{1}{\sqrt{N}} e^{i\vec{k} \cdot \vec{R}} C_{\vec{k}\sigma}^{\dagger}$$

Substitute this into the Hamiltonian:

$$H = \sum_{\vec{k}\sigma} \frac{1}{N} \sum_{\vec{R}\vec{R}'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} E_{\vec{k}} C_{\vec{R}\sigma}^{\dagger} C_{\vec{R}'\sigma}$$

$$E_{\vec{k}} = \varepsilon - \delta \sum_{\vec{\lambda}} \cos(\vec{k} \cdot \vec{\lambda}) =$$

$$= \varepsilon - \frac{\delta}{2} \sum_{\vec{\lambda}} \left[ e^{i\vec{k} \cdot \vec{\lambda}} + e^{-i\vec{k} \cdot \vec{\lambda}} \right]$$

$$H = \sum_{\vec{k}\sigma} \frac{1}{N} \sum_{\vec{R}\vec{R}'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} \left[ \varepsilon - \frac{\delta}{2} \sum_{\vec{\lambda}} \left( e^{i\vec{k} \cdot \vec{\lambda}} + e^{-i\vec{k} \cdot \vec{\lambda}} \right) \right]$$

$$C_{\vec{R}\sigma}^{\dagger} C_{\vec{R}'\sigma} = \varepsilon \sum_{\vec{k}} C_{\vec{k}\sigma}^{\dagger} C_{\vec{k}\sigma} - \delta \sum_{\vec{R}\vec{\lambda}} C_{\vec{R}\sigma}^{\dagger} C_{\vec{R}+\vec{\lambda}\sigma}$$

$$H = \varepsilon \sum_{\vec{k}\sigma} C_{\vec{k}\sigma}^{\dagger} C_{\vec{k}\sigma} - \delta \sum_{\vec{R}\vec{\lambda}} C_{\vec{R}\sigma}^{\dagger} C_{\vec{R}+\vec{\lambda}\sigma}$$

$$H = \varepsilon \sum_{\vec{R}\sigma} C_{\vec{R}\sigma}^{\dagger} C_{\vec{R}\sigma} - \gamma \sum_{\vec{R}\vec{\lambda}} C_{\vec{R}\sigma}^{\dagger} C_{\vec{R}+\vec{\lambda}\sigma}$$

The first ~~term~~ term is just the energy of the atomic orbital. The second corresponds to tunneling of electrons from one atom ~~to the nearest~~ to one of its nearest neighbors, with amplitude  $\gamma$ .