TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

SFB 1143

Solid State Theory (SS2020)

Lecture 10: Nearly free electron & tight-binding model

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§ 3.2 Nearly free electrons

- General consideration:

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

$$V(x)=0 : \quad \varepsilon_k = \frac{\hbar^2}{2m}k^2 \quad \phi_k(x) = \frac{1}{\sqrt{L}}e^{ikx} \quad \text{(free electron)}$$

$$V(x)\neq 0 : \quad E_k = ? \quad \psi_k(x) = ?$$

Periodic potential: $V(x) = \sum_{m\in\mathbb{Z}} V_m e^{iG_m x} = \sum_{m\in\mathbb{Z}} V_m e^{im\frac{2\pi}{a}x}$, where $G_m = m\frac{2\pi}{a}$

§ 3.2 Nearly free electrons

- General consideration:

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

$$H e^{ikx} = \left(\frac{\hbar^2}{2m}k^2 + V_0\right) e^{ikx} + V_1 e^{i(k+\frac{2\pi}{a})x} + \cdots$$

Due to the (discrete) translation symmetry, we could work within subspaces S_k ($k \in$ FBZ).

$$S_k = \{\phi_k, \phi_{k\pm\frac{2\pi}{a}}, \phi_{k\pm\frac{4\pi}{a}}, \cdots\}$$

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- General consideration:

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

Subspace: $S_k = \{ \phi_k, \phi_{k\pm\frac{2\pi}{a}}, \phi_{k\pm\frac{4\pi}{a}}, \dots \}$

Label basis: $\phi_{k,m}(x) = \frac{1}{\sqrt{L}} e^{i(k+m\frac{2\pi}{a})x}$

$k \in FBZ$
$m \in \mathbb{Z}$
$L = Na$
# of unit cells

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- General consideration:

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

  - $\phi_{k,m}$ provide an orthogonal and complete basis for each subspace.

$$\langle \phi_{k,m} | \phi_{k,n} \rangle = \frac{1}{L}\int_0^L dx\, e^{i(n-m)\frac{2\pi}{a}x} = \delta_{n,m}$$

Diagonalize Hamiltonian in this basis?

§ 3.2 Nearly free electrons

$k \in \mathrm{FBZ}$

$$\langle \phi_{k,m} | H | \phi_{k,n} \rangle$$

$$= \frac{1}{L} \int_0^L dx \; e^{-i(k+m\frac{2\pi}{a})x} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] e^{i(k+n\frac{2\pi}{a})x}$$

$$= \frac{1}{L} \int_0^L dx \; \left[\frac{\hbar^2}{2m} (k + n\tfrac{2\pi}{a})^2 + V(x) \right] e^{i(n-m)\frac{2\pi}{a}x}$$

$$V(x) = \sum_{l \in \mathbb{Z}} V_l \, e^{il\frac{2\pi}{a}x}$$

$$= \frac{\hbar^2}{2m} (k + n\tfrac{2\pi}{a})^2 \delta_{mn} + V_{m-n}$$

$$\equiv \left[H(k) \right]_{m,n}$$

$\begin{cases} V_{-l} = V_l^* \\ V_0 : \text{overall shift of energy} \end{cases}$

(taken as $V_0 = 0$ below)

§ 3.2 Nearly free electrons

Diagonalizing $\hat{H}(k)$ allows us to obtain E_k and ψ_k:

$$\det\left(E - \hat{H}(k)\right) = 0 \quad \Rightarrow E_k$$

$$\psi_k(x) = \sum_{m \in \mathbb{Z}} f_{k,m}\, \phi_m(x)$$

$f_{k,m}$: eigenvector of $\hat{H}(k)$

In practice this might be hard because $\hat{H}(k)$ is in general an infinite-dimensional matrix (unless $V(x)$ has special forms).

- We may truncate $H(k)$ into a finite-dimensional matrix -- The quality of this approximation would depend on whether the true eigenstates can be well approximated with a few plane waves.

§ 3.2 Nearly free electrons

- Perturbation theory: $V(x)$ weak

Zero-th order energy : $\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} k^2$

Degenerate or non-degenerate perturbation theory?

§ 3.2 Nearly free electrons

- Perturbation theory: $V(x)$ weak

In $k = \frac{\pi}{a}$ subspace:

$$\mathcal{H}\left(k=\frac{\pi}{a}\right) = \begin{array}{c} \\ \langle\phi_{\frac{\pi}{a}}| \\ \langle\phi_{-\frac{\pi}{a}}| \\ \langle\phi_{\frac{3\pi}{a}}| \\ \langle\phi_{-\frac{3\pi}{a}}| \\ \vdots \end{array} \begin{pmatrix} |\phi_{\frac{\pi}{a}}\rangle & |\phi_{-\frac{\pi}{a}}\rangle & |\phi_{\frac{3\pi}{a}}\rangle & |\phi_{-\frac{3\pi}{a}}\rangle & \cdots \\ \varepsilon^{(0)}_{\frac{\pi}{a}} & V_1 & V_1^* & V_2 & \\ V_1^* & \varepsilon^{(0)}_{-\frac{\pi}{a}} & V_2^* & V_1 & \cdots \\ V_1 & V_2 & \varepsilon^{(0)}_{\frac{3\pi}{a}} & V_3 & \\ V_2^* & V_1^* & V_3^* & \varepsilon^{(0)}_{-\frac{3\pi}{a}} & \\ \cdots & & & & \ddots \end{pmatrix}$$

§ 3.2 Nearly free electrons

- Perturbation theory:

2×2 degenerate subspace from $k = \pm \frac{\pi}{a}$:

$$\det \begin{pmatrix} \varepsilon^{(0)}_{\frac{\pi}{a}} - E & V_1 \\ V_1^{*} & \varepsilon^{(0)}_{-\frac{\pi}{a}} - E \end{pmatrix} = 0 \quad \Rightarrow \quad \varepsilon^{(1)}_{\frac{\pi}{a}} = \varepsilon^{(0)}_{\frac{\pi}{a}} \pm |V_1|$$

Degeneracy at $k = \pm \frac{\pi}{a}$ lifted !

§ 3.2 Nearly free electrons

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Degeneracy at $k = \pm \frac{\pi}{a}$ lifted !

Degenerate perturbation theory at first order :

coupling to $\phi_{\pm \frac{3\pi}{a}}$, ... ignored since $\varepsilon^{(0)}_{\pm \frac{3\pi}{a}} \gg \varepsilon^{(0)}_{\pm \frac{\pi}{a}}$.

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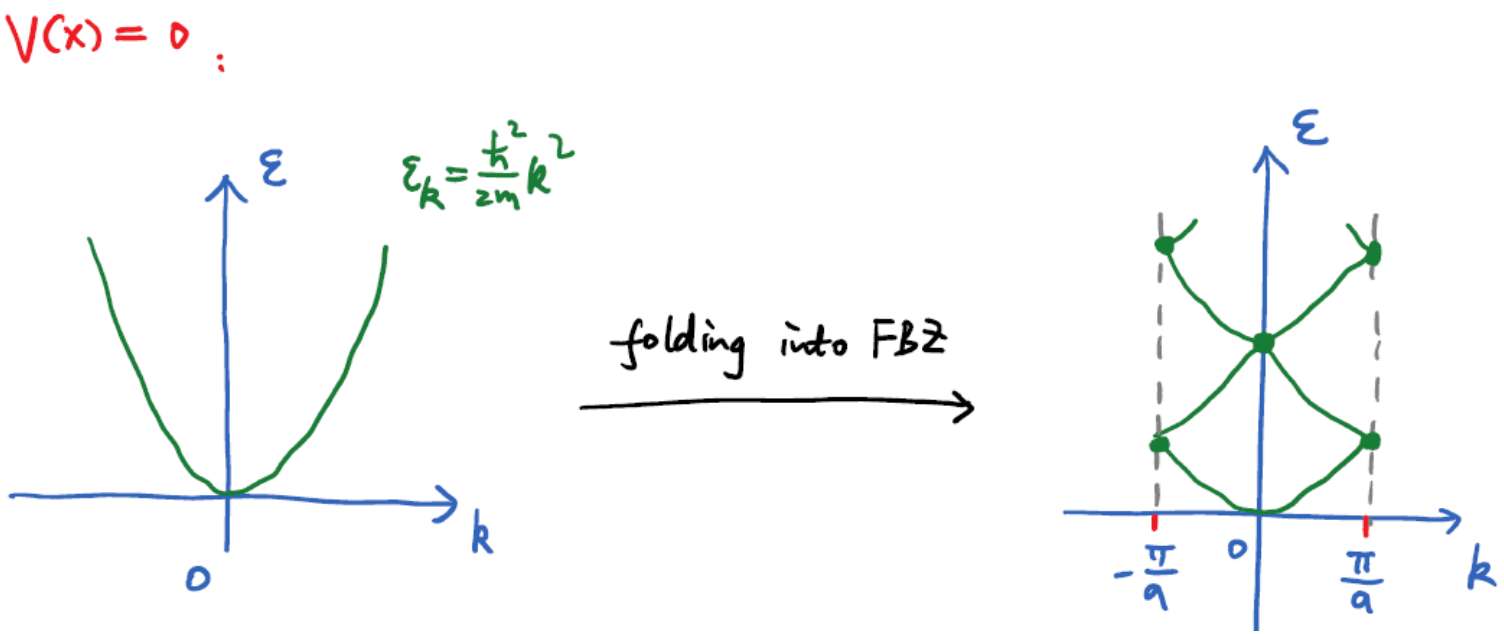
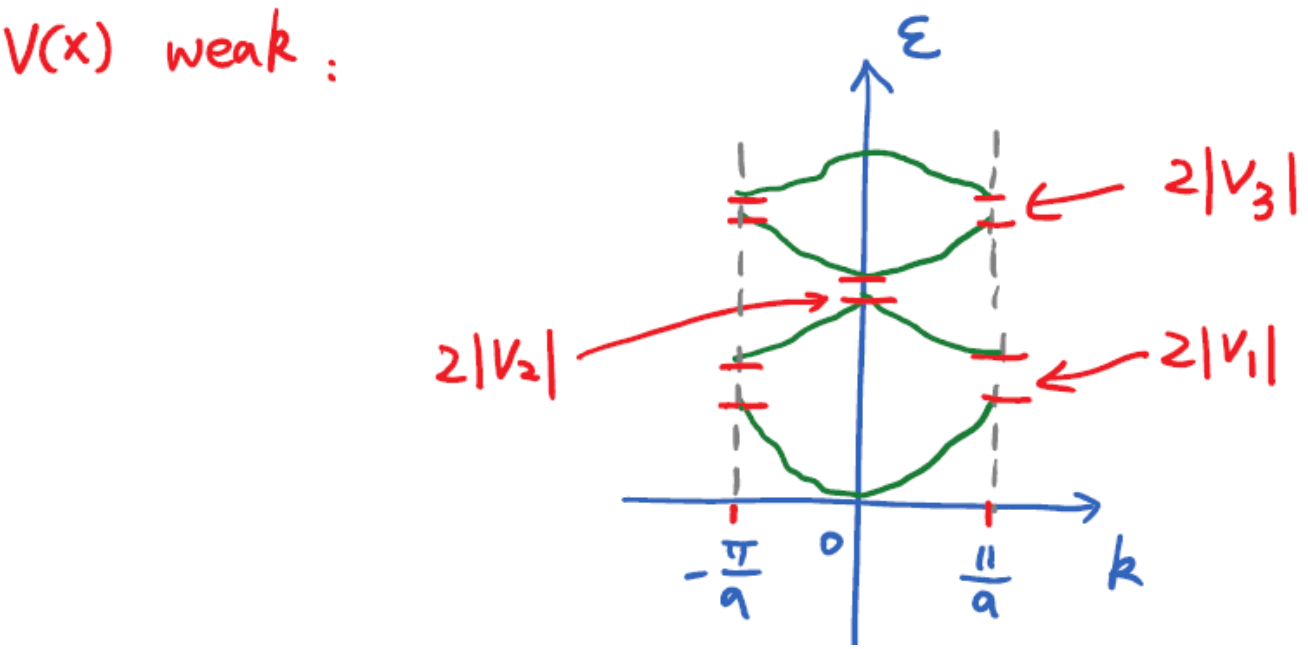
- Perturbation theory:



§ 3.2 Nearly free electrons

- Perturbation theory:



➢ Degenerate perturbation theory for $k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \ldots$

§ 3.2 Nearly free electrons

- Perturbation theory:

Key message: Single-particle energies form "energy bands"!

The gaps open due to the lift of degeneracy.

It happens for $\varepsilon_k^{(0)} = \varepsilon_{k'}^{(0)}$ and $k - k' = m\frac{2\pi}{a}$, $m \in \mathbb{Z}$.

k & k' related by reciprocal vectors.

Other k-points also get corrections in energy.

(non-degenerate perturbation theory)

§ 3.2 Nearly free electrons

- Degenerate perturbation theory near $k = \pi/a$:

$$k = \frac{\pi}{a} + \Delta k \quad \& \quad k' = -\frac{\pi}{a} + \Delta k \qquad (\Delta k \text{ small})$$

$$\mathcal{H}(k,k') = \begin{pmatrix} \varepsilon_k & V_1 \\ V_1^* & \varepsilon_{k'} \end{pmatrix}$$

$$\begin{cases} \varepsilon_k = \frac{\hbar^2}{2m}\left(\frac{\pi}{a} + \Delta k\right)^2 \\ \varepsilon_{k'} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a} - \Delta k\right)^2 \end{cases}$$

$$\varepsilon^{\pm}_{\Delta k} = \frac{1}{2}\left(\varepsilon_k + \varepsilon_{k'} \pm \sqrt{(\varepsilon_k - \varepsilon_{k'})^2 + 4|V_1|^2}\right)$$

$$= \varepsilon_0 + \frac{\hbar^2}{2m}\Delta k^2 \pm \sqrt{4\varepsilon_0 \frac{\hbar^2}{2m}\Delta k^2 + |V_1|^2} \qquad \varepsilon_0 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$$

§ 3.2 Nearly free electrons

- Degenerate perturbation theory near $k = \pi/a$:

$$\varepsilon_{\Delta k}^{\pm} \overset{\Delta k \to 0}{\simeq} \varepsilon_0 + \frac{\hbar^2}{2m}\Delta k^2 \pm |V_1| \left(1 + \frac{2\varepsilon_0}{|V_1|^2}\frac{\hbar^2}{2m}\Delta k^2\right) + \cdots$$

$$= \varepsilon_0 \pm |V_1| + \frac{\hbar^2}{2m}\left(1 \pm \frac{2\varepsilon_0}{|V_1|}\right)\Delta k^2 + \cdots$$

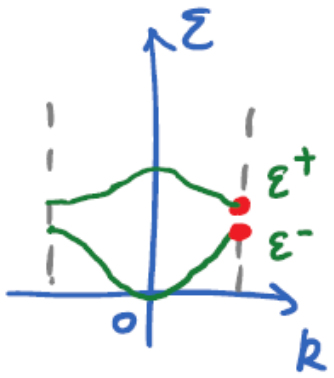
gap

dominant since $|V_1| \ll \varepsilon_0$

Effective mass of electrons:

$$\varepsilon_{\Delta k}^{\pm} \equiv \frac{\hbar^2}{2m_{\pm}^*}\Delta k^2$$

$$\Rightarrow \quad m_{\pm}^* \simeq \pm m \frac{|V_1|}{2\varepsilon_0} \ll m$$



§ 3.2 Nearly free electrons

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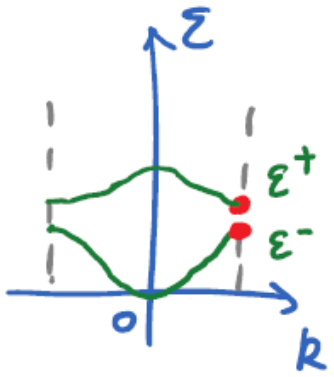
$$= \varepsilon_0 \pm |V_1| + \frac{\hbar^2}{2m}\left(1 \pm \frac{2\varepsilon_0}{|V_1|}\right)\Delta k^2 + \cdots$$

gap

dominant since $|V_1| \ll \varepsilon_0$

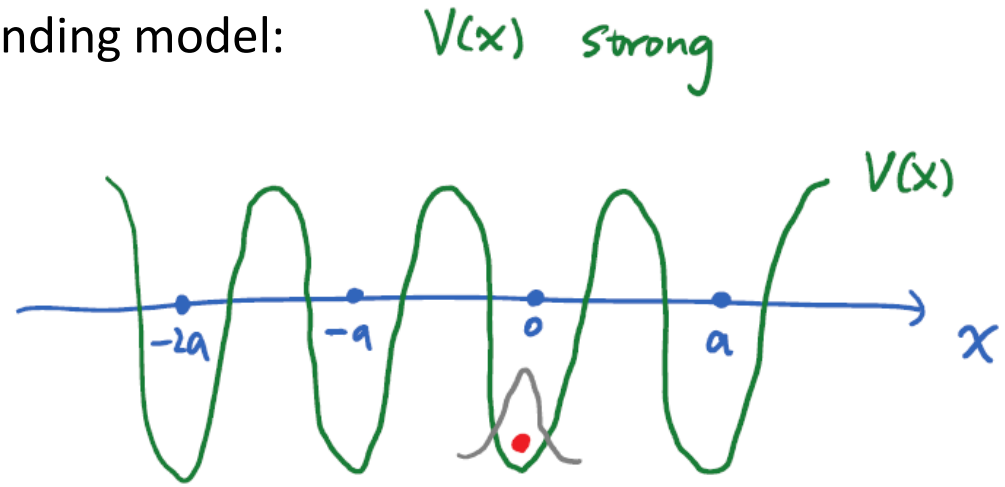
Effective mass of electrons:

- Bands are rather flat near the band edge, so mass of electrons is strongly renormalized.



§ 3.3 Tight-binding model

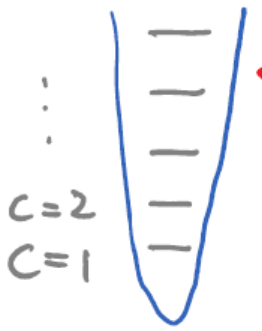
- Tight-binding model:



  - It may not be a good idea to approximate the eigenstates with plane waves (you need many to approximate localized wave packets).

§ 3.3 Tight-binding model

- Tight-binding model: $V(x)$ strong



← discrete energy levels E_c
(labeled by $c = 1, 2, \ldots$)

Eigenstates ϕ_c : localized

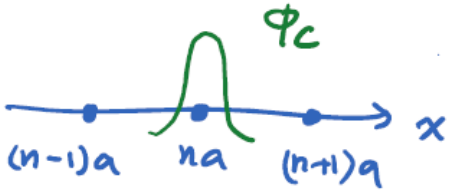
$|\phi_c(x-na)|^2$ localized near $x = na$.

§ 3.3 Tight-binding model

- Tight-binding model:

We could make use of the "atomic" wave functions:

$\phi_c(x-na)$



One issue: ϕ_c is a localized wave packet,

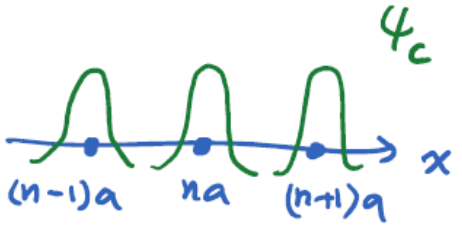
so it does not satisfy the Bloch theorem.

§ 3.3 Tight-binding model

- Tight-binding model:

We could use linear combinations of ϕ_c in different wells to build a good ansatz:

$$\psi_k^c(x) = \frac{1}{\sqrt{N}} \sum_{n \in \mathbb{Z}} \phi_c(x-na)\, e^{ikna}$$



$$\psi_k^c(x) = u_k^c(x)\, e^{ikx} \qquad u_k^c(x+a) = u_k^c(x) \quad \checkmark$$

$$u_k^c(x) = \frac{1}{\sqrt{N}} \sum_{n \in \mathbb{Z}} \phi_c(x-na)\, e^{-ik(x-na)}$$

§ 3.3 Tight-binding model

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We could use linear combinations of ϕ_c in different wells to build a good ansatz:

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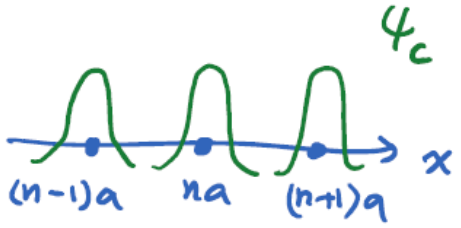


Subtle issue: $\psi_k^c(x)$ are generally NOT orthogonal!

$$\langle \psi_k^c | \psi_k^{c'} \rangle \not\propto \delta_{cc'}$$

§ 3.3 Tight-binding model

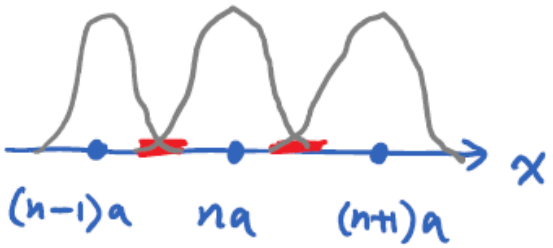
- Tight-binding model:

Let's postpone the orthogonalization issue for a while.

Below we assume the mixings are small.

(non-orthogonal part)

- $H\phi_c(x-na)$ generates mostly $\phi_c(x-na)$, $\phi_c(x-na-a)$ and $\phi_c(x-na+a)$ (with some coefficients). The rest are ignored.



§ 3.3 Tight-binding model

- Tight-binding model:

Let's postpone the orthogonalization issue for a while.

Below we assume the mixings are small.

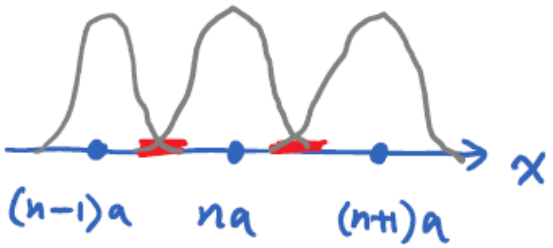
(non-orthogonal part)

$$\langle \phi_c(x-na) | H | \phi_c(x-na) \rangle$$

$$= \int_0^L dx\ \phi_c^*(x-na) \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right] \phi_c(x-na)$$

dominant contribution from $x \simeq na$

$$\simeq E_c$$ (local energy levels)



§ 3.3 Tight-binding model

- Tight-binding model:

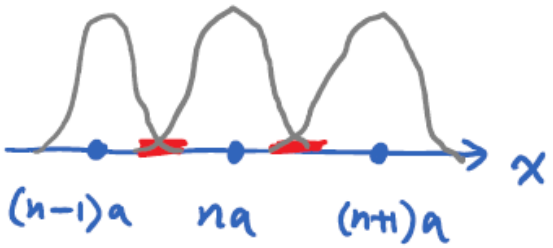
Let's postpone the orthogonalization issue for a while.

Below we assume the mixings are small.

(non-orthogonal part)

$$\langle \phi_c(x-na) \,|\, H \,|\, \phi_c(x-(n\pm1)a) \rangle \equiv t_c$$

"exchange integral" between nearest neighbors



§ 3.3 Tight-binding model

- Tight-binding model (simplest version):

$$H\phi_c(x-na) \simeq E_c\phi_c(x-na)$$

$$+ t_c\phi_c(x-(n+1)a) + t_c\phi_c(x-(n-1)a)$$

  - Eigenstates of the Hamiltonian in the tight-binding limit:

$$\psi_k^c(x) = \frac{1}{\sqrt{N}} \sum_{n\in\mathbb{Z}} \phi_c(x-na)\, e^{ikna}$$

§ 3.3 Tight-binding model

- Tight-binding model (simplest version):

Proof: $$H\varphi_k^c(x) = \frac{1}{\sqrt{N}} \sum_{n\in\mathbb{Z}} H\phi_c(x-na)\, e^{ikna}$$

previous page

$$= \left(E_c + t_c e^{-ika} + t_c e^{ika}\right) \varphi_k^c(x)$$

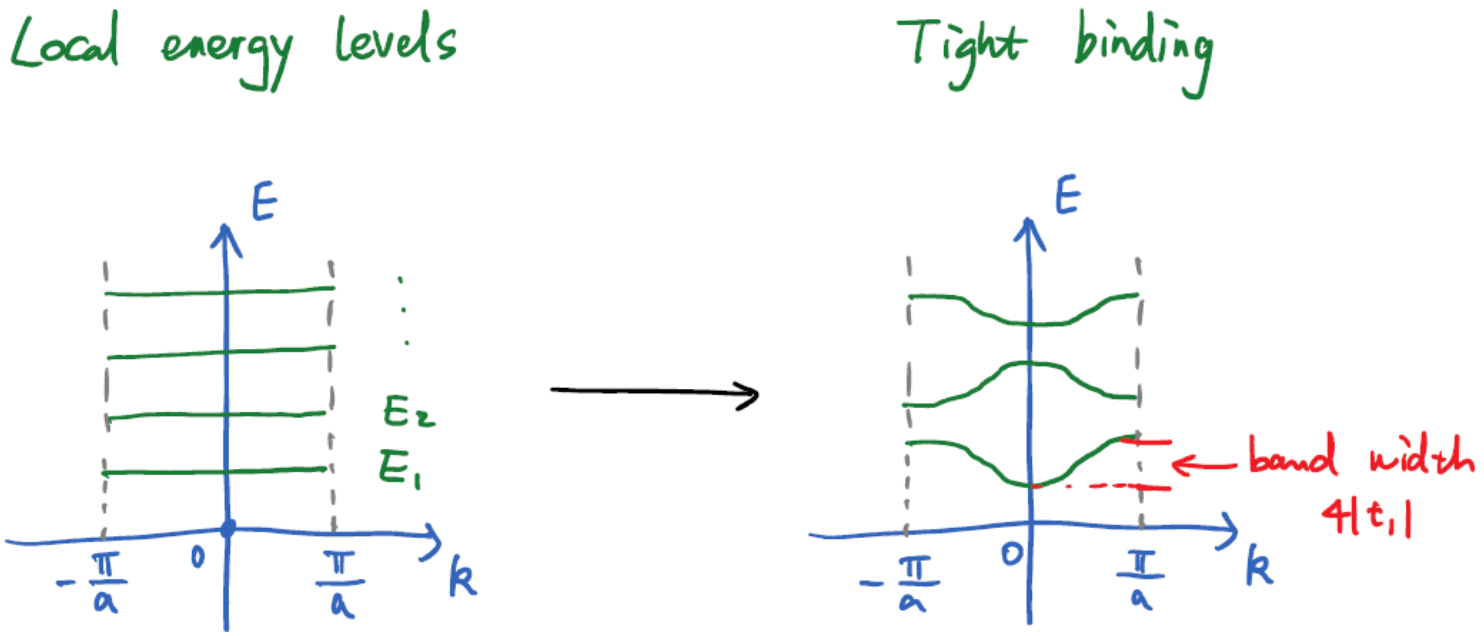
$$= \left[E_c + 2t_c \cos(ka)\right] \varphi_k^c(x)$$

Single-particle energy

Key message: Single-particle energies also form "energy bands"!

§ 3.3 Tight-binding model

- Tight-binding model (simplest version):



§ 3.3 Tight-binding model

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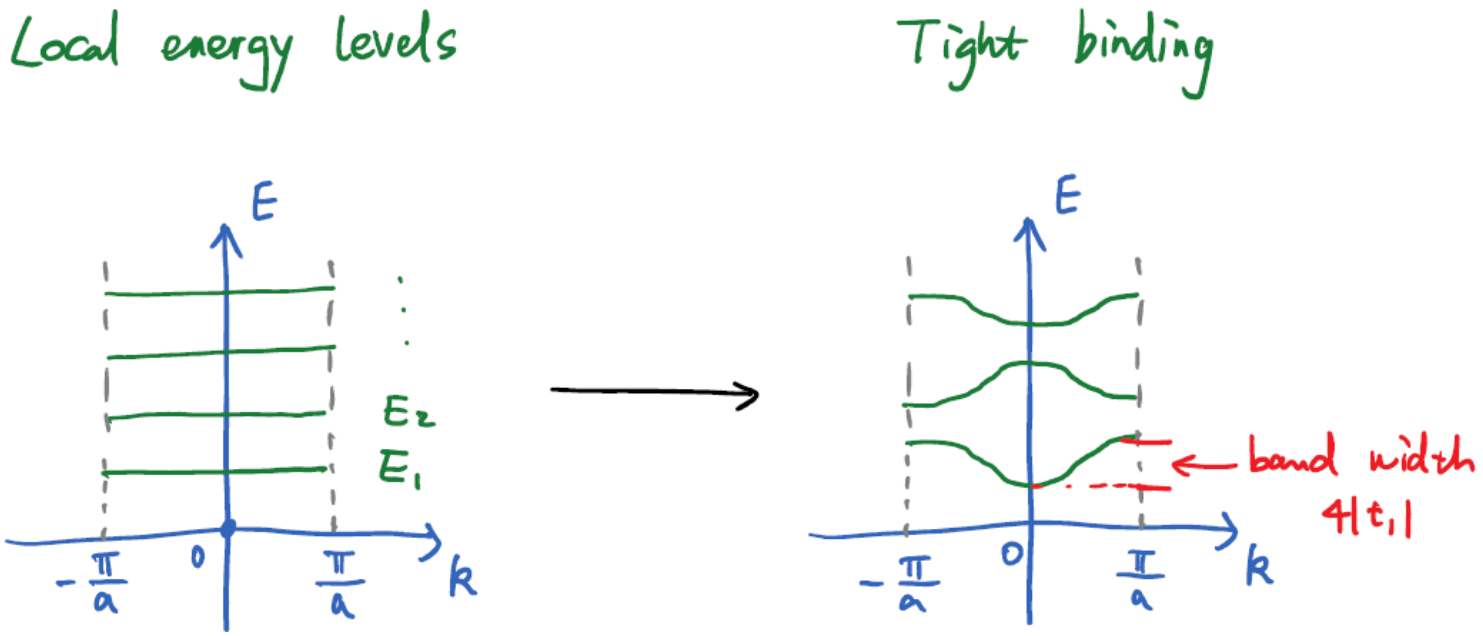

➢ For both weak and strong $V(x)$, single-particle energies form bands!
So we expect that this is quite generic for electrons in a periodic potential.