

§3. Band electrons

*1) Nearly free electrons

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

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

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

$$V(x) = \sum_{m \in \mathbb{Z}} V_m e^{im \frac{2\pi}{a} x} = \sum_{m \in \mathbb{Z}} V_m e^{im \frac{2\pi}{a} x}$$

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

Due to the (discrete) translation symmetry,
we could work within subspaces S_k ($k \in FB\mathbb{Z}$):

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

Label plane-wave basis in S_k :

$$\phi_{k,m}(x) = \frac{1}{\sqrt{L}} e^{i(k+m\frac{2\pi}{a})x}, \quad \begin{array}{l} k \in FB\mathbb{Z} \\ m \in \mathbb{Z} \\ L = \underbrace{Na}_{\# \text{ of unit cells}} \end{array}$$

$\phi_{k,m}$ form orthogonal / complete basis:

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

Thus, we could diagonalize H in this basis.

Matrix element of H :

$$\begin{aligned} & \langle \phi_{k,m} | H | \phi_{k,n} \rangle \quad k \in \text{FBZ} \\ &= \frac{1}{L} \int_0^L dx e^{-i(k+m\frac{2\pi}{a})x} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] e^{i(k+n\frac{2\pi}{a})x} \\ &= \frac{1}{L} \int_0^L dx \left[\frac{\hbar^2}{2m} (k+n\frac{2\pi}{a})^2 + \underbrace{V(x)}_{\parallel} \right] e^{i(n-m)\frac{2\pi}{a}x} \\ &= \frac{\hbar^2}{2m} (k+n\frac{2\pi}{a})^2 \delta_{mn} + V_{m-n} \\ &\equiv [f(k)]_{m,n} \end{aligned}$$

$\left\{ \begin{array}{l} V_{-l} = V_l^* \\ V_0 : \text{overall shift of energy} \\ (\text{taken as } V_0 = 0 \text{ below}) \end{array} \right.$

Diagonalizing $f(k)$ allows us to obtain E_k and ψ_k :

$$\det(E - f(k)) = 0 \Rightarrow E_k$$

$$\begin{aligned} \psi_k(x) &= \sum_{m \in \mathbb{Z}} f_{k,m} \phi_m(x) \\ &\text{eigenvector of } f(k) \end{aligned}$$

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

— Perturbation theory ($V(x)$ weak)

degenerate vs. non-degenerate ?

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

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

| | $ \Phi_{\frac{\pi}{a}}\rangle$ | $ \Phi_{-\frac{\pi}{a}}\rangle$ | $ \Phi_{\frac{3\pi}{a}}\rangle$ | $ \Phi_{-\frac{3\pi}{a}}\rangle$ | ... |
|------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|-----|
| $\langle \Phi_{\frac{\pi}{a}} $ | $\varepsilon_{\frac{\pi}{a}}^{(0)}$ | V_1 | V_1^* | V_2 | |
| $\langle \Phi_{-\frac{\pi}{a}} $ | V_1^* | $\varepsilon_{-\frac{\pi}{a}}^{(0)}$ | V_2^* | V_1 | ... |
| $\langle \Phi_{\frac{3\pi}{a}} $ | V_1 | V_2 | $\varepsilon_{\frac{3\pi}{a}}^{(0)}$ | V_3 | |
| $\langle \Phi_{-\frac{3\pi}{a}} $ | V_2^* | V_1^* | V_3^* | $\varepsilon_{-\frac{3\pi}{a}}^{(0)}$ | |
| : | | ... | | | ... |

$$H(k = \frac{\pi}{a}) =$$

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

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

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

(Degenerate perturbation theory at first order :

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

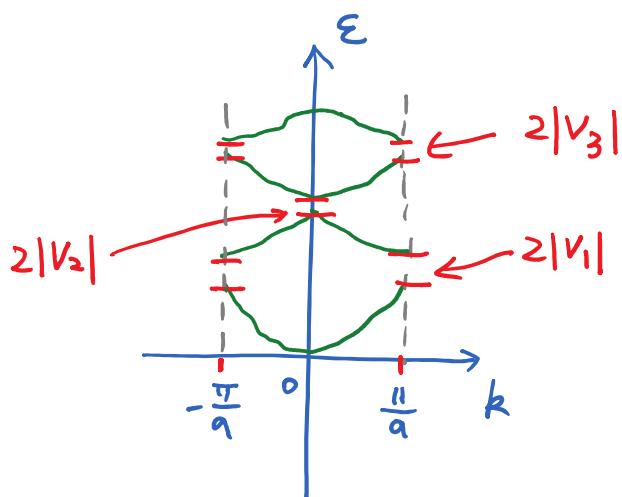
Similar analysis can be carried out for $k = \pm \frac{2\pi}{a}$,

Single-particle energies from $V(x)=0$ to weak $V(x)$:

$V(x) = 0$:



$V(x)$ weak:



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

The gaps open due to the lift of degeneracy.

It happens for $\epsilon_k^{(0)} = \epsilon_{k'}^{(0)}$ 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)

- Degenerate perturbation theory near $k = \frac{\pi}{a}$:

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

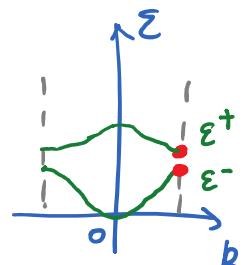
$$H(k, k') = \begin{pmatrix} \varepsilon_k & V_1 \\ V_1^* & \varepsilon_{k'} \end{pmatrix} \quad \begin{cases} \varepsilon_k = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} + \Delta k \right)^2 \\ \varepsilon_{k'} = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} - \Delta k \right)^2 \end{cases}$$

$$\begin{aligned} \Rightarrow \varepsilon_{\Delta k}^{\pm} &= \frac{1}{2} \left(\varepsilon_k + \varepsilon_{k'} \pm \sqrt{(\varepsilon_k - \varepsilon_{k'})^2 + 4|V_1|^2} \right) \\ &= \frac{1}{2} \left[\frac{\hbar^2}{m} \left(\frac{\pi^2}{a^2} + \Delta k^2 \right) \pm \sqrt{\left(\frac{\hbar^2}{m} \frac{2\pi}{a} \Delta k \right)^2 + 4|V_1|^2} \right] \\ &= \varepsilon_0 + \frac{\hbar^2}{2m} \Delta k^2 \pm \sqrt{4\varepsilon_0 \frac{\hbar^2}{2m} \Delta k^2 + |V_1|^2} \quad \varepsilon_0 = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2 \\ &\stackrel{\Delta k \rightarrow 0}{\simeq} \varepsilon_0 + \frac{\hbar^2}{2m} \Delta k^2 \pm |V_1| \left(1 + \frac{2\varepsilon_0}{|V_1|^2} \frac{\hbar^2}{2m} \Delta k^2 \right) + \dots \\ &= \underbrace{\varepsilon_0 \pm |V_1|}_{\text{gap}} + \frac{\hbar^2}{2m} \left(1 \pm \frac{2\varepsilon_0}{|V_1|^2} \right) \Delta k^2 + \dots \quad \text{dominant since } |V_1| \ll \varepsilon_0 \end{aligned}$$

Effective mass of electrons near $k = \frac{\pi}{a}$:

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

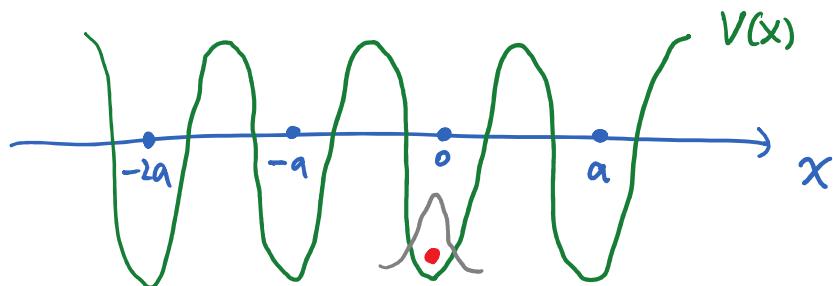
$$\Rightarrow m_{\pm}^* \simeq \pm m \frac{|V_1|}{2\varepsilon_0} \ll m$$



(Bands are flat near the band edge,
so mass of electron are strongly renormalized.)

* Tight-binding model

Now we consider the other limit: $V(x)$ strong.



Single well:

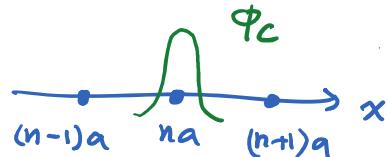


$|\phi_c(x-na)|^2$ localized near $x = na$.

\Rightarrow Plane waves are not a good starting point.
(A large # of plane waves needed.)

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

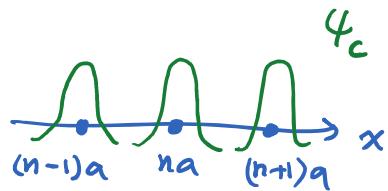
$$\phi_c(x-na)$$



One issue: ϕ_c is a localized wave packet,
so it does not satisfy the Bloch theorem.

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

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



Check the Bloch function:

$$\psi_k^c(x) = \underbrace{u_k^c(x)}_{\downarrow} e^{ikx}$$

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

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

define $n' = n-1 \in \mathbb{Z}$

(periodic boundary assumed)

$$= \frac{1}{\sqrt{N}} \sum_{n' \in \mathbb{Z}} \phi_c(x-n'a) e^{-ik(x'-n'a)}$$

$$= u_k^c(x) \quad \checkmark$$

$\psi_k^c(x)$ satisfies the Bloch theorem.

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

$$\langle \psi_k^c | \psi_k^{c'} \rangle \times \delta_{cc'}$$

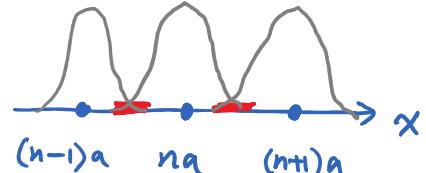
Let's postpone the orthogonalization issue for a while.

Below we assume the mixings are small.

(non-orthogonal part)

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

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



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

dominant contribution from $x \approx na$

$$\simeq E_c \quad (\text{local energy levels})$$

$$\langle \phi_c(x-na) | H | \phi_c(x-(n\pm 1)a) \rangle \equiv t_c$$

"exchange integral" between nearest neighbors

The (simplest) tight-binding model :

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

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

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

Below we show that the constructed ansatz

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

is the eigenstate of H under the tight-binding limit.

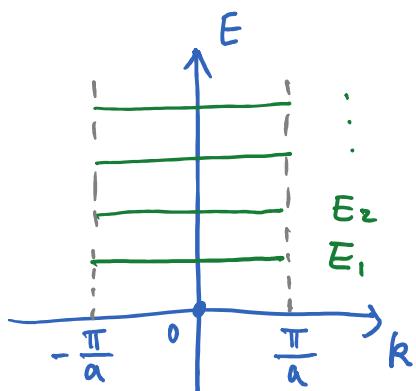
$$\begin{aligned} H \psi_k^c(x) &= \frac{1}{\sqrt{N}} \sum_{n \in \mathbb{Z}} \underbrace{H \phi_c(x-na)}_{E_c \phi_c(x-na)} e^{ikna} \\ &= \frac{1}{\sqrt{N}} \sum_{n \in \mathbb{Z}} E_c \phi_c(x-na) e^{ikna} \\ &\quad + \frac{1}{\sqrt{N}} \sum_{n \in \mathbb{Z}} t_c \phi_c(x-(\underbrace{n+1}_{n'=n+1})a) e^{ikna} \\ &\quad + \frac{1}{\sqrt{N}} \sum_{n \in \mathbb{Z}} t_c \phi_c(x-(\underbrace{n-1}_{n'=n-1})a) e^{ikna} \\ &= (E_c + t_c e^{-ika} + t_c e^{ika}) \psi_k^c(x) \\ &= \underbrace{[E_c + 2t_c \cos(ka)]}_{\sim} \psi_k^c(x) \end{aligned}$$

Single-particle energy:

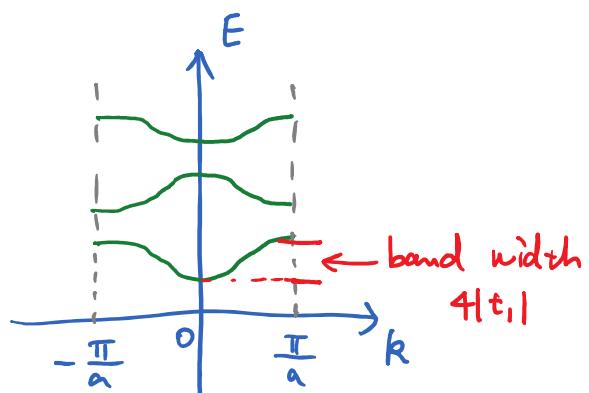
$$E_k^c = E_c + 2t_c \cos(ka)$$

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

Local energy levels



Tight binding



Effective mass in the lowest band close to $k=0$:

$$\begin{aligned} E_K^{c=1} &= E_1 + 2t_1 \cos(ka) \\ &\stackrel{k \rightarrow 0}{\simeq} E_1 + 2t_1 - t_1 a^2 k^2 \\ &\quad \underbrace{\qquad}_{\text{III}} \\ \Rightarrow m^* &= -\frac{t_1^2}{2t_1 a^2} \end{aligned}$$

(large band width \Rightarrow small effective mass)

In both weak and strong $V(x)$ limits,
single-particle energies form energy bands.

So we expect that the formation of energy bands
is generic for electrons in a periodic potential.