X. Energy Bands

Two different viewpoints on the formation of energy bands

Starting Point: Free Electron

Q: How does a periodic $V(\vec{r})$ affect the free electron $\mathcal{E}(\vec{k})$?

Steps:

- Periodicity ⇒ $\vec{k}$'s in 1st B.Z. (band folding)
- Strength of $V(\vec{r})$ ⇒ formation of bands and band gaps
- Periodic $V(\vec{r})$ is treated as a perturbation on the free electron states
- Expected to be good for metals.

Nearly free electron Model

Starting Point: Atomic orbitals

Q: How do atomic electronic states (e.g., 1s, 2s, 2p, 3s, ...) from different atoms evolve into energy bands?

Steps:

- Construct Bloch functions from atomic states
- Treat deviation of $V(\vec{r})$ from atomic potential as perturbation
- Mixing of neighboring atomic states ⇒ bands
- Expected to be good for electrons tightly-binded to atoms (e.g. 3d electrons in transition metals)

Tight-binding Model

A. Formal Set up for Band Structure Calculations

- The problem is to solve

$$\boxed{\frac{-\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) + V(\vec{r})\psi_{\vec{k}}(\vec{r}) = \mathcal{E}(\vec{k})\psi_{\vec{k}}(\vec{r}) \quad \text{with } V(\vec{r}+\vec{R}) = V(\vec{r})} \qquad (1)$$

- As in other QM problems, we can choose a basis set and turn the problem into a matrix eigenvalue problem.

Plane Wave Expansion

- Use plane waves as the basis functions
- Recall $V(\vec{r})$ is periodic, the Fourier expansion involves $\vec{G}$'s only, where $\vec{G}$ = reciprocal lattice vectors

$$\boxed{V(\vec{r}) = \sum_{\vec{G}'} V(\vec{G}')\, e^{i\vec{G}'\cdot\vec{r}}}$$

$$\text{where } V(\vec{G}') = \frac{1}{\Omega_c}\int_{\Omega_c} d^3r\, V(\vec{r})\, e^{-i\vec{G}'\cdot\vec{r}} \qquad (*)$$

Ω_c = volume of a unit cell

- Real $V(\vec{r}) \Rightarrow V(-\vec{G}) = V^*(\vec{G})$

- Bloch's theorem says that $\psi_{\vec{k}}$ is of the form of

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, \underbrace{u_{\vec{k}}(\vec{r})}_{\text{periodic in direct space}} \qquad \text{Bloch function}$$

$$\therefore\ u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{k}}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}}$$

thus,

$$\boxed{\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{k}}(\vec{G})\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}}} \qquad (**)$$

Substituting (*) and (**) into the Schrödinger Eq. (1):

$$\sum_{\vec{G}} \left(\varepsilon(\vec{k}) - V(\vec{0}) - \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2\right) u_{\vec{k}}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}} = \sum_{\vec{G}} \sum_{\substack{\vec{G}' \\ (\vec{G}'\neq 0)}} u_{\vec{k}}(\vec{G})\, V(\vec{G}')\, e^{i(\vec{G}+\vec{G}')\cdot\vec{r}}$$

Then do the following:

(i) multiply both sides by $e^{-i\vec{G}''\cdot\vec{r}}$

(ii) $\int_{\Omega_c} d^3r$ over a unit cell

(iii) note that $\int_{\Omega_c} d^3r\, e^{i(\vec{G}-\vec{G}'')\cdot\vec{r}} = \Omega_c\, \delta_{\vec{G},\vec{G}''}$

The Schrödinger Equation (1) is turned into:

$$\boxed{\left(\varepsilon(\vec{k}) - V(\vec{0}) - \frac{\hbar^2}{2m}|\vec{k}+\vec{G}''|^2\right) u_{\vec{k}}(\vec{G}'') = \sum_{\substack{\vec{G}' \\ (\vec{G}'\neq 0)}} V(\vec{G}')\, u_{\vec{k}}(\vec{G}''-\vec{G}')} \qquad (2)$$

What is this?

- For each $\vec{k}$, this is an $(\infty \times \infty)$ matrix equation for $u_{\vec{k}}(\vec{G})$.
- Solving the many eigenvalues $\varepsilon(\vec{k})$ for each $\vec{k}$ amounts to finding the eigenvalues of an $\infty \times \infty$ matrix.
- This may be called the Central Equation. (See Eq. (27) in Kittel's Ch. 7)
- Given $V(\vec{r}) \Rightarrow V(\vec{G})$ are known

  For each $\vec{k} \Rightarrow$ many $\varepsilon(\vec{k})$ and thus $\varepsilon_n(\vec{k})$ ← band index
- From (1) to (2): Exact! (No approximation)
- (2) is the starting point of many serious band structure calculations
- Same procedure is good for other periodic structures, e.g. photonic crystals, phononic crystals, etc.
- Practically, Eq. (2) is truncated to include only finite number of terms.

- There is one equation of the form (2) for each $\vec{k}$ in 1st B.Z.

  Eq. (2) is of the form

$$\begin{pmatrix} & & \\ & \text{a big matrix} & \\ & & \end{pmatrix} \begin{pmatrix} u_{\vec{k}}(\vec{G}_1) \\ u_{\vec{k}}(\vec{G}_2) \\ \vdots \\ u_{\vec{k}}(\vec{G}_n) \\ \vdots \end{pmatrix} = \mathcal{E}(\vec{k}) \begin{pmatrix} u_{\vec{k}}(\vec{G}_1) \\ u_{\vec{k}}(\vec{G}_2) \\ \vdots \\ u_{\vec{k}}(\vec{G}_n) \\ \vdots \end{pmatrix}$$

  ↑ for an allowed $\vec{k}$

  Infinite many $\vec{G}$'s in principle ⇒ $\infty \times \infty$ matrix!

- Practically, "truncate" to include a number n of shortest $\vec{G}$'s ⇒ $n \times n$ matrix

  Bigger matrix ⇒ Results are more accurate.

- Mathematically, we have written

$$\hat{H}\psi = \mathcal{E}\psi$$

  into a matrix equation using the basis $\{e^{i\vec{k}\cdot\vec{r}}, e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}}, e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}}, \ldots\}$ for each allowed $\vec{k}$.

One can write down the matrix directly as follows:

	$e^{i\vec{k}\cdot\vec{r}}$	$e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}}$	$e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}}$	$e^{i(\vec{k}+\vec{G}_3)\cdot\vec{r}}$	⋯
$e^{i\vec{k}\cdot\vec{r}}$	$\mathcal{E}^0(\vec{k})+\overline{V}$	$V(-\vec{G}_1)$	$V(-\vec{G}_2)$	$V(-\vec{G}_3)$	⋯
$e^{i(\vec{k}+\vec{G}_1)\cdot\vec{r}}$	$V(\vec{G}_1)$	$\mathcal{E}^0(\vec{k}+\vec{G}_1)+\overline{V}$	$V(\vec{G}_1-\vec{G}_2)$	$V(\vec{G}_1-\vec{G}_3)$	⋯
$e^{i(\vec{k}+\vec{G}_2)\cdot\vec{r}}$	$V(\vec{G}_2)$	$V(\vec{G}_2-\vec{G}_1)$	$\mathcal{E}^0(\vec{k}+\vec{G}_2)+\overline{V}$	$V(\vec{G}_2-\vec{G}_3)$	⋯
$e^{i(\vec{k}+\vec{G}_3)\cdot\vec{r}}$	$V(\vec{G}_3)$	$V(\vec{G}_3-\vec{G}_1)$	$V(\vec{G}_3-\vec{G}_2)$	$\mathcal{E}^0(\vec{k}+\vec{G}_3)+\overline{V}$	⋯
⋮	⋮	⋮	⋮	⋮	

- The left column and top row give the basis set.
- Each matrix element is $\int \psi_i^* \hat{H} \psi_j \, d^3r$
- Diagonal elements: $\mathcal{E}^0(\vec{k}) = \frac{\hbar^2 k^2}{2m}$; $\overline{V} = V(\vec{0})$ = average of $V(\vec{r})$ = a constant
- Off-diagonal elements $V(\vec{G})$ where $\vec{G}$ "connects" ψ_j to ψ_i
- Eigenvalues give electronic states (infinitely many) for one allowed $\vec{k}$.

B. Empty lattice approximation : Band folding

Question: What is the effect of an infinitely-weak but periodic $V(\vec{r})$?

Thus, practically $V=0$. But we imagine that we have a periodic direct lattice

$\Rightarrow$ reciprocal lattice, Brillouin zones, Bloch's theorem, $\vec{k} \in$ 1st B.Z., etc. all follows!

Take 1D example

- $V=0$ (no invisible periodic potential)

  $E(k) = \frac{\hbar^2 k^2}{2m}$, k takes on any value (not restricted to 1st B.Z., as the notion of B.Z. is not there)

- $V=0$ (with invisible periodic potential) [empty lattice]

  $\Rightarrow$ B.Z.'s

  1st B.Z. $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$

  and many bands

Look at Central Equation (2), for $V=0$,

$$E(\vec{k}) = \underbrace{\frac{\hbar^2}{2m} |\vec{k}+\vec{G}|^2}_{\text{infinitely many values depend on } \vec{G}}$$

$\vec{k}$: in 1st B.Z.

"0" labels empty lattice case

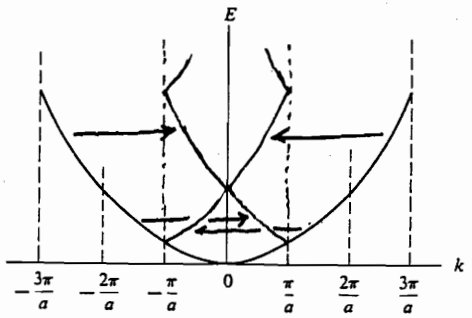
1D case: $E^0(k) = \frac{\hbar^2}{2m} |k+G|^2$

k: in 1st B.Z.

$\vec{G} = h\frac{2\pi}{a}\hat{x}$

$h = 0, \pm 1, \pm 2, \pm 3, \ldots$

What does it mean? Band folding



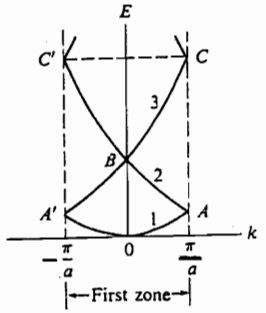
$\vec{G}_1 = \frac{2\pi}{a}\hat{x}$

$-\vec{G}_1 = -\frac{2\pi}{a}\hat{x}$

- Using different $\vec{G}$'s, translate k's outside 1st B.Z. into 1st B.Z.

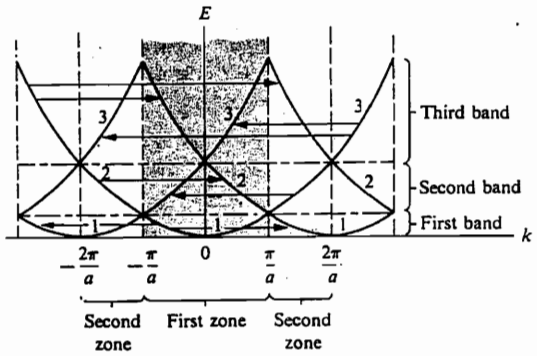
This gives: Many $E(k)$ for each k in 1st B.Z.
Something that resembles band structure
But no gaps!

After band folding:



- Already see 1st, 2nd, 3rd bands, ...
- reduced zone scheme
- See a feature that:
  - lowest bands are narrower
  - higher bands are wider
  - → true in real materials!

One can also show the result in the periodic zone scheme that emphasizes $\mathcal{E}_n(k) = \mathcal{E}_n(k+G)$



periodic zone scheme

Nearly free electron model:

What is the effect of a weak (but not infinitely small) periodic potential?

Band folding in higher dimensions

- same procedure, but much harder to visualize!

[Ex.: Try 2D square empty lattice]

3D cubic lattice

$$\vec{G} = h\frac{2\pi}{a}\hat{x} + k\frac{2\pi}{a}\hat{y} + l\frac{2\pi}{a}\hat{z}$$

$$= G_x\hat{x} + G_y\hat{y} + G_z\hat{z}$$

$h, k, l = 0, \pm 1, \pm 2, \ldots$

For any $\vec{k}'$ outside 1st B.Z., there is a $\vec{k}$ in 1st B.Z. that

$$\vec{k} + \vec{G} = \vec{k}'$$

For $\vec{k} = (k_x, k_y, k_z) \in$ 1st B.Z.,

$$\mathcal{E}^0(k_x, k_y, k_z) = \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2$$

$$= \frac{\hbar^2}{2m}\left[(k_x+G_x)^2 + (k_y+G_y)^2 + (k_z+G_z)^2\right]$$

with $\vec{G}$ runs over choices of h, k, l

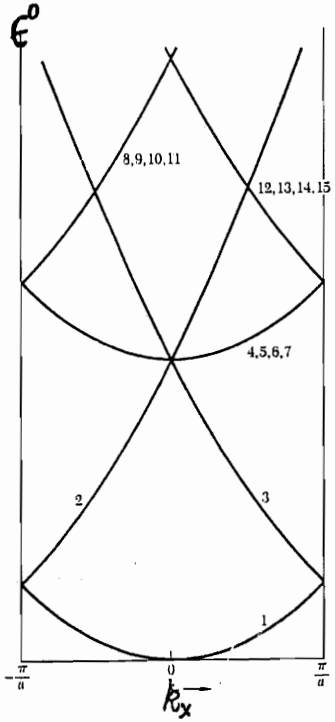
Empty lattice approximation

3D cubic crystal

factor of $\frac{\hbar^2}{2m}$ ignored.

Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x00)$
1	000	0	k_x^2
2,3	$100,\bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	$010,0\bar{1}0,001,00\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	$110,101,1\bar{1}0,10\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10,\bar{1}01,\bar{1}\bar{1}0,\bar{1}0\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
16,17,18,19	$011,0\bar{1}1,01\bar{1},0\bar{1}\bar{1}$	$2(2\pi/a)^2$	$k_x^2 + 2(2\pi/a)^2$

$$\epsilon^0(k_x,0,0) = \frac{\hbar^2}{2m}\left[(k_x+G_x)^2 + G_y^2 + G_z^2\right]$$



band crossings

$\vec{k} = (k_x, 0, 0)$

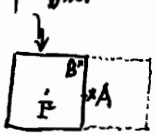
Low-lying free electron energy bands of the empty sc lattice, as transformed to the first Brillouin zone and plotted vs. (k_x00). The free electron energy is $\hbar^2(k + G)^2/2m$, where the G's are given in the second column of the table. The bold curves are in the first Brillouin zone, with $-\pi/a \le k_x \le \pi/a$. Energy bands drawn in this way are said to be in the reduced zone scheme.

Ex: How about $\vec{k} = (k, k, k)$? i.e. along [111] direction in the B.Z.?

After band folding, we see that in higher dimensions, it is possible to have:

- degenerate bands
- overlapping bands

↳ 2D example



$\mathcal{E}^0(A) < \mathcal{E}^0(B)$

↑ 2nd band ↑ 1st band

C. Nearly free electron model

Empty lattice: periodic, but $V = 0$

$\Rightarrow$ bands, but no gaps

Nearly free electron model: turn on a weak periodic potential

- $V(\vec{r}) \neq 0$
- weakly dependent on $\vec{r}$

$\Downarrow$

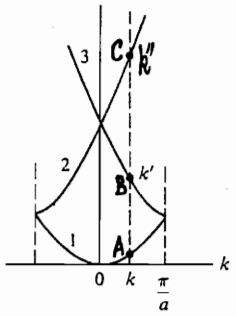
V is quite flat

$\Downarrow$

empty lattice results can be treated as unperturbed system and $V(\vec{r})$ as perturbation

Key results

(a) k's with no band crossing



empty lattice

Q: Unperturbed state in Band 1 at k (pt. A) with $\mathcal{E}^0(k) = \frac{\hbar^2 k^2}{2m}$, turn on $V(x)$, how is the energy altered?

Turn on $V(x) \Rightarrow V(x) = \sum_G V(G)\, e^{iGx}$, $G = h\frac{2\pi}{a}$

- Look at Central Equation,

the state at k (pt. A) is affected only by the state k' (pt. B) and the state k'' (pt. C), etc., i.e.

> state at k (pt. A) is affected only be states with the same k in the 1st B.Z.

↑ a consequence of periodic $V(x)$

Note: state at k (pt. A) is non-degenerate, i.e., only one state with that $\mathcal{E}^0(k)$

Effect of $V(x) \neq 0$? Think perturbatively

Let $\mathcal{E}(k)$ be the energy with $V(x)$ turned on.

Non-degenerate perturbation theory

Zeroth order: $\mathcal{E}(k) \approx \mathcal{E}^0(k) = \frac{\hbar^2 k^2}{2m}$

(pretend that $V(x)$ is not there)
[equivalent to empty lattice approximation]

First order correction:

$\langle \psi^{(0)}_{1,k} | V | \psi^{(0)}_{1,k} \rangle$ = Expectation value of $V(x)$ w.r.t. unperturbed state

unperturbed

$$\psi^{(0)}_{1,k} = \frac{1}{\sqrt{L}} e^{ikx}$$

band 1, at k

$$\langle \psi^{(0)}_{1,k} | V | \psi^{(0)}_{1,k} \rangle = \frac{1}{L}\int e^{-ikx} V(x) e^{ikx} dx$$

$$= \frac{1}{L}\int V(x)\, dx \equiv \overline{V} = \text{averaged potential} = \text{a constant} = V(\vec{G}=\vec{0})$$

∴ 1st order correction is to shift $\mathcal{E}^0(k)$ by a constant

↳ true for all non-degenerate k

↳ an unimportant shift of all bands by $\overline{V}$ or $V(\vec{G}=\vec{0})$

Second order corrections:

Consider 2nd order perturbation in "physical terms"†

(i) State k (pt. A) is related to state k' (pt. B) by

$$k - \frac{2\pi}{a} = k' \quad \text{since} \quad \mathcal{E}^0(k') = \frac{\hbar^2}{2m}\left(k - \frac{2\pi}{a}\right)^2$$

$\therefore$ The Fourier component in $V(x)$ that "connects" state k and state k' is $V(-\frac{2\pi}{a})$.

Similarly, the Fourier component that connects state k' and state k is $V(+\frac{2\pi}{a})$.

(But $V(-G) = V^*(G)$)

(ii) Consider how state k and state k' influence each other in the presence of V

The "interaction" is represented by

$$\begin{pmatrix} \mathcal{E}^0(k) & V(+\frac{2\pi}{a}) \\ V(-\frac{2\pi}{a}) & \mathcal{E}^0(k') \end{pmatrix}$$

Note: $V(\frac{2\pi}{a}) = V^*(-\frac{2\pi}{a})$

† The discussion that follows is a physical interpretation of the result in non-degenerate perturbation theory. It is a practical way to think about a theoretical approach.

or more correctly,

$$\begin{pmatrix} \mathcal{E}^0(k) + \overline{V} & V(+\frac{2\pi}{a}) \\ V(-\frac{2\pi}{a}) & \mathcal{E}^0(k') + \overline{V} \end{pmatrix}$$

including the first order constant shift

this ignored the effects of the states above
[or we can consider the effect pair by pair]

setting up this matrix does not require non-degenerate state
$\Rightarrow$ valid even for $\mathcal{E}^0(k) = \mathcal{E}^0(k')$

The perturbed energies $\mathcal{E}(k)$ and $\mathcal{E}(k')$ are given by the eigenvalues of this matrix.

Non-degenerate: $\mathcal{E}^0(k) \neq \mathcal{E}^0(k')$

Weak potential $\Rightarrow |V(-\frac{2\pi}{a})| \ll |\mathcal{E}^0(k) - \mathcal{E}^0(k')|$

Under these conditions:

$$\mathcal{E}(k) \approx \mathcal{E}^0(k) + \overline{V} + \frac{|V(-\frac{2\pi}{a})|^2}{\mathcal{E}^0(k) - \mathcal{E}^0(k')}$$

$$= \mathcal{E}^0(k) + \overline{V} - \frac{|V(-\frac{2\pi}{a})|^2}{\mathcal{E}^0(k') - \mathcal{E}^0(k)}$$

zeroth order; first order; 2nd order correction to energy

$\mathcal{E}_1^{(0)}(k)$ is "pushed" downward by the state $(2,k)$ above!

Similarly,

$$\mathcal{E}(k') \approx \mathcal{E}^0(k') + \overline{V} + \frac{|V(+\frac{2\pi}{a})|^2}{\mathcal{E}^0(k') - \mathcal{E}^0(k)}$$

$\mathcal{E}_2^{(0)}(k)$ is "pushed" upward by the state $(1,k)$ below!

Back to consider the state k in Band 1:

taking into account the effects of all states with same k

$$\mathcal{E}_1(k) \approx \mathcal{E}_1^{(0)}(k) + \overline{V} + \sum_{\substack{\text{all other} \\ \text{bands}}} \frac{|V(G)|^2}{\mathcal{E}_1^{(0)}(k) - \mathcal{E}_n^{(0)}(k)}$$

where G connects k to the state (n,k)

[This is the result of 2nd order non-degenerate perturbation theory.]

What is the effect?

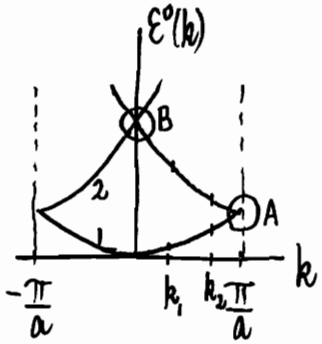
Most "important" term comes from nearby band(s)

$$\mathcal{E}_1(k) \approx \mathcal{E}_1^0(k) + \overline{V} - \underbrace{\frac{|V(-\frac{2\pi}{a})|^2}{\mathcal{E}_2^{(0)}(k) - \mathcal{E}_1^{(0)}(k)}}_{\text{small! (weak potential, non-degenerate)}}$$

even smaller effects from other bands!

⇒ for states k that the other bands are far apart, $V(x)$ does not alter $\mathcal{E}_n^0(k)$ significantly!

(b) k's with nearby bands: Gap Opening



$\mathcal{E}_2^0(k_1) - \mathcal{E}_1^0(k_1) \gg |V(-\frac{2\pi}{a})|$

⇒ effect of V is negligible

- But $(1,k_2)$ and $(2,k_2)$ are connected by the same $V(-\frac{2\pi}{a})$

Obviously, $\mathcal{E}_2^0(k_2) - \mathcal{E}^0(k_1)$ is smaller, thus the "pushing" becomes more important at k's where two (or more) bands come closer.

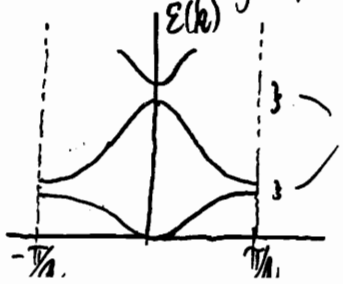
How about at $k = \frac{\pi}{a}$ (pt. A) and pt. B?

$\mathcal{E}_1^0(k) = \mathcal{E}_2^0(k)$ $\qquad$ $\mathcal{E}_2^0(k=0) = \mathcal{E}_3^0(k=0)$

↑ effect of V becomes significant!

[and non-degenerate perturbative approach fails]

From the idea of "pushing" between bands:

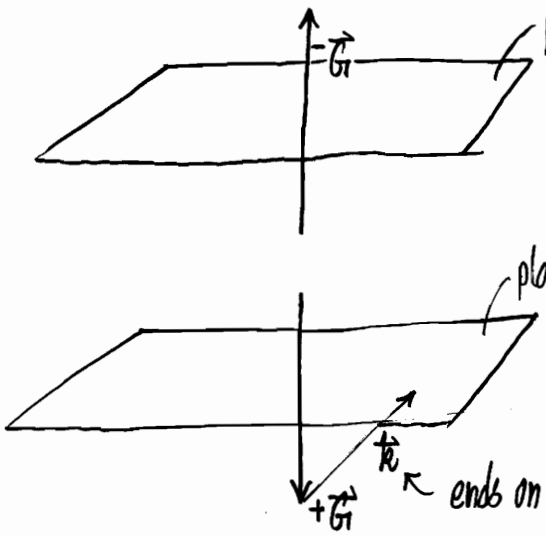


gaps opened up!

Thus, gaps will appear at places where $\mathcal{E}^0(k) \approx \mathcal{E}^0(k+G)$

- Be careful at Brillouin zone edges

Recall: Construction of Brillouin Zones



$$\vec{k}\cdot\frac{\vec{G}_1}{|\vec{G}_1|} = -\frac{1}{2}|\vec{G}_1| \Rightarrow 2\vec{k}\cdot\vec{G}_1 = -|\vec{G}_1|^2$$

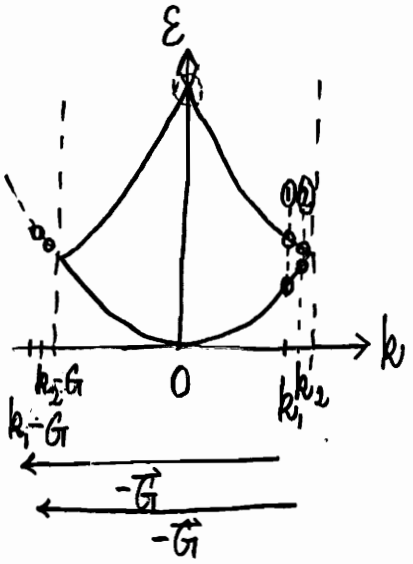
for $\vec{k}$ on plane that bisects $\vec{G}_1$

Now, for $\vec{k}$ and a $\vec{G}_1$ that satisfy $2\vec{k}\cdot\vec{G}_1 = -|\vec{G}_1|^2$,

$$\underbrace{\frac{\hbar^2}{2m}|\vec{k}+\vec{G}_1|^2}_{\mathcal{E}^0(\vec{k})} = \frac{\hbar^2}{2m}\left(k^2 + G_1^2 + 2\vec{k}\cdot\vec{G}_1\right) = \underbrace{\frac{\hbar^2}{2m}k^2}_{\mathcal{E}^0(\vec{k}+\vec{G}_1)}$$

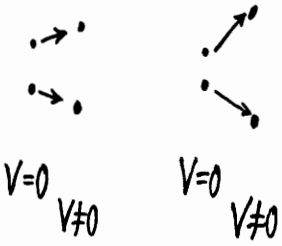
$\mathcal{E}^0(\vec{k}) = \mathcal{E}^0(\vec{k}+\vec{G}_1)$

$\therefore$ Must be careful for $\vec{k}$'s near the B.Z. edges!



"pushing" effect smaller ①

"pushing" effect larger ②



c.f. molecular bonding, and antibonding orbitals

$\mathcal{E}(k_{1,2}) \approx \mathcal{E}(k_{1,2}-G_1)$

for $k_{1,2}$ near B.Z. edge

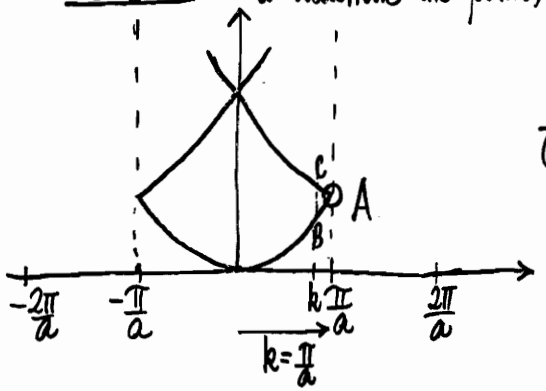
$\Rightarrow$ Need to be more careful!

Generally, when we have

$\mathcal{E}(\vec{k}+\vec{G}_1) \approx \mathcal{E}(\vec{k}+\vec{G}_2)$

then we need to be more careful!

1D case: (to illustrate the point)



$\vec{G}_1 = \frac{2\pi}{a}\hat{x}$

When $\vec{k} = \frac{\pi}{a}\hat{x} = \frac{1}{2}\vec{G}_1$ ($-\vec{G}_1$)

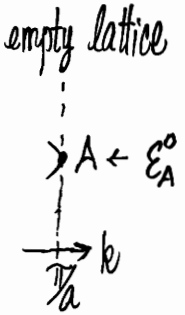
$\mathcal{E}^0(\vec{k}) = \mathcal{E}^0(\vec{k}-\vec{G}_1) = \mathcal{E}^0(\vec{k}+(-\frac{\pi}{a}\hat{x}))$

• Consider pt. A where band 1 ($\mathcal{E}_1^0(k=\frac{\pi}{a})$) and band 2 ($\mathcal{E}_2^0(k=\frac{\pi}{a})$) meet.

Let's set up a 2×2 matrix to describe the pushing:

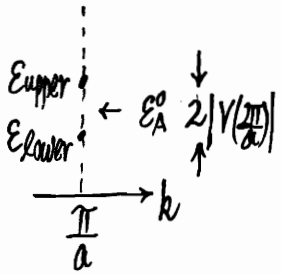
Call $\mathcal{E}_1^0(k=\frac{\pi}{a}) = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 \equiv \mathcal{E}_A^0$

$$\begin{pmatrix} \mathcal{E}_A^0 + \overline{V} & V(+\frac{2\pi}{a}) \\ V(-\frac{2\pi}{a}) & \mathcal{E}_A^0 + \overline{V} \end{pmatrix}$$



The eigenvalues give the perturbed values:
↑ can be found exactly!

$$\begin{cases} \mathcal{E}_{upper} = \mathcal{E}_A^0 + \overline{V} + |V(-\frac{2\pi}{a})| \\ \mathcal{E}_{lower} = \mathcal{E}_A^0 + \overline{V} - |V(-\frac{2\pi}{a})| \end{cases}$$



∴ Band 2 is pushed up
Band 1 is pushed down

A gap is opened up!

Gap = $2|V(\vec{G})|$
where $\vec{G}$ connects the two unperturbed states.

This treatment is called degenerate perturbation theory. Here, it amounts to treating the 2×2 matrix exactly.

• Looking closer at the gap opening at $k=\frac{\pi}{a}$

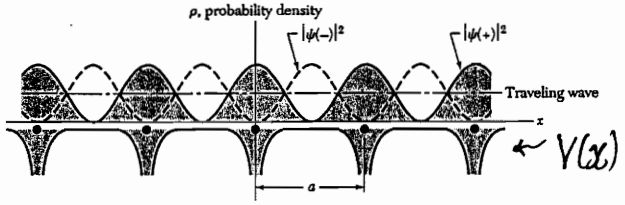
$$\begin{matrix} \psi^{(0)}_{k=\frac{\pi}{a}}(x) \\ \psi^{0}_{k=-\frac{\pi}{a}}(x) \end{matrix} \begin{pmatrix} \mathcal{E}_A^0 + \overline{V} & V(+\frac{2\pi}{a}) \\ V(-\frac{2\pi}{a}) & \mathcal{E}_A^0 + \overline{V} \end{pmatrix} \qquad \psi^0_k(x) \sim e^{ikx}$$

↑ Basis functions used in writing down the matrix

The two eigenvectors (new or perturbed eigenfunctions) with energies $\mathcal{E}_{Lower}$ and $\mathcal{E}_{upper}$ have "equal mix" of $\psi^0_{\frac{\pi}{a}}(x)$ and $\psi^0_{-\frac{\pi}{a}}(x)$. [from the form of matrix]

$$\psi(+) \sim \psi^0_{\frac{\pi}{a}}(x) + \psi^0_{-\frac{\pi}{a}}(x) \sim 2\cos\frac{\pi x}{a} = \psi_{lower}$$

$$\psi(-) \sim \psi^0_{\frac{\pi}{a}}(x) - \psi^0_{-\frac{\pi}{a}}(x) \sim 2i\sin\frac{\pi x}{a} = \psi_{upper}$$



$|\psi(+)|^2$ piles up electronic charge around cores where $V(x)$ is small

$|\psi(-)|^2$ piles up electronic charge between cores where $V(x)$ is not small

- For a value of k close to A, e.g.

$$\mathcal{E}^0(k) \approx \mathcal{E}^0(k+G) \qquad \text{(pts. B and C)}$$

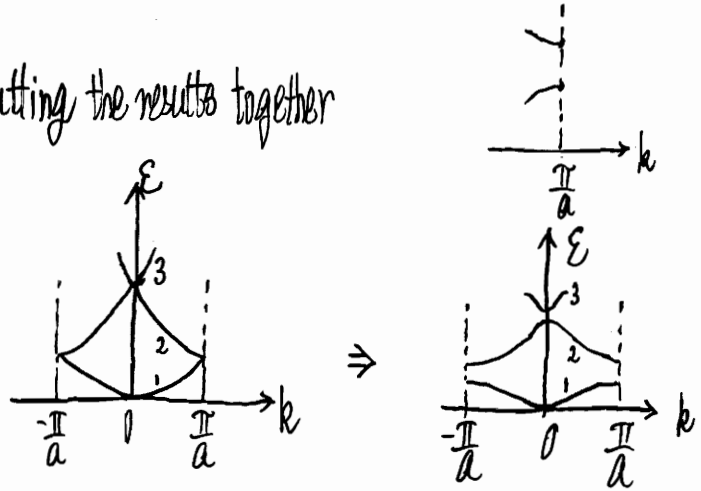
Setting up a 2×2 matrix to describe the pushing:

$$\begin{pmatrix} \frac{\hbar^2k^2}{2m} + \overline{V} & V(-\vec{G}) \\ V(+\vec{G}) & \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2 + \overline{V} \end{pmatrix}$$

The two eigenvalues are:

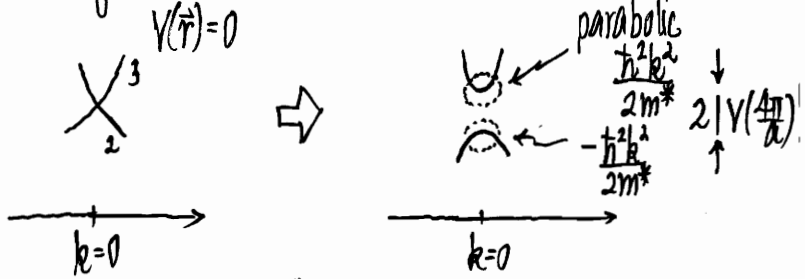
$$\mathcal{E}(k) = \overline{V} + \frac{\hbar^2}{2m}\left(k^2 + |\vec{k}+\vec{G}|^2\right) \pm \frac{1}{2}\sqrt{\left(\frac{\hbar^2}{2m}\right)^2\left(k^2 - |\vec{k}+\vec{G}|^2\right)^2 + 4|V(\vec{G})|^2}$$

Putting the results together



The band structure near $k \approx 0$ between band 2 and band 3 is also interesting!

Zoom in:



m^* = effective mass $\neq m_e$ (in general)

Summary: Nearly free-electron model

Periodic $V(\vec{r})$ ⇒ only states with the same $\vec{k}$ (in 1st B.Z.) in the empty lattice approximation are "connected" by $V(\vec{r})$ through the Fourier components $V(\vec{G})$.

- for states well separated in energy
  $V(\vec{r}) \neq 0$ only shifts the energy slightly
- for states close in energy
  $V(\vec{r}) \neq 0$ ⇒ "pushing" against each other

Consequence: bands and band gaps

Refs: Kittel Ch.7 ; Christman Sec. 7.4 ; Omar Ch.5.