J. Nearly Free Electron Model (Viewpoint)

- **Idea:** Take Eq. (45), see effects of $V(\vec{r})$ as "corrections" (perturbations) to the free-electron (empty lattice folded bands) behavior ($\mathcal{E}^0(\vec{k}+\vec{G})$'s)

  i.e. $V(\vec{r})$ is "weak"

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\text{k.e. term}} + \overbrace{V(\vec{r})}^{\text{periodic}} = \underbrace{\hat{H}_0}_{\text{thought to be important}} + \underbrace{\hat{H}'}_{\text{regarded as perturbation (微擾)}} \qquad (47)$$

(k.e. term: free-electron part)

$$\hat{H}_0\, \psi_{\vec{k}}^{(0)} = \mathcal{E}^0(\vec{k})\, \psi_{\vec{k}}^{(0)} = \frac{\hbar^2 k^2}{2m}\, \psi_{\vec{k}}^{(0)} \qquad \text{(unperturbed theorem)}$$

$\psi_{\vec{k}}^{(0)} \sim$ plane waves

$\{\psi_{\vec{k}}^{(0)}\}$ form a complete set

Eq. (45) is TISE written into a matrix using the basis functions $\{\psi_{\vec{k}}^{(0)}\}$. It is Exact.

For a $\vec{k} \in$ 1st B.Z. with no degenerate states nearby a state "n", i.e.

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

(↑ quite far away,)

The whole matrix can be visualized as

	$e^{i\vec{k}\cdot\vec{r}}$	$e^{i(\vec{k}+\vec{G}_{11})\cdot\vec{r}}$	$e^{i(\vec{k}+\vec{G}_{12})\cdot\vec{r}}$	$e^{i(\vec{k}+\vec{G}_{13})\cdot\vec{r}}$	... ← help you think
$e^{i\vec{k}\cdot\vec{r}}$	$\mathcal{E}^0(\vec{k})+\overline{V}$	$V(-\vec{G}_{11})$	$V(-\vec{G}_{12})$	$V(-\vec{G}_{13})$	...
$e^{i(\vec{k}+\vec{G}_{11})\cdot\vec{r}}$	$V(\vec{G}_{11})$	$\mathcal{E}^0(\vec{k}+\vec{G}_{11})+\overline{V}$	$V(\vec{G}_{11}-\vec{G}_{12})$	$V(\vec{G}_{11}-\vec{G}_{13})$	...
$e^{i(\vec{k}+\vec{G}_{12})\cdot\vec{r}}$	$V(\vec{G}_{12})$	$V(\vec{G}_{12}-\vec{G}_{11})$	$\mathcal{E}^0(\vec{k}+\vec{G}_{12})+\overline{V}$	$V(\vec{G}_{12}-\vec{G}_{13})$	...
$e^{i(\vec{k}+\vec{G}_{13})\cdot\vec{r}}$	$V(\vec{G}_{13})$	$V(\vec{G}_{13}-\vec{G}_{11})$	$V(\vec{G}_{13}-\vec{G}_{12})$	$\mathcal{E}^0(\vec{k}+\vec{G}_{13})+\overline{V}$	...
⋮	⋮	⋮	⋮	⋮	⋱

↑ Basis functions

(45)

e.g.

$$\mathcal{E}_1(\vec{k}) \approx \mathcal{E}_1^{(0)}(\vec{k}) + \overline{V} + \sum_{\substack{i\,(i\neq 1) \\ (\vec{G}\neq 0)}} \frac{|V_{\vec{G}}|^2}{\mathcal{E}^{(0)}(\vec{k}) - \mathcal{E}_i^{(0)}(\vec{k}+\vec{G})} \qquad (48)$$

(↑ lowest band)

This is H'_{nn} $=$ $\frac{1}{\Omega_c}\int_{\Omega_c} V(\vec{r})\, d^3r$

($\vec{G}=0$ gives lowest band)

Just a small modification to $\mathcal{E}_1^{(0)}(\vec{k})$

Similar for other bands!

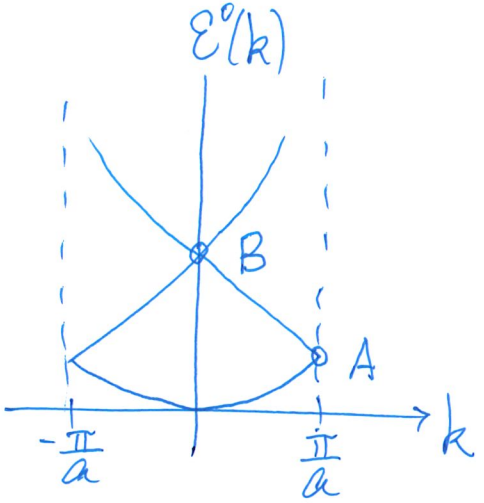
But be careful when $\underbrace{\mathcal{E}^{(0)}(\vec{k}) \approx \mathcal{E}_i^{(0)}(\vec{k}+\vec{G}_1)}$

when two bands cross in empty lattice picture

e.g. $\mathcal{E}^0\left(\frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 = \mathcal{E}^0\left(\frac{\pi}{a} \underbrace{-\frac{2\pi}{a}}_{-G_{1,1}\ (1D\ case)}\right) = \mathcal{E}^0\left(-\frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$ (point A)

or $\mathcal{E}^0\left(\frac{\pi}{a} \underbrace{+\frac{2\pi}{a}}_{+G_1}\right) = \frac{\hbar^2}{2m}\left(\frac{3\pi}{a}\right)^2 = \mathcal{E}^0\left(\frac{\pi}{a} \underbrace{-\frac{4\pi}{a}}_{-G_2}\right) = \frac{\hbar^2}{2m}\left(\frac{3\pi}{a}\right)^2$ (point B)

some $\vec{G}_1$ ← $\vec{G}_1' = -\frac{2\pi}{a}\hat{x}$ connects them → another $\vec{G}_1$



Can't use case (ii) [lazy 2×2 folding] or Eq. (A10)!

But the point of reading out 2×2 matrices remains valid!

What to do? Try case (iii), do 2×2 exactly for cases like $\begin{pmatrix} \mathcal{E} & \Delta \\ \Delta^* & \mathcal{E} \end{pmatrix}$,

giving $\mathcal{E} - |\Delta|$ and $\mathcal{E} + |\Delta|$

$$\mathcal{E}^0(\vec{k}) = \mathcal{E}^0(\vec{k}+\vec{G}_1) \quad \text{or} \quad \mathcal{E}^0(\vec{k}) \approx \mathcal{E}^0(\vec{k}+\vec{G}_1),$$

$$\begin{pmatrix} \mathcal{E}^0(\vec{k}) + \overline{V} & V(\vec{G}_1) \\ V^*(\vec{G}_1) & \underbrace{\mathcal{E}^0(\vec{k})}_{\mathcal{E}^0(\vec{k}+\vec{G}_1)=\mathcal{E}^0(\vec{k})} + \overline{V} \end{pmatrix}$$

find eigenvalues (49)

(This is Degenerate Perturbation Theory)

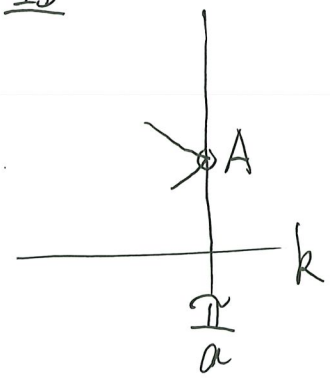
$$\Rightarrow \boxed{\mathcal{E}_{lower} = \mathcal{E}^0(\vec{k}) + \overline{V} - |V(\vec{G}_1)| \;;\; \mathcal{E}_{upper} = \mathcal{E}^0(\vec{k}) + \overline{V} + |V(\vec{G}_1)|} \quad (50)$$

$$\psi_{lower} \cong \psi^{(0)}_{\vec{k}} + \psi^{(0)}_{\vec{k}+\vec{G}_1} \;;\; \psi_{upper} \cong \psi^{(0)}_{\vec{k}} - \psi^{(0)}_{\vec{k}+\vec{G}_1}$$

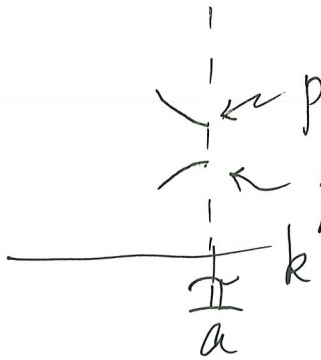
↑ equal mixing ↑ equal mixing ↑ equal mixing ↑

[standing waves] $\psi^{(0)}_{\frac{\pi}{a}} \pm \psi^{(0)}_{-\frac{\pi}{a}}$

1D

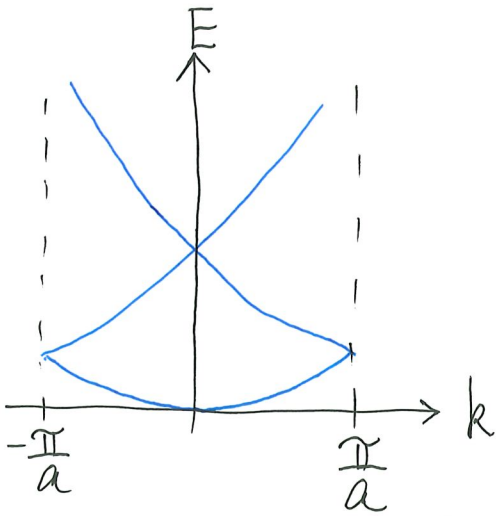


Near A:



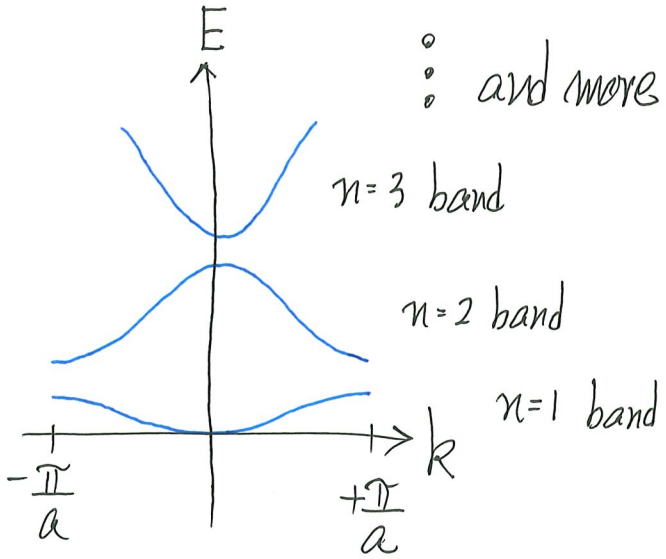
$2|V(\vec{G}_1)|$

the Fourier Component that has the $\vec{G}_1$ connecting degenerate states



$U(\vec{r}) \to 0$ (but retain period)

(empty lattice)/band folding



$U(\vec{r}) \neq 0$

band formations resulting from states pushing each other

High-Dimensions

- Same idea, but open a gap needs to consider all $\vec{k}$'s in 1st B.Z. (but just a line)

(overlapping of bands occur more readily)

Technical Remark

- After doing the 2×2 (e.g. at $k=\frac{\pi}{a}$) exactly, what about the contributions of the other states? [those have different $\mathcal{E}^0$'s]

use 2nd order perturbation [matrix folding] ⇒ some smaller corrections

$$\begin{array}{c|cc|cc|c}
 & \psi^{(0)}_{\frac{\pi}{a}} & \psi^{(0)}_{-\frac{\pi}{a}} & \psi^{(0)}_3 & \psi^{(0)}_4 & \cdots \\
\hline
\psi^{(0)}_{\frac{\pi}{a}} & \mathcal{E}^0 & \Delta & H'_{13} & H'_{14} & \cdots \\
\psi^{(0)}_{-\frac{\pi}{a}} & \Delta^* & \mathcal{E}^0 & H'_{23} & H'_{24} & \cdots \\
\hline
\psi^{(0)}_3 & H'_{31} & H'_{32} & \mathcal{E}^{(0)}_3 & H'_{34} & \cdots \\
\psi^{(0)}_4 & H'_{41} & H'_{42} & H'_{43} & \mathcal{E}^{(0)}_4 & \cdots \\
\vdots & \vdots & \vdots & & & \ddots
\end{array}
\rightarrow
\begin{array}{c|cc|cc|c}
 & \phi_A \sim \psi^{(0)}_{\frac{\pi}{a}} + \psi^{(0)}_{-\frac{\pi}{a}} & \phi_B \sim \psi^{(0)}_{\frac{\pi}{a}} - \psi^{(0)}_{-\frac{\pi}{a}} & \psi^{(0)}_3 & \psi^{(0)}_4 & \cdots \\
\hline
\phi_A & \mathcal{E}^0 - |\Delta| & 0 & H'_{A3} & H_{A4} & \cdots \\
\phi_B & 0 & \mathcal{E}^0 + |\Delta| & H'_{B3} & H'_{B4} & \cdots \\
\hline
\psi^{(0)}_3 & H'_{3A} & H'_{3B} & \mathcal{E}^{(0)}_3 & H'_{34} & \\
\psi^{(0)}_4 & H'_{4A} & H'_{4B} & H'_{43} & \mathcal{E}^{(0)}_4 & \\
\vdots & \vdots & \vdots & & & \ddots
\end{array}$$

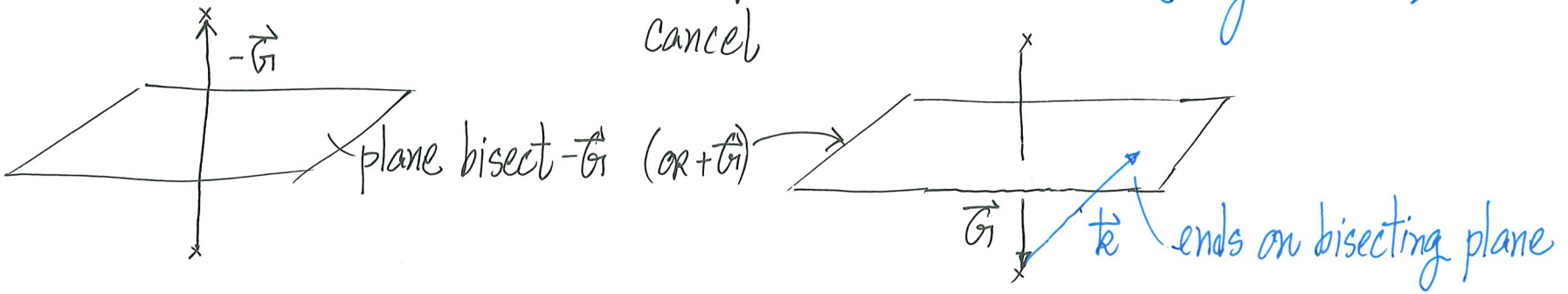
elements are altered by transformation to ϕ_A and ϕ_B

- Do it 2×2 at corner exactly
- But formally, not done yet!

When should we be careful? When $\frac{\hbar^2}{2m}|\vec{k}+\vec{G}_1|^2 = \frac{\hbar^2 k^2}{2m}$

Consider a $\vec{k}$ and a $\vec{G}_1$ that satisfy $2\vec{k}\cdot\vec{G}_1 = -|\vec{G}_1|^2$ or $\vec{k}\cdot\frac{\vec{G}_1}{2} = -\left|\frac{\vec{G}_1}{2}\right|^2$

then $\frac{\hbar^2}{2m}|\vec{k}+\vec{G}_1|^2 = \frac{\hbar^2}{2m}(k^2 + \underbrace{G_1^2 + 2\vec{k}\cdot\vec{G}_1}_{\text{cancel}}) = \frac{\hbar^2}{2m}k^2$ (Degenerate!)



$$\vec{k}\cdot\underbrace{\frac{\vec{G}_1}{|\vec{G}_1|}}_{\text{unit vector in } \vec{G} \text{ direction}} = -\frac{|\vec{G}_1|}{2} \Rightarrow 2\vec{k}\cdot\vec{G}_1 + G_1^2 = 0$$

∴ $\vec{k}$'s that are near to Brillouin Zone(s) Edges should be treated with care!

not only 1st B.Z. but 2nd, 3rd, ... Zones!

The Idea can be carried over to 2D and 3D.

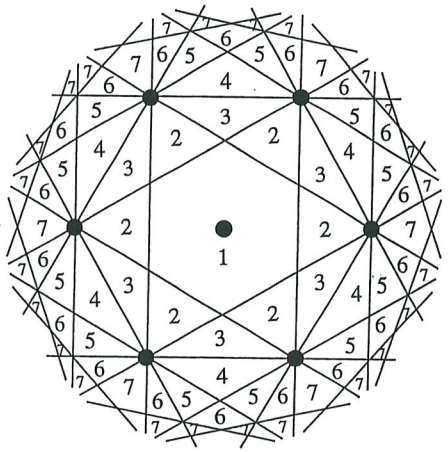
B.Z.'s of 2D Hexagonal Lattice

Higher Dimension, points with Higher degeneracy

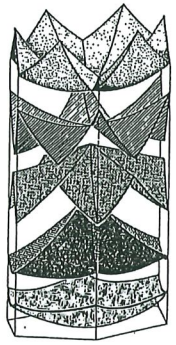
Band Folding ($U=0$)

$U \neq 0$

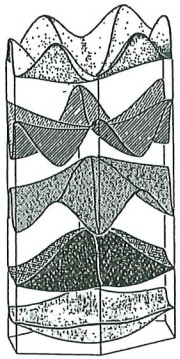
---- empty lattice



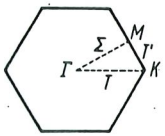
(a)

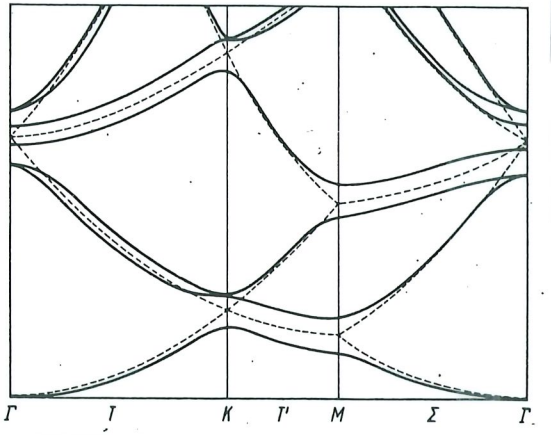


(c)

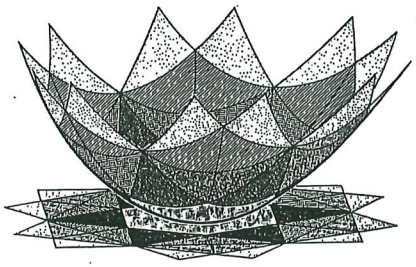


(d)





$E(k) = \frac{\hbar^2 k^2}{2m}$

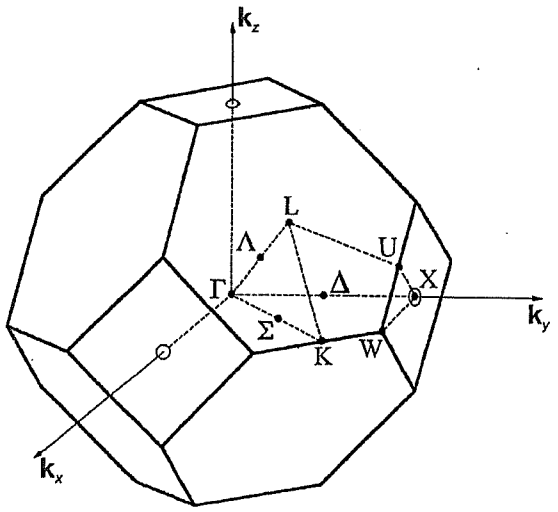


(b)

a) Brillouin zones for a two-dimensional hexagonal lattice. b) Energy paraboloid for free electrons ($E = \hbar^2k^2/2m$) above the k-plane for the two-dimensional hexagonal lattice. Regions of the free-electron energy surface falling in different Brillouin zones are shaded differently. c) The energy paraboloid of (b) reduced to the first Brillouin zone. d) The bands of (c) smoothed by the effect of a weak lattice potential.

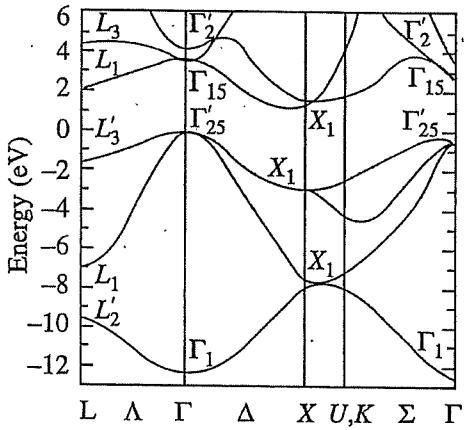
[Taken from Snoke, "Solid State Physics". See also Madelung, "Introduction to Solid State Theory"]

- Pushing at M does not result in a gap!
- $U(\vec{r}) \neq 0$ makes $E(\vec{k})$ smoother (after pushing)



1st B.Z.

Silicon



Band structure of Si (after Chelikowsky and Cohen 1976).

I hope that you now have a better sense on what is involved in obtaining band structures.

Non-trivial Aspects

Need $V(\vec{r})$ (periodic) to start the calculation

What $V(\vec{r})$ to use? Big Problem

$$V(\vec{r}) = \sum_{\vec{R}_n} \underbrace{U_{atomic}(\vec{r} - \vec{R}_n)}_{\text{what is this? Including Core electrons or not? How about el-el interaction?}} \quad \text{or} \quad V(\vec{r}) = \sum_{\vec{R}_n} \frac{-Ze^2}{4\pi\epsilon_0 |\vec{r} - \vec{R}_n|}$$

How about el-el interaction?

Once $V(\vec{r})$ is specified, then $V(\vec{r}) = \sum_{\vec{G}_1} V(\vec{G}_1) e^{i\vec{G}_1 \cdot \vec{r}}$ and so

$$V(\vec{G}_1) = \frac{1}{\Omega_c} \int_{\Omega_c} V(\vec{r}) e^{-i\vec{G}_1 \cdot \vec{r}} d^3r$$

go into the Huge Matrix

Ω_c: one primitive unit cell

- Only after such non-trivial treatment, we can fill the electrons into the states as given by $E_n(\vec{k})$.

  ↑ N allowed values in 1st B.Z.
  ↑ 2N sites for electrons in each band

[Need Density of States AND Rules to fill electrons]

- See

$$E_v(\vec{k}) \approx -\frac{\hbar^2 k^2}{2m_e^*}$$

↑ like "free electron" even with $V(\vec{r})$

⇒ effective mass

(Why electrons living in the forest of ions/nuclei behave freely?)