

Periodic solids continued

Translational symmetry:

$$\underline{R}_n = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$$

$$T_{\underline{R}_n} f(\underline{r}) := f(\underline{r} + \underline{R}_n)$$

[Last lecture: further symmetries \rightarrow group theory]

Today: What can we learn about $\varphi_{0i}(\underline{r})$
from translational symmetry of $V^{\text{eff}}(\underline{r})$?

Bloch theorem

- $h \psi_{0_i}(\underline{r}) = E_{0_i} \psi_{0_i}(\underline{r})$

- $T_{\underline{R}_L} \psi_{0_i}(\underline{r})$ is also EF to h for E_{0_i}

Case a) E_{0_i} is non-degenerate

Since Observables are periodic $\rightarrow |\psi_{0_i}(\underline{r})|^2$ periodic

$$T_{\underline{R}_L} \psi_{0_i}(\underline{r}) = e^{i\alpha} \psi_{0_i}(\underline{r})$$

in general, $\alpha = \alpha(\underline{R}_L)$

$$\begin{aligned} \text{and } T_{\underline{R}_M} T_{\underline{R}_L} \psi_{0_i}(\underline{r}) &= e^{i\alpha(\underline{R}_M)} e^{i\alpha(\underline{R}_L)} \psi_{0_i}(\underline{r}) \\ &\stackrel{!}{=} T_{\underline{R}_M + \underline{R}_L} \psi_{0_i}(\underline{r}) = e^{i\alpha(\underline{R}_M + \underline{R}_L)} \psi_{0_i}(\underline{r}) \end{aligned}$$

$$\alpha(\underline{R}_M + \underline{R}_L) = \alpha(\underline{R}_M) + \alpha(\underline{R}_L) \text{ linear!}$$

$$\rightarrow \text{can write } \alpha(\underline{R}_L) = \underline{k} \cdot \underline{R}_L$$

$$T_{\underline{R}_L} \psi_{0_i}(\underline{r}) = e^{i\underline{k} \cdot \underline{R}_L} \psi_{0_i}(\underline{r})$$

\hookrightarrow the eigenvalues of $T_{\underline{R}_L}$ are $e^{i\underline{k} \cdot \underline{R}_L}$

$\rightarrow \underline{k}$ is quantum number to label

$$\psi_{0_i}(\underline{r}) = \psi_{\underline{k}}(\underline{r})$$

$$E_{0_i} = E(\underline{k}).$$

b) E_{0_i} degenerate.

\rightarrow there exist $l=1, \dots, f$ eigenfunctions $\psi_l(\underline{r})$

for the same ϵ_0 .

In general, $T_{\underline{R}_n} \varphi_{\underline{k}}(\underline{r}) = \sum_{m=1}^f \overline{T}_{m,\underline{k}} \varphi_m(\underline{r})$ possible

$$\overline{T}_{m,\underline{k}} = \langle \varphi_m | T_{\underline{R}_n} | \varphi_{\underline{k}} \rangle$$

"representation of the translational group"

But $T_{\underline{R}_n}$ form Abelian group

$\Rightarrow \overline{T}_{m,\underline{k}}$ can be diagonalized
to the form $\widehat{\overline{T}}_{m,\underline{k}}$

\Rightarrow we can transform $\varphi_{\underline{k}} \rightarrow \widetilde{\varphi}_{\underline{k}}$

$$T_{\underline{R}_n} \widehat{\overline{T}}_{\underline{k},\underline{k}} \widetilde{\varphi}_{\underline{k}}(\underline{r}) = \widehat{\overline{T}}_{\underline{k},\underline{k}} \widetilde{\varphi}_{\underline{k}}(\underline{r})$$

Rest as before.

In a nutshell:

$$T_{\underline{R}_n} \varphi_{\underline{k}}(\underline{r}) = \varphi_{\underline{k}}(\underline{r} + \underline{R}_n) = e^{i\underline{k} \cdot \underline{R}_n} \varphi_{\underline{k}}(\underline{r})$$

Bloch theorem.

Form of $\varphi_{\underline{k}}(\underline{r})$:

$$\varphi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\underline{r}} u_{\underline{k}}(\underline{r})$$

general Ansatz. Why is this helpful

[note: $e^{i\underline{k}\underline{r}}$ are eigenfns. for Translation.

Ansatz: means we just "modify" these.]

$$\begin{aligned} T_{\underline{R}_n} \varphi_{\underline{k}}(\underline{r}) &= e^{i\underline{k}(\underline{r} + \underline{R}_n)} \cdot u_{\underline{k}}(\underline{r} + \underline{R}_n) \\ &= e^{i\underline{k}\underline{R}_n} \varphi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\underline{R}_n} e^{i\underline{k}\underline{r}} u_{\underline{k}}(\underline{r}) \\ &\quad \uparrow \\ &\quad \text{Bloch} \end{aligned}$$

$$\text{Thus: } u_{\underline{k}}(\underline{r} + \underline{R}_n) = u_{\underline{k}}(\underline{r})$$

same periodicity as V^{eff} .

Second form of Bloch's theorem:

if V periodic \rightarrow Eigenfunctions have form

$$\varphi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\underline{r}} u_{\underline{k}}(\underline{r})$$

where $u_{\underline{k}}(\underline{r})$ is also periodic.

The reciprocal lattice

- eigenvalues of $T_{\underline{R}_n}$ are $e^{i\underline{k}\underline{R}_n}$
- but, different \underline{k} can yield the same $e^{i\underline{k}\underline{R}_n}$

$$e^{i\underline{k}'\underline{R}_n} = e^{i\underline{k}\cdot\underline{R}_n}$$

$$\text{if } \underline{k}' = \underline{k} + \underline{G}_m$$

$$\text{for } \underline{G}_m \cdot \underline{R}_h = 2\pi N, \quad N \text{ integer.}$$

Let's define:

$$\underline{b}_1 = \frac{2\pi}{\Omega} (\underline{a}_2 \times \underline{a}_3)$$

$$\underline{b}_2 = \frac{2\pi}{\Omega} (\underline{a}_3 \times \underline{a}_1)$$

$$\underline{b}_3 = \frac{2\pi}{\Omega} (\underline{a}_1 \times \underline{a}_2)$$

This means

$$\underline{a}_i \cdot \underline{b}_j = 2\pi \delta_{ij}$$

[math.: \underline{b}_j define "dual space"]

$$\Omega = \underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)$$

All possible \underline{G}_m can be listed:

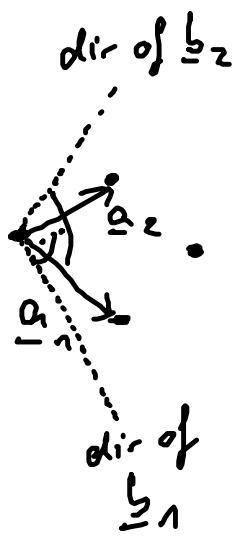
$$\underline{G}_m = m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3$$

This set $\{\underline{G}_m\}$ is called "reciprocal lattice".

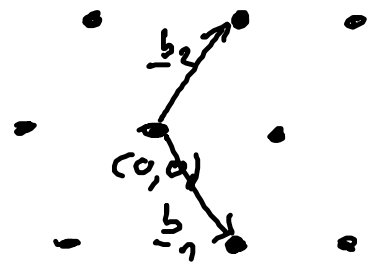
Note: units $\frac{1}{\text{length}}$

Example: 2D

real space



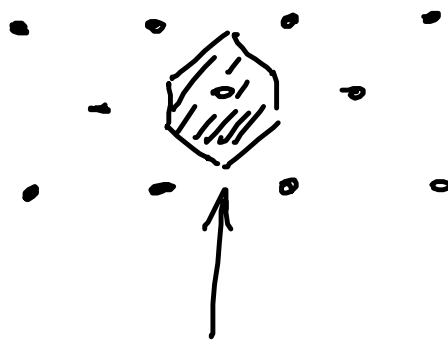
reciprocal space



Looking at \underline{k} space, note:

$\{\underline{k} + \underline{G}_m\}$ all label the same $\epsilon_{\underline{k}}$, $\psi_{\underline{k}}$!

But any \underline{k} that are closer to $\underline{k} = 0$ than to any other \underline{G}_m should be unique.



"1st Brillouin zone"
(Wigner-Seitz cell of the reciprocal lattice)

3d: harder to draw

| | | |
|-------------|------------|------------------|
| - examples: | Real space | reciprocal space |
| | sc | sc |
| | hexagonal | hexagonal |
| | fcc | bcc |
| | bcc | fcc |

Note labelling of special symmetry points

e.g. Γ point $\leftrightarrow \underline{k} = 0$

Let's look at

$$\hbar \phi_{\underline{k}}(\underline{r}) = \epsilon(\underline{k}) \phi_{\underline{k}}(\underline{r})$$

$$\text{note } v^{\text{eff}}(\underline{r}) = \sum_{\underline{G}_e} v^{\text{eff}}(\underline{G}_e) e^{i \underline{G}_e \cdot \underline{r}} \quad \text{Fourier series}$$

$$\begin{aligned} \text{and } \phi_{\underline{k}}(\underline{r}) &= e^{i \underline{k} \cdot \underline{r}} u_{\underline{k}}(\underline{r}) = \\ &= e^{i \underline{k} \cdot \underline{r}} \sum_{\underline{G}_m} C_{\underline{G}_m} e^{i \underline{G}_m \cdot \underline{r}} \end{aligned}$$

Rewrite Schrödinger Eq.:

$$\begin{aligned} &\sum_m \frac{\hbar^2}{2m} (\underline{k} + \underline{G}_m)^2 C_{\underline{G}_m}(\underline{k}) e^{i(\underline{k} + \underline{G}_m) \cdot \underline{r}} \\ &+ \sum_e v^{\text{eff}}(\underline{G}_e) \sum_m C_{\underline{G}_m}(\underline{k}) e^{i(\underline{k} + \underline{G}_e + \underline{G}_m) \cdot \underline{r}} \\ &= \epsilon(\underline{k}) \sum_m C_{\underline{G}_m}(\underline{k}) \cdot e^{i(\underline{k} + \underline{G}_m) \cdot \underline{r}} \end{aligned}$$

\Rightarrow Coupled set of linear equations:

$$\frac{\hbar^2}{2m} (\underline{k} + \underline{G}_n)^2 C_{\underline{G}_n}(\underline{k}) + \sum_m v^{\text{eff}}(\underline{G}_n - \underline{G}_m) C_{\underline{G}_m}(\underline{k}) = E(\underline{k}) C_{\underline{G}_n}(\underline{k})$$

$v^{\text{eff}}(\underline{G}_n - \underline{G}_m)$ couple $C_{\underline{G}_m}(\underline{k})$!

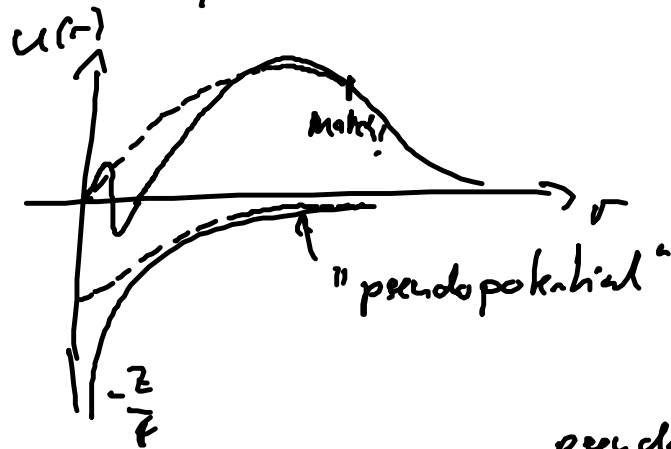
- define \underline{k} points that you need
- make sure that $v^{\text{eff}}(\underline{G}_n)$ falls off rapidly with $|\underline{G}_n|$

excursion (quadr.)

v^{eff} contains $-\frac{Z}{r}$ for nuclei.

⇒ instead (1950's):

replace $-\frac{Z}{r}$ by "pseudopotential" and treat only valence electrons.



note $v^{\text{eff}}(\underline{G})$ smooth if we use $v^{\text{pseudo}}(r)$ for atoms

"plane-wave pseudo pot. method".

can we continue to work:

$$\sum_n h_{m,n} C_{\underline{G}_n}(\underline{k}) = E(\underline{k}) C_{\underline{G}_n}(\underline{k})$$

$$h_{m,n} = \frac{\hbar^2}{2m} (\underline{k} + \underline{G}_n)^2 \delta_{n,m} + V^{\text{eff}}(\underline{G}_n - \underline{G}_m)$$

\Rightarrow for each \underline{k} point:

set of discrete solutions

$$E_n(\underline{k}), \psi_{n,\underline{k}}(\underline{r})$$

"band structure"

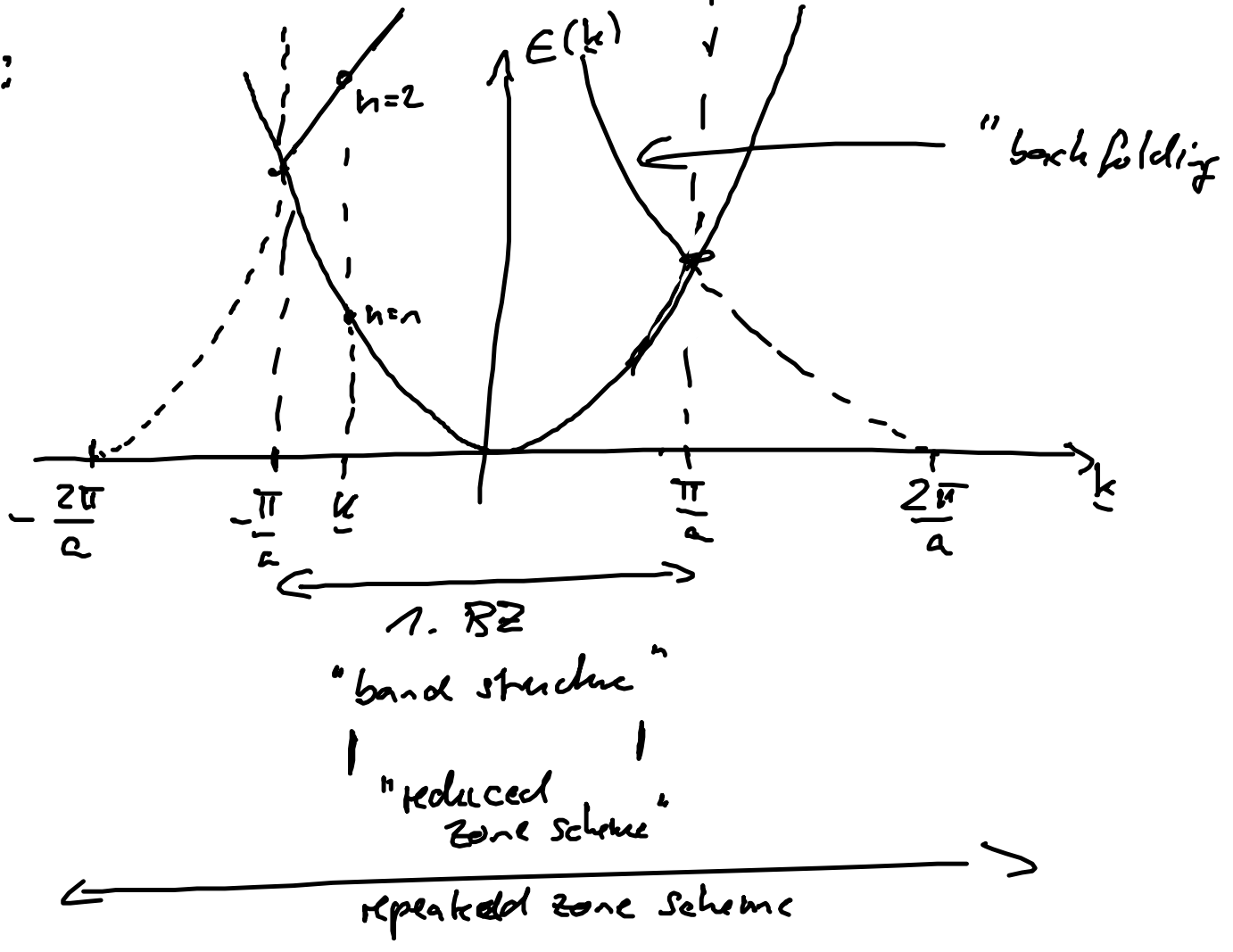
\underline{k} points in 1. BZ are all independent of each other.

How about nearly free electrons?

(weakly varying potential $V^{\text{eff}}(\underline{G}_i) \rightarrow 0$)

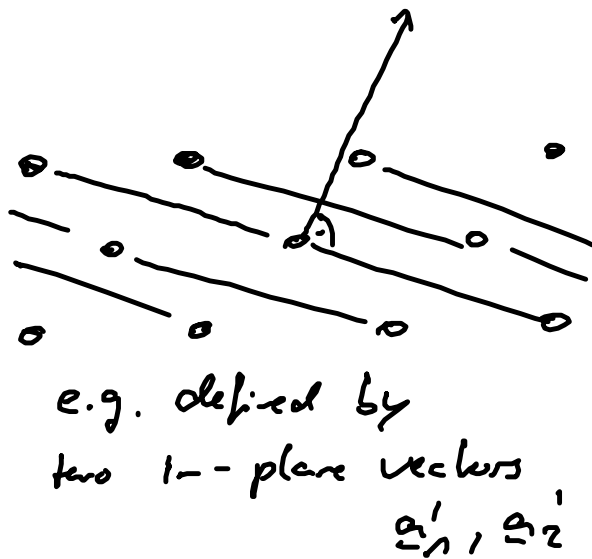
Limiting case $E_n(\underline{k}) \rightarrow \approx \frac{\hbar^2}{2m} (\underline{k} + \underline{G})^2$

1- AD:



Reciprocal lattice, real-space lattice, diffraction

Real space



many lattice planes possible

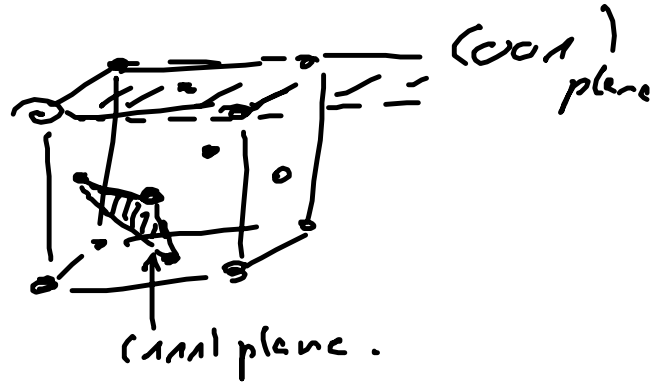
Normal vector to lattice plane must be a reciprocal lattice point $\underline{G}_m \equiv \underline{G}_{hkl}$

Shortest possible $\underline{G}_m = \underline{G}_{hkl}$

can be used to label lattice planes

→ Miller indices hkl

Example: fcc



note:

typically use

conventional cell for

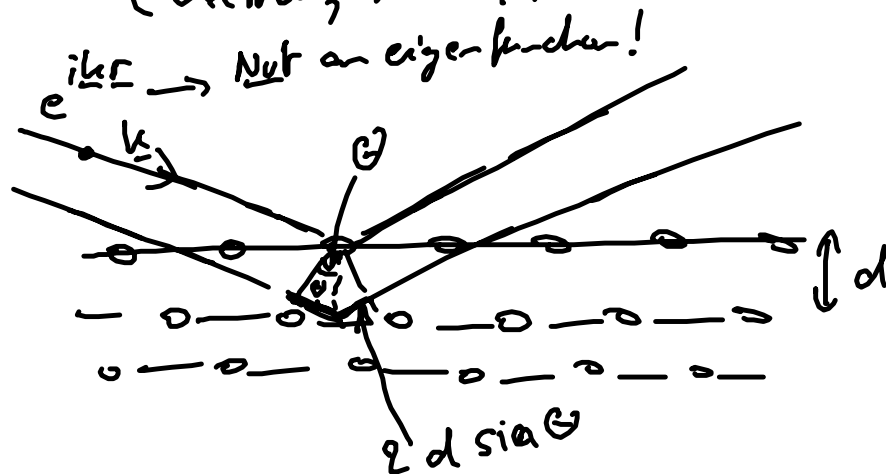
fcc, bcc, sc

but in fact: - simple cubic lattice does have all \underline{G}_m

- fcc has \underline{G}_{hkl} if (hkl) all even or all odd

- bcc has \underline{G}_{hkl} if $h+k+l$ even

Reflection of waves at a crystal
(electrons, X-rays, etc.)



Constructive interference for

$$2d \sin \Theta = m \lambda = m \frac{2\pi}{|\underline{k}|}$$

But: $|\underline{G}_m| = m \cdot \frac{2\pi}{d} \perp$ plane $d = m \cdot \frac{2\pi}{|\underline{G}_m|}$

hok $\sin \Theta = \frac{\underline{k} \cdot \underline{G}_m}{|\underline{k}| \cdot |\underline{G}_m|}$

$$\rightarrow 2 \cdot \frac{2\pi}{|\underline{G}_m|} \cdot m \cdot \frac{\underline{k} \cdot \underline{G}_m}{|\underline{k}| \cdot |\underline{G}_m|} = m \frac{2\pi}{|\underline{k}|}$$

$$2 \underline{k} \cdot \underline{G}_m = |\underline{G}_m|^2 \quad | + \underline{k}^2$$

$$\underline{k}^2 = (\underline{k} - \underline{G}_m)^2 \quad \text{Bragg condition}$$

Only \underline{k} for which we can find such a \underline{G}_m lead to a reflection!

$$\underline{k} = \frac{\underline{G}_m}{2} \text{ at BZ boundary curves}$$

Chapter 5 The band structure of the electron

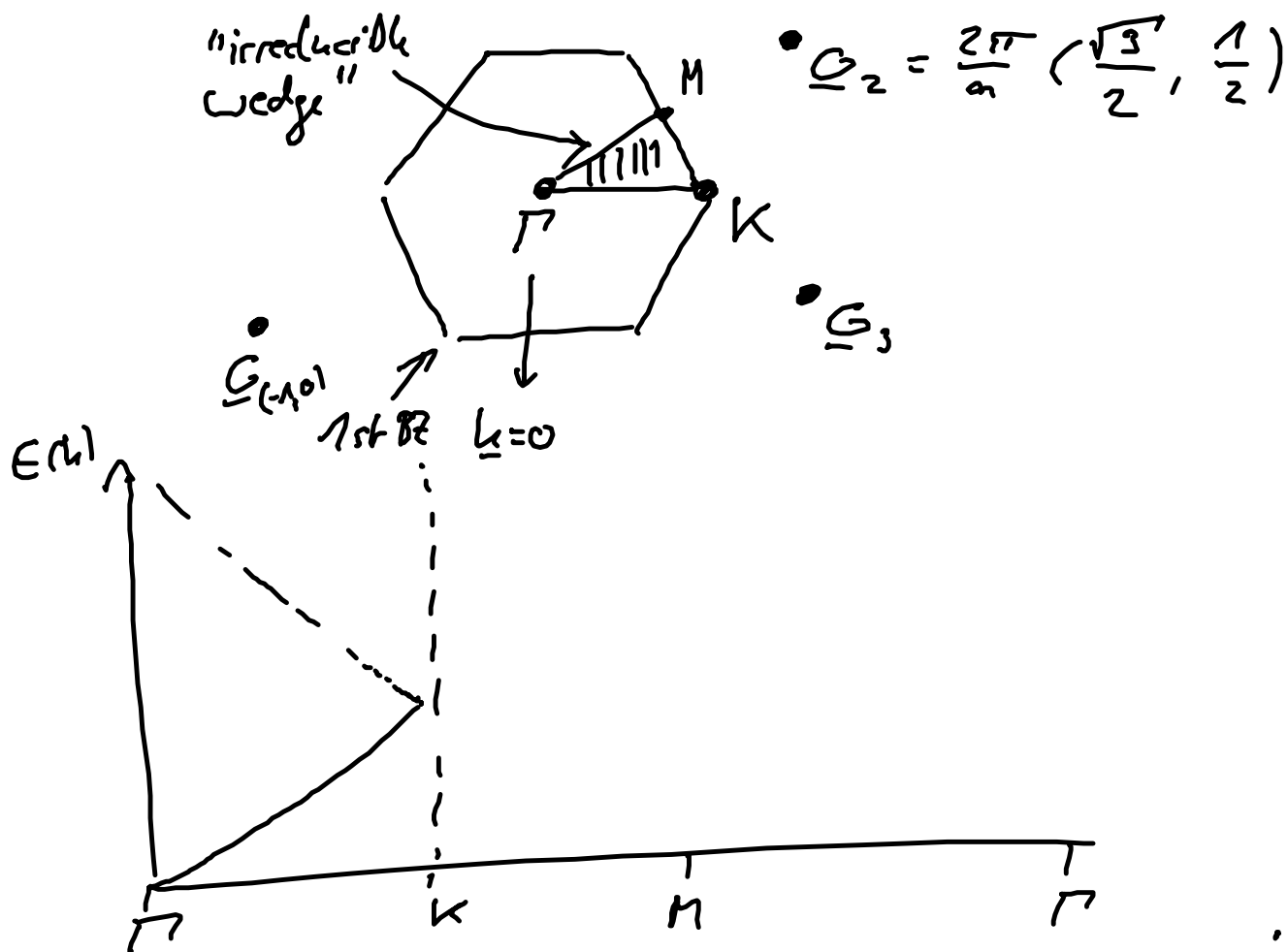
We saw: $\psi_{\underline{k}}(\underline{r}) = \sum_m C_{\underline{G}_m}(\underline{k}) e^{i(\underline{k} + \underline{G}_m) \cdot \underline{r}}$

$$h_{n,m} = \frac{\hbar^2}{2m} (\underline{k} + \underline{G}_m) \cdot \delta_{n,m} + V^{\text{eff}}(\underline{G}_m - \underline{G}_n)$$

\rightarrow can get $E_n(\underline{k})!$

What does this look like in more than 1D?

Example: hexagonal lattice: $\underline{G}_1 = \frac{2\pi}{a}(0, 1)$



$$n=0: \quad E_0(\underline{k}) = \frac{\hbar^2}{2m} k^2$$

$$E_0(0) = 0$$

$$E_0(\underline{k}) = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \cdot \frac{1}{\sqrt{3}} \right)^2$$

$$n=1; \quad \Gamma-K : \underline{k} = (k_x, 0)$$

$$E_1(\underline{k}) = \frac{\hbar^2}{2m} (\underline{k} - \underline{G}_3)^2$$

$$= \dots$$

$$= \frac{\hbar^2}{2m} \left(k^2 - \frac{2\pi}{a} \sqrt{3} k + \left(\frac{2\pi}{a} \right)^2 \right)$$

$$E_1(\underline{k}) = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 \frac{1}{3} \checkmark$$

how about

$v^{\text{eff}}(\underline{G}_n)$ small but $\neq 0$?

$v^{\text{eff}}(\underline{G})$ couples

$$\frac{1}{\sqrt{V_g}} e^{i(\underline{k} + \underline{G}_n) \cdot \underline{r}} \rightarrow$$

$$\left\{ \begin{array}{l} \psi_{\underline{k}\underline{k}} = \sum_n C_{\underline{G}_n}(\underline{k}) e^{i(\underline{k} + \underline{G}_n) \cdot \underline{r}} \\ E_n(\underline{k}) \rightarrow E_n^{\text{free}}(\underline{k}) + \Delta_n(\underline{k}) \end{array} \right.$$

perturbation theory,

$$\Delta_n(\underline{k}) \sim |v^{\text{eff}}(\underline{G}_n)|^2$$

for non-degenerate n

$$\text{but } \Delta_n(\underline{k}) \sim |v^{\text{eff}}(\underline{G}_n)|$$

for degenerate $E_n(\underline{k})$