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 → group theory]

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

Bloch theorem

- $h\,\varphi_{0i}(\underline{r}) = \epsilon_{0i}\,\varphi_{0i}(\underline{r})$
- $T_{\underline{R}_n}\,\varphi_{0i}(\underline{r})$ is also EF to h for ϵ_{0i}

Case a) ϵ_{0i} is non-degenerate

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

$$T_{\underline{R}_n}\,\varphi_{0i}(\underline{r}) = e^{i\alpha}\,\varphi_{0i}(\underline{r})$$

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

and $T_{\underline{R}_m}\,T_{\underline{R}_n}\,\varphi_{0i}(\underline{r}) = e^{i\alpha(\underline{R}_m)}\,e^{i\alpha(\underline{R}_n)}\,\varphi_{0i}(\underline{r})$

$$\overset{!}{=} T_{\underline{R}_m+\underline{R}_n}\,\varphi_{0i}(\underline{r}) = e^{i\alpha(\underline{R}_m+\underline{R}_n)}\varphi_{0i}(\underline{r})$$

$\alpha(\underline{R}_m+\underline{R}_n) = \alpha(\underline{R}_m)+\alpha(\underline{R}_n)$ linear!

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

$$T_{\underline{R}_n}\,\varphi_{0i}(\underline{r}) = e^{i\underline{k}\underline{R}_n}\,\varphi_{0i}(\underline{r})$$

the eigenvalues of $T_{\underline{R}_n}$ are $e^{i\underline{k}\underline{R}_n}$

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

$$\varphi_{0i}(\underline{r}) = \varphi_{\underline{k}}(\underline{r})$$
$$\epsilon_{0i} = \epsilon(\underline{k}).$$

b) ϵ_{0i} degenerate.

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

for the same ϵ_0.

In general, $T_{\underline{R}_n} \varphi_\ell(\underline{r}) = \sum_{m=1}^{f} \Gamma_{m,\ell} \varphi_m(\underline{r})$ possible

$$\Gamma_{m,\ell} = \langle \varphi_m | T_{\underline{R}_n} | \varphi_\ell \rangle$$

"representation of the translational group"

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

$\Rightarrow$ $\Gamma_{m,\ell}$ can be diagonalized

to the form $\tilde{\Gamma}_{m,\ell}$

$\Rightarrow$ we can transform $\varphi_\ell \to \tilde{\varphi}_\ell$

$$T_{\underline{R}_n} \tilde{\varphi}_\ell(\underline{r}) = \tilde{\Gamma}_{\ell,\ell} \tilde{\varphi}_\ell(\underline{r})$$

Rest as before.

In a nutshell:

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

Bloch theorem.

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

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{\underline{k}}(\underline{r})$$

general Ansatz. Why is this helpful

[note: $e^{i\underline{k}\cdot\underline{r}}$ are eigenfcts. for Jellium.
Ansatz: means we just "modify" those.]

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

$$\vdots = e^{i\underline{k}\underline{R}_n}\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\underline{R}_n} e^{i\underline{k}\underline{r}} u_{\underline{k}}(\underline{r})$$

↑ Bloch

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 h periodic → Eigenfunctions have form

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{\underline{k}}(\underline{r})$$

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 $e^{i\underline{k}\underline{R}_n}$

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

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

for $\underline{G}_m \cdot \underline{R}_n = 2\pi N$, N 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"]

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

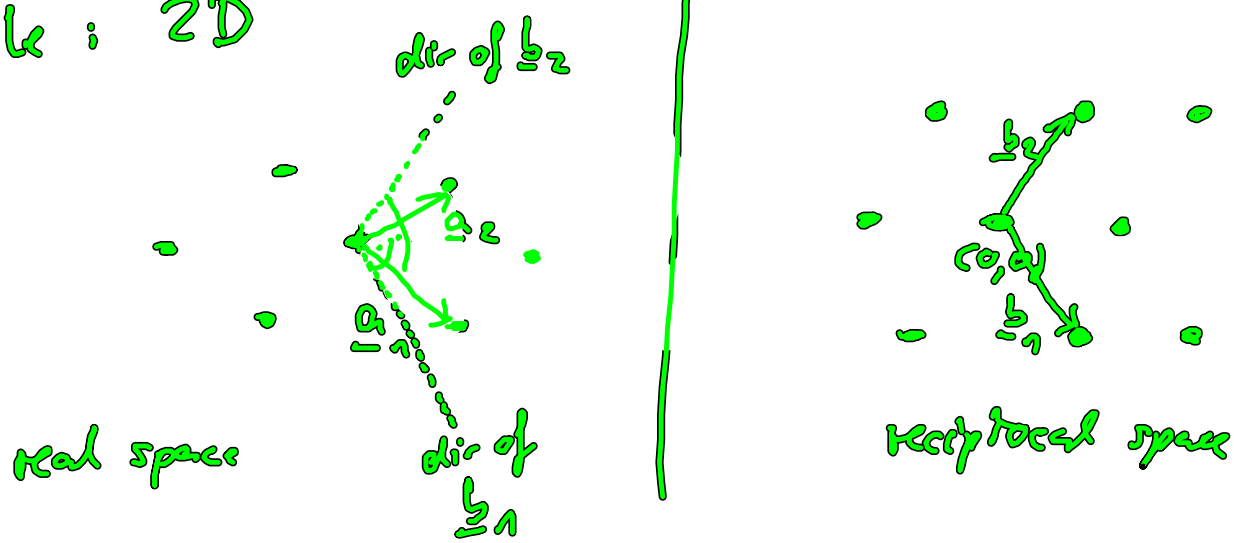
All possible $\underline{G}_m$ can be listed:

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

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

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

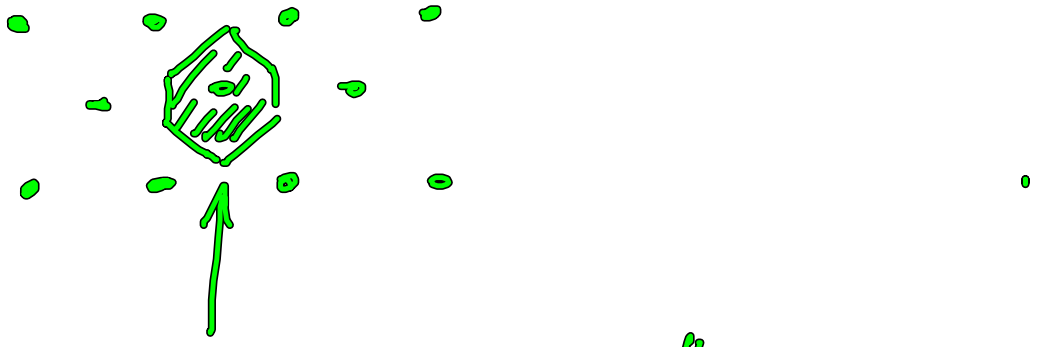
Example: 2D



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

Usual labelling of special symmetry points

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

Let's look at

$$\hat{h}\,\psi_{\underline{k}}(\underline{r}) = \epsilon(\underline{k})\,\psi_{\underline{k}}(\underline{r})$$

with $V^{eff}(\underline{r}) = \sum_{\underline{G}} V^{eff}(\underline{G})\, e^{i\underline{G}\cdot\underline{r}}$ Fourier series

and $\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{\underline{k}}(\underline{r}) =$

$$= e^{i\underline{k}\cdot\underline{r}} \sum_{\underline{G}_m} C_{\underline{G}_m}\, e^{i\underline{G}_m\cdot\underline{r}}$$

Rewrite Schrödinger Eq.:

$$\sum_m \frac{\hbar^2}{2m}(\underline{k}+\underline{G}_m)^2\, C_{\underline{G}_m}(\underline{k})\, e^{i(\underline{k}+\underline{G}_m)\cdot\underline{r}}$$

$$+ \sum_{\underline{G}_l} V^{eff}(\underline{G}_l) \sum_m C_{\underline{G}_m}(\underline{k})\, e^{i(\underline{k}+\underline{G}_l+\underline{G}_m)\cdot\underline{r}}$$

$$= \epsilon(\underline{k}) \sum_m C_{\underline{G}_m}(\underline{k}) \cdot e^{i(\underline{k}+\underline{G}_m)\cdot\underline{r}}$$

$\Rightarrow$ Coupled set of linear equations:

$$\frac{\hbar^2}{2m}(\underline{k}+\underline{G}_n)^2 C_{\underline{G}_n}(\underline{k}) + \sum_{\underline{G}_m} V^{eff}(\underline{G}_n - \underline{G}_m) C_{\underline{G}_m}(\underline{k})$$

$$= \epsilon(\underline{k})\, C_{\underline{G}_n}(\underline{k})$$

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

- define $\underline{k}$ points that you need
- make sure that $V^{eff}(\underline{G}_{max})$ falls off rapidly with $|\underline{G}_i|$

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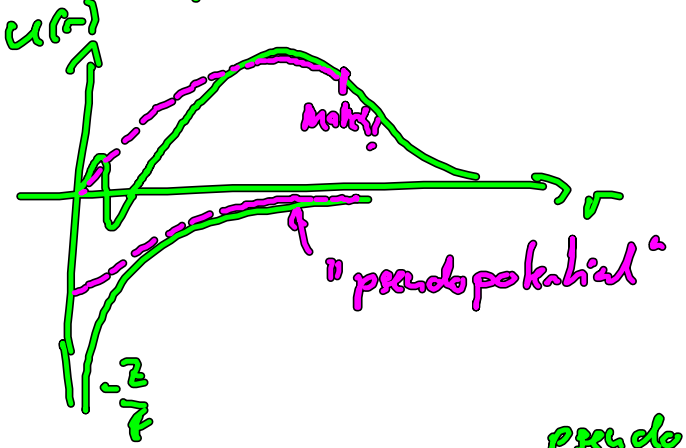
excursion (quadrt.)

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

⟹ instead (1950's):

replace $-\frac{Z}{r}$ by "pseudopotential"

and treat only valence electrons.



note $V^{eff}(\underline{G})$ smooth if we use $V^{pseudo}(r)$

for atoms

"plane-wave pseudopot.-method".

can now continue to write:

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

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

$\Rightarrow$ for each $\underline{k}$ point:

set of discrete solutions

$$\epsilon_n(\underline{k}),\ \varphi_{n,\underline{k}}(\underline{r})$$

"band structure"

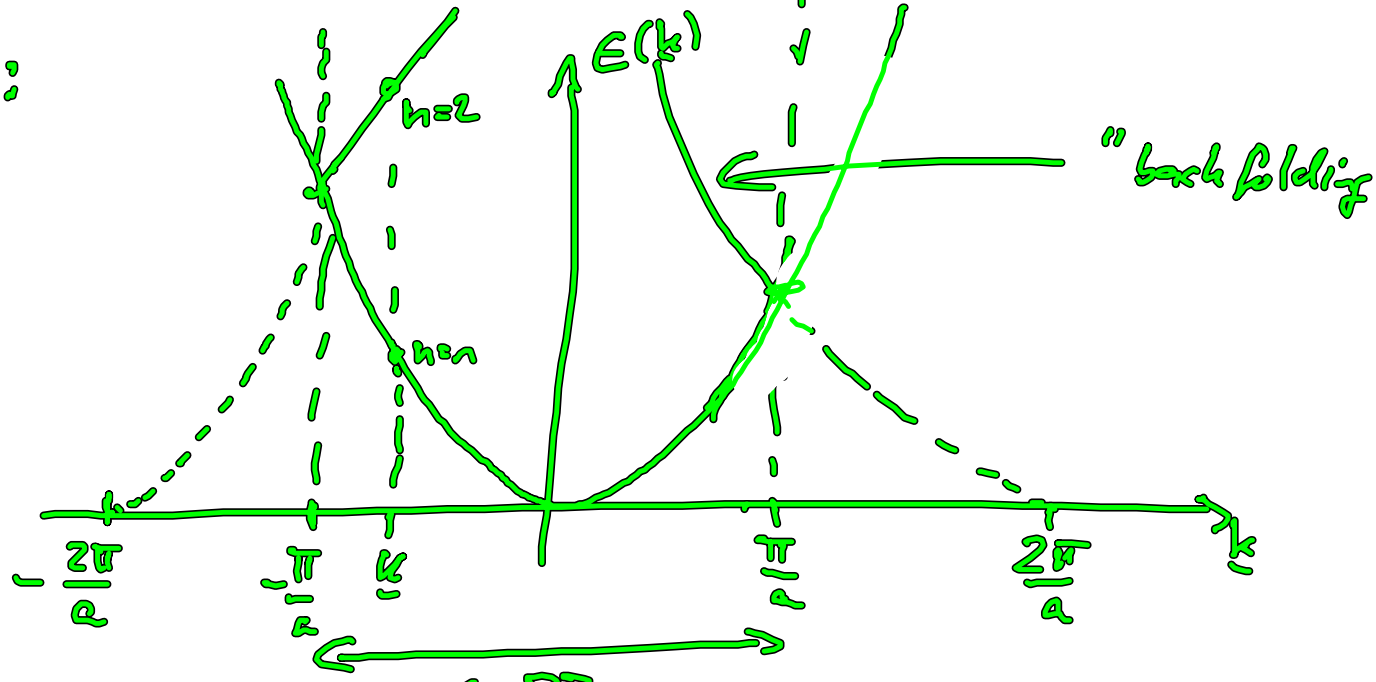
$\underline{k}$ points in 1. BZ are all independent of each other.

How about nearly free electrons?

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

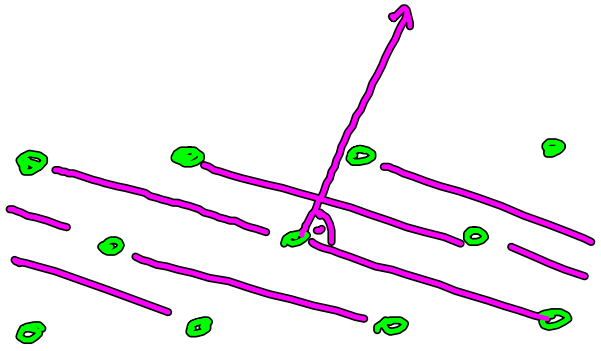
Limiting case $\epsilon_n(\underline{k}) \longrightarrow \simeq \frac{\hbar^2}{2m}(\underline{k}+\underline{G})^2$

1. 1D:



Reciprocal lattice, real-space lattice, diffraction

Real space



e.g. defined by two 1-- plane vectors a_1', a_2'

many lattice planes possible

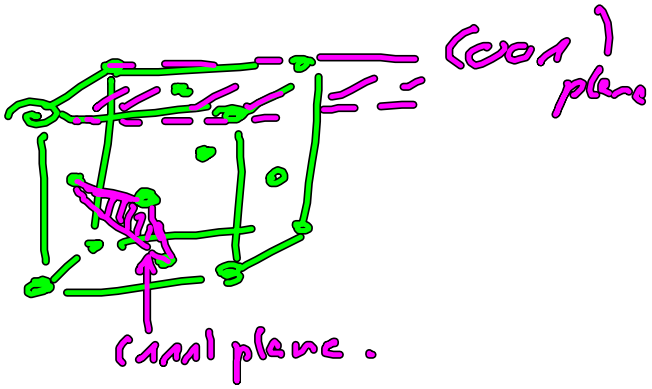
Normal vector to lattice plane must be a reciprocal lattice part $\underline{G}_m \equiv$ "$\underline{G}_{hkl}$"

Shortest possible $G_m = a G_{hkl}$

can be used to label lattice planes

→ Miller indices hkl

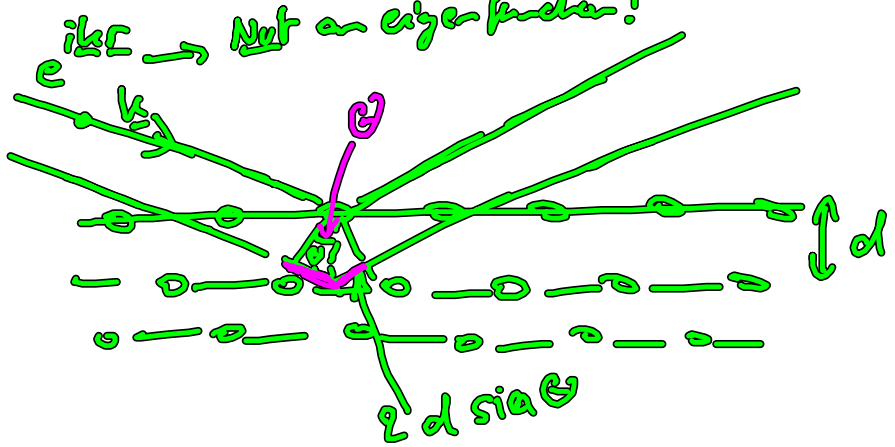
Example: fcc



note:
typically use
conventional cell for
fcc, bcc, sc

but in fact:
- simple cubic lattice does have all G_m
- fcc has G_{hkl} if (hkl) all even or all odd
- bcc has G_{hkl} if h+k+l even

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



Constructive interference for

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

But: $|G_m| = m \cdot \frac{2\pi}{d}$ $\perp$ plane $\quad d = m \cdot \frac{2\pi}{|G_m|}$

not $\sin\Theta = \frac{k \cdot G_m}{|k| \cdot |G_m|}$

$$\rightarrow \quad 2 \cdot \frac{2\pi}{|G_m|} \cdot m \cdot \frac{k \cdot G_m}{|k| \cdot |G_m|} = m\frac{2\pi}{|k|}$$

$$2\, k \cdot G_m = |G_m|^2 \quad | + k^2$$

$$k^2 = (k - G_m)^2$$ Bragg condition

Only k for which we can find such a G_m lead to a reflection!

$k = \frac{G_m}{2}$ at BZ boundary everywhere

Chapter 5 The band structure of the electron

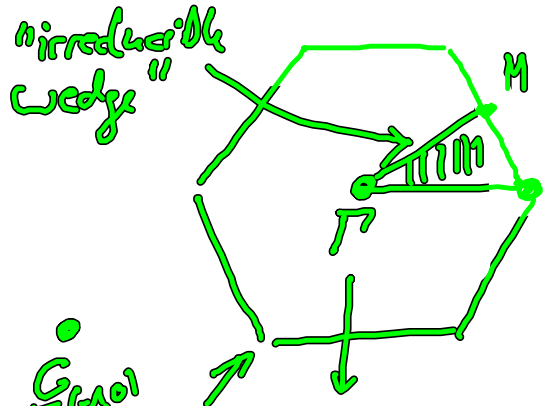
We saw: $\psi_k(r) = \sum_m C_{G_m}(k)\, e^{i(k+G_m)r}$

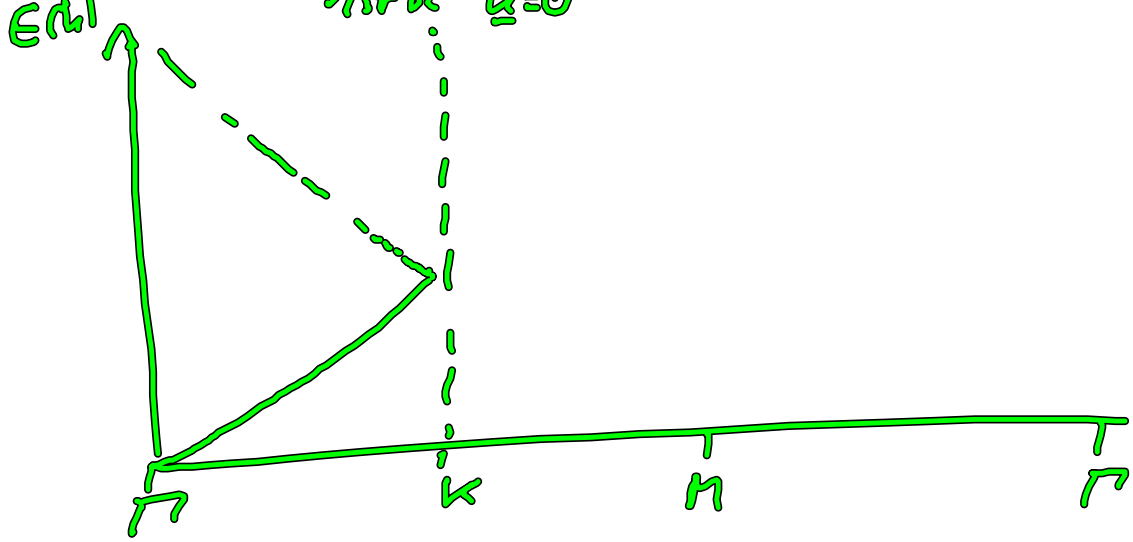
$$H_{k,m} = \frac{\hbar^2}{2m}(k+G_m)\,\delta_{k,m} + V^{eff}(G_k - G_m)$$

$\rightarrow$ can get $\epsilon_n(k)$!

What does this look like in more than 1D?

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





$n=0$: $\epsilon_0(\underline{k}) = \frac{\hbar^2}{2m}\underline{k}^2$

$\epsilon_0(0) = 0$

$\epsilon_0(K) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\cdot\frac{1}{\sqrt{3}}\right)^2$

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

$\epsilon_1(\underline{k}) = \frac{\hbar^2}{2m}(\underline{k} - \underline{G}_3)$

$= \dots$

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

$\epsilon_1(K) = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2\frac{1}{3}$ ✓

how about $V^{eff}(G_n)$ small but $\neq 0$?

$V^{eff}(G)$ couples

$$\frac{1}{\sqrt{V_g}} e^{i(k+G_n)r} \rightarrow \begin{cases} \psi_{nk} = \sum_m C_{G_m}(k) e^{i(k+G)r} \\ \epsilon_n(k) \rightarrow \epsilon_n^{free}(k) + \Delta_n(k) \end{cases}$$

perturbation theory:

$\Delta_n(k) \sim |V^{eff}(G_n)|^2$ for non-degenerate $\epsilon_n(k)$

but $\Delta_n(k) \sim |V^{eff}(G_n)|$ for degenerate $\epsilon_n(k)$