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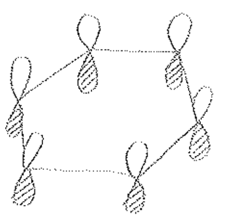
① Hückel model

$$H c = S c E$$

$$\begin{pmatrix} \langle 1|\hat{H}|1\rangle & \langle 1|\hat{H}|2\rangle & \cdots & \langle 1|\hat{H}|n\rangle \\ \langle 2|\hat{H}|1\rangle & \langle 2|\hat{H}|2\rangle & & \vdots \\ \vdots & & & \vdots \\ \langle n|\hat{H}|1\rangle & & & \langle n|\hat{H}|n\rangle \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} \langle 1|1\rangle & \cdots & \langle 1|n\rangle \\ \vdots & & \vdots \\ \langle n|1\rangle & \cdots & \langle n|n\rangle \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix} E$$

Hückel nearest neighbor / π system

$\mathbb{1}$



$$\begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ & \beta & \alpha & \beta & & \\ & & \beta & \alpha & \beta & \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix}$$

negative

$\alpha - 2\beta$ } virtual

$\alpha - \beta$ (×2)

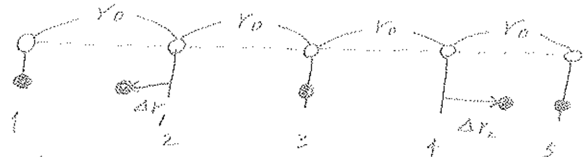
} frontier

↑↓ ↑↓ $\alpha + \beta$ } occupied

↑↓ $\alpha + 2\beta$

② Su-Schrieffer-Heeger (SSH) model

Rev. Mod. Phys. <u>60</u> 781 ('88)

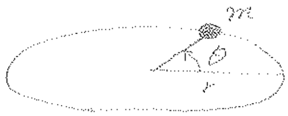


$$\begin{pmatrix} \alpha & \beta+\beta'\Delta r_1 & & & \\ \beta+\beta'\Delta r_1 & \alpha & \beta-\beta'\Delta r_1 & & \\ & \beta-\beta'\Delta r_1 & \alpha & \beta+\beta'\Delta r_2 & \\ & & \beta+\beta'\Delta r_2 & \alpha & \beta-\beta'\Delta r_2 \\ & & & \beta-\beta'\Delta r_2 & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{pmatrix} = E_i \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{pmatrix}$$

$$E = \sum_i^{occ.} 2E_i + \sum_j \frac{1}{2} k \Delta r_j^2$$

③ Band theory (primer)

i) A particle on a ring

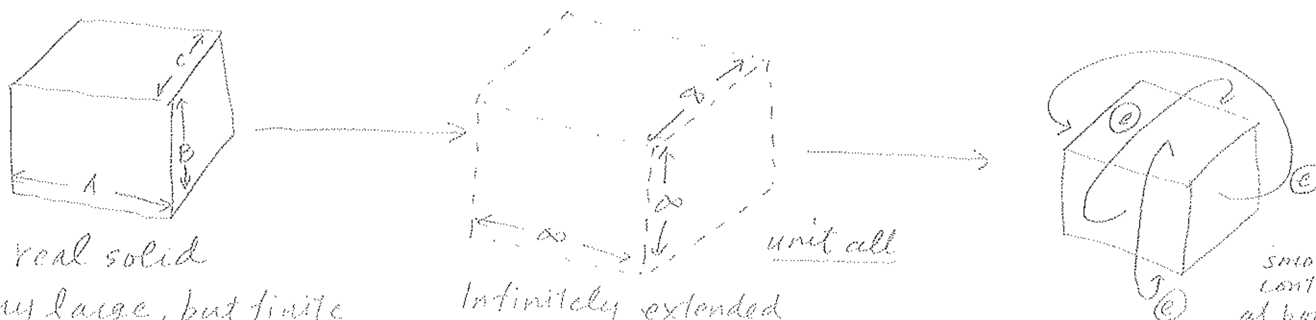


$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\theta^2}\psi = E\psi \longrightarrow \psi = \frac{1}{\sqrt{2\pi}}e^{im\theta}$$

$m = 0, \pm 1, \pm 2, \cdots$

$$-i\hbar\frac{\partial}{\partial\theta}\psi = \underbrace{m\hbar}_{\text{angular momentum}}\psi$$

ii) Periodic boundary conditions aka Born-von Karman condition



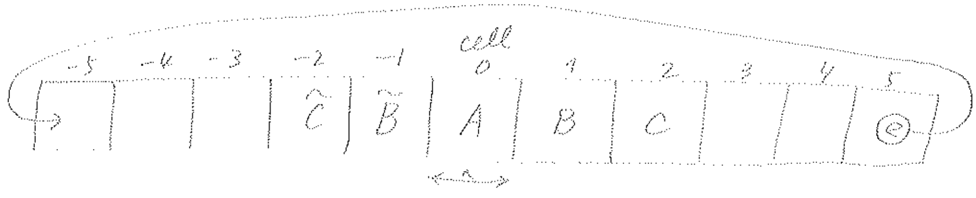
real solid
very large, but finite

Infinitely extended system

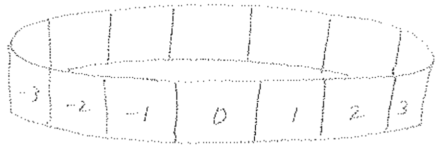
PBC

smooth continuous at boundary
cf. particle in a box

In 1D,



or



matrix of size $n \times n$
n = # basis fxn in a cell

PBC

$$\mathbb{H} = \begin{pmatrix} A & B & C & & & \tilde{C} & \tilde{B} \\ \tilde{B} & A & B & C & & & \tilde{C} \\ \tilde{C} & \tilde{B} & A & B & C & & \\ & & & \ddots & & & \\ C & & & \tilde{C} & \tilde{B} & A & B \\ B & C & & & \tilde{C} & \tilde{B} & A \end{pmatrix}$$

PBC

iii) Dynamical matrix

The $\mathbb{H}$ matrix can be <u>analytically block diagonalized</u>!

because of its systematic structure.

wave vector

lattice constant

$$
\begin{pmatrix}
\hat{C} & \hat{B} & A & B & C & & \\
 & \hat{C} & \hat{B} & A & B & C & \\
 & & \hat{C} & \hat{B} & A & B & C
\end{pmatrix}
\begin{pmatrix}
\boxed{c}\, e^{-2ika} \\
\boxed{c}\, e^{-ika} \\
\boxed{c} \\
\boxed{c}\, e^{ika} \\
\boxed{c}\, e^{2ika}
\end{pmatrix}
=
\begin{pmatrix}
\hat{C}\boxed{c}\, e^{-3ika} + \hat{B}\boxed{c}\, e^{-2ika} + A\boxed{c}\, e^{-ika} + B\boxed{c} + C\boxed{c}\, e^{ika} \\
\hat{C}\boxed{c}\, e^{-2ika} + \hat{B}\boxed{c}\, e^{-ika} + A\boxed{c} + B\boxed{c}\, e^{ika} + C\boxed{c}\, e^{2ika} \\
\hat{C}\boxed{c}\, e^{-ika} + \hat{B}\boxed{c} + A\boxed{c}\, e^{ika} + B\boxed{c}\, e^{2ika} + C\boxed{c}\, e^{3ika}
\end{pmatrix}
$$

$$
= \begin{pmatrix}
D(k)\boxed{c}\, e^{-2ika} \\
D(k)\boxed{c}\, e^{-ika} \\
D(k)\boxed{c} \\
D(k)\boxed{c}\, e^{ika} \\
D(k)\boxed{c}\, e^{2ika}
\end{pmatrix}
= E \begin{pmatrix}
\boxed{c}\, e^{-2ika} \\
\boxed{c}\, e^{-ika} \\
\boxed{c} \\
\boxed{c}\, e^{ika} \\
\boxed{c}\, e^{2ika}
\end{pmatrix}
$$

$$\Leftrightarrow \boxed{D(k)}\boxed{c} = E\boxed{c}$$

block diagonalization by e^{imka}

$$
\begin{pmatrix}
D(k) & & & & \\
 & D(k) & & & \\
 & & D(k) & & \\
 & & & \ddots & \\
 & & & & D(k)
\end{pmatrix}
$$

$$\boxed{D(k)} = \boxed{\hat{C}}\, e^{-2ika} + \boxed{\hat{B}}\, e^{-ika} + \boxed{A} + \boxed{B}\, e^{ika} + \boxed{C}\, e^{2ika}$$

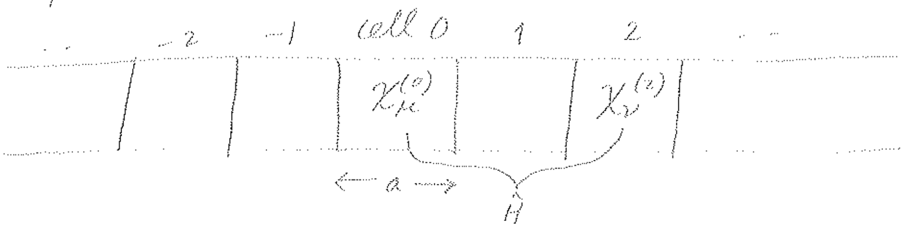
Dynamical matrix (k-dependent)

Diagonalization of a very large (or infinitely large) matrix

$\Longrightarrow$ Diagonalization of $n \times n$, k-dependent matrix for various k's

$$\boxed{D(k)}\boxed{c}(k) = E(k)\boxed{c}(k)$$

iv) Computational steps

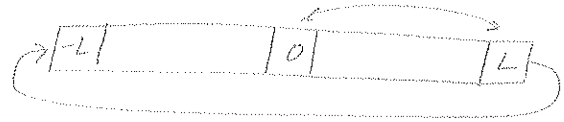


$$H_{\mu\nu}^{(m)} = \langle \chi_\mu^{(0)} | \hat{H} | \chi_\nu^{(m)} \rangle$$ (For simplicity, $\{\chi\}$ are orthonormal)

$$H_{\mu\nu}(k) = \sum_{m=-\infty}^{+\infty} H_{\mu\nu}^{(m)} \exp(imka)$$

$$\approx \sum_{m=-L}^{+L} H_{\mu\nu}^{(m)} \exp(imka)$$ L : long-range cutoff

interaction sufficiently small



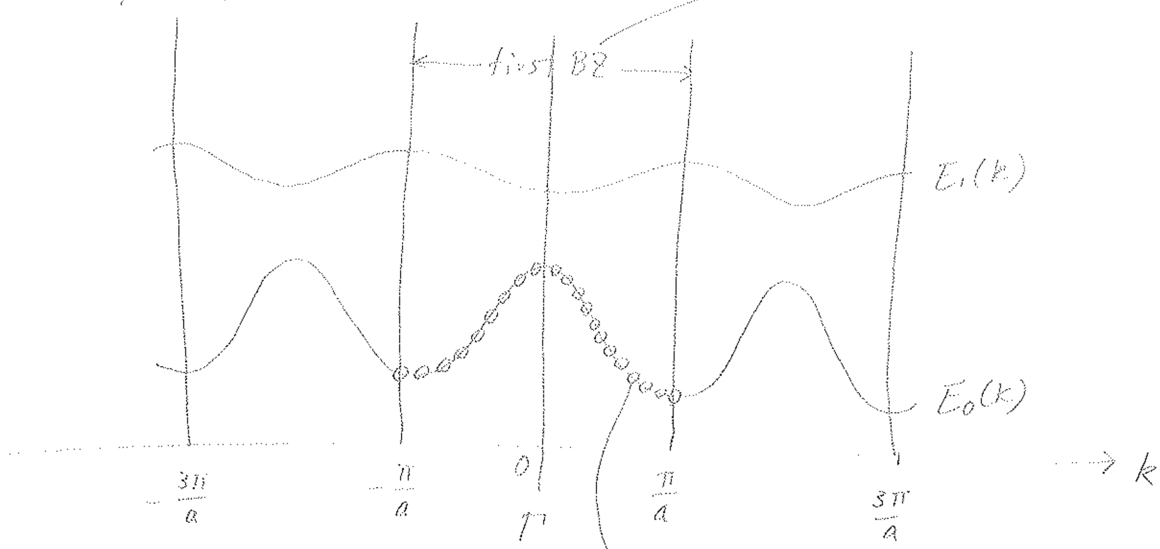
$$\sum_\nu \underbrace{H_{\mu\nu}(k)}_{\text{Dynamical Hamiltonian}} C_{\nu p}(k) = \underbrace{E_p(k)}_{\text{Energy band}} \underbrace{C_{\mu p}(k)}_{\text{MO, Bloch orbital coefficient}}$$

periodic in every $\frac{2\pi}{a}$ period

$\boxed{k\hbar = \text{momentum}}$

$$\exp(im(k+\frac{2\pi}{a})a) = \exp(imka)$$

Brillouin zone



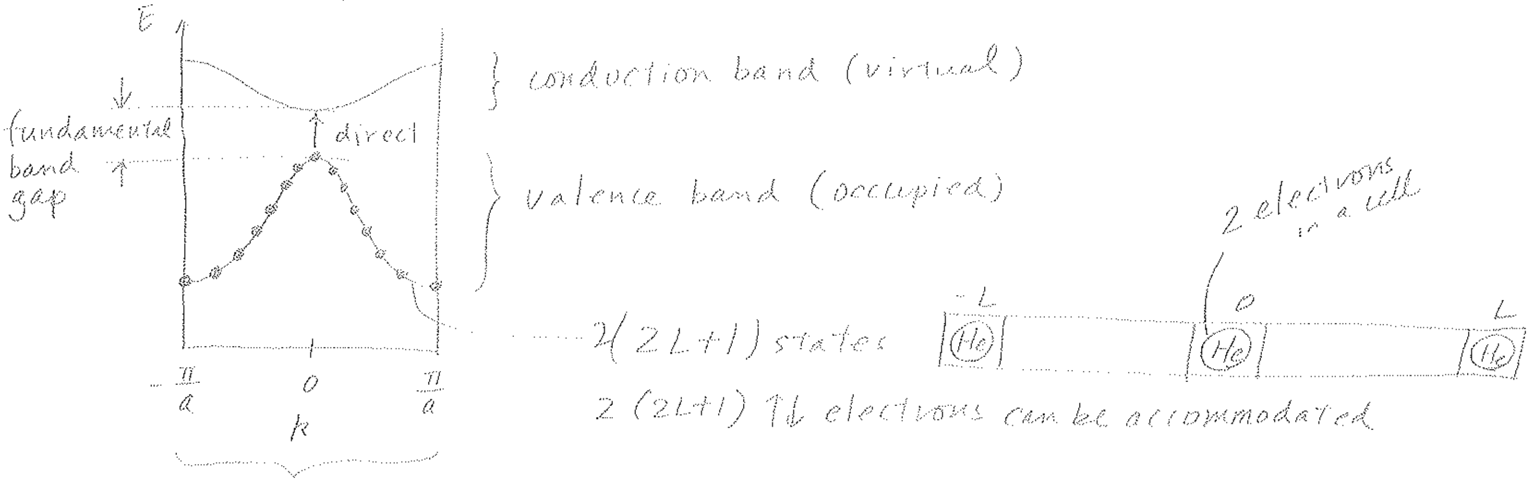
if there's only 1 basis function per cell there should be $2(2L+1)$ one electron state for each band

$$k = 0, \frac{\pm 1}{2L+1}\frac{\pi}{a}, \ldots \pm \frac{\pi}{a}$$

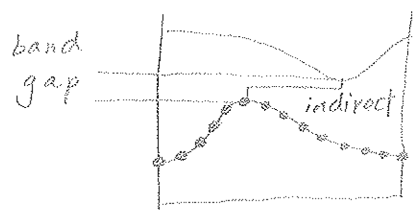
$$\varphi_p(k) = \frac{1}{\sqrt{2L+1}} \sum_\mu \sum_m C_{\mu p}(k) e^{imka} \chi_\mu^{(m)}(\mathbf{r})$$ — Bloch orbital

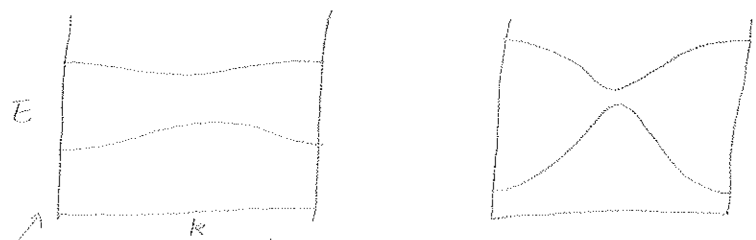
V) Metal versus insulators / semi conductors

ⓐ Insulator / semi conductors



Σ momentum = 0





small mobility

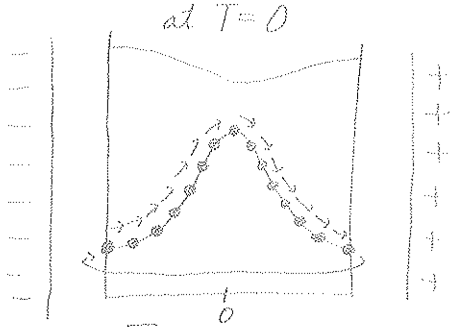
$\frac{\partial E}{\partial k}$ = group velocity

dispersion

large mobility

Conductivity and resistivity

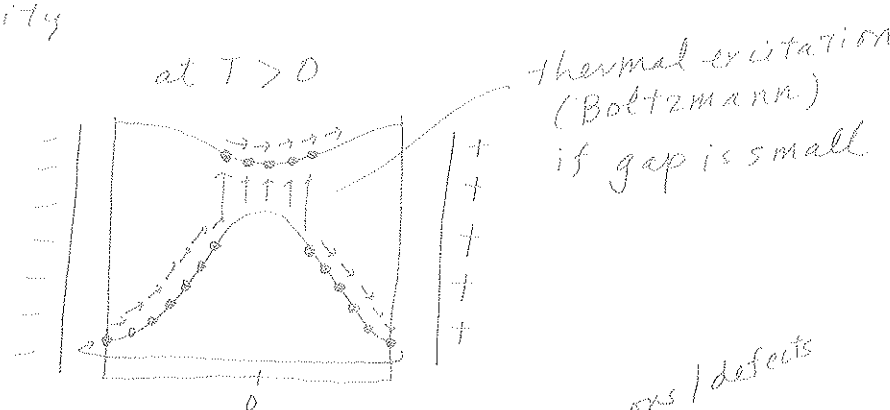
at T = 0



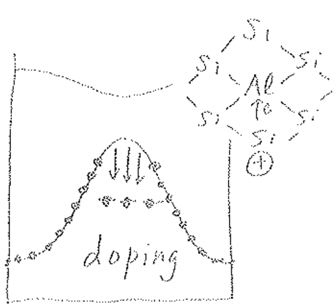
Σ momentum = 0!

NO conductivity

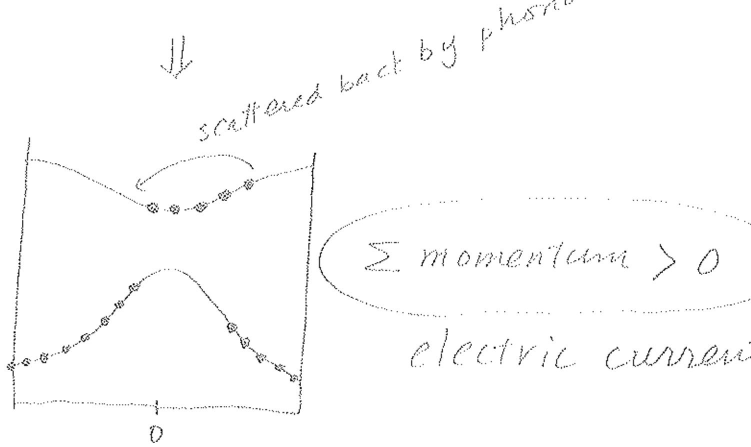
at T > 0



⇓



In semi conductors T increases / doping more excitations more current

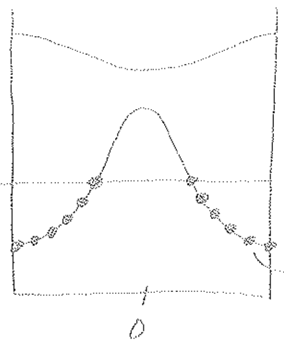


Σ momentum > 0

electric current

(b) Metals / semimetals

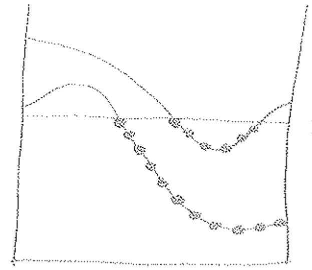
zero gap



Fermi level

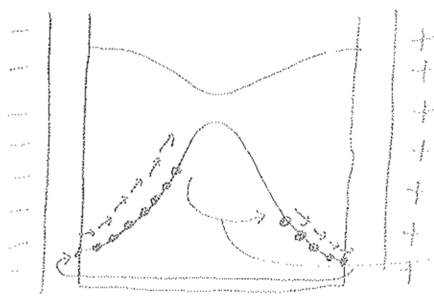
2(2L+1) states.

one electron / cell → the band is only half filled



semimetal

zero gap



scattering by phonons and defects tends to restore Σ momentum = 0 state

in metals higher T more phonons lower current

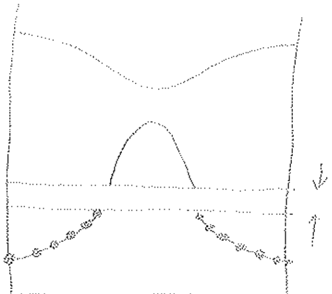
Σ momentum > 0

current

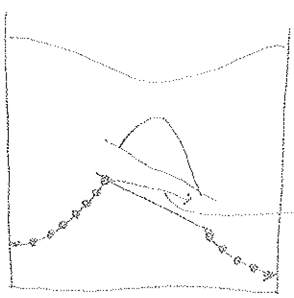
(c) Superconductors

(March et al "The Many-Body Problem in QM"
Tinkham "Intro to Superconductivity"
Phillips "Advanced Solid State Phys.")

Bardeen - Schrieffer - Cooper (BCS) theory



gap created by electron phonon interaction



scattering to restore the Σ momentum = 0 state prohibited by the gap

permanent current

Σ momentum > 0