~~Lect 14~~ LECTURE 14

Tight Binding Model illustrated.

As usual life is simpler in 1D

N sites with a periodic boundary condition:

$$H = K + \sum_j V_j \qquad K = \frac{P^2}{2m} \qquad V_j = V(r - R_j)$$

$$H|m\rangle = (K + V_m)|m\rangle + \sum_{j \neq m} V_j |m\rangle$$

$$(K + V_m)|m\rangle = \epsilon_{atomic}|m\rangle$$

ϵ_{atom} = energy of e⁻ on site m in the absence of other nuclei.

$$H_{n,m} = \langle n|H|m\rangle = \epsilon_{atomic}\,\delta_{m,n} + \sum_{j \neq m} \langle n|V_j|m\rangle$$

The simplest model is to assume that an electron can hop only from the site n to the site m

$$\sum_{j \neq m} \langle n|V_j|m\rangle = \begin{cases} V_0 & n = m \\ -t & n = m \pm 1 \\ 0 & \text{otherwize} \end{cases}$$

$$\begin{cases} H_{n,m} = \epsilon_{atomic}\,\delta_{n,m} - t\,(\delta_{n,m+1} + \delta_{n,m-1}) \\ \quad + V_0 \end{cases}$$

→ This hamitonian is very popular and is known ~~as~~ as the tight binding chain. Notice, no spin involved.

Lets solve this model:

Since the electrons have very large m.f.p. we should consider the solution in a form:

$$\phi_n = \frac{e^{-ikna}}{\sqrt{N}} \times e^{i\omega t}$$

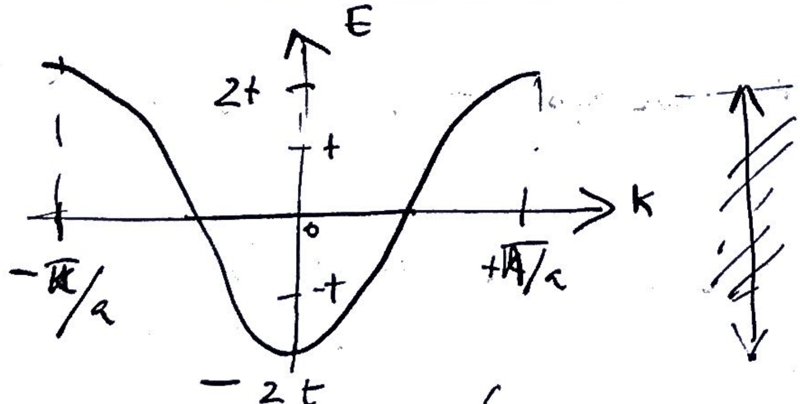
$\uparrow$ # of sites in chain

B/c of the periodic b.c. the momentum is quantaised $\Rightarrow$ $L = NA$ ~~ϕc~~

$$\sum_m H_{n,m}\phi_m = \epsilon_0 \frac{e^{-ikna}}{\cancel{\sqrt{N}}} - t\left(\frac{e^{-ik(n+1)a}}{\cancel{\sqrt{N}}} + \frac{e^{-ik(n-1)a}}{\cancel{\sqrt{N}}}\right) = E\frac{e^{-ikna}}{\cancel{\sqrt{N}}} \Rightarrow$$

$$\epsilon_0 - t\left(e^{-ika} + e^{+ika}\right) = E \Rightarrow$$

$$\boxed{E = \epsilon_0 - 2t\cos ka} \qquad \phi_n = \frac{1}{\sqrt{N}} e^{-ikna}$$



allowed energy band $= 4t$.
$\equiv$ band width $= W$

Within the band for any k exists at least 1 E.

Not $W \sim 4t \leftarrow$ amplitude of hopping between the nn sites.

— if there are N sites in the system:
The total size of the chain: $N \cdot a$

and $k = \frac{2\pi}{L = Na} \cdot m$ $\quad m = 1, 2, 3, \ldots$

Lets return to $E = \epsilon_0 - 2t \cos ka$
and for small ka $\quad \cos x \sim x \Rightarrow$

$$E = \text{const} + |t| a^2 k^2 = \frac{\hbar^2 k^2}{2m^*} \Rightarrow$$

$$\boxed{m^* = \frac{\hbar^2}{(2|t|a^2)}}$$

mass of the electron in the chain.

The density of states $\frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE}$

$\frac{dN}{dk} = \frac{L}{2\pi} = \frac{N \cdot a}{2\pi}$ $\quad$ New

from $E(k) = \epsilon_0 - 2|t| \cos ka$

$$\frac{dE}{dk} = 2ta \sin ka = 2ta\sqrt{1 - ((E-\varepsilon)/(2t))^2}$$

$\cos^2 x + \sin^2 x = 1$
$\sin^2 x = \sqrt{1 - \cos^2 x}$

Thus $\quad \frac{dN}{dE} = \underbrace{\frac{dN}{dk}}_{\frac{N \cdot a}{2\pi}} \cdot \frac{dk}{dE} =$

$$= \frac{N\cancel{a}}{\cancel{2}\pi} \frac{1}{\cancel{2}t\cancel{a}\sqrt{1 - ((E-\varepsilon)(2t))^2}} \cdot \cancel{2} \times \cancel{2} \text{ spins}$$

2 energy states per each k

$$= \frac{N}{\pi t\sqrt{1 - ((E-\varepsilon) \cdot (2t))^2}}$$

if the chain is monovalent then band is half

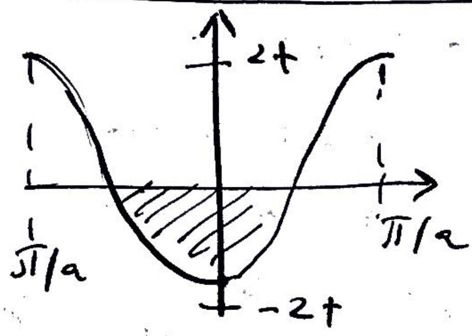
$$\frac{dN}{dE} = \frac{N}{\pi |t|}$$

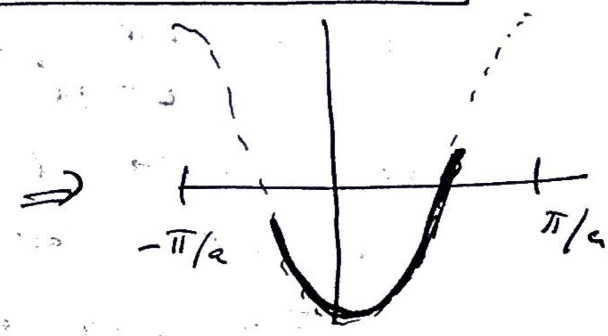
$\varepsilon = \epsilon_{\text{field}}$ $\Rightarrow$

The system is a metal.

With 2 electrons per atom the system is completely full and the system is dielectric

$\boxed{\text{So filled band carries no current}}$





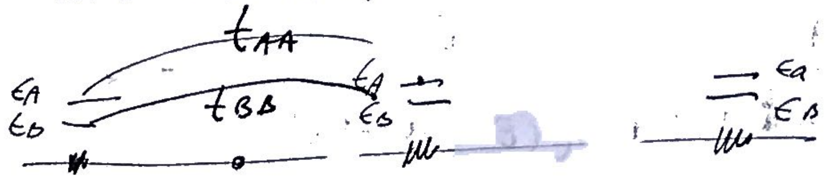
electric field E means extra momentum $\vec{p}$

Multiple Bands

We can expand our LCAO model to the case when:

- multiple orbitals per atom
- multiple atom per U.C. (THIS WILL BE YOUR HW)

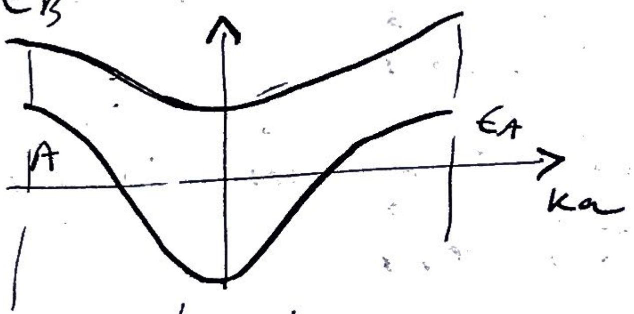
Consider an atom with 2 orbitals having eigenstates ϵ_a and ϵ_b – all atomic.



the terms
$\langle n | V | n \rangle = V_0$
$\langle m | V | m \rangle = V_0 \neq 0$
just the energy shift

To make our life easier let me assume that those orbitals are independent from each other; Each dispersion is:

$$\begin{cases} E = \epsilon_A - 2t_{AA}\cos ka \\ E = \epsilon_B - 2t_{BB}\cos ka \end{cases}$$



$t_{AA} = 1$
$t_{BB} = 2$
$\epsilon_A = 0$
$\epsilon_B = 4$

> Notice!
> This is the case which we call **divalent** and **NOT DIATOMIC**!

if Bands overlap = a metal
not overlap = Insulator

for top the band ~~expand~~ extends from
$\epsilon_A - 2t_{AA}$ to $\epsilon_A + 2t_{AA}$
and so is for ϵ_B

if $\begin{cases} \epsilon_A + 2t_{AA} < \epsilon_B - 2t_{BB} \\ \text{or} \\ \epsilon_B + 2t_{BB} < \epsilon_A - 2|t_{AA}| \end{cases}$ NO OVERLAP DIALECTRIC

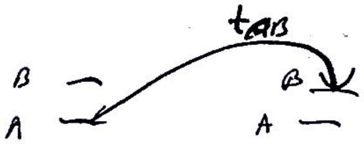
OTHERWISE IT IS A METAL

or

$$|\epsilon_A - \epsilon_B| > 2(|t_{AA}| - |t_{BB}|)$$ a condition for dielectric

$\epsilon_A \simeq \epsilon_A^{atomic} + v_0$

Lets assume that we can allow t_{AB} hoping.



$$\begin{cases} E\phi_n^A = \epsilon_A \phi_n^A - t_{AA}\phi_{n+1}^A - t_{AA}^*\phi_{n-1}^A \\ - t_{AB}\phi_{n+1}^B - t_{AB}^*\phi_{n-1}^B \\ E\phi_n^B = \epsilon_B\phi_n^B - t_{BB}\phi_{n+1}^B - t_{BB}^*\phi_{n-1}^B - \\ - t_{AB}\phi_{n+1}^A - t_{AB}^*\phi_{n-1}^A \end{cases}$$

using $\phi_n^A = A e^{ikna}$
$\phi_n^B = B e^{ikna}$ $\Rightarrow$

$$\begin{cases} EA = (\epsilon_A - t_{AA}e^{ika} - t^*_{AA}e^{-ika})A + \\ (-t_{AB}e^{ika} - t_A^* e^{-ika})B \\ EB = (\epsilon_B - t_{BB}e^{ika} - t_{BB}^* e^{-ika})B + \\ + (-t_{AB}e^{ika} - t_{AB}^* e^{-ika})A \end{cases} \Rightarrow$$

You get E!

Lets simplify

$T_{AA} = t_{AA}e^{ika} + t^*_{AA}e^{-ika}$
$= 2\mathrm{Re}[t_{AA}e^{ika}]$

The secular eqn. $\Leftarrow$

$0 = E^2 + E(T_{AA} + T_{BB} - \epsilon_A - \epsilon_B) + (\epsilon_A - T_{AA})(\epsilon_B - T_{BB}) - T_{AB}^2 \Rightarrow$

$T_{BB} = 2\mathrm{Re}[t_{BB}e^{ika}]$

$T_{AB} = 2\mathrm{Re}[t_{AB}e^{ika}]$

$$E = \frac{1}{2}\left(\epsilon_A + \epsilon_B - T_{AA} - T_{BB} \pm \sqrt{(\epsilon_A - \epsilon_B - T_{AA} + T_{BB})^2 - 4T_{AB}^2}\right)$$

THE end.