Electronic properties of solids - Tight-binding and Band Theory

Lecture 14

CHM 637

Chemistry & Physics of Materials

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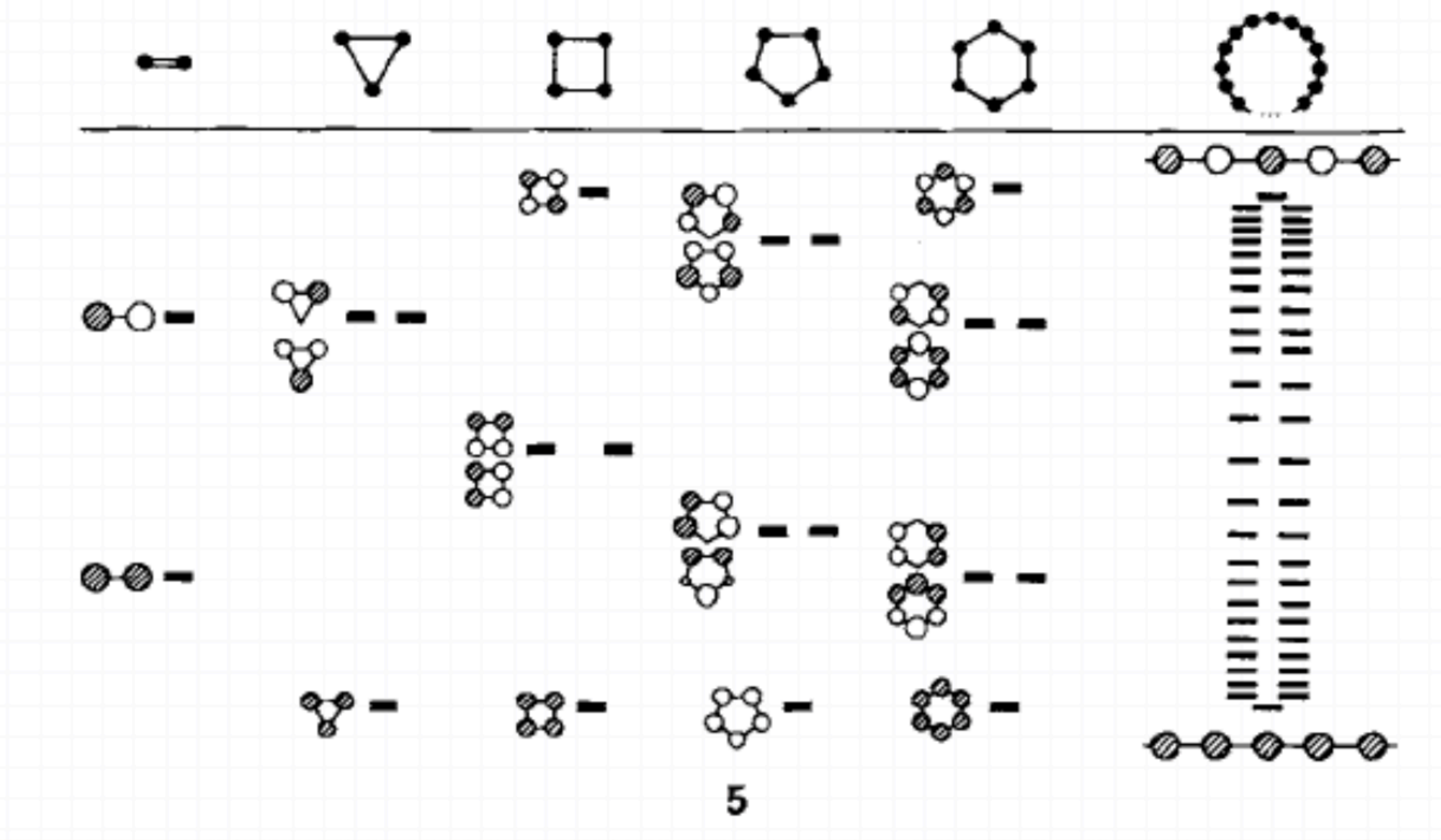
Lecture Plan

- Simple motivation to the tight-binding approach
- Energy bands, Brillouin zones and band-structure
- Typical semiconductors and insulators

Simple Motivation to T-B approach

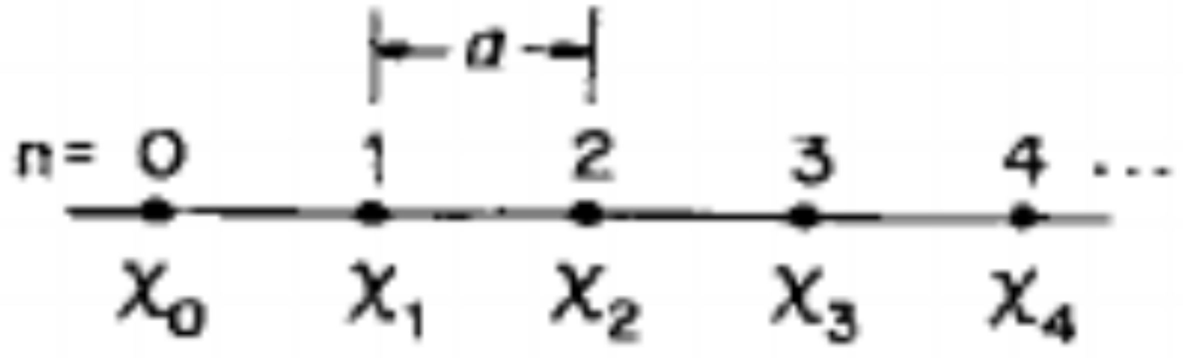
Evolution of levels in *N*-atom rings



Source: R. A. Hoffman, How Chemistry Meets Physics in the Solid State

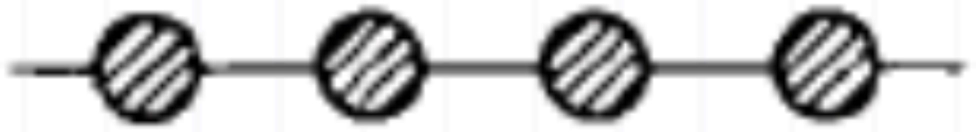
Simple Motivation to T-B approach

Meaning of k values

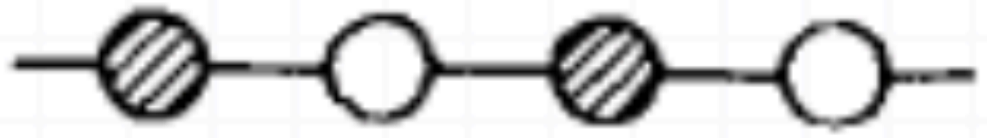


$$\psi_k = \sum_n e^{ikna} \chi_n$$

$$k = 0 \qquad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$



$$k = \frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \chi_n = \sum_n (-1)^n \chi_n = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$



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Simple Motivation for T-B approach

electron-lattice interactions cannot be ignored.

electron-electron interactions can be neglected (or taken into account in an average manner)

IPA

$$\boxed{\hat{H} = -\frac{\nabla^2}{2} + V(\vec{r})}$$

$$= \sum_{\vec{R}}{}' \tilde{V}_{at}(\vec{r}-\vec{R})$$

el-latt + mean el-el interaction

$$V_{cryst}(\vec{r}) = \sum_{\vec{R},\, b} v_{ion}(\vec{r} - \vec{R} - \vec{u}_b)$$

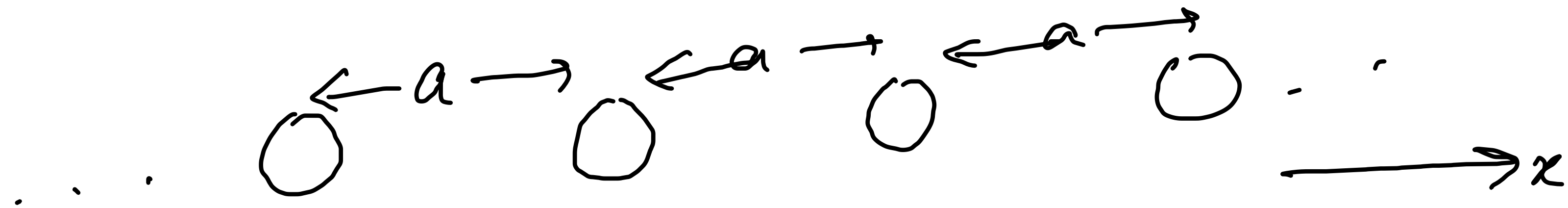
$\vec{u}_b \to$ coord. of the basis atoms

$\vec{R}$ – lattice vector

$$V_{cry}(\vec{r} + \vec{R}') = V_{cryst}(\vec{r})$$

periodic w/ lattice periodicity

1-d lattice of H atoms



N atoms

Molecular Orbital using LCAO

Let $\underline{\varphi_j(x)} \equiv \varphi_{1s}(x - \underline{j}a)$ $\quad j = 0, 1, 2 \ldots N-1$

LCAO: $\psi(x) = \sum_{j=0}^{N-1} c_j \varphi_j(x)$

Assumptions: Suppose the hamiltonian of the system is $\hat{H}$. Then we assume that

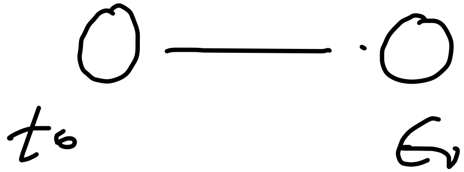
(1) $\langle \varphi_i | \hat{H} | \varphi_j \rangle = h_{ij} = \begin{cases} \epsilon_0 & \text{if } i=j \\ t & \text{if } |i-j|=1 \\ 0 & \text{if } |i-j|>1 \end{cases}$

n-n TBA (Hückel model)

(2) $\langle \varphi_i | \varphi_j \rangle = S_{ij} = \delta_{ij}$

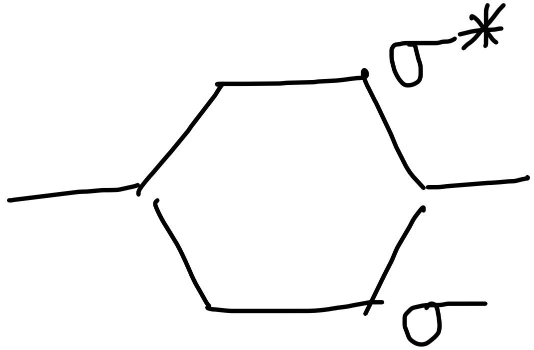
orthogonal TB.

$N = 2$



$\longrightarrow \epsilon_{\pm} = \epsilon_0 \pm t$

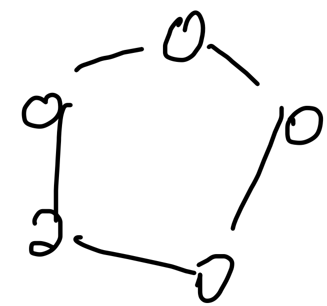
bonding and and antibonding level



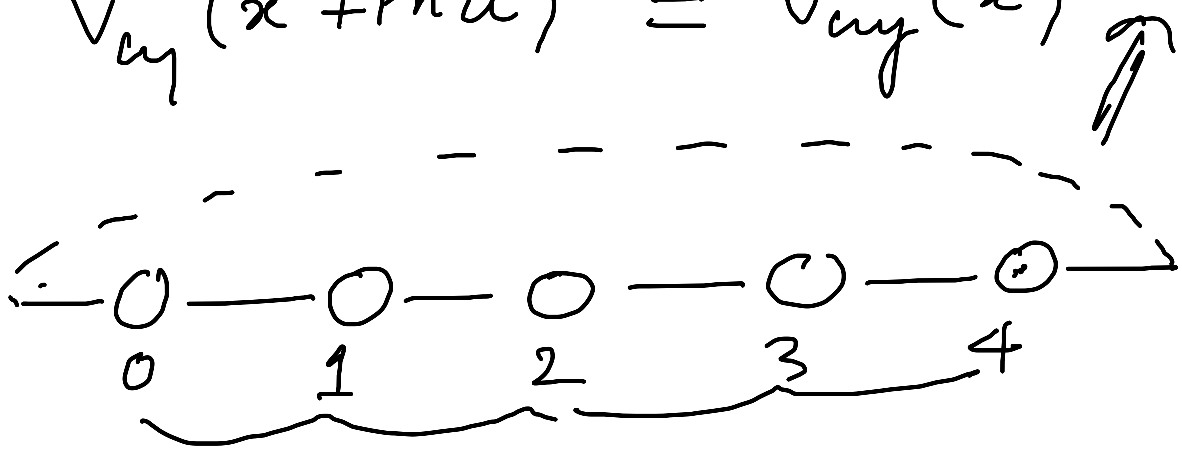
as $N \to \infty$, we get $N \to \infty$ levels spaced very closely resulting in a "band" of energies.

For treating large lattices it is convenient to assume periodic boundary conditions (Born-von Karman):

$$V_{cry}(x) = \sum_{j=0}^{N-1} v_{ion}(x - ja)$$



PBC $\Rightarrow$ $$V_{cry}(x + Na) = V_{cry}(x)$$



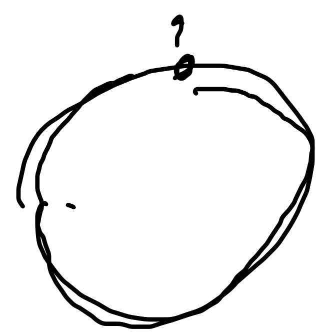
On a 1-d lattice of N atoms w/ P.B.C.

Let $$\psi_k(x) = \sum_{j=0}^{N-1} c_j(k)\,\phi_j(x).$$ (L.C.A.O)

be a solution to the lattice Schrödinger eqn $$\hat{H}\psi_k(x) = \mathcal{E}(k)\psi_k(x)$$

$$\psi_k(x+Na) = \psi_k(x) \;\therefore$$

(single-valued)



$$\psi_k(x+Na) = \sum_{j=0}^{N-1} C_j(k)\,\varphi_j(x+Na).$$

$$\varphi_j(x+Na) = \varphi_{1s}(x - ja + Na)$$

$$= \varphi_{1s}(x-(j-N)a) = \varphi_{j-N}(x)$$

$$= \sum_{j=0}^{N-1} C_j(k)\,\underbrace{\varphi_{j-N}}(x) \qquad \boxed{C_{j+N}(k) = C_j(k)}.$$

$$= \sum_{j=0}^{N-1} C_{j+N}(k)\,\varphi_j(x).$$

$$\boxed{\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{ikja} \varphi_j(x)}$$

$$\boxed{k = \frac{2\pi m}{Na}, \quad m = 0, 1, 2, \dots, N-1}$$

$$C_j(k) = \frac{1}{\sqrt{N}} e^{ikja}$$

$$\psi_k(x+a) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{ikja} \varphi_j(x+a)$$

$$= \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{ikja} e^{ika} \varphi_j(x)$$

$$= \underbrace{e^{ika}\psi_k(x) = \psi_k(x+a)}_{\text{Bloch Theorem}}$$

First Brillouin zone

Conventionally, k is taken in the range $\boxed{-\pi/a \leq k < \pi/a}$ allowed quantum no's

$\left(m = -\frac{N}{2}, -\frac{N}{2}+1, \ldots, \frac{N}{2}-1 \right)$

if $N \to \infty$, k becomes continuous.

$$E(k) = \frac{\langle \Psi_k | \hat{H} | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle} = E_0 + 2t\cos(ka)$$

resonance integral $\leftarrow t = \langle \varphi_i | \hat{H} | \varphi_{i+1} \rangle$

(β)

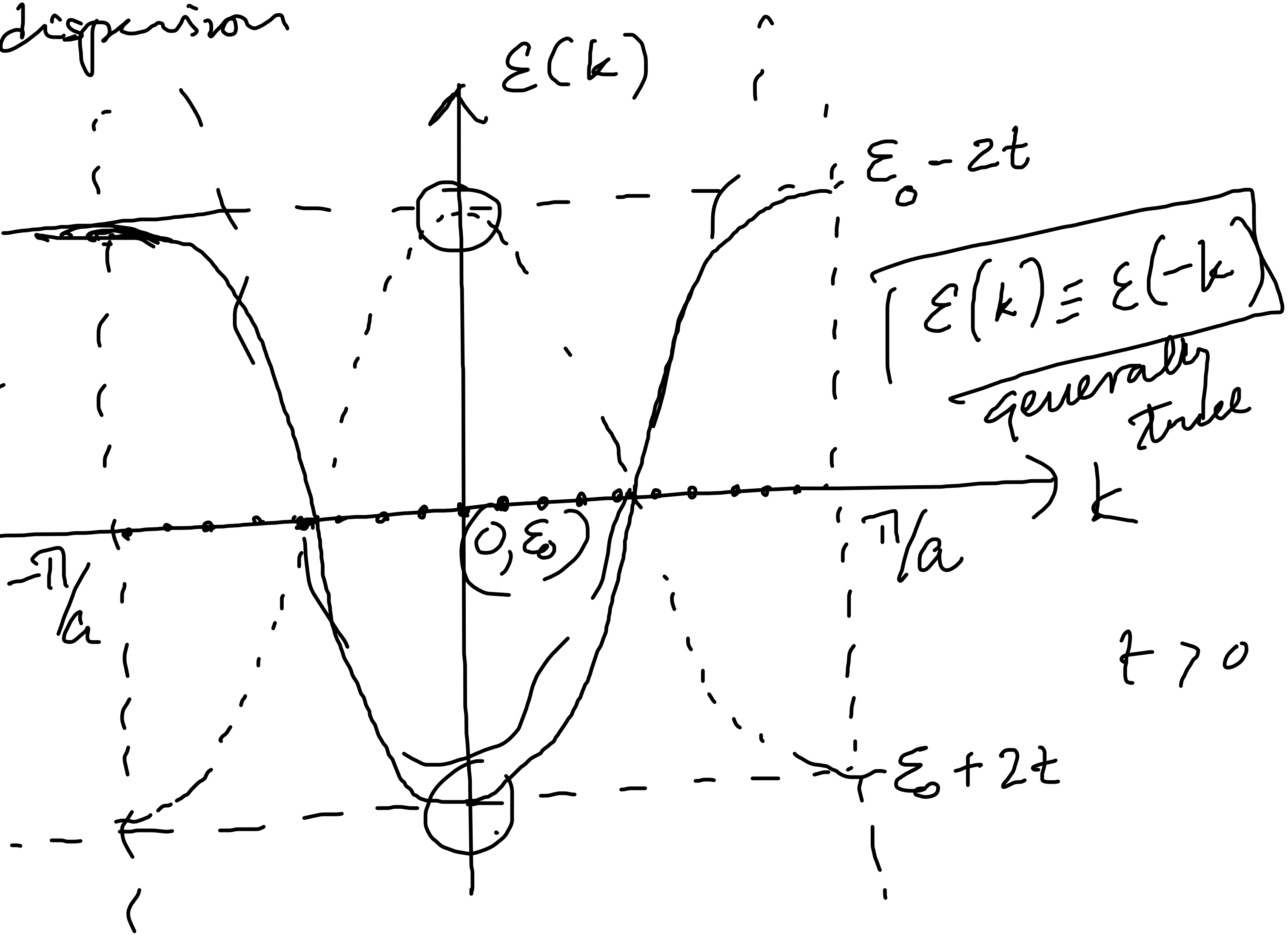
α

$E_0 \leftrightarrow \alpha$

$$t_{1s} \approx \left\langle \varphi_1 \left| \frac{-1}{|\vec{r} - \vec{R}_2|} \right| \varphi_2 \right\rangle < 0$$

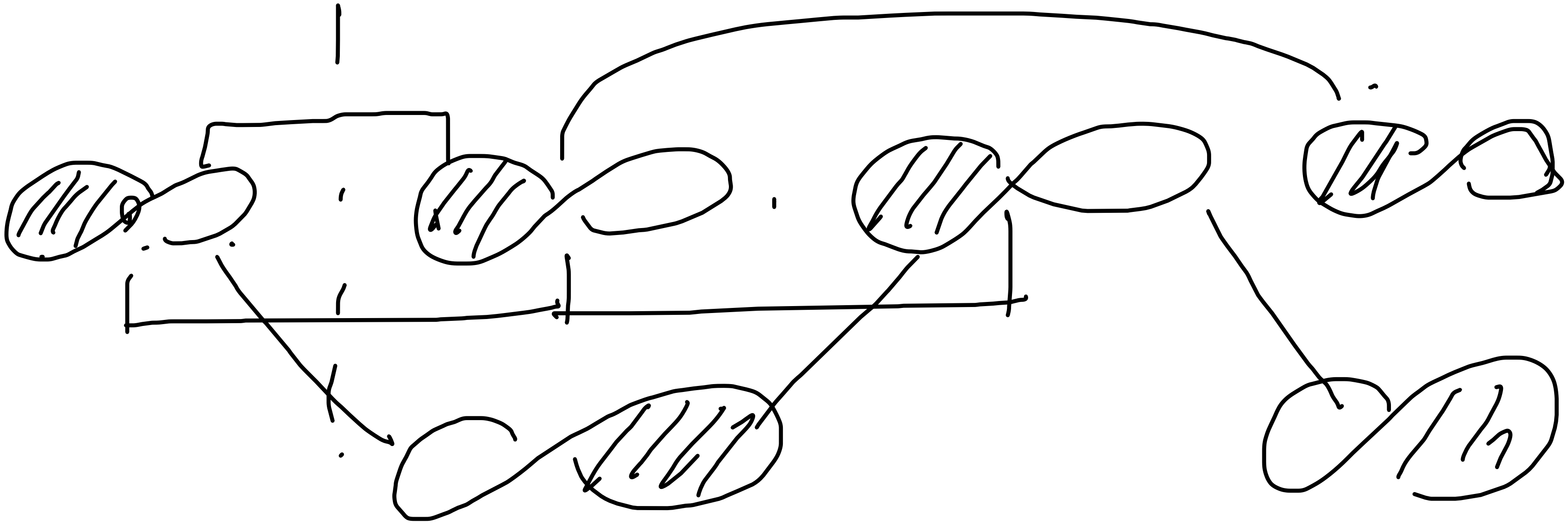
Band dispersion

$k \sim 1/a$



$\frac{2\pi m}{a}$

$\frac{2\pi j}{Na}$



$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{ikja} \varphi_j(x)$$

$$k = 0, \quad \psi_0(x) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \overset{1}{\swarrow} \varphi_j(x)$$

$$e^{i \frac{\pi}{\cancel{a}} \times j \times \cancel{a}} = e^{i(\pi j)} \qquad \psi_{\pi/a}(x) = \frac{1}{\sqrt{N}} \sum_{j=0}^{(N-1)} (-1)^j \varphi_j(x)$$

Band theory for solids: Tight-binding Approach

$$V_{cry}(\vec{r}+\vec{R}) = V_{cry}(\vec{r})$$

$$V_{cry}(\vec{r}) = \sum_{\vec{G}} V_{cry}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}}$$

$\vec{G} \longrightarrow$ reciprocal lattice vector

for ex. in 1-d w/ periodicity a

$$V_{cry}(x) = \sum_{G} V_{cry}(G)\, e^{iGx}$$

where $G = \frac{2\pi}{a} m \;,\; m \in \mathbb{Z}$

Bloch Theorem :

$$\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi_{k}(\vec{r})$$

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

where $u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$

$$\hat{H} = -\frac{\nabla^2}{2} + V_{cry}(\vec{r})$$

$$[\hat{T}_{\vec{a}}, \hat{H}] = 0$$

when $\hat{T}_{\vec{a}}\psi(\vec{r}) = \psi(\vec{r}-\vec{a})$

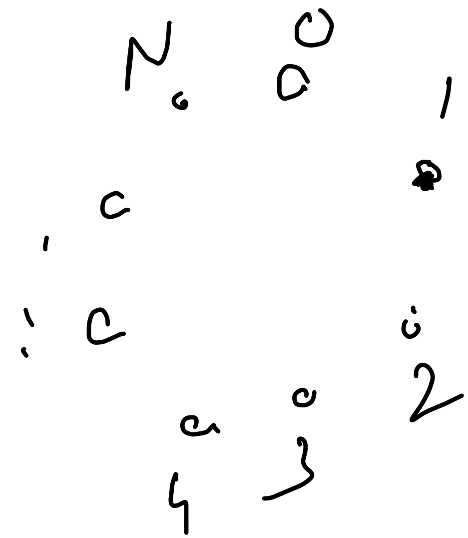
Translation operator

$\Rightarrow$

$$\hat{T}_{\vec{a}}\,\psi(\vec{r}) = \lambda\,\psi(\vec{r})$$

for eg. let's take 1-d,

$$\Rightarrow \hat{T}_a\,\psi(x) = \lambda\,\psi(x)$$



$$\Rightarrow \hat{T}_{Na} \equiv \left(\hat{T}_a\right)^N = \hat{\mathbb{1}}$$

$$\hat{T}_{Na}\,\psi(x) = \psi(x)$$

$$\lambda^N\,\psi(x) = \psi(x)$$

$\Rightarrow \lambda$ is the N^{th} root of 1

$$\Rightarrow \quad \lambda_m = \exp\left(i\frac{2\pi m}{N}\right), \quad m = 0, 1, 2, \dots N-1$$

or

$$\underline{N/2 \leq m < \frac{N}{2} - 1}$$

$$k : k = \frac{2\pi m}{Na}$$

$$\boxed{\hat{T}_a \psi_k(x) = e^{ika} \psi_k(x)}$$

$\because [\hat{T}_a, \hat{H}] = 0 \quad \{\psi_k(x)\}$ are also simultan eigenfunction of $\hat{H}$.

$$\Rightarrow \boxed{\hat{H}\psi_k(x) = E_k \psi_k(x)}$$

In T.B.A. (L.C.A.O.)

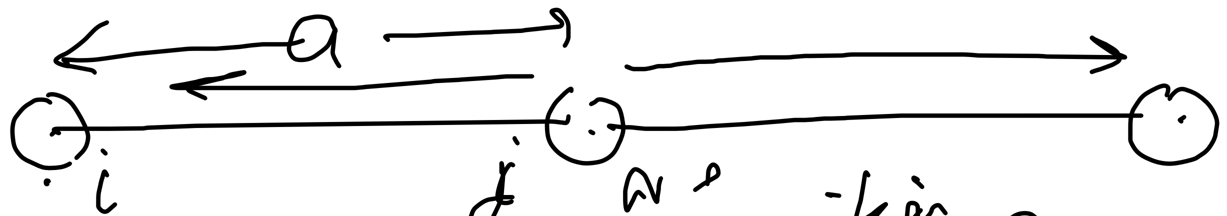
$$\psi_k(x) = \sum_{j=0}^{N-1} C_j(k)\, \varphi_j(x)$$

$$\varphi_j(x) \equiv \varphi_{nlm}(x - ja)$$

$$\hat{T}_a \psi_k(x) = e^{ika} \psi_k(x) \quad , \quad \hat{T}_{Na} = \mathbb{1}$$

$$C_j(k) = \frac{1}{\sqrt{N}} e^{ikja}$$

$$\boxed{\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{ikja} \varphi_j(x)}$$



$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{ikja} \varphi_j(x)$$

$$E(k) = \langle \psi_k | \hat{H} | \psi_k(x) \rangle$$

$$\hat{H} = \sum_{j=0}^{N-1} \epsilon |\varphi_j\rangle\langle\varphi_j| + t\sum_{j=0}^{N-1}\left\{ |\varphi_j\rangle\langle\varphi_{j+1}| + h.c. \right\}$$

$$|\varphi_j\rangle \equiv \varphi_j(x)$$

$$\langle x|\varphi_j\rangle$$

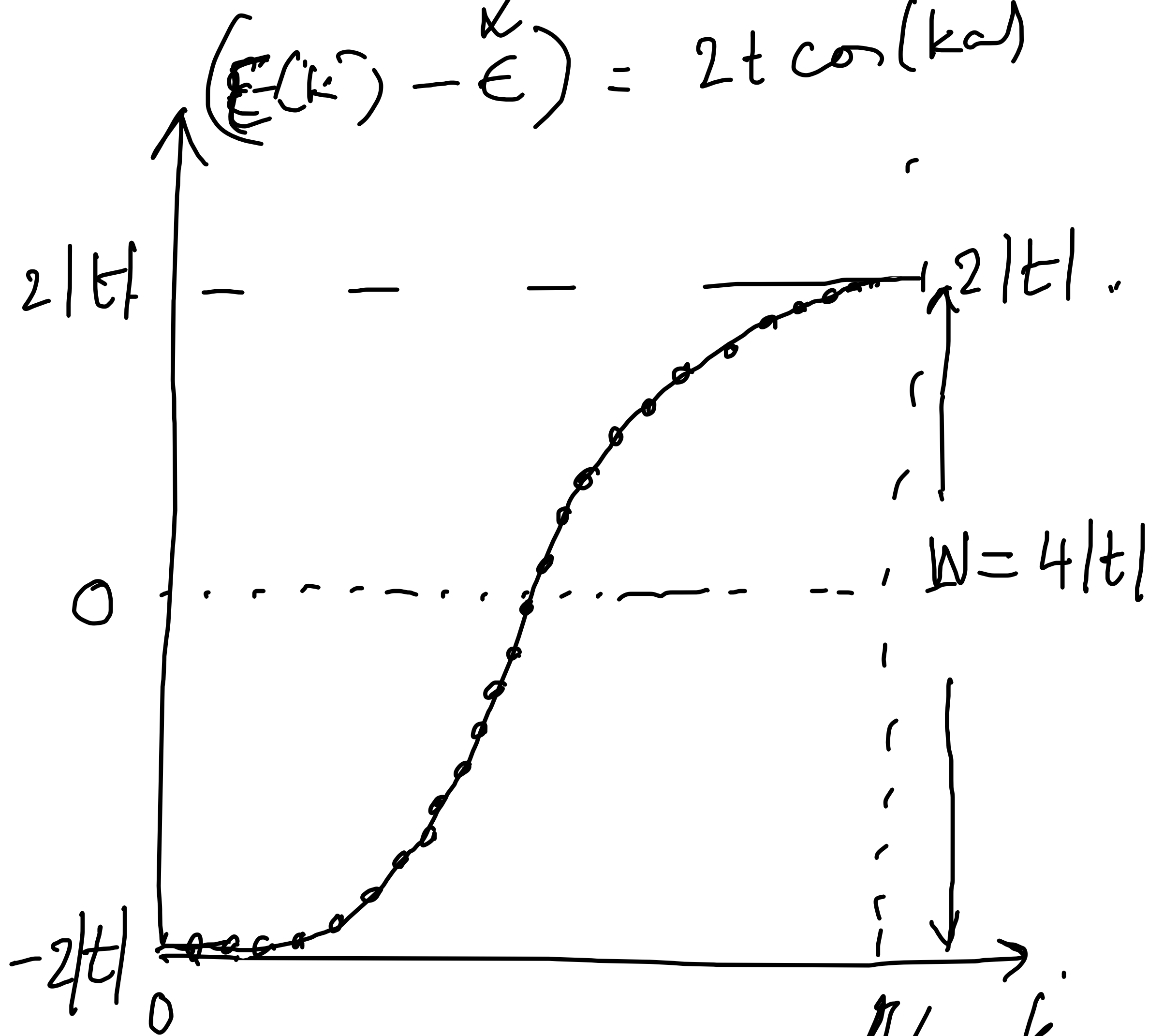
$$\boxed{E(k) = \epsilon + 2t\cos(ka)}$$

$E(k) = E(-k)$

$t < 0$

Band/dispersion curve $\equiv$ plotting energy vs quantum number

$\Delta k \sim \frac{2\pi}{Na} \to 0$ as $N \to \infty$



doubly occupied due spin degeneracy

No. of occupied levels in a 1-d lattice w/ one electron per site = $N/2$

$\Rightarrow$ In the (hypothetical) H 1-d lattice the band is half-filled

Length of each k-pt in the B.Z.

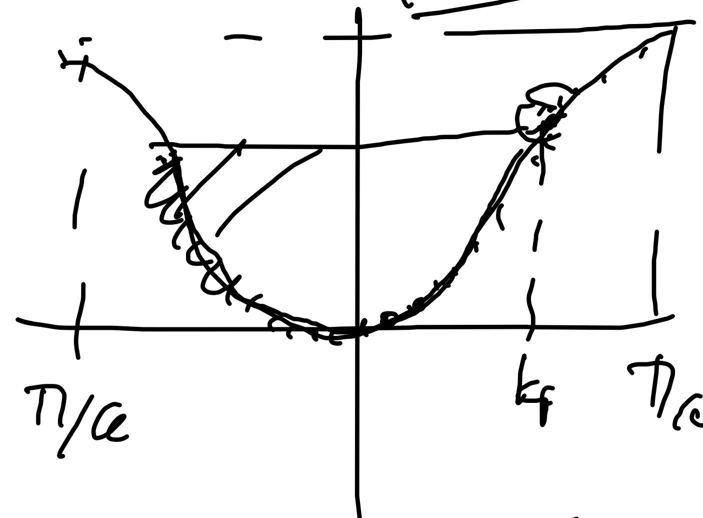
$$= \frac{2\pi}{Na} = \frac{2\pi}{L}$$

$\Rightarrow$ No. of k-pts per unit length of B.Z.

$= L/2\pi$

Let k_F be the quantum no. of the last level occupied. Then

$$\boxed{\langle \vec{v} \rangle = 0}$$



the no. of states in a length $2k_F$ of the B.Z. is

$$= 2k_F \times \frac{L}{2\pi}$$

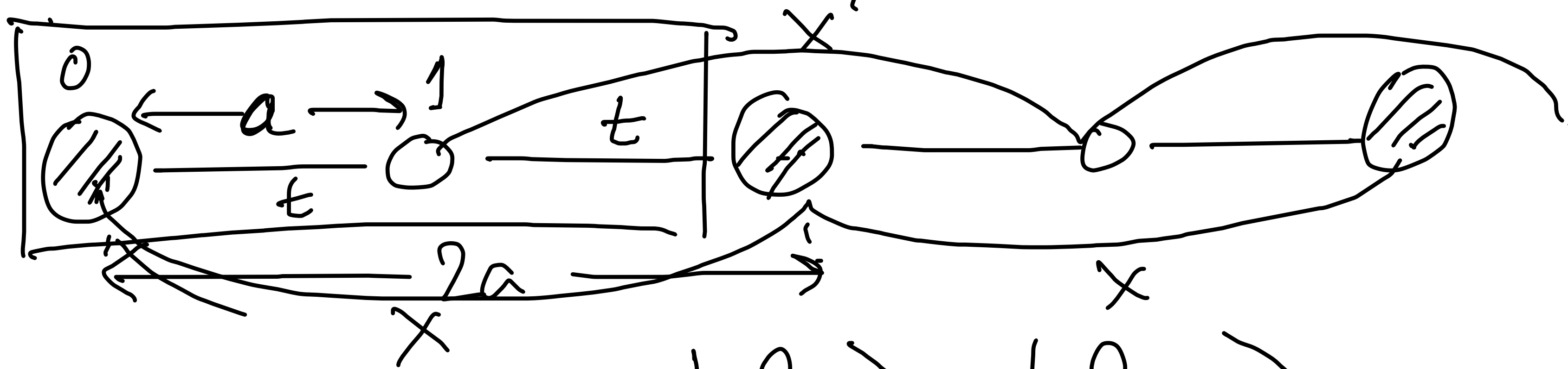
$$= N/2 \implies k_F = \frac{\pi}{2} \times n \rightarrow (N/L)$$

fermi eln $\rightarrow E_F - \epsilon = -2t\cos(k_F a)$

$$= -2t\cos\left(\frac{n\pi a}{2}\right)$$

$\Rightarrow$ partially filled bands lead to metallic conduction.

1-d chain/lattice w/ basis 2.



$$|\varphi_{\mu,j}\rangle \longrightarrow |\varphi_{0,j}\rangle, |\varphi_{1,j}\rangle$$

Nearest-neighbours, orthogonal, T.B

$$\hat{H} = \sum_{j=0}^{N-1} \left\{ \epsilon_0 |\varphi_{0,j}\rangle\langle\varphi_{0,j}| + \epsilon_1 |\varphi_{1,j}\rangle\langle\varphi_{1,j}| \right\}$$

$$+ t \sum_{j=0}^{N-1} \left\{ |\varphi_{0,j}\rangle\langle\varphi_{1,j}| + |\varphi_{0,j}\rangle\langle\varphi_{1,j-1}| + h.c. \right\}.$$

$$\langle \varphi_{\mu,j} | \hat{H} | \varphi_{\mu',j'} \rangle = \begin{cases} 0 & \text{if } \mu = \mu' \,\&\, j \neq j' \\ 0 & \text{if } |j - j'| > 1 \\ t & \text{otherwise} \\ \epsilon_\mu & \text{if } \mu = \mu' \,\&\, j = j' \end{cases}$$

L.C.M.O.

$$|\psi_k\rangle = \sum_{j=0}^{N-1} \underline{\underline{c_j(k)}} \left\{ a_0(k) |\varphi_{0,j}\rangle + a_1(k) |\varphi_{1,j}\rangle \right\}$$

$$\hat{T}_a |\psi_k\rangle = e^{ik2a} |\psi_k\rangle$$

$$\Rightarrow \underline{\underline{c_j(k) = e^{i2kja}}}$$

$$\langle \varphi_{0,j} | \hat{H} | \psi_k \rangle = \langle \varphi_{0,j} | \psi_k \rangle E(k)$$

$$\langle \varphi_{1,j} | \hat{H} | \psi_k \rangle = \langle \varphi_{1,j} | \psi_k \rangle E(k)$$

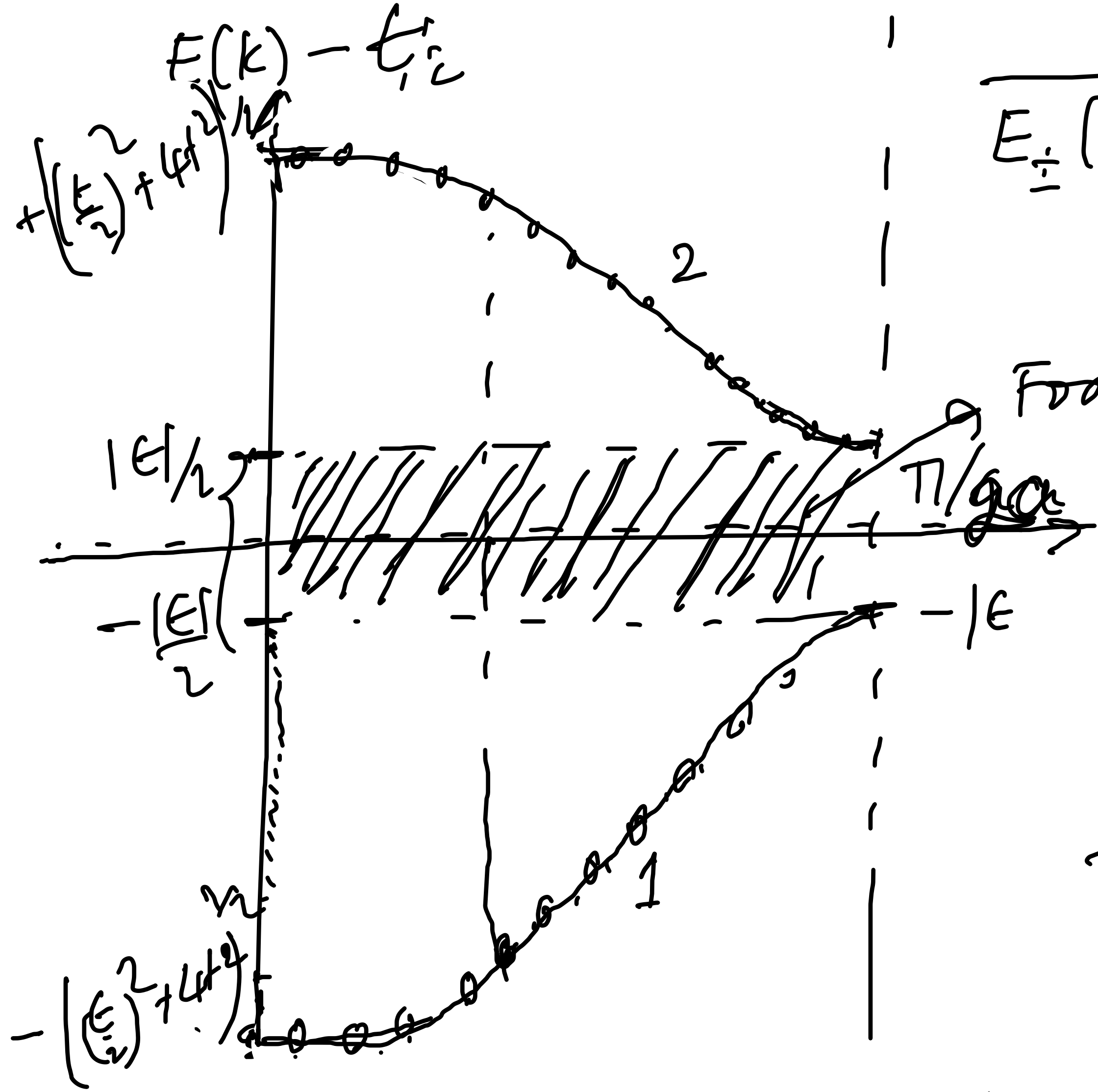
$$\Downarrow$$

$$\left|\begin{array}{l} (\epsilon_0 - E(k))\, a_0(k) + \underline{2t\, e^{-ika} \cos}(ka) = 0 \\ \underline{2t\, e^{ika} \cos}(ka)\, a_0(k) + (\epsilon_1 - E(k))\, a_1(k) = 0 \end{array}\right.$$

For simplicity let $\epsilon_0 \equiv 0$, $\epsilon_1 \equiv \epsilon$

$$\begin{vmatrix} -E(k) & 2t\,e^{-ika}\cos(ka) \\ 2t\,e^{ika}\cos(ka) & \epsilon - E(k) \end{vmatrix} = 0$$

$$\boxed{E_\pm(k) = \frac{\epsilon}{2} \pm \sqrt{\left(\frac{\epsilon}{2}\right)^2 + 4t^2\cos^2(ka)}}$$



$\nearrow \tilde{E}(k)$

$$E_\pm(k) = \frac{\epsilon}{2} = \pm\sqrt{\left(\frac{\epsilon}{2}\right)^2 + 4t^2\cos^2(ka)}$$

Forbidden energy gap or band gap

when $k=0$

$$\tilde{E}_\pm(0) = \pm\sqrt{\left(\frac{\epsilon}{2}\right)^2 + 4t^2}$$

$$\tilde{E}_\pm(\pi/2a) = \pm\sqrt{\left(\frac{\epsilon}{2}\right)^2}$$

$$= \pm\frac{|\epsilon|}{2}$$

$$E_g = \underline{\underline{|\epsilon|}}$$

Total no. of solution = Tot. no. of unit cells (N) x no. of basis atoms/orbitals per unit cell

Each energy level can occupy 2 $\bar{e}$'s w/ opposite spin

No. of states is the same in both band
= N,

$\Rightarrow$ Only the lower band is filled at 0K and it is completely filled.
$\Rightarrow$ poor conductor. i.e. insulating.