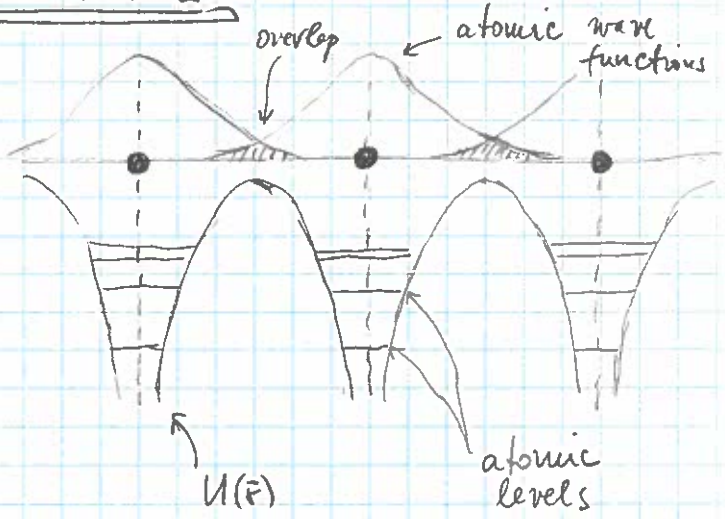
(III) TIGHT-BINDING MODEL



- Assumes electrons are tightly bound in atomic orbitals; "hopping" occurs due to small wavefunction overlaps

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \sum_i U_{at}(\vec{r}-\vec{R}_i) \qquad (1)$$

atomic potential

- We work in the basis of atomic wavefunctions $\phi_n(\vec{r})$

$$H_{at}\phi_n = E_n\phi_n, \qquad H_{at} = -\frac{\hbar^2\nabla^2}{2m} + U_{at}(\vec{r}) \qquad (2)$$

- Second quantization: Introduce operator $c_n^+(R_i)$ which creates electron is state $\phi_n(\vec{r}-\vec{R}_i)$ represented by ket $|n,\vec{R}_i\rangle$

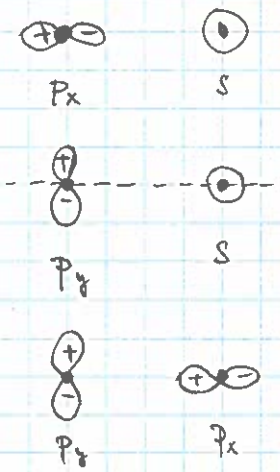
→ then, the most general tight-binding Hamiltonian can be written as:

$$\boxed{\hat{H} = \sum_{m,n}\sum_{i,j} \langle n,\vec{R}_i|H|m,\vec{R}_j\rangle\, c_n^+(\vec{R}_i)\, c_m(\vec{R}_j)} \qquad (3)$$

- Because the atomic wf $\phi_n(\vec{r})$ decay exponentially $\sim e^{-r/a_0}$ we expect matrix elements $t_{ij}^{mn} = \langle n,\vec{R}_i|H|m,\vec{R}_j\rangle$ to become negligible when $|\vec{R}_i-\vec{R}_j| \gg a_0$

→ in practice it is usually sufficient to include first (potentially second and third) neighbor hopping

- There are well-established techniques to calculate t_{ij}^{mn} for a given material but they require detailed knowledge of relevant atomic orbitals.
- The form of t_{ij}^{mn} is constrained by symmetries:

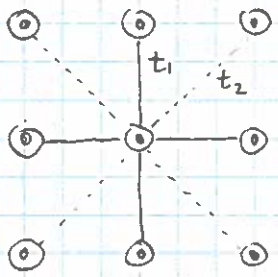


– here $t_{12}^{Ps} \neq 0$, no symmetry constraint

– here $t_{12}^{P_y s} = 0$ as the overlap integral has to be odd under reflection $y \to -y$

– similarly $t_{12}^{P_y P_x} = 0$.

<u>EXAMPLE 1:</u> <u>Single, non-degenerate orbital in 2D</u>



$$\hat{H} = \sum_i E_i\, c^\dagger(\vec{R}_i)\, c(\vec{R}_i) - \sum_{i \neq j} t_{ij}\, c^\dagger(\vec{R}_i)\, c(R_j) \qquad (4)$$

- E_i is "on-site energy", $E_i = \varepsilon_0$ for all i in monatomic lattice.
- for t_{ij} we consider only firs & second neighbor tunneling amplitudes as indicated in the figure.

$$t_{ij} = \begin{cases} t_1, & \text{first neighbor} \\ t_2, & \text{second neighbor} \\ 0, & \text{otherwise} \end{cases}$$

$$\rightarrow \hat{H} = \varepsilon_0 \sum_i c^\dagger(\vec{R}_i)\, c(\vec{R}_i) - \sum_{i,\vec{\delta}} t_{\vec{\delta}}\, c^\dagger(\vec{R}_i + \vec{\delta})\, c(\vec{R}_i) \qquad (5)$$

$\vec{\delta}$ - vectors pointing from site i to its first & second neighbors

- fourier-transform:

$$c(\vec{R}_i) = \frac{1}{\sqrt{N}} \sum_k e^{i\vec{k}\vec{R}_i} c_k$$
$$c^+(\vec{R}_i) = \frac{1}{\sqrt{N}} \sum_k e^{-i\vec{k}\cdot\vec{R}_i} c^+_k \qquad (6)$$

$$\hat{H} = \varepsilon_0 \sum_{k,k'} c^+_k c_{k'} \underbrace{\frac{1}{N}\sum_i e^{-i\vec{R}_i\cdot(\vec{k}-\vec{k}')}}_{\delta_{kk'}} - \sum_{k,k'} c^+_k c_{k'} \frac{1}{N} \sum_{i,\delta} t_\delta e^{-i\vec{R}_i\cdot(\vec{k}-\vec{k}')-i\vec{\delta}\cdot\vec{k}}$$

$$\hat{H} = \varepsilon_0 \sum_k c^+_k c_k - \sum_k c^+_k c_k \left(\sum_\delta t_\delta e^{-i\vec{\delta}\cdot\vec{k}}\right) \qquad (7)$$

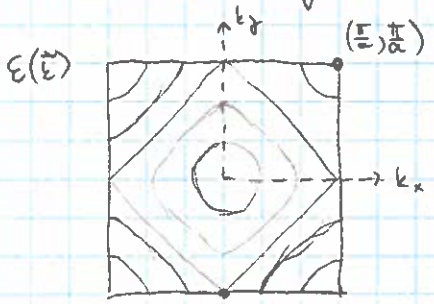
$$\boxed{\begin{aligned} \hat{H} &= \sum_k \varepsilon(\vec{k})\, c^+_k c_k \\ \varepsilon(\vec{k}) &= \varepsilon_0 - \sum_\delta t_\delta e^{-i\vec{k}\cdot\vec{\delta}} \end{aligned}} \qquad (8)$$

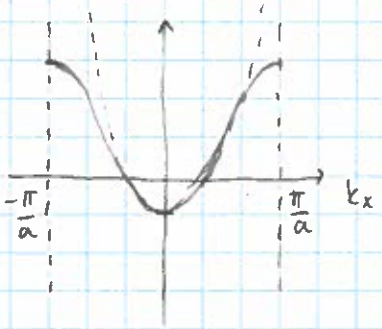
- For our model with t_1, t_2 we have:

$$\vec{\delta}_1 = a(\pm\hat{x}, \pm\hat{y}), \qquad \vec{\delta}_2 = a(\hat{x}\pm\hat{y}, -\hat{x}\pm\hat{y})$$

$$\rightarrow \quad \varepsilon(\vec{k}) = \varepsilon_0 - 2t_1(\cos ak_x + \cos ak_y) - 2t_2\left(\cos a(k_x+k_y) + \cos a(k_x-k_y)\right) \qquad (9)$$

- For simplicity now illustrate the case with $t_2 = 0$





$\varepsilon_{MIN} = \varepsilon(\vec{k}=0) = \varepsilon - 4t$

$\varepsilon_{MAX} = \varepsilon(\frac{\pi}{a}, \frac{\pi}{a}) = \varepsilon + 4t$

$W = \varepsilon_{MAX} - \varepsilon_{MIN} = 8t$

"bandwidth"

- Effective mass: Near band minima and maxima we can expand $\varepsilon(\vec{k})$ to second order to study long-wavelength behavior

(i) <u>near $\vec{k}=0$:</u>

$$\varepsilon(\vec{k}) \simeq \varepsilon_0 - 2t\left[1-\frac{(ak_x)^2}{2}+\dots + 1-\frac{(ak_y)^2}{2}+\dots\right]$$

$$= (\varepsilon_0 - 4t) + \underbrace{ta^2k^2}_{\frac{\hbar^2k^2}{2m^*}} + \dots \qquad (10)$$

$$m^* = \frac{\hbar^2}{2ta^2} \quad \text{"effective mass"}$$

$\Rightarrow$ Near $\vec{k}=0$ (the Γ point of BZ) the tight-binding electron behaves as a free particle with mass m^*.

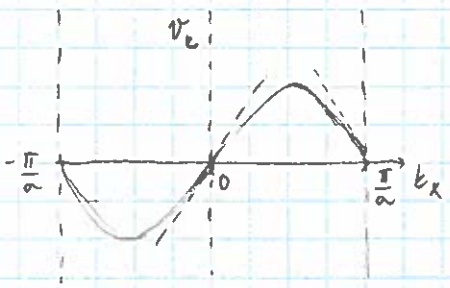
(ii) <u>near $\vec{k}=(\frac{\pi}{a},\frac{\pi}{a}) = \vec{K}$:</u>

$$\varepsilon(\vec{K}+\vec{k}) = (\varepsilon_0+4t) - ta^2k^2 + \dots \qquad (11)$$

$$m^* = -\frac{\hbar^2}{2ta^2}$$ negative effective mass, carriers are HOLES

- <u>Band velocity</u>

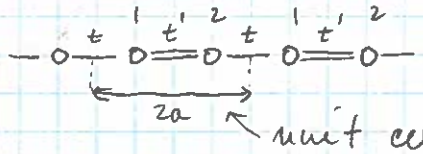
$$\vec{v}_k = \frac{1}{\hbar}\frac{\partial\varepsilon(\vec{k})}{\partial\vec{k}} = \frac{2ta}{\hbar}(\sin ak_x, \sin ak_y)$$



- near $\vec{k}=0$ we have $\vec{v}_k \simeq \frac{2ta^2}{\hbar}\vec{k} = \frac{\hbar\vec{k}}{m^*}$ as expected for a free particle of mass m^*
- near $k_x = \frac{\pi}{a}$ we have $v_k = -\frac{2ta^2}{\hbar}\delta k_x$

  i.e. velocity is OPPOSITE to change in crystal momentum! This is consistent with effective mass being negative here.

EXAMPLE 2: Lattice with a basis, dimerized chain



unit cell with two sites

$$H = \varepsilon_0 \sum_i \left[c_1^+(R_i) c_1(R_i) + c_2^+(R_i+a) c_2(R_i+a) \right]$$
$$+ t \sum_i \left[c_1^+(R_i) c_2(R_i+a) + h.c. \right] \qquad (12)$$
$$+ t' \sum_i \left[c_1^+(R_i) c_2(R_i-a) + h.c. \right]$$

"h.c." means hermitian conjugate

f.t.: $c_\alpha(\vec{r}) = \frac{1}{\sqrt{N}} \sum_k e^{ik\cdot r} c_{\alpha k}$, $\alpha = 1,2$

$$\rightarrow \quad H = \varepsilon_0 \sum_{\alpha,k} c_{\alpha k}^+ c_{\alpha k} + t \sum_k \left(c_{1k}^+ c_{2k} e^{ika} + h.c. \right) + t' \sum_k \left(c_{1k}^+ c_{2k} e^{-ika} + h.c. \right) \qquad (13)$$

- To solve we define a 2-component "spinor" operator

$$\chi_k = \begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix}, \qquad \chi^+ = \left(c_{1k}^+, c_{2k}^+ \right) \qquad (14)$$

and express the Hamiltonian as (setting $a=1$)

$$H = \sum_k \chi_k^+ h_k \chi_k, \qquad h_k = \begin{pmatrix} \varepsilon_0 & te^{ik} + t'e^{-ik} \\ te^{-ik} + t'e^{ik} & \varepsilon_0 \end{pmatrix} \qquad (15)$$

The band structure of H is given by eigenvalues of h_k:

$$\det(h_k - \mathbb{1}\varepsilon) = 0$$

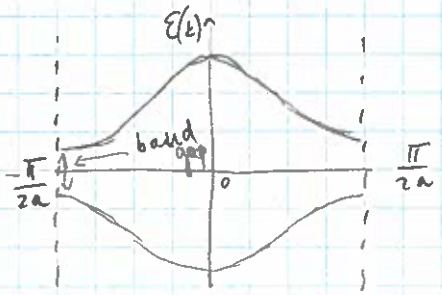
$$\rightarrow (\varepsilon_0 - \varepsilon)^2 - (te^{ik} + t'e^{-ik})(te^{-ik} + t'e^{ik}) = 0 \qquad (16)$$

$$\boxed{\varepsilon(k) = \varepsilon_0 \pm \sqrt{t^2 + t'^2 + 2tt'\cos 2k}} \qquad (17)$$

Analyze:

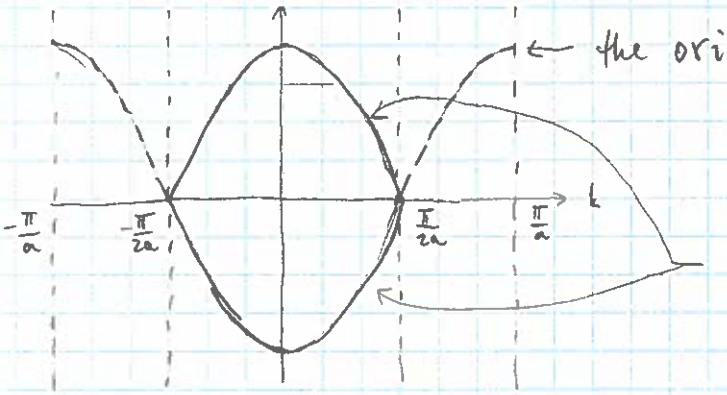
$k=0$: $\quad \varepsilon(0) = \varepsilon_0 \pm |t+t'|$

$k=\frac{\pi}{2}$: $\quad \varepsilon(\frac{\pi}{2}) = \varepsilon_0 \pm |t-t'|$



- <u>Special case $t' = t$</u>: how do we recover the monatomic limit?

For $t' = t$ we have
$$\varepsilon(k) = \varepsilon_0 \pm t\sqrt{2(1+\cos 2k)} = \varepsilon_0 \pm 2t|\cos k| \qquad (19)$$



← the original monatomic dispersion $\varepsilon(k) = \varepsilon_0 - 2t\cos k$

the "reconstructed" dispersion in smaller Brillouin zone