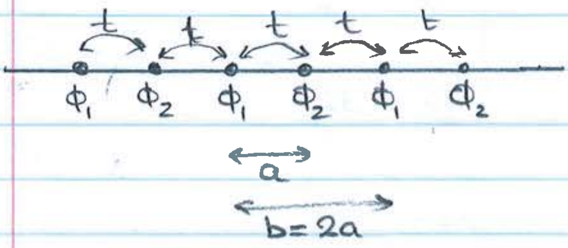
2-sites per basis – 1D chain/ring



$$\varepsilon_1 = \langle \phi_1(r) | H | \phi_1(r) \rangle$$
$$\varepsilon_2 = \langle \phi_2(r) | H | \phi_2(r) \rangle$$

$$t = \langle \phi_1(r) | H | \phi_2(r-a) \rangle$$
$$t = \langle \phi_1(r) | H | \phi_2(r+a) \rangle$$

$$k = \frac{2\pi}{b} \cdot \frac{n}{N}$$

$$0 = \langle \phi_1(r) | H | \phi_1(r \pm b) \rangle$$
$$0 = \langle \phi_2(r) | H | \phi_2(r \pm b) \rangle$$

$$\psi_1^k(r) = \frac{1}{\sqrt{N}} \sum_{R_1} e^{ikR_1} \phi_1(r-R_1)$$

$$\psi_2^k(r) = \frac{1}{\sqrt{N}} \sum_{R_2} e^{ikR_2} \phi_2(r-R_2)$$

$$\langle \psi_1^k(r) | H | \psi_1^k(r) \rangle = \sum_R e^{ikR} \langle \phi_1(r) | H | \phi_1(r-R) \rangle = \varepsilon_1 \quad (R=0 \text{ only})$$

$$\langle \psi_2^k(r) | H | \psi_2^k(r) \rangle = \qquad = \varepsilon_2 \quad (R=0 \text{ only})$$

$$\langle \psi_1^k(r) | H | \psi_2^k(r) \rangle = (R=a)\, e^{ika} \cdot t + (R=-a)\, e^{-ika} \cdot t = 2t\cos(ka)$$

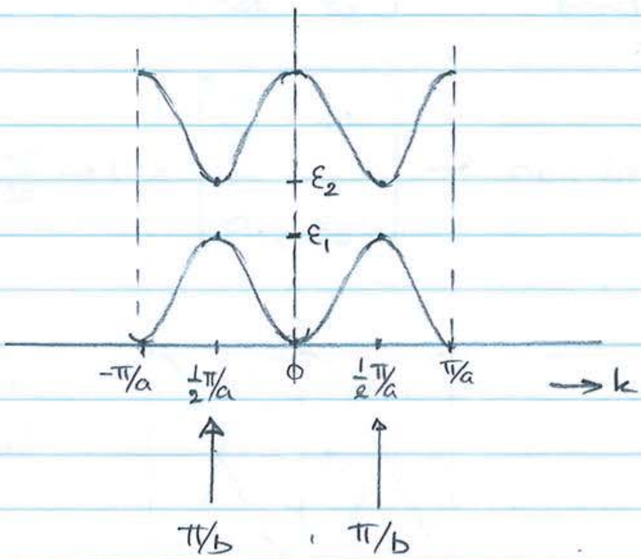
$$\langle \psi_2^k(r) | H | \psi_1^k(r) \rangle = \qquad = 2t\cos(ka)$$

$$H_{\psi_1^k, \psi_2^k} = \begin{bmatrix} \varepsilon_1 & 2t\cos(ka) \\ 2t\cos(ka) & \varepsilon_2 \end{bmatrix}$$

$$k=0 \rightarrow \quad H=\begin{bmatrix} \varepsilon_1 & 2t \\ 2t & \varepsilon_2 \end{bmatrix}$$

$$k=\frac{\pi}{a} \rightarrow \quad H=\begin{bmatrix} \varepsilon_1 & -2t \\ -2t & \varepsilon_2 \end{bmatrix}$$ → same eigenvalues as for $k=0$

$$k=\frac{1}{2}\cdot\frac{\pi}{a} \rightarrow \quad H=\begin{bmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{bmatrix}$$ → non bonding !



$b=2a$.

Brillouin Zone

Special case: $\varepsilon_1 = \varepsilon_2 = \varepsilon_0$

$$H_{\varphi_1^k \varphi_2^k} = \begin{bmatrix} \varepsilon_0 & 2t\cos(ka) \\ 2t\cos(ka) & \varepsilon_0 \end{bmatrix}$$

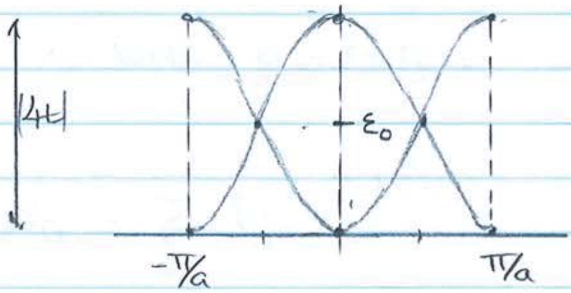
$$k=0 \rightarrow H = \begin{bmatrix} \varepsilon_0 & 2t \\ 2t & \varepsilon_0 \end{bmatrix} \rightarrow E_+ = \varepsilon_0 - |2t|, \quad E_- = \varepsilon_0 + |2t|$$

bonding, antibonding

$$k=\frac{\pi}{a} \rightarrow H = \begin{bmatrix} \varepsilon_0 & -2t \\ -2t & \varepsilon_0 \end{bmatrix} \rightarrow E_- = \varepsilon_0 - |2t|, \quad E_+ = \varepsilon_0 + |2t|$$

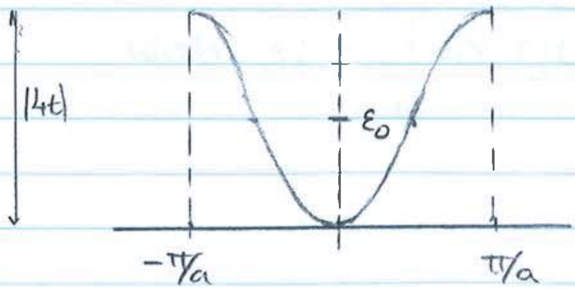
bonding, antibonding

$$k=\frac{\pi}{2a} \rightarrow H = \begin{bmatrix} \varepsilon_0 & 0 \\ 0 & \varepsilon_0 \end{bmatrix} \rightarrow \text{non bonding, degenerate.}$$



"wrong Brillouin Zone"

Backfolding around $k = \frac{\pi}{2a} = \frac{\pi}{b}$.



"correct Brillouin Zone"

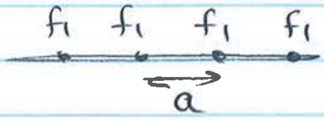
X-ray diffraction

- $F = \int dV\, n(\underline{r})\, e^{-i(\underline{k}'-\underline{k}).\underline{r}} = \int dV\, n(\underline{r})\, e^{-i\Delta\underline{k}.\underline{r}}$ Scattering amplitude
- $\Delta\underline{k} = \underline{G}$ (reciprocal lattice vector - Bragg condition)
- $F_{\underline{G}} = \int dV\, n(\underline{r})\, e^{-i\underline{G}.\underline{r}} = N \int_{cell} V\, n(\underline{r})\, e^{-i\underline{G}.\underline{r}} = N . S_{\underline{G}}$
- $S_{\underline{G}} = \int_{cell} dV\, n(\underline{r})\, e^{-i\underline{G}.\underline{r}}$ Structure factor.
- $n(\underline{r}) = \sum_{j=1}^{m} n_j(r - r_j)$ inside cell : m-atoms (basis)
- $S_{\underline{G}} = \sum_j \int_{cell} dV\, n_j(r-r_j)\, e^{-i\underline{G}.\underline{r}} = \sum_j e^{-i\underline{G}.\underline{r}_j} \int_{cell} dV\, n_j(\rho) e^{-i\underline{G}.\underline{\rho}}$

  with $\underline{\rho} = \underline{r} - \underline{r}_j$

- $S_G = \sum_j f_j . e^{-i\underline{G}.\underline{r}_j}$

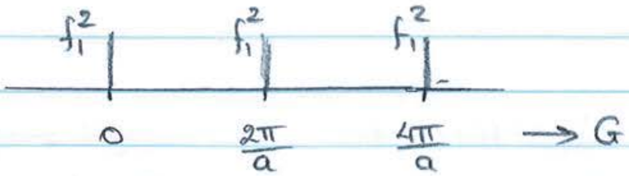
  with $f_j = \int_{cell} dV\, n_j(\rho) e^{-i\underline{G}.\underline{\rho}}$ form factor example 1 :



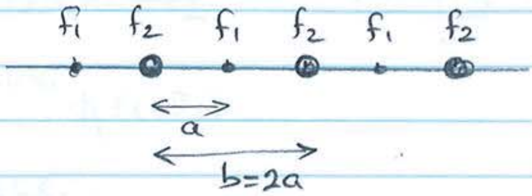
$G = \frac{2\pi}{a} . h$ $\quad h = \text{integer}$

$m = 1 , j = 1 \rightarrow r_j = r_1 = 0 \rightarrow S_G = f_1 \rightarrow |S_G|^2 = f_1^2$

intensity ↑



example 2 :



$G = \frac{2\pi}{b} . h = \frac{\pi}{a} . h$

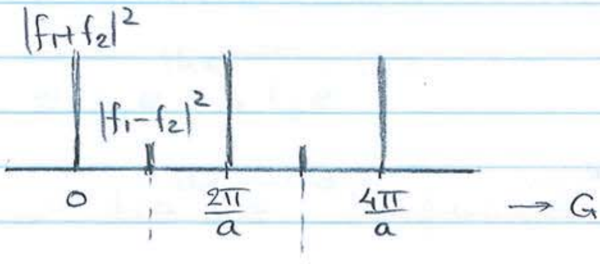
$$\left.\begin{array}{l} m=2 , j=1 \rightarrow r_1 = 0 \\ m=2 , j=2 \rightarrow r_2 = a \end{array}\right\} S_G = f_1 + f_2 e^{-iG.a}$$

$h=0 \rightarrow S_G = f_1 + f_2 \rightarrow |S_G|^2 = |f_1+f_2|^2 \quad h = \text{even}$

$h=1 \rightarrow S_G = f_1 + f_2 e^{-i\pi} = f_1 - f_2 \rightarrow |S_G|^2 = |f_1 - f_2|^2 \quad h = \text{odd}$

$h=2 \rightarrow S_G = f_1 + f_2 e^{-2i\pi} = f_1 + f_2$

intensity ↑



When $f_1 = f_2$ then peaks at π/a, $3\pi/a$ etc disappears !