

# Origin of Energy Gaps



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consider free-electron-like wavefunctions

$$\psi_{\vec{k}} = e^{i\vec{k}\cdot\vec{r}}$$

for free-electron case, these are running waves with

$$\vec{p} = \hbar\vec{k}$$

Now consider a weak periodic potential

$$U(\vec{r}) = U(\vec{r} + \vec{R})$$

$\Rightarrow$  Bragg reflections of the electron waves

$\Rightarrow$  energy gaps

How?

Consider 1D chain with lattice constant  $a$   
(1-D case)

Bragg condition ~~condition~~

$$|\vec{K}| = |\vec{k} - \vec{k}'|$$

or in 1-D

~~$$K = 2k$$~~

$$K^2 = (2k)^2 \Rightarrow k^2 = \frac{K^2}{2^2}$$

~~$$K = 2k$$~~

$$k = \pm \frac{K}{2}$$

and  $\vec{R} \cdot \vec{R} = 2\pi m$

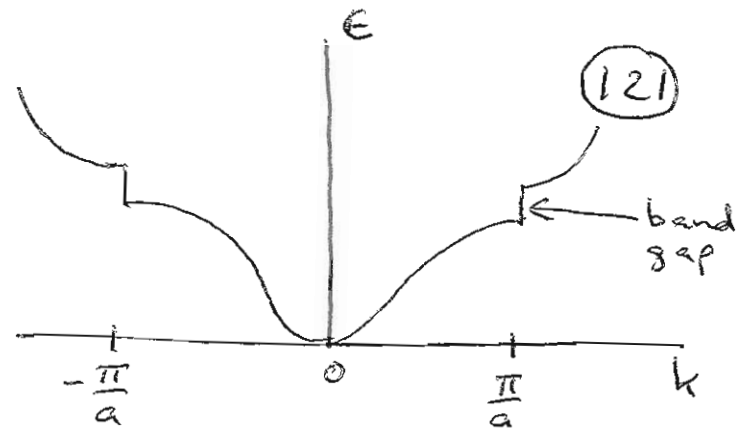
$$\Rightarrow a^2 (2k)^2 = 2\pi m \Rightarrow$$

$$k = \pm \frac{\pi m}{a}$$

$$\text{At } k = \pm \frac{\pi m}{a},$$

Bragg reflection

$\Rightarrow$  waves travelling to left and right will superimpose to form standing waves



$\Rightarrow$  2 kinds of solutions at  $k = \pm \frac{\pi}{a}$

$$\psi^+ = e^{i\pi x/a} + e^{-i\pi x/a}$$

$$\psi^- = e^{i\pi x/a} - e^{-i\pi x/a}$$

$$\Rightarrow \psi^+ = 2 \cos \frac{\pi x}{a} \Rightarrow \sqrt{2} \cos \frac{\pi x}{a}$$

$$\psi^- = 2i \sin \frac{\pi x}{a} \Rightarrow \sqrt{2} i \sin \frac{\pi x}{a}$$

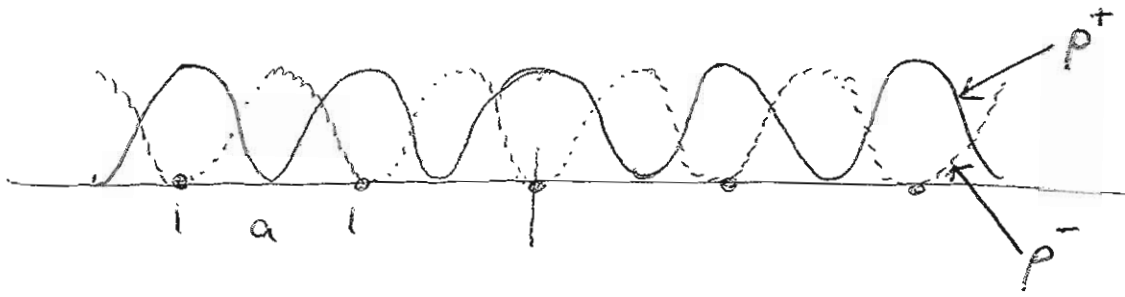
after normalizing

probability density of a particle

$$\rho = \psi^* \psi = |\psi|^2$$

$$\Rightarrow \rho^+ = 2 \cos^2 \frac{\pi x}{a}$$

$$\rho^- = 2 \sin^2 \frac{\pi x}{a}$$



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$\rho^+$  piles up charge at ion core positions

$\rho^-$  piles up charge at midpoints between ions

$\Rightarrow$   $\rho^+$  charge will have lower potential energy compared to  $\rho^-$  charge

$$\mathcal{E}(\rho^+) - \mathcal{E}(\rho^-) = \bar{E}_g = \text{band-gap}$$

potential energy

$$U(x) = U_0 \cos \frac{2\pi x}{a} \quad \left. \vphantom{U(x)} \right\} \begin{array}{l} \text{periodic with} \\ \text{period } \frac{2\pi}{a} \end{array}$$

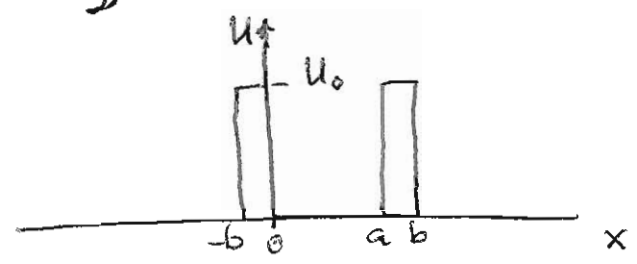
$$\bar{E}_g \approx \int_0^a dx U(x) [|\psi^+|^2 - |\psi^-|^2]$$

to first-order

$$E_g = 2 \int dx U_0 \cos \frac{2\pi x}{a} \left[ \cos^2 \frac{\pi x}{a} - \sin^2 \frac{\pi x}{a} \right]$$

can show that  $\bar{E}_g = U$

Another more rigorous derivation of energy gap in 1-D case is the Kronig-Penney model



U(x) has period = a+b

Return to Bloch wavefunctions

Apply the Born-Von Karman boundary conditions

$$\psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r}) \quad i = 1, 2, 3$$

$$N = \prod_i N_i = \text{total \# of primitive cells in the crystal}$$

Now Bloch theorem

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

but  $N_i \vec{a}_i$  is an  $\vec{R}$

$$\Rightarrow \psi(\vec{r} + N_i \vec{a}_i) = e^{i\vec{k} \cdot N_i \vec{a}_i} \psi(\vec{r}) = \psi(\vec{r})$$

$$\Rightarrow e^{i\vec{k} \cdot N_i \vec{a}_i} = 1$$

$$\Rightarrow \vec{k} \cdot N_i \vec{a}_i = 2\pi m_i$$

$$\vec{k} = \sum x_i \vec{b}_i$$

$$\vec{k} \cdot N_i \vec{a}_i = x_i N_i \vec{b}_i \cdot \vec{a}_i = 2\pi x_i N_i$$

$$\Rightarrow x_i N_i = m_i = \text{integer}$$

$$\Rightarrow \boxed{x_i = \frac{m_i}{N_i}}$$

$$\Rightarrow \vec{h} = \sum_i^3 \frac{m_i}{N_i} \vec{b}_i \quad m_i = \text{integer}$$

these are the allowed  $\vec{h}$ -vectors of the Bloch waves

$$\psi(x) = e^{i\vec{h} \cdot \vec{r}} u_{\vec{h}}(\vec{r})$$

? how many such  $\vec{h}$ -vectors are existing inside 1 primitive cell of the reciprocal lattice?

$\Rightarrow$  what  $\vec{h}$ -space volume is occupied by 1 such  $\vec{h}$ -vector?

$$\vec{k}_i = \frac{m_i \vec{b}_i}{N_i} = \left\{ \frac{1\vec{b}_i}{N_i}, \frac{2\vec{b}_i}{N_i}, \frac{3\vec{b}_i}{N_i}, \dots \right\}$$

$$\Rightarrow \Delta k_i = \frac{\vec{b}_i}{N_i}$$

in 3-Dimensions

$$\Delta \vec{h} = \frac{\vec{b}_1}{N_1} \cdot \left( \frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right) = \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3}$$

So, volume of  $\vec{k}$ -space occupied by

1 Bloch wave vector is

$$\Delta \vec{k} = \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N}$$

$N$  = number of primitive cells in real space

but  $\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)$  = volume of reciprocal space unit (primitive) cell

$\Rightarrow$  number of Bloch wavevectors per reciprocal space unit cell

$$= \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{\Delta \vec{k}} = N$$

= number of real space primitive cells of the crystal

$$\text{but } \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{(2\pi)^3}{v}$$

$v$  = primitive cell volume in real space lattice

So

$$\Delta \vec{k} = \frac{(2\pi)^3}{\frac{V}{N}} \frac{1}{N} = \frac{(2\pi)^3}{V}$$

$v = \frac{V}{N}$  ← crystal total volume

(same as for free-electron case)