# Electrons in a weak periodic potential

# Outline

# The "nearly free electron" model

## From empty lattice to non-null potential

### Recap and motivation

- The "empty lattice" model: $U(\boldsymbol{r}) = 0$ exactly — a very special, non-physical case
- In any real crystal $U(\boldsymbol{r}) \neq 0$: a new feature, absent in the empty lattice, enters the game
- In the empty lattice, energy bands are contiguous: passing from any band to the next occurs with continuity
- With $U(\boldsymbol{r}) \neq 0$: bands become separated by forbidden energy intervals $\longrightarrow$ band gaps
- Band gaps play a fundamental role in determining the properties of crystalline solids

# The "nearly free electron" model

## Definition of the model

### Two key assumptions

1. Fourier coefficients of the potential are negligibly small:

$$U(\boldsymbol{r}) = \sum_{\boldsymbol{G}} U_{\boldsymbol{G}}\, e^{i\boldsymbol{G}\cdot\boldsymbol{r}}, \qquad U_{\boldsymbol{G}} \to 0 \;\; \forall\, \boldsymbol{G}$$

2. Eigenvalues differ from the empty lattice by an infinitesimal amount:

$$\epsilon(\boldsymbol{k}-\boldsymbol{G}) = \underbrace{\frac{\hbar^2|\boldsymbol{k}-\boldsymbol{G}|^2}{2m}}_{\text{empty lattice model}} + \alpha, \quad |\alpha| \to 0$$

- The model is more realistic than the empty lattice while remaining mathematically tractable

# Mathematical justification of the band gap

## The 1D crystal: setup

### The central equation subsystem

- 1D crystal, primitive cell length $a$, $g = 2\pi/a$, first BZ: $[-\pi/a, \pi/a]$
- Reciprocal lattice vectors: $G = pg$, $p \in \mathbb{Z}$
- Subsystem of the central equation for allowed $k$ inside the first BZ:

$$\left( \frac{\hbar^2 (k - jg)^2}{2m} - \varepsilon \right) C_{k-jg} + \sum_{i=-\infty}^{\infty} U_{ig} \, C_{k-jg-ig} = 0, \quad j \in \mathbb{Z}$$

- Rewrite as an expression for the generic coefficient $C_{k-jg}$:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} \, C_{k-jg-ig}}{\varepsilon - \frac{\hbar^2 (k - jg)^2}{2m}}, \quad j \in \mathbb{Z}$$

# Mathematical justification of the band gap

## Solutions far from $k = 0, \pm\pi/a$

Band nr. 1 $\implies \varepsilon_1 = \dfrac{\hbar^2 k^2}{2m} + \alpha,\ |\alpha| \to 0$

- $j \neq 0$: numerator $\to 0$; denominator is finite
  ($\hbar^2 k^2/2m - \hbar^2(k - jg)^2/2m$ is finite and grows with $|j|$)

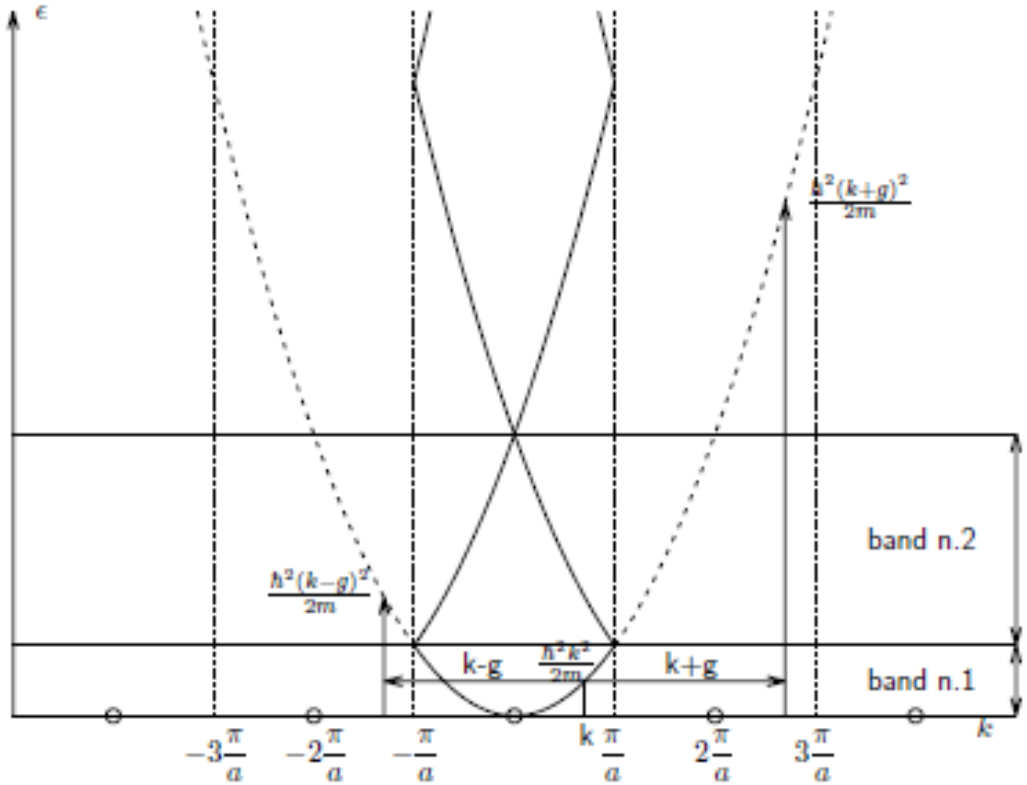
$$C_{k-jg} = \frac{\overbrace{\sum U_{ig}\, C_{k-jg-ig}}^{\to 0}}{\underbrace{\hbar^2 k^2/2m + \alpha - \hbar^2(k - jg)^2/2m}_{\text{finite}}} \approx 0$$

- $j = 0$: numerator $\to 0$; denominator $= \alpha \to 0$; ratio finite $\implies C_k \neq 0$
  - $\implies \Psi_{1k}(r) \approx C_k\, e^{ikr}$, $\epsilon_1(k) \approx \frac{\hbar^2 k^2}{2m}$

# Mathematical justification of the band gap

## Solutions far from $k = 0, \pm\pi/a$

Band nr. 1 $\Longrightarrow \varepsilon_1 = \dfrac{\hbar^2 k^2}{2m} + \alpha,\ |\alpha| \to 0$



# Mathematical justification of the band gap

## Solutions far from $k = 0, \pm\pi/a$

Band nr. 2 $\implies \varepsilon = \dfrac{\hbar^2(k-g)^2}{2m} + \alpha,\ |\alpha| \to 0$

- $j \neq 1$: denominator is finite $\implies C_{k-jg} \approx 0$
- $j = 1$: denominator $= \alpha \to 0 \implies C_{k-g} \neq 0$
- Only one coefficient survives
  - $\implies \Psi_{k2}(r) \approx C_{(k-g)2}\, e^{i(k-g)r},\ \epsilon_2(k) \approx \frac{\hbar^2(k-g)^2}{2m}$
- Same procedure for $k \in [-\frac{\pi}{a}, 0] \implies C_{k+g} \neq 0\ (j = -1)$

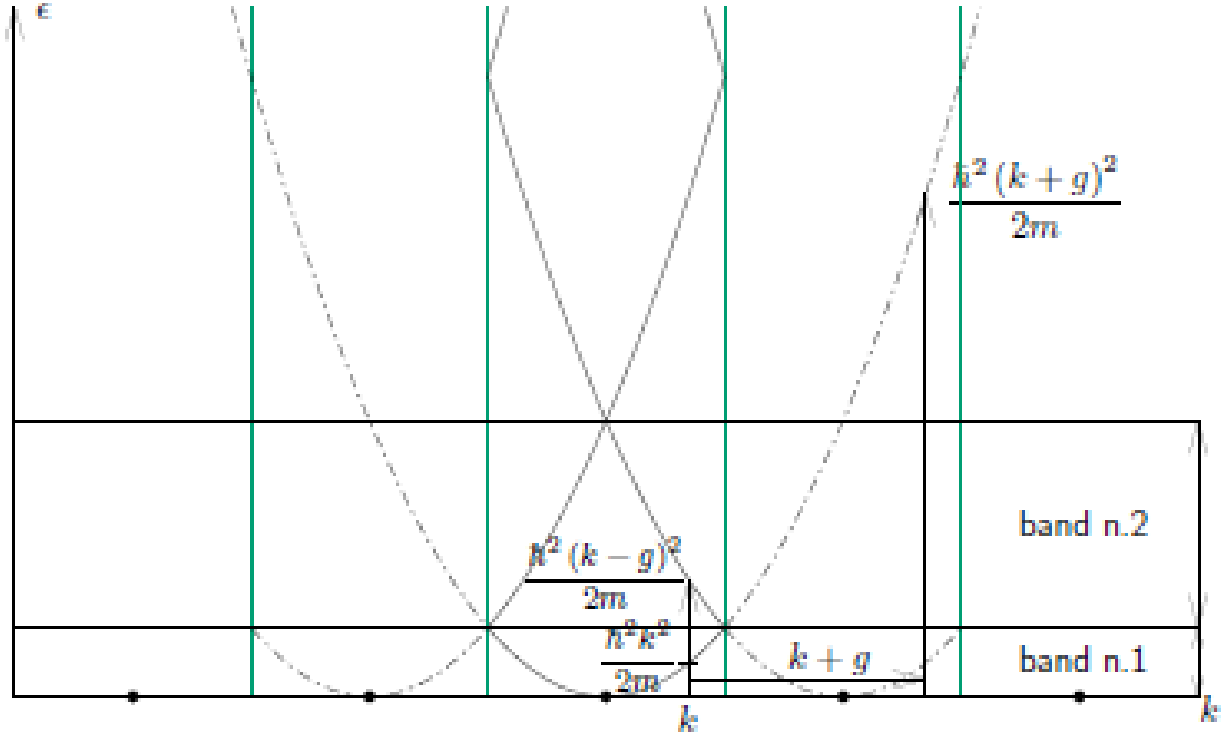
Generic band $n$ ($k$ far from $k = 0, \pm\pi/a$)

- For band $n$ only $C_{k-pg} \neq 0$
  - $\implies p = p(n,k) \in \mathbb{Z}$ defines the $n$th eigenvalue (e.g. $p(3,k) = -1$)
  - $\implies \varepsilon_n(k) = \dfrac{\hbar^2(k-pg)^2}{2m} + \alpha$
  - $\implies \psi_{nk}(r) \approx C_{(k-pg)n}\, e^{i(k-pg)r}$

# Mathematical justification of the band gap

## Solutions far from $k = 0, \pm\pi/a$

Band nr. 2 $\Longrightarrow \varepsilon = \dfrac{\hbar^2(k-g)^2}{2m} + \alpha,\ |\alpha| \to 0$



# Mathematical justification of the band gap

## The special point $k \approx \pi/a$

### Degeneracies

- In the empty lattice: $\varepsilon_1(g/2) = \varepsilon_2(g/2) \longrightarrow$ doubly degenerate
- For $k \approx g/2$: $\varepsilon \approx \dfrac{\hbar^2 (g/2)^2}{2m} + \alpha$
- The denominator becomes $\approx \alpha$ for two values of $j$:

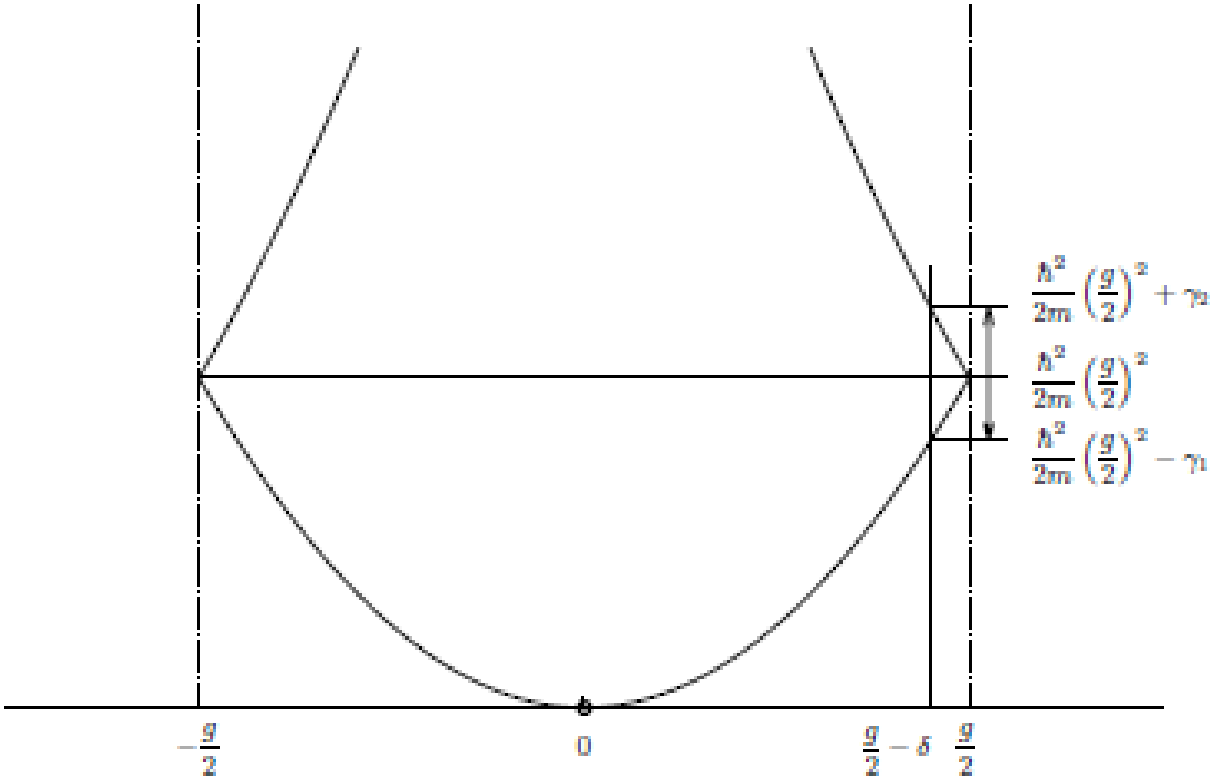
$$\frac{\hbar^2 (g/2)^2}{2m} - \frac{\hbar^2 (g/2 - jg)^2}{2m} = 0 \iff j = 0,\ 1$$

- For $j \neq 0, 1$: denominator is finite $\Longrightarrow C_{k-jg} \approx 0$
- For $j = 0, 1$: both $C_k \neq 0$ and $C_{k-g} \neq 0$
- Two coefficients survive instead of one

# Mathematical justification of the band gap

## The special point $k \approx \pi/a$

$k \in [g/2 - \delta,\, g/2]$



# Mathematical justification of the band gap

## The special point $k \approx \pi/a$

### The $2 \times 2$ homogeneous system

- Keep only the $C_k$ and $C_{k-g}$ terms in each sum
- Set $U_0 = 0$ and $U_{ig} = U_{-ig}$ (real and even potential):

$$\begin{cases} \left( \dfrac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} + U_g \, C_k = 0 \\ U_g \, C_{k-g} + \left( \dfrac{\hbar^2 k^2}{2m} - \epsilon \right) C_k = 0 \end{cases}$$

- Non-trivial solution:

$$\det \begin{pmatrix} \lambda_{k-g} - \epsilon & U_g \\ U_g & \lambda_k - \epsilon \end{pmatrix} = 0, \quad \lambda_k = \frac{\hbar^2 k^2}{2m}$$

# Mathematical justification of the band gap

## Solution of the $2 \times 2$ system

### Dispersion relation near $k = \pi/a$

Solving the secular equation:

$$\boxed{\varepsilon_{\pm} = \frac{1}{2}(\lambda_k + \lambda_{k-g}) \pm \left\{ \frac{1}{4}(\lambda_k - \lambda_{k-g})^2 + U_g^2 \right\}^{1/2}}$$

- If $U_g = 0$ recovers empty lattice bands n.1 and n.2
- $\varepsilon_{\pm}$ depends quadratically on $k$ near $k = g/2$
- Two allowed energies for each $k \in [g/2 - \delta,\, g/2] \longrightarrow$ bands n.1 and n.2 respectively

# Mathematical justification of the band gap

## Opening of the band gap at $k = \pi/a$

### Degeneracy removed: the band gap

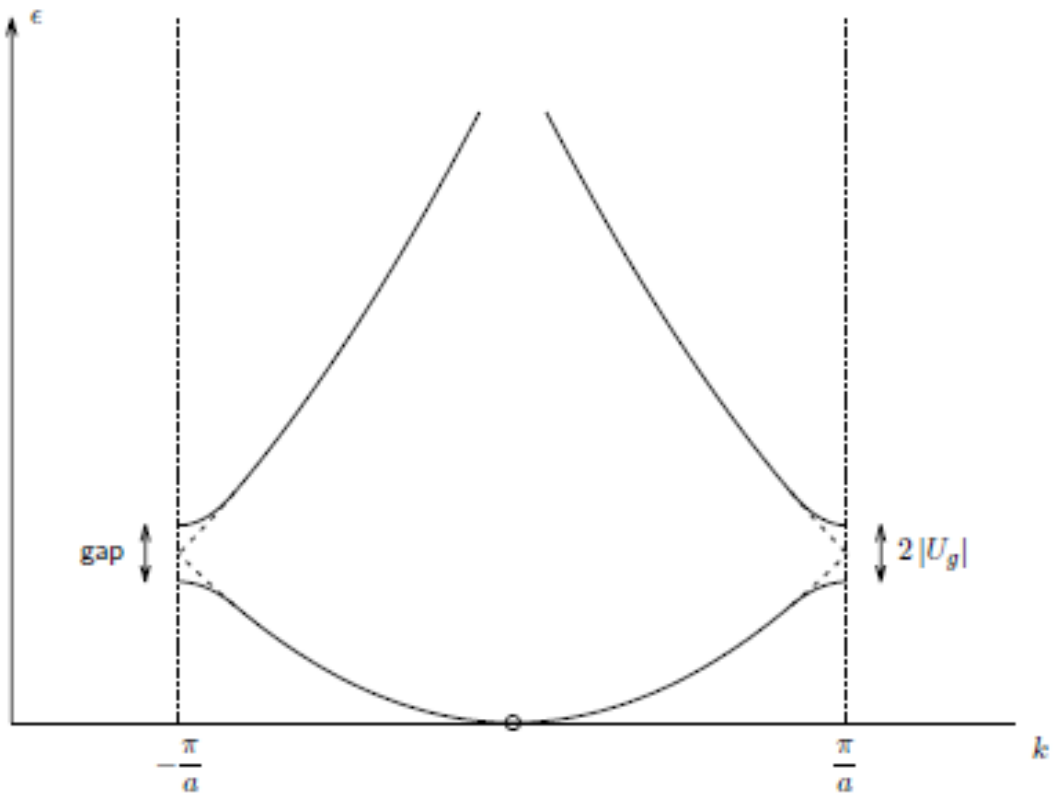
At $k = g/2$ exactly: $\lambda_k = \lambda_{k-g} = \dfrac{\hbar^2 (g/2)^2}{2m}$, so:

$$\varepsilon_\pm = \underbrace{\frac{\hbar^2 (g/2)^2}{2m}}_{\text{free electron value}} \pm |U_g|$$

- Band gap amplitude: $\varepsilon_+ - \varepsilon_- = 2|U_g|$
- Forbidden interval $[\varepsilon_-, \epsilon_+]$: no allowed eigenvalues exist
- $\varepsilon_-$: maximum of band n.1; $\varepsilon_+$: minimum of band n.2
- Bands enter the BZ boundary orthogonally: $\left(\dfrac{d\varepsilon}{dk}\right)_{k=g/2} = 0$

# Mathematical justification of the band gap

## Bands n.1 and n.2: empty lattice vs nearly free electron model

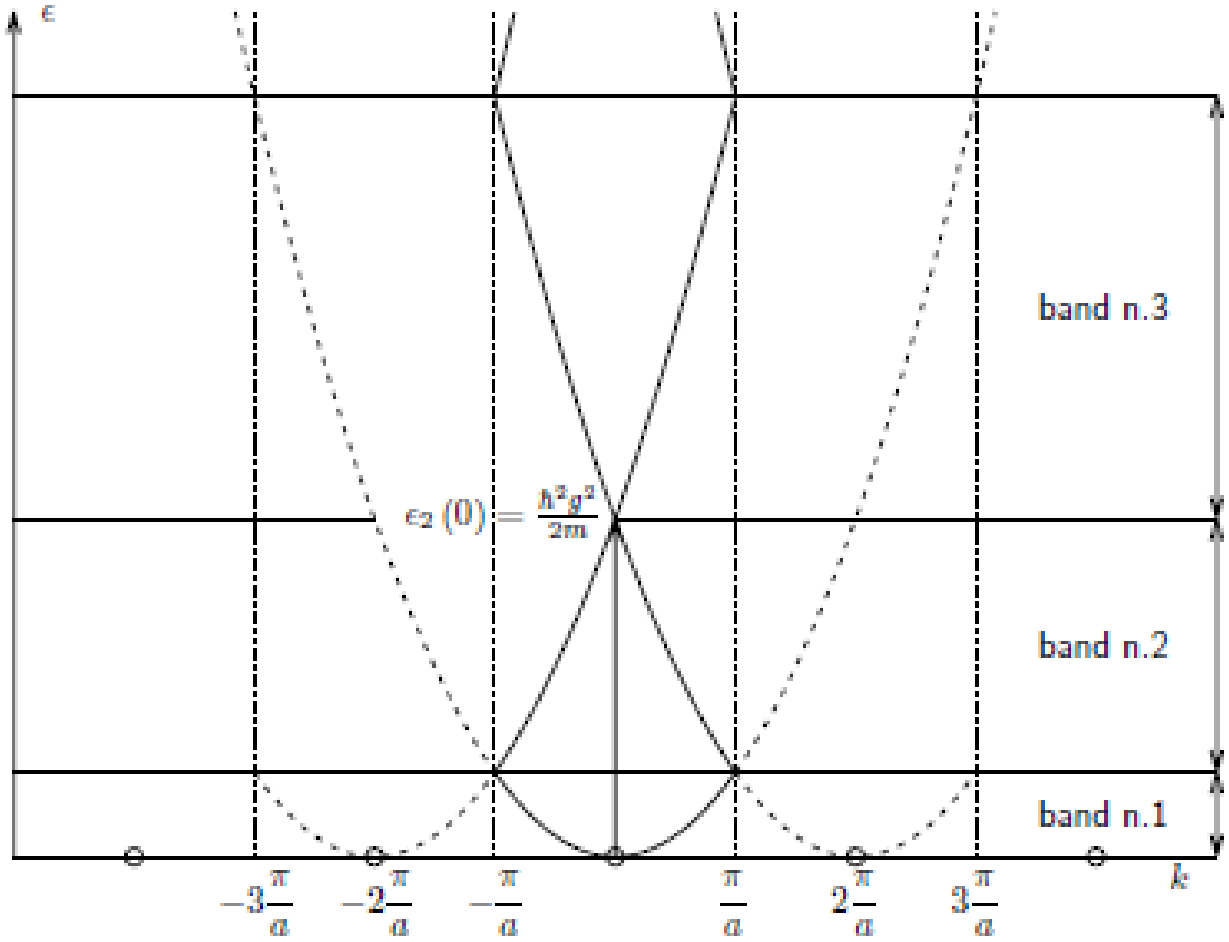



Dashed: empty lattice (degenerate at $k = \pi/a$); solid: nearly free electron model

(gap $= 2|U_g|$, orthogonal entry at BZ boundary)

# Mathematical justification of the band gap

## The special point $k \approx 0$



# Mathematical justification

## The special point $k \approx 0$

### Band gap between bands n.2 and n.3

- In the empty lattice: $\epsilon_2(0) = \epsilon_3(0) \longrightarrow$ doubly degenerate
- For $k \in [-\delta, \delta]$ around $k = 0$: two non null coefficients $C_{k-g}$ and $C_{k+g}$ (i.e. $C_{k-jg}$ with $j = 1$ and $j = -1$)
- Reduced $2 \times 2$ system:

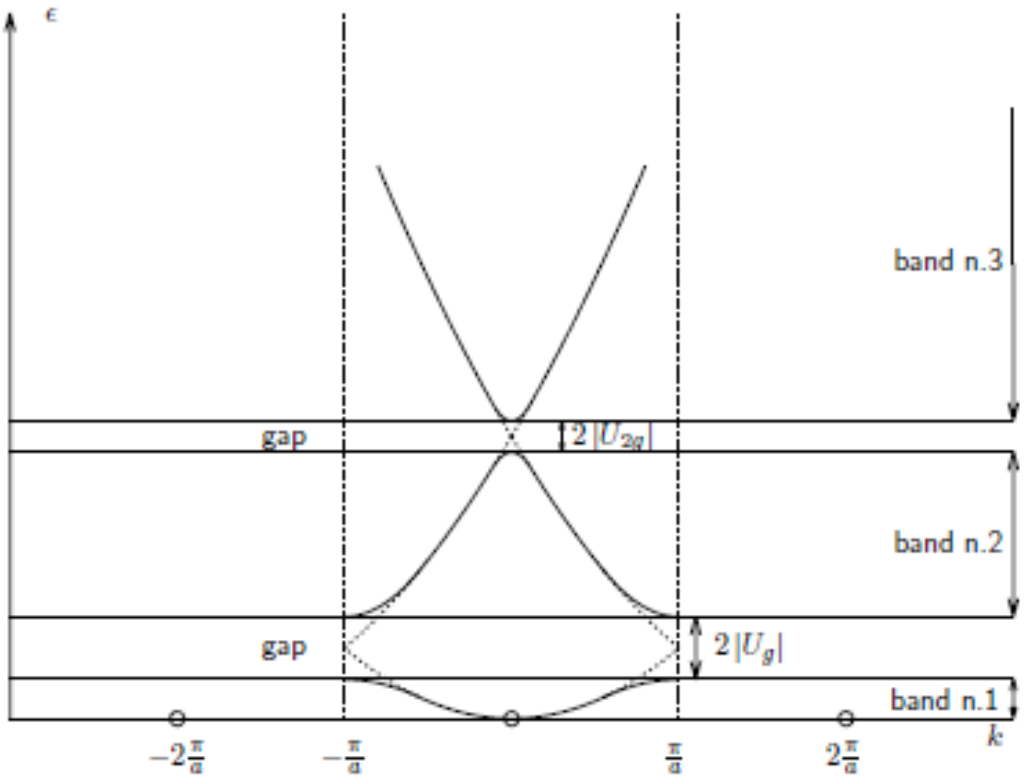
$$\begin{cases} \left( \dfrac{\hbar^2 (k+g)^2}{2m} - \epsilon \right) C_{k+g} + U_{2g}\, C_{k-g} = 0 \\ U_{2g}\, C_{k+g} + \left( \dfrac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} = 0 \end{cases}$$

- Band gap between bands n.2 and n.3:

$$\epsilon_{\pm} = \frac{\hbar^2 g^2}{2m} \pm |U_{2g}|, \qquad \Delta\epsilon = 2|U_{2g}|$$

# Mathematical justification of the band gap

## Bands n.1, n.2, n.3: empty lattice vs nearly free electron model




Band gaps between n.1–2 (amplitude $2|U_g|$) and n.2–3 (amplitude $2|U_{2g}|$);

dashed: empty lattice; solid: nearly free electron model

# Mathematical justification of the band gap

## Extrapolating to the general case

### Band gap between bands $i$ and $(i+1)$

- Gap opens at the boundary of every Brillouin zone (and at $k = 0$)
- Amplitude of the gap between bands $i$ and $(i+1)$:

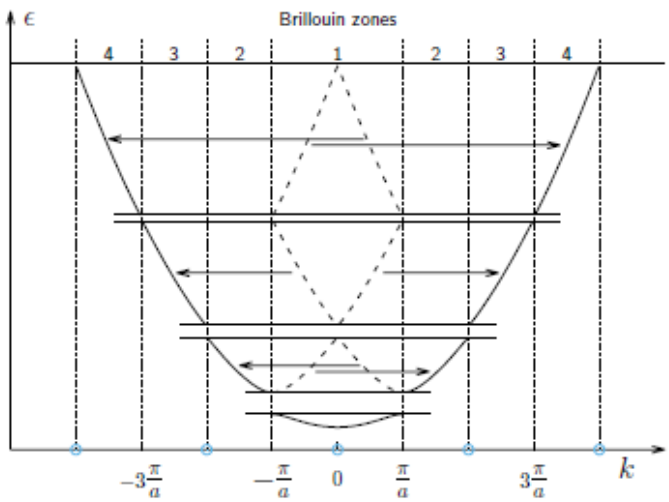
$$\Delta\epsilon = 2|U_{ig}|$$

  where $U_{ig}$ is the $i$-th Fourier coefficient of the periodic potential
- Since $|U_{ig}|$ decreases with $i$: band gaps become narrower at higher energies
- Analogy with confined quantum systems: level spacing $\to 0$ as energy $\to \infty$
- In a crystal: discrete atomic energy levels $\longrightarrow$ energy bands; spacing between bands $\longrightarrow 0$ with increasing band index

# Mathematical justification of the band gap

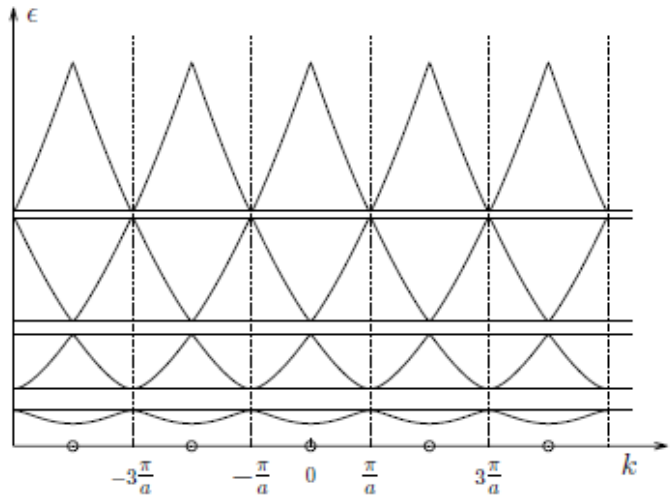
## Extended and repeated zone representations

### Extended zone




First four bands; band gaps highlighted; arrows show how the reduced zone representation maps to this one

### Repeated zone




Same four bands; band gaps shown as horizontal shaded regions; obtained by periodic replication of the reduced zone

# Physical interpretation of the band gap

## Stationary waves at $k = \pi/a$

### Ratio of the two surviving coefficients

At $k = g/2$: $\lambda_k = \lambda_{k-g} = \lambda$, $\varepsilon = \lambda \pm |U_g|$:

$$\frac{C_{g/2}}{C_{-g/2}} = \pm 1$$

- $C_{g/2} = +C_{-g/2} = C$:

$$\psi_+(r) \propto e^{i\frac{g}{2}r} + e^{-i\frac{g}{2}r} = 2\cos\left(\frac{\pi}{a}r\right)$$

- $C_{g/2} = -C_{-g/2} = C$:

$$\psi_-(r) \propto e^{i\frac{g}{2}r} - e^{-i\frac{g}{2}r} = 2i\sin\left(\frac{\pi}{a}r\right)$$

# Physical interpretation of the band gap

## Probability densities and energy

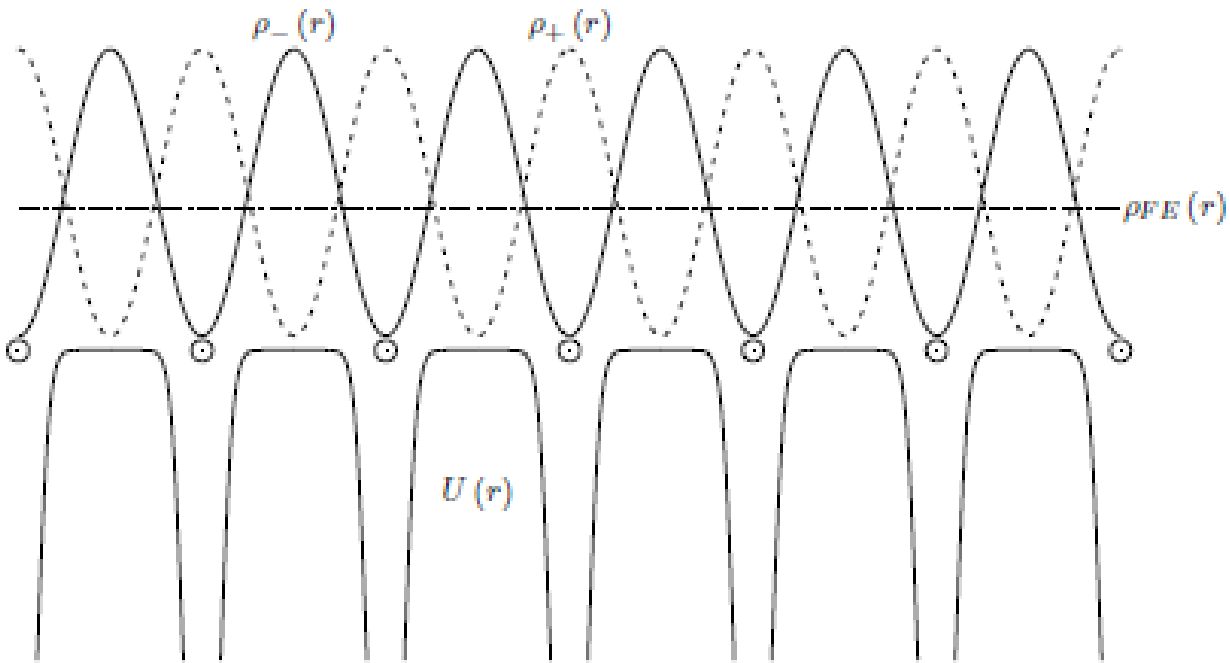
### Charge distribution near the nuclei

$$\rho_+ \propto \cos^2\left(\frac{\pi}{a}r\right), \quad \rho_- \propto \sin^2\left(\frac{\pi}{a}r\right), \quad \rho_{FE} = \text{const}$$

- $\rho_+$ and $\rho_-$ are out of phase by $a/2$: maximum of one $\leftrightarrow$ minimum of the other
- $\rho_+$: maxima near the nuclei $\longrightarrow$ lower potential energy $\longrightarrow$ lower $\epsilon_-$
- $\rho_-$: maxima between the nuclei $\longrightarrow$ higher potential energy $\longrightarrow$ higher $\epsilon_+$
- $\rho_{FE} = \text{const}$: no preference $\longrightarrow$ intermediate energy
- Energy splitting $2|U_g|$ is a direct consequence of this charge redistribution

# Physical interpretation of the band gap

## Probability densities — figure




Periodic potential $U(r)$ (bottom); $\rho_+$ peaks at nuclei (lower energy); $\rho_-$ peaks between nuclei (higher energy); $\rho_{FE} = \text{const}$ (free electron); circles: nuclear positions; vertical positions of plots are arbitrary

# Band gap and diffraction

## Connection to the Laue condition

### Electrons as waves in a lattice

- Electrons have a wave character $\longrightarrow$ they can be diffracted by the lattice (exactly like X-rays)
- Laue condition in 1D ($\boldsymbol{k} \cdot \hat{\boldsymbol{G}} = G/2$):

$$k = j\,\frac{g}{2}, \quad j = 0, \pm 1, \pm 2, \ldots$$

- Far from $jg/2$: electron $\approx$ free particle; interaction with lattice negligible
- At $k = jg/2$: Bragg reflection; in 1D diffraction $\equiv$ pure reflection

# Band gap and diffraction

## Two diffracted waves at $k = \pi/a$

### Superposition of incoming and reflected waves

- Incoming wave ($k = g/2$, wavelength $\lambda = 2a$): $\psi \propto e^{i\frac{g}{2}r}$
- Ions at spacing $a$ ($= \lambda/2$): Bragg condition satisfied separately by even and odd lattice points $\longrightarrow$ two reflected waves, phase difference $a$:

$$\psi' \propto e^{-i\frac{g}{2}r}, \qquad \psi'' \propto e^{-i\frac{g}{2}(r+a)}$$

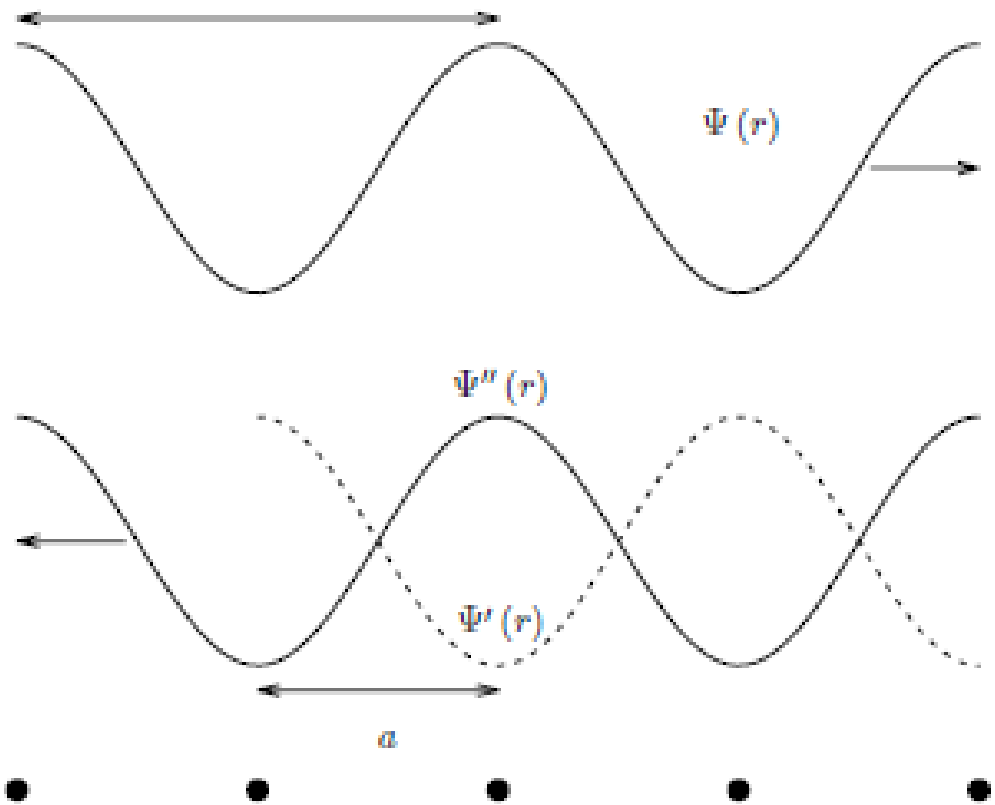
- Superposition gives two distinct states:

$$\psi_+ = \psi + \psi' \propto 2\cos\left(\frac{\pi}{a}r\right), \quad \psi_- = \psi + \psi'' \propto 2i\sin\left(\frac{\pi}{a}r\right)$$

- Same stationary waves as derived from the $2 \times 2$ system

# Band gap and diffraction

## Superposition of incoming and reflected waves




Upper: incoming electron ($k = \pi/a$, $\lambda = 2a$) travelling right; lower: two sets of reflected waves from even (solid) and odd (open) lattice sites, phase difference $a$; their interference with the incoming wave produces the two stationary states $\Psi_{\pm}$

# Band gap and diffraction

## The nearly free electron model

### Summary

- For $k$ far from BZ boundaries and $k = 0$: eigenfunctions and eigenvalues are essentially those of the free electron / empty lattice model
- When $k$ satisfies the Laue condition: Bragg reflection occurs; the resulting standing waves localize electrons differently relative to the nuclei
- This charge redistribution removes the degeneracy present in the empty lattice and opens a band gap of amplitude $2|U_G|$
- Bands are now separated; no allowed eigenvalue exists inside the gap
- Bands enter BZ faces orthogonally

# Band gaps in 2D and 3D

## Extensions to higher dimensions

### Generalization to higher dimensions

- Band gaps open whenever $\boldsymbol{k}$ satisfies the Laue condition:

$$\boldsymbol{k} \cdot \hat{\boldsymbol{G}} = \frac{1}{2} G$$

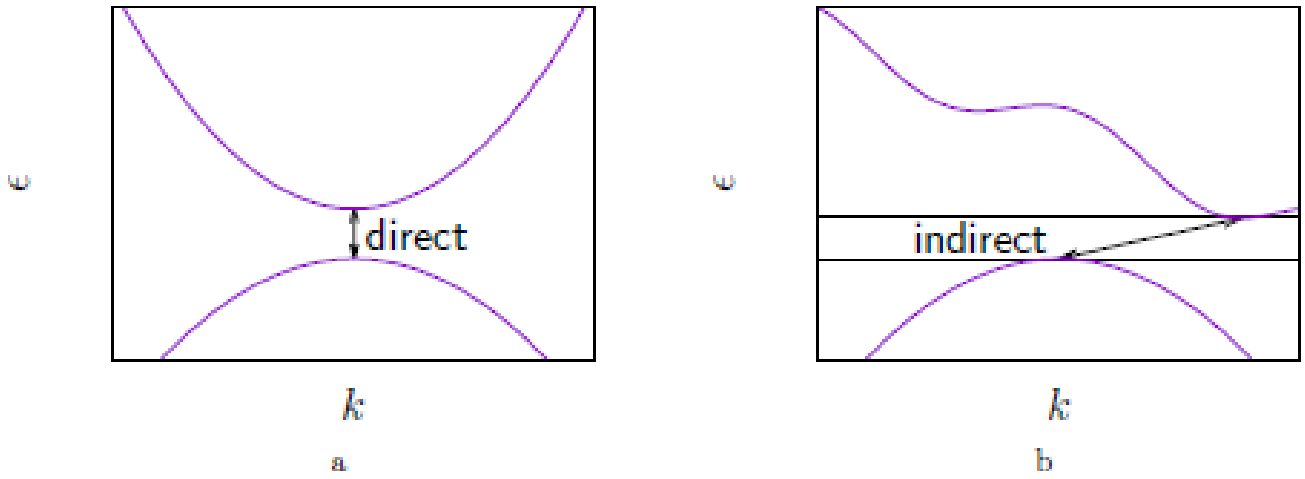
- In $3D$: Laue condition satisfied on planes (faces of Brillouin zones) $\longrightarrow$ BZ faces are the origin of band gaps in any dimension
- Band structure obtained exactly as for the empty lattice model: plot $\epsilon_n(\boldsymbol{k})$ along segments inside the first BZ
- Bands are no longer contiguous: band gaps separate consecutive bands

# Band gaps in 2D and 3D

## Direct and indirect band gaps

### Classification

- Direct band gap: minimum of upper band and maximum of lower band occur at the same $\boldsymbol{k}$
- Indirect band gap: minimum of upper band and maximum of lower band occur at different $\boldsymbol{k}$ points
- Band overlap: if two bands overlap there is no gap between them (as can occur in the empty lattice model)



# Band gaps in 2D and 3D

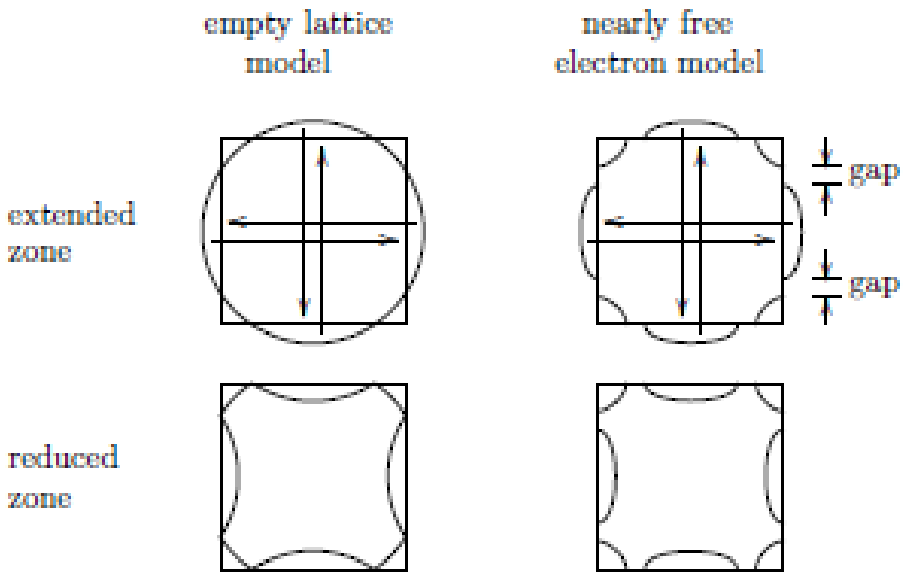
## The Fermi surface in the NFE model

**Qualitative changes with respect to the empty lattice**

- $\epsilon_F$ small: Fermi surface entirely inside the first BZ $\longrightarrow$ no difference from empty lattice
- Fermi surface intersects BZ boundaries: discontinuities appear at intersections (diffraction conditions met)
- Near BZ boundaries: bands repel each other; Fermi surface enters boundary orthogonally
- Net effect: broadening of all cusps present in the empty lattice Fermi surface

# Band gaps in 2D and 3D

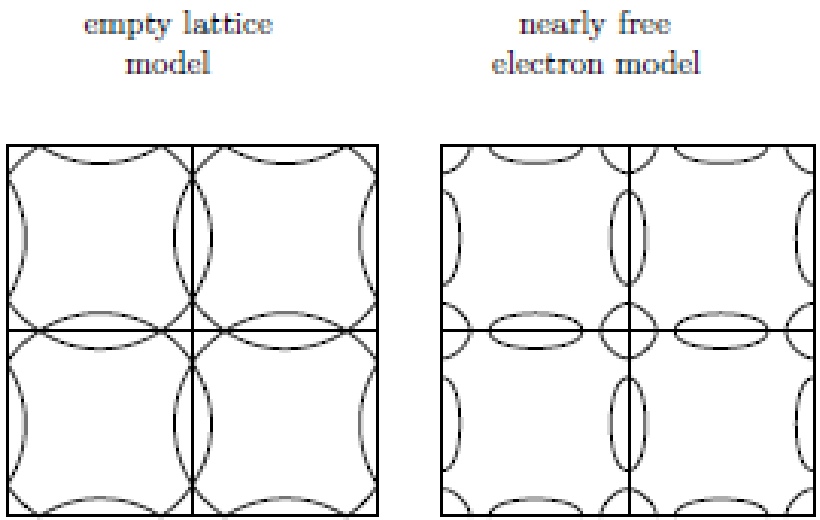
## Fermi surface: reduced zone (2D)




Left: empty lattice; right: nearly free electron model; reduced zone representation; branches from bands n.1 and n.2; note orthogonal entry at BZ boundaries and gap openings (marked by arrows)

# Band gaps in 2D and 3D

## Fermi surface: repeated zone (2D)




Left: empty lattice; right: nearly free electron model; repeated zone representation (four cells); note gap openings and the broadening of cusps induced by the non-null periodic potential