Lecture 2 – 18/09/2024

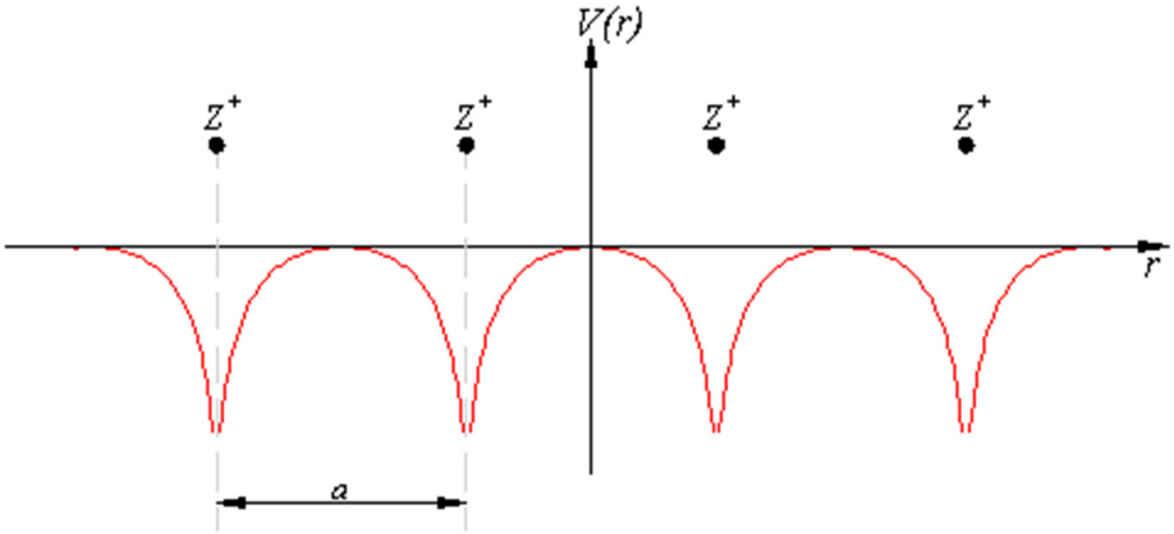
Origin of the bandgap: the "Physicist's view"

- Kronig-Penney model

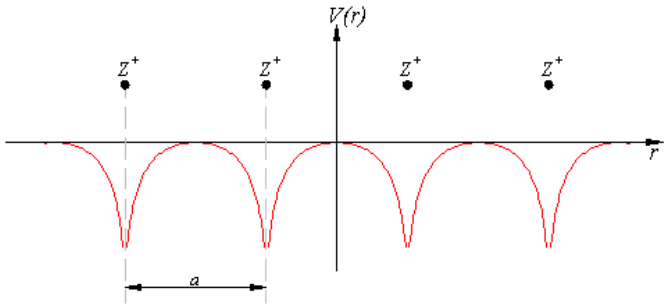
- Nearly-free electron model

Origin of the bandgap

In a crystal ⇒ periodic potential created by the atoms

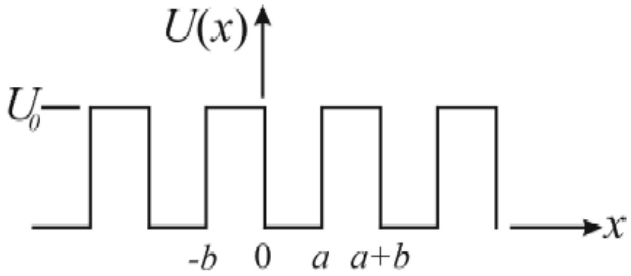


Kronig-Penney model



$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi$$

Mean crystal field



$$\psi_I(x)=Ae^{iKx}+Be^{-iKx}$$

$$\psi_{II}(x)=Ce^{Qx}+De^{-Qx}$$

Exercise and solution available on demand!

Free electrons

The **potential *V* is zero** and the solutions to Schrödinger's equation write as plane waves

$$H_e\psi_n(\mathbf{r}) = \frac{p^2}{2m}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}) \quad \text{with} \quad p = \frac{\hbar}{i}\nabla$$

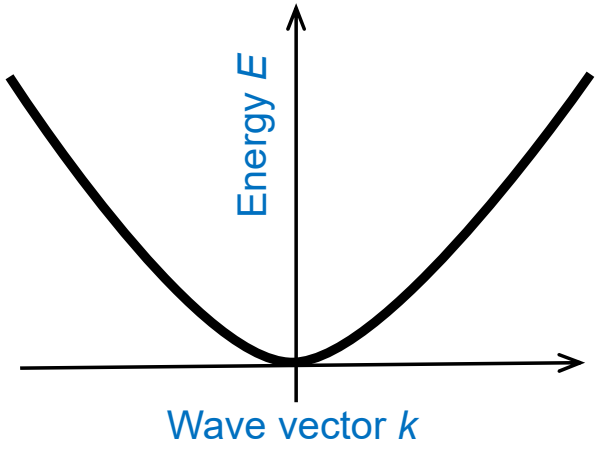
$$\psi_n(\mathbf{r}) = \psi_0\, exp(i\mathbf{kr})$$

The wave function is characterized by its wave vector **k**

Free electrons

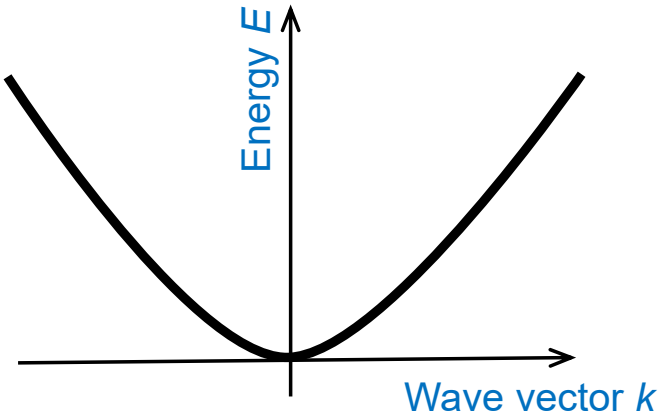
Energy and wave vector relationship (dispersion curve):

$$E = \frac{p^2}{2m_0} = \frac{\hbar^2 k^2}{2m_0} = \frac{\hbar^2}{2m_0}\left(k_x^2 + k_y^2 + k_z^2\right)$$

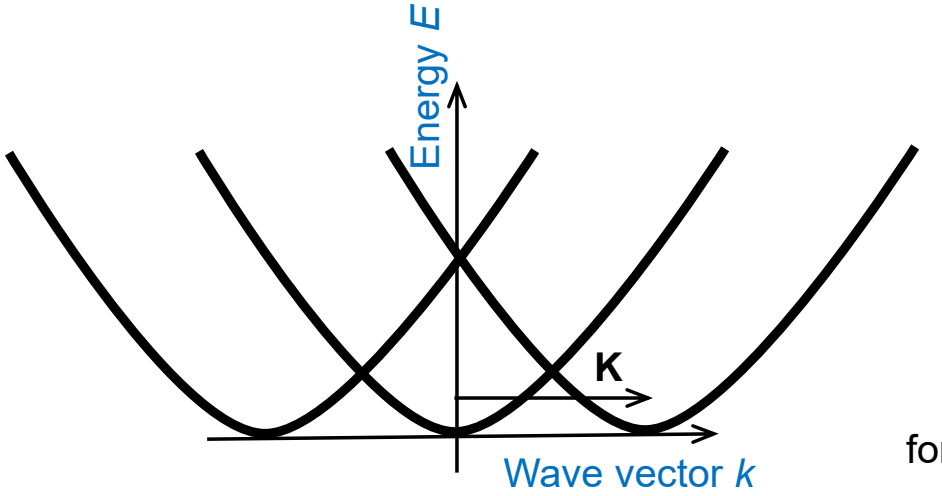


What does happen in a crystal?

1D dispersion curves



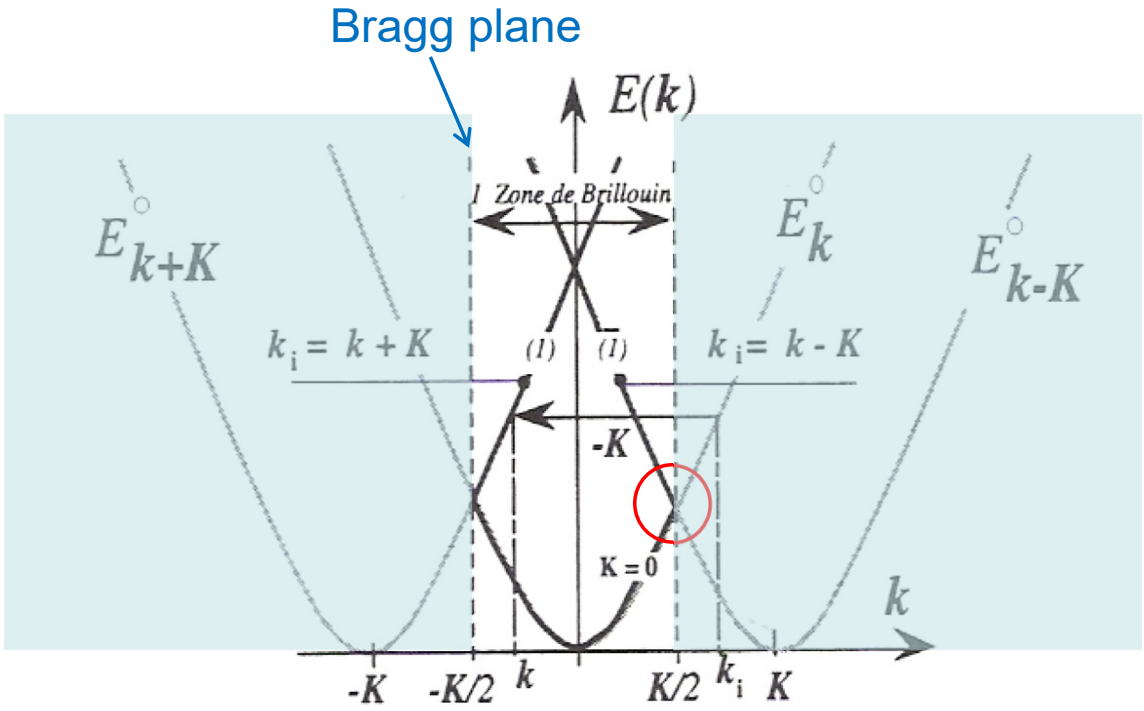
Free electron $E(k) = \frac{\hbar^2 k^2}{2m_0}$



$E(k) = \frac{\hbar^2 (k+K)^2}{2m_0}$

for any **K** vector of the reciprocal lattice

1D dispersion curves

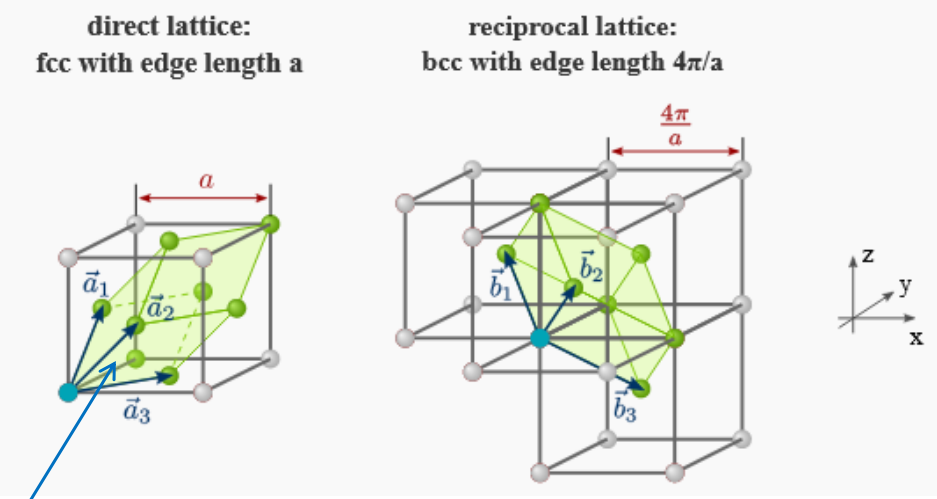


Folding in the 1st Brillouin zone

≡ reduced-zone scheme (vs. extended-zone scheme)

Reciprocal space (brief reminder)

The set of all wave vectors **K** that yield plane waves with the periodicity of a given Bravais lattice (real space) is known as its reciprocal lattice (when so doing, **k**s correspond to points in the reciprocal lattice space)



$$\mathbf{b_i} \cdot \mathbf{a_j} = 2\pi\delta_{ij}$$

Primitive unit cell

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad ; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad ; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Volume of the primitive cell

$\mathbf{a}_i$ are primitive vectors of the direct lattice while $\mathbf{b}_i$ are primitive vectors of the reciprocal lattice

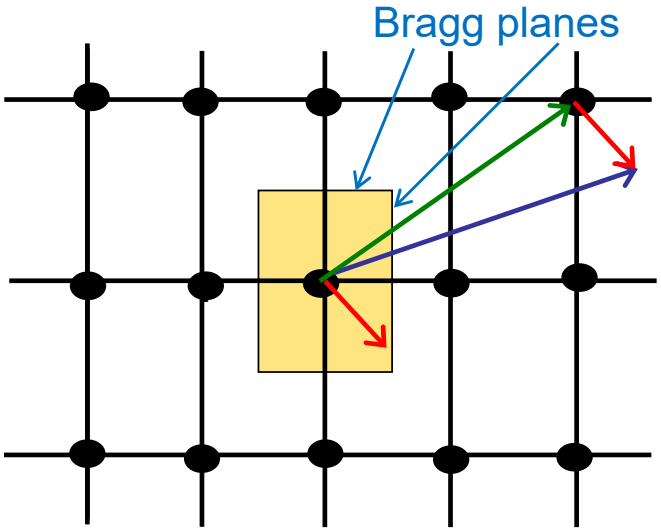
Brillouin zone (2D case)

The 1st Brillouin zone is the region of space about a lattice point that is closer to that point than to any other lattice point

$$E(k_i) = \frac{\hbar^2 k_i^{\,2}}{2m_0}$$ with $\mathbf{k_i}$ a given wave vector

$\mathbf{k_i} = \mathbf{k} + \mathbf{K_i}$,

$\mathbf{k}$ vector within the first Brillouin zone and $\mathbf{K_i}$ vector of the reciprocal lattice



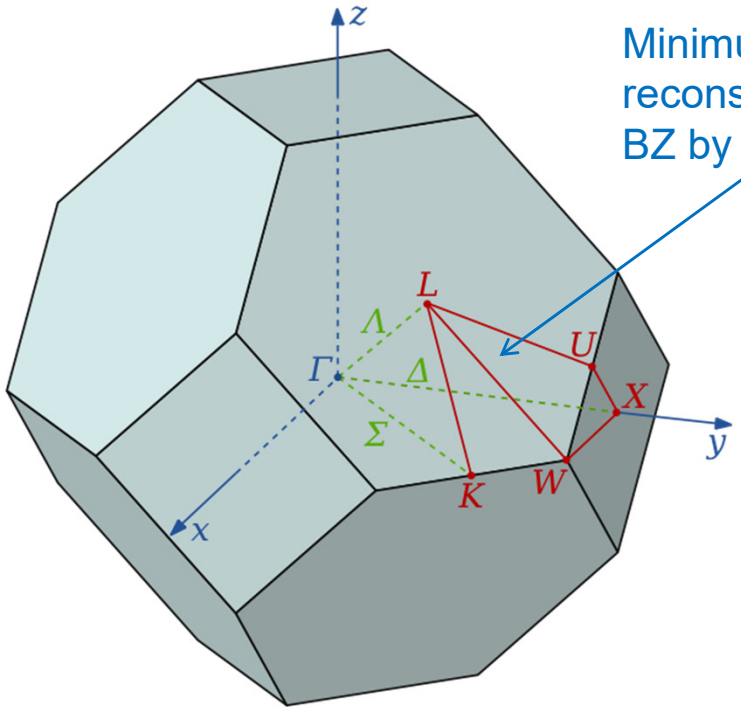
$$E(k_i) = \frac{\hbar^2 (k + K_i)^2}{2m_0}$$

- **Due to the crystalline symmetry, we can restrict the study of the dispersion curve to the 1st BZ** (translational invariance of the lattice)
- 1st BZ ≡ Wigner-Seitz primitive cells of the reciprocal lattice, which are all equivalent*

*See, e.g., Ashcroft-Mermin, Chap. 5

Brillouin zone (3D case)

High symmetry points: Γ, L, X, and K are within the 1st Brillouin zone (joined by high-symmetry lines)



Minimum volume allowing for reconstructing a complete 1st BZ by symmetry

$[100]$ direction: $\dot{\Gamma}\ \overline{\Delta}\ \dot{X}$

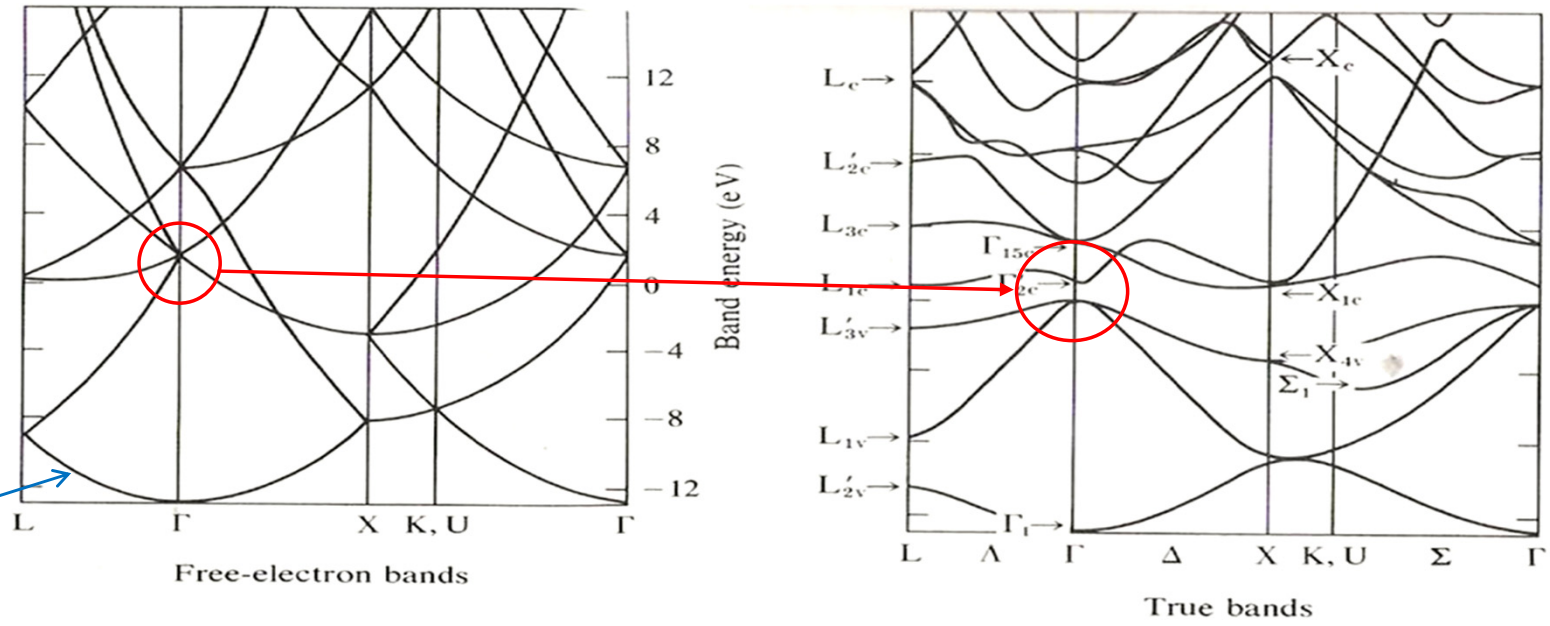
$[111]$ direction: $\dot{\Gamma}\ \overline{\Lambda}\ \dot{L}$

$[110]$ direction: $\dot{\Gamma}\ \overline{\Sigma}\ \dot{K}$

1st Brillouin zone of the fcc lattice

Dispersion curves: free electrons (e^-) and e^- in a crystal

Case of Ge



Dispersion of core electrons

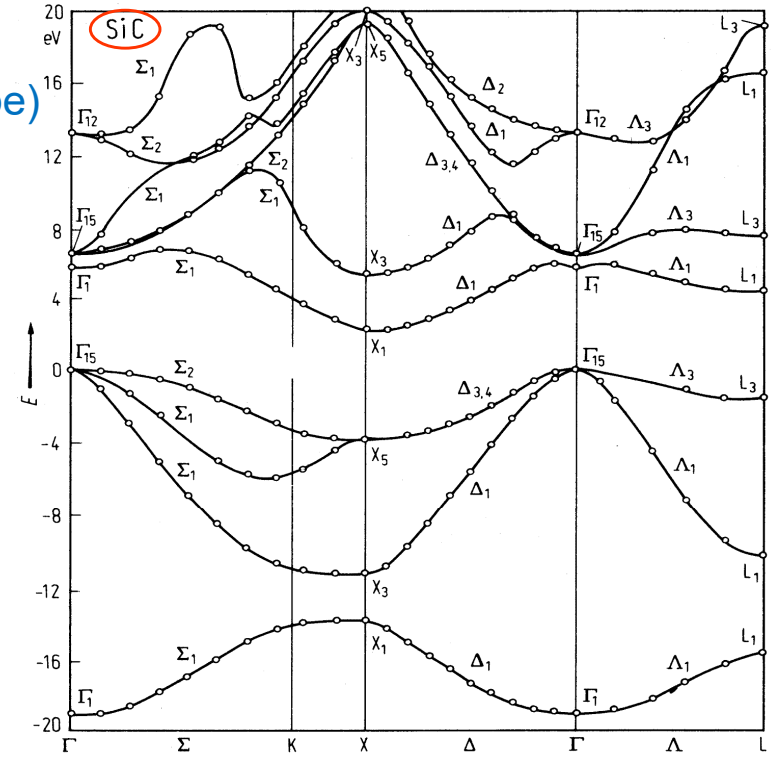
$V = 0$

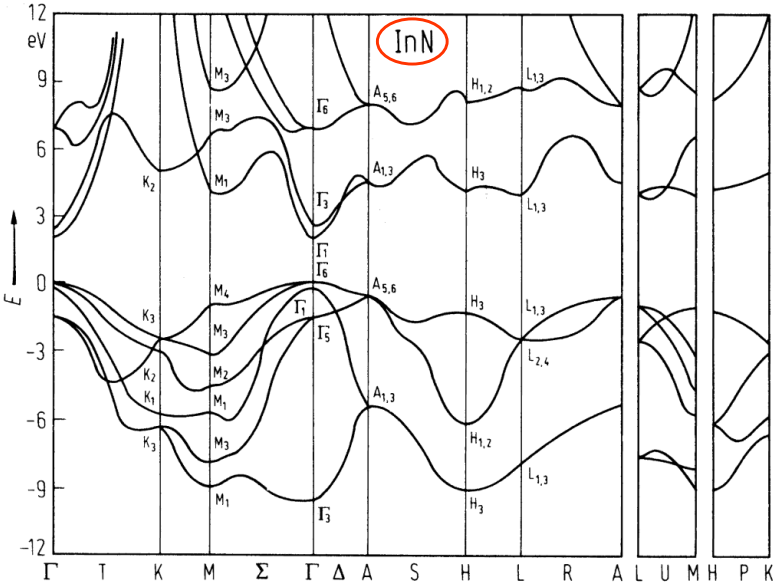
$V \neq 0$

In a true crystal: degeneracy lift due to the non-zero periodic potential

Dispersion curves: band structure

3C-SiC
(cubic polytype)

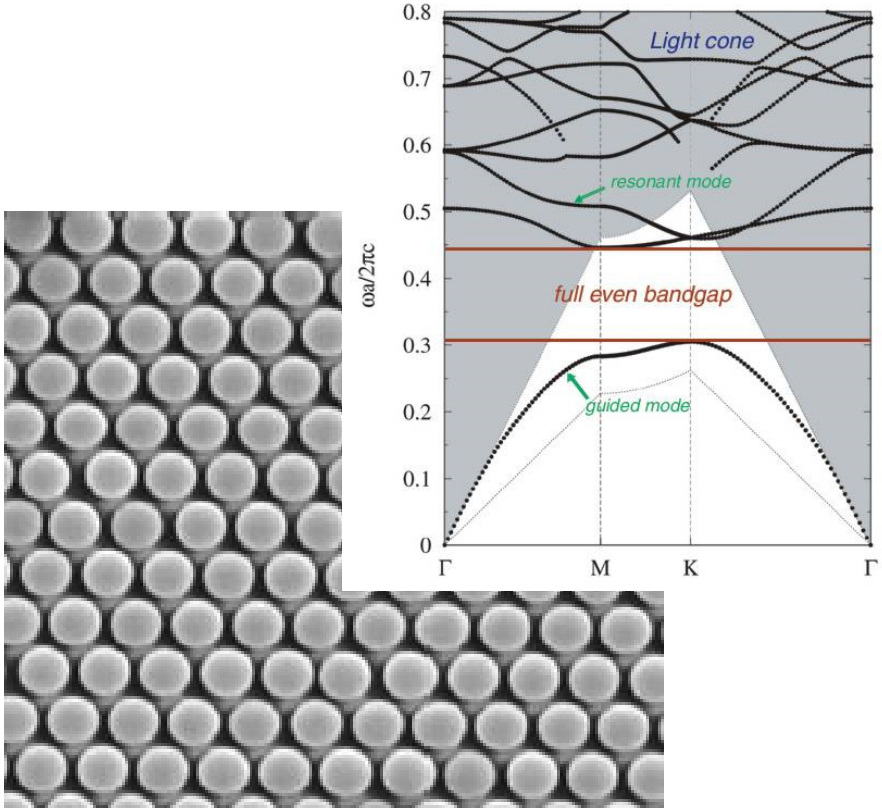




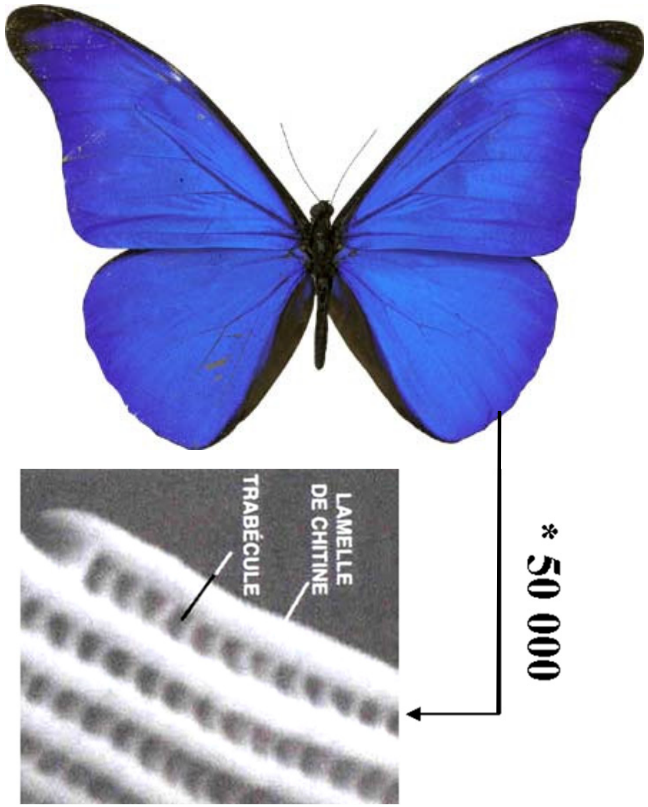
Case of InN with predicted bandgap of 1.9 eV
To be compared to true value of 0.7 eV !

Issue solved through the introduction of bandgap-corrected-approaches based on hybrid functional and quasiparticle methods

Dispersion curves and bandgap: also with photons

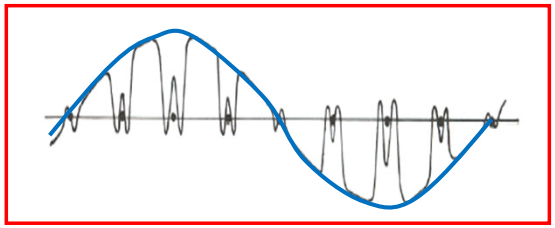


Photonic crystal



Bloch waves: particle wavefunctions in a periodic potential

$$H_e\psi_n(\mathbf{r}) = \left(\frac{p^2}{2m} + V(\mathbf{r})\right)\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$$



with $V(\mathbf{r})$ which is periodic: $V(\mathbf{r}+\mathbf{T}) = V(\mathbf{r})$

The eigenfunctions can be written as follows:

To be admitted

$$\psi_n(\mathbf{r}) = u_{n,k}(\mathbf{r})\, e^{i\mathbf{k}.\mathbf{r}}$$

Plane wave (envelope part)

Bloch functions:

- $u_{n,k}$ (atomic wave functions) vary rapidly at the lattice scale
- same symmetry as $V(\mathbf{r})$, i.e., $u_{n,k}(\mathbf{r}+\mathbf{T}) = u_{n,k}(\mathbf{r})$

Electronic band structure (1st summary)

To be admitted

r: vector in the direct lattice
k: vector in the reciprocal space
n: index of the n^{th} band (1, 2, 3 ...)

The $E_n(k)$ curves are the dispersion curves of electrons in the crystal.
Therefore, they account for the electronic band structure.

To be admitted

The $E_n(k)$ curves exhibit the symmetry of the reciprocal space.
One can thus reduce $E_n(k)$ to the first Brillouin zone and have a description of the crystal properties as a whole.

Nearly-free electron model

Let us consider electrons in a crystal with a periodic potential $V(x+a) = V(x)$

Note that the potential V is small with respect to the kinetic energy of the electrons
⇒ weak perturbation of the free electron energy

The Hamiltonian writes

$$H = -\frac{\hbar^2}{2m_0}\nabla^2 + V(x)$$

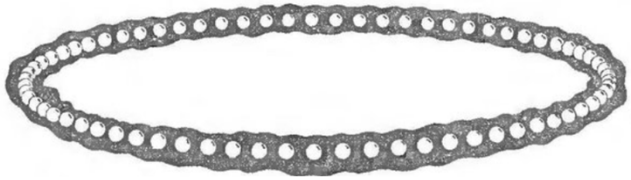
The potential being periodic it can be expressed as a Fourier series:

$$V(x) = \sum_G V_G \, e^{iGx}$$

where G is a reciprocal space vector such that $G = n' \times 2\pi / a$ (integer: n'; potential periodicity: a)

Nearly-free electron model

$$H\psi(x) = \left(\frac{p^2}{2m_0} + \sum_G V_G e^{iGx} \right) \psi(x) = E\psi(x) \qquad (1)$$



The wave functions can also be expressed as Fourier series using Born – von Kármán boundary conditions that imply $\psi(x) = \psi(x + L)$. The wave vectors are then quantized such that $K = n'' \times 2\pi / L$ with $n'' \in \mathbb{N}$ and $L = Na$ is the crystal length. The wave function then writes

K values form a quasicontinuum because *L* is large

$$\psi(x) = \sum_K C(K) e^{-iKx} \qquad (2)$$

$$(2) \text{ in } (1) \Rightarrow \quad \sum_K \left[\left(\frac{\hbar^2 K^2}{2m_0} - E \right) C(K) e^{-iKx} + \left(\sum_G V_G C(K) e^{-i(K-G)x} \right) \right] = 0$$

Nearly-free electron model

$$\sum_K \left[\left(\frac{\hbar^2 K^2}{2m_0} - E \right) C(K) e^{-iKx} + \left(\sum_G V_G C(K) e^{-i(K-G)x} \right) \right] = 0$$

This equation is multiplied by a plane wave term e^{-ikx} and further integrated over the whole crystal volume. The only non-zero terms are those such that *G-K = k*. In other words if a *k* term is present, all the other terms can be deduced by adding a *G* vector of the reciprocal lattice. This is the signature of the crystal periodicity.

Wave functions can then be identified via a *k* vector arbitrarily chosen in the 1st BZ.

$$\psi_k(x) = \sum_G C(k-G) e^{-i(k-G)x}$$ **Bloch-Floquet theorem**

Schrödinger's equation applied to Bloch functions then becomes:

$$\left(\frac{\hbar^2 k^2}{2m_0} - E_k \right) C(k) + \sum_G V_G C(k-G) = 0$$

This is the so-called **secular equation**

Nearly-free electron model

$$\left(\frac{\hbar^2 k^2}{2m_0} - E_k\right) C(k) + \sum_G V_G C(k-G) = 0$$

Non trivial solutions to the secular equation if and only if the determinant = 0

$$\begin{vmatrix} \frac{\hbar^2 (k-G)^2}{2m_0} - E(k) & V & V' & V'' \\ V & \frac{\hbar^2 k^2}{2m_0} - E(k) & V & V' \\ V' & V & \frac{\hbar^2 (k+G)^2}{2m_0} - E(k) & V \\ V'' & V' & V & \text{etc.} \end{vmatrix} = 0$$

Red, **blue** and **green** **blocks** are all equivalent (inherited from the crystalline symmetry)

Number of lines = number of points in the reciprocal space $\Rightarrow$ "infinity" of solutions

In general, it is assumed that periodicity plays a major role and in the limit $|V| >> |V'| >> |V''|$ only a single Fourier component is kept (i.e., only $V \neq 0$)

Nearly-free electron model

Particular case: *k* nearby the 1st Brillouin zone edge, i.e., $k \approx G/2 = \pi/a$ and interactions such that a single Fourier component dominates over the others (V',V'' ...<<V, very periodic case ≡ sine function)

In that case, *k* and *G*-*k* have the same value and we end up with a (2 × 2) sub-matrix with identical terms

$$\begin{bmatrix} \frac{\hbar^2 G^2}{8m_0} - E & V \\ V & \frac{\hbar^2 G^2}{8m_0} - E \end{bmatrix}$$

$k = G - k$

The potential *V* lifts the degeneracy between the free electron energy levels, which have the same energy for $k = G/2$ and $V = 0$

Nearly-free electron model

$$\begin{vmatrix} \frac{\hbar^2 (k-G)^2}{2m_0} - E & V \\ V & \frac{\hbar^2 k^2}{2m_0} - E \end{vmatrix} = 0$$ *Determinant leading to the lift of degeneracy*

There are two different solutions:

$$E_{\pm} = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\left[(E_1 - E_2)^2 + 4V^2\right]^{1/2} \text{ where } E_1 = \frac{\hbar^2 k^2}{2m_0} \text{ and } E_2 = \frac{\hbar^2 (k-G)^2}{2m_0}$$

or

$$E_{\pm} = \frac{1}{2}\frac{\hbar^2}{2m_0}\left((k-G)^2 + k^2\right) \pm \frac{1}{2}\sqrt{\left[\frac{\hbar^2}{2m_0}\left((k-G)^2 - k^2\right)\right]^2 + 4V^2}$$

Nearly-free electron model

Let us take $q = k - G/2$

$$E_{\pm} = \frac{\hbar^2}{2m_0}\left(q^2 + \frac{G^2}{4}\right) \pm \sqrt{\frac{\hbar^2 G^2}{2m_0}\frac{\hbar^2 q^2}{2m_0} + V^2}$$

We then introduce E_0 the energy of the free electron for $k = G/2$: $E_0 = \hbar^2 G^2 / 8m_0$

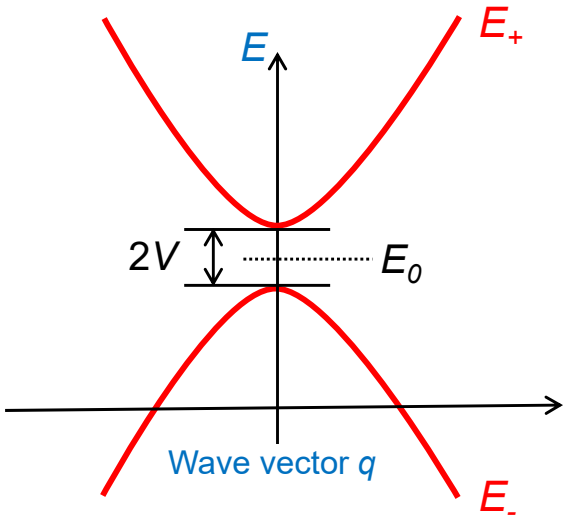
Using a first order expansion we get:

$$E_{\pm} = \frac{\hbar^2 q^2}{2m_0} + \frac{\hbar^2 G^2}{8m_0} \pm V\sqrt{1 + \frac{4}{V^2}\frac{\hbar^2 G^2}{8m_0}\frac{\hbar^2 q^2}{2m_0}}$$

$$E_{\pm} = E_0 \pm V + \frac{\hbar^2 q^2}{2m_0}\left(1 \pm \frac{2E_0}{V}\right)$$

Nearly-free electron model

$$E_{\pm} = E_0 \pm V + \frac{\hbar^2 q^2}{2m_0}\left(1 \pm \frac{2E_0}{V}\right) \qquad (1)$$



The bandgap is equal to $E_g = 2V$ ($q = 0$)

due to the degeneracy lift between right and left travelling waves e^{ikr} and $e^{i(k-G)r}$

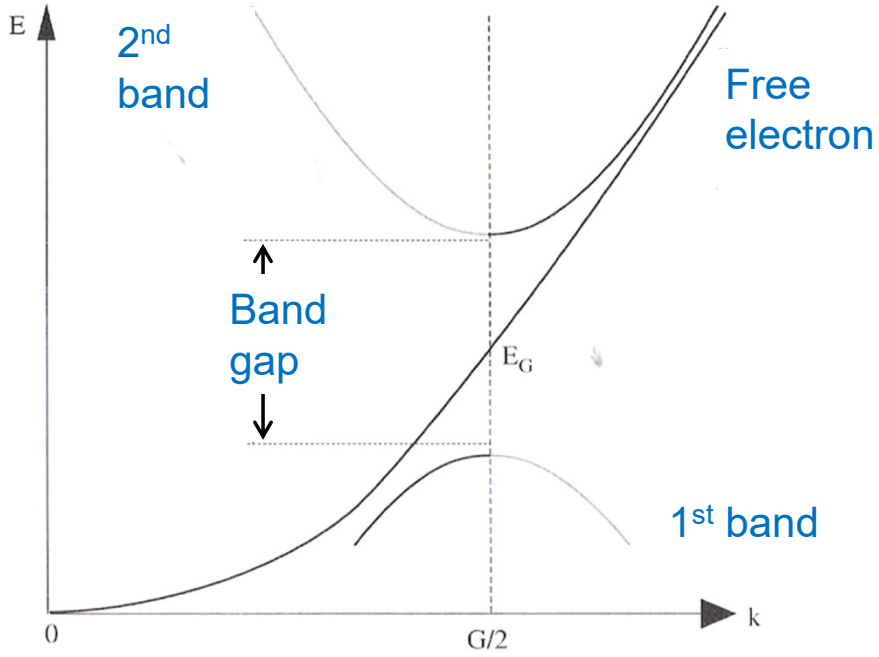
Equation (1) can then be written in a form similar to the free electron case provided we introduce an effective mass m^*

$$E_+ = E_0^+ + \frac{\hbar^2 q^2}{2m_+^*} \qquad E_- = E_0^- + \frac{\hbar^2 q^2}{2m_-^*}$$

$$m_{\pm}^* = \hbar^2 \left(\frac{\mathrm{d}^2 E}{\mathrm{d}q^2}\right)^{-1} = m_0 \frac{1}{1 \pm \frac{2E_0}{V}} \approx \pm m_0 \frac{V}{2E_0}$$

An identical mass is predicted for the two bands with the nearly-free electron model!

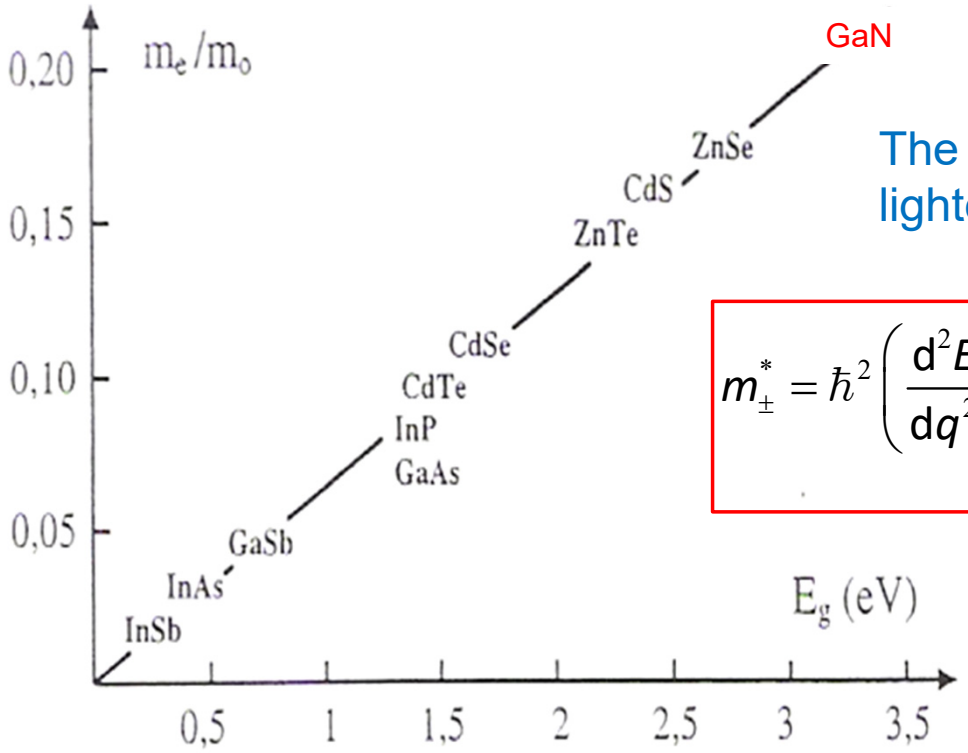
Nearly-free electron model



1. Far from the Brillouin zone edges, the band structure is that of the free electrons
2. The bandgap value is $2V$ for $q = 0$
3. Parabolic dispersion as q^2

Effective mass

Case of the electron



The smaller the bandgap, the lighter the effective mass

$$m_{\pm}^{*} = \hbar^2 \left(\frac{\mathrm{d}^2 E}{\mathrm{d}q^2} \right)^{-1} = m_0 \frac{1}{1 \pm \frac{2E_0}{V}} \approx \pm m_0 \frac{V}{2E_0}$$