# The nearly free electron approximation

**Javier Junquera**

# Basic references, where most of the information is taken from

**Charles Kittel**
"Introduction to Solid-State Physics"
John-Wiley & Sons, New York, 1996
ISBN 0-471-11181-3

Chapter 9

**Harald Ibach and Hans Lüth**
"Solid-State Physics"
Springer-Verlag, Berlin, 1993
ISBN 3-540-56841-7

Chapter 7

**N. W. Ashcroft and N. D. Mermin**
"Solid State Physics"
Saunders College Publishers, Fort Worth, 1976
ISBN 0-03-083993-9

Chapter 3 and 8

# Proos of the free electron model

Free electron model succesfully accounts for a wide range of metallic properties

Stricking deficiencies of Drude’s model (due to the use of classical statistics):

- Thermoelectric fields
- Heat capacities
- Wiedemann-Franz law

(hundreths of times too large even at room temperature

(fortuitous compensation of errors)

Fermi-Dirac statistics eliminated this class of difficulties

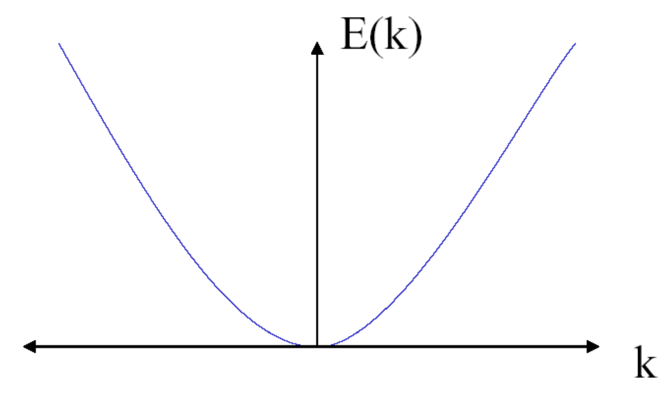
# Inedequacies of the free electron model

- The Hall coefficient
- The magnetoresistance
- The thermoelectric field
- The Wiedemann-Franz law
- Temperature dependence of the DC electrical conductivity
- Directional dependence of the DC electric conductivity
- AC conductivity
- Optical properties (Sharp resonance-like structures observed in the optical spectra of solids)

# Failures of the free electron model

**Too simple model to explain the difference between insulator, semiconductors and metals**

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$



**All the energies are allowed**

**Independent of the material!**

# Reviews of basic assumptions

**Free electron approximation**
The metallic ions play a very minor role

**Independent electron approximation**
The interaction of electrons with one another are ignored

**Relaxation time approximation**
The outcome of a collision is assumed not to depend on the configuration of the electrons at the moment of collision

**Supersimplifications to be abandoned if we want to obtain an accurate model of the solid**

# Next approximation:
# abandon the free electron approximation

Significant progress can be made by maintaining (2) and (3), concentrating on revising the free electron approximation (1)

# One step forward: consideration of a periodic potential

**All the physics of the system can be described from its Hamiltonian**

$$\hat{H}^{\mathrm{el}}_{\{\vec{R}_\alpha\}} = \sum_i -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,\alpha}\frac{1}{4\pi\epsilon_0}\frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}$$

**Kinetic energy of the electrons**

**Captures the electron-electron interaction**

**Coulomb-like**
**Repulsive**

**Captures the electron-lattice (or electron-phonon) interaction**

**Coulomb-like**
**Attractive**

**We will enrich the physical phenomenology of the crystal considering that the electrons move in the periodic potential resulting from a distribution of positive particles located in the static positions of the Bravais lattice.**

**The electrons will move within a potential that will fulfill**

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

“This chapter is not the easiest one in the book, but is the most important”

**Ch. Kittel**

**Starting sentence of chapter 9**

# Electron in a potential with the periodicity of the underlying Bravais lattice

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

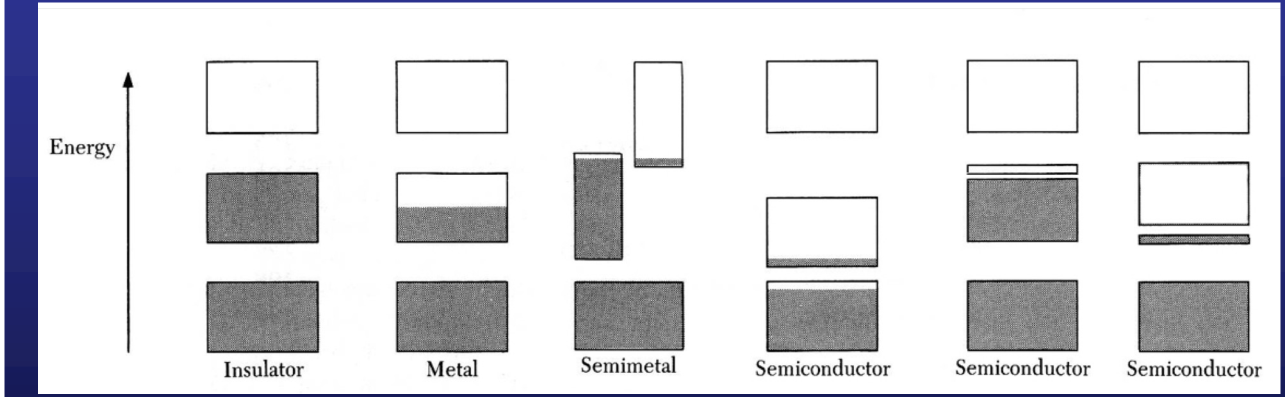
Deviations of perfect periodicity (defects, lattice vibrations,…) will be neglected
Assumption of an infinitely extended potential means the neglect all surface effects

The periodicity of the potential is of the order of $10^{-10}$ m
( ≈ de Broglie's wave length in the Sommerfeld's free electron model)

A quantum formalism is still required

New concepts:

- Energy bands
- Band gaps
- Fermi surfaces
- Effective masses



From Kittel

Electrons within the Fermi surface will occupy energy levels distributed in bands separated by gaps of forbidden energy

# From the free electron model to the energy bands

On the free electron model the allowed energy values are distributed continuosly from zero to infinity

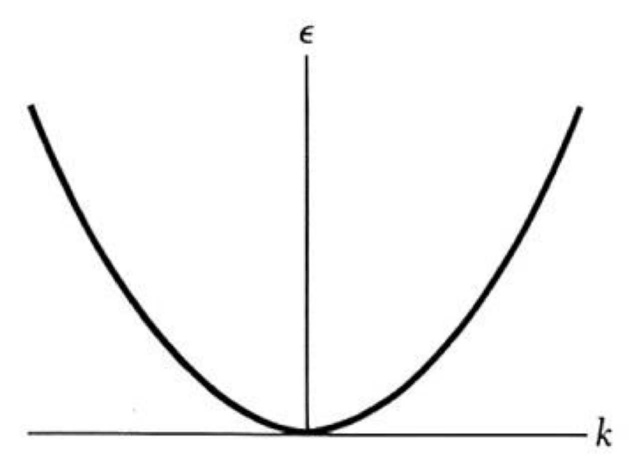
$$\epsilon(\vec{k}) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

For periodic boundary conditions over a cube of side $L$

$$k_i = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots \quad (i = x, y, z)$$

The free electron wave functions are of the form $\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$

Free electron model



# From the free electron model to the energy bands

**On the free electron model the allowed energy values are distributed continuosly from zero to infinity**

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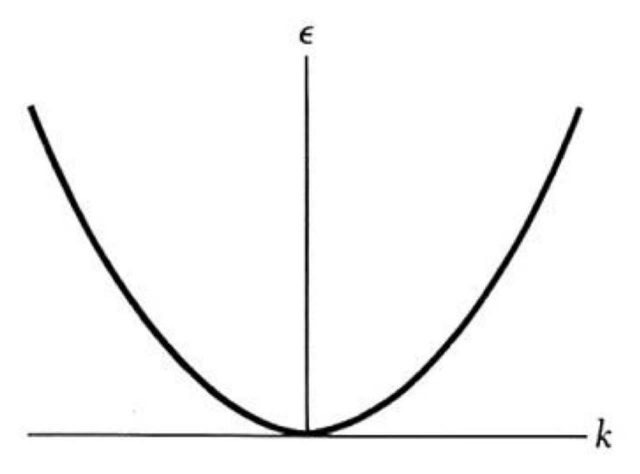
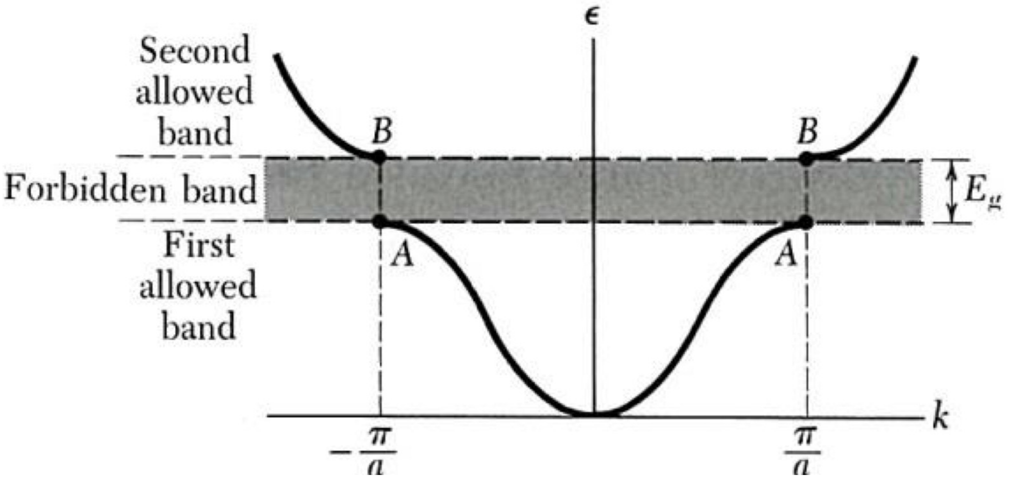
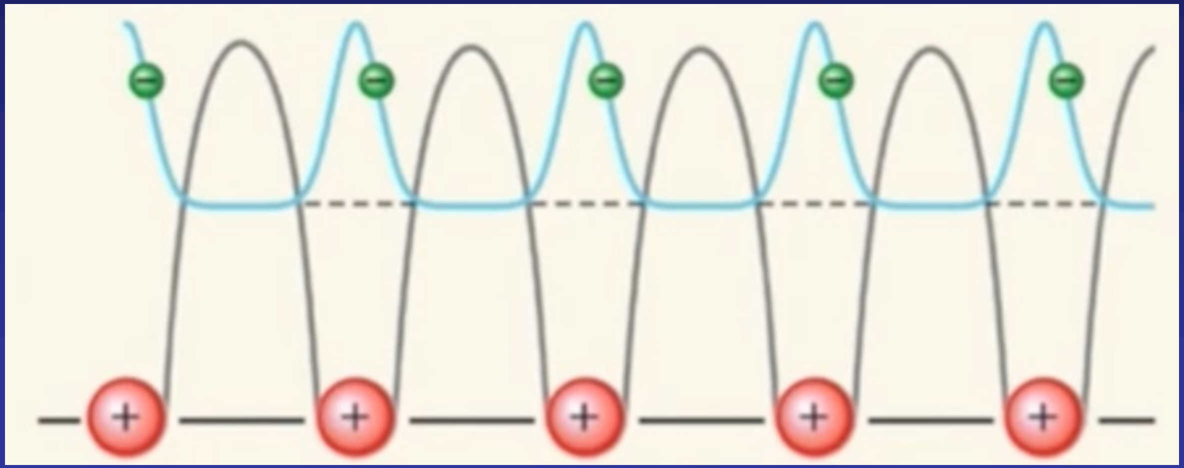
**Free electron model**



**Nearly free electron model**



# Two different aspects to analyze



1. General symmetry properties

What kind of symmetry properties will impose the periodic potential on the electronic wave function

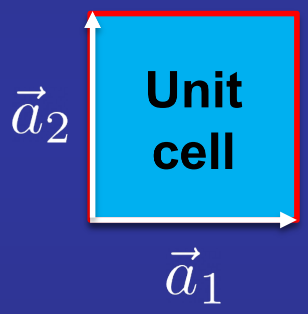
The Bloch theorem

2. Interaction with a weak periodic potential

The nearly free electron model

Energy bands

# The infinitely extended solid is described using Born-von-Karman boundary conditions

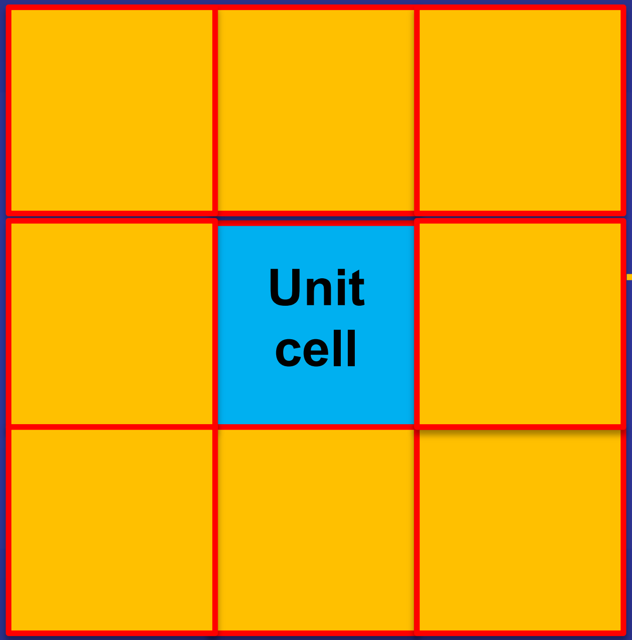


$\vec{a}_1, \vec{a}_2$ **are the primitive vectors of the Bravais lattice**

# The infinitely extended solid is described using Born-von-Karman boundary conditions

We build a supercell that contains $N = N_1 N_2 N_3$ unit cells

We repeat the unit cell $N_i$ times along the direction of the $\vec{a}_i$ Bravais lattice vector



This is the Born-von-Karman supercell

For the electronic states, we apply the periodic boundary conditions within the Born-von-Karman supercell

(the bulk properties of the solid will not depend on the choice of the boundary conditions, wich can be dictated by analytical convenience)

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

# Allowed values of $\vec{k}$ points

Let us search for plane waves compatible with the periodic boundary conditions

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

Where the wave vectors are given in a basis of the reciprocal lattice vectors

$$\vec{k} = x_1\ \vec{g}_1 + x_2\ \vec{g}_2 + x_3\vec{g}_3$$

$\vec{g}_i$ are the reciprocal lattice vectors $\quad \vec{g}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$

$$e^{iN_i\vec{k}\cdot\vec{a}_i} = 1 \Rightarrow e^{i2\pi N_i x_i} = 1$$

Consequently, we must have

$$x_i = \frac{m_i}{N_i} \qquad m_i \in \mathbb{Z}$$

The general form for allowed wave vectors is

$$\vec{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\vec{g}_i$$

There will be

$$N_1 \times N_2\ \times N_3 = N$$

Allowed wave vectors in the first Brillouin zone

# General symmetry properties
# The periodic potential

**Time independent Schrödinger equation with a finite and periodic potential**

$$\hat{\mathcal{H}}\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

**where** $V(\vec{r}+\vec{R}) = V(\vec{r})$ $\qquad \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

**Since the potential has the same periodicity as the lattice, it can be expanded in the following Fourier series**

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

**where** $\vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$ **is a reciprocal lattice vector**

**Besides, we will take into account the Born von Karman boundary conditions**

# General symmetry properties
# The electronic wave function

**We can expand a wave function that obeys the Born-von-Karman boundary conditions as plane wave expansion**

$$\psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

**where $\vec{k}$ is a point in the reciprocal space that is compatible with the periodic boundary conditions**

# General symmetry properties
# The time independent Schrödinger equation (TISE)

**Kinetic energy** $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\left(\sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\right) = \sum_{\vec{k}}\left(-\frac{\hbar^2}{2m}\right) C_{\vec{k}}\nabla^2 e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{k}}\frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$

**Potential energy** $V(\vec{r})\psi(\vec{r}) = \left(\sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}\right)\left(\sum_{\vec{k}'} C_{\vec{k}'} e^{i\vec{k}'\cdot\vec{r}}\right) = \sum_{\vec{G},\vec{k}'} V_{\vec{G}} C_{\vec{k}'} e^{i(\vec{G}+\vec{k}')\cdot\vec{r}}$

**TISE** $\sum_{\vec{k}}\frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \sum_{\vec{G},\vec{k}'} V_{\vec{G}} C_{\vec{k}'} e^{i(\vec{G}+\vec{k}')\cdot\vec{r}} = E\sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$

**Renaming the summation indices** $\vec{G}+\vec{k}' = \vec{k}$

$$\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\left[\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}}\right] = 0$$

# General symmetry properties
# The time independent Schrödinger equation (TISE)

$$\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \left[ \left( \frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} \right] = 0$$

This condition is valid for every position vector $\vec{r}$

The expression in brackets, independent of the position, must vanish for every $\vec{k}$ point

$$\left( \frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

This expression couples only expansion coefficients $C_{\vec{k}}$ of $\psi(\vec{r})$ whose value of $\vec{k}$ differ only from one another by a reciprocal lattice vector $\vec{G}$

The original problem separates into $N$ problems
($N$= number of unit cells in the Born-von-Karman supercell)
Each of them corresponds to a $\vec{k}$ vector in the unit cell of the reciprocal lattice

# Decoupling of the equations in reciprocal space

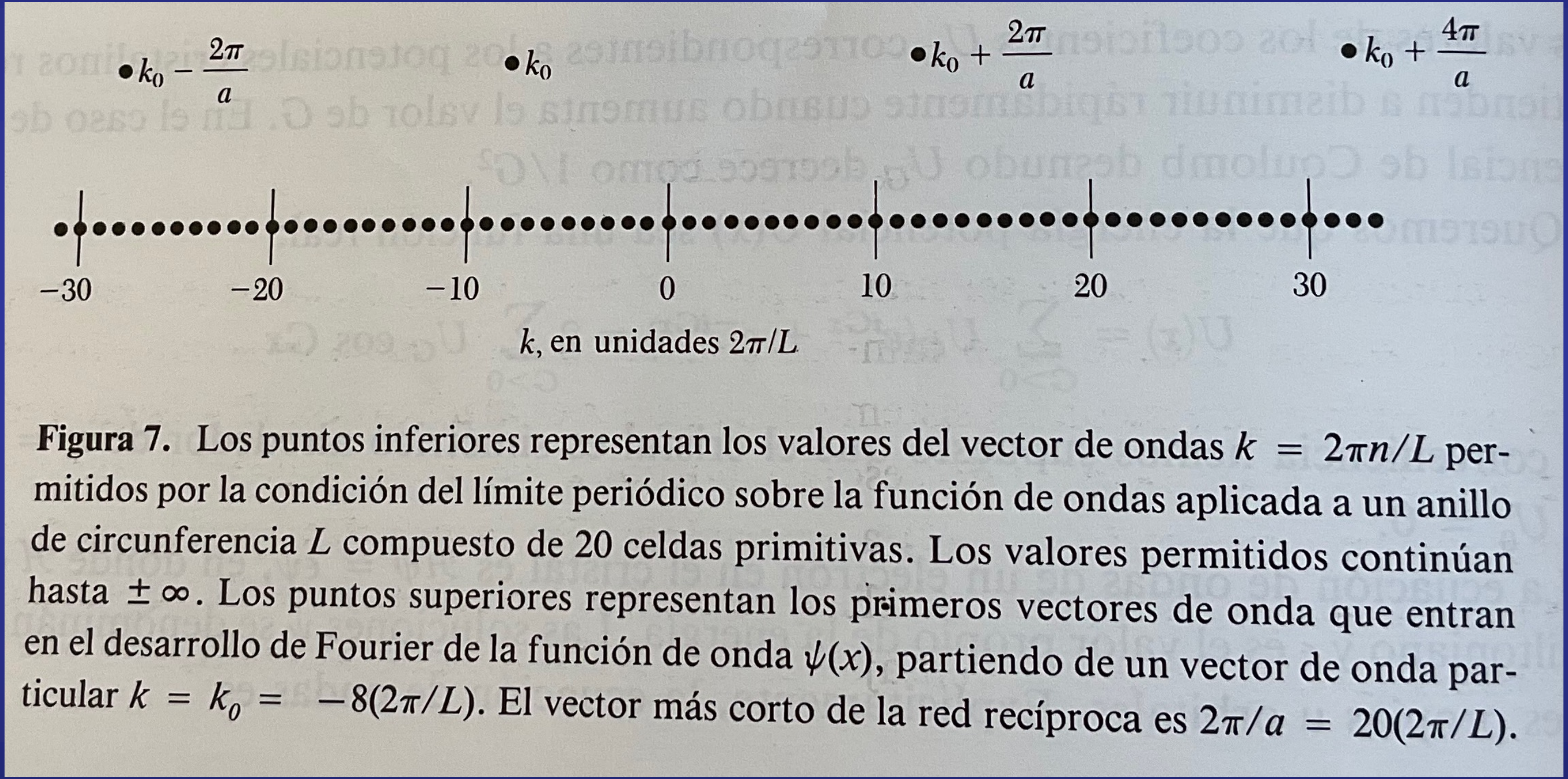


**Figura 7.** Los puntos inferiores representan los valores del vector de ondas $k = 2\pi n/L$ permitidos por la condición del límite periódico sobre la función de ondas aplicada a un anillo de circunferencia $L$ compuesto de 20 celdas primitivas. Los valores permitidos continúan hasta $\pm\infty$. Los puntos superiores representan los primeros vectores de onda que entran en el desarrollo de Fourier de la función de onda $\psi(x)$, partiendo de un vector de onda particular $k = k_0 = -8(2\pi/L)$. El vector más corto de la red recíproca es $2\pi/a = 20(2\pi/L)$.

From Kittel

# General symmetry properties
# The time independent Schrödinger equation (TISE)

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

Each of the $N$ system of equations yields a solution that can be represented as a superposition of plane waves whose wave vectors differ by reciprocal lattice vectors

The eigenvalue $E$ of the Schrödinger equation can be indexed according to $\vec{k}$

$$E_{\vec{k}} = E(\vec{k})$$

And the wave functions belonging to $\vec{k}$

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}}$$

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} = \left(\sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{-i\vec{G}\cdot\vec{r}}\right) e^{i\vec{k}\cdot\vec{r}} = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

Fourier series over reciprocal lattice vector
and thus has the periodicity of the lattice

# General symmetry properties
# Quantization of the wave vector

**The wave vector for periodic boundary conditions can take the values**

$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \pm\frac{2\pi n_x}{L}$$

$$k_y = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \pm\frac{2\pi n_y}{L}$$

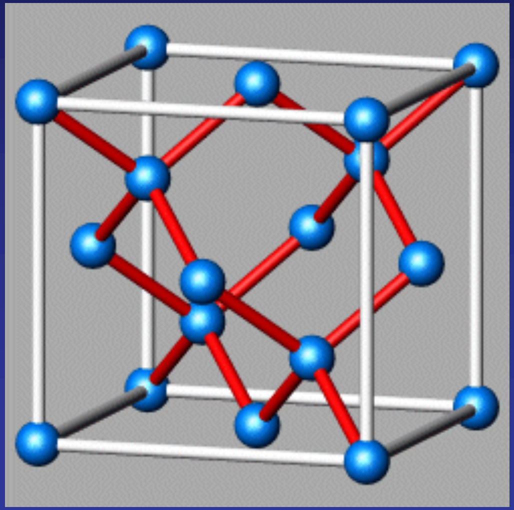
$$k_z = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \pm\frac{2\pi n_z}{L}$$

$L$ **is the macroscopic dimension of the crystal**

**yields the correct quantum numbers** $(k_x, k_y, k_z)$ or $(n_x, n_y, n_z)$ **according to which the energy eigenvalues and quantum states may be indexed**

# Summary of the Bloch theorem

**Periodic solid**



$$V\left(\vec{r}\right) = V\left(\vec{r} + \vec{R}\right)$$

$$\psi_{\vec{k}}\left(\vec{r}\right) = e^{i\vec{k}\vec{r}} u_{\vec{k}}\left(\vec{r}\right) \qquad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

**Bloch's Theorem:**

**The wave function of an electron within a mean periodic potential can be written as the product of a plane wave times a periodic function with the periodicity of the lattice**

**The wave functions are called Bloch states or Bloch waves**

# The Bloch wave functions are not eigenstates of the momentum operator

Bloch's theorem introduces a wave vector $\vec{k}$ which play a similar role to that of the free electron wave vector $\vec{k}$ plays in the Sommerfeld theorem

However, in the periodic potential case

$\vec{k}$ is not proportional to the electronic momentum

The Bloch wave function is not an eigenstate of the mometum operator

$$
\begin{aligned}
-i\hbar\nabla\psi_{n\vec{k}} &= -i\hbar\nabla\left[e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}\left(\vec{r}\right)\right] \\
&= -i\hbar\left(i\vec{k}\right)e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}\left(\vec{r}\right) - i\hbar e^{i\vec{k}\cdot\vec{r}}\nabla u_{n\vec{k}}\left(\vec{r}\right) \\
&= \hbar\vec{k}e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}} - i\hbar e^{i\vec{k}\cdot\vec{r}}\nabla u_{n\vec{k}} \\
&= \hbar\vec{k}\psi_{n\vec{k}} - i\hbar e^{i\vec{k}\cdot\vec{r}}\nabla u_{n\vec{k}}
\end{aligned}
$$

$\hbar\vec{k}$ is known as the crystal momentum

(a natural extension of $\vec{p}$ to the case of a periodic potential)

# For a given $\vec{k}$ there are many solutions to the Schrödinger equation, labeled by the band index $n$

**Look for all the solutions to the Schrödinger equation that have the Bloch form**

Replacing the solution of the Bloch theorem

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

into the Schrödinger equation

$$\hat{\mathcal{H}}\psi(\vec{r}) = \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}),$$

we arrive to

$$\begin{aligned} \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) &= \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \left( e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) \right) \\ &= \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\vec{r}) \right] \left( e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) \right) \end{aligned}$$

# For a given $\vec{k}$ there are many solutions to the Schrödinger equation, labeled by the band index $n$

$$\begin{aligned}\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r}) &= \left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right)\\ &= \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\vec{r})\right]\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right)\end{aligned}$$

Let us take the derivative with respect to $x$

$$\frac{\partial}{\partial x}\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right)=ik_x e^{i\vec{k}\cdot\vec{r}}u(\vec{r})+e^{i\vec{k}\cdot\vec{r}}\frac{\partial u(\vec{r})}{\partial x}$$

$$\begin{aligned}\frac{\partial^2}{\partial x^2}\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) &= \frac{\partial}{\partial x}\left[ik_x e^{i\vec{k}\cdot\vec{r}}u(\vec{r})+e^{i\vec{k}\cdot\vec{r}}\frac{\partial u(\vec{r})}{\partial x}\right]\\ &= (ik_x)^2 e^{i\vec{k}\cdot\vec{r}}u(\vec{r})+2ik_x e^{i\vec{k}\cdot\vec{r}}\frac{\partial u(\vec{r})}{\partial x}+e^{i\vec{k}\cdot\vec{r}}\frac{\partial^2 u(\vec{r})}{\partial x^2}\\ &= e^{i\vec{k}\cdot\vec{r}}\left[(ik_x)^2+2ik_x\frac{\partial}{\partial x}+\frac{\partial^2}{\partial x^2}\right]u(\vec{r})\end{aligned}$$

Adding the results for the three cartesian directions

$$\begin{aligned}\nabla^2\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) &= e^{i\vec{k}\cdot\vec{r}}\left[(i\vec{k})^2+2i\vec{k}\cdot\nabla+\nabla^2\right]u(\vec{r})\\ &= e^{i\vec{k}\cdot\vec{r}}\left(i\vec{k}+\nabla\right)^2 u(\vec{r})\end{aligned}$$

# For a given $\vec{k}$ there are many solutions to the Schrödinger equation, labeled by the band index $n$

$$\begin{aligned}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) &= \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) \\ &= \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(\vec{r})\right]\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right)\end{aligned}$$

Let us take the derivative with respect to $x$

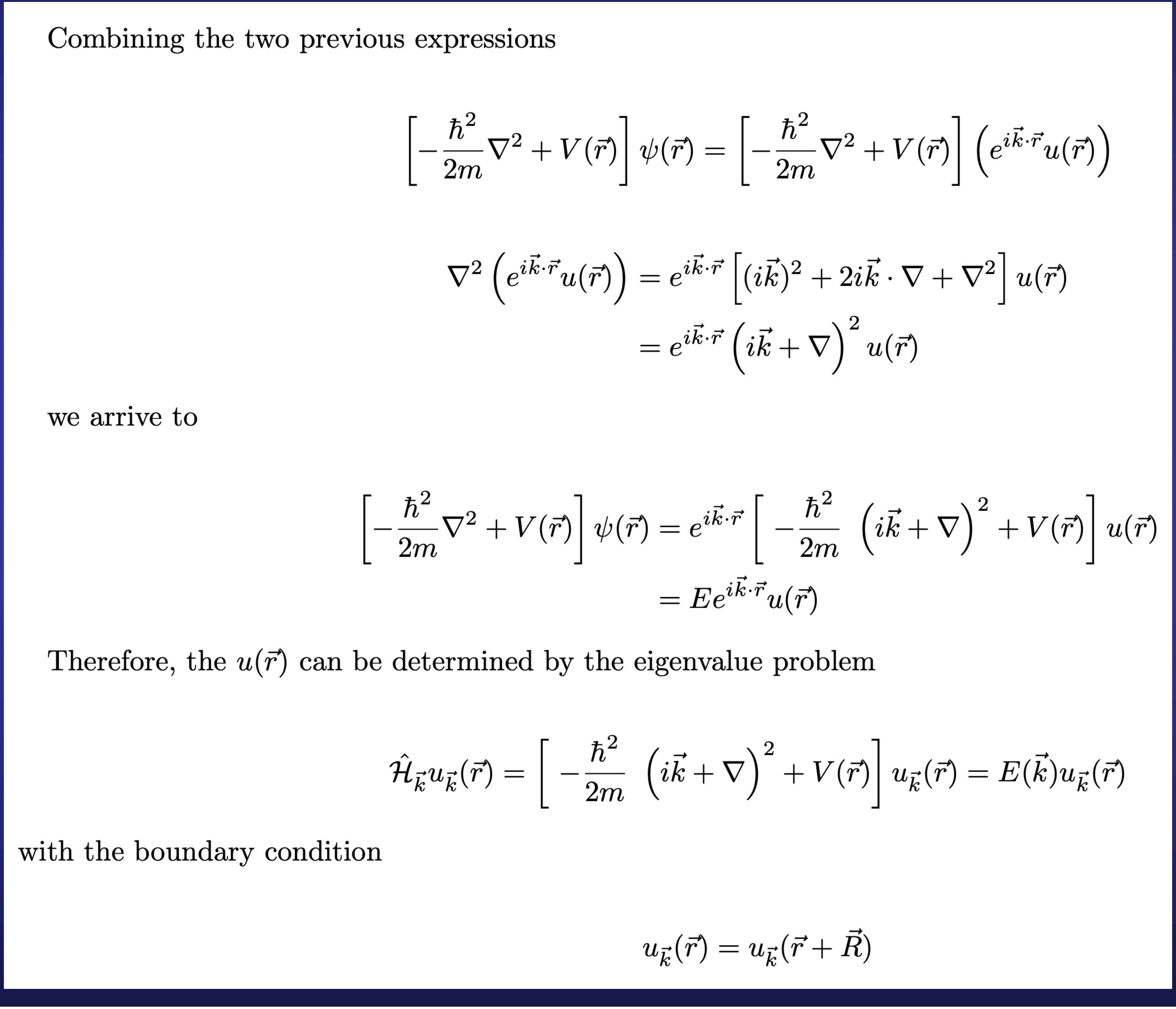
$$\frac{\partial}{\partial x}\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) = ik_x e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\frac{\partial u(\vec{r})}{\partial x}$$

$$\begin{aligned}\frac{\partial^2}{\partial x^2}\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) &= \frac{\partial}{\partial x}\left[ik_x e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\frac{\partial u(\vec{r})}{\partial x}\right] \\ &= (ik_x)^2 e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) + 2ik_x e^{i\vec{k}\cdot\vec{r}}\frac{\partial u(\vec{r})}{\partial x} + e^{i\vec{k}\cdot\vec{r}}\frac{\partial^2 u(\vec{r})}{\partial x^2} \\ &= e^{i\vec{k}\cdot\vec{r}}\left[(ik_x)^2 + 2ik_x\frac{\partial}{\partial x} + \frac{\partial^2}{\partial x^2}\right]u(\vec{r})\end{aligned}$$

Adding the results for the three cartesian directions

$$\begin{aligned}\nabla^2\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) &= e^{i\vec{k}\cdot\vec{r}}\left[(i\vec{k})^2 + 2i\vec{k}\cdot\nabla + \nabla^2\right]u(\vec{r}) \\ &= e^{i\vec{k}\cdot\vec{r}}\left(i\vec{k} + \nabla\right)^2 u(\vec{r})\end{aligned}$$

# For a given $\vec{k}$ there are many solutions to the Schrödinger equation, labeled by the band index $n$



Combining the two previous expressions

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right)$$

$$\begin{aligned}\nabla^2\left(e^{i\vec{k}\cdot\vec{r}}u(\vec{r})\right) &= e^{i\vec{k}\cdot\vec{r}}\left[(i\vec{k})^2 + 2i\vec{k}\cdot\nabla + \nabla^2\right]u(\vec{r}) \\ &= e^{i\vec{k}\cdot\vec{r}}\left(i\vec{k}+\nabla\right)^2 u(\vec{r})\end{aligned}$$

we arrive to

$$\begin{aligned}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) &= e^{i\vec{k}\cdot\vec{r}}\left[-\frac{\hbar^2}{2m}\left(i\vec{k}+\nabla\right)^2 + V(\vec{r})\right]u(\vec{r}) \\ &= Ee^{i\vec{k}\cdot\vec{r}}u(\vec{r})\end{aligned}$$

Therefore, the $u(\vec{r})$ can be determined by the eigenvalue problem

$$\hat{\mathcal{H}}_{\vec{k}}u_{\vec{k}}(\vec{r}) = \left[-\frac{\hbar^2}{2m}\left(i\vec{k}+\nabla\right)^2 + V(\vec{r})\right]u_{\vec{k}}(\vec{r}) = E(\vec{k})u_{\vec{k}}(\vec{r})$$

with the boundary condition

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$$

# For a given $\vec{k}$ there are many solutions to the Schrödinger equation, labeled by the band index $n$

$$\hat{\mathcal{H}}_{\vec{k}} u_{\vec{k}}(\vec{r}) = \left[ -\frac{\hbar^2}{2m} \left( i\vec{k} + \nabla \right)^2 + V(\vec{r}) \right] u_{\vec{k}}(\vec{r}) = E(\vec{k}) u_{\vec{k}}(\vec{r})$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

Hermititian eigenvalue problem restricted to a single primitive cell
(fixed finite volume)

Infinite family of solutions with discretely spaced eigenvalues,
that will be labelled with the band index $n$

The wave vector $\vec{k}$ appears as a parameter in the Hamiltonian $\hat{\mathcal{H}}_{\vec{k}}$

We expect each of the energy levels for a given $\vec{k}$ to vary continuously as $\vec{k}$ varies

We arrive at the description of the levels of an electron in a periodic potential
in terms of a family of continuous functions $E_n(\vec{k})$
(ENERGY BANDS)

# Both the Bloch wave functions and the eigenvalues are periodic functions in reciprocal space

$$\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n\,\vec{k}}(\vec{r})$$

$$E_n(\vec{k}+\vec{G}) = E_n(\vec{k})$$

The wave vector $\vec{k}$ appearing in Bloch's theorem can always be confined to the first Brillouin zone

Any vector $\vec{k}'$ not in the first Brillouin zone can be written as

$$\vec{k}' = \vec{k} + \vec{G}$$

where $\vec{G}$ is a reciprocal lattice vector and $\vec{k}$ lie in the first Brillouin zone

# The energy eigenfunctions are periodic functions of the wave vectors of the Bloch waves

$$\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n\,\vec{k}}(\vec{r})$$

**Demonstration**

$$\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = e^{i(\vec{k}+\vec{G})\cdot\vec{r}} u_{n\,\vec{k}+\vec{G}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \left[ e^{i\vec{G}\cdot\vec{r}} u_{n\,\vec{k}+\vec{G}}(\vec{r}) \right]$$

$$\begin{aligned}
e^{i\vec{G}\cdot\vec{r}} u_{n\,\vec{k}+\vec{G}}(\vec{r}) &= e^{i\vec{G}\cdot\vec{r}} \sum_{\vec{G}'} C_{n\,\vec{k}+\vec{G}-\vec{G}'} e^{-i\vec{G}'\cdot\vec{r}} && \longleftarrow \quad u_{n\,\vec{k}}(\vec{r}) = \sum_{\vec{G}'} C_{n\,\vec{k}-\vec{G}'} e^{-i\vec{G}'\cdot\vec{r}} \\
&= \sum_{\vec{G}'} C_{n\,\vec{k}+\vec{G}-\vec{G}'} e^{-i(\vec{G}'-\vec{G})\cdot\vec{r}} \\
&= \sum_{\vec{G}''} C_{n\,\vec{k}-\vec{G}''} e^{-i\vec{G}''\cdot\vec{r}} && \longleftarrow \quad \vec{G}'' = \vec{G}' - \vec{G} \\
&= u_{n\,\vec{k}}(\vec{r})
\end{aligned}$$

$$\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\,\vec{k}}(\vec{r}) = \psi_{n\,\vec{k}}(\vec{r})$$

# The energy eigenvalues are periodic functions of the wave vectors of the Bloch waves

$$E_n(\vec{k}+\vec{G}) = E_n(\vec{k})$$

**Demonstration**

$$\hat{\mathcal{H}}\psi_{n\,\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n\,\vec{k}}(\vec{r})$$

$$\hat{\mathcal{H}}\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = E_n(\vec{k}+\vec{G})\psi_{n\,\vec{k}+\vec{G}}(\vec{r})$$

**But since** $\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\,\vec{k}}(\vec{r}) = \psi_{n\,\vec{k}}(\vec{r})$

$$\hat{\mathcal{H}}\psi_{n\,\vec{k}}(\vec{r}) = E_n(\vec{k}+\vec{G})\psi_{n\,\vec{k}}(\vec{r})$$

**So, finally, comparing the first equation with this last one**

$$E_n(\vec{k}) = E_n(\vec{k}+\vec{G})$$

# Upper and lower bounds in the band structure

$$E_n(\vec{k} + \vec{G}) = E_n(\vec{k})$$

Since the bands are periodic in $\vec{k}$ and continuous,
they have an upper and lower bound,
so that all the levels $E_n(\vec{k})$ lie in the band of energyes lying between these limits

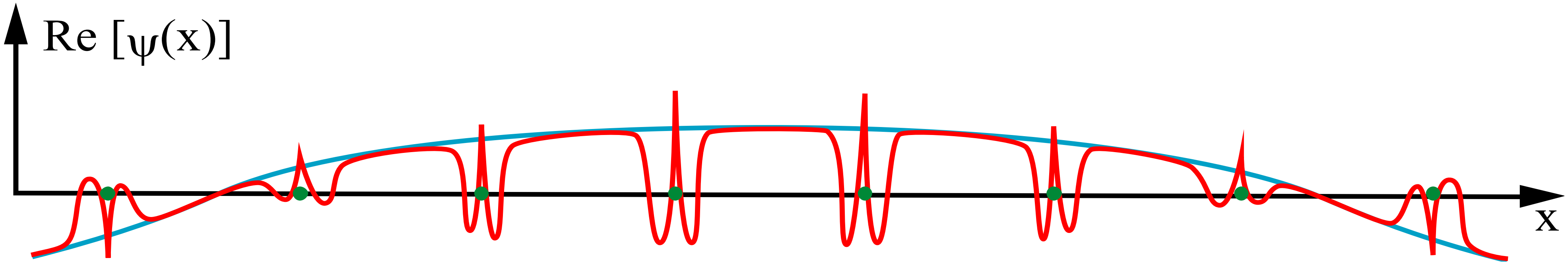
# Bloch functions are not periodic in real space

**Bloch functions are not periodic in real space**

$$\psi_{n\vec{k}}\left(\vec{r}+\vec{R}\right)=e^{i\vec{k}\cdot\left(\vec{r}+\vec{R}\right)}u_{n\vec{k}}\left(\vec{r}+\vec{R}\right)=e^{i\vec{k}\cdot\vec{R}}e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}\left(\vec{r}\right)=e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}\left(\vec{r}\right)$$

**Its square (associated with the probability of finding an electron in a given position) is periodic**

$$\left|\psi_{n\vec{k}}\left(\vec{r}+\vec{R}\right)\right|^{2}=\left|\psi_{n\vec{k}}\left(\vec{r}\right)\right|^{2}$$



# Electron velocity

An electron in a level specified by a band index $n$ and a wave vector $\vec{k}$ has a non-vanishing mean velocity

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} E_n(\vec{k})$$

There are stationary (time independent) levels of an electron in a periodic potential in which, in spite of the interaction of the electrons with the fixed lattice, it moves forever without any degradation of its mean velocity

Contrast with Drude's model:

Collisions were simply encounters between the electrons and the statis ions

# The nearly-free-electron approximation

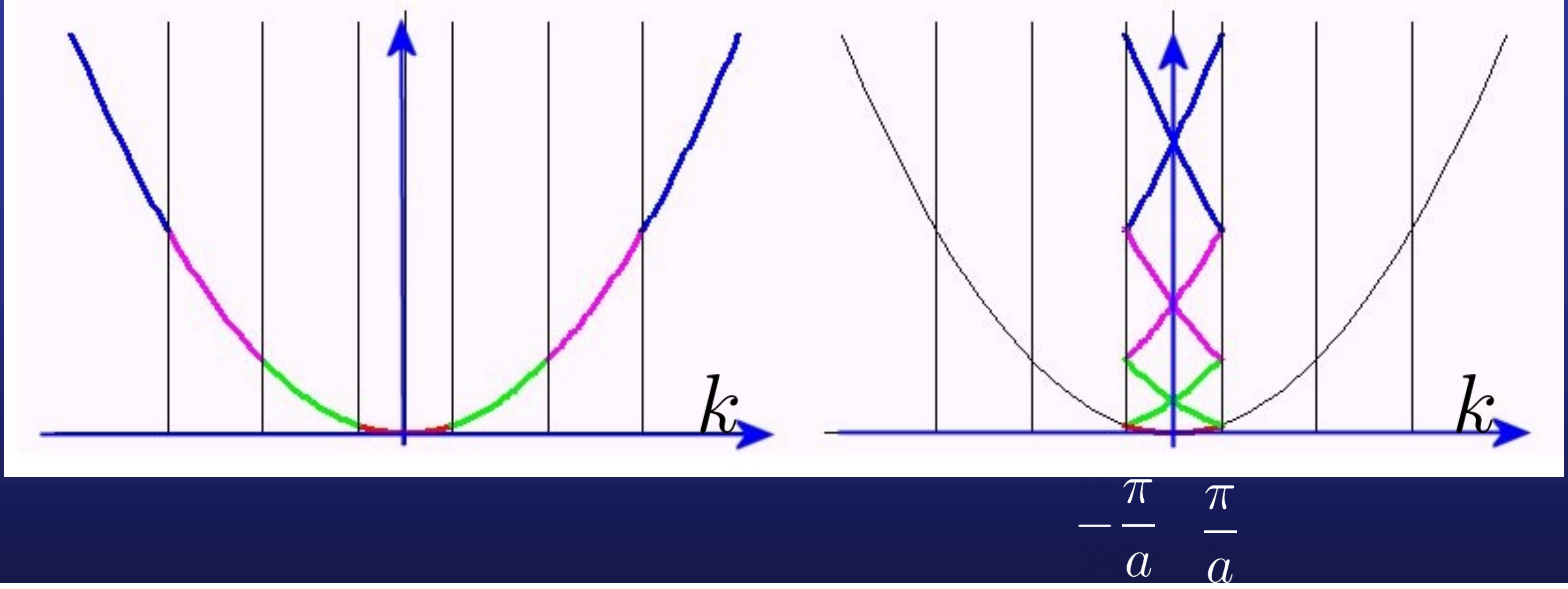
We shall consider the case of a vanishingly small periodic potential

We shall imagine that the periodic potential starts at zero and is gradually “switched on”

What happens then to the energy states of the free electrons?

We shall start with the energy states of free electrons in the square-well potential

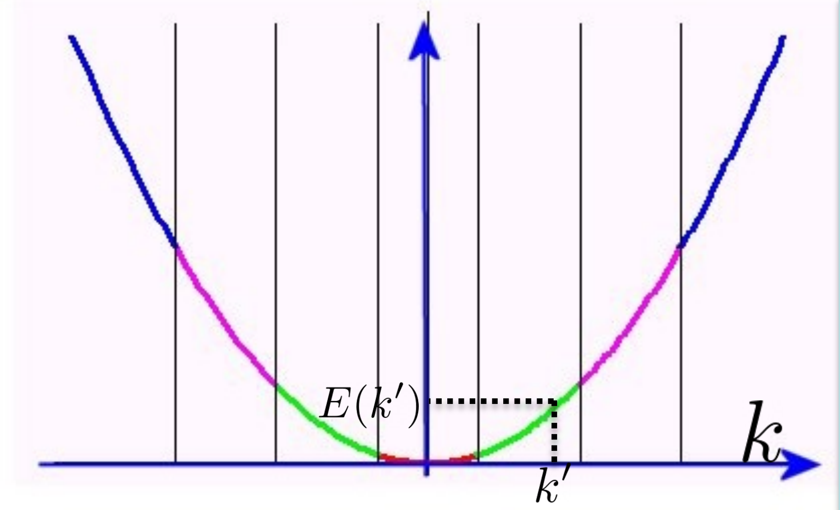
$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$



**Extended zone scheme**

**Reduced zone scheme**

# Extended zone scheme

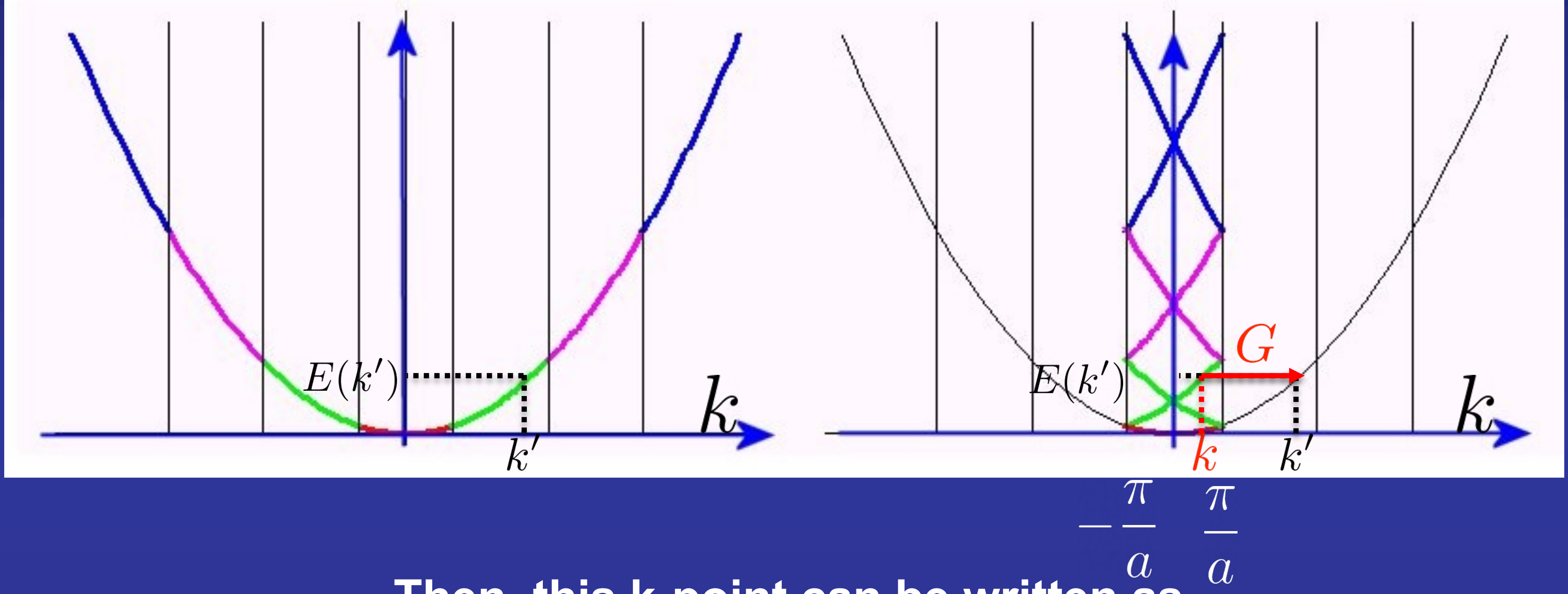


Only one band plotted for
all the kpoints
(including those outside
the first Brillouin zone)

Let us take a k-point outside the first Brillouin zone, $k', |k'| > \pi/a$
with an associated eigenvalue $E(k')$

# From the extended zone scheme to the reduced zone scheme

**Extended zone scheme** **Reduced zone scheme**



Then, this k-point can be written as

$$k' = k + G$$

It follows than any energy for wave vector outside the first-Brillouin zone is equal to an eigenvalue in the first-Brillouin zone
(might be with other band index)

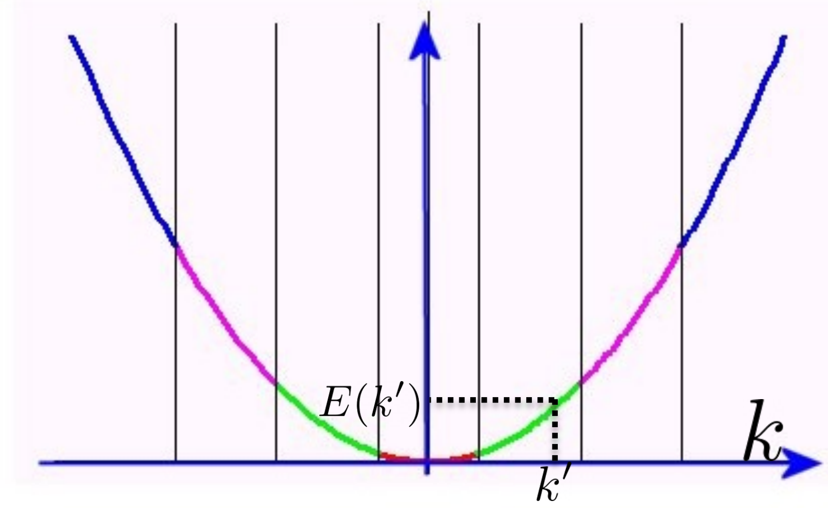
In the example above, there is one red band and one green band below our translated band

$$E_1^{\text{extended}}(k') = E_1^{\text{extended}}(k+G) = E_3^{\text{reduced}}(k)$$

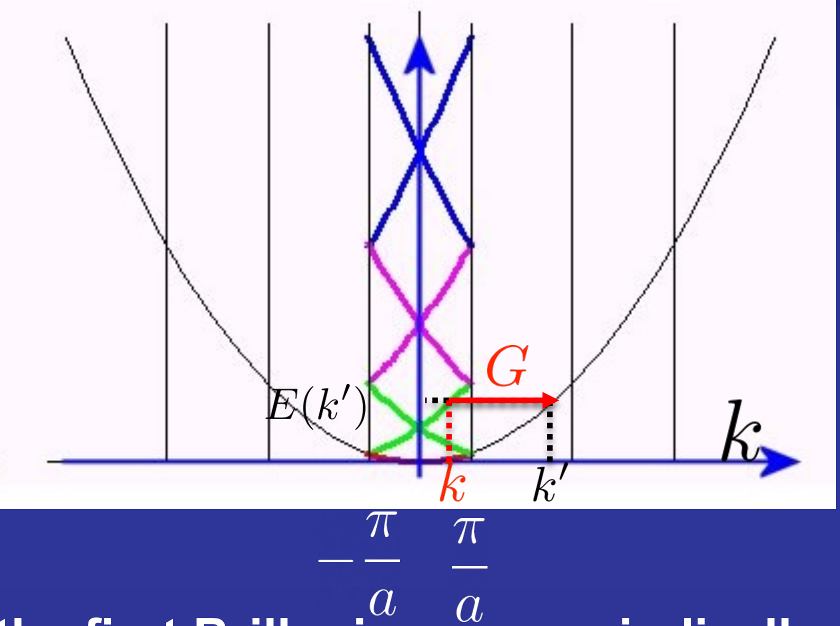
**We need solve for the energy only in the first Brillouin zone for each band**

# From the reduced zone scheme to the periodic zone scheme

**Extended zone scheme**

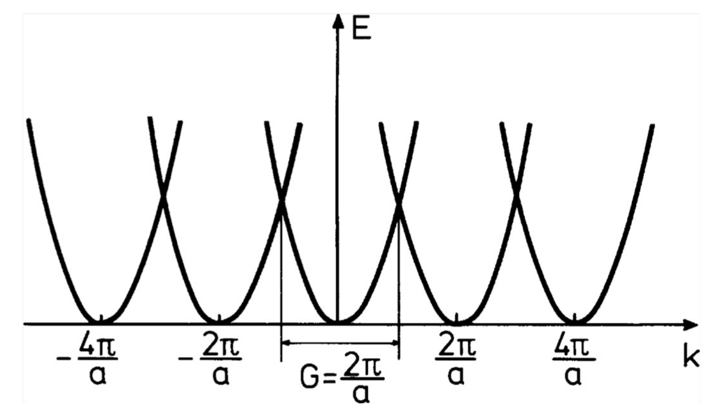


**Reduced zone scheme**



Sometimes it is helpful to repeat the first Brillouin zone periodically through all the reciprocal space.

**Periodic zone scheme**



If we can translate the contents of other zones into the first zone, then we can translate the first zone into any or every other zone

$$E_n(k) = E_n(k+G)$$

# The nearly-free-electron approximation

We shall consider the case of a vanishingly small periodic potential

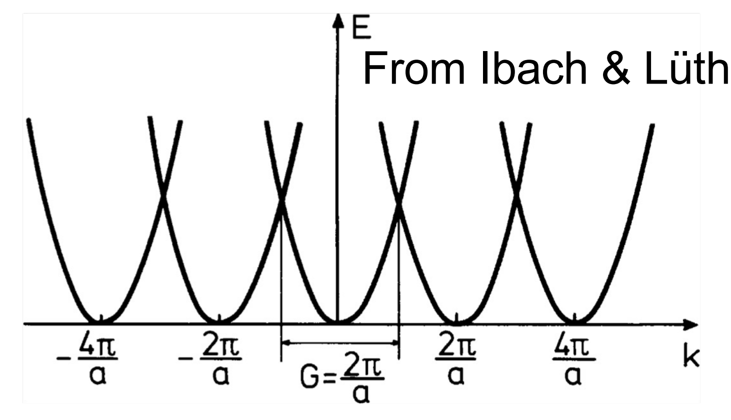
We shall imagine that the periodic potential starts at zero and is gradually “switched on”

What happens then to the energy states of the free electrons?

We shall start with the energy states of free electrons in the square-well potential

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$

In the extreme case, where the potential is still zero ($V_{\vec{G}} = 0 \ \forall \ \vec{G}$ )
one must consider the symmetry requirements of the periodicity
The possible electron states are not restricted to a single parabola in $\vec{k}$ space
but can be found equally well on parabolas shifted by any $\vec{G}$ vector



From Ibach & Lüth

$$E(\vec{k}) = E(\vec{k}+\vec{G}) = \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2$$

# Reduction to the first Brillouin zone

Since the behaviour of $E(\vec{k})$ is periodic in $\vec{k}$ space,
it is sufficient to represent this in the first Brilloun zone only

From Ibach & Lüth

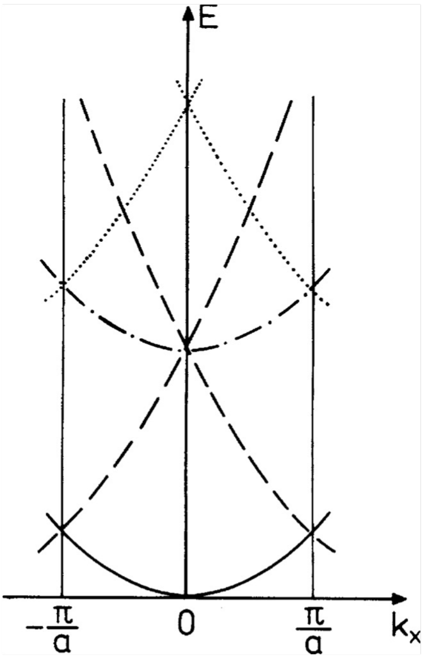


**Fig. 7.3.** Bandstructure for a free electron gas in a primitive cubic lattice (lattice constant $a$), represented on a section along $k_x$ in the first Brillouin zone. The periodic potential is assumed to be vanishing ("empty" lattice). The various branches stem from parabolas whose origin in reciprocal space is given by the Miller indices $hkl$. (——) 000; (– – –) 100, $\bar{1}00$; (–·–) 010, $0\bar{1}0$, 001, $00\bar{1}$; (· · ·) 110, 101, $1\bar{1}0$, $10\bar{1}$, $\bar{1}10$, $\bar{1}01$, $\bar{1}\bar{1}0$, $\bar{1}0\bar{1}$

There is a degeneracy of the energy values at the edges of the first Brillouin zone, $+\frac{G}{2} = \frac{\pi}{a}$ and $-\frac{G}{2} = -\frac{\pi}{a}$ ,

where two parabolas intersect

The description of the state of an electron with these $\vec{k}$ values is necessarily a superposition of at least two corresponding plane waves

# The nearly-free-electron approximation: solutions at the Brillouin zone border

For a vanishing potential (zero order approximation) these waves are

$$e^{iGx/2} \quad \text{and} \quad e^{i[(G/2)-G]x} = e^{-iGx/2}$$

The approximate expressions for a perturbation calculation of the influence of a small potential are of the form

$$\psi_+ \sim \left(e^{iGx/2} + e^{-iGx/2}\right) = 2\cos\left(\frac{Gx}{2}\right) = 2\cos\left(\frac{2\pi}{a}\frac{x}{2}\right) \sim \cos\left(\frac{\pi x}{a}\right)$$

$$\psi_- \sim \left(e^{iGx/2} - e^{-iGx/2}\right) = 2i\sin\left(\frac{Gx}{2}\right) = 2i\sin\left(\frac{2\pi}{a}\frac{x}{2}\right) \sim \sin\left(\frac{\pi x}{a}\right)$$

These are standing waves possessing zeros at fixed position in space

They can be represented as a superposition of an

- incoming wave and
- a counter-propagating “Bragg-reflected” wave

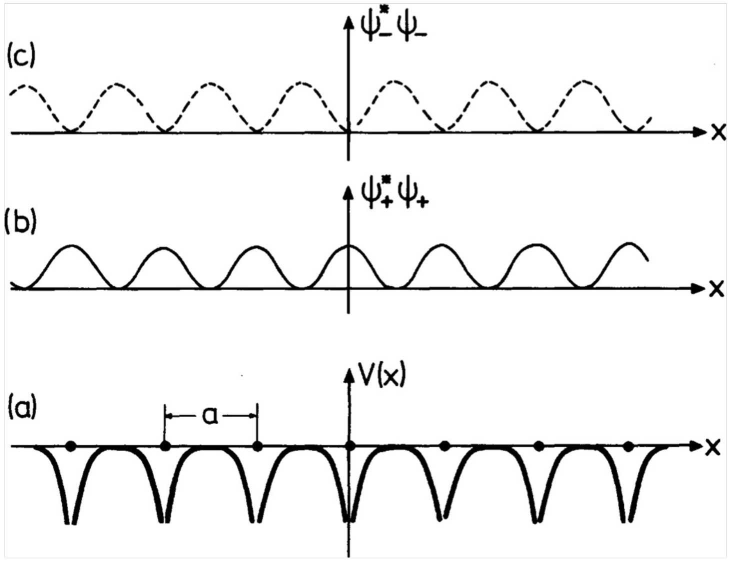
# The nearly-free-electron approximation: solutions at the Brillouin zone boundary (density)

$$\psi_+ \sim \left(e^{iGx/2} + e^{-iGx/2}\right) = 2\cos\left(\frac{Gx}{2}\right) = 2\cos\left(\frac{2\pi}{a}\frac{x}{2}\right) \sim \cos\left(\frac{\pi x}{a}\right)$$

$$\psi_- \sim \left(e^{iGx/2} - e^{-iGx/2}\right) = 2i\sin\left(\frac{Gx}{2}\right) = 2i\sin\left(\frac{2\pi}{a}\frac{x}{2}\right) \sim \sin\left(\frac{\pi x}{a}\right)$$

**The corresponding probability densities are**

$$\rho_+ = \psi_+^*\psi_+ \sim \cos^2\left(\frac{\pi x}{a}\right) \qquad \rho_- = \psi_-^*\psi_- \sim \sin^2\left(\frac{\pi x}{a}\right)$$



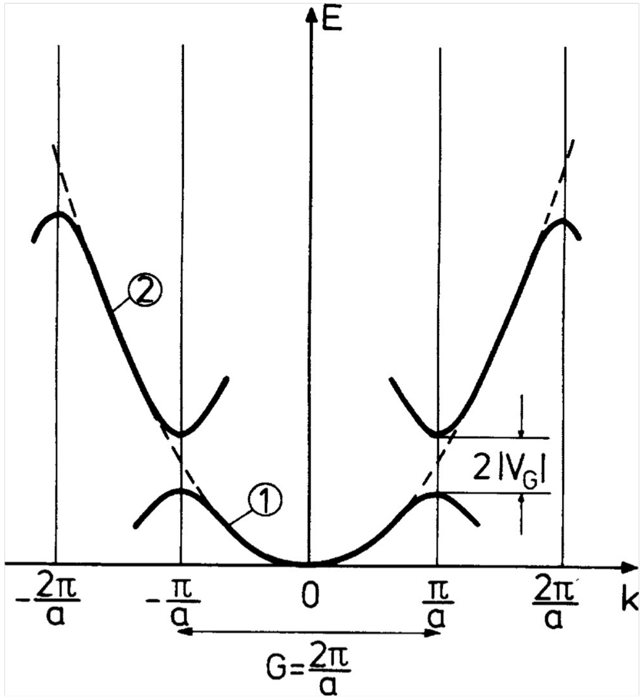
From Ibach & Lüth

**Fig. 7.4. (a)** Qualitative form of the potential energy $V(x)$ of an electron in a one-dimensional lattice. The positions of the ion cores are indicated by the points with separation $a$ (lattice constant). **(b)** Probability density $\varrho_+ = \psi_+^*\psi_+$ for the standing wave produced by Bragg reflection at $k = \pm\pi/a$ (upper edge of band ① in Fig. 7.5). **(c)** Probability density $\varrho_- = \psi_-^*\psi_-$ for the standing wave at the lower edge of band ② (Fig. 7.5) at $k = \pm\pi/a$

# The nearly-free-electron approximation: solutions at the Brillouin zone boundary (energy)

$\psi_+$ has lower total energy (particularly potential energy) than that of a free electron

$\psi_-$ has higher total energy (particularly potential energy) than that of a free electron



From Ibach & Lüth

**Fig. 7.5.** Splitting of the energy parabola of the free electron (– – –) at the edges of the first Brillouin zone $\mathbf{k} = \pm\pi/a$ in the one-dimensional case). To a first approximation the gap is given by twice the corresponding Fourier coefficient $V_G$ of the potential. Periodic continuation over the whole of $\mathbf{k}$-space gives rise to continuous bands ① and ②, shown here only in the vicinity of the original energy parabola

This increase and decrease in the energy of the electron of the states at the zone boundary represents a deviation from the free-electron energy parabola

A gap is opened at $\pi/a$ where $a$ is determined by the lattice

# The nearly-free-electron approximation: quantitative solution

The solution can be considered from a
perturbation of the eigenstates at zero potencial

$$\psi^0_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

Trivially verifies the Bloch theorem.
The function with the periodicity of the lattice is $\frac{1}{\sqrt{V}}$

The associated eigenvalue is

$$E^0(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$

# Fourier transform of a weak periodic potential

Let us assume that $V(\vec{r})$ is a weak periodic potential
with the periodicity of the lattice

Therefore, it can be expanded in a basis of plane waves with
wave vectors that are vectors of the reciprocal lattice

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

The Fourier components $V(\vec{G})$ are related with $V(\vec{r})$ by

$$V(\vec{G}) = \frac{1}{\Omega} \int_{\text{cell}} d\vec{r} e^{-i\vec{G}\cdot\vec{r}} V(\vec{r})$$

Integral over the
primitive cell of volume $\Omega$

Since we are at liberty to change the potential energy by an additive constant,
we fix this constant by requiring that the spatial average of the potential over
a primitive cell vanishes

$$V(\vec{G}=0) \equiv V_0 = \frac{1}{v} \int_{\text{cell}} d\vec{r}\, V(\vec{r}) = 0$$

Since the potential is real $V(-\vec{G}) = V^*(\vec{G})$

In a weak periodic potential $|V(\vec{G})|$ are small $\forall\ \vec{G}$

# Electronic wave function in a weak periodic potential

A function that complies with the Bloch theorem

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} = \left[\sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{-i\vec{G}\cdot\vec{r}}\right] e^{i\vec{k}\cdot\vec{r}}$$

If the potential is weak, we expect that the wave functions differ only slightly from the unperturbed wave functions

$$\psi^0_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

In other words, we expect that

$$|C_{\vec{k}-\vec{G}}| << C_{\vec{k}} = \frac{1}{\sqrt{V}} \ \forall \ \vec{G}$$

# Consequences of $|C_{\vec{k}-\vec{G}}| << C_{\vec{k}} = \frac{1}{\sqrt{V}} \ \forall \ \vec{G}$

Starting from the general representation of the Schrödinger equation in reciprocal space

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

Where $E$ is the eigenvalue of

$$\hat{\mathcal{H}}\psi_{\vec{k}}(\vec{r}) = E\psi_{\vec{k}}(\vec{r})$$

And translating by a reciprocal lattice vector

$$\left(E - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2\right) C_{\vec{k}-\vec{G}} = \sum_{\vec{G}'} V_{\vec{G}'} C_{\vec{k}-\vec{G}-\vec{G}'} \underset{\substack{\uparrow \\ \vec{G}+\vec{G}'=\vec{G}''}}{=} \sum_{\vec{G}''} V_{\vec{G}''-\vec{G}} C_{\vec{k}-\vec{G}''}$$

In the sum, the only relevant term will be the one with $C_{\vec{k}}$ , i.e. with $\vec{G}'' = 0$

$$\left(E - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2\right) C_{\vec{k}-\vec{G}} = V_{-\vec{G}} C_{\vec{k}}$$

Solving for $C_{\vec{k}-\vec{G}}$

$$\frac{C_{\vec{k}-\vec{G}}}{C_{\vec{k}}} \approx \frac{V_{-\vec{G}}}{E - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2} \quad \forall \ \vec{G} \neq 0$$

# Consequences of $|C_{\vec{k}-\vec{G}}| << C_{\vec{k}} = \frac{1}{\sqrt{V}} \ \forall\ \vec{G}$

For small perturbations, a first approximation of $C_{\vec{k}-\vec{G}}$
Can be made by setting the true eigenvalue we are seeking equal to the energy of the free electron

$$\frac{C_{\vec{k}-\vec{G}}}{C_{\vec{k}}} \approx \frac{V_{-\vec{G}}}{\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2} \qquad \forall\ \vec{G} \neq 0$$

Remember that the Fourier coefficients are small

**In a weak periodic potential** $|V(\vec{G})|$ are small $\forall\ \vec{G}$

So $\frac{C_{\vec{k}-\vec{G}}}{C_{\vec{k}}}$ will be small…

When this happens, we expect the wave function of the electrons for a given $\vec{k}$ in a weak periodic potential to be well described by the component of the plane wave $C_{\vec{k}}$ .

Those electrons are essentially plane waves.

# Behaviour under the Bragg condition

For small perturbations, a first approximation of $C_{\vec{k}-\vec{G}}$
Can be made by setting the true eigenvalue we are seeking equal to
the energy of the free electron

$$\frac{C_{\vec{k}-\vec{G}}}{C_{\vec{k}}} \approx \frac{V_{-\vec{G}}}{\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2} = -\frac{m}{\hbar^2}\frac{V_{-\vec{G}}}{\vec{k}\cdot\vec{G} + \frac{1}{2}G^2} \quad \forall\ \vec{G} \neq 0$$

Remember that the Fourier coefficients are small

In a weak periodic potential $|V(\vec{G})|$ are small $\forall\ \vec{G}$

So $\frac{C_{\vec{k}-\vec{G}}}{C_{\vec{k}}}$ will be small…

…unless the demonitator will be also small. When

$$\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2 \approx 0 \Rightarrow \quad \vec{k}\cdot\vec{G} + \frac{1}{2}\vec{G}^2 \approx 0$$

This happens at the edges of
the Brillouin zone

$k = \pi/2 \qquad k - G = -\pi/2$

The right term can be arbitrarily large and $|C_{\vec{k}-\vec{G}}|$ cannot be ignored

Both $C_{\vec{k}-\vec{G}}$ and $C_{\vec{k}}$ appear in the expansión of the wave function

# Behaviour under the Bragg condition

In such a case, we need to know both the coefficient of $C_{\vec{k}}$ and $C_{\vec{k}-\vec{G}}$

Starting from

$$\left(E-\frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2\right)C_{\vec{k}-\vec{G}}=\sum_{\vec{G}'}V_{\vec{G}'}C_{\vec{k}-\vec{G}-\vec{G}'}=\sum_{\vec{G}''}V_{\vec{G}''-\vec{G}}C_{\vec{k}-\vec{G}''}$$

From here, we get the equation for $C_{\vec{k}}$

$$\left(E-\frac{\hbar^2}{2m}k^2\right)C_{\vec{k}}-V_{\vec{G}}C_{\vec{k}-\vec{G}}=0$$

Making $\vec{G}''=0$ we get the equation for $C_{\vec{k}-\vec{G}}$

$$\left(E-\frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2\right)C_{\vec{k}-\vec{G}}-V_{-\vec{G}}C_{\vec{k}}=0$$

We thus obtain the secular equation for the energy value

$$\begin{vmatrix}\left(\frac{\hbar^2k^2}{2m}-E\right) & V_{\vec{G}} \\ V_{-\vec{G}} & \left(\frac{\hbar^2|\vec{k}-\vec{G}|^2}{2m}-E\right)\end{vmatrix}=0$$

# Value of the gap at the zone boundary

We thus obtain the secular equation for the energy value

$$\begin{vmatrix} \left(\frac{\hbar^2 k^2}{2m} - E\right) & V_{\vec{G}} \\ V_{-\vec{G}} & \left(\frac{\hbar^2 |\vec{k}-\vec{G}|^2}{2m} - E\right) \end{vmatrix} = 0$$

The two solutions of this secular equation might be written as

$$E^{\pm} = \frac{E^0_{\vec{k}-\vec{G}} + E^0_{\vec{k}}}{2} \pm \sqrt{\frac{\left(E^0_{\vec{k}-\vec{G}} - E^0_{\vec{k}}\right)^2}{4} + |V_{\vec{G}}|^2}$$

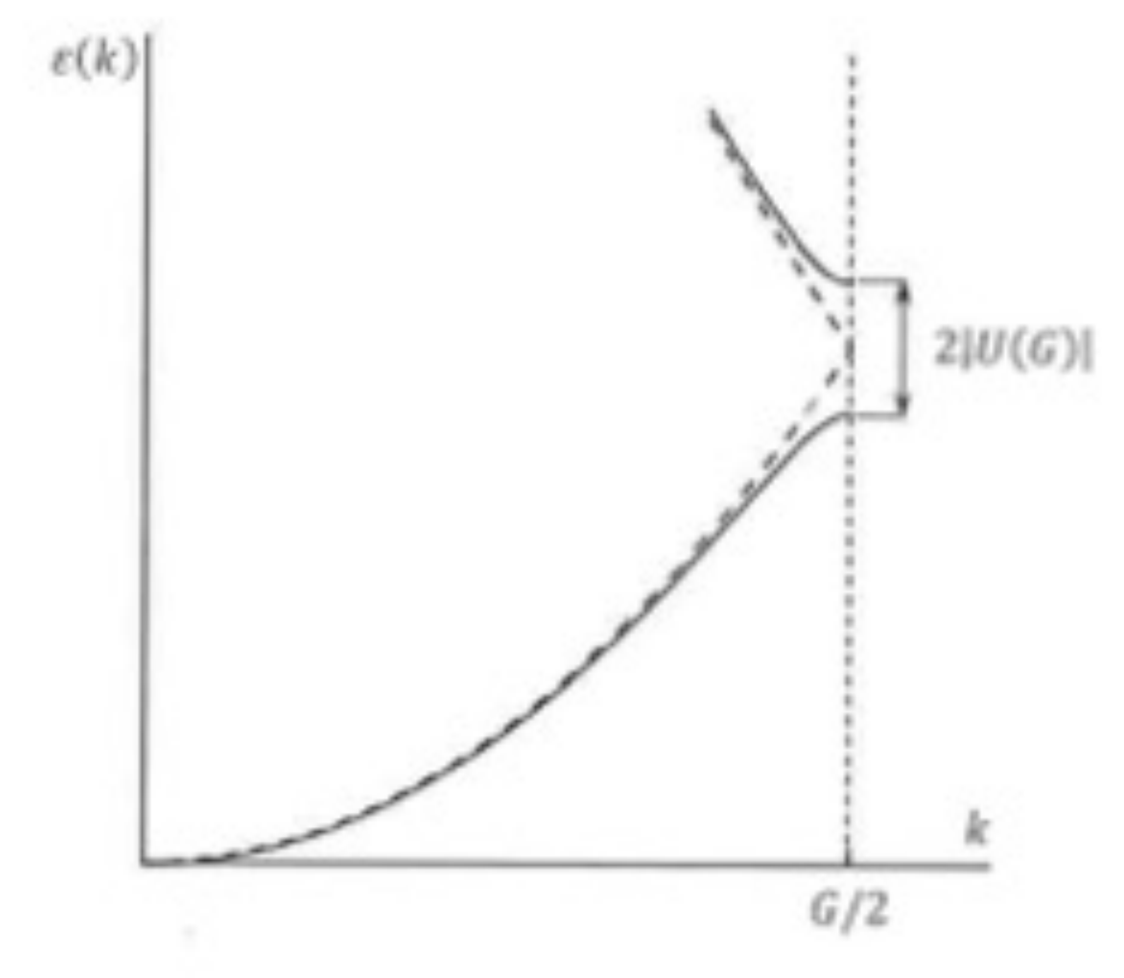
Where we have defined $E^0_{\vec{k}-\vec{G}} = \frac{\hbar^2}{2m}|\vec{k} - \vec{G}|^2$

At the zone boundary, where the contributions of the two waves with $C_{\vec{k}}$ and $C_{\vec{k}-\vec{G}}$ are equal and $E^0_{\vec{k}-\vec{G}} = E^0_{\vec{k}}$

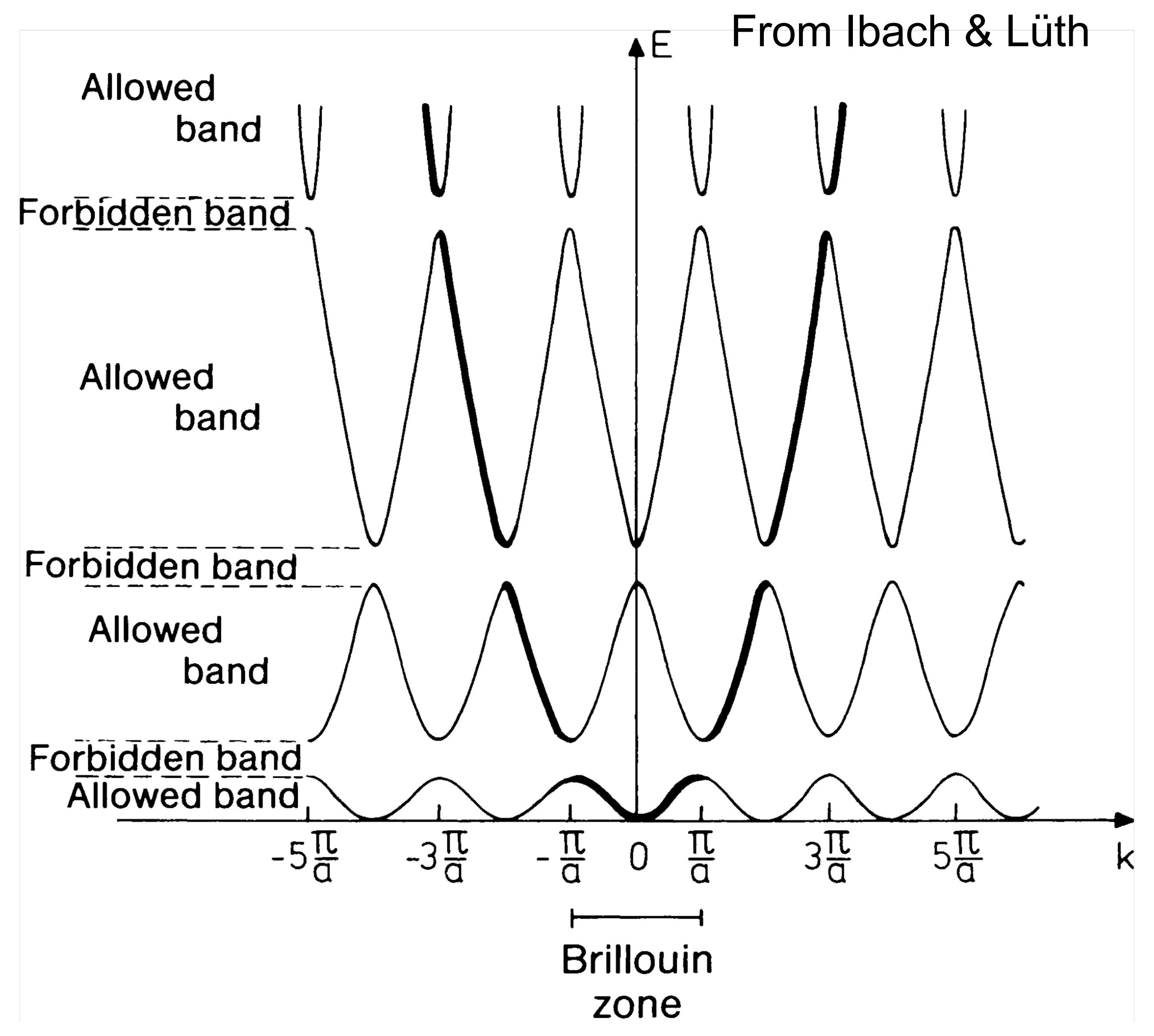
$$E^{+} = E^0_{\vec{k}} + |V_{\vec{G}}| \qquad E^{-} = E^0_{\vec{k}} - |V_{\vec{G}}|$$

$$\Delta E = E^{+} - E^{-} = 2|V_{\vec{G}}|$$

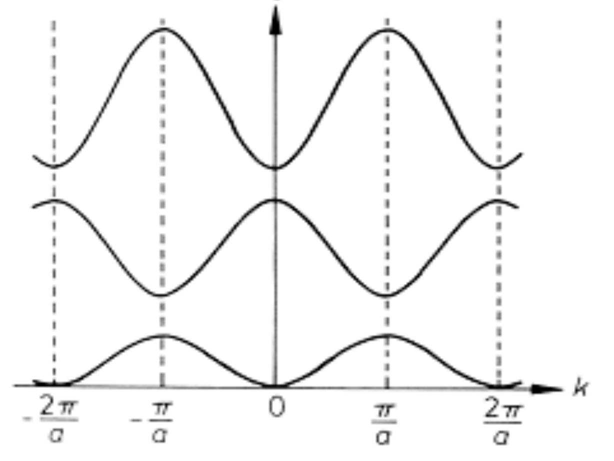
# Dispersion relation for the nearly-free electron model



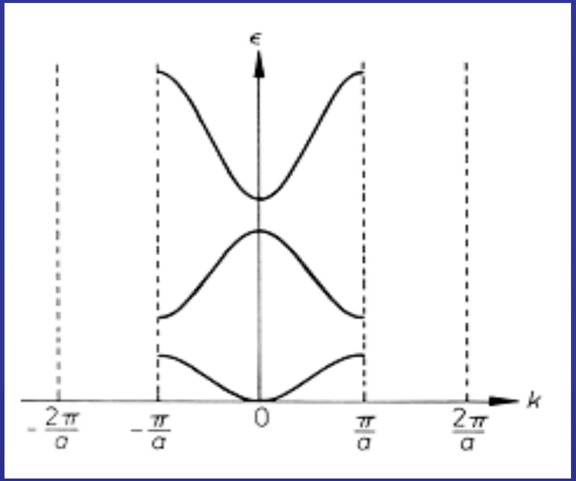
# The nearly-free-electron approximation: formal calculation of the band splitting


From Ibach & Lüth

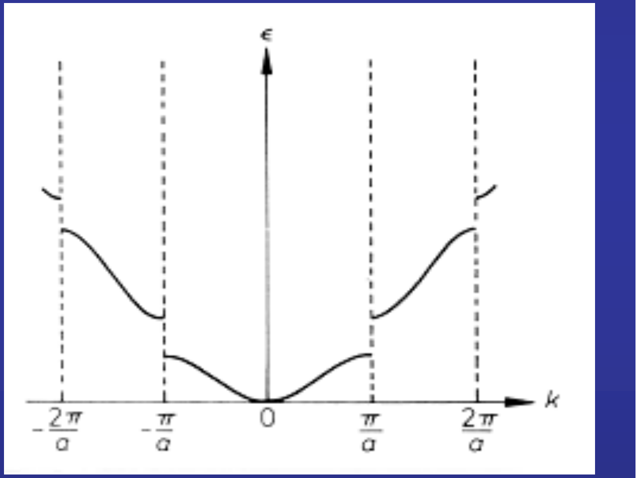
# Band structure in the three schemas



Periodic zone



Reduced zone



Extended zone