In this lecture you will learn:

- Properties of Bloch functions
- Periodic boundary conditions for Bloch functions
- Density of states in k-space
- Electron occupation statistics in energy bands

**Bloch Functions - Summary**

- Electron energies and solutions are written as (\( k \) is restricted to the first BZ):
  \[
  \psi_{n,k}(\vec{r}) \quad \text{and} \quad E_n(\vec{k})
  \]

- The solutions satisfy the Bloch’s theorem:
  \[
  \psi_{n,k}(\vec{r} + \vec{R}) = e^{i \vec{k} \cdot \vec{R}} \psi_{n,k}(\vec{r})
  \]
  and can be written as a superposition of plane waves, as shown below for 3D:
  \[
  \psi_{n,k}(\vec{r}) = \sum_j c_n(\vec{k} + \vec{G}_j) \frac{1}{V} e^{i(\vec{k} + \vec{G}_j) \cdot \vec{r}}
  \]

- Any lattice vector and reciprocal lattice vector can be written as:
  \[
  \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad \vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3
  \]

- Volume of the direct lattice primitive cell and the reciprocal lattice first BZ are:
  \[
  \Omega_3 = | \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) | \quad \Pi_3 = | \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) |
  \]
Bloch Function – Product Form Expression

A Bloch function corresponding to the wavevector \( \vec{k} \) and energy band “n” can always be written as superposition over plane waves in the form:

\[
\psi_{n,k}(\vec{r}) = \sum_j c_n(\vec{k} + \vec{G}_j) \frac{1}{V} e^{i(\vec{k} + \vec{G}_j) \cdot \vec{r}}
\]

The above expression can be re-written as follows:

\[
\psi_{n,k}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \sum_j c_n(\vec{k} + \vec{G}_j) \frac{1}{V} e^{i\vec{G}_j \cdot \vec{r}}
= \frac{1}{V} e^{i\vec{k} \cdot \vec{r}} \sum_j c_n(\vec{k} + \vec{G}_j) e^{i\vec{G}_j \cdot \vec{r}}
= \frac{1}{V} e^{i\vec{k} \cdot \vec{r}} u_{n,k}(\vec{r})
\]

Where the function \( u_{n,k}(\vec{r}) \) is lattice periodic:

\[
u_{n,k}(\vec{r} + \vec{R}) = \sum_j c_n(\vec{k} + \vec{G}_j) e^{i\vec{G}_j \cdot (\vec{r} + \vec{R})} = \sum_j c_n(\vec{k} + \vec{G}_j) e^{i\vec{G}_j \cdot \vec{r}}
= u_{n,k}(\vec{r})
\]

Note that: \( \psi_{n,k}(\vec{r}) = \frac{1}{V} e^{i\vec{k} \cdot \vec{r}} u_{n,k}(\vec{r}) \) satisfies Bloch’s theorem:

\[
\psi_{n,k}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n,k}(\vec{r})
\]

Allowed Wavevectors for Free-Electrons (Sommerfeld Model)

We used periodic boundary conditions:

\[
\psi(x + L_x, y, z) = \psi(x, y, z)
\]

\[
\psi(x, y + L_y, z) = \psi(x, y, z)
\]

\[
\psi(x, y, z + L_z) = \psi(x, y, z)
\]

The boundary conditions dictate that the allowed values of \( k_x, k_y, \) and \( k_z \), are such that:

\[
e^{i(k_xL_x)} = 1 \quad \Rightarrow \quad k_x = n \frac{2\pi}{L_x} \quad n = 0, \pm 1, \pm 2, \ldots
\]

\[
e^{i(k_yL_y)} = 1 \quad \Rightarrow \quad k_y = m \frac{2\pi}{L_y} \quad m = 0, \pm 1, \pm 2, \ldots
\]

\[
e^{i(k_zL_z)} = 1 \quad \Rightarrow \quad k_z = p \frac{2\pi}{L_z} \quad p = 0, \pm 1, \pm 2, \ldots
\]

\[
\Rightarrow \text{There are} \ \frac{V}{(2\pi)^3} \ \text{grid points per unit volume}
\]
Bloch Functions – Periodic Boundary Conditions

- Any vector \( \vec{k} \) in the first BZ can be written as:
  \[
  \vec{k} = \alpha_1 \vec{b}_1 + \alpha_2 \vec{b}_2 + \alpha_3 \vec{b}_3
  \]
  where \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) range from \(-1/2\) to \(+1/2\):
  \[
  -\frac{1}{2} < \alpha_1 \leq \frac{1}{2} \quad -\frac{1}{2} < \alpha_2 \leq \frac{1}{2} \quad -\frac{1}{2} < \alpha_3 \leq \frac{1}{2}
  \]

Volue of the entire crystal is:

\[
V = N_1 a_1 \times (N_2 a_2 \times N_3 a_3) = N_1 N_2 N_3 \Omega_3
\]
The periodic boundary condition in the $\bar{a}_1$ direction implies:

\[ e^{i \bar{k} \cdot N_1 \bar{a}_1} = 1 \]
\[ \bar{k} \cdot N_1 \bar{a}_1 = 2\pi m_1 \quad \{ m_1 \text{ is an integer} \} \]
\[ 2\pi \alpha_1 N_1 = 2\pi m_1 \quad \{ \text{recall that} \ : \bar{a}_j \cdot \bar{b}_k = 2\pi \delta_{jk} \} \]
\[ \alpha_1 = \frac{m_1}{N_1} \]

Since: \[ -\frac{1}{2} < \alpha_1 \leq \frac{1}{2} \quad \Rightarrow \quad -\frac{N_1}{2} < m_1 \leq \frac{N_1}{2} \]
\[ \Rightarrow m_1 \text{ can have } N_1 \text{ different integral values} \]

between $-N_1/2$ and $+N_1/2$

Similarly, the periodic boundary conditions in the directions of $\bar{a}_2$ and $\bar{a}_3$ imply:

\[ e^{i \bar{k} \cdot N_2 \bar{a}_2} = 1 \quad \& \quad e^{i \bar{k} \cdot N_3 \bar{a}_3} = 1 \]
\[ \bar{k} \cdot N_2 \bar{a}_2 = 2\pi m_2 \quad \& \quad \bar{k} \cdot N_3 \bar{a}_3 = 2\pi m_3 \]
\[ \alpha_2 = \frac{m_2}{N_2} \quad \& \quad \alpha_3 = \frac{m_3}{N_3} \]
\[ -\frac{N_2}{2} < m_2 \leq \frac{N_2}{2} \quad \& \quad -\frac{N_3}{2} < m_3 \leq \frac{N_3}{2} \]
\[ \Rightarrow m_2 \text{ can have } N_2 \text{ different integral values} \]
\[ m_3 \text{ can have } N_3 \text{ different integral values} \]

Since any $k$-vector in the FBZ is given as:
\[ k = \alpha_1 \bar{b}_1 + \alpha_2 \bar{b}_2 + \alpha_3 \bar{b}_3 \]
\[ \Rightarrow \text{there are } N_1 N_2 N_3 \text{ different allowed } k\text{-values} \]
\[ \Rightarrow \text{There are as many different allowed } k\text{-values} \]
\[ \text{in the FBZ as the number of primitive cells in the crystal} \]
Density of States in k-Space

Reciprocal lattice for a 2D lattice

Reciprocal lattice vectors:

\[ \mathbf{b}_1 = \frac{2\pi}{a_1} \mathbf{a}_1 \]
\[ \mathbf{b}_2 = \frac{2\pi}{a_2} \mathbf{a}_2 \]

\[ \mathbf{b}_3 = \mathbf{b}_1 \times \mathbf{b}_2 \]

Density of states in k-space:

\[ \mathbf{k} = \alpha_1 \mathbf{b}_1 + \alpha_2 \mathbf{b}_2 + \alpha_3 \mathbf{b}_3 \]

\[ \alpha_1 = \frac{m_1}{N_1} \quad \{ - \frac{N_1}{2} < m_1 \leq \frac{N_1}{2} \} \]
\[ \alpha_2 = \frac{m_2}{N_2} \quad \{ - \frac{N_2}{2} < m_2 \leq \frac{N_2}{2} \} \]
\[ \alpha_3 = \frac{m_3}{N_3} \quad \{ - \frac{N_3}{2} < m_3 \leq \frac{N_3}{2} \} \]

Volume of the first BZ:

\[ \Pi_3 = \left| \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) \right| \]

\[ = \frac{N_1 N_2 N_3}{\Omega_3} \]

\[ = \frac{V}{(2\pi)^3} \]

where \( V \) is the volume of the crystal.

Question: Since \( \mathbf{k} \) is allowed to have only discrete values, how many allowed k-values are there per unit volume of the k-space?

3D Case:

Volume of the first BZ is:

\[ \Pi_3 = \left| \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) \right| \]

\[ = \frac{N_1 N_2 N_3}{\Omega_3} \]

\[ = \frac{V}{(2\pi)^3} \]

where \( V \) is the volume of the crystal.

1D Case:

Length of the crystal:

\[ L = N_1 \mid \mathbf{a}_1 \mid = N_1 \Omega_1 \]

Length of the first BZ is:

\[ \Pi_1 = \left| \mathbf{b}_1 \right| = \frac{2\pi}{\Omega_1} \]

• In the first BZ, there are \( N_1 \) allowed k-values

• The number of allowed k-values per unit length in k-space are:

\[ \frac{N_1}{\Pi_1} = \frac{N_1 \Omega_1}{(2\pi)} = \frac{L}{(2\pi)} \]

2D Case:

Area of the crystal:

\[ A = \left| N_1 \mathbf{a}_1 \times N_2 \mathbf{a}_2 \right| = N_1 N_2 \Omega_2 \]

Area of the first BZ is:

\[ \Pi_2 = \left| \mathbf{b}_1 \times \mathbf{b}_2 \right| = \frac{(2\pi)^2}{\Omega_2} \]

• In the first BZ, there are \( N_1 N_2 \) allowed k-values

• The number of allowed k-values per unit area in k-space are:

\[ \frac{N_1 N_2}{\Pi_2} = \frac{N_1 N_2 \Omega_2}{(2\pi)^2} = \frac{A}{(2\pi)^2} \]
States in k-Space and Number of Primitive Cells

1D Case:
- Reciprocal lattice is: \( \vec{a}_1 = a \hat{x} \) and \( \vec{b}_1 = \frac{\pi}{a} \hat{y} \).
- Length of the first BZ is: \( \Pi_1 = \frac{2\pi}{a} \).
- In the first BZ, there are \( N_1 \) allowed k-values.
- The number of allowed k-values per unit length in k-space are:
  \[
  \frac{N_1}{\Pi_1} = \frac{N_1 \Omega_1}{(2\pi)^2} = \frac{L}{(2\pi)}
  \]
- There are \( N_1 \) allowed k-values in k-space.
  \( \Rightarrow \) There are \( N_1 \) allowed k-values per energy band.
  \( \Rightarrow \) There are as many allowed k-values per energy band as the number of primitive cells in the entire crystal.

2D Case:
- Reciprocal lattice is: \( \vec{a}_1 = \frac{2\pi}{N_1 a_1} \hat{x}, \vec{a}_2 = \frac{2\pi}{N_2 a_2} \hat{y}, \vec{b}_1 = \frac{2\pi}{a_1}, \vec{b}_2 = \frac{2\pi}{a_2} \).
- In the first BZ, there are \( N_1 N_2 \) allowed k-values.
  \( \Rightarrow \) There are \( N_1 N_2 \) allowed k-values per energy band.
  \( \Rightarrow \) There are as many allowed k-values per energy band as the number of primitive cells in the entire crystal.
Statistics of Electrons in Energy Bands

Suppose I want to find the total number of electrons in the n-th band — how should I find it?

The probability that the quantum state of wavevector $\mathbf{k}$ is in the n-th energy band is occupied by an electron is given by the Fermi-Dirac distribution:

$$f_n(k) = \frac{1}{1 + e^{(E_n(k) - E_F)/kT}}$$

Then the total number $N$ of electrons in the n-th band must equal the following sum over all the allowed values in k-space in the first BZ:

$$N = 2\times \sum_{\text{all } k \text{ in FBZ}} f_n(k)$$

1D Case:

The number of allowed k-values per unit length in k-space is $L/2\pi$, therefore:

$$\Rightarrow N = 2\times \sum_{\text{all } k \text{ in FBZ}} f_n(k) = 2\times L \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} f_n(k)$$

Statistics of Electrons in Energy Bands

Need to find the total number of electrons in the n-th band

$$N = 2\times \sum_{\text{all } k \text{ in FBZ}} f_n(k)$$

2D Case:

The number of allowed k-values per unit area in k-space is:

$$A/(2\pi)^2$$

Therefore:

$$N = 2\times \sum_{\text{all } k \text{ in FBZ}} f_n(k) = 2\times A \int_{FBZ} \frac{d^2k}{(2\pi)^2} f_n(k)$$

3D Case:

The number of allowed k-values per unit volume in k-space is:

$$V/(2\pi)^3$$

Therefore:

$$N = 2\times \sum_{\text{all } k \text{ in FBZ}} f_n(k) = 2\times V \int_{FBZ} \frac{d^3k}{(2\pi)^3} f_n(k)$$
Band Filling at $T\approx 0K$ for a 1D lattice

Suppose the number of primitive cells $= N_1$

**Question:** suppose we have 2 electrons per primitive cell. How will the bands fill up at $T\approx 0K$? Where will be the Fermi level?

2 electrons per primitive cell
$\Rightarrow 2N_1$ total number of electrons

Number of k-values per band $= N_1$
Number of quantum states per band $= 2xN_1$ spin

$\Rightarrow$ First band will be completely filled. All higher bands will be empty

**Question:** Suppose we have 3 electrons per primitive cell. How will the bands fill up at $T\approx 0K$?

3 electrons per primitive cell
$\Rightarrow 3N_1$ total number of electrons

$\Rightarrow$ First band will be completely filled. Second band will be half filled. All higher bands will be empty

Important lesson:
In an energy band (whether in 1D, 2D or 3D) the total number of quantum states available is twice the number of primitive cells in the direct lattice. How the bands get filled depends on the number of electrons per primitive cell.

Band Filling at $T\approx 0K$ for a 2D lattice

Suppose the number of primitive cells $= N_1N_2$

**Question:** suppose we have 2 electrons per primitive cell. How will the bands fill up at $T\approx 0K$? Where will be the Fermi level?

2 electrons per primitive cell
$\Rightarrow 2N_1N_2$ total number of electrons

Number of k-values per band $= N_1N_2$
Number of quantum states per band $= 2xN_1N_2$ spin

$\Rightarrow$ First band will be completely filled. All higher bands will be empty
Fermi Surfaces (3D) and Contours (2D) in Solids

Fermi circle for a free electron gas in 2D

What happens in solids when the energy bands are more complex?

First energy band of a 2D lattice

Fermi contours for different electron densities corresponding to the energy band shown on the left
Fermi Surfaces (3D) and Contours (2D) in Solids

Fermi surface of a simple cubic direct lattice shown inside the first BZ

Fermi surface of a FCC lattice shown inside the first BZ (the figure shows the Fermi surface of Copper)

Band Filling at $T=0K$ for Silicon

Silicon:

Atomic number: 14
Electron Configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
Number of electrons in the outermost shell: 4

- The electrons in the outermost shell can move from atom to atom in the lattice – they are not confined to any individual atom. Their energies are described by the energy bands
- The electrons in the inner shells remain confined to individual atoms

- Silicon lattice is FCC
- There are 2 Silicon atoms per primitive cell (2 basis atoms)

⇒ There are 4 electrons contributed by each Silicon atom and so there are 8 electrons per primitive cell that are available to fill the energy bands
Band Filling at $T=0K$ for Silicon

- There are 8 electrons per unit cell available to fill the energy bands
- Recall that in each energy band the number of states available is twice the number of primitive cells in the crystal
- In Silicon, the lowest 4 energy bands will get completely filled at $T=0K$ and all the higher energy bands will be empty

Energy Bands in Silicon

- The highest filled energy band is called the valence band. In silicon the valence band is double degenerate at most points in the first BZ
- The lowest empty energy band is called the conduction band
- In energy, the valence band maximum and the conduction band minimum need not happen at the same point in k-space (as is the case in Silicon)
- The lowest energy of the conduction band is called $E_c$ and the highest energy of the valence band is called $E_v$
Energy vs. $k$ and Energy vs. $(k_x, k_y)$