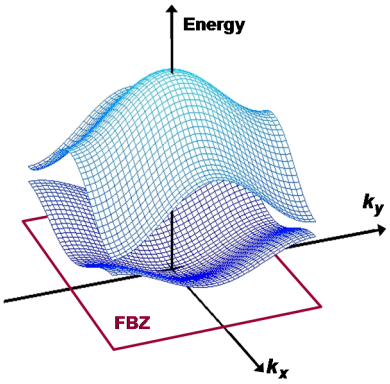
Handout 7

Properties of Bloch States and Electron Statistics in Energy Bands

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 ($\vec{k}$ is restricted to the first BZ):**

$$\psi_{n,\vec{k}}(\vec{r}) \qquad \text{and} \qquad E_n(\vec{k})$$

- **The solutions satisfy the Bloch's theorem:**

$$\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$$

and can be written as a superposition of plane waves, as shown below for 3D:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_n(\vec{k}+\vec{G}_j)\sqrt{\frac{1}{V}}\,e^{i\,(\vec{k}+\vec{G}_j).\,\vec{r}}$$

- **Any lattice vector and reciprocal lattice vector can be written as:**

$$\vec{R} = n_1\,\vec{a}_1 + n_2\,\vec{a}_2 + n_3\,\vec{a}_3 \qquad\qquad \vec{G} = m_1\,\vec{b}_1 + m_2\,\vec{b}_2 + m_3\,\vec{b}_3$$

- **Volume of the direct lattice primitive cell and the reciprocal lattice first BZ are:**

$$\Omega_3 = \left|\,\vec{a}_1\,.\,(\vec{a}_2\times\vec{a}_3)\,\right| \qquad\qquad \Pi_3 = \left|\,\vec{b}_1\,.\,(\vec{b}_2\times\vec{b}_3)\,\right|$$

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:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_n\left(\vec{k}+\vec{G}_j\right)\sqrt{\frac{1}{V}}\, e^{i\left(\vec{k}+\vec{G}_j\right).\vec{r}}$$

The above expression can be re-written as follows:

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\,\vec{k}\,.\,\vec{r}}\sum_j c_n\left(\vec{k}+\vec{G}_j\right)\sqrt{\frac{1}{V}}\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

$$= \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}\sum_j c_{n,\vec{k}}\left(\vec{G}_j\right)\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

$$= \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}\, u_{n,\vec{k}}(\vec{r})$$

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

$$u_{n,\vec{k}}\left(\vec{r}+\vec{R}\right) = \sum_j c_{n,\vec{k}}\left(\vec{G}_j\right)\, e^{i\,\vec{G}_j\,.\,\left(\vec{r}+\vec{R}\right)} = \sum_j c_{n,\vec{k}}\left(\vec{G}_j\right)\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

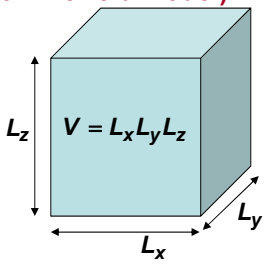
$$= u_{n,\vec{k}}(\vec{r})$$

Note that: $\psi_{n,\vec{k}}(\vec{r}) = \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}\, u_{n,\vec{k}}(\vec{r})$ satisfies Bloch's theorem $\Rightarrow$ $\psi_{n,\vec{k}}\left(\vec{r}+\vec{R}\right) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$

Allowed Wavevectors for Free-Electrons (Sommerfeld Model)

We used periodic boundary conditions:

$$\psi(x+L_x,y,z) = \psi(x,y,z)$$
$$\psi(x,y+L_y,z) = \psi(x,y,z)$$
$$\psi(x,y,z+L_z) = \psi(x,y,z)$$

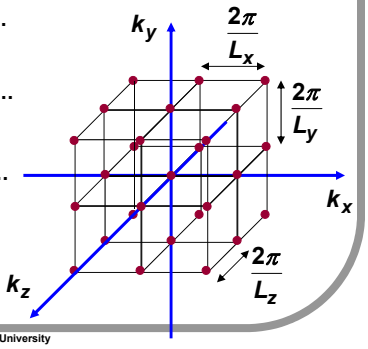


The boundary conditions dictate that the allowed values of k_x, k_y, and k_z, are such that:

$$e^{i(k_xL_x)} = 1 \Rightarrow k_x = n\frac{2\pi}{L_x} \quad n = 0, \pm1, \pm2, \ldots.$$

$$e^{i(k_yL_y)} = 1 \Rightarrow k_y = m\frac{2\pi}{L_y} \quad m = 0, \pm1, \pm2, \ldots.$$

$$e^{i(k_zL_z)} = 1 \Rightarrow k_z = p\frac{2\pi}{L_z} \quad p = 0, \pm1, \pm2, \ldots.$$



$\Rightarrow$ There are $\frac{V}{(2\pi)^3}$ grid points per unit volume of k-space

Bloch Functions – Periodic Boundary Conditions

Direct lattice

Reciprocal lattice for a 2D lattice

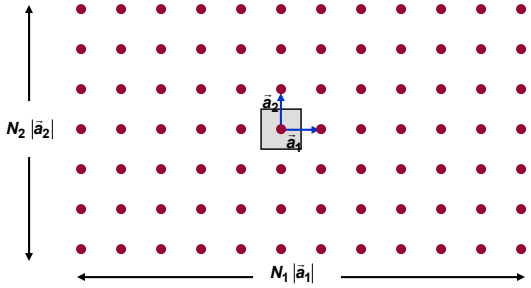
• Any vector $\vec{k}$ in the first BZ can be written as:

$$\vec{k} = \alpha_1 \vec{b}_1 + \alpha_2 \vec{b}_2 + \alpha_3 \vec{b}_3$$

where α_1, α_2, and α_3 range from -1/2 to +1/2:

$$-\frac{1}{2} < \alpha_1 \leq \frac{1}{2} \qquad -\frac{1}{2} < \alpha_2 \leq \frac{1}{2} \qquad -\frac{1}{2} < \alpha_3 \leq \frac{1}{2}$$

Bloch Functions – Periodic Boundary Conditions



For the 2D crystal :

$A = |\, N_1\vec{a}_1 \times N_2\vec{a}_2 \,|$
$= N_1 N_2\, \Omega_2$

• Consider a 3D crystal made up of N_1 primitive cells in the $\vec{a}_1$ direction, N_2 primitive cells in the $\vec{a}_2$ direction and N_3 primitive cells in the $\vec{a}_3$ direction

$\Rightarrow$ Volume of the entire crystal is: $V = \left|\, N_1\vec{a}_1 \,.\, \left(N_2\vec{a}_2 \times N_3\vec{a}_3\right) \right| = N_1 N_2 N_3\, \Omega_3$

Assuming periodic boundary conditions in all three directions we must have:

$$\psi\left(\vec{r} + N_1\, \vec{a}_1\right) = e^{i\, \vec{k}\,.\, N_1\, \vec{a}_1}\; \psi\left(\vec{r}\right) = \psi\left(\vec{r}\right)$$

$$\psi\left(\vec{r} + N_2\, \vec{a}_2\right) = e^{i\, \vec{k}\,.\, N_2\, \vec{a}_2}\; \psi\left(\vec{r}\right) = \psi\left(\vec{r}\right)$$

$$\psi\left(\vec{r} + N_3\, \vec{a}_3\right) = e^{i\, \vec{k}\,.\, N_3\, \vec{a}_3}\; \psi\left(\vec{r}\right) = \psi\left(\vec{r}\right)$$

Bloch Functions – Periodic Boundary Conditions

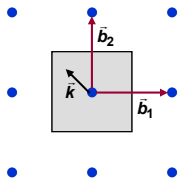
The periodic boundary condition in the $\vec{a}_1$ direction implies:

$$\Rightarrow e^{i\,\vec{k}\,.\,N_1\,\vec{a}_1} = 1 \qquad \left\{ \vec{k} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2 + \alpha_3\,\vec{b}_3 \right.$$

$$\Rightarrow \vec{k}\,.\,N_1\,\vec{a}_1 = 2\pi\,m_1 \qquad \left\{ m_1 \text{ is an integer} \right.$$

$$\Rightarrow 2\pi\,\alpha_1\,N_1 = 2\pi\,m_1 \qquad \left\{ \text{recall that} : \vec{a}_j\,.\,\vec{b}_k = 2\pi\,\delta_{j\,k} \right.$$

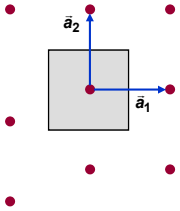
$$\Rightarrow \alpha_1 = \frac{m_1}{N_1}$$



Reciprocal lattice for a 2D lattice

Since: $-\frac{1}{2} < \alpha_1 \le \frac{1}{2} \quad \Rightarrow \quad -\frac{N_1}{2} < m_1 \le \frac{N_1}{2}$

$\Rightarrow m_1$ can have N_1 different integral values between $-N_1/2$ and $+N_1/2$



Direct lattice

Bloch Functions – Periodic Boundary Conditions

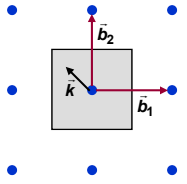
Similarly, the periodic boundary conditions in the directions of $\vec{a}_2$ and $\vec{a}_3$ imply:

$$\Rightarrow e^{i\,\vec{k}\,.\,N_2\,\vec{a}_2} = 1 \quad \& \quad e^{i\,\vec{k}\,.\,N_3\,\vec{a}_3} = 1$$

$$\Rightarrow \vec{k}\,.\,N_2\,\vec{a}_2 = 2\pi\,m_2 \quad \& \quad \vec{k}\,.\,N_3\,\vec{a}_3 = 2\pi\,m_3$$

$$\Rightarrow \alpha_2 = \frac{m_2}{N_2} \quad \& \quad \alpha_3 = \frac{m_3}{N_3}$$

$$\Rightarrow \quad -\frac{N_2}{2} < m_2 \le \frac{N_2}{2} \quad \& \quad -\frac{N_3}{2} < m_3 \le \frac{N_3}{2}$$



Reciprocal lattice for a 2D lattice

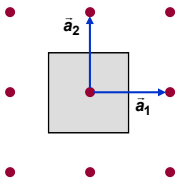
$\Rightarrow m_1$ can have N_1 different integral values
$\Rightarrow m_2$ can have N_2 different integral values
$\Rightarrow m_3$ can have N_3 different integral values

Since any k-vector in the FBZ is given as:

$$\vec{k} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2 + \alpha_3\,\vec{b}_3$$

$\Rightarrow$ there are $N_1\,N_2\,N_3$ different allowed k-values in the FBZ

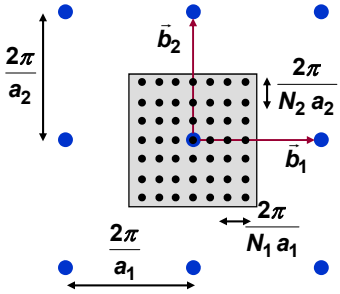
$\Rightarrow$ There are as many different allowed k-values in the FBZ as the number of primitive cells in the crystal



Direct lattice

Density of States in k-Space

Reciprocal lattice for a 2D lattice



$$\vec{k} = \alpha_1 \vec{b}_1 + \alpha_2 \vec{b}_2 + \alpha_3 \vec{b}_3$$

$$\alpha_1 = \frac{m_1}{N_1} \quad \left\{ -\frac{N_1}{2} < m_1 \le \frac{N_1}{2} \right.$$

$$\alpha_2 = \frac{m_2}{N_2} \quad \left\{ -\frac{N_2}{2} < m_2 \le \frac{N_2}{2} \right.$$

$$\alpha_3 = \frac{m_3}{N_3} \quad \left\{ -\frac{N_3}{2} < m_3 \le \frac{N_3}{2} \right.$$

Question: Since $\vec{k}$ 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:

$$\Pi_3 = \left| \vec{b}_1 . \left(\vec{b}_2 \times \vec{b}_3 \right) \right|$$

- In this volume, there are $N_1\ N_2\ N_3$ allowed k-values
- The number of allowed k-values per unit volume in k-space are:

$$= \frac{N_1 N_2 N_3}{\Pi_3}$$

$$= N_1 N_2 N_3 \frac{\Omega_3}{(2\pi)^3}$$

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

where V is the volume of the crystal

Density of States in k-Space

1D Case:

Length of the crystal: $L = N_1 \left| \vec{a}_1 \right| = N_1\ \Omega_1$

Length of the first BZ is: $\Pi_1 = \left| \vec{b}_1 \right| = \frac{2\pi}{\Omega_1}$

- In the first BZ, there are N_1 allowed k-values
- The number of allowed k-values per unit length in k-space are:

$$= \frac{N_1}{\Pi_1} = N_1 \frac{\Omega_1}{(2\pi)^1} = \frac{L}{(2\pi)}$$

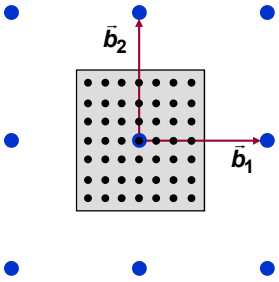
2D Case:

Area of the crystal: $A = \left| N_1 \vec{a}_1 \times N_2 \vec{a}_2 \right| = N_1\ N_2\ \Omega_2$

Area of the first BZ is: $\Pi_2 = \left| \vec{b}_1 \times \vec{b}_2 \right| = \frac{(2\pi)^2}{\Omega_2}$

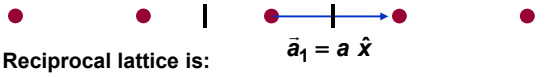
- In the first BZ, there are $N_1 N_2$ allowed k-values
- The number of allowed k-values per unit area in k-space are:

$$= \frac{N_1 N_2}{\Pi_2} = N_1 N_2 \frac{\Omega_2}{(2\pi)^2} = \frac{A}{(2\pi)^2}$$

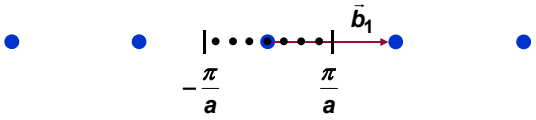


States in k-Space and Number of Primitive Cells

1D Case:



Reciprocal lattice is:

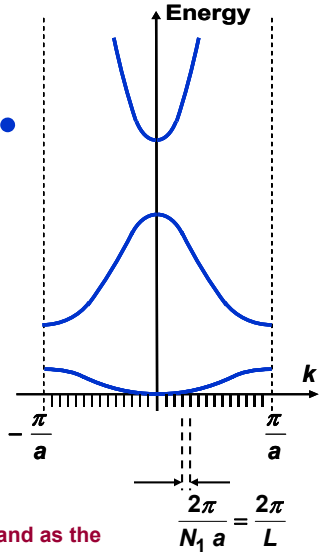


Length of the crystal: $L = N_1 \left| \vec{a}_1 \right| = N_1 \Omega_1 = N_1 a$

Length of the first BZ is: $\Pi_1 = \left| \vec{b}_1 \right| = \frac{2\pi}{a}$

- In the first BZ, there are N_1 allowed k-values
- The number of allowed k-values per unit length in k-space are:

$$= \frac{N_1}{\Pi_1} = N_1 \frac{\Omega_1}{(2\pi)^1} = \frac{L}{(2\pi)}$$

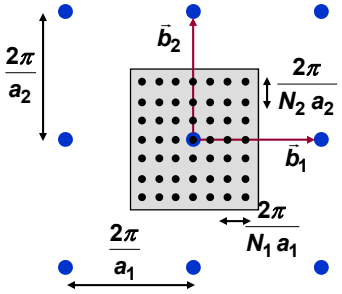


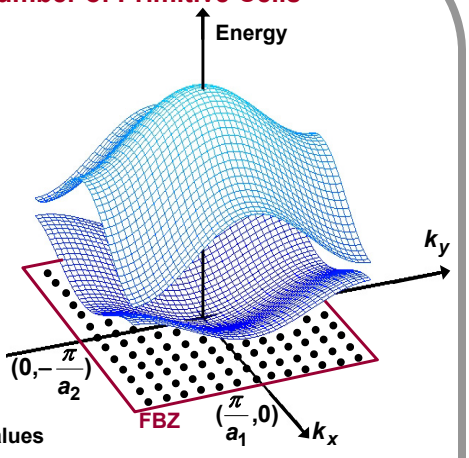
There are N_1 allowed k-values in k-space
⇒There are N_1 allowed k-values per energy band
⇒There are as many allowed k-values per energy band as the number of primitive cells in the entire crystal

States in k-Space and Number of Primitive Cells

2D Case:

Reciprocal lattice is:





- In the first BZ, there are $N_1 N_2$ allowed k-values

⇒There are $N_1 N_2$ allowed k-values per energy band

⇒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?

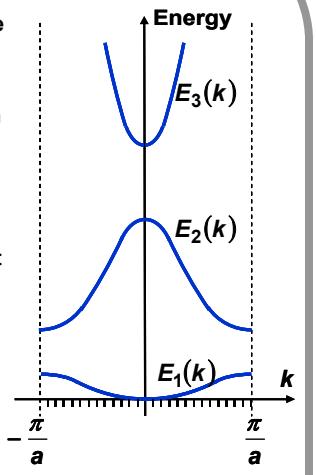
The probability that the quantum state of wavevector $\vec{k}$ is in the n-th energy band is occupied by an electron is given by the Fermi-Dirac distribution:

$$f_n(\vec{k}) = \frac{1}{1 + e^{(E_n(\vec{k}) - E_f)/KT}}$$

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:

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

spin



1D Case:

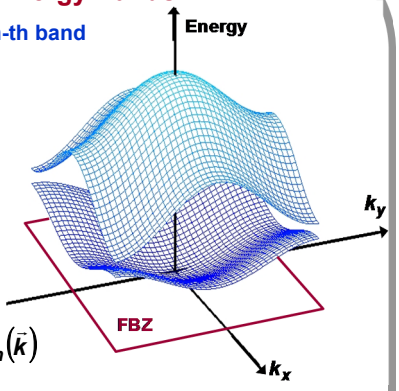
The number of allowed k-values per unit length in k-space is $L / 2\pi$, therefore:

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

Statistics of Electrons in Energy Bands

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

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



2D Case:

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

$$\frac{A}{(2\pi)^2}$$

Therefore:

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

3D Case:

The number of allowed k-values per unit volume in k-space is: $\frac{V}{(2\pi)^3}$

Therefore:

$$N = 2 \times \sum_{\text{all } \vec{k} \text{ in FBZ}} f_n(\vec{k}) = 2 \times V \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3} f_n(\vec{k})$$

Band Filling at $T \approx 0$K 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 $T \approx 0$K? Where will be the Fermi level?

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

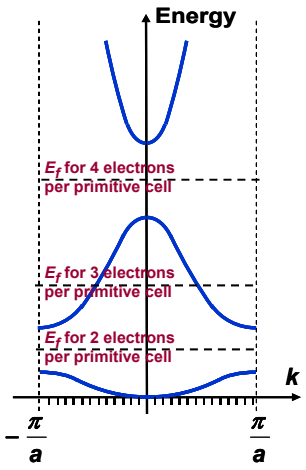
Number of k-values per band = N_1
Number of quantum states per band = $2 \times N_1$
spin

$\Rightarrow$ 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 $T \approx 0$K?

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



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

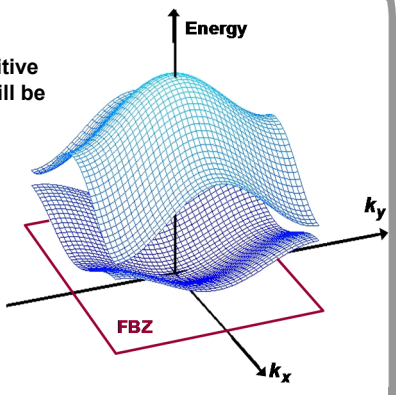
Suppose the number of primitive cells = $N_1 N_2$

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

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

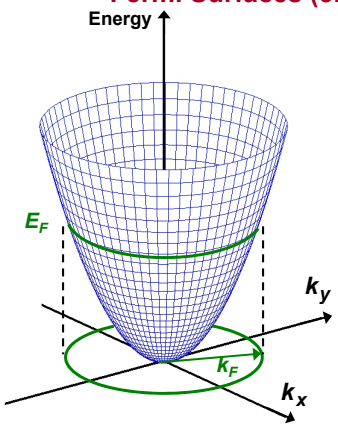
Number of k-values per band = N_1N_2
Number of quantum states per band = $2 \times N_1N_2$
spin

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

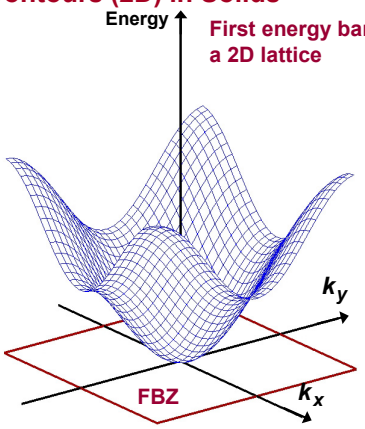


Important lesson:
In an energy band (whether in 1D, 2D or 3D) the total number of quantum states available is twice the number of primitive cells in the direct lattice. How the bands get filled depends on the number of electrons per primitive cell.

Fermi Surfaces (3D) and Contours (2D) in Solids

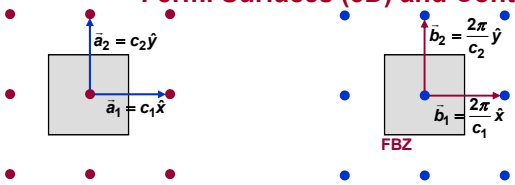


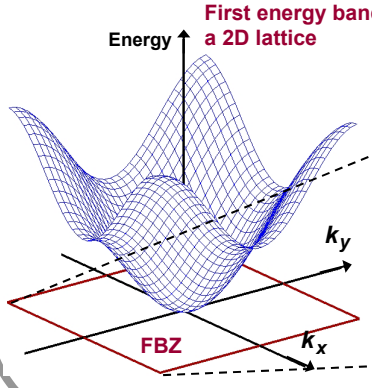
Fermi circle for a free electron gas in 2D



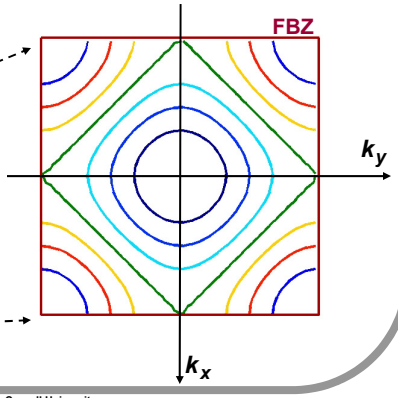
What happens in solids when the energy bands are more complex?

Fermi Surfaces (3D) and Contours (2D) in Solids

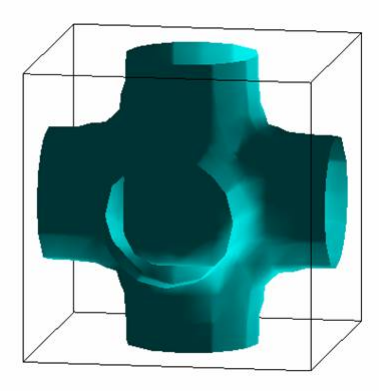




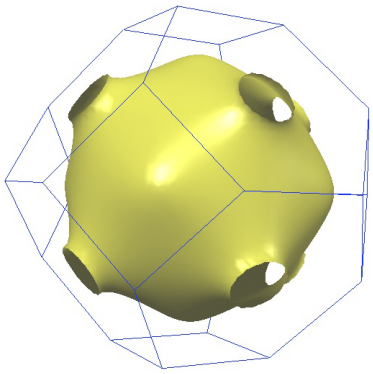
Fermi contours for different electron densities corresponding to the energy band shown on the left



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 $T \approx 0$K for Silicon

Silicon:

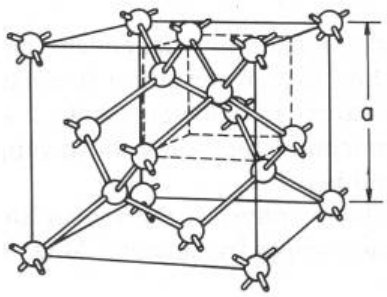
Atomic number: 14

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



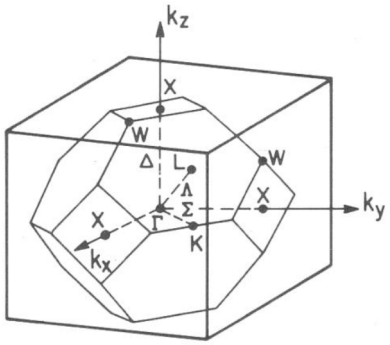
• Silicon lattice is FCC

• There are 2 Silicon atoms per primitive cell (2 basis atoms)

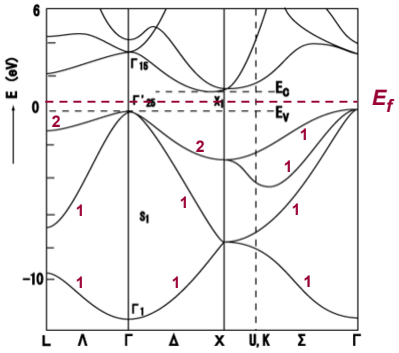
⇒ There are 4 electrons contributed by each Silicon atom and so there are 8 electrons per primitive cell that are available to fill the energy bands

Band Filling at $T \approx 0$K 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 $T \approx 0$K and all the higher energy bands will be empty



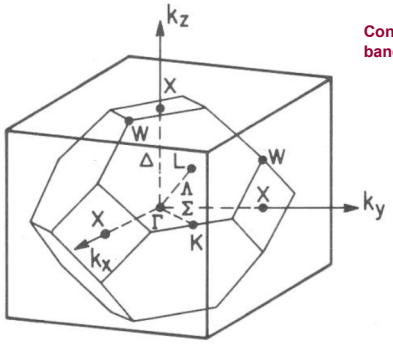
FBZ (for FCC lattice)



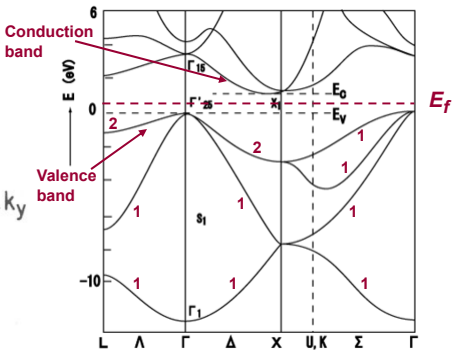
Silicon Energy Bands

Energy Bands in Silicon

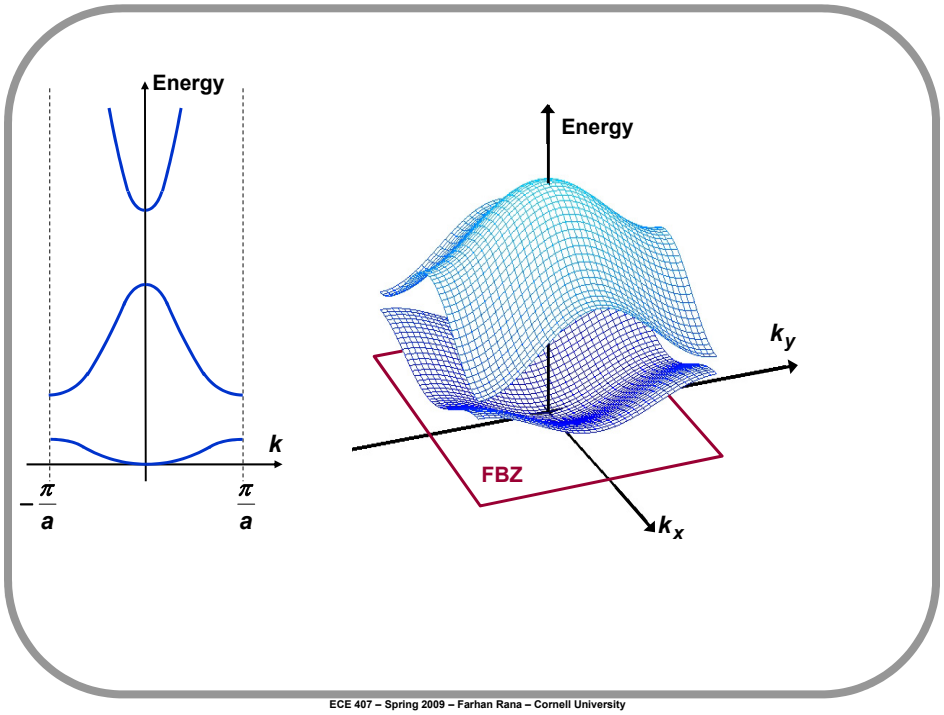
- The highest filled energy band is called the valence band. In silicon the valence band is double degenerate at most points in the first BZ
- The lowest empty energy band is called the conduction band
- In energy, the valence band maximum and the conduction band minimum need not happen at the same point 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



FBZ (for FCC lattice)



Silicon Energy Bands


Energy
k
$-\frac{\pi}{a}$
$\frac{\pi}{a}$
Energy
k_y
FBZ
k_x