

Lecture 12 Nearly Free Electron Model

Reading Kittel: Chapter 7, p162-168, Simon: Chapter 15: p163-170; Ashcroft and Mermin: Chapter 3 (available on duo)

In the free electron model we ignored two possible interactions:

1. Electron – atom interactions (free electron approximation)
2. Electron – electron interactions (independent electron approximation)

The nearly free electron model includes the electron-atom interactions.

We continue to use the independent electron interactions and ignore electron-electron interactions.

It is remarkable that using this approximation gives such good results. The assumption can be justified only in part by the Pauli Exclusion Principle.

The nearly-free electron model will resolve many of the limitations of the free electron model and will also allow us to explain the difference between insulators – semiconductors – metals. It will also help explain some of the failures of the free electron model.

Failures of Free electron model

- Hall coefficients
- Temperature dependence of conductivity
- Specific heat

Crystal Lattices

As we saw earlier in the course any crystal is composed of a repeating array of atoms with a well defined spatial relationship.

A lattice is described by a lattice vector \mathbf{R}

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Where $\mathbf{a}_{1,2,3}$ are the lattice unit vectors.

| TABLE The Fourteen Bravais Lattices and Conventional Unit Cells in Three Dimensions* | | | | |
|--|--|--------------------------|--|--|
| SYSTEM | NUMBER OF LATTICES IN SYSTEM | LATTICE SYMBOLS | NATURE OF UNIT-CELL AXES AND ANGLES | LENGTHS AND ANGLES TO BE SPECIFIED |
| Triclinic | 1 | P | $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ | a, b, c α, β, γ |
| Monoclinic | 2 | P C | $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$ | a, b, c β |
| Orthorhombic | 4 | P C I F | $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ | a, b, c |
| Tetragonal | 2 | P I | $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ | a, c |
| Rhombohedral (Trigonal) | 1 | R | $a = b = c$ $\alpha = \beta = \gamma$ $< 120^\circ, \neq 90^\circ$ | a α |
| Hexagonal | 1 | P | $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ | a, c |
| Cubic | 3 | P I F | $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$ | a |

The number of parameters needed to describe a crystal are given in the table.

Each crystal can be described using one of the 14 Bravais Lattices shown below.

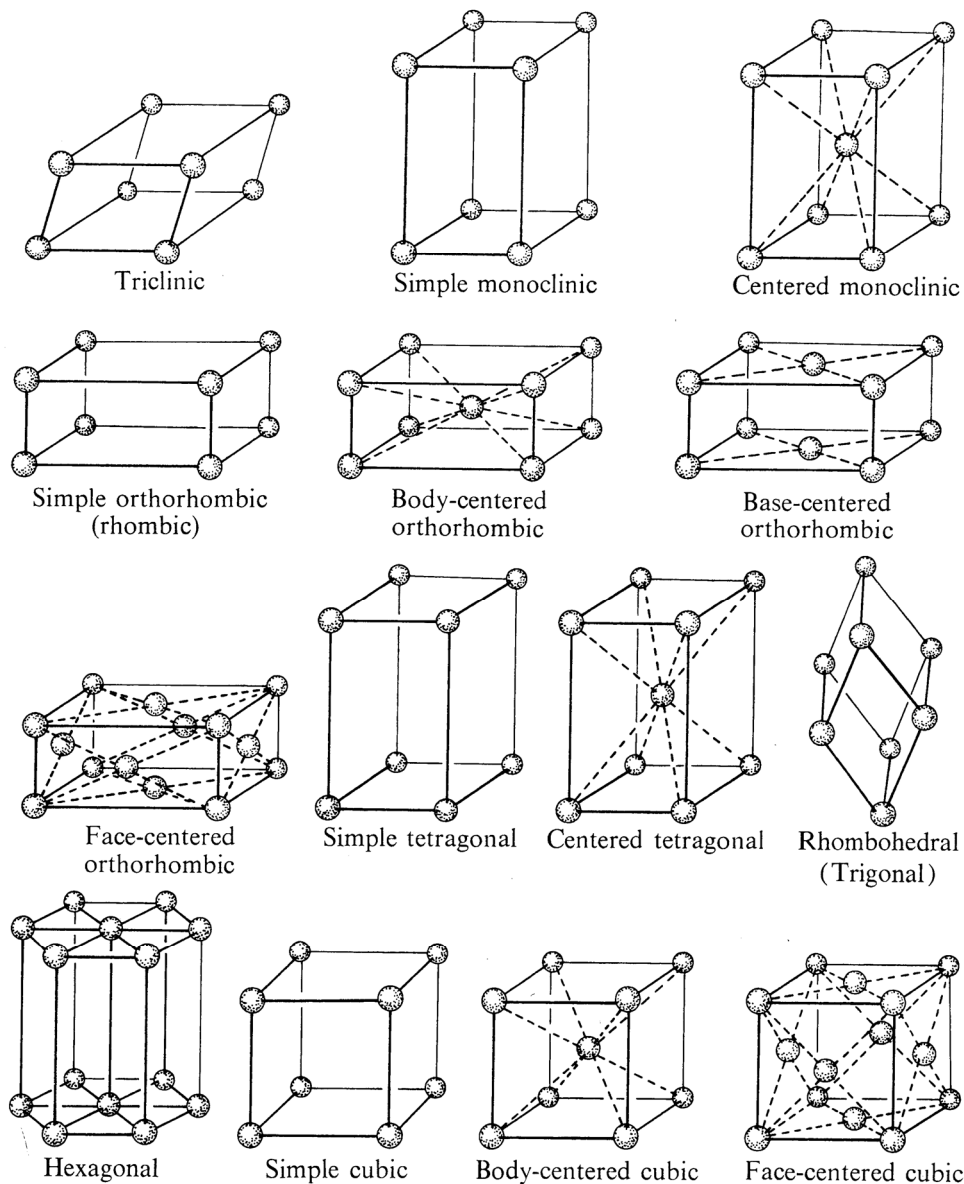


Fig. The fourteen three-dimensional Bravais lattices.

The nearly free electron model includes the interaction between the electrons and a periodic potential due to the presence of atoms at points in the lattice defined by the vector \mathbf{R} .

When considering the interaction between the electrons and the atoms in the nearly free electron model we first need to investigate **Bloch's Theorem**. Bloch's theorem comes about as a result of the periodic nature of crystals.

Bloch's Theorem provides significant insight into the behaviour of nearly free electrons i.e. those electrons moving in a periodic potential.

Bloch states refers to energy states of electrons in a periodic potential.

Bloch's Theorem

This section gives a derivation of the Bloch Theorem.

Consider a 1D crystal system:

Suppose that a wavefunction $\psi(x)$ satisfies a 1D time independent Schrodinger equation with a periodic potential $V(x)$ at an energy eigenvalue of E .

Consider the function $\phi(x) = \psi(x + R)$ where R is a lattice vector.

The Schrodinger equation evaluated at $x+R$ must give the same solution when evaluated at x . This is a direct consequence of the periodic nature of crystals. The local electronic environment at x and $x+R$ must be identical (assuming an infinite array of atoms in the crystal).

Therefore $\phi(x)$ also satisfies the same Schrodinger equation with an energy eigenvalue of E .

If we assume that ψ and ϕ are unique solutions to the Schrodinger equation then we can write:

$$\psi(x + R) = c(R)\psi(x)$$

where $c(R)$ is a constant.

In the situation described above the constant $c(R) = 1$.

If we perform a series of lattice translations we can show that:

$$c(R_1 + R_2) = c(R_1)c(R_2)$$

Therefore:

$$c(nR) = [c(R)]^n, \quad n = 0, 1, 2, \dots$$

The wavefunction ψ has then to satisfy periodic boundary conditions over M lattice translations where $Ma = L$.

This is a key step in the development of Bloch's Theorem and comes about when bringing together the requirements of the periodic boundary conditions primarily determined by L , with the periodicity of the lattice, primarily determined by a .

From this we have:

$$\psi(x + Ma) = \psi(x) \quad \text{which implies that} \quad [c(a)]^M = 1$$

This allows us to write a solution which satisfies this requirement:

$$c(a) = \exp ika$$

where

$$ka = \frac{2\pi l}{M}, \quad l = 0, \pm 1, \pm 2, \dots$$

M is the total number of atoms, and a is the lattice constant.

Therefore for any lattice translation $\underline{R} = m\underline{a}$ we have:

$$c(R) = [c(a)]^M = \exp iMka = \exp ikR$$

Where:

$$k = \frac{2\pi l}{L}, \quad l = 0, \pm 1, \pm 2, \dots$$

L is the total dimension of our 1D system.

These statements set out Bloch's Theorem.

The allowed values of k are exactly those allowed for the free electron model.

Free electron model:

$$\psi(x) = C \exp ikx \quad (\text{a plane wave, with constant energy})$$

Nearly Free electron model:

$$\psi(x + R) = C \exp ik(x + R) = C \exp ikR \quad \psi(x) = C \exp ikR \exp ikx = C u_k(R) \exp ikx$$

This is true for any value of R (a lattice vector).

Bloch's theorem applies only when the potential is periodic and when R corresponds to a lattice translation.

The function $\exp ikR$ is called the Bloch function and is written as $u_k(R)$.

The Bloch theorem tells us that the nearly free electron wavefunctions for electrons in a periodic potential are composed of two parts

1. a plane wave $\exp i(\mathbf{k} \cdot \mathbf{r})$ [or $\exp ikx$ in one dimension]
2. a Bloch function $u_k(R)$ which has the periodicity of the lattice and which modulates the intensity of the plane wave.

In other words the fundamental nature of the wavefunction of electrons in a periodic potential (Bloch states) is similar to free electron wavefunctions.

Another consequence of the Bloch Theorem is that adding multiples of $2\pi/a$ to the Bloch wavevector does not alter the phase of the wavefunction. This means that only k values in a range $2\pi/a$ along the k axis are physically distinct. All other k values can be mapped onto this unique range.

Convention is that the unique region is centred about the origin between $-\pi/a < k < +\pi/a$

This region or zone of wavevector corresponds to the first Brillouin zone (in a simple cubic lattice).

All points on the k -axis can be mapped onto the first Brillouin zone by adding or subtracting an integer multiple of $2\pi/a$.

Energy Band Diagrams

We can plot out the different possibilities of the energy dependence on wavevector k . These are called energy bands.

Energy band diagrams are commonly used to illustrate the properties of crystalline solids.

For the free electron model we have

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

If this were mapped onto the first Brillouin zone we would have an energy band diagram showing the relationship between energy and wavevector.

The free electron behaviour follows the $E \propto k^2$ curve. This is consistent with a free electron and we can determine the momentum $\hbar k$ the group velocity $\partial\omega/\partial k$ from this relationship.

In the free electron model the value of the wavevector is unrestricted. However we know that in describing crystals that the Brillouin zone contains a full set of information that can uniquely describe all the properties of the crystal.

Any wavevector which lies outside the Brillouin zone can be mapped inside the first Brillouin zone by adding/subtracting multiples of $2\pi/a$ to the wavevector. No physical information is lost in making this transition.

When representing the behaviour of electrons on $E(k)$ diagrams the same principle is used. Generally the wavevector k can be mapped inside the first Brillouin zone when considering the interaction between the electron and the periodic potential of the crystal.

The solid curve below represents the free electron behaviour with no restriction on the value of k . It follows the k^2 behaviour.

The representation is called the **extended scheme**.

Mapping the wavevector k onto the range contained within the first Brillouin zone is shown by adding/subtracting multiples of $2\pi/a$ to the wavevector. This is called the **reduced zone scheme**.

The reduced zone scheme is generally used in energy band diagrams.

Free Electron Model

$$E = \hbar^2 k^2 / 2m_e$$

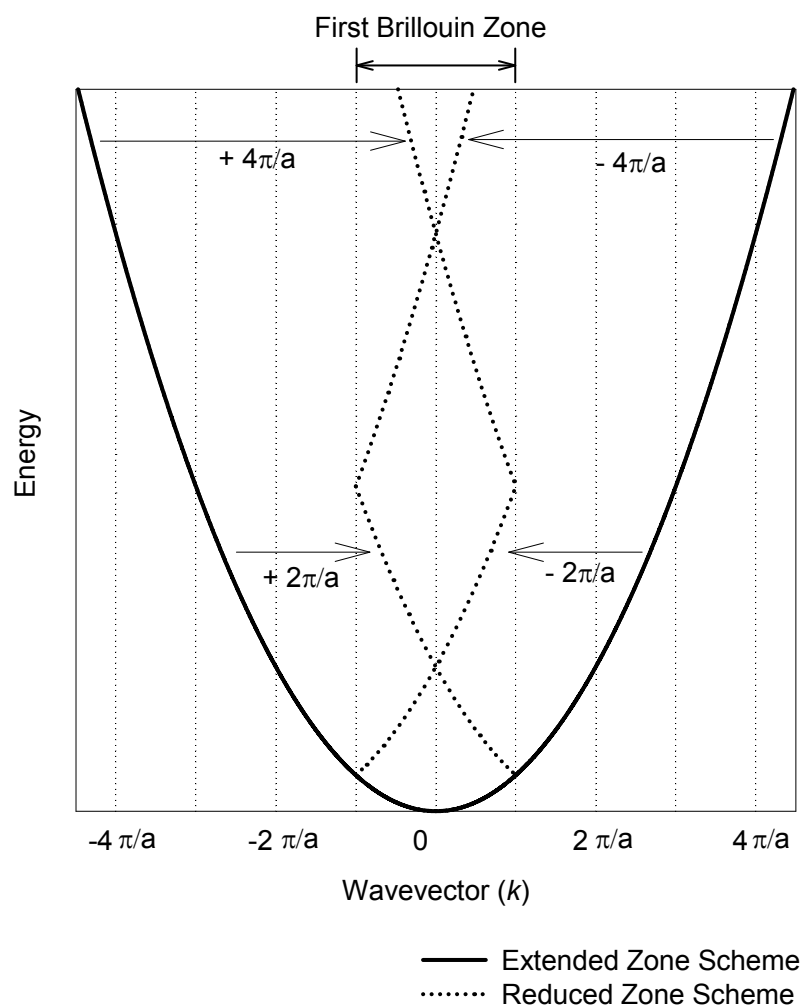


Diagram showing energy bands produced by Bloch state in the first Brillouin zone for the free electron model.

The allowed energy levels form a series of lines traversing the Brillouin zone. Each line corresponds to a different E dependence on k . These curves are called energy bands.

The lines represent the start of the energy bands with the number of states increasing according to the density of states.

If there are M unit cells in the length L of the 1D solid then each band can accommodate $(2\pi/a) \times (L/\pi) = 2M$ electrons.

Electrons states in energy bands subject to a periodic potential are described as **Bloch states**. This implies the motion of the electron is modified by the periodic potential.

The Bloch Theorem has not involved developing solutions to the Schrodinger equation with a periodic potential. The Bloch Theorem is a consequence of linking the requirements of periodic boundary conditions with the requirements that crystals are highly periodic structures with a periodicity given by the lattice constant a .

In the next lecture we will look at the solution of the Schrodinger equation for electrons in a periodic potential. We will find that gaps appear in the energy spectrum as a consequence of the interference between electron waves and the periodic potential. This leads to the formation of energy bands.