

Unit I

Semester 6th

Solid materials are classified on the basis of arrangement of atoms within the solid. There are two main categories: Materials in which atoms are placed randomly (lack regular arrangement) in a long range are called amorphous. Examples are pitch, plastic. Materials in which atoms are placed in a high ordered structure (regular and regular pattern) in a long range are called crystalline. Examples are diamond, quartz. Polycrystalline materials are materials with a high degree of short-range order and no long-range order. These materials consist of small crystalline regions with random orientation called grains, separated by grain boundaries. Crystals are categorized by their crystal structure and the underlying lattice. While some crystals have a single atom placed at each lattice point, most crystals have a combination of atoms associated with each lattice point. This combination of atoms is also called the basis. OR we can say that basis is an aggregate of atoms occupying space point's position. The classification of lattices, the common semi-conductor crystal structures and the growth of single-crystal semiconductors are discussed in the following sections.

Bravais lattices.

In 1848 A. Bravais, the French Crystallographer proved that there are only 14 space lattices in total, which are required to describe all possible arrangements of points in space. These are the distinct lattice types, which when repeated can fill the whole space. It is subjected to the condition that each lattice point has exactly identical environment. The lattice can therefore be generated by three unit vectors, $\vec{a}_1, \vec{a}_2, \vec{a}_3$ and a set of integers k, l and m so that each lattice point, identified by \vec{r} a vector can be obtained from:

$$k\vec{a}_1 + l\vec{a}_2 + m\vec{a}_3$$

The construction of the lattice points based on a set of unit vectors is illustrated by Figure

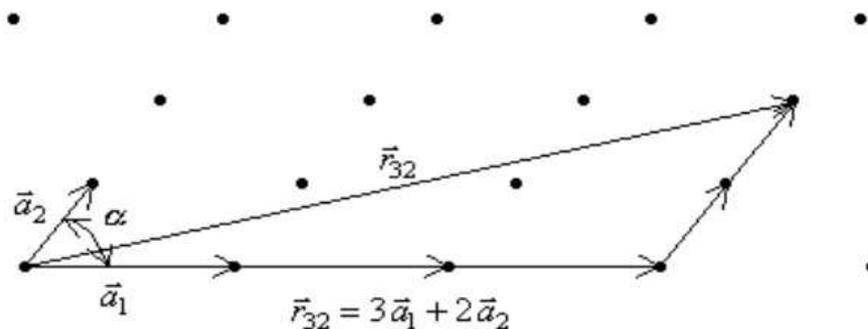


Figure: The construction of lattice points using unit vectors.

In two dimensions, there are five distinct Bravais lattices, while in three dimensions there are

fourteen—broadly classified into seven types known as seven crystal systems or classes. The lattices in two dimensions are the square lattice, the rectangular lattice, the centered rectangular lattice, the hexagonal lattice and the oblique lattice as shown in Figure:

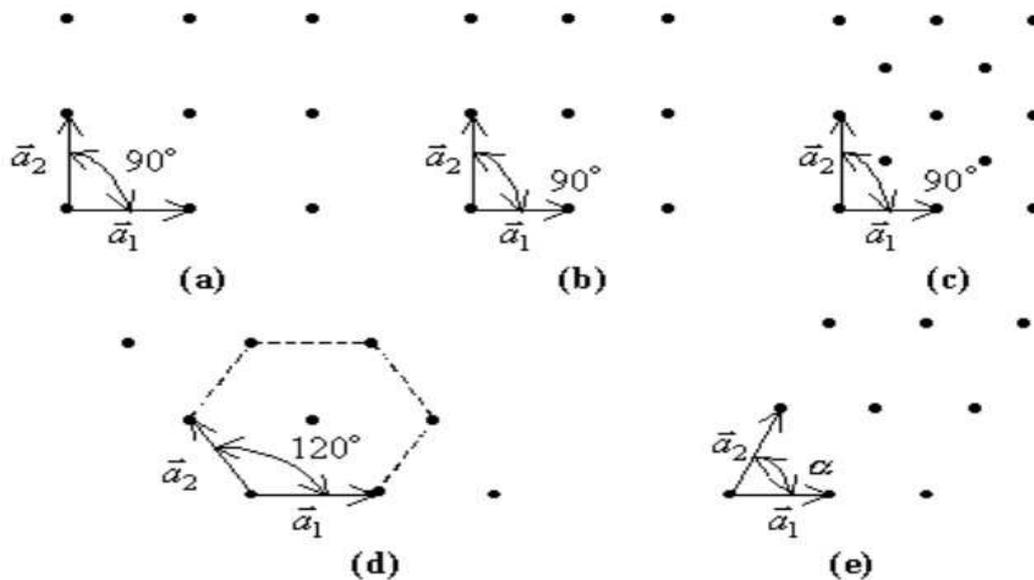


Figure: The five Bravais lattices of two-dimensional crystals: (a) cubic, (b) rectangular, (c) centered rectangular, (d) hexagonal and (e) oblique.

It is customary to organize these lattices in groups which have the same symmetry. An example is the rectangular and the centered rectangular lattice. As can be seen on the figure, all the lattice points of the rectangular lattice can be obtained by a combination of the lattice vectors. The centered rectangular lattice can be constructed in two ways. It can be obtained by starting with the same lattice vectors as those of the rectangular lattice and then adding an additional atom at the center of each rectangle in the lattice. This approach is illustrated by Figure (c). The lattice vectors generate the traditional unit cell and the center atom is obtained by attaching two lattice points to every lattice point of the traditional unit cell. The alternate approach is to define a new set of lattice vectors, one identical to and another starting from the same origin and ending on the center atom. These lattice vectors generate the so-called primitive cell and directly define the centered rectangular lattice.

These lattices are listed in Table below a_1 and a_2 are the magnitudes of the unit vectors and α is the angle between them.

Name	Number of Bravais lattices	Conditions
Square	1	$a_1 = a_2, \alpha = 90^\circ$
Rectangular	2	$a_1 \neq a_2, \alpha = 90^\circ$
Hexagonal	1	$a_1 = a_2, \alpha = 120^\circ$
Oblique	1	$a_1 \neq a_2, \alpha \neq 120^\circ, \alpha \neq 90^\circ$

The same approach is used for lattices in three dimensions. The fourteen lattices of three-dimensional crystals are classified as shown in Table below where a_1 , a_2 and a_3 are the magnitudes of the unit vectors defining the traditional unit cell and α , β and γ are the angles between these unit vectors.

Name	Number of Bravais lattices	Conditions
Triclinic	1	$a_1 \neq a_2 \neq a_3, \alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3, \alpha = \beta = 90^\circ \neq \gamma$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3, \alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3, \alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3, \alpha = \beta = \gamma < 120^\circ \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3, \alpha = \beta = 90^\circ, \gamma = 120^\circ$

Table: Bravais lattices of three-dimensional crystals.

The cubic lattices are an important subset of these fourteen Bravais lattices since a large number of semiconductors are cubic. The three cubic Bravais lattices are the simple cubic lattice, the body-centered cubic lattice and the face-centered cubic lattice as shown in Figure below. Since all unit vectors identifying the traditional unit cell have the same size, the crystal structure is completely defined by a single number. This number is the lattice constant, a .

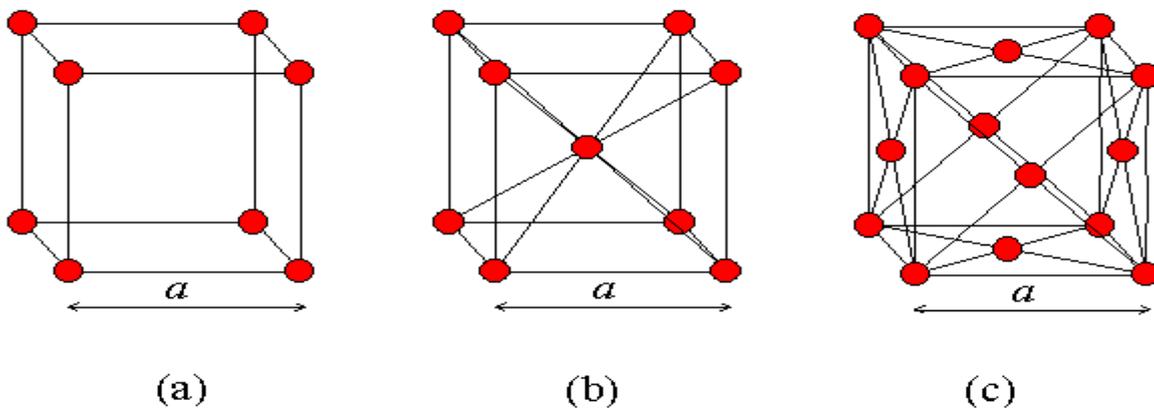


Figure: The simple cubic (a), the body-centered cubic (b) and the face centered cubic (c) lattice.

Reciprocal lattice.

We know that there exist many sets of planes in a crystal lattice with different orientation and spacings. If we draw from a common origin, normals to all set of planes, length of each normal being proportional to the reciprocal of the interplanar spacing of the corresponding set, then the end points of the normals form a lattice known as reciprocal lattice. Each point in the reciprocal lattice preserves the characteristics of the set of the planes. Its direction with respect the origin represents the orientation of the plane and its distance from the origin represents the interplanar spacing of the planes. If $\vec{a}, \vec{b}, \vec{c}$ are the basis vectors of a direct lattice, then the basis vectors $\vec{a}^*, \vec{b}^*, \vec{c}^*$ of the

reciprocal lattice are defined as:

$$\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \quad \vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \quad \vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

The common denominator in each case represents the volume of the direct crystal lattice. The vectors \vec{a} , \vec{b} and \vec{c} have the dimensions of length. And the vectors \vec{a}^* , \vec{b}^* and \vec{c}^* have the dimensions of $length^{-1}$.

Properties of Reciprocal lattice.

Every crystal structure has two lattices associated with it-- The Direct crystal lattice and the Reciprocal lattice. Reciprocal lattice has following properties:

1. Volume of a unit cell of reciprocal lattice is inversely proportional to the volume of unit cell of the direct lattice.
2. Magnitude of every reciprocal lattice vector is inversely proportional to the interplanar spacing of the corresponding set of lattice planes.
3. Every vector of the reciprocal lattice is normal to a set of lattice planes of the crystal lattice.

The concept of reciprocal is useful in understanding the X-ray diffraction phenomena in a very simple way. And also provides ample understanding of electron behavior in a periodic crystal lattice.

Density of States of Continuous Medium

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy. Bulk properties such as specific heat, paramagnetic susceptibility, and other transport phenomena of conductive solids depend on this function. DOS calculations allow one to determine the general distribution of states as a function of energy and can also determine the spacing between energy bands in semi-conductors.

Before we get involved in the derivation of the DOS of electrons in a material, it may be easier to first consider just an elastic wave propagating through a solid. Elastic waves are in reference to the lattice vibrations of a solid comprised of discrete atoms. Though, when the wavelength is very long, the atomic nature of the solid can be ignored and we can treat the material as a continuous medium.

We know that 1-D wave equation is given by:

$$\frac{\partial^2 u}{\partial x^2} - \frac{\rho}{Y} \frac{\partial u}{\partial t^2} = 0$$

$$u = Ae^{i(qx - \omega t)}$$

solution for a propagating plane wave:(1)

Where the terms have their usual meanings.

In equation(1), the temporal factor $- \omega t$, can be omitted because it is not relevant to the derivation of the DOS. So now we will use the solution:

$$u = Ae^{i(qx)} \dots\dots\dots(2)$$

To begin, we must apply some type of boundary conditions to the system. The easiest way to do this is to consider a periodic boundary condition. With a periodic boundary condition we can imagine our system having two ends, one being the origin, 0, and the other, L. We now say that the origin end is constrained in a way that it is always at the same state of oscillation as end L.

This boundary condition is represented as: $u(x = 0) = u(x = L)$

Now we apply the boundary condition to equation (2) to get: $e^{iqL} = 1$

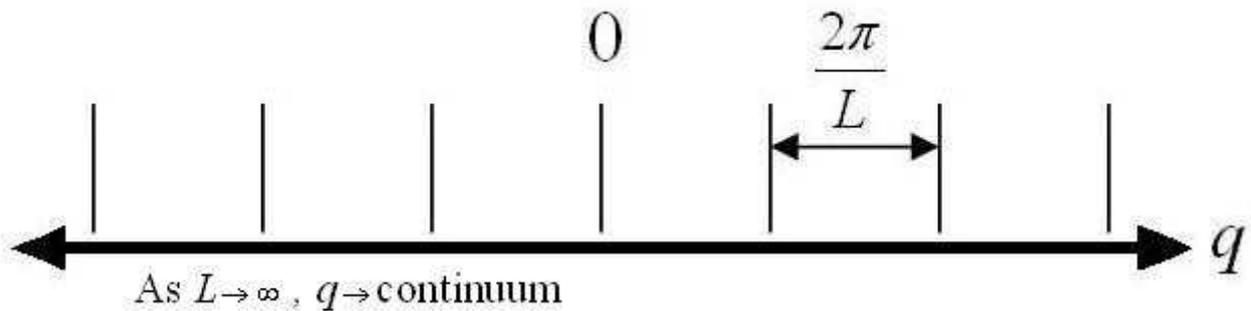
Now, using Euler's identity; $e^{ix} = \cos(x) + i \sin(x)$

we can see that there are certain values of $qL = 2n\pi$ which satisfy the above equation. Those values are for any integer, n. Leaving the relation:

$$q = n \frac{2\pi}{L}$$

If you choose integer values for n and plot

them along an axis q you get a 1-D line of points, known as modes, with a spacing of $2\pi/L$ between each mode.



We now have that the number of modes in an interval dq in q-space equals:

$$\frac{dq}{\frac{2\pi}{L}} = \frac{L}{2\pi} dq$$

Using the dispersion relation we can find the number of modes within a frequency range $d\omega$ that lies within $(\omega, \omega + d\omega)$. This number of modes in that range is represented by $g(\omega)d\omega$, where $g(\omega)$ is defined as the density of states. So now we see that $g(\omega)d\omega = \frac{L}{2\pi} dq$

Implies that,

$$g(\omega) = \left(\frac{L}{2\pi}\right) \left/ \left(\frac{d\omega}{dq}\right)\right.$$

Now

$$\frac{d\omega}{dq} = v_s$$

Therefore, we have

$$g(\omega) = \left(\frac{L}{2\pi}\right) \frac{1}{v_s} \Rightarrow g(\omega) = 2 \left(\frac{L}{2\pi}\right) \frac{1}{v_s}$$

we multiply by a factor of two because there are modes in positive and negative q-space, and we get the density of states for a phonon in 1-D:

$$g(\omega) = \frac{L}{\pi v_s}$$

2-D:

We can now derive the density of states for two dimensions. Equation(2) becomes: $u = Ae^{i(q_x x + q_y y)}$

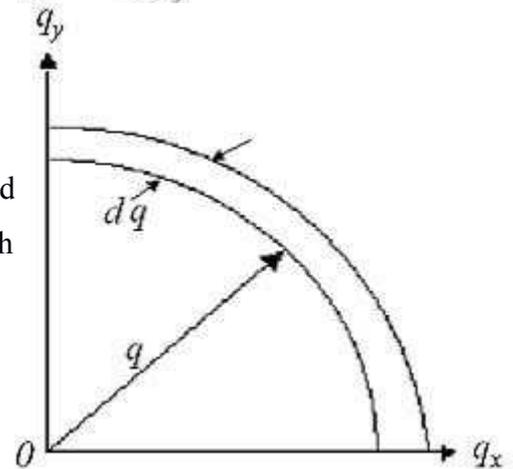
Now apply the same boundary conditions as in the 1-D case:

$$e^{i[q_x L + q_y L]} = 1 \Rightarrow (q_x, q_y) = \left(n \frac{2\pi}{L}, m \frac{2\pi}{L} \right)$$

We now consider an area for each point in q-space $= (2\pi/L)^2$ and find the number of modes that lie within a flat ring with thickness dq , a radius q and area: πq^2

Number of modes inside interval:

$$\frac{d}{dq} \left(\frac{L}{2\pi} \right)^2 \pi q^2 \Rightarrow \left(\frac{L}{2\pi} \right)^2 2\pi q dq$$



Now account for transverse and longitudinal modes (multiply by a factor of 2) and set equal to $g(\omega)d\omega$ We get

$$g(\omega)d\omega = 2 \left(\frac{L}{2\pi} \right)^2 2\pi q dq$$

Apply dispersion relation we get

$$2 \left(\frac{L}{2\pi} \right)^2 2\pi \left(\frac{\omega}{v_s} \right) \frac{d\omega}{v_s}$$

which simplifies to the 2-D result:

$$g(\omega) = \frac{L^2}{\pi v_s^2} \omega$$

3-D:

We can now derive the density of states for three dimensions. Equation(2) becomes: $u = Ae^{i(q_x x + q_y y + q_z z)}$

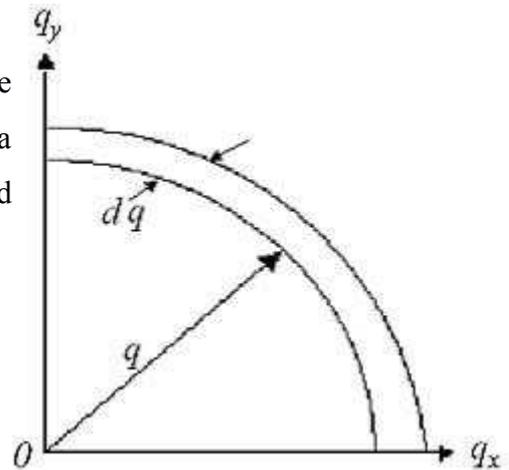
Apply the boundary conditions as in the 1-D case to get:

$$e^{i[q_x L + q_y L + q_z L]} = 1 \Rightarrow (q_x, q_y, q_z) = \left(n \frac{2\pi}{L}, m \frac{2\pi}{L}, l \frac{2\pi}{L} \right)$$

We now consider a volume for each point in q-space $= (2\pi/L)^3$ and find the number of modes that lie within a spherical shell, thickness dq , with a radius q and volume: $4/3\pi q^3$.

Number of modes inside shell:

$$\frac{d}{dq} \left(\frac{L}{2\pi} \right)^3 \frac{4}{3} \pi q^3 \Rightarrow \left(\frac{L}{2\pi} \right)^3 4\pi q^2 dq$$



Assuming a common velocity for transverse and longitudinal waves we can account for one longitudinal and two transverse modes for each value of q (multiply by a factor of 3) and set equal to $g(\omega)d\omega$:

$$g(\omega)d\omega = 3 \left(\frac{L}{2\pi} \right)^3 4\pi q^2 dq$$

Apply dispersion relation and let $L^3=V$ to get

$$3 \frac{V}{(2\pi)^3} 4\pi \left(\frac{\omega}{v_s} \right)^2 \frac{d\omega}{v_s}$$

Implies that

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

Specific Heat

Specific heat is mathematically represented as heat capacity per unit mass of a substance. It is defined as a measure of number of degrees of freedom of a system. Since the degrees of freedom imply freedom to absorb potential or kinetic or potential energy,-- this depends on the number of ways energy is given to the system.

Different systems need different amounts of heat energy to raise their temperature by a given temperature interval. For example, it takes 4184 joules to raise temperature of 1Kg of water by 1K. But the same heat energy raises the temperature of 1 Kg of copper by 11 K. Thus water has large heat capacity as compared to copper. The heat capacity at constant volume C_v is the most useful quantity than the specific heat at constant pressure C_p because the former can be obtained immediately from the energy of the system. Whole analysis is based on the following thermodynamic relations.

$$dQ = dU - dW = dU - PdV$$

Then the specific heat at constant volume is

$$C_v = \left[\frac{\partial Q}{\partial T} \right]_v = \left[\frac{\partial U}{\partial T} \right]_v$$

On the other hand, it is easy to measure the heat capacity of solid at constant pressure than at constant volume. At low temperatures the difference between C_p and C_v vanishes for solids and is only 5% at room temperature. C_v can be calculated from C_p if the volume expansion coefficient α and the compressibility β of a material are known by applying the following relations.

$$C_p - C_v = \frac{\alpha^2 TV}{\beta}$$

Where V is the volume of the solid.

Any theory used to calculate lattice vibration heat capacities of crystalline solids must explain two things:

1. Near room temperature, the heat capacity of most solids is around $3k$ per atom (the molar heat capacity for a solid consisting of n -atom molecules is $\sim 3nR$). This is the well-known Dulong and Petit law.
2. At low temperatures, C_v decreases, becoming zero at $T=0$. Heat capacities have a temperature dependence of the form $\alpha T^3 + \gamma T$, where the T^3 term arises from lattice vibrations, and the linear term from conduction electrons. Classical mechanics would predict $C_v = 3R$ at all temperatures, in violation of both experiment and the third law of thermodynamics

Einstein's theory of Specific Heat.

Einstein treated the atoms in a crystal as N simple harmonic oscillators, all having the same frequency ν_E . The frequency ν_E depends on the strength of the restoring force acting on the atom, i.e. the strength of the chemical bonds within the solid. Since the equation of motion for each atom decomposes into three independent equations for the x , y and z components of displacement, and N -atom solid is equivalent to $3N$ harmonic oscillators, each vibrating independently at frequency ν_E . Note that this treatment is a gross approximation, since in reality the lattice vibrations are very complicated coupled oscillations.

The energy levels of the harmonic oscillators are given by

$$\epsilon_\nu = h\nu_E (\nu + 1/2), \quad \nu = 0, 1, 2, \dots$$

Assuming the oscillators are in thermal equilibrium at temperature T , the partition function for a single oscillator is

$$q = \sum_{\nu=0}^{\infty} \exp[-\beta\epsilon_\nu] = \sum_{\nu=0}^{\infty} \exp[-\beta h\nu_E (\nu + 1/2)] = e^{-x/2} \sum_{\nu=0}^{\infty} e^{-x\nu} = \frac{e^{-x/2}}{1 - e^{-x/2}} \text{ where } x = \beta h\nu_E$$

In the above, we have used the fact that

$$\sum_{\nu=0}^{\infty} X^\nu = \frac{1}{1 - X}$$

The mean energy per oscillator is then

$$u = -\frac{d \ln q}{d\beta} = -\frac{d}{d\beta} \left(\frac{\beta h\nu_E}{2} + \ln(1 - e^{-\beta h\nu_E}) \right) = \frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E} - 1}$$

The first term above, $h\nu/2$, is simply the zero point energy. Using the fact that energy is an extensive property, the energy of the $3N$ oscillators in the N -atom solid is

$$U = 3Nu = 3N \left(\frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h \nu_E} - 1} \right)$$

The heat capacity at constant volume is therefore

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 3N \left(\frac{\partial U}{\partial \beta} \right)_v \frac{\partial \beta}{\partial T} = 3Nk \frac{x^2 e^x}{(e^x - 1)^2} \quad \text{where} \quad x = \frac{h\nu_E}{kT} = \frac{\theta_E}{T}$$

θ_E is the 'Einstein temperature', which is different for each solid, and reflects the rigidity of the lattice. At the high temperature limit, when $T \gg \theta_E$ (and $x \ll 1$), the Einstein heat capacity reduces to $C_v = 3Nk$, the Dulong and Petit law [prove by setting $e^x \sim 1+x$ in the denominator].

At the low temperature limit, when $T \ll \theta_E$ (and $x \gg 1$), $C_v \rightarrow 0$ as $T \rightarrow 0$, as required by the third law of thermodynamics. [Prove by setting $e^x - 1 \sim e^x$ in the denominator for large x].

Debye's theory of heat capacities.

Debye improved on Einstein's theory by treating the coupled vibrations of the solid in terms of $3N$ normal modes of vibration of the whole system, each with its own frequency. The lattice vibrations are therefore equivalent to $3N$ independent harmonic oscillators with these normal mode frequencies.

For low frequency vibrations, defined as those for which the wavelength is much greater than the atomic spacing, $\lambda \gg a$, the crystal may be treated as a homogeneous elastic medium. The normal modes are the frequencies of the standing waves that are possible in the medium.

Debye derived an expression for the number of modes with frequency between ν and $\nu+d\nu$ in such a medium.

$$g(\nu) d\nu = \frac{4\pi V \nu^2}{v^3} d\nu = \alpha \nu^2 d\nu$$

where V is the crystal volume and v is the propagation velocity of the wave. As outlined above, this expression applies only to low frequency vibrations in a crystal. Debye used the approximation that it applied to all frequencies, and introduced a maximum frequency ν_D (the Debye frequency) such that there were $3N$ modes in total.

$$\int_0^{\nu_D} g(\nu) d\nu = 3N$$

The Debye frequency corresponds to $\lambda = 2a$, when neighbouring atoms vibrate in anti-phase with each other. With this approximation in place, Debye integrated over all of the frequencies to find the

internal energy of the crystal, and then calculated $C_v = \left(\frac{\partial U}{\partial T} \right)_v$. The resulting expression is given below.

$$C_v = 3Nk \left(\frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \right)$$

Where

$$x = \frac{h\nu}{kT}, \text{ and } x_D = \frac{h\nu_D}{kT} = \frac{\theta_D}{T}$$

The Debye heat capacity depends only on the Debye temperature θ_D . The integral cannot be evaluated analytically, but the bracketed function is tabulated.

At high temperatures ($T \gg \theta_D$, $x_D \ll 1$), we may rewrite the integrand as follows:

$$\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4}{(e^x - 1)(1 - e^{-x})} = \frac{x^4}{2(\cosh(x) - 1)} = \frac{x^4}{2(x^2/2! + x^4/4! + \dots)}$$

Retaining only the x^2 term in the denominator gives

$$C_v = 3Nk \left(\frac{3}{x_D^3} \int_0^{x_D} x^2 dx \right) = 3Nk$$

To determine the low temperature limit ($T \ll \theta_D$, $x_D \gg 1$), we note that the integrand tends towards zero rapidly for large x . This allows us to replace the upper limit by ∞ and turn the integral into a standard integral, to give

$$C_v = 3Nk \left(\frac{T}{\theta_D} \right)^3 \left(3 \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} \right) = \frac{12}{5} \pi^4 Nk \left(\frac{T}{\theta_D} \right)^3$$

We see that the Debye heat capacity decreases as T^3 at low temperatures, in agreement with experimental observation. This is a marked improvement on Einstein's theory.

Concept of Phonons

Phonons are a quantum mechanical version of a special type of vibrational motion, known as normal modes in classical mechanics, in which each part of a lattice oscillates with the same frequency. These normal modes are important because, according to a well-known result in classical mechanics, any arbitrary vibrational motion of a lattice can be considered as a superposition of normal modes with various frequencies; in this sense, the normal modes are the

elementary vibrations of the lattice. Although normal modes are wave-like phenomena in classical mechanics, they acquire certain particle-like properties when the lattice is analyzed using quantum mechanics (see wave-particle duality.) They are then known as phonons.

Lattice waves

Consider the elastic vibrations of a crystal with one atom in the primitive cell. We want to find the frequency of an elastic wave in terms of the wave vector k and the elastic constants. When a wave propagates along the x -direction, entire planes of atoms move in phase with displacements either parallel or perpendicular to the direction of k . We can describe with a single co-ordinate u_s the displacement of the plane s from its equilibrium position.

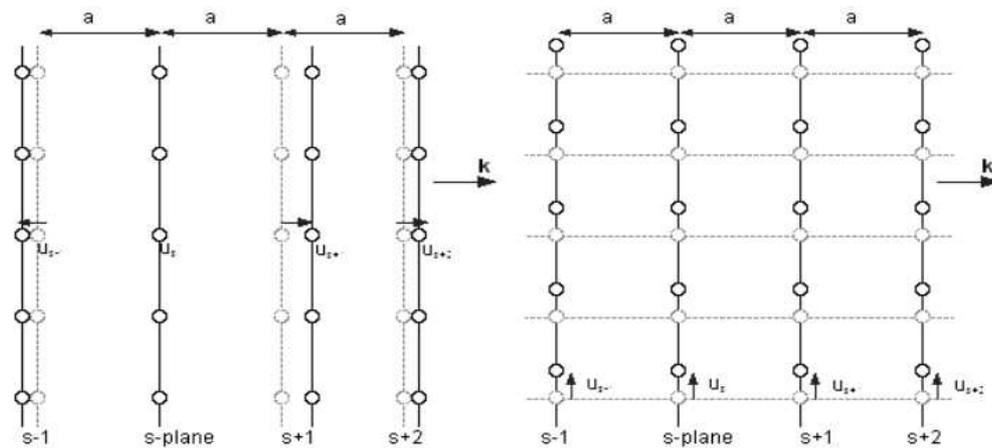


Fig.1 (Left figure) (Dashed lines) Planes of atoms when in equilibrium. (Solid lines) Planes of atoms when displaced as for a longitudinal wave. The coordinate u measures the displacement of the planes. (Right figure) Plane of atoms as displaced during passage of transverse wave.

For each wave vector there are three modes; one of longitudinal polarization, two of transverse polarization. We assume that the elastic response of the crystal is a linear function of the forces. Or the elastic energy is a quadratic function of the relative displacement of any two points in the crystal. The forces on the plane s caused by the displacement of the plane $s+p$ is proportional to the difference $u_{s+p} - u_s$ of their displacements. For brevity, we consider only nearest-neighbor interactions, so that $p = \pm 1$. The total force on s comes from planes $s \pm 1$.

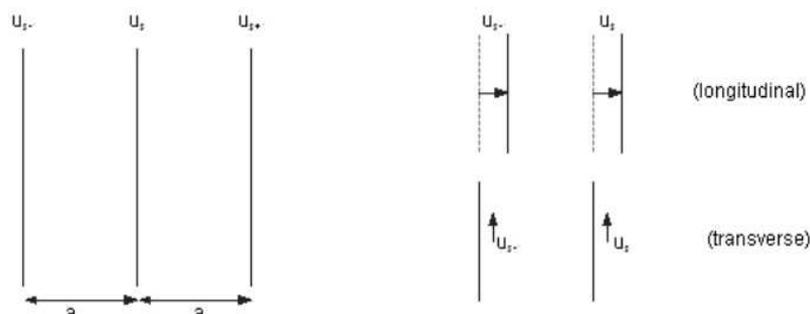
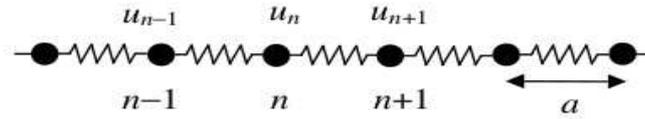


Fig.2 The displacements of atoms with mass M are denoted by u_{s-1} , u_s , and u_{s+1} . The repeated

distance is a in the direction of the wave vector k . The direction of u is parallel to the direction of the wave vector k for the longitudinal wave and is perpendicular to the direction of the wave vector k for the transverse wave.

One Dimensional Monoatomic Lattice

For simplicity we consider, first, a one-dimensional crystal lattice and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions.



This is known as the harmonic approximation, which holds well provided that the displacements are small. One might think about the atoms in the lattice as interconnected by elastic springs. Therefore, the force exerted on n -th atom in the lattice is given by

$$F_n = C (u_{n+1} - u_n) + C (u_{n-1} - u_n) \quad (1)$$

where C is the interatomic force (elastic) constant. Applying Newton's second law to the motion of the n -th atom we obtain

$$M \frac{d^2 u_n}{dt^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) = -C(2u_n - u_{n+1} - u_{n-1}) \quad (2)$$

where M is the mass of the atom. Note that we neglected here by the interaction of the n -th atom with all but its nearest neighbors. A similar equation should be written for each atom in the lattice, resulting in N coupled differential equations, which should be solved simultaneously (N is the total number of atoms in the lattice). In addition the boundary conditions applied to the end atom in the lattice should be taken into account.

Now let us attempt a solution of the form

$$u_n = A e^{i(qx_n - \omega t)} \quad (3)$$

where x_n is the equilibrium position of the n -th atom so that $x_n = na$. This equation represents a traveling wave, in which all the atoms oscillate with the same frequency ω and the same amplitude A and have wave vector q . Note that a solution of the form (3) is only possible because of the translational symmetry of the lattice.

Now substituting Eq.(3) into Eq.(2) and canceling the common quantities (the amplitude and the time-dependent factor) we obtain

$$M (-\omega^2) e^{iqna} = -C [2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}] \quad (4)$$

This equation can be further simplified by canceling the common factor e^{iqna} , which leads to

$$M \omega^2 = C(2 - e^{iqa} - e^{-iqa}) = 2C(1 - \cos qa) = 4C \sin^2 \frac{qa}{2}. \quad (5)$$

We find therefore the dispersion relation for the frequency

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{qa}{2} \right|, \quad (6)$$

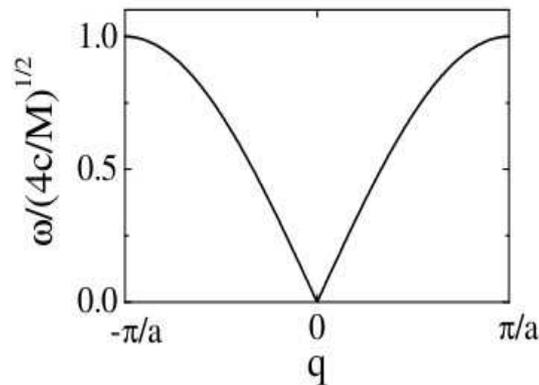
which is the relationship between the frequency of vibrations and the wave vector q . This dispersion relation has a number of important properties.

(i) Reducing to the first Brillouin zone. The frequency (6) and the displacement of the atoms (3) do not change when we change q by $q + 2\pi/a$. This means that these solutions are physically identical.

This allows us to set the range of independent values of q within the first Brillouin zone, i.e.

$$\frac{-\pi}{a} \leq q \leq \frac{\pi}{a} \quad (7)$$

Within this range of q the ω versus q is shown in Figure below:



The maximum frequency is $\sqrt{4C/M}$. The frequency is symmetric with respect to the sign change in q , i.e. $\omega(q) = \omega(-q)$. This is not surprising because a mode with positive q corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative q corresponds to the wave traveling from the right to the left. Since these two directions are equivalent in the lattice the frequency does not change with the sign change in q .

At the boundaries of the Brillouin zone $q = \pm\pi/a$ the solution represents a standing wave

: atoms oscillate in the opposite phases depending on whether n is even or odd. At the

boundaries of the Brillouin zone $q = \pm\pi/a$ the solution represents a standing wave

$u_n = A(-1)^n e^{it}$: atoms oscillate in the opposite phases depending on whether n is even or odd.

The wave moves neither right nor left.

(ii) Phase and group velocity. The phase velocity is defined by

$$v_p = \frac{\omega}{q} \quad (8)$$

and the group velocity by

$$v_g = \frac{d\omega}{dq} \quad (9)$$

The physical distinction between the two velocities is that v_p is the velocity of the propagation of the plane wave, whereas the v_g is the velocity of the propagation of the wave packet. The latter is the velocity for the propagation of energy in the medium. For the particular dispersion relation (6) the group velocity is given by,

$$v_g = \sqrt{\frac{Ca^2}{M}} \cos \frac{qa}{2}. \quad (10)$$

As is seen from Eq.(10) the group velocity is zero at the edge of the zone where $q = \pm\pi/a$. Here the wave is standing and therefore the transmission velocity for the energy is zero.

(iii) Long wavelength limit. The long wavelength limit implies that $\lambda \gg a$. In this limit $qa \ll 1$. We can then expand the sine in Eq.(6) and obtain for the positive frequencies:

$$\omega = \sqrt{\frac{C}{M}} qa. \quad (11)$$

We see that the frequency of vibration is proportional to the wave vector. This is equivalent to the statement that velocity is independent of frequency. In this case

$$v_p = \frac{\omega}{q} = \sqrt{\frac{C}{M}} a. \quad (12)$$

This is the velocity of sound for the one dimensional lattice which is consistent with the expression we obtained earlier for elastic waves.

Elastic Waves in Solids

Elasticity is a solid's most important property for restoring its shape and volume after the termination of the action of the external forces applied to it, while for liquids and gases, only volume is restored. Therefore the medium, whose typical feature is elasticity, is referred to as "elastic medium." Accordingly, elastic vibrations are vibrations of mechanical systems, elastic medium, or its part that arises under mechanical disturbances. Elastic or acoustic waves are mechanical disturbances that reproduce in an elastic medium. A partial case of acoustic waves is a sound, which is audible to man; thus the term "acoustics" (from the Greek "akustikos," which means "auditory") was given to this phenomenon. In the widest sense, acoustics involves the study of elastic waves, and in the narrowest, it is often used to define their sound range only.

Elastic vibrations and acoustic waves are widely used in nondestructive testing and technical diagnostics of materials and products, in various engineering devices and equipment. For example, powerful ultrasonic vibrations are used for the local fracture of brittle high-strength materials (ultrasonic crushing); dispersion (fine crushing of solid or liquid bodies in any medium—for example, fats in water); coagulation (enlargement of particles of a substance, such as smoke); and for other purposes. Elastic vibrations and waves are very important for the investigation of the processes of initiation and propagation of the volume damaging and fracture of solids; this is what has made it possible to use them widely in fundamental and applied scientific studies of these processes from the viewpoint of fracture mechanics.

Types of Elastic Waves

Some General Ideas on Elastic Strain.

Elastic vibrations in liquids and gases are characterized by one of the following parameters: change in pressure p or density ρ ; particle shift from an equilibrium state u ; vibration motion velocity v ; or shear potential χ , i.e., vibration velocity ϕ . It is essential to distinguish the change in pressure or density caused by acoustic wave propagation from their statistical (average) value. All the above-mentioned parameters are interconnected, for example: $u = \text{grad}\chi$, $v = \text{grad}\phi$, $v = \partial u / \partial t$; $p = \rho \partial \phi / \partial t$; Unlike liquids and gases, the acoustic field in a solid is of a more complicated nature, because a solid possesses not only the volume elasticity as liquids and gases do, but also the elasticity of their shape, i.e., shear elasticity. The concept of stress is introduced for solids instead of pressure, i.e., the force related to a surface unit. In the mechanics of a deformed solid there are normal (tensile or compressive) .

A Wave Equation for a Solid

It is derived by using the second Newton's law for an elementary volume $dx dy dz$. The difference of forces applied to its opposite faces is equated to the product of mass and acceleration. As a result, we get for axis x

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z}. \quad (1)$$

By analogy, it is possible to write the equation for axes y and z. By substituting strains instead of stresses, the equation of wave propagation in an elastic medium is obtained:

$$\rho \frac{\partial^2 u_x}{\partial t^2} - (\Lambda + \mu) \frac{\partial \epsilon_x}{\partial x} - \mu \nabla^2 u_x = 0, \quad (2)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (3)$$

is the Laplace operator. The wave equations (2) include second-order time, and coordinate derivatives with different signs with respect to some variable. Using a vector analysis, the equation of (2) type for all coordinates can be written as one expression:

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = (\Lambda + \mu) \text{grad div } \mathbf{u} + \mu \nabla^2 \mathbf{u}. \quad (4)$$

When $\mu = 0$, and assuming the displacement $u_x = u_y = u_z = u$ to be the same in all directions (scalar), Eq. (4) is transformed to a wave equation for a liquid or a gas:

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = c^2 \nabla^2 u, \quad (5)$$

where $c = \sqrt{\frac{\Lambda}{\rho}}$ is the velocity of propagation of elastic waves. The same equations are valid for other elastic values, i.e., pressure, potential, etc.

Density of States in Lattice

The density of states gives the number of allowed electron (or hole) states per volume at a given energy. It can be derived from basic quantum mechanics.

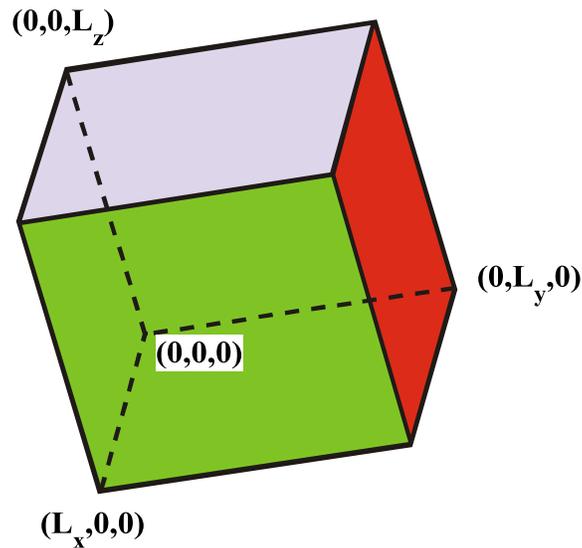
Electron Wavefunction

The position of an electron is described by a wavefunction $\psi(x, y, z)$. The probability of finding the electron at a specific point (x, y, z) is given by $|\psi(x, y, z)|^2$, where total probability $\int_{\text{all space}} |\psi(x, y, z)|^2 dx dy dz$ is normalized to one.

Particle in a Box

The electrons at the bottom of a conduction band (and holes at the top of the valence band) behave approximately like free particles (with an effective mass) trapped in a box. We will consider here conduction band electrons, but the result for holes is similar. For our parabolic conduction band:

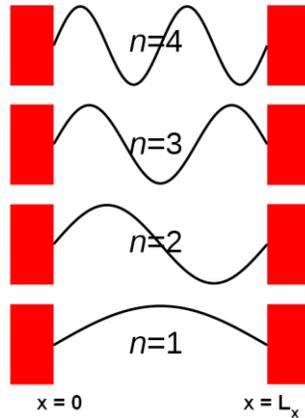
$$(E - E_c) = \frac{\hbar^2 k^2}{2m^*}$$



For electrons in a rectangular volume L_x by L_y by L_z with an infinite confining potential ($U(x, y, z) = 0$ inside the box and ∞ outside), the electron wavefunction ψ must go to zero on the boundaries, and takes the form of a harmonic function within the region. The wavefunction solution is:

$$\psi(x, y, z) = \sin(k_x x) \sin(k_y y) \sin(k_z z) \quad (1)$$

and k_x, k_y , and k_z are the wavevectors for an electron in the x, y , and z directions. The real wavefunction in a solid is more complex and periodic (with the crystal lattice), but this is a good approximation for the parabolic regions near the band edges.



First 4 particle in a box wavefunctions across the x direction.
Orthogonal directions are analogous.

Enforcing the boundary conditions: At x, y , or $z = 0$, the sine functions go to zero. At the opposite boundaries of the rectangular region, $\sin(k_x L_x) = 0$, $\sin(k_y L_y) = 0$, and $\sin(k_z L_z) = 0$ for the x, y , and z directions. The allowed wavevectors satisfy:

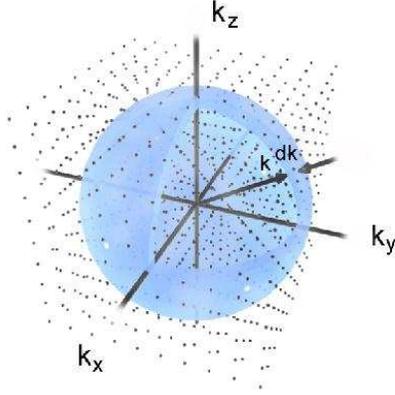
$$k_x L_x = \pi n_x, k_y L_y = \pi n_y, k_z L_z = \pi n_z, \text{ for } n_x, n_y, n_z \text{ integers} \quad (2)$$

K Space

The allowed states can be plotted as a grid of points in k space, a 3-D visualization of the directions of electron wavevectors. Allowed states are separated by $\pi / L_{x,y,z}$ in the 3 directions in k space.

The k space volume taken up by each allowed state is $\pi^3 / L_x L_y L_z$. The reciprocal is the state density in k space (# of states per volume in k space), V / π^3 where V is the volume of the semiconductor (in real space).

The number of states available for a given magnitude of wavevector $|k|$ is found by constructing a spherical shell of radius $|k|$ and thickness dk . The volume of this spherical shell in k space is $4\pi k^2 dk$.



Allowed wavevector states in k space form a lattice.
 A spherical shell gives the number of allowed states at a specific radius $|k|$.

The number of k states within the spherical shell, $g(k)dk$, is (approximately) the k space volume times the k space state density:

$$g(k)dk = 4\pi k^2 \left[\frac{V}{\pi^3} \right] dk \quad (3)$$

Each k state can hold 2 electrons (of opposite spins), so the number of electron states is:

$$g(k)dk = 8\pi k^2 \left[\frac{V}{\pi^3} \right] dk \quad (4a)$$

Finally, there is a relatively subtle issue. Wavefunctions that differ only in sign are indistinguishable. Hence we should count only the positive n_x, n_y, n_z states to avoid multiply counting the same quantum state. Thus, we divide (4a) by 1/8 to get the result:

$$g(k)dk = \pi k^2 \left[\frac{V}{\pi^3} \right] dk = \left[\frac{Vk^2}{\pi^2} \right] dk \quad (4b)$$

This is an expression for the number of unique electron states available at a given $|k|$ over a range dk . We need an expression in terms of energy rather than wavevector k . We proceed from the relationships between wavevector, momentum p , and energy E :

$$p = \hbar k, E = p^2 / 2m^* \quad E = \frac{\hbar^2 k^2}{2m^*} \quad (5)$$

with m^* as the effective mass. Rewriting, and noting that the energy of carriers in the conduction band is given with respect to the conduction band edge energy E_c :

$$k^2 = \frac{(E - E_c)2m^*}{\hbar^2} \quad (6)$$

Differentiating:

$$2kdk = \frac{2m^* dE}{\hbar^2} \quad (7a)$$

Combining (6) and (7a):

$$\begin{aligned}
 dk &= \frac{2m^* dE}{2k\hbar^2} = \frac{m^* dE}{k\hbar^2} = \frac{m^* dE}{\hbar^2 \sqrt{2m^* (E - E_c)}/\hbar^2} \\
 &= \frac{m^* dE}{\hbar \sqrt{2m^* (E - E_c)}}
 \end{aligned} \tag{7b}$$

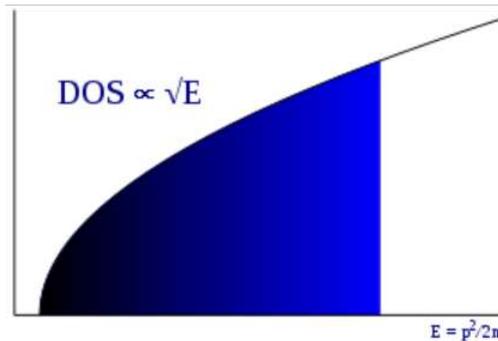
Plugging (6) and (7) into (4b):

$$\begin{aligned}
 g(k)dk &= \frac{Vk^2}{\pi^2} \frac{m^* dE}{\hbar \sqrt{2m^* (E - E_c)}} \\
 &= \frac{V [2m^* (E - E_c) / \hbar^2] (m^* dE)}{\pi^2 \hbar [2m^* (E - E_c)]^{1/2}} \\
 &= \frac{Vm^* [2m^* (E - E_c)]^{1/2}}{\pi^2 \hbar^3} dE
 \end{aligned} \tag{8}$$

Dividing through by V , the number of electron states in the conduction band per unit volume over an energy range dE is:

$$g(E)dE = \frac{m^* [2m^* (E - E_c)]^{1/2}}{\pi^2 \hbar^3} dE \tag{9}$$

This is equivalent to the density of the states given without derivation in the textbook.



3-D density of states, which are filled in order of increasing energy.

Dimensionality

The derivation above is for a 3 dimensional semiconductor volume. What happens if the semiconductor region is very thin and effectively 2 dimensional?

Confining the electron in the x - y plane, the wavevector z component $k_z=0$. The allowed states in k space becomes a 2 dimensional lattice of k_x and k_y values, spaced $\pi / L_{x,y}$ apart.

The 2-D k space area taken up by each state is $\pi^2 / L_x L_y$. The number of states per area in k space is A / π^2 with A as the real-space area of the thin semiconductor.

The number of states available at a given $|k|$ is found using an annular region of radius $|k|$ and thickness dk rather than the spherical shell from the 3-D case. There is a factor of $1/4$ due to the equivalent nature of the \pm states (just as there was $1/8$ in the 3D case). The area is $\pi k dk$. The number of k space states is:

$$g(k)dk = \left[\frac{A}{\pi^2} \right] 2\pi k dk \times 2 \text{ spin states} \div 4 \text{ equivalent states} = k \left[\frac{A}{\pi} \right] dk \quad (10)$$

Converting to energy using (7b):

$$g(k)dk = k \left[\frac{A}{\pi} \right] dk = \frac{A \left[2m^* (E - E_c) / \hbar^2 \right]^{1/2}}{\pi} \left(\frac{m^*}{\hbar \left[2m^* (E - E_c) \right]^{1/2}} \right) dE \quad (11)$$

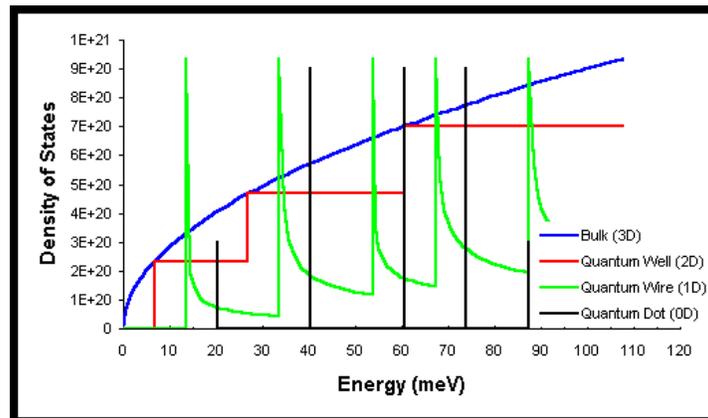
Cleaning up and dividing through by area, the density of states per area at an energy E over a range dE is:

$$g(E)dE = \frac{m^* dE}{\pi \hbar^2} \quad (12)$$

Unlike the 3-D case, this expression is independent of energy E !

In a real structure (which is not perfectly 2-D), there are finite energy ranges over which the energy independence holds (the derivation holds for each single, well separated possible value of k_z). The resulting density of states for a quantum well is a staircase, as below in red.

Further restriction of the semiconductor dimensionality to 1-D (quantum wire) and 0-D (quantum dot) results in more and more confined density of states functions.



Density of states for 0-D through 3-D regions.

Low dimensional and confining nanostructures have lots of applications controlling carriers in semiconductor devices.

Sommerfeld-Drude model

Recap of Drude model:

1. Treated electrons as free particles moving in a constant potential background.
2. Treated electrons as *identical* and *distinguishable*.
3. Applied classical (Maxwell-Boltzmann) statistics on them.

Drawbacks of this approach:

1. electrons cannot be treated classically – they are Fermions
2. They are *identical* and *indistinguishable*.
3. They obey Pauli exclusion principle

These observations imply that electrons obey Fermi-Dirac (FD) statistics.

Sommerfeld Drude model: - Retains almost all aspects of Drude model with the following modifications:

1. Treats electrons using FD statistics.
2. Recognizes that their energies are discrete – treats them like a particle in a box of constant energy.
3. Uses Pauli principle to distribute them in the available energy states.

Ground state of ideal electron gas

Electron confined in a cube of sides L at $T=0$, potential inside the cube is constant (take it to be zero) – potential at boundaries ∞ . Assume non-interacting electrons i.e.

$$\psi(r_1, r_2, \dots, r_N) = \psi(r_1)\psi(r_2) \dots \dots \psi(r_N)$$

Hamiltonian is:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi$$

Using the periodic boundary condition $\psi(x + L, y, z) = \psi(x, y, z)$ and so on,

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

with the energy eigenvalues $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$ - this is the dispersion relation for free electrons.

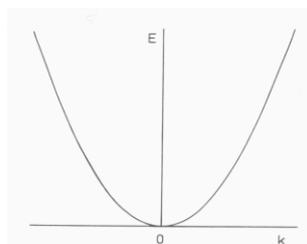


Figure 1: Dispersion relation for free electrons

\mathbf{k} is a position independent wave vector, each value of \mathbf{k} label a distinct state.

$$\mathbf{p}\psi = \hbar\mathbf{k}\psi$$

implying that \mathbf{k} plays the role of wave-vector for the free electrons

Allowed values of k are given by the quantization condition $\psi(x + L, y, z) = \psi(x, y, z)$ to be

$$k_x = \frac{2\pi}{L} n_x \text{ where } n_x \text{ is an integer}$$

Now we have levels – put electrons in them following Pauli exclusion principle (Pauli exclusion principle is a manifestation of e-e interaction although we did not put it in explicitly in the Hamiltonian) – can do this as electrons are treated to be independent - each level denoted by a particular value of k can accommodate two electrons (for two values of the spin projection).

For large N the filled states form a sphere in k -space (remember $(k) \propto k^2$) – its radius is k_F (this is called the Fermi wave-vector) and volume $\frac{4}{3}\pi k_F^3$. This is the *Fermi sphere*. k_F is given by:

$$2 \times \frac{4}{3}\pi k_F^3 \times \frac{1}{\left(\frac{2\pi}{L}\right)^3} = N$$

$$k_F = \left(3\pi^2 n\right)^{\frac{1}{3}} \quad (1)$$

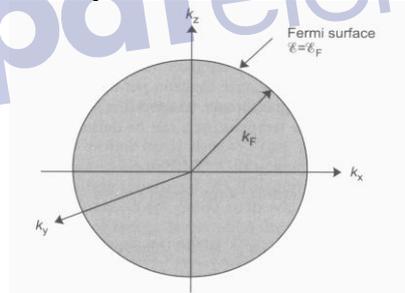


Figure 2: Fermi sphere at T=0

The highest occupied energy level in the ground state is called the *Fermi energy*. This separates the completely filled states from the completely empty ones in the ground state. For free electrons $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$. For metallic systems *Fermi energy* $\varepsilon_F \sim eV$ and *Fermi velocity* $v_F = \frac{\hbar k_F}{m} \sim 10^6$ m/s.

Total ground state energy is

$$E = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m}$$

For large N ; the values of k are arbitrarily close to each other – can treat as continuum:

$$\sum_K \rightarrow \frac{V}{8\pi^3} \int d\mathbf{k}$$

thus the total energy of the electronic system is

$$E = 2 \frac{V}{8\pi^3} \int \frac{\hbar^2 k^2}{2m} d\mathbf{k} = 2 \frac{V}{8\pi^3} \int \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk = \frac{1}{10} \frac{\hbar^2}{\pi^2 m} k_F^5$$

Average energy per particle is

$$\frac{E}{N} = \frac{E}{V} / \frac{N}{V} = \left(\frac{1}{10} \frac{\hbar^2}{\pi^2 m} k_F^5 \right) / \left(k_F^3 / 3\pi^2 \right) = \frac{3}{5} \varepsilon_F = \frac{3}{5} k_B T_F$$

In contrast to a classical gas, the degenerate quantum mechanical electron gas has appreciable ground-state energy. The Fermi temperature $T_F \sim 10^5$ K; hence compared to classical gas at room temperature the average energy of electrons is about 100 times more.

Ideal electron gas at finite temperatures

Probability that a state with energy ε is occupied at temperature T is

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}$$

where μ is the chemical potential and equals ε_F at $T=0$. Nominally it is the value of energy at which the probability of occupation is $1/2$.

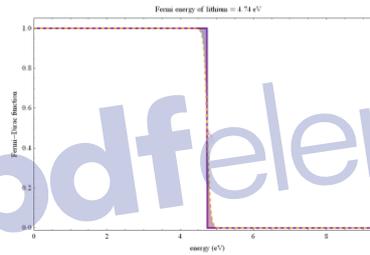


Figure 3: Fermi function at zero temperature and at a finite temperature

The total energy of the electron gas at a finite temperature is:

$$E = 2 \frac{V}{8\pi^3} \int f(\varepsilon) \varepsilon(k) d\mathbf{k}$$

Or the energy density $u = E/V$ is

$$u = \frac{1}{4\pi^3} \int f(\varepsilon) \varepsilon(k) d\mathbf{k}$$

Similarly number density n is:

$$n = \frac{1}{4\pi^3} \int f(\varepsilon) d\mathbf{k}$$

Change the integral form from over k to over energy:

$$\frac{d\mathbf{k}}{4\pi^3} = \frac{1}{4\pi^3} 4\pi k^2 dk = \frac{1}{\pi^2} k^2 dk = \frac{1}{\pi^2} \frac{2m\varepsilon}{\hbar^2} \sqrt{\frac{m}{2\hbar^2}} \frac{d\varepsilon}{\sqrt{\varepsilon}}$$

or

$$n = \frac{1}{4\pi^3} \int f(\varepsilon) d\mathbf{k} = \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon$$

where

$$g(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} = \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

is the density of states, $g(\varepsilon)d\varepsilon = \#$ states per unit volume in the energy interval ε and $d\varepsilon$.

Similarly,

$$u = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon$$

This is a general form independent of any approximations regarding the interaction of the electrons (which enters only through the specific form of $g(\varepsilon)$ used).

The number density in Sommerfeld model is given by:

$$n = \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \sqrt{\varepsilon} f(\varepsilon) d\varepsilon$$

or,

$$n = 2 \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2} \left(\frac{\mu}{k_B T} \right)$$

where $F_{1/2}(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{y^{1/2}}{e^{(y-x)} + 1} dy$ is Fermi integral of order $1/2$ - can be solved exactly only in two extreme limits.

1. $\frac{\mu}{k_B T} \ll 1$ (valid for low-density systems like semiconductors):

$$n = 2 \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} e^{\frac{\mu}{k_B T}}$$

2. $\frac{\mu}{k_B T} \gg 1$ (valid for high-density systems like metals):

$$F_{1/2}(x) \approx \frac{4}{3\sqrt{\pi}} x^{3/2} \left[1 + \frac{\pi^2}{8} \frac{1}{x^2} + \dots \right]$$

$$n = \frac{1}{3\pi^2} \left(\frac{2m\mu}{\hbar^2} \right)^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \text{---(2)}$$

Also, from equation (1) we have

$$n = \frac{1}{3\pi^2} k_F^3 = \frac{1}{3\pi^2} \left(\frac{2m\varepsilon_F}{\hbar^2} \right)^{3/2} \text{----(3)}$$

Combining eqns. 2 and 3 we get,

$$\varepsilon_F = \mu \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right]^{2/3}$$

This gives the expression for μ in terms of ε_F (in the limit $\frac{k_B T}{\mu} \ll 1$):

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right]$$

Even near the melting point of metals, $k_B T / \varepsilon_F \ll 1$, hence for metals at all temperatures $\mu \sim \varepsilon_F$.

The energy density in Sommerfeld mode can be similarly calculated:

$$u = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon = u_0 + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)$$

The specific heat then becomes:

$$c_V = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F) = \frac{\pi^2}{2} \frac{k_B T}{\varepsilon_F} n k_B$$

Compared to classical value $\sim n k_B$ the Sommerfeld electronic contribution is $\sim \frac{k_B T}{\varepsilon_F} \sim 100$ times smaller.

Physically $c_V \sim T$ easy to understand – at any finite temperature the Fermi distribution changes appreciably from its zero temperature value only in a narrow region of width few $k_B T$ around μ . The Fermi edge is smeared out over this narrow energy range by the thermally created electron–hole pairs. The states are neither fully occupied nor completely empty here. At energies that are farther than a few times $k_B T$ from the chemical potential μ , states within the Fermi sphere continue to be completely filled, as if they were frozen in, while states outside the Fermi sphere remain empty. Thus, the majority of the electrons are frozen in states well below the Fermi energy: only electrons in a region of a few times $k_B T$ in width around ε_F – i.e., about a fraction $k_B T / \varepsilon_F$ of all electrons – can be excited thermally, giving finite contributions to the specific heat.

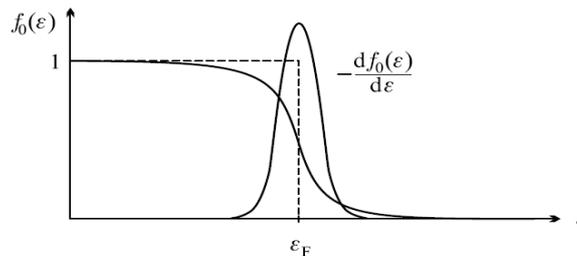


Figure 4: Derivative of Fermi function at a finite temperature

Number of electrons excited at any temperature T is $\propto g(\varepsilon_F) k_B T$. Each of them gains energy $\sim k_B T$. Total energy gain $\sim (k_B T)^2 g(\varepsilon_F)$. So

$$c_V = \frac{\partial u}{\partial T} \sim k_B^2 T g(\varepsilon_F)$$

$c_V \propto T$ is not seen at room temperature, rather the specific heat over any extended temperature range goes as $c_V = \gamma T + AT^3$.

The values of γ measured for Alkali metals match quite well with the experimental values. The difference in the calculated and experimental values can be attributed to an apparent change in the mass of the electrons in response to the periodic potential due to the ions in the crystal. For certain compounds (called *Heavy Fermions*) like CeAl_3 and CeCu_6 γ_{ex} can be hundreds of times larger than γ_{th} – to account for these we need strong e-e interactions.

Other properties of electron gas from Sommerfeld model: τ does not depend on the distribution function – only properties that explicitly depend on v or l will change from the Drude value.

- Thermal conductivity $\kappa = \frac{1}{3} v l C_v$ remains unchanged.
- Thermo power $Q = -\frac{1}{3ne} c_v = -\frac{\pi^2}{6} \left(\frac{k_B}{e}\right) \left(\frac{k_B T}{\epsilon_F}\right) \sim \frac{k_B T}{\epsilon_F} \times 10^{-4} \text{V/K}$ - 100 times smaller than Drude value, closer to measured values of Q .
- Electrical properties remain unchanged.
- Wiedemann-Franz law still remains theoretically valid (experimentally valid only at very low T and at high T).

How can we use quantum statistics in a classical dynamical theory? – Why does Sommerfeld model work?

We can use classical description if uncertainty principle is not violated. For typical electron $p \sim \hbar k_F$ so maximum $\Delta p \sim \hbar k_F$; implying the uncertainty in its position is $\Delta x \sim \frac{\hbar}{\Delta p} \sim \frac{1}{k_F}$ which is of the order of the lattice spacing. If we do not want to probe electron dynamics in the scale of lattice spacings classical description is OK. Conduction electrons are delocalized – need not probe them on atomic scale – mean free path ~ 100 Angstroms. Probing with visible light (wavelength ~ 1000 Angstroms) also poses no problems. Cannot study electron dynamics under X-ray excitation ($\lambda \sim 1$ Angstrom) by using this model.

Kronig–Penney Model - Free-Electron / Quasifree-Electron Approximation: Density of States Function



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1 Free electron and nearly free electron model & concepts leading to Kronig – Penney model

1.1 Free Electron Theory

In 1900, Drude first proposed that the large electrical and thermal conductivity of metals and semiconductors is due to the presence of free electrons. Also Drude and Lorentz jointly explained these properties based on the following assumptions,

1. Free electrons that move through the specimen suffer collisions with the atoms
2. These free electrons are treated as free particles in ideal gas
3. Hence these particles obey Maxwell-Boltzmann statistics

One of the supporting points for the acceptance of this classical free electron theory was that it is in agreement with the Wiedmann-Frantz law, which relates electrical and thermal conductivity.

1.2 Free Electron Model

In this model, a bulk specimen is assumed to be consisting of two parts: one is the fixed positive charges and the other is free electrons which are nothing but the valance electrons. And these electrons are assumed to be free except at the specimen's surface and have the effect of confining them to the interior. Thus, according to this model, the conduction electrons are free to move anywhere in the sample (totally free) except for rare reflection from the surface and resembles much like molecules in ideal gas.

The free electron approximation, which allows the conduction electrons to move freely within the solid material boundary implies that the total energy depends mainly on kinetic energy and not potential energy. This model which is mainly applied for metals considers the specimen to be a box filled with electrons. These electrons are free and the only constraint they experience is that they are in a box.

1.3 Electron gas in one dimensional box

Let the length of the box be L with infinite potential barrier at the distance $x=0$ and $x=L$ and let an electron of mass m be represented by the wave function $\psi(x)$ can be equated as,

$$H\psi = E\psi \quad (1)$$

where H is Hamiltonian and E is total energy (sum of potential and kinetic energy) also it is allowed eigen values (energies) of the electron in the orbital (i.e., here the study is for a

system of single electron and the orbital model is valid only if when there is no interactions between electrons)

As the total energy considered is mainly kinetic equation (1) takes the form

$$H = \frac{P^2}{2m} \quad (2)$$

where P is the momentum and $P = -i\hbar \frac{d}{dx}$ in quantum mechanics, hence,

$$H\psi_n = -\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = E_n\psi_n \quad (3)$$

The expected boundary conditions are $\psi_n(0)=\psi_n(L)=0$, i.e., the electron present inside the box of dimension L. Rewriting Eqn. 3,

$$\frac{d^2\psi_n}{dx^2} = -\frac{2m}{\hbar^2} E_n\psi_n \quad (4)$$

The general solution of Eqn.4 is,

$$\psi_n(x) = Ae^{ikx} + Be^{-ikx} \quad (5)$$

where $k^2 = \frac{2m}{\hbar^2} E_n$ (6)

We get A=-B by substituting the first boundary condition $\psi_n(0)=0$ and this shows that the wave function takes the sine like shape.

Applying the second boundary condition $\psi(L)=0$,

we get, $\text{SinkL}=0 \implies k=n\pi/L$; with $n=1,2,3,\dots$

On substituting in Eqn. 6, $E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2$ (7)

And their wave function representation is,

$$\psi_n = A \sin\left(\frac{n\pi x}{L}\right) \quad (8)$$

1.4 Inferences

1. Hence the wave function exists only for integral values of n , ultimately n is the quantum number.
2. From Eqn.7 the energy consists of discrete value with their spacing depends on the terms $\left(\frac{n^2}{L^2}\right)$, the energy levels are closer when L is large.
3. The value of the constant A in Eqn.8 is determined by considering the normalization condition (i.e. the electron exists somewhere within the box) and their probability is maximum, 1. Hence,

$$\int_0^L \psi_n^*(x)\psi_n(x)dx = 1$$

$$\int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) = 1 \Rightarrow A^2 = \frac{2}{L} \text{ or } A = \sqrt{\frac{2}{L}}$$

$$\text{So the existing wave function is } \psi_n(x) = \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right)$$

4. Suppose if the box has to accommodate N number of electrons, the placing of electrons in the allowed energy levels is done by following Pauli's exclusion principle. Hence each quantum level with quantum number n obeying Pauli's principle can accommodate two electrons; one with spin up and another with spin down.

Considering even number of electrons N , these electrons are filled sequentially from the bottom most level ($n=1$) to the top most energy level (n_f), with

$$2n_f = N$$

The upper most energy is nothing but the Fermi energy at 0K, which can be obtained from Eqn. 7 with $n=n_f$,

$$E_f = \frac{\hbar^2}{2m} \left(\frac{n_f \pi}{L}\right)^2 = \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L}\right)^2$$

Now the total energy E_o is obtained by individually summing the energies E_n between $n=1$ and $n_f = N/2$. (Where 2 is introduced due to spin degeneracy)

$$\text{Therefore, } E_o = \sum_{n=1}^{N/2} E_n = \frac{2\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \sum_{n=1}^{N/2} n^2$$

On simplification, we get,

$$E_o \cong \frac{1}{3} N E_f$$

1.5 Conclusion

Free electron model helps in better understanding of several key parameters of metals like heat capacity, thermal conductivity, electrical conductivity, magnetic susceptibility and electrostatics.

However, it fails to explain the positive values of Hall coefficient observed, fails to differentiate insulator, semiconductor and conductor materials. It also fails to relate conduction electron in metals to the valence electron of free atoms and cannot explain transport properties like magnetoresistance.

1.6 Nearly Free Electron Model

The concept of energy bands was introduced to have a better understanding of metals and crystals. Every solid has electrons. However, to understand the difference in the behavior of these electrons in insulators and conductors, we have to take into account, the presence of lattice in the specimen. Hence the electrons from now are not totally free instead they are nearly free since the presence of lattice (ions) has its own influence (though weak).

Following the free electron model, the allowed energy values when the form extends in 3 dimension takes,

$$E_k = \frac{\hbar^2}{2m} (K_x^2 + K_y^2 + K_z^2)$$

Over a cube of side L, where $K_x, K_y, K_z = \pm n\pi/L$; $n=0,2,4,\dots$

According to nearly free electron model, electrons present in a specimen are slightly perturbed by the weak periodic potential produced by the lattice. Qualitative analysis about the metals and crystals can be done by studying their band structures.

Energy gaps are caused when electrons' undergo Bragg's reflection. In these gaps Schrodinger equation which depicts the wave like nature of electron does not exist. These energy gaps detected plays a vital role in discriminating / identifying a solid as an insulator or a conductor. The energy of the electron based on free electron and nearly free electron model are shown in Fig. 1a. and Fig. 1b respectively.

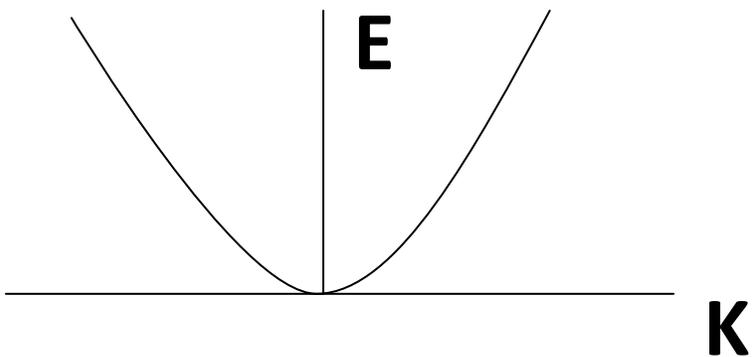


Fig. 1a. Energy curve of a free electron.

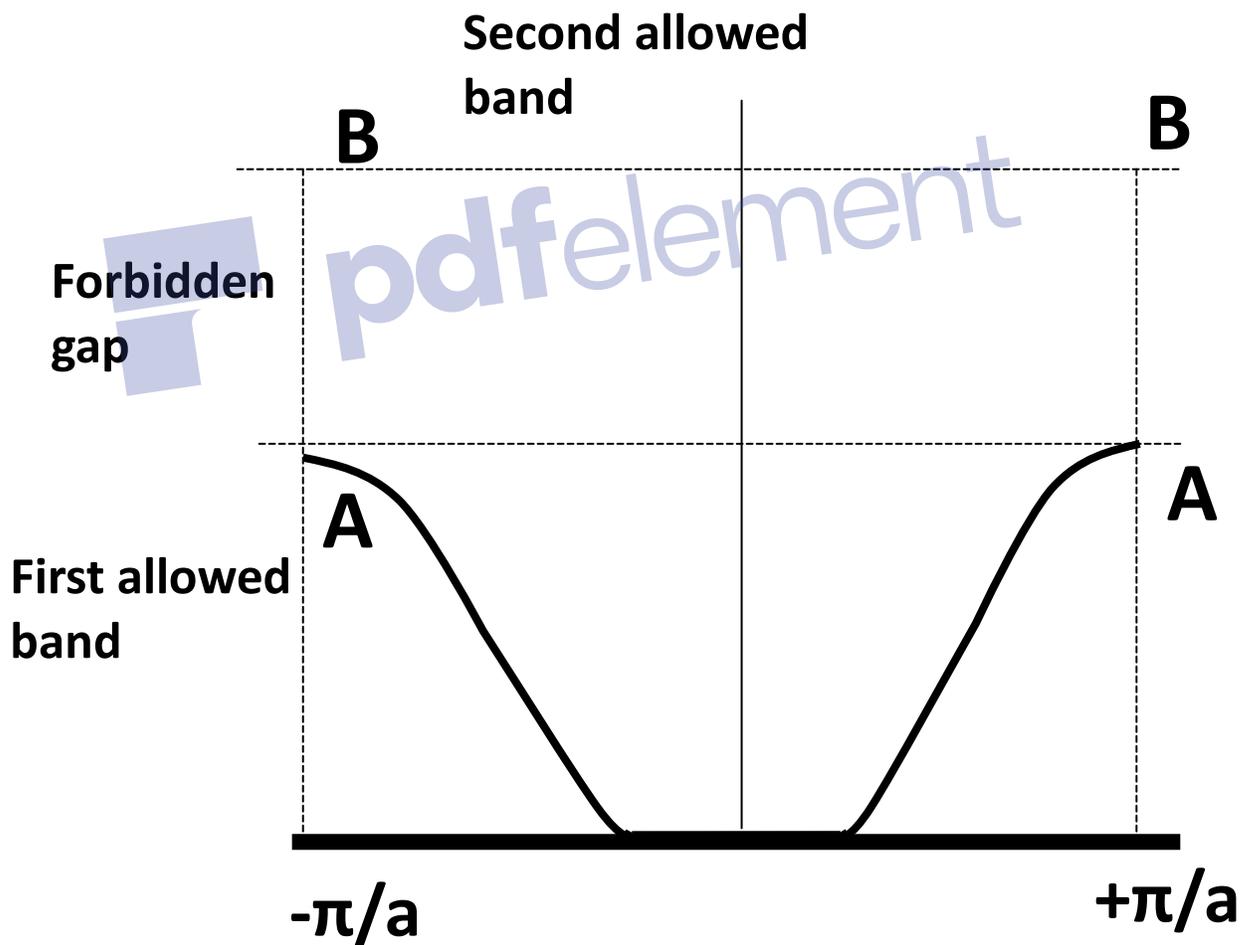


Fig. 1b. Energy curve of an electron in a monoatomic linear lattice; a – lattice constant. i.e., Γ reflection at $\pm \pi/a$

The Fig. 1b shows an energy gap at $k=\pm\pi/a$, where Bragg's first reflection is observed. As per Bragg's concept other gaps occur for integer values of n . The reason for the occurrence of reflection at $k=\pm\pi/a$ is because the reflected wave from one atom in the linear lattice interferes constructively with a phase difference of 2π .

1.7 Reason for energy gap formation

The wave function at the point $k=\pm\pi/a$ do not have traveling waves instead standing waves. The standing waves are formed when wave is Bragg reflected; its direction of travel is opposite to its incident direction and subsequent reflection reverses the direction again there by producing standing waves since the wave by itself should be time independent. The two different forms of standing waves in terms of traveling waves $e^{i\pi x/a}$ and $e^{-i\pi x/a}$ are,

$$\psi(+)=e^{i\pi x/a}+e^{-i\pi x/a}=2\text{Cos}\left(\frac{\pi x}{a}\right) \quad (\text{real part})$$

$$\psi(-)=e^{i\pi x/a}-e^{-i\pi x/a}=2i\text{Sin}\left(\frac{\pi x}{a}\right) \quad (\text{imaginary part})$$

These two different standing waves $\psi(+)$ and $\psi(-)$ group electron at different region with different potential energy. This gives raise to the formation of forbidden energy gap.

1.8 Concepts leading to Kronig–Penney Model

The fundamental nature of insulators, conductors and semiconductors can be functionally explained based on band theory. The recent development in semiconductor physics, the semiconductor hetero-structures are also analyzed using the concept of band theory.

Another notable theory, the free-electron theory, can help in understanding the electron movement in metals. It assumes that, the valence electron in a metal absorbs thermal energy which ultimately is converted into kinetic energy with an average of $(3/2)K_B T$ based on law of equipartition of energy. But the calculated molar electronic specific heat does not match with the experimental value.

Hence it can be concluded that the equipartition law and the classical Maxwell-Boltzmann statistics are not adequate for evaluating electronic specific heat in metals. Another failure of classical free electron theory is that, it does not account for the magnetic moment of electron due to its spin.

The free-electron theory, which neglects the magnetic moment of electrons arising from their spin predicts that, paramagnetic susceptibility is proportional to the temperature for each electron. On the contrary, the experimental results show that the susceptibility is almost independent (constant) of temperature.

The reason is, the classical theory allows all the free electrons to gain energy which does not actually happen in reality, which leads to drastic difference between the calculated and the observe values.

At this juncture, the quantum free-electron theory steps in, assumes that an electron in a metal experiences a constant or zero potential and hence is free to move within the lattice.

The quantum free-electron theory thus successfully explains the specific heat, electrical conductivity, thermionic emission, thermal conductivity and para magnetism of materials. However, the concept fails to differentiate the conductivities in conductors, semiconductors and insulators.

In a real crystal, electrons move in a regularly arranged lattice of positive ions. The electrons have the zero potential at the positive ion site and possess maximum value at the intermediate lattice points.

This could be schematically represented as shown in Fig. 2(sine wave notation). The observed potential is periodical as the lattice planes. Bloch has the solution as $\psi(x) = U_k(x)e^{ikx}$ for the Schrödinger equation, which describes the electron motion:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0 \quad (9)$$

where, ψ is the wave function and $U_k(x)$ in the Bloch's solution, which has the periodicity of the lattice.

Hence, the wave function includes both a plane wave e^{ikx} which is modulated by the periodic function $U_k(x)$ and the state of motion of electron, which is represented by the wave vector k . However, it is difficult (not tractable) to solve the Schrödinger's equation with the sinusoidal periodicity. Therefore, Kronig and Penney suggested a simpler model, where the inner potential of the crystal system has the rectangular shaped potential.

Thus, in the Kronig Penney model, instead of experiencing a gradual variation in the strength of the potential electrons experience a maximum potential (potential well) and minimum value (potential barrier) in the presence of the lattice planes.

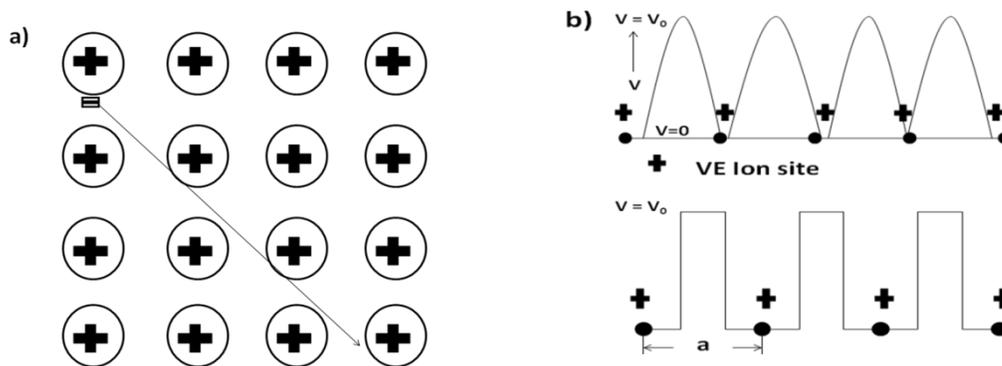


Fig. 2. One dimensional periodic potential distribution for a crystal

2 ELECTRON IN A PERIODIC FIELD OF A CRYSTAL (THE KRONIG - PENNEY MODEL)

For the treatment of our problem, a periodic repetition of the potential well of Fig.3, i.e., a periodic arrangement of potential wells and potential barriers, is most probably very close to reality and is also best suited for the calculation. Such a periodic potential is shown in Fig. 3 for the one-dimensional case.

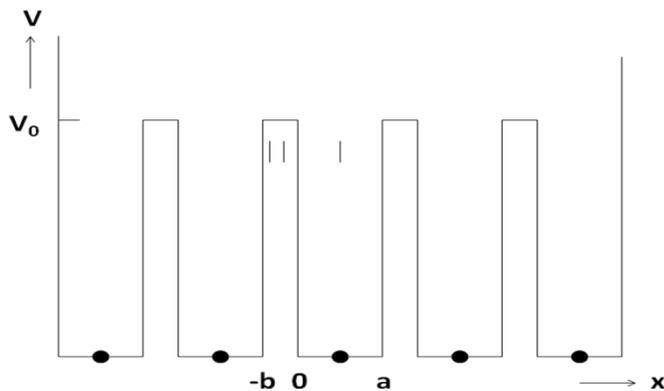


Fig. 3. Ideal periodic square well potential used by Kronig and Penney.

Although this model is highly artificial, yet it illustrates many of the characteristic features of the behaviour of electrons in a periodic lattice. The wave functions associated with this model can

be calculated by solving Schrodinger equations for the two regions I and II. The time-independent Schrodinger equation takes the following forms for the two regions

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2} E\Psi = 0; \text{ for } 0 < x < a \quad (10)$$

And

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V_0) = 0; \text{ for } -b < x < 0 \quad (11)$$

Making use of Bloch's theorem, the solution can be written in the form

$$\Psi(x) = u_K(x) e^{iKx} \quad (12)$$

Assuming that the total energy E of the electron is less than the potential energy V_0 , we define two real quantities α and β such that

$$\alpha^2 = \frac{8\pi^2mE}{h^2} \quad (13)$$

$$\text{and } \beta^2 = \left(\frac{8\pi^2m}{h^2} (V_0 - E) \right) \quad (14)$$

Thus

$$\frac{d^2\Psi}{dx^2} + \alpha^2 \Psi = 0; \text{ for } 0 < x < a \quad (15)$$

$$\frac{d^2\Psi}{dx^2} - \beta^2 \Psi = 0; \text{ for } -b < x < 0 \quad (16)$$

The solution that will be appropriate for both the regions suggested by Bloch is of the form

$$\Psi(x) = u_K(x) e^{iKx} \quad (17)$$

On differentiating this equation, one gets

$$\frac{d\Psi}{dx} = e^{ikx} \frac{du_K}{dx} + u_K iK e^{ikx}$$

$$\text{and } \frac{d^2\Psi}{dx^2} = e^{ikx} \frac{d^2u_K}{dx^2} + iK e^{ikx} \frac{du_K}{dx} + iK e^{ikx} \frac{du_K}{dx} - K^2 e^{ikx} u_K$$

$$\text{i.e., } \frac{d^2\Psi}{dx^2} = -K^2 e^{ikx} u_K + 2iK e^{ikx} \frac{du_K}{dx} + e^{ikx} \frac{d^2u_K}{dx^2}$$

Substituting these values, we get

$$\frac{d^2u_1}{dx^2} + 2iK \frac{du_1}{dx} + (\alpha^2 - K^2)u_1 = 0; \quad \text{for } 0 < x < a \quad (18)$$

$$\text{and } \frac{d^2u_2}{dx^2} + 2iK \frac{du_2}{dx} - (\beta^2 + K^2)u_2 = 0; \quad \text{for } -b < x < 0 \quad (19)$$

where u_1 represents the value of $u_K(x)$ in the interval $0 < x < a$ and u_2 the value of $u_K(x)$ in the interval $-b < x < 0$.

The solution of the differential Eqn. (18) is of the form

$$u_1 = e^{mx}$$

$$\frac{du_1}{dx} = m e^{mx} \quad \text{and} \quad \frac{d^2u_1}{dx^2} = m^2 e^{mx}$$

Substituting these values in Eqn. (18), we get

$$m^2 e^{mx} + 2iK e^{mx} + (\alpha^2 - K^2) e^{mx} = 0$$

$$m^2 + 2iKm + (\alpha^2 - K^2) = 0$$

$$m = \frac{-2iK \pm \sqrt{(-4K^2) - 4((\alpha^2 - K^2))}}{2}$$

$$m = -iK \pm i\alpha$$

$$\text{i.e., } m_1 = -iK + i\alpha = i(\alpha - K)$$

and $m_2 = -iK - i\alpha = -i(\alpha + K)$

Thus the general solution is

$$\begin{aligned} u_1 &= A e^{m_1 x} + B e^{m_2 x} \\ u_1 &= A e^{i(\alpha-K)x} + B e^{-i(\alpha+K)x} \quad (20) \end{aligned}$$

Where A and B are constants.

Similarly Eqn. (19) can be written as

$$m^2 + 2iKm - (\beta^2 + K^2) = 0$$

$$m = \frac{-2iK \pm \sqrt{-4K^2 + 4(\beta^2 + K^2)}}{2}$$

$$m = -iK \pm i\beta$$

i.e., $m_1 = -iK + \beta = (\beta - iK)$

and $m_2 = -iK - \beta = -(\beta + iK)$

Thus

$$u_2 = C e^{m_1 x} + D e^{m_2 x}$$

$$u_2 = C e^{(\beta-iK)x} + D e^{-(\beta+iK)x} \quad (21)$$

Where C and D are constants. The values of the constants A, B, C and D can be obtained by applying the boundary conditions.

$$[[u]_1(x)]_{x=0} = [[u]_2(x)]_{x=0} ; \quad \left[\frac{du_1(x)}{dx} \right]_{x=0} = \left[\frac{du_2(x)}{dx} \right]_{x=0}$$

$$\text{and } [[u]_1(x)]_{x=a} = [[u]_2(x)]_{x=-b} ; \quad \left[\frac{du_1(x)}{dx} \right]_{x=a} = \left[\frac{du_2(x)}{dx} \right]_{x=-b}$$

Applying these conditions, we get

$$(i) \quad (A + B) = (C + D) \quad (22)$$

$$(ii) \quad [Ai(\alpha - K)e^{i(\alpha-K)x} - Bi(\alpha + K)e^{-i(\alpha+K)x}]_{x=0}$$

$$= \left[C(\beta - iK)e^{(\beta - iK)x} - D(\beta + iK)e^{-(\beta + iK)x} \right]_{x=0}$$

$$\text{i.e.,} \quad i(\alpha - K)A - i(\alpha + K)B = (\beta - iK)C - (\beta + iK)D \quad (23)$$

$$\text{(iii)} \quad A e^{i(\alpha - K)a} + B e^{-i(\alpha + K)a} = C e^{-(\beta - iK)b} + D e^{(\beta + iK)b} \quad (24)$$

$$\text{(iv)} \quad [Ai(\alpha - K)e^{i(\alpha - K)x} - Bi(\alpha + K)e^{-i(\alpha + K)x}]_{x=a}$$

$$= \left[C(\beta - iK)e^{(\beta - iK)x} - D(\beta + iK)e^{-(\beta + iK)x} \right]_{x=-b}$$

$$\text{i.e.,} \quad Ai(\alpha - K)e^{i(\alpha - K)a} - Bi(\alpha + K)e^{-i(\alpha + K)a}$$

$$= C(\beta - iK)e^{-(\beta - iK)b} - D(\beta + iK)e^{-(\beta + iK)b} \quad (25)$$

Eqn. 22,23,24 and 25 will have non- vanishing solutions if and only if the determinant of the coefficients A, B,C and D vanishes. This requires that

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - K) & -i(\alpha - K) & (\beta - iK) & -(\beta - iK) \\ e^{i(\alpha - K)a} & e^{-i(\alpha + K)a} & e^{-(\beta - iK)b} & e^{(\beta + iK)b} \\ i(\alpha - K) e^{i(\alpha - K)a} & -i(\alpha - K) e^{-i(\alpha + K)a} & (\beta - iK) e^{-b(\beta - iK)b} & -(\beta - iK) e^{(\beta + iK)b} \end{vmatrix} = 0$$

Thus the solution of the determinant (Eqn. 25) is

$$\frac{(\beta^2 - \alpha^2)}{2\alpha\beta} \sin \alpha a \sin \beta b \cos \alpha a = \cos K(\alpha + b) \quad (26)$$

Eqn. (26) is complicated but a simplification is possible. Kronig and Penney considered the possibility that V_{0b} remains finite. Such a function is called delta function. Under these circumstances, $\sin \beta b \rightarrow \beta b$ and $\cos \beta b \rightarrow 1$ as $b \rightarrow 0$.

Hence Eqn. (26) becomes

$$\frac{(\beta^2 - \alpha^2)}{2\alpha\beta} \beta b \sin \alpha a + \cos \alpha a = \cos K a$$

$$(\beta^2 - \alpha^2) = \frac{8\pi^2 m}{h^2} (V_0 - E) - \frac{8\pi^2 m}{h^2} E = \left(\frac{8\pi^2 m}{h^2} \right) [V_0 - 2E]$$

Since $V_0 \gg E$,

$$\beta^2 - \alpha^2 = \frac{8\pi^2 m}{h^2} (V_0)$$

Substituting this in the above equation, we get

$$\left(\frac{8\pi^2 m V_0}{2\alpha\beta h^2} \right) \beta b \sin \alpha a + \cos \alpha a = \cos K a$$

$$P = \frac{m V_0 a b}{h^2}$$

Where

$$\left(\frac{m V_0 a b}{h^2} \right) \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos K a$$

$$\text{ie., } \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos K a \quad (27)$$

The term $V_0 b$ is called the barrier *strength*. The term $P = \frac{m V_0 a b}{h^2}$ in Eqn. (27) is sometimes referred as the *scattering power* of the potential barrier. It is a measure of the strength with which electrons in a crystal are attracted to the ions on the crystal lattice sites. Also

$$\alpha^2 = \frac{8\pi^2 m E}{h^2}, \text{ or } E = \frac{\alpha^2 h^2}{8\pi^2 m}$$

$$\text{and } K = \frac{2\pi}{\lambda} \quad (28)$$

Eqn. (27) is a condition of the existence of a solution for the electron wave function.

There are only two variables in Eqn. (27), namely α and K . The right hand side of Eqn. (27) is bounded since it can only assume values between +1 and -1. If we plot the left-hand side of this equation against αa , it will be possible to determine those value of α (and hence

energy) which are permissible; that is, permit $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ to take values between +1 and -1. This has been plotted in Fig.4.

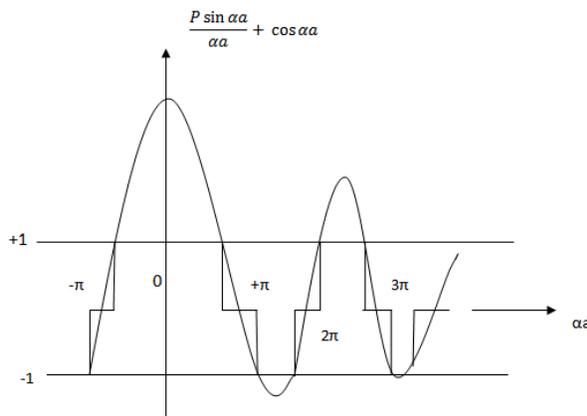


Fig. 4. Plot of $\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka$ with $P = 3\pi/2$.

3. Quasifree-Electron Approximation: Density of States Function

3.1 Inferences

1. The permissible limit of the term $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ lies between +1 to -1. By varying αa , a wave mechanical nature could be plotted as shown in Fig. 5, the shaded portion of the wave shows the bands of allowed energy with the forbidden region as unshaded portion.

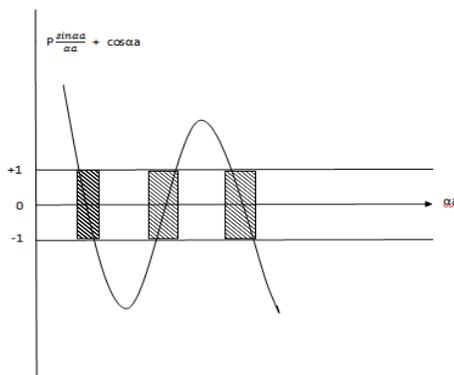


Fig. 5. Left hand side of Eqn. 28

2. With increase of αa , the allowed energy states for a electron increases there by increasing the band width of the bands, i.e., the strength of the potential barrier diminishes. This also leads to increase of the distance between electrons and the total energy possessed by the individual electron.

3. Conversely if suppose the effect of potential barrier dominate i.e., if P is large, the resultant wave obtained in terms of $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ shows a stepper variation in the region lies between $+1$ to -1 . This results in the decrease of allowed energy and increase of forbidden energy gap. Thus at extremities,

Case (i) when $P \rightarrow \infty$, the allowed energy states are compressed to a line spectrum. (Fig. 6b)

Case (ii) when $P \rightarrow 0$ the energy band is broadened and it is quasi continuous. (Fig. 6c)

3.2 Energy Spectrum

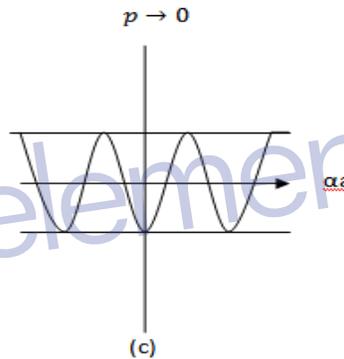
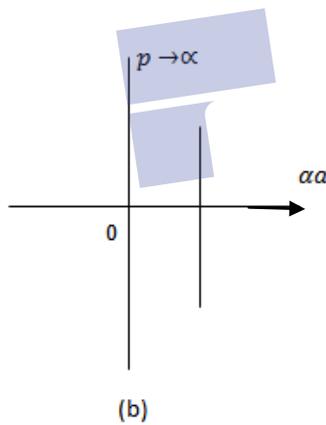


Fig. 6b. Line spectrum of energy bands

6c. Quasi state spectrum

Case (i): At one of the extremities, $p \rightarrow \infty$

$$\sin \alpha a = 0; \text{ or } \alpha a = \pm n \pi \Rightarrow \alpha^2 = \frac{n^2 \pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

on rearranging,

$$E = \frac{n^2 \pi^2 \hbar^2}{a^2 2m} = \frac{n^2 \pi^2 \hbar^2}{a^2 2m (2\pi)^2} = \frac{n^2 \hbar^2}{8ma^2} \quad (29)$$

Here the energy depends on the width of the potential rather than any other parameter. The energy level of electron in the crystal lattice is discrete and is similar to the particle in a potential box with an atomic dimensions. This is because with a large value of potential strength barrier the tunneling effect is explicitly improbable.

Case (ii): When $p \rightarrow 0$, with the same equation $\cos \alpha a = \cos ka \Rightarrow \alpha = k$

Substituting the values $k^2 = \alpha^2 = \frac{2mE}{\hbar^2}$ on rearranging,

$$E = \left(\frac{\hbar^2}{2m} \right) k^2 \quad (30)$$

$$= \frac{\hbar^2}{8\pi^2 m} \left(\frac{2\pi}{\lambda} \right)^2 = \frac{\hbar^2}{2m\lambda^2}$$

λ here refers to the wave nature of the electron and is equated as de Broglie's wavelength

$$E = \frac{\hbar^2}{2m} \frac{P^2}{\hbar^2} = \frac{P^2}{2m} \quad (31)$$

$$= \frac{m^2 v^2}{2m} = \frac{1}{2} m v^2$$

The energy obtained above corresponds to the energy of the completely free particles and is depicted in Fig. 7.

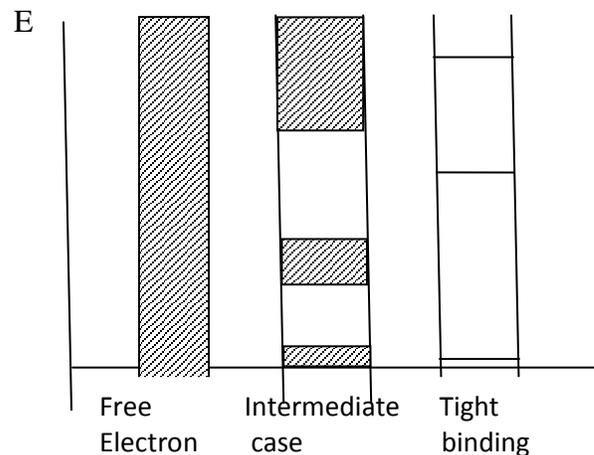


Fig. 7. Energy level structure for differentiating degrees of binding.

Thus using this model a system can be analyzed from the free state condition to the extremely bounded condition.

3.3 Number of Possible Wave Functions in a Band

Let us consider a one-dimensional crystal of N lattices. The length L of the lattice is $N(a+b)$. Imposing the periodic boundary conditions for obtaining the running wave picture of the de Broglie wave, we find that the wave function must be periodic in 'L'. That is

$$\Psi(x) = \Psi(x + L)$$

The wave function in one dimensional periodic potential lattice is given by

$$\Psi(x) = u_k(x)e^{ikx} \text{ and}$$

$$\Psi(x + L) = u_k(x + L)e^{ik(x+L)}$$

Imposing the periodic boundary conditions, we get

$$u_k(x)e^{ikx} = u_k(x + L)e^{ik(x+L)} \quad (32)$$

We have already seen that the modulating function $u_k(x)$ has the periodicity of the lattice.

$$\text{i.e.,} \quad u_k(x) = u_k(x + a) = u_k(x + 2a) = \dots u_k(x + Na)$$

Where Na is the length 'L' of the crystal. Substituting this in Eqn. (32), we get

$$e^{ikx} = e^{ikx} e^{ikL}$$

$$e^{ikL} = 1$$

$$\text{or} \quad K = \frac{2\pi n}{L} \quad (33)$$

$$\text{with} \quad n = \pm 1, \pm 2, \pm 3, \dots$$

$$\text{Now} \quad n = \frac{KL}{2\pi}$$

Thus the number of possible wave functions in the interval dK is

$$dn = \left(\frac{L}{2\pi} \right)$$

Hence total number of possible states in a band is

$$n = \int dn = \frac{L}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dK$$

$$n = \frac{L}{2\pi \left[K \right]_{-\frac{\pi}{a}}^{\frac{\pi}{a}}} = \frac{L}{a}$$

i.e., $na = L$ (34)

with $b \rightarrow 0$, $a+b \cong a$. Also length of the crystal $L = N(a+b) = Na$. Comparing this with Eqn.6, we get $n = N$, where N is the number of unit cells. Thus the total number of possible states in a band is the number of unit cells. Taking into account the spin of the electron and Pauli's exclusion principle, each state can be occupied at most by two electrons, and hence the total number of electrons in a band is $2N$.

3.4 Density of states

Density of states for electron is nothing but the number of available energy states for the electron to occupy. Knowledge about this helps us to understand the electronic transport phenomena. Let it be denoted as $D(E)$ and this is dealt with in the energy range of E and $E+dE$ with the representation as $D(E)dE$.

The expression for density states of free electrons for in metals and in crystals are the same except the considered mass in metals has been replaced by effective mass in crystals.

The density of states in one dimension is given by the equation

$$n(E) = \frac{2}{\pi} \frac{dk}{dE} \quad (35)$$

But the dispersion relation given by Kronig Penny is,

$$\frac{P \sin \alpha L}{\alpha L} + \cos \alpha L = \cos kL \quad (36)$$

With the aid of this equation, the density of state equation becomes,

$$n(E) = \frac{(2m)^{1/2} \left[P \left(\frac{\sin \alpha L}{(\alpha L)^2} - \frac{\cos \alpha L}{\alpha L} \right) + \sin \alpha L \right]}{\pi \hbar \sqrt{E} \left[1 - \left(\frac{P \sin \alpha L}{\alpha L} + \cos \alpha L \right)^2 \right]^{1/2}} \quad (37)$$

The effective masses m_e of electron in the range $k=n\pi/L$ are defined as,

$$\frac{1}{m_e} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \left(\frac{n\pi}{L} \right); \quad n=0,1,2,\dots \quad (38)$$

then with the dispersion equation the effective mass could be rewritten as

$$m_e = \beta m_o$$

where, $\beta = \frac{1}{L} \left(\frac{\hbar^2}{2mE} \right)^{1/2} \left[P \left(\frac{\sin \alpha L}{(\alpha L)^2} - \frac{\cos \alpha L}{\alpha L} \right) + \sin \alpha L \right] x (\cos \alpha L)^{-1}$

where, $k= n\pi/L$ and E is the energy at the lower edge of the upper band at $k= n\pi/L$.

4 References

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Part III

Concept of Brillouin zones

The electron moving in a periodic potential lattice can have energy values only between allowed regions or zones. From Kronig-Penney model, we arrive at the solution of the electron wave function as

$$\left(\frac{mV_0ab}{\hbar^2}\right) \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka$$

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka \dots \dots (1)$$

Where $P = \frac{mV_0ab}{\hbar^2}$ is called as the scattering power of the potential barrier. It is a measure of the strength with which electrons in a crystal are attracted to the ions on the crystal lattice sites.

Also

$$\alpha^2 = \frac{8\pi^2mE}{h^2} \text{ or } E = \frac{\alpha^2 h^2}{8\pi^2m}$$

And $K = \frac{2\pi}{\lambda}$

We can plot the total energy E of the electron versus the wave number or the propagation vector K as shown in figure 1.

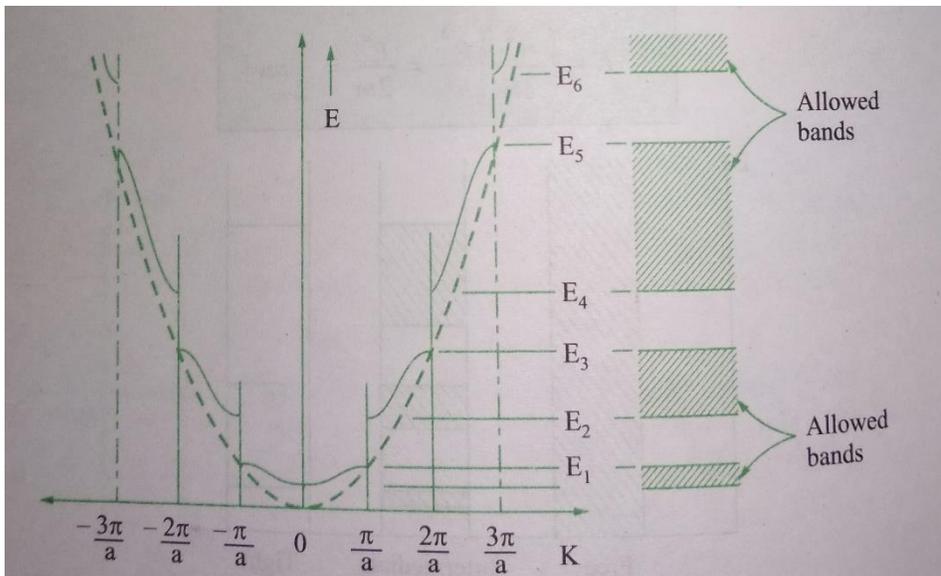


Figure 1. The relation between energy and wave number of a one dimensional lattice

The RHS of equation (1) becomes ± 1 for values of $K = \frac{n\pi}{a}$ and hence the discontinuities in the E versus K graph occur at $K = \frac{n\pi}{a}$, where n takes the values of $\pm 1, \pm 2, \pm 3, \dots$ etc. the dotted curve shows the free electron parabola. From the graph we see that the electron has allowed energy

values in the region extending from $K = -\frac{\pi}{a}$ to $K = +\frac{\pi}{a}$. The zone is called the first Brillouin zone. After a break in the energy values called the forbidden region or band or zone, we get another allowed zone of energy values in the region extending from $K = -\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and $K = +\frac{\pi}{a}$ to $+\frac{2\pi}{a}$. This zone is called the second Brillouin zone. Similarly the other higher order Brillouin zones can be defined.

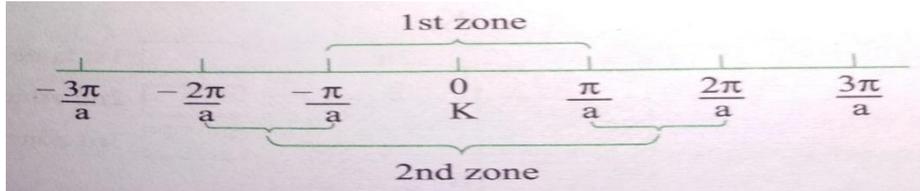


Figure 2. The first two Brillouin zones for one-dimensional case.

Brillouin zones in two Dimensions

The motion of the electron in two dimensions can be discussed using a wave number K , which is measured in the direction of propagation of the wave. The wave number K can be analyzed into components along the x and y axes, which are respectively, K_x and K_y

The first Brillouin zone is sketched in fig (3), the value of $\pm \frac{\pi}{a}$ represent the limits of the zone along K_x . Similarly along the K_y axis the value of $\pm \frac{\pi}{a}$ also represent the limits of the zone. In general, the condition for any energy discontinuity is

$$K = \pm \frac{n\pi}{a}$$

So in two dimensions the condition reads

$$K_x n_1 + K_y n_2 = \frac{\pi}{a} (n_1^2 + n_2^2)$$

Where, n_1 and n_2 are integers corresponding to the single integer n and referring to each of the axes. To sketch the first zone n_1 and n_2 are made equal to ± 1 , or 0. The equations of the lines bordering the first zone are therefore

$$n_1 = \pm 1, n_2 = 0, \text{ giving } K_x = \pm \frac{\pi}{a}$$

$$n_1 = 0, n_2 = \pm 1, \text{ giving } K_y = \pm \frac{\pi}{a}$$

Thus a square passing through the points A, B, C and D gives the first Brillouin zone.

The second Brillouin zone should obviously pass through the points E, F, G and H. The complete picture of the second zone is obtained by taking n_1 and n_2 as the next integers in the series above those used for the first zone. These are $n_1 \pm 1$ and $n_2 \pm 1$. The equations giving the boundaries of the second zone are

$$n_1 = +1, n_2 = +1, \text{ giving } K_x + K_y = \frac{2\pi}{a}$$

$$n_1 = -1, n_2 = +1, \text{ giving } -K_x + K_y = \frac{2\pi}{a}$$

$$n_1 = +1, n_2 = -1, \text{ giving } K_x - K_y = \frac{2\pi}{a}$$

$$n_1 = -1, n_2 = -1, \text{ giving } -K_x - K_y = \frac{2\pi}{a}$$

The above four equations describe a set of lines at 45° to the K_x and K_y axes passing through E, F, G and H. the second Brillouin zone is thus the region between the squares ABCD and EFGH. The third Brillouin zone is obtained giving n_1 and n_2 values of $0, \pm 1$ and ± 2 .

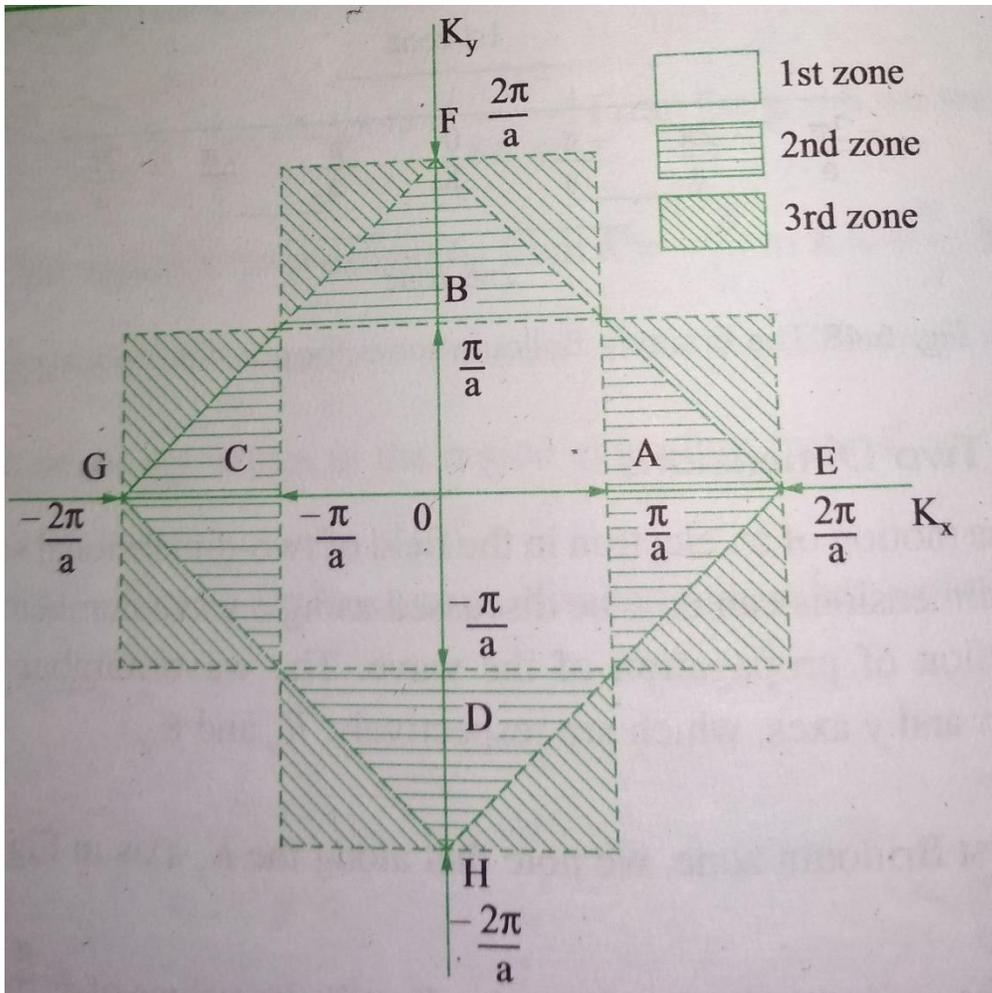


Figure 3. The first three Brillouin zones for a two-dimensional square lattice.

Brillouin zones in three dimensions

The equation used to describe the zones in three dimensions is given by

$$K_x n_1 + K_y n_2 + K_z n_3 = \frac{\pi}{a} (n_1^2 + n_2^2 + n_3^2)$$

The first zone for a simple cubic lattice is clearly a cube intersecting the K_x , K_y and K_z axes at the points $\frac{\pi}{a}$. Just as in the triangular form of the second zone in two dimensions, the second zone in three dimensions is obtained by adding a pyramid to each face to the first zone cube.

Brillouin Zones and the Origin of Bands

In this class we will plot the reciprocal lattice information as well as the wave vector information on the same plot and examine the interaction between them in a pictorial manner.

We have noted that while the E Vs k relationship is the same for free electrons, nearly free electrons, as well as the bound electrons, it is a continuous curve only for free electrons. For nearly free electrons as well as bound electrons, confinement of the electron results in only specific values of k to be permitted, and therefore only the corresponding values of energy to be permitted. The resulting plot has discrete points that are laid out in the form of the parabola consistent with

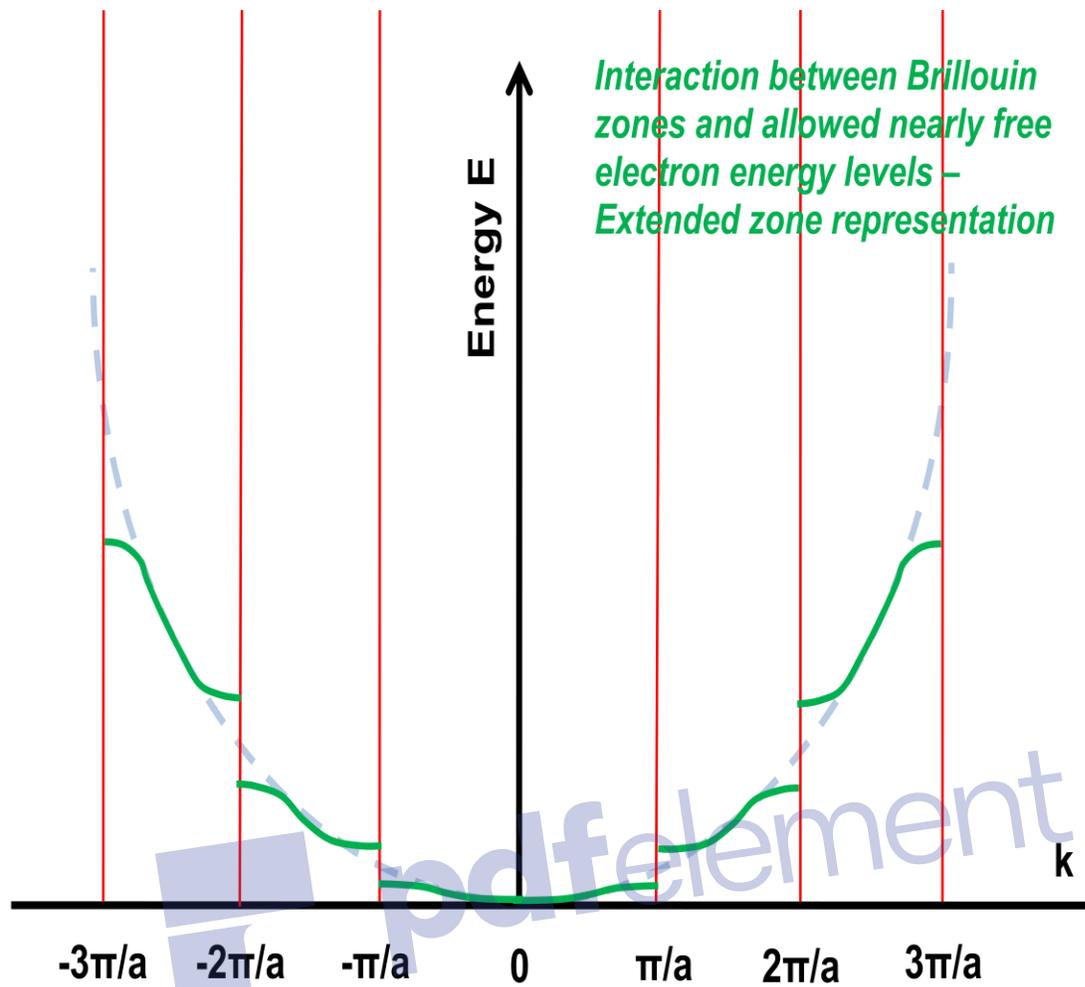
$$E = \frac{\hbar^2 k^2}{2m}$$

We wish to plot the periodicity of the lattice as well as the wave vectors on the same plot. The reciprocal space differs from k space only in the scaling factor 2π . Therefore reciprocal lattice information is multiplied by 2π to enable it to be plotted in k space. Therefore real lattice vector 'a' which is plotted in reciprocal space as $\frac{1}{a}$, is now plotted in k space as $\frac{2\pi}{a}$. We note that a , which is of the order of inter-atomic spacing, is of the order of 10^{-10} m, while L , the extent of confinement of the nearly free electrons, is of the order of meters. Therefore the reciprocal lattice points, plotted in k space as $\frac{2n\pi}{a}$, where n is an integer, can contain 10^{10} allowed wave vectors of nearly free electrons which are of the form $\frac{n\pi}{L}$ between two adjacent reciprocal lattice points. This is the reason that allowed wave vector plots drawn on the scale of the order of $\frac{2n\pi}{a}$, will look continuous even though they contain discrete points spaced $\frac{\pi}{L}$ apart.

We have noted that diffraction occurs when one end of a wave vector touches a Bragg plane. In the context of nearly free electrons, diffraction causes the E Vs k relationship to distort in the vicinity of the Bragg planes (or Brillouin zone boundaries). This distortion causes some of the energy levels to become forbidden to the nearly free electrons – which results in the presence of band gaps in the material.

In this class we will present this interaction between wave vectors and the Brillouin zones pictorially and not focus on the exact values of the band gaps that result. We will look at examples of one dimensional, two dimensional, and three dimensional lattices and the interaction of wave vectors with the Brillouin zones corresponding to these lattices in k space. In the next class we will examine the formation of band gaps in a mathematical manner.

Since a one dimensional real lattice of spacing 'a' is plotted in k space as $\frac{2\pi}{a}$, the Brillouin zone boundaries occur in intervals of $\frac{\pi}{a}$, i.e. at $\frac{\pi}{a}$, $\frac{2\pi}{a}$, $\frac{3\pi}{a}$ etc. The Figure 32.1 below shows the interaction of the E Vs k relationship of nearly free electrons with the Brillouin zone boundaries of a one dimensional lattice of spacing a



- E Vs k of nearly free electrons, without accounting for the Brillouin Zones
- E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones
- Brillouin zone boundaries

Figure 1 Interaction of the E Vs k relationship of nearly free electrons with the Brillouin zone boundaries of a one dimensional lattice of spacing a

The distortion of the E Vs k relationship at the Brillouin zone boundaries and the resulting energy gaps, can be described as follows: the travelling waves of nearly free electrons undergo diffraction at the Brillouin boundaries and result in standing waves – as a result energy gaps appear.

The above form of representing the interaction between the allowed energy values and the Brillouin zones of the material is called the ‘Extended zone’ representation, since the information is presented spread across several lattice points, but has a single origin.

The band gaps described here, and the remaining allowed energy levels, are in concept the same as the band gaps and the allowed bands, we are familiar with in the band structure of materials. However, in high school texts, bands of allowed energy levels are represented as boxes, separated by gaps which represent the band gaps, and such a diagram is called a 'Flat band diagram'. How does the flat band diagram relate to Figure 1 above? This relationship is shown in Figure 2 below.

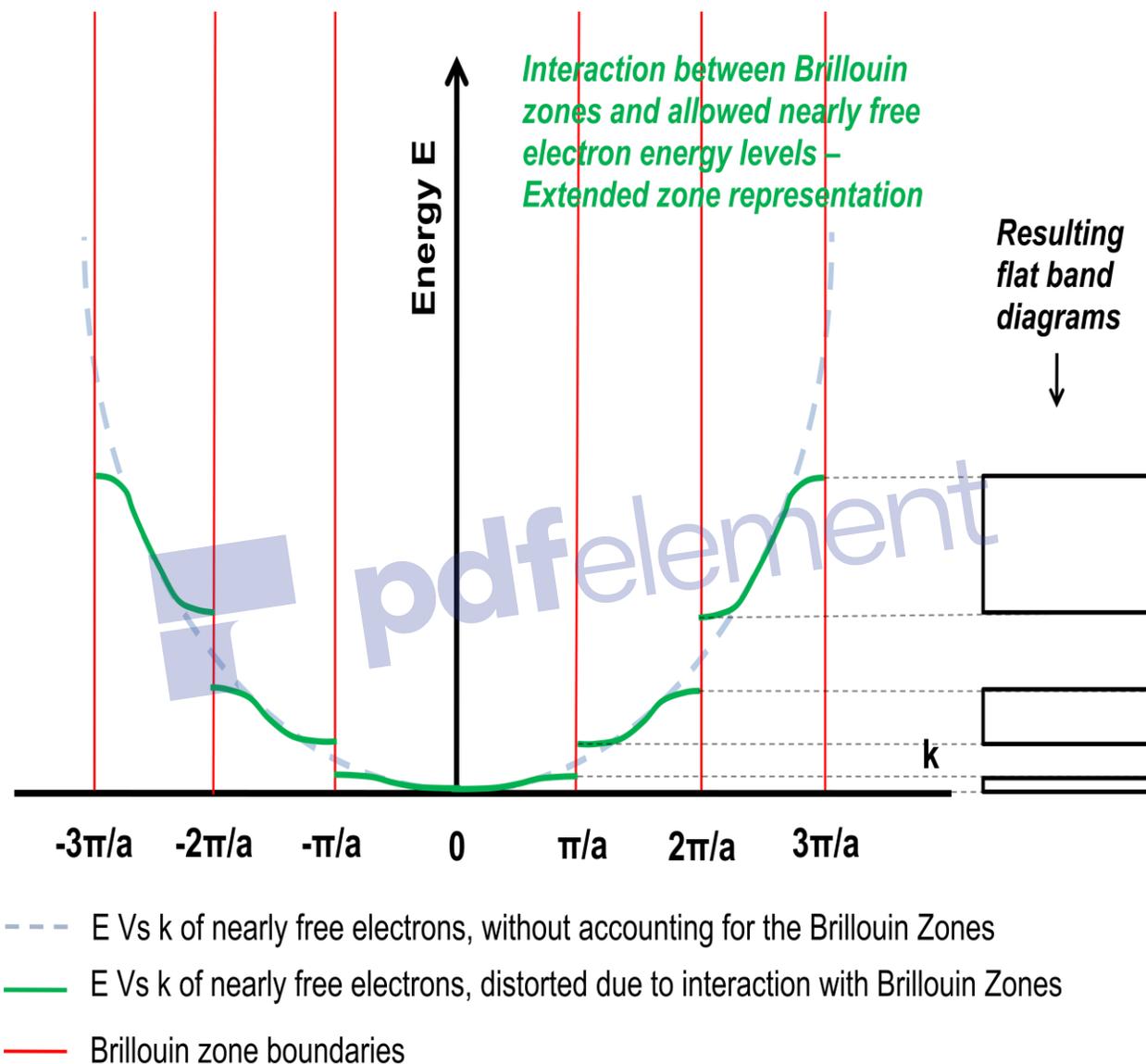


Figure 2: Relationship between the extended zone representation and the flat band structure.

The flat band diagram is sufficient to explain specific material phenomena, but is insufficient to explain many others. The other representations we are presenting in this class, including the extended zone representation and some more that will follow, are much more capable of explaining a variety of material phenomena when compared to the flat band diagram.

We have also noted that at 0 Kelvin the Fermi energy represents the highest occupied energy level in the system, and interaction of electrons with the outside world begins here. Where does this fit into our representations of the allowed energy levels, and how does that relate to the flat band diagram? Figure 3 below shows an example of this.

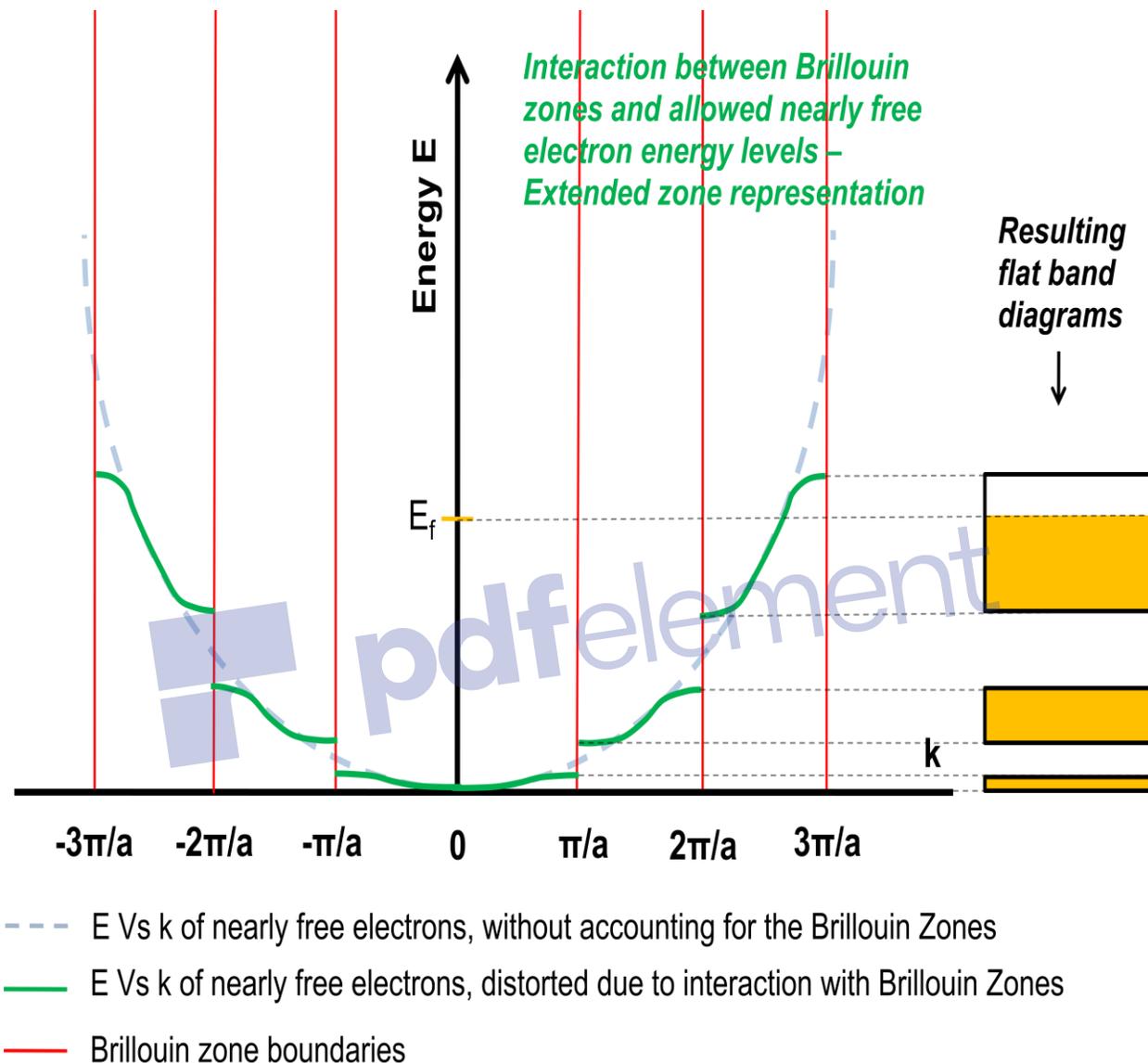


Figure 3: The Fermi energy in the extended zone scheme and in the flat band diagram.

While the extended zone scheme plots the essential details, it is important to note that the choice of origin of k space is arbitrary. Due to symmetry, each lattice point is the same as every other lattice point. Therefore the E Vs k diagram can be repeated at each lattice point, to give a more complete picture of the situation in the material. This type of a diagram is called a 'Repeated zone' representation, and is shown in Figure 4 below.

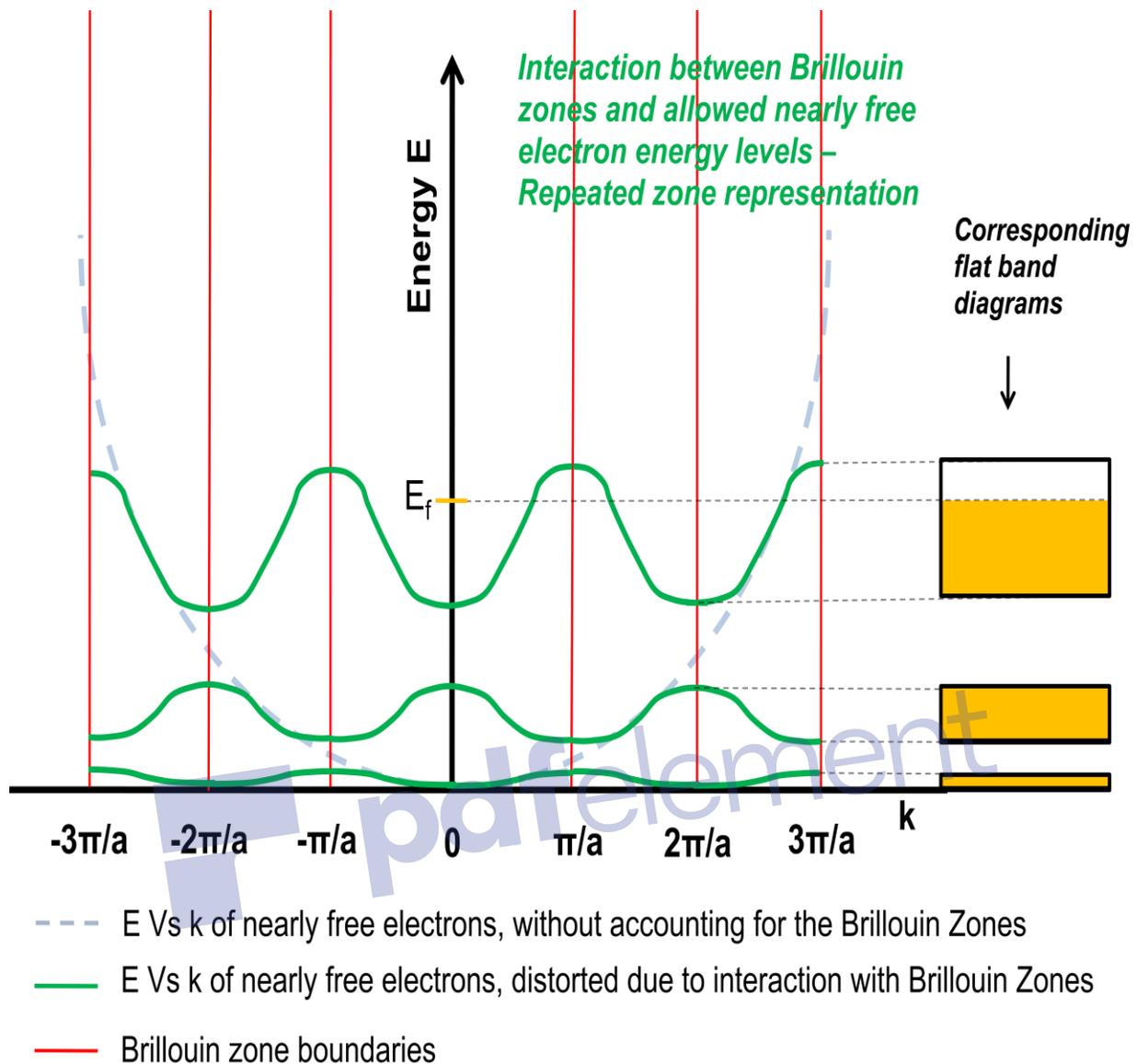


Figure 4: The repeated zone representation

Looking at the repeated zone representation, it can be concluded that the region in the first Brillouin zone, between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$, contains all of the information in a compact manner. Therefore it is often considered sufficient to show all of the allowed wave vectors and energy levels within the first Brillouin zone itself. Such a representation is referred to as the 'Reduced zone' representation, and is as shown in Figure 5 below.

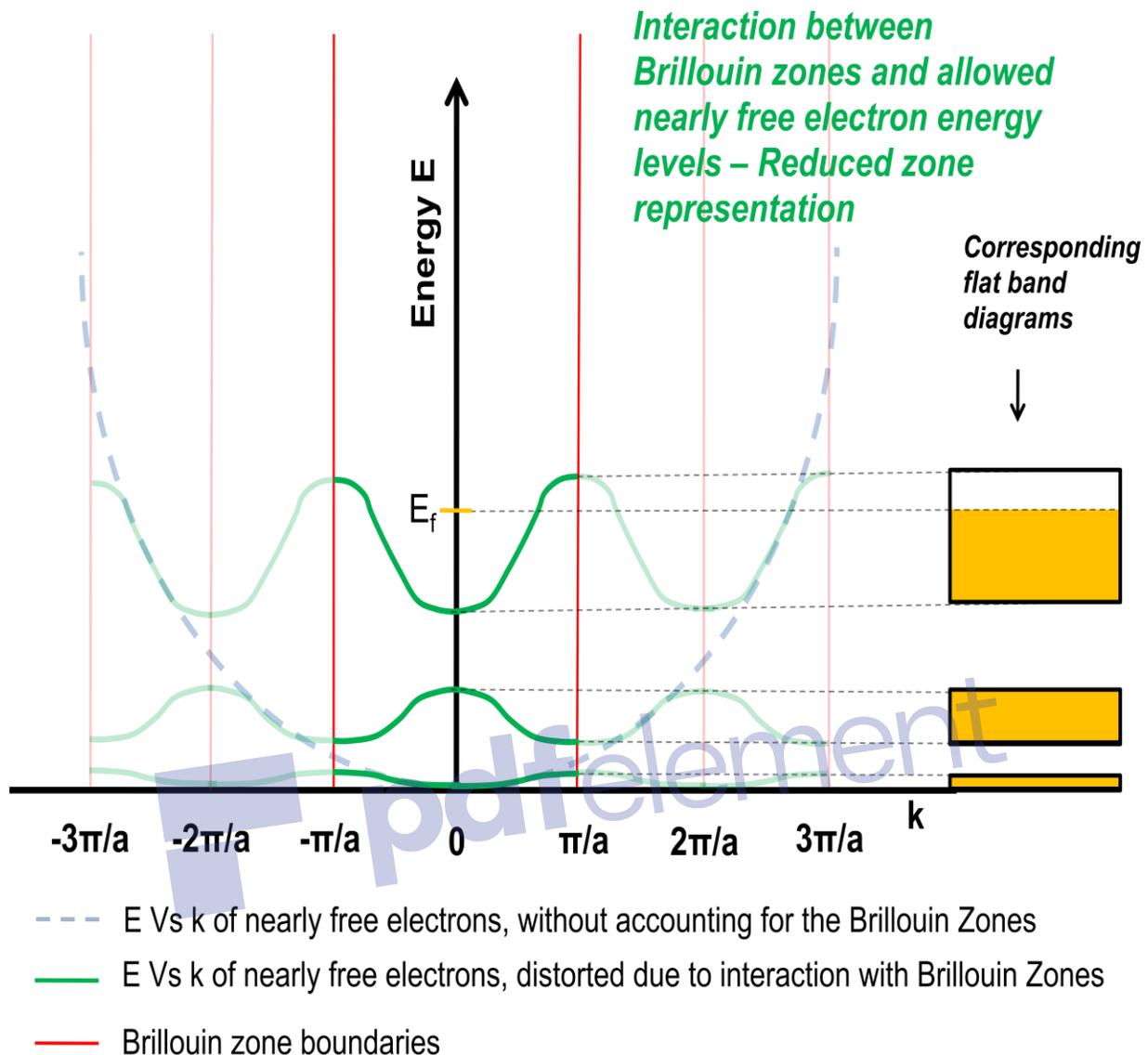


Figure 5: The reduced zone representation

In all of these diagrams, it is the location of the Fermi energy, E_f , which decides whether the material is metallic, semiconducting, or insulating. In the diagrams drawn here, E_f is in the middle of a band, therefore the material being depicted is metallic.

The above diagrams were for a one dimensional lattice. Let us consider a two dimensional square lattice and schematically consider its interaction with the wave vectors of nearly free electrons. In two dimensional k space, electrons of the same energy are represented by a circle. The Fermi energy corresponds to the largest such circle, and we are therefore interested its interaction with the two dimensional Brillouin zone boundaries. Figure 6 below shows the first two Brillouin zones of a two dimensional lattice and consider four possible values of N_f , resulting in four different values of E_f , and hence circles of corresponding diameters. As long as the circle is far

from the Brillouin zone boundary, it does not interact with the boundary, and remains undistorted. When the circle gets close to the boundary, diffraction effects cause it to distort. When the circle is slightly larger than the Brillouin zone, distorted sections of the circle appear inside the first Brillouin zone as well as in the second Brillouin zone.

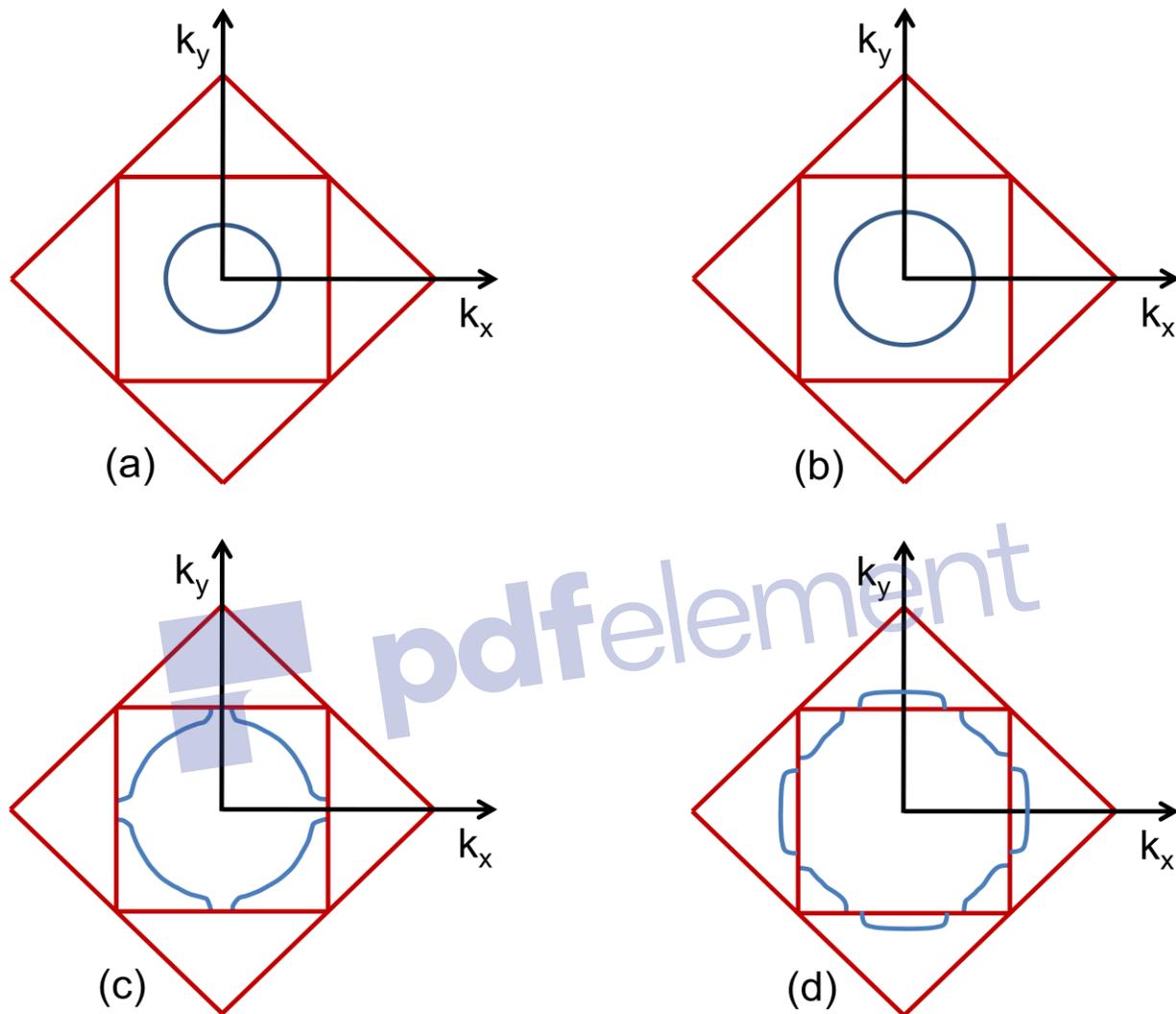


Figure 6: Interaction between allowed wave vectors of nearly free electrons and Brillouin zones of a two dimensional square lattice. The figures (a), (b), (c), and (d) differ in the value of N_f being depicted. N_f in (a) $<$ N_f in (b) $<$ N_f in (c) $<$ N_f in (d). The allowed wave vectors are contained within the first Brillouin zone in figures (a), (b), and (c), In figure (d) the allowed wave vectors appear in the first as well as the second Brillouin zones.

In two dimensions, as well as in three dimensions, it is possible to plot in the reduced zone representation, in just the manner it was accomplished in the one dimensional case. The figures get complicated but the concept is the same. By moving higher Brillouin zones by valid lattice vectors in k space, the information corresponding to higher Brillouin zones can be represented in

the first Brillouin zone itself. Figure 7 below shows this for the two dimensional square lattice.

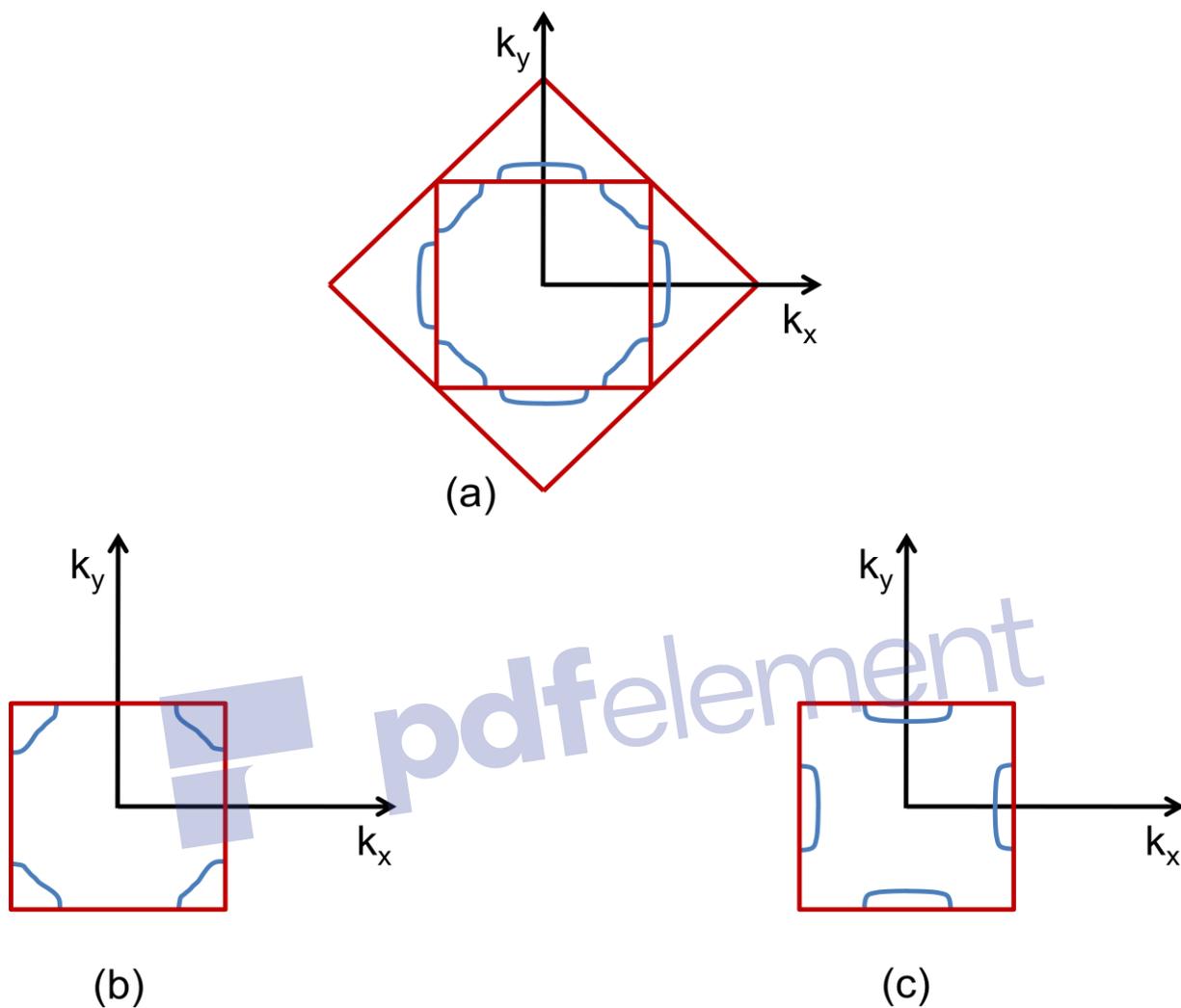


Figure 7: (a) Extended zone representation, (b) and (c) Reduced zone representation





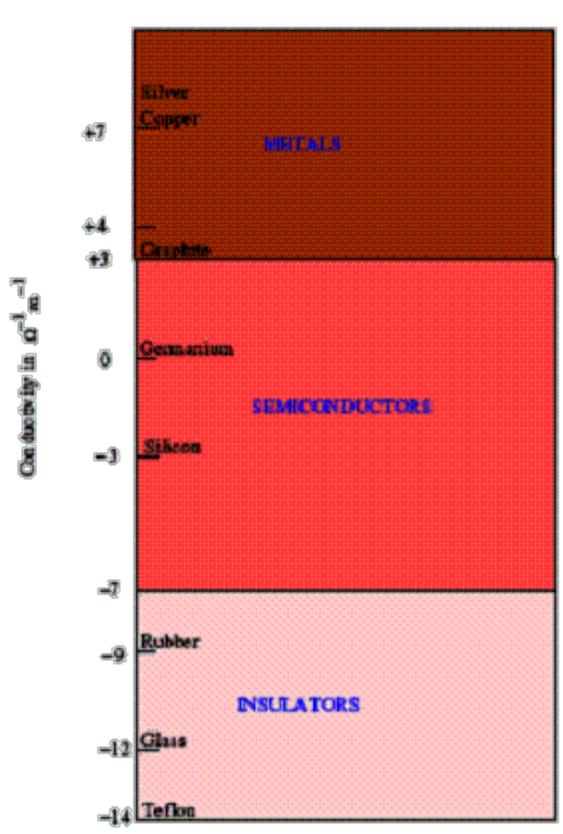
PHYSICS OF SEMICONDUCTOR DEVICES

Energy Band Diagram

Modern electronics, which has revolutionized our way of life, is based on interesting properties of a class of material known as **semiconductors**.

Semiconductors have resistivity values intermediate between those of metals and insulators. While typical metallic resistivity is between 10^{-8} to 10^{-6} ohm-m, that of silicon, which is a representative semiconductor is 3×10^3

ohm-m. Materials with resistivities higher than 10^8 ohm-m are considered to be insulators. Glass, rubber and many plastics are typical insulators.



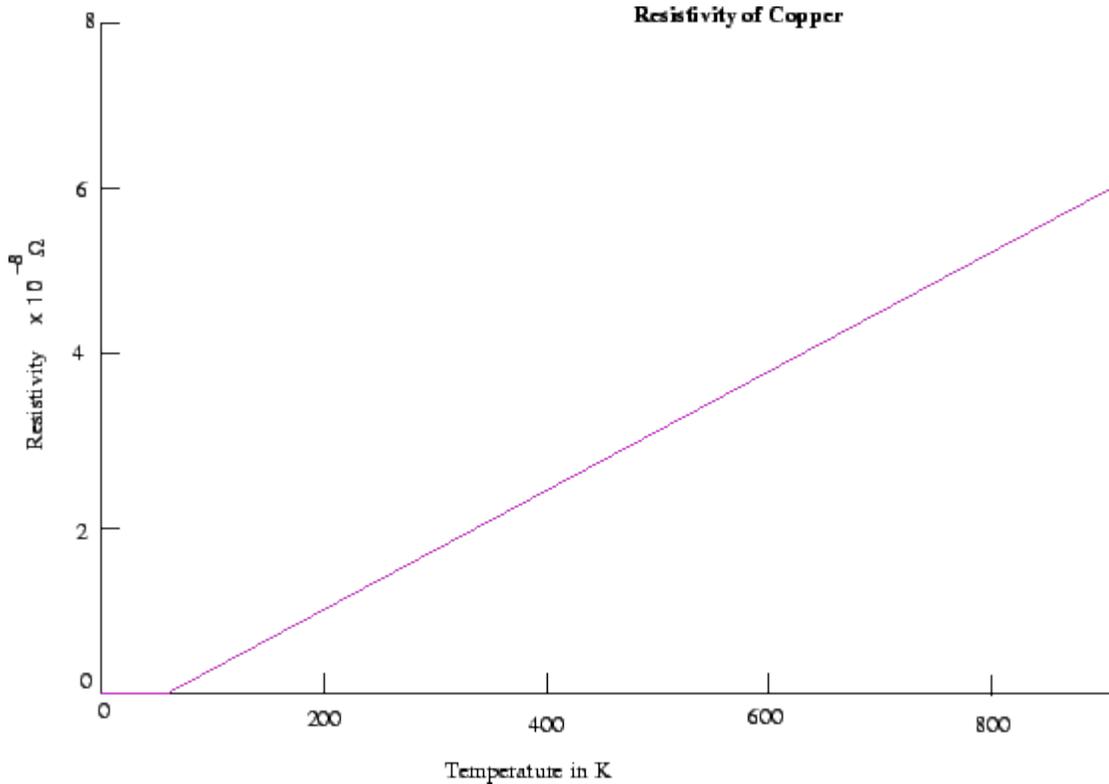
Temperature coefficient of resistivity :

The resistivity of metals increase with the increase of temperature. This is because with increase in temperature, ions in a solid vibrate more causing electrons to scatter more frequently from them. The semiconductors, on the other hand, have a negative temperature coefficient of resistivity, i.e., their resistivity decreases with increase in temperature.

An empirical formula for resistivity of metal is

$$\rho(T) = \rho_{T_{ref}}[1 + \alpha(T - T_{ref})]$$

where $\rho_{T_{ref}}$ is the resistivity at a reference temperature T_{ref} , usually taken to be 0 °C or 20 °C. The constant α is known as the coefficient of resistivity, which is a small positive number (For Cu $\alpha \simeq 0.004 / ^\circ\text{C}$).

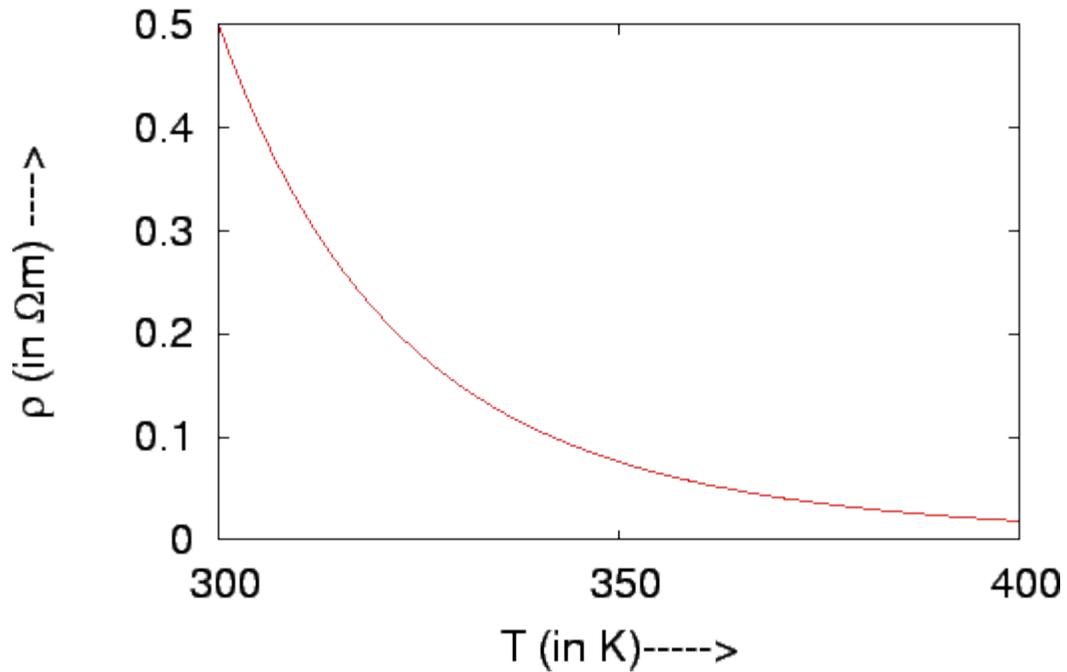


An corresponding formula for resistivity of semiconductors (or of insulators) is

$$\rho(T) = \rho_0 \exp\left[\left(\frac{1}{T} - \frac{1}{T_0}\right) \frac{\Delta E}{2k}\right]$$

where ρ_0 is the resistivity at 0 °C (i.e. at 273 K) and T is the absolute temperature at which the resistivity is measured. Here k is Boltzmann constant and ΔE is the bandgap energy, which, for semiconductors is of the order of 1 eV and much larger for insulators.

Resistivity (ρ) of Ge with Temperature (T)



Charge carriers

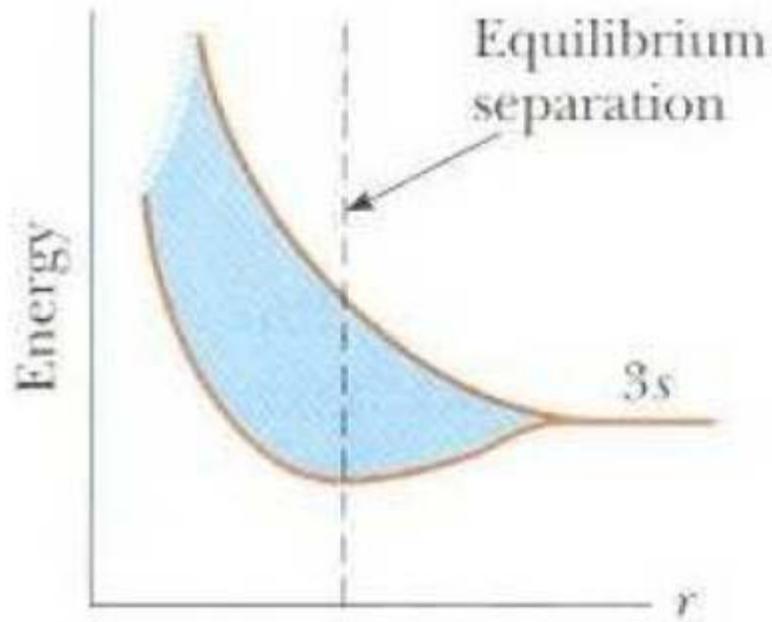
Conductivity arises due to motion of charge carriers in a material when placed in an electric field. The primary charge carriers in a metal are electrons. In gases and solutions, the carriers could be charged ions. The density of carriers in a metal is very high, being of the order of 10^{29} per m^3 .

Charge carriers in semiconductors are electrons and vacancies, the latter being known as **holes**. Typical carrier density in a semiconductor is about 10^{16} which is substantially lower than that of metals. Insulators have negligible carrier densities.

Energy Band Diagram

Electrical properties of materials are best understood in terms of their electronic structure. We know that the energy levels of isolated atoms are discrete. When atoms are brought together to form a solid, these energy levels spread out into **bands** of allowed energies. The effect is qualitatively understood as follows by considering what happens when a collection of N atoms, which are initially far apart are brought closer.

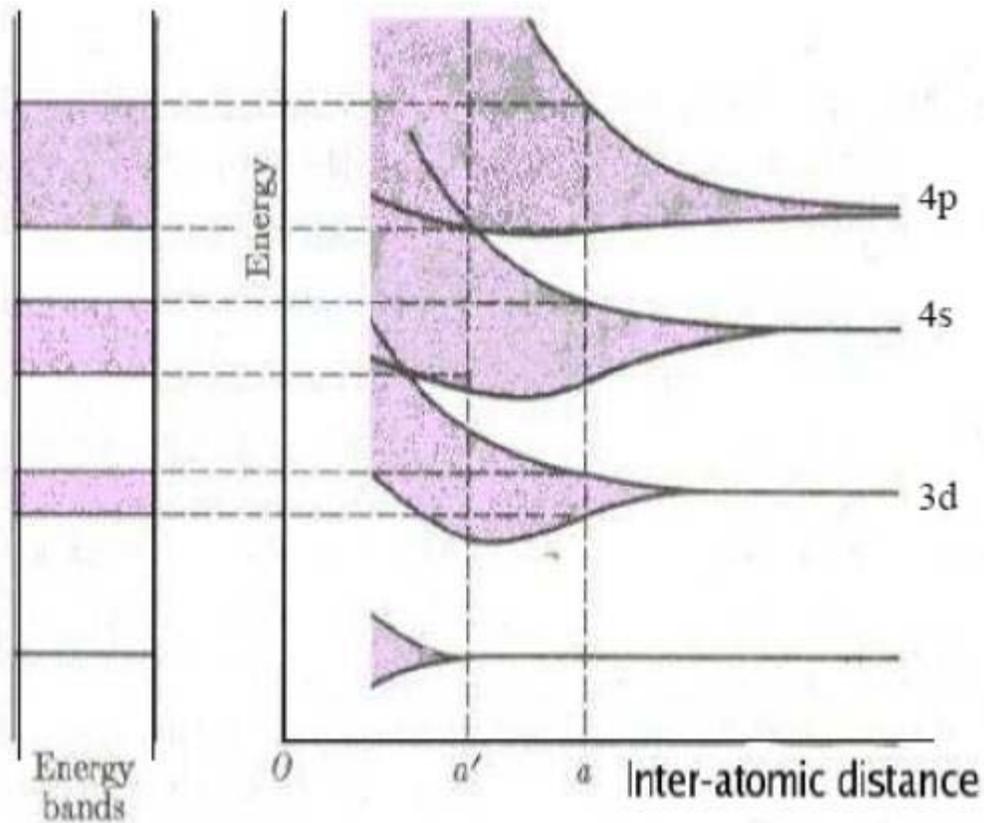
When the spacing r between adjacent atoms is large, each atom has sharply defined energy levels which are denoted by $1s, 2s, 2p, 3s$ etc. As the atoms are far apart their orbitals do not overlap. In particular if each atom is in its ground state, the electrons in each atom occupy identical quantum states. As the distance starts decreasing, the orbitals overlap. The electrons of different atoms cannot remain in the same state because of **Pauli Exclusion Principle**. Pauli principle states that a particular state can at most accommodate two electrons of opposite spins. Thus when N atoms are brought together, the levels must split to accommodate electrons in different states. Though they appear continuous, a band is actually a very large number of closely spaced discrete levels.



Conductors, Insulators and Semiconductors :

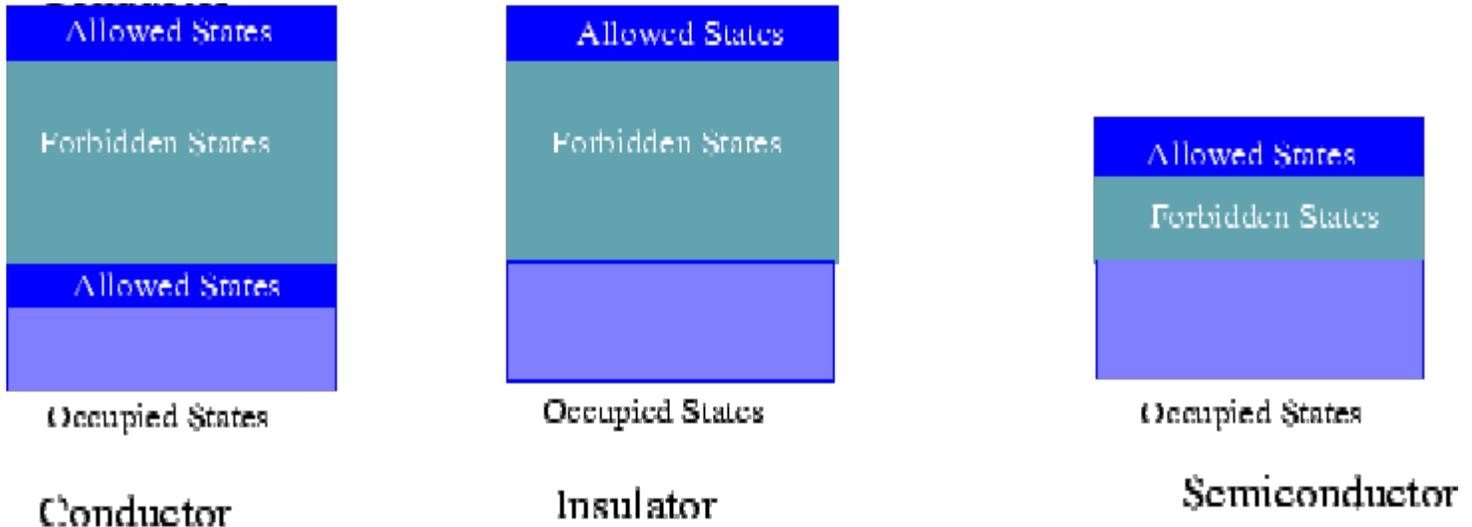
When an electric field is applied to any substance, the electrons can absorb energy from the field and can move to higher energy levels. However, this is possible only when empty states with higher energies exist close to the initial states in which the electrons happen to be in. If there is a substantial energy difference between the occupied electron state and the higher unoccupied state, the electron cannot absorb energy from the electric field and conduction cannot take place. Thus **conduction takes place only in partially occupied bands**.

In case of a metal, the bands which arise from different atomic orbitals overlap and the electrons can absorb energy from an electric field (or absorb thermal or light energy). The electrons in such partially filled bands are called **free electrons**.



For an insulator there is a wide gap (eV) between the lower occupied band, known as the **valence band**,

and the higher unoccupied band, called the **conduction band**. No electron can exist in this **forbidden gap**. To promote electrons from lower levels to higher levels would require a great amount of energy. It is incorrect to say that electrons in an insulator are not free to move around. In fact, they do. However, as there are as many electrons as there are states, the electrons only trade places resulting in no net movement of charges.



Semiconductors, like insulator have band gaps. However, the gap between the top of the valence band and the bottom of the conduction band is much narrower than in an insulator. For comparison, the gap in case of Silicon is 1.1 eV while that for diamond, which is an insulator is about 6 eV.

Quantum Mechanical Concepts

Formation of bands can only be understood on the basis of quantum mechanics. Earlier, we had seen that an object behaves both as particle and as wave. According to de Broglie theory, an electron having a momentum p has an associated wave with a wavelength h/p . Schrödinger proposed an equation for the wave associated with a particle of

mass m having a total energy E which is moving in a potential V . The Schrödinger equation, which is as fundamental to quantum mechanics as Newton's laws are to classical mechanics, is given by

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = (E - V) \psi$$

According to quantum mechanical hypothesis, the **wavefunction** $\psi(\vec{r})$ is interpreted as the probability amplitude of a particle of energy E being at a point \vec{r} . The square of the wavefunction $|\psi(\vec{r})|^2$ gives the probability density at the point, so that the probability of finding the particle anywhere in space given by $\int_{\text{all space}} |\psi(\vec{r})|^2 d^3r$ is unity.

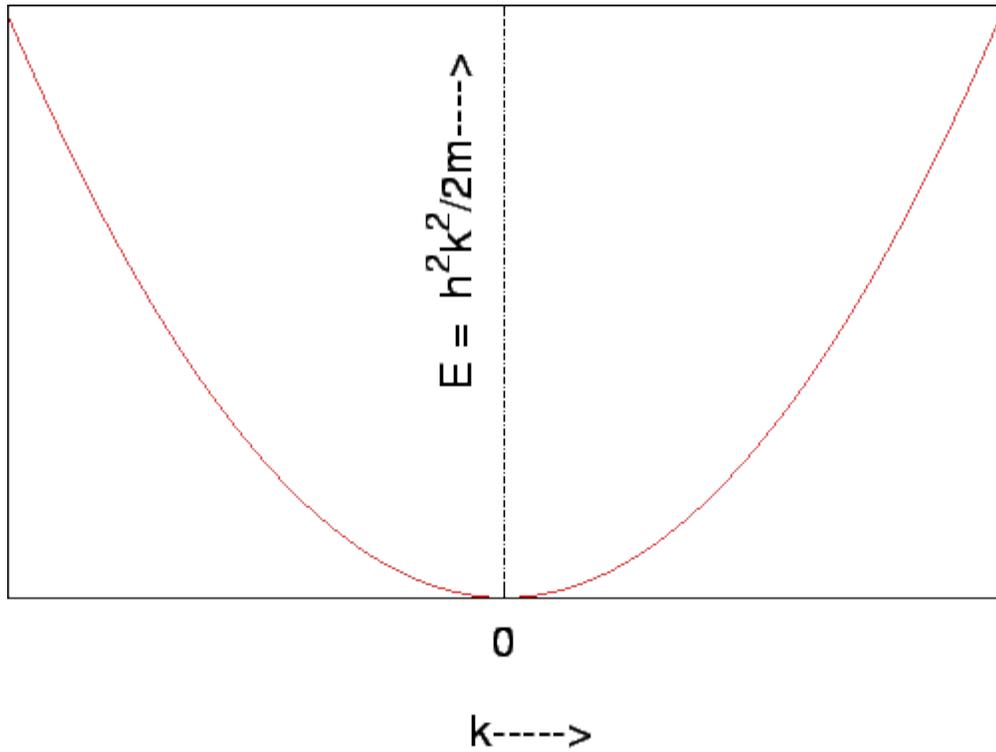
This is called the normalization of the wavefunction. It is also postulated that the wavefunction and its first derivative are continuous and single valued.

Wavefunction of a Free Electron

The energy- momentum relationship for a free electron is given by

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

The $E - k$ relationship (known as the *dispersion relation*) is a parabola.



Free Electron Model of a Metal

The valence electrons in a metal are detached from the individual atoms and move in the metal like a gas of free particles. This leaves the atomic cores positively charged. In the free electron model of a metal, it is assumed that this positive charge of the cores is uniformly distributed throughout the metal. Such an assumption essentially removes any details of the crystal structure of the metal. Nevertheless, it is a good starting point in understanding behaviour of electrons in a metal.

As the interaction between the electrons themselves are also ignored, one can simply consider the motion of a single electron which is moving in a constant potential, which can be conveniently taken to be zero. The electron can be taken to be confined within a box of dimension $L \times L \times L$ within which the potential is constant (taken to be zero)

and outside which it is infinite. The Schrödinger equation for the electron within the box is

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] = E\psi$$

Defining $k^2 = 2mE/\hbar^2$, the equation reads

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + k^2 \psi = 0 \quad (A)$$

The equation may be solved by separation of variables by substituting

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

in eqn. (A) and dividing the resulting equation by $\psi_x\psi_y\psi_z$. We get

$$\frac{1}{\psi_x} \frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{\psi_y} \frac{\partial^2 \psi_y}{\partial y^2} + \frac{1}{\psi_z} \frac{\partial^2 \psi_z}{\partial z^2} + k^2 = 0$$

Since k^2 is constant and the first three terms depend upon x, y, z separately, the above equation can be satisfied

for all values of x, y, z only if each of the three terms is constant, i.e.

x, y, z

$$\frac{1}{\psi_x} \frac{\partial^2 \psi_x}{\partial x^2} + k_x^2 = 0$$

$$\frac{1}{\psi_y} \frac{\partial^2 \psi_y}{\partial y^2} + k_y^2 = 0$$

$$\frac{1}{\psi_z} \frac{\partial^2 \psi_z}{\partial z^2} + k_z^2 = 0$$

with $k_x^2 + k_y^2 + k_z^2 = 0$.

The solutions of the above with boundary condition (i.e. vanishing of wavefunction at the walls) gives

$$\psi_x(x) = A \sin(k_x x)$$

where $k_x = n_x \pi / L$, n_x being any non-zero positive integer. Thus the complete solution (with normalization constant) is

$$\psi(x, y, z) = \frac{2^{3/2}}{\sqrt{V}} \sin k_x x \sin k_y y \sin k_z z$$

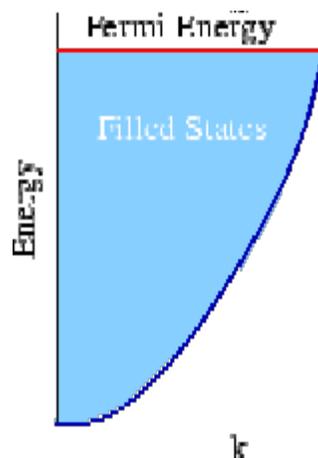
and the energy

$$E = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2} \right) (B)$$

where $V = L^3$ is the volume of the crystal.

At absolute zero temperature, electrons fill up available states from minimum energy upwards satisfying Pauli exclusion principle. Each distinct energy level, specified by a combination of n_x, n_y and n_z is occupied by two electrons of

opposite spins. The maximum value of energy is known as **Fermi energy** and is denoted by E_F .



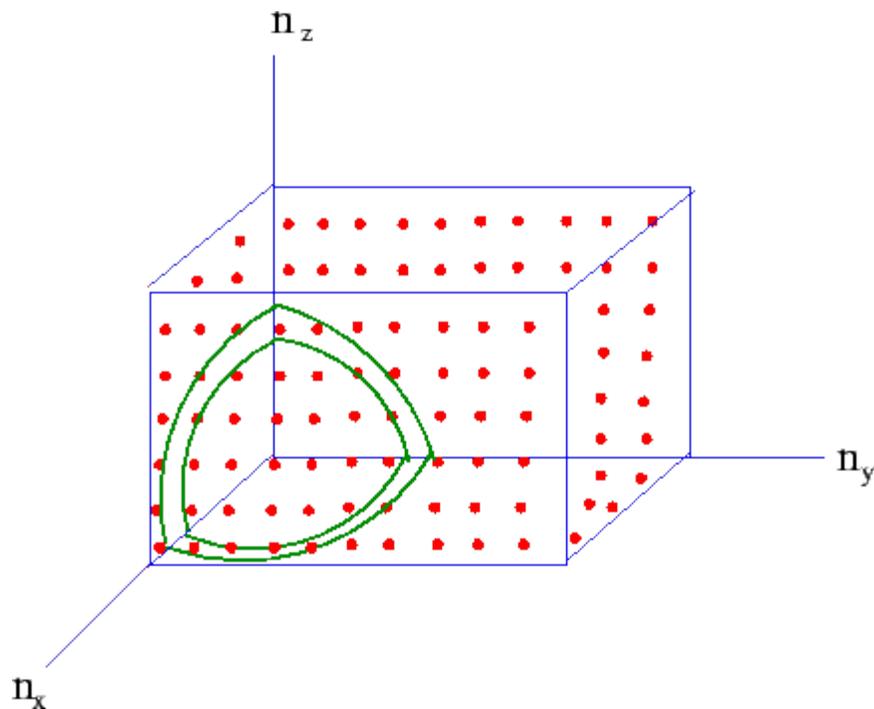
Density of States

Density of states at an energy E is the number of states per unit volume available per unit energy interval with

energy between E and $E + dE$. This would require counting of states, i.e., enumeration of different values of n_x, n_y, n_z corresponding to the energy of states within this interval. This is obviously a difficult task. However, given the large dimension of a crystal, the states are very closely packed and one can essentially treat the k -values as continuous.

Equation of constant energy given by eqn. (B) is a sphere in $n_x - n_y - n_z$ space with a radius $\sqrt{2mEL}/\pi\hbar$.

As the points in this space are separated from the adjacent ones by one unit in each direction, each point effectively occupies a volume $(2\pi)^3/V$ in the k -space. Thus a unit volume in k -space contains $V/(2\pi)^3$ number of states. As each k -state can accommodate two electrons (corresponding to two distinct spin states), the number of electrons per unit volume of k -space is $V/4\pi^3$.



Since the constant energy surface in k -space is a sphere, we can define **Fermi wave vector** k_F as the radius of a sphere corresponding to the Fermi energy E_F by

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

The volume of Fermi sphere being $4\pi k_F^3/3$, the number of electrons N that lie within such a sphere is

$$N = \frac{4\pi}{3} k_F^3 \times \frac{V}{4\pi^3} \equiv \frac{V}{3\pi^2} \left(\frac{2mE_F}{\hbar^2} \right)^{3/2} \quad (C)$$

which gives the density n as equal to

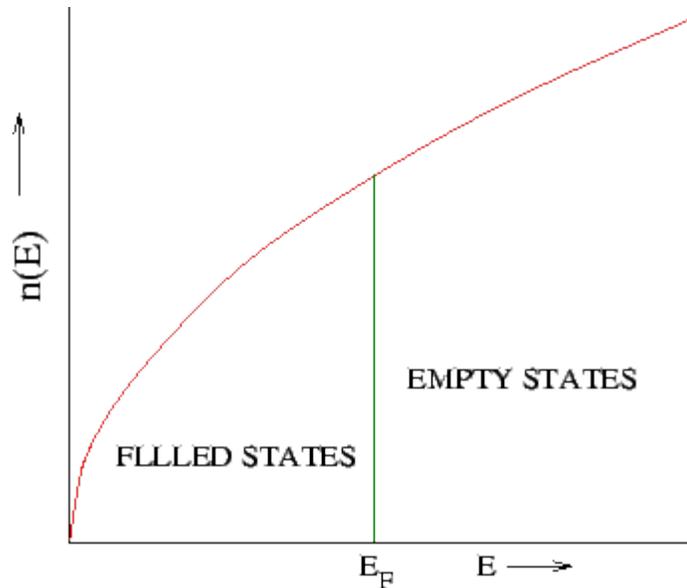
$$n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

Using eqn. (C), we can obtain an expression for the density of states $n(E)$. Since, by definition, $n(E)dE$ is the number of states lying within energy interval E and $E + dE$, we may simply subtract the number of states below energy E from the number below $E + dE$. We have

$$\begin{aligned} n(E)dE &= \frac{1}{3\pi^2} \left[\frac{2m}{\hbar^2} \right]^{3/2} [(E + dE)^{3/2} - E^{3/2}] \\ &\simeq \frac{1}{3\pi^2} \left[\frac{2m}{\hbar^2} \right]^{3/2} \left[E^{3/2} \left(1 + \frac{3dE}{2E} \right) - E^{3/2} \right] \\ &= \frac{1}{2\pi^2} \left[\frac{2m}{\hbar^2} \right]^{3/2} E^{1/2} dE \end{aligned}$$

The unit of density of states $n(E)$ is $(\text{eV})^{-1} \text{m}^{-3}$.

Density of States and Fermi Energy

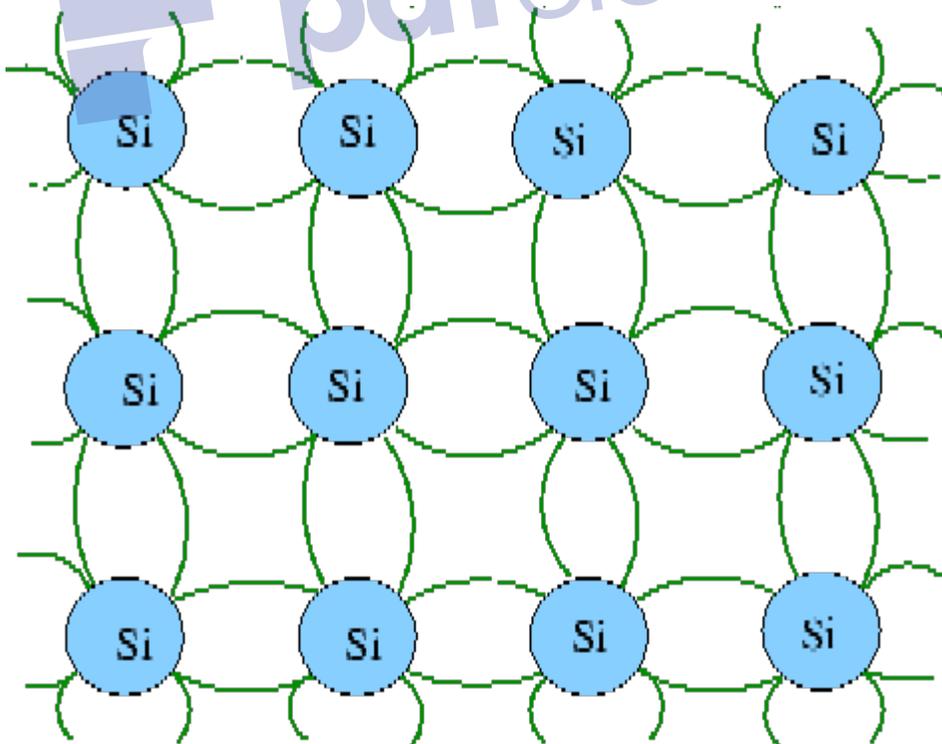


Free electron theory can be used to explain, reasonably satisfactorily, several qualitative properties of metals, such as, thermal and electrical conductivity, magnetic properties, heat capacity etc. However, as the theory totally ignores the crystalline structure of metals, it fails to provide a distinction between metals, semiconductors and insulators. The atoms in a crystal are arranged in a periodic arrangement. Consequently, the electrons in the crystal are subject to a periodic potential rather than a uniform potential assumed in the free electron model. If this potential is assumed to be weak, the electrons do not become completely free but nearly so. The model is known as **nearly free electron model**.

- Metals have free charge carriers. With increase in temperature, the resistivity of a metal increases.
- Pure (intrinsic) semiconductors are very similar to insulators. For a semiconductor, the resistivity decreases with increase in temperature.
- Metals have partially occupied band which allow charge carriers to move even when a small amount of energy is supplied. Semiconductors have occupied valence band and unoccupied conduction band. Carriers can be thermally excited from valence band to conduction band.
- Insulators are similar to semiconductor in their band structure. However, the band gap is much larger than in a semiconductor.
- Behaviour of simple metals can be described by a free electron theory in which an electron is taken to move in a constant potential. At zero temperature the electron states are occupied from the lowest energy state to a state of maximum energy, known as Fermi energy.
- Density of state is the number of states per unit volume of a substance per unit energy interval. For free electrons the density of state is proportional to the square root of energy.

Intrinsic Semiconductors

An intrinsic semiconductor is a pure semiconductor, i.e., a sample without any impurity. At absolute zero it is essentially an insulator, though with a much smaller band gap. However, at any finite temperature there are some charge carriers are thermally excited, contributing to conductivity. Semiconductors such as silicon and germanium, which belong to Group IV of the periodic table are covalently bonded with each atom of Si(or Ge) sharing an electron with four neighbours of the same species. A bond picture of silicon is shown in the figure where a silicon atom and its neighbour share a pair of electrons in covalent bonding.



Gallium belongs to Group III and bonds with arsenic which belongs to Group V to give a III-V semiconductor. In GaAs, the bonding is partly covalent and partly ionic. Other commonly known III-V semiconductors are GaN, GaP, InSb etc. Like the III-V compounds, Group II elements combine with Group VI elements to give semiconductors like CdTe, CdS, ZnS etc. Several industrially useful semiconductors are alloys such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

The number of carriers in a band at finite temperatures is given by $\int n(E)f(E)dE$, where

$$N_c = \frac{1}{4} \left(\frac{2m_c kT}{\pi \hbar^2} \right)^{3/2} \quad \text{is the density of state and } f(E) \text{ is the Fermi function which gives the}$$

thermal probability. If $E - E_F \gg kT$, we may ignore the term 1 in the denominator of the Fermi function and approximate it as

$$f_c(E) \simeq e^{(E-E_F)/kT}$$

Using this the density of electrons in the conduction band (n) may be written as follows.

$$\begin{aligned} n &= \int_{E_c}^{\infty} e^{(E_F-E)/kT} \frac{1}{2\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} dE \\ &= \frac{1}{2\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} e^{(E_F-E)/kT} (E - E_c)^{1/2} dE \\ &= \frac{1}{2\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} \int_0^{\infty} e^{(E_F - xkT - E_c)/kT} (kT)^{3/2} x^{1/2} dx \\ &= \frac{1}{2\pi^2} \left(\frac{2m_c kT}{\hbar^2} \right)^{3/2} e^{(E_F - E_c)/kT} \int_0^{\infty} e^{-x} x^{1/2} dx \end{aligned}$$

where we have substituted

$$x = \frac{E - E_c}{kT}$$

The integral $\int_0^{\infty} e^{-x} x^{1/2} dx$ is a gamma function $\Gamma(3/2)$ whose value is $\sqrt{\pi}/2$. Substituting this value, we get for the density of electrons in the conduction band

$$n = \frac{1}{4} \left(\frac{2m_c kT}{\pi \hbar^2} \right)^{3/2} e^{(E_F - E_c)/kT} = N_c e^{(E_F - E_c)/kT} \quad (A)$$

where

$$N_c = \frac{1}{4} \left(\frac{2m_c kT}{\pi \hbar^2} \right)^{3/2}$$

One can in a similar fashion one can calculate the number density of holes, p , by evaluating the expression

$$p = \int_{E_v}^{-\infty} n_h(E) f_h(E) dE$$

where $f_h(E) = 1 - f_c(E)$ is the Fermi function for the occupancy of holes which is the same as the probability that an electron state at energy E is unoccupied. For $E_F - E \gg kT$, the density of holes is given by

$$p = \frac{1}{4} \left(\frac{2m_h kT}{\pi \hbar^2} \right)^{3/2} e^{(E_v - E_F)/kT} = N_v e^{(E_v - E_F)/kT} \quad (B)$$

where

$$N_v = \frac{1}{4} \left(\frac{2m_h kT}{\pi \hbar^2} \right)^{3/2}$$

The following table gives generally accepted values of some of the quantities associated with the three most common semiconductors at room temperature (300 K).

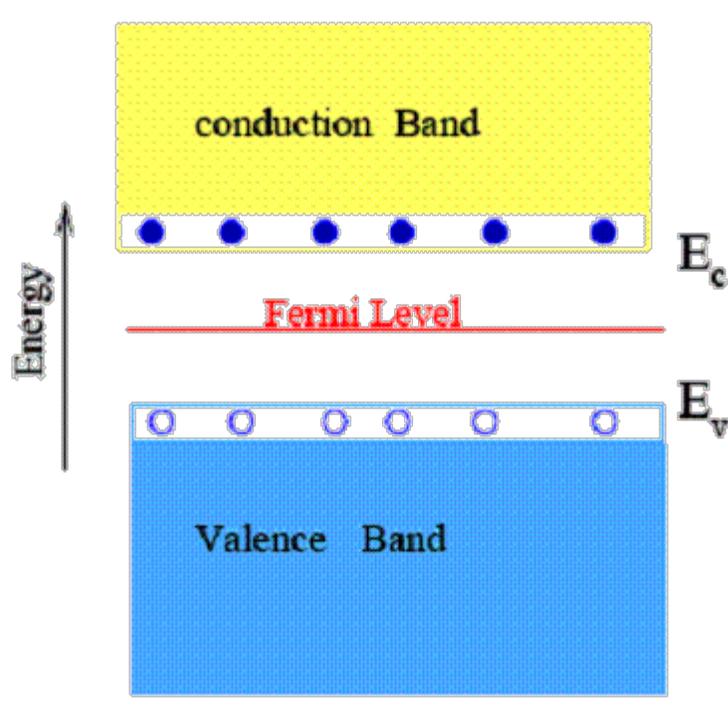
	Δ	m_c/m_0	m_h/m_0	N_c	N_v	n_i
	in eV			/m ³	/m ³	/m ³
Si	1.12	1.08	0.56	2.8×10^{25}	1.0×10^{25}	1.5×10^{16}
Ge	0.66	0.55	0.37	1.0×10^{25}	6.0×10^{24}	2.4×10^{19}
GaAs	1.4	0.04	0.48	4.7×10^{24}	7.0×10^{24}	1.8×10^{12}

For an intrinsic semiconductor the number of electrons in the conduction band is equal to the number of holes in the valence band since a hole is left in the valence band only when an electron makes a transition to the conduction band,

$$n = p$$

Using this and assuming that the effective masses of the electrons and holes are the same one gets

$$e^{(E_F - E_c)/kT} = e^{(E_v - E_F)/kT}$$



giving

$$E_F = \frac{E_c + E_v}{2} \quad (C)$$

i.e. **the Fermi level lies in the middle of the forbidden gap**. Note that there is no contradiction with the fact that no state exists in the gap as E_F is only an energy level and not a state.

By substituting the above expression for Fermi energy in (A) or (B), we obtain an expression for the number density of electrons or holes ($n = p = n_i$)

$$n_i = \frac{1}{4} \left(\frac{2kT}{\pi \hbar^2} \right)^{3/2} (m_e m_h)^{3/4} e^{-\Delta/2kT} \quad (D)$$

where Δ is the width of the gap.

Exercise 1

For a two band model of silicon, the band gap is 1.11 eV. Taking the effective masses of electrons and holes as $m_e = 1.08m_0$ and $m_h = 0.81m_0$, calculate the intrinsic carrier concentration in silicon at 300 K.

(Ans. $1.2 \times 10^{16} \text{ m}^{-3}$.)

Exercise 2

Show that, if the effective masses of electrons and holes are not equal, the position of the Fermi energy for an intrinsic semiconductor is given by

$$E_F = \frac{E_c + E_v}{2} + \frac{3}{4}kT \ln \frac{m_c}{m_h}$$

Current in an intrinsic semiconductor

For semiconductors both electrons and holes contribute to electric current. Because of their opposite charge, their contribution to the current add up. For an intrinsic semiconductor with a single valence band and a conduction band, the current density is given by

$$J = q(nv_e + pv_h)$$

where n and v_e are respectively the electron density and speed while p and v_h are the hole density and speed. Using $v_e = \mu_e \mathcal{E}$ and $v_h = \mu_h \mathcal{E}$ and the fact that $n = p = n_i$, we have

$$J = q\mathcal{E}n_i(\mu_e + \mu_h)$$

which gives the conductivity as

$$\sigma = qn_i(\mu_e + \mu_h)$$

Example 1

Estimate the electrical conductivity of intrinsic silicon at 300 K, given that the electron and hole mobilities are $\mu_e = 0.15 \text{ m}^2/\text{V}\cdot\text{s}$ and $\mu_h = 0.05 \text{ m}^2/\text{V}\cdot\text{s}$.

Solution

The conductivity arises due to both electrons and holes

$$\sigma = qn_i(\mu_e + \mu_h)$$

The intrinsic carrier concentration n_i was calculated to be $1.2 \times 10^{16}/\text{m}^3$ at 300 K. Thus

$$\sigma = 1.6 \times 10^{-19} \times 1.2 \times 10^{16} \times 0.2 = 3.84 \times 10^{-4} \text{ ohm}^{-1} \text{ m}^{-1}$$

Exercise 3

A sample of an intrinsic semiconductor has a band gap of 0.7 eV, assumed independent of temperature.

Taking $\mu_h = 0.5\mu_e$ and $m_h = 2m_e$, find the relationship between the conductivity at 200 K and 300 K.

(Ans. ratio of conductivity = 2014.6, $E_F(300\text{K}) - E_F(200\text{K}) = 4.33 \times 10^{-3} \text{ eV}$)

Extrinsic Semiconductors

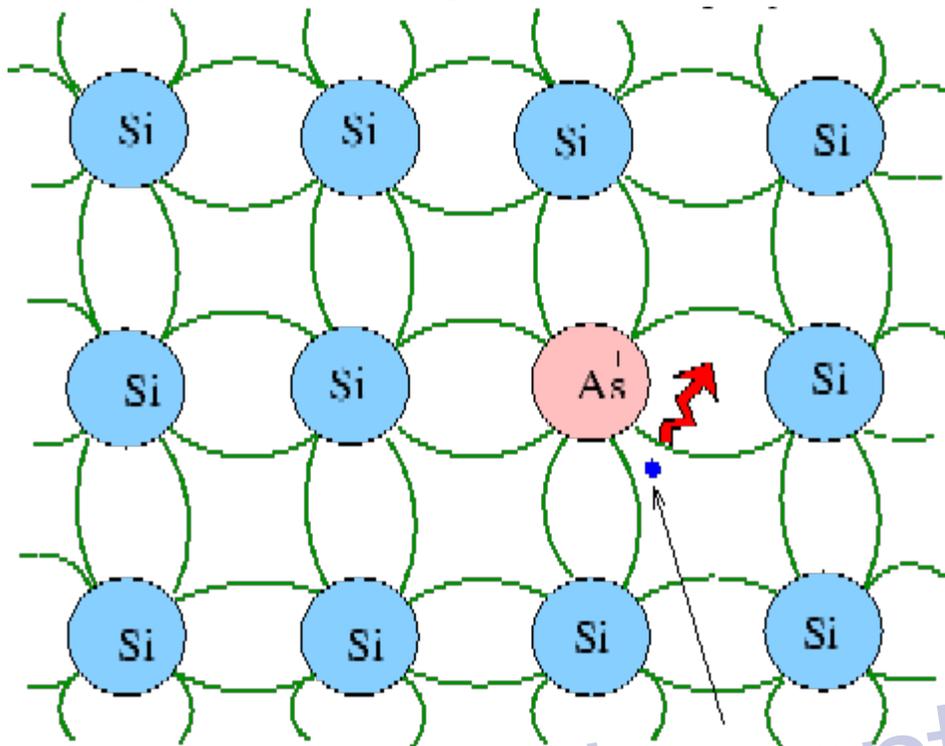
An extrinsic semiconductor is formed by adding impurities, called **dopants** to an intrinsic semiconductor to modify the former's electrical properties. There are two types of such impurities - those which provide electrons as majority carriers are known as **n-type** and those which provide holes as majority carriers are known as **p-type**.

Using this and assuming that the effective masses of the electrons and holes are the same one gets

n- type Semiconductors

Consider a matrix of silicon where the atoms are covalently bonded.

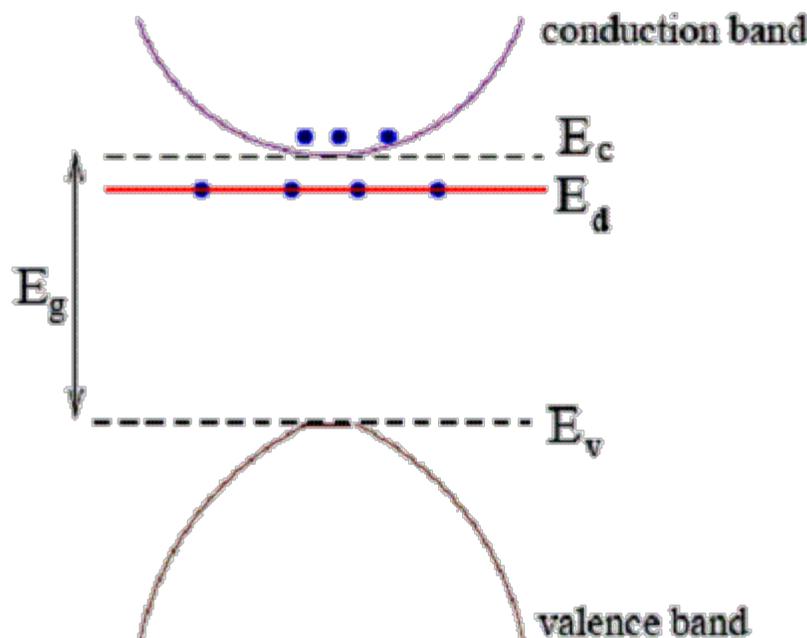
If we add a pentavalent atom (As, P etc.) as an impurity, the dopant atom replaces a silicon atom substitutionally. As the dopant has five electrons, only four of these can be used in forming covalent bonds while the fifth electron is loosely bonded to the parent atom. This electron can become detached from the dopant atom by absorbing thermal energy.



Extra electron from impurity atom

In the band picture, the energy level of the additional electron lies close to the bottom of the conduction band. Such an energy level E_d is called a *donor level* as it can donate an electron to the empty conduction band by thermal excitation.

We may see this by assuming that the fifth electron of the donor is orbiting around a hydrogen-like nucleus consisting of the core of the donor atom with the following modifications made into the formula for the energy of an electron in the hydrogen atom.



- permittivity of the free space ϵ_0 is replaced by ϵ , the permittivity of the medium (silicon).
- free electron mass being replaced by the effective mass of the donor electron.

Recalling that the energy of an electron in the the hydrogen atom is given by

$$-\frac{me^4}{8\epsilon_0^2 h^2 n^2} = -\frac{13.6}{n^2} \text{ eV}$$

where $n = 1, 2, 3, \dots$, we need to replace m by m^* and e^2/ϵ_0 by $e^2/\kappa\epsilon_0$, where κ is the relative dielectric constant of the medium. Using $\kappa = 12$ for Si and $m^* \simeq m$, the free electron mass, the ionization energy of the electron bound to the donor atom is $13.6/(12)^2 \simeq 0.094$ eV, if

the electron is in the ground state. Thus the donor energy level lies close to the bottom of the conduction band. In case of semiconductors, the donor **ionization energy** is defined as the energy required to elevate the donor electron to the conduction band.

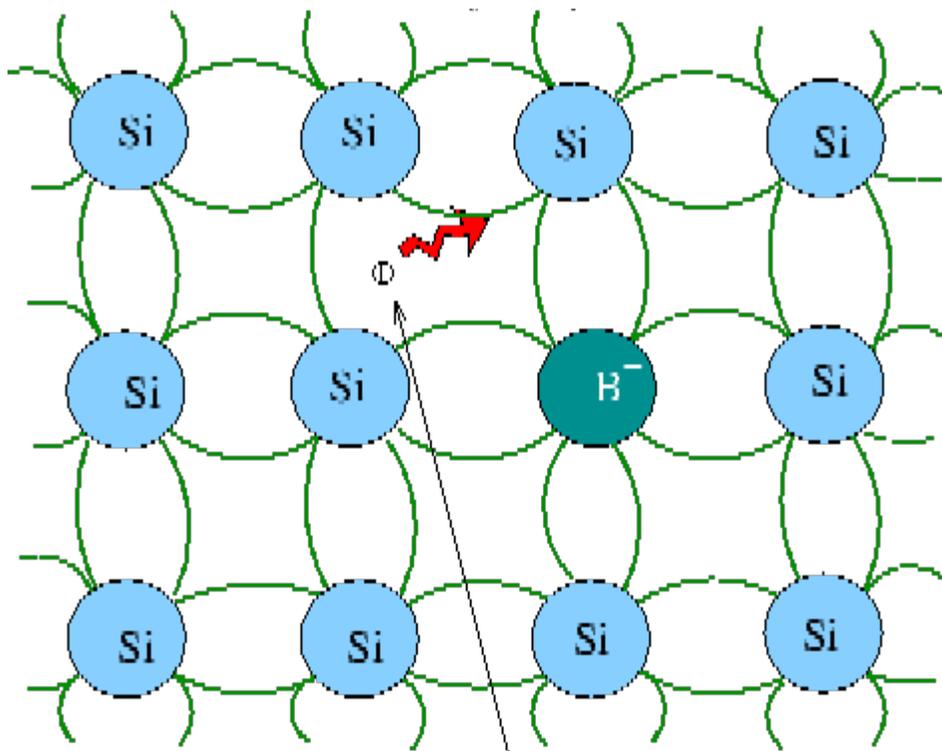
Exercise 4

Calculate the ionization energy of a donor impurity in Ge. The effective mass of electrons is $0.12m_0$ and the dielectric constant is 16.

(6.4 meV)

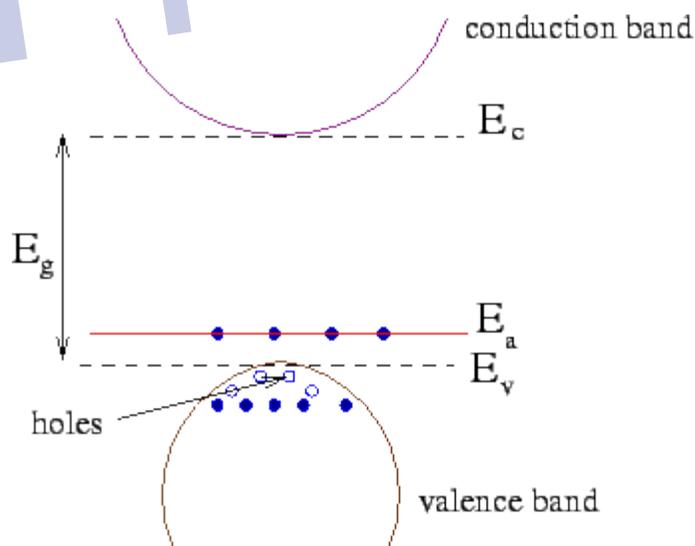
p- type Semiconductors

If the Si matrix is doped with Group III impurities like boron or aluminium, it cannot provide electrons to complete the covalent bonds. However, the impurity readily accepts an electron from a nearby Si-Si bond to complete its own bonding scheme. A hole is thereby created which can freely propagate in the lattice.



deficiency in a bond
(a hole)

In the band picture, the acceptor energy level E_a lies close to the top of the valence band. Electrons near the top of the valence band can be thermally excited to the acceptor level leaving holes near the top of the valence band. In these semiconductors, known as P-type semiconductors, the primary current is due to majority carriers which are holes.



Example 2

In an n-type semiconductor 25% of the donor atoms are ionized at 300 K. Determine the location of the Fermi level with respect to the donor level.

Solution

As 25% of donor atoms are ionized, the occupation probability of donor level is 0.75. Thus

$$F(E_D) = \frac{1}{1 + \exp\left(\frac{E_D - E_F}{kT}\right)} = 0.75$$

Solving, $E_D - E_F = -0.028$ eV.

Exercise 5

In a p-type semiconductor 40% of atoms are ionized at 300 K. Find the location of the Fermi level with respect to the acceptor level.

$$(E_a - E_F = 0.016 \text{ eV})$$

A **compensated semiconductor** contains both donor and acceptor impurities. The compensation is said to be complete if $N_d = N_a$ in which case the semiconductor behaves like an intrinsic semiconductor.









