

Unit I b (Part II)

Part – A

1. What is meant by degenerate and Non - degenerate state?

For several combination of quantum numbers, if the Eigen value are same with different set of Eigen functions, such states and energy levels are called Degenerate states

For several combination of quantum numbers, if the Eigen value and Eigen functions are same, such states and energy levels are called Non - Degenerate states

2. What are the difference between quantum theory and zone theory?

S.No	Quantum Theory	Zone Theory
01.	Here the electron is assumed to move in a region of constant potential	Here the electron is assumed to move in a region of periodic potential
02.	The mass of the electron remains constant , when it moves through the constant potential	The mass of the electron varies as they move in a periodic potential called effective mass
03.	It fails to explain the classification of conductors, semiconductor and insulators	It explains the classification of conductors, semiconductor and insulators

3. Define scattering power of the potential barrier?

It is defined as the strength with which the electrons are attracted by the positive ions and is given by $P = mV_0ba / \hbar^2$.

m – Mass of electron; a, b – limits with which the electrons assumed to move

4. What is Brillouin zone?

Brillouin zone are the boundaries that are marked by the values of propagation vector \vec{k} in which the electrons can have allowed energy values without diffraction.

5. What is effective mass of electron?

When an electron is accelerated in a periodic potential within the lattice due to external electric or magnetic field, then the mass of the electron varies with respect to the applied field. This varying mass is called effective mass (m^*)

6. Will the effective mass of the electron be negative? Justify your answer?

Yes, the effective mass of the electron can also have a negative value.

Justification: the effective mass of the electron is the mass of the electron when it is

accelerated in a periodic potential and is given by
$$m^* = \frac{\hbar^2}{d^2E / dk^2}$$

Here, $\frac{d^2E}{dk^2}$ can vary from positive to negative value. Therefore if $\frac{d^2E}{dk^2}$ is negative, then

m^* will also have negative value. Also, this negative effective mass of an electron leads to the concept of hole.

Physically speaking the electrons with negative mass has same positive mass as that an electron but it has positive charge rather than negative charge

7. Explain the concept of hole and give its importance

When the electrons are accelerated in a periodic potential, its mass varies and it moves in the direction opposite to the direction of the applied field. This variation of mass of an electron is called as negative mass behaviour of electron. The electrons with negative mass is called hole which has same positive mass as that an electron but instead of negative charge, the hole will possess positive charge.

Importance: If we have n number of empty states in a nearly filled band then these n number of empty states can be considered as n number of holes

8. What are the phenomenon that explains the concept of hole?

- (i) Hall effect (ii) Thomson effect

9. What is meant by effective mass approximation?

For an electron moving in a constant potential field $m^* = m$. But for an electron moves in a periodic potential $m^* \neq m$. Thus, when an electron moves in a periodic potential the free electron mass m should be replaced by the effective mass m^* and this process is called as effective mass approximation.

10. Compare free electron and tight binding approximations

Sl.No	Free electron approximation	Tight binding approximation
1.	The potential energy of electron is assumed to be lesser than its total energy	The potential energy of electron is nearly equal to its total energy
2.	The width of forbidden bands are smaller than the allowed bands	The width of forbidden bands are larger than the allowed bands
3.	The interaction between neighbouring atoms will be very strong	The interaction between neighbouring atoms will be weak
4.	As the atoms come closer, the interatomic distance decreases and hence the wave function overlap with each other	As the atoms come closer, the interatomic distance increases and hence the wave function do not overlap with each other

11. What do you understand from Fermi-Dirac statistics and what are fermions?

- (i) The particles are indistinguishable
 (ii) The electrons which obey Fermi-Dirac statistics are called fermions
 (iii) Each energy state can have only one particle with one spin
 (iv) The number of energy states should be greater than or equal to number of particles.
 (v) The total energy of the system = sum of all the energies of the particles.

12. Compare drift velocity and thermal velocity.

Sl.No	Drift velocity	Thermal velocity
1.	It is the average velocity acquired by the free electron in the presence of the electric field	It is the velocity of an electron without any external field
2.	The electrons moving in a direction opposite to the direction of the applied electric field.	The direction of the electrons moving with thermal velocity is random.

Part – B

1. Explain the behaviour of an electron moving in a field of periodic potential using Kronig and Penny model?

Kronig and Penny treated a simplest example for one dimensional periodic potential. In this model, it assumed that the potential energy of an electron has the form of periodic array of square well as shown in figure.

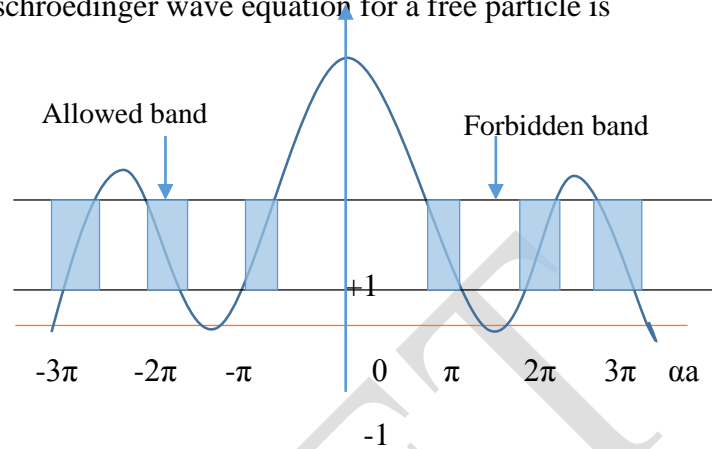
Here we are having 2 regions. viz

Region I: $0 < x < a$, here the potential energy is zero and hence the electron is assumed to be free particle. Therefore, the 1 – D schroedinger wave equation for a free particle is

$$\frac{d^2\psi}{dt^2} + \frac{2m}{\hbar^2}[E - 0]\psi = 0$$

$$(or) \frac{d^2\psi}{dt^2} + \alpha^2\psi = 0 \quad (1)$$

$$Where \quad \alpha^2 = \frac{2mE}{\hbar^2}$$



Region II: $-b < x < 0$, here the potential energy of the electron is V_0 .

Therefore, the 1 – D schroedinger wave equation for a free particle in a periodic potential is

$$\frac{d^2\psi}{dt^2} + \frac{2m}{\hbar^2}[E - V_0]\psi = 0$$

$$(or) \frac{d^2\psi}{dt^2} - \beta^2\psi = 0 \quad (2)$$

$$Where \quad \beta^2 = \frac{2m}{\hbar^2}[V_0 - E] \quad (since \quad V_0 > E)$$

For both the region, the appropriate solution suggested by Bloch's is of the form is

$$\psi(x) = e^{ikx} u_k(x) \quad (3)$$

Differentiating equation (3) and substituting it in equation (1) and (2) and then further solving it under boundary conditions, we get

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad (4)$$

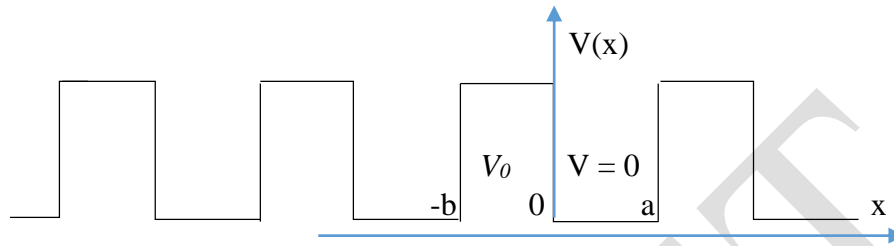
Where $P = mV_0ba / \hbar^2$ is called scattering power of the potential barrier, which is the measure of the strength with which the electrons are attracted by the positive ions.

In equation (4) there are only two variables α and k . we know $\cos ka$ can take values only from -1 to 1, therefore the left hand side of equation (4) must also fall in this range. A plot is made between the LHS of equation (4) and αa for a value of $P = 3\pi/2$ (arbitrary) as shown in figure.

Conclusion

- (i) The energy spectrum has a number of allowed energy bands denoted by solid horizontal line separated by forbidden band gaps denoted by dotted lines
- (ii) The width of allowed energy band increases with the increase in αa

- (iii) When P is increased, the binding energy of the electrons with the lattice points is also increased. Therefore the electron will not be able to move freely and hence the width of the allowed energy band is decreased. Especially for $P \rightarrow \infty$, then allowed energy band becomes infinitely narrow and the energy spectrum becomes a line spectrum as shown in figure.
- (iv) When P is decreased, the binding energy of the electron decreases and thus it moves freely over the lattice points and hence we get a wide range of allowed energy levels as shown in figure
- (v) Thus by varying P from zero to infinity we get the energy spectra of all ranges.



2. Explain free electron approximation and tight binding approximation with suitable diagrams?

Free electron approximation

We know in solids there exists the ionic cores which are tightly bounded to the lattice location, while the electrons are free to move here and there throughout the solid. This is called free electron approximation.

In free electron approximation the following points are observed:

- (i) The potential energy of the electron is assumed to be lesser than its total energy.
- (ii) The width of the forbidden bands (E_g) are smaller than the allowed bands as shown in the figure
- (iii) Therefore, the interaction between the neighbouring atoms will be very strong.
- (iv) As the atoms are closer to each other, the inter atomic distance decreases and hence the wave functions overlap with each other as shown in figure

Tight binding approximation

Tight binding approximation is exactly an opposite approach of discussing the atomic arrangements, when compared to free electron approximation.

Here instead of beginning with solid core, we begin with the electrons, i.e., All the electrons are bounded to the atoms. In other way we say that the atoms are free, while the electrons are tightly bounded. Hence, this is called tight binding approximation

The following points are observed in tight binding approximation:

- (i) The potential energy of the electron is assumed to be almost equal to its total energy.
- (ii) The width of the forbidden bands (E_g) are larger than the allowed bands as shown in the figure

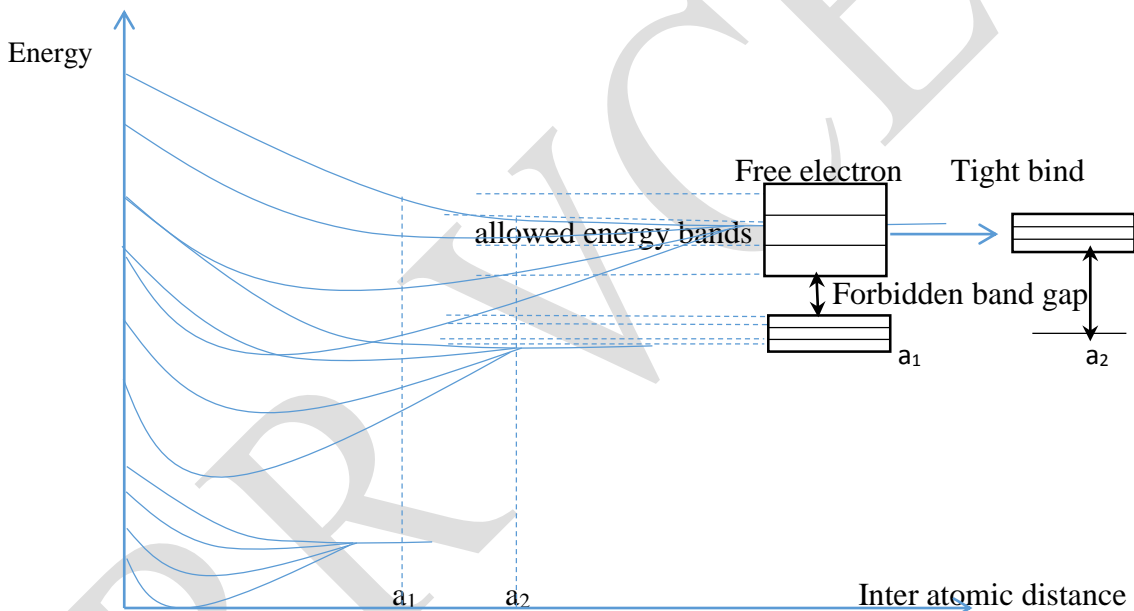
- (iii) Therefore, the interaction between the neighbouring atoms will be weak.
- (iv) As the atoms are not closer, the inter atomic distance increases and hence the wave functions will not overlap with each other as shown in figure

Explanation

Let us consider the atoms with larger inter atomic distance (a_2) as shown in figure. Here the atoms are far apart, and all the bounded electrons have fixed energy levels. Therefore when a solid is formed by using the same element, then the energy levels occupied by the electrons in each atom will be identical, which lead to *tight binding approximation*.

Now, when we bring the atoms closer to each other to form the solid, then inter atomic distance (a_1) decreases. Therefore, the outer shell electrons begin to overlap and the energy levels also splits as shown in figure.

If the inter atomic distance is further reduced, then the splitting of energy level happens for the inner shall electrons also, which lead to *free electron approximation*.



3. Explain zone theory and get the relationship between wave vector and the energy of the electron in a constant potential? Construct first two Brillouin zone for the electron in two dimensional lattice

Brillouin zones are the boundaries that are marked by the values of propagation vector \vec{k} in which the electrons can have allowed energy values without diffraction. since k is a vector, it has different values along different directions.

Explanation:

The relationship between the wave vector and the energy of the electron in constant potential field can be got as follows.

We know, in a length of potential box ' l ' the energy of the electron in a constant potential field.

$$E = \frac{n^2 h^2}{8ma^2} \quad (1)$$

Also, we know that wave vector $k = \frac{n\pi}{a}$ (or) $a^2 = \frac{n^2 \pi^2}{k^2}$ (2)

Substituting equation (2) in (1) we get $E = \frac{k^2 h^2}{8m\pi^2}$ (3)

a plot is made between the total energy 'E' and the wave vector k, for different values of k with $n = \pm 1, k = \pm\pi/a$

$n = \pm 2, k = \pm 2\pi/a, \text{ etc.,}$

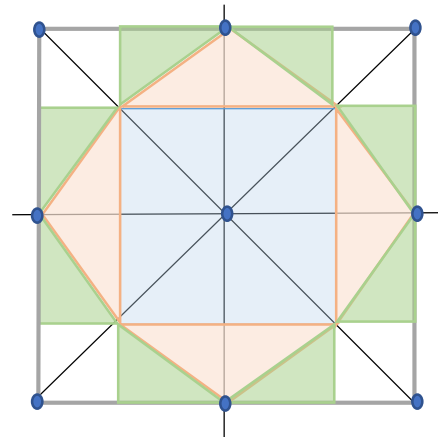
For the above values of k, the curve is obtained as shown in figure, which is in the form of a parabola with discontinuities.

From the figure it can be seen that the energy of the electron increases continuously from 0 to $\pm\pi/a$ then the electron meets the wall and is reflected. This range of allowed energy values in the region between $-\pi/a$ to π/a is called first Brillouin zone. The second allowed energy values consists of two parts: one from π/a to $2\pi/a$ and another from $-\pi/a$ to $-2\pi/a$ is called second Brillouin zone and so on.

Therefore we can conclude that the electron can go from one Brillouin zone to the other only if it is supplied with an energy equal to forbidden gap energy. This forbidden gap is the one which decides whether the solid is an insulator, semiconductor (or) conductor.

Brillouin zone can be constructed by drawing vectors from the origin to the nearest lattice point and then draw Bragg planes perpendicularly between these two points. The region below this plane are said to Brillouin zone.

- First Brillouin Zone ($-\pi/a$ to π/a)
- Second Brillouin Zone ($-2\pi/a$ to $-\pi/a$ & $2\pi/a$ to π/a)
- Third Brillouin Zone ($-3\pi/a$ to $-2\pi/a$ & $3\pi/a$ to $2\pi/a$)



4. Define effective mass of an electron. Deduce an expression for the effective mass. Draw E – k curve and explain the concept of hole?

*Effective mass of an electron is the mass of the electron when it is accelerated in a periodic potential and is denoted by m^**

When an electron of mass m is placed in a periodic potential and if it is accelerated with the help of an electric or magnetic field, then the mass of the electron is not constant, rather it varies with respect to the field applied. That varying mass is called as *effective mass (m^*)*

To study the effect of electric field on the motion of an electron in one dimensional periodic potential, let us consider the Brillouin zone which contains only one electron of charge e in

the state k , placed in an external field 'E'. Due to the field applied the electrons gains a group velocity quantum mechanically and therefore the acceleration changes.

$$\text{The group velocity with which the electron can travel is } V_g = \frac{d\omega}{dk} \quad (1)$$

$$\text{Where } k \rightarrow \text{wave vector; } \omega \rightarrow \text{angular velocity of electron } \omega = 2\pi\nu \text{ (or) } \omega = \frac{2\pi E}{h} \quad (2)$$

Substituting equation (2) in equation (1) we get

$$\text{Group velocity } V_g = \frac{2\pi}{h} \times \frac{dE}{dk} \text{ (or) } V_g = \frac{1}{\hbar} \times \frac{dE}{dk} \quad (3)$$

$$\text{If the electron moving in a crystal lattice with momentum } P, \text{ then the wavelength associated is } \lambda = \frac{h}{p} \text{ (or) } p = \frac{2\pi}{\lambda} \times \frac{h}{2\pi} \text{ (or) } P = \hbar k \quad (4)$$

$$\text{Differentiating equation (4) w.r.t to } t \quad \frac{dP}{dt} = \hbar \frac{dk}{dt} \quad (5)$$

$$\text{(or) } F = \hbar \frac{dk}{dt} \text{ (or) } \frac{F}{\hbar} = \frac{dk}{dt} \quad (6)$$

$$\begin{aligned} \text{we know acceleration } a &= \frac{dV_g}{dt} = \frac{d}{dt} \left[\frac{1}{\hbar} \times \frac{dE}{dk} \right] \\ &= \frac{1}{\hbar} \frac{d^2 E}{dk^2} \times \frac{dk}{dt} \end{aligned} \quad (7)$$

Substituting equation (6) in equation (7), we get

$$a_g = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \times \frac{F}{\hbar} \text{ (or) } a_g = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F \text{ (or) } F = \frac{\hbar^2}{d^2 E / dk^2} a_g \quad (8)$$

Equation (8) resembles with newton's force equation

$$\text{i.e., } F = eE = m^* a \quad (9)$$

Where m^* is the effective mass of the electron.

$$\text{Comparing equation (7) and (8), we can write } m^* = \frac{\hbar^2}{d^2 E / dk^2} \quad (10)$$

Equation (10) represents the effective mass of an electron in a periodic potential, which depend on $\frac{d^2 E}{dk^2}$

Special cases:

(i) If $\frac{d^2 E}{dk^2}$ is +ve, then effective mass m^* is also positive

(ii) If $\frac{d^2 E}{dk^2}$ is -ve, then effective mass m^* is also negative

(iii) If $\frac{d^2E}{dk^2}$ is zero, then effective mass m^* becomes infinity

Negative effective mass (or) concept of hole

To show that the effective mass has negative value. Let us take the Energy - wave vector ($E-k$) of a single electron in a periodic potential. i.e., consider the 1st Brillouin zone (allowed energy band) alone as shown in figure.

In the $E - k$ curve, the band can be divided into two bands viz. upper band and lower band with respect to a point (P) called a **Point of inflection**.

(i) In the **lower band** the value of $\frac{d^2E}{dk^2}$ is a decreasing function from the point of inflection

$\therefore \frac{d^2E}{dk^2}$ is +ve and hence m^* should be +ve in the lower band. If a plot is made between m^* and k for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

(ii) In the **Upper band** of $E - k$ the value of $\frac{d^2E}{dk^2}$ is an increasing function from the point of inflection

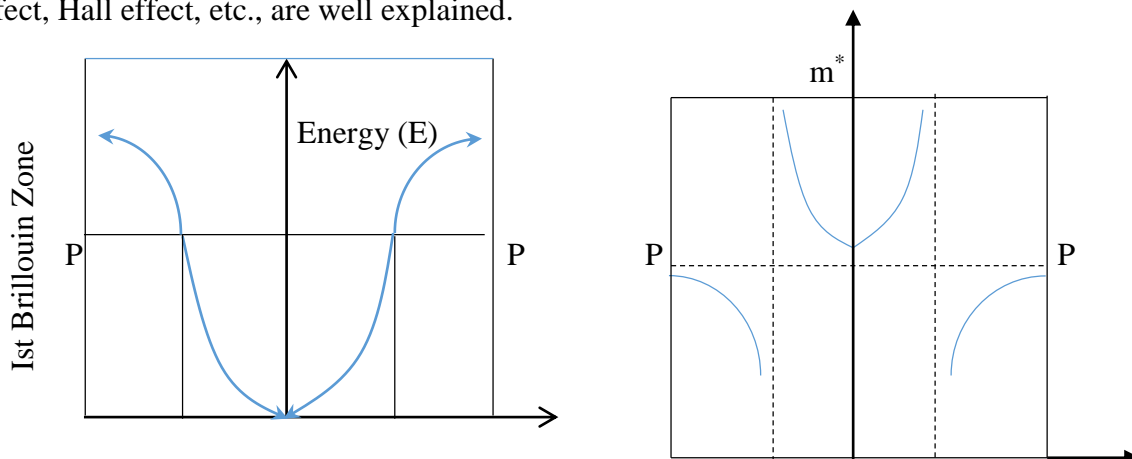
$\therefore \frac{d^2E}{dk^2}$ is -ve and hence m^* should be -ve in the upper band. If a plot is made between m^* and k for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

(iii) **At the point of inflection**, the value of $\frac{d^2E}{dk^2} = 0$ and hence in $m^* - k$ plot, effective mass goes to infinity.

The electron with the negative effective mass is called **Hole**, in other words the electron in the upper band which behaves as a positively charged particle is called hole. It has the same mass as that of an electron but with positive charge.

Therefore, the advantage of the concept of hole is, for a nearly filled band with n number of empty states as shown in figure n number of holes arises

In other words, we can say that the presence of hole is attributed to an empty state, for an electron to be filled. Thus, based on the hole concept several phenomena like Thompson effect, Hall effect, etc., are well explained.

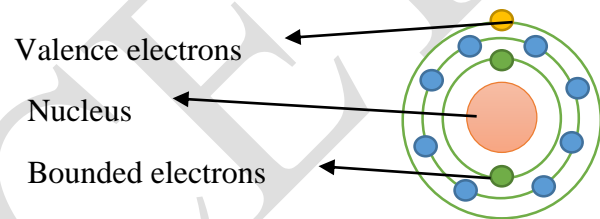


$$-\pi/a \quad -k_0 \quad O \quad k_0 \quad \pi/a \quad K \qquad \pi/a \quad -k_0 \quad O \quad k_0 \quad \pi/a \quad K$$

5. Discuss qualitatively how band theory of solids leads to the classification of solids into conductors, semiconductors and insulators

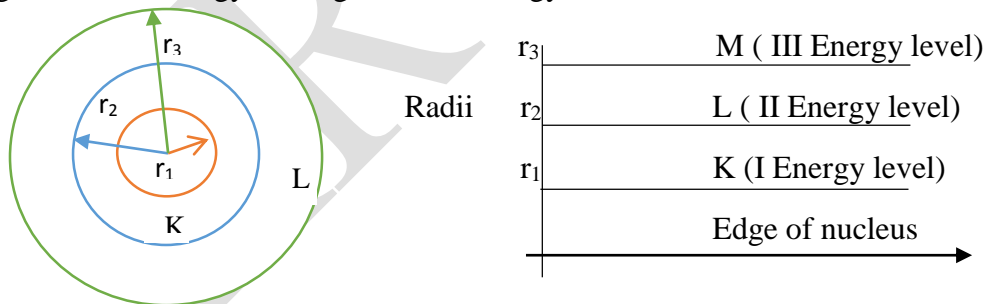
(i) Free and bound electrons

In an isolated atom all the electrons are tightly bounded with the central positive nucleus and revolves around various orbits. The number of electrons the outermost orbit are called *valence electrons*. In the outermost orbits, the attractive force between the nucleus and electrons will be very less, so that the electrons can be easily detached from the nucleus. These detached electrons from the outermost orbits are called *free electrons*. But as far as the innermost orbits are concerned, the electrons are tightly bounded with positive nucleus, and hence they are termed as *bound electrons*.



(ii) Energy levels

We know that each orbit of an atom has fixed amount of energy associated with it. The electrons moving in a particular orbit possess the energy of that orbit. The larger the orbit, the greater is its energy. So, the outermost orbit electrons possess more energy than the inner orbit electrons. A convenient way of representing the energy of different orbits are called *energy levels* as shown in figure. Let E_1 be the energy level of K shell, E_2 be the energy level of L shell, E_3 be the energy level of M shell and so on. The larger the orbit of an electron, the greater is its energy and higher is the energy level.

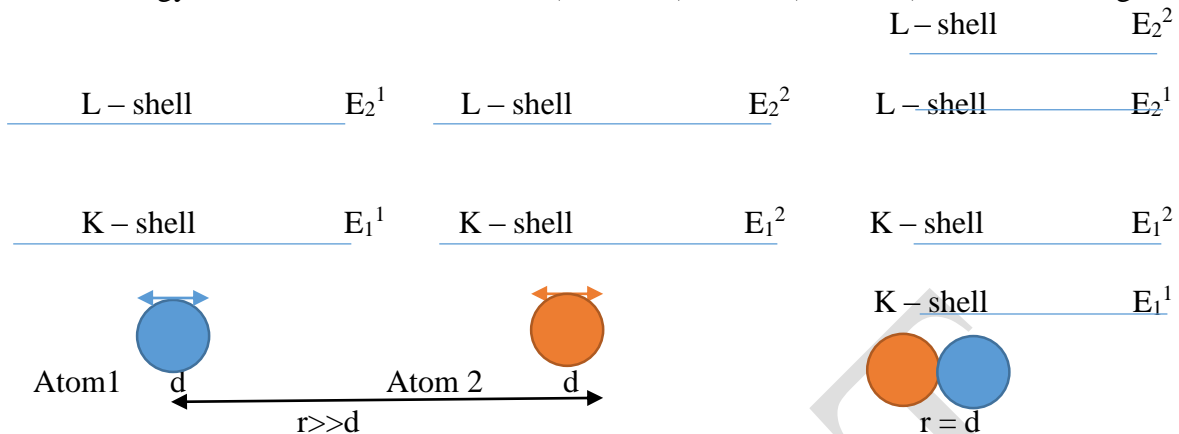


From the figure it is clear that the electrons can revolve only in certain permitted orbits of radii r_1 , r_2 and r_3 etc., and not in any arbitrary orbit. Since the electrons are not allowed in between the radii r_1 and r_2 or between the radii r_2 and r_3 etc., there won't be any electronic energy levels in between those radii so called *forbidden radii*. These unallowed energy levels are called *forbidden energy levels*.

(iii) Energy bands

It has to be noted that as long as the atoms are widely separated, they have identical energy levels. But, once the atoms are brought together the interatomic force of attraction between the atoms in the solid may modify the energy levels of a solid as energy bands. Now let us discuss how energy levels of single free atom becomes bands in solids.

Let us consider two identical atoms of diameter (d) separated at a distance (r), so that the electronic energy levels of one atom [$E_1^1(K - shell)$ and $E_2^1(L - shell)$] do not affect the electronic energy levels of the other atom [$E_1^2(K - shell)$ and $E_2^2(L - shell)$] as shown in figure



Now when the atoms are brought closer to each other, some force of attraction occurs between them and according to quantum mechanics, their wave functions will start overlapping. Therefore when two atoms are brought closer, it does not remain as two independent atoms, rather it forms a **single two-atom** system with two different energy levels to form an energy band as shown in figure.

Origin of energy band formation in solids

We know that when two atoms of equal energy levels are brought closer to each other, the original energy levels *viz* E_1 and E_2 split each into two energy levels. i.e., the K-shell energy E_1 splits into E_1^1 and E_2^1 . Similarly the L-shell energy E_2 splits into E_1^2 and E_2^2 . Now when three atoms are brought closer together, the original energy levels *viz* E_1 and E_2 split each into three energy levels *viz* E_1^1 , E_1^2 , and E_1^3 and E_2^1 , E_2^2 , and E_2^3 respectively. This type of transformation from the original energy levels into two (or) more energy levels is known as *Energy level splitting*.

Energy bands

Therefore, if ' N ' number of atoms of equal energy levels are brought closer to form a solid, then it forms a closely spaced continuous energy level, so called **energy bands**.

Hence an energy band can be defined as, *the range of energies possessed by an electron in a solid*. The magnified view of the energy band which consists of a large number of very closely spaced energy levels as shown in figure.

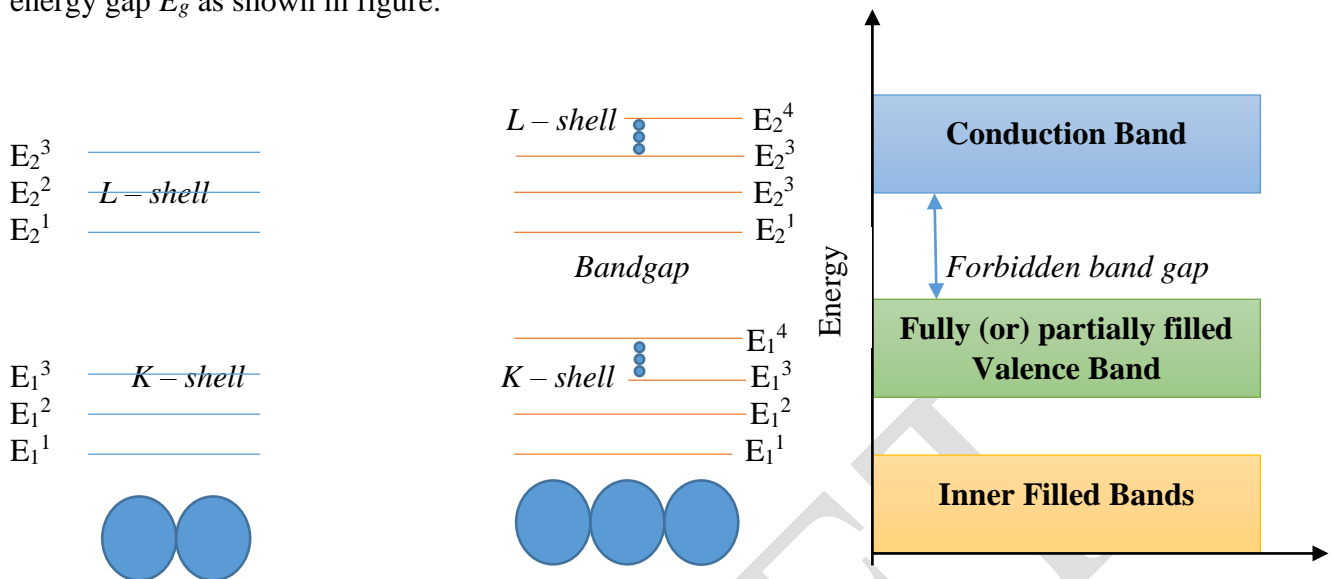
Inner Filled Bands, Valence band and Conduction band

During the formation of energy bands, the inner filled energy levels form an energy band called *inner filled bands*. Similarly the electrons in the outermost shells of atoms form an energy band called *valence band*. The valence band will be completely filled (or) partially filled with electrons, based on the type of materials.

If an electron comes out from the valence band for conduction, then they form an energy level corresponding to the energy band called *conduction band*.

Forbidden gap

While referring to energy bands, they are separated by small regions which does not allow any energy levels. Such regions between the energy bands are called forbidden gaps (or) forbidden energy gap E_g as shown in figure.



Based on band theory and the presence of forbidden band gap the materials are classified in to three categories viz:

(i) **Metals (or) Conductors**

Here, there is no forbidden band gap. Hence the valence band and conduction band overlap with each other. Since the free electron are relatively available in large number, even a small external field induces the electrons from the valence band to conduction band and hence conduction easily occurs.

Example: Copper, Aluminium, etc.

(ii) **Semiconductors**

Here, the forbidden band gap is small (say 0.5 to 1.5 eV) and hence the width of forbidden gap is smaller than allowed energy bands. Generally, the free electrons in valence band is comparatively less compared to conductors because of finite forbidden gap and hence the semiconductor requires external field with energy greater than or equal to this forbidden gap energy such that conduction process occurs.

Example: Germanium, Silicon, etc.

(iii) **Insulators**

Here the width of the forbidden gap is wider (say 3 to 5.47 eV) and hence the width of forbidden gap is larger than allowed energy bands. Therefore in case of insulator, a sufficiently large energy is required for conduction to occur.

Example: Diamond, Dielectrics, etc,