

BAND THEORY

In free electron theory it was assumed that the electrons move freely inside a region of constant potential. The free electron theory is able to explain the observed phenomena such as electrical conductivity, thermionic emission etc but it fails to explain why some materials are good conductors while some are insulators and semi conductors.

In order to explain the conductivity shown by different materials, it is necessary to incorporate the variation of potential inside the crystal due to the presence of positive ion cores in the free electron model. It may be assumed that the potential inside a crystal to be periodic with the periodicity of lattice.

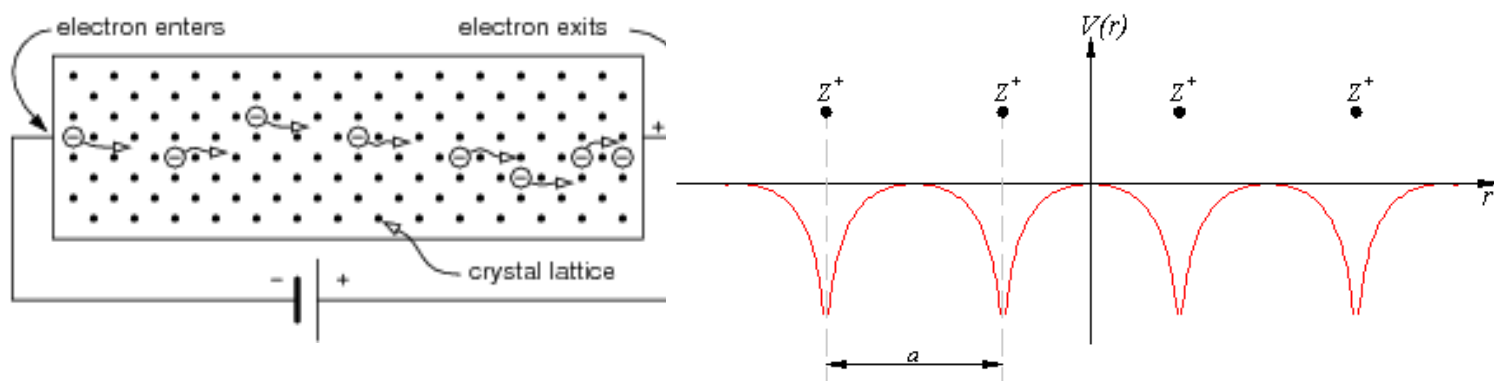


Fig-1

The potential is minimum at the +ve ion sites and maximum between the two ions.

The one dimensional Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} [E - V(x)]\psi = 0 \quad \dots\dots\dots(1)$$

The potential $V(x)$ is periodic with lattice constant

$$V(x) = V(x+a) \quad \dots\dots\dots(2)$$

Bloch has shown that the one dimensional solution of the Schrödinger equation takes the form

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

These solutions are called Bloch Functions. The free electron waves are modulated by the periodic function $U_k(x)$ where $U_k(x)$ has the same periodicity as that of the lattice.

$$U_k(n) = U_k(x + a) \dots\dots\dots(4)$$

$$\psi(x+a) = e^{ikx(x+a)} U_k(x+a) \dots\dots\dots(5)$$

Applying (4)

$$\psi(x+a) = e^{ika} e^{ikx} U_k(x) \dots\dots\dots(6)$$

$$\psi(x+a) = e^{ika} \psi(x) \dots\dots\dots(7)$$

The complex conjugate equation is

$$\psi^\square(x+a) = e^{-ika} \psi^\square(x) \dots\dots\dots(8)$$

(7) × (8) ⇒

$$\text{ie } \psi(x+a)\psi^\square(x+a) = \psi(x)\psi^\square(x) \dots\dots\dots(9)$$

Thus $e^{ika} = 1$

$$\cos ka + i \sin ka = 1$$

$$\text{S } \sin ka = 0 \quad \text{ie } ka = \pm n\pi$$

$$\therefore k = \pm \frac{n\pi}{a}$$

$$\text{If } n = 1 \quad k = \pm \frac{\pi}{a}$$

The range $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ is known as the first Brillouin zone.

Kroneig – Penny Model

If we assume a well defined potential for $V(n)$, the relationship between Energy E and k can be frond out. In Kronieg – Penny Model the crystal potential is assumed to be a periodic square well potential.

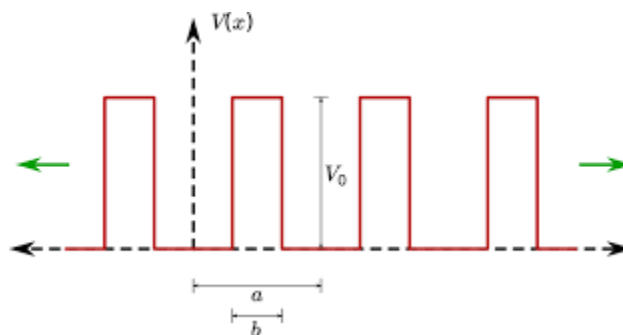


Fig-2

The Schrödinger equation for region I where $V(x) = 0$ is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} E\psi = 0 \dots\dots\dots(1) \quad 0 < x < a$$

$$\text{ie } \frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \dots\dots\dots(2)$$

where $\alpha^1 = \frac{8\pi^2 mE}{h^2}$ (3)

In region II Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V_0)\psi = 0$$
(4)

$$-b < x < 0$$

Where $V(x) = V_0$ (5)

$$(4) \Rightarrow \frac{d^2\psi}{dx^2} - \beta^2\psi = 0$$
(6)

Where

$$\beta^2 = \frac{8\pi^2 m}{h^2} (V_0 - E)$$
(7)

The solution for equation (2) can be written as

$$\psi_1(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$$
(8)

$$\psi_2(x) = Ce^{\beta x} + Ee^{-\beta x}$$
(9) $E < V_0.$

Where A, B, C and D are constants where values can be found out by applying boundary conditions.

The wave function ψ has to be well behaved. This requires that both ψ and $\frac{d\psi}{dx}$ has to be continuous through out the crystal.,

ie $\psi_1(x)|_{x=0} = \psi_2(x)|_{x=0}$ (10)

$$\frac{d\psi_1(x)}{dx}|_{x=0} = \frac{d\psi_2(x)}{dx}|_{x=0}$$
(11)

and

$$\psi_1(x)|_{x=0} = \psi_2(x)|_{x=-b}$$
(12)

$$\frac{d\psi_1(x)}{dx}|_{x=0} = \frac{d\psi_2(x)}{dx}|_{x=-b}$$
(13)

Applying Bloch solutions

$$\psi_k(x) = e^{ikx} U_k(x)$$
(14)

$$\therefore \psi_k(x+a+b) = e^{ik(x,a+b)} U_k(x+a+b)$$
(15)

$$\psi_k(x+a+b) = e^{ikx} \cdot e^{ik(a+b)} U_k(x)$$
(16)

ie $\psi_k(x+a+b) = e^{ik(a+b)} e\psi_k(x)$ (17)

or $\psi_k(x) = \psi_k(x+a+b) e^{-ik(a+b)}$ (18)

Applying this at $n = -b$ and $x = a$ we get

$$\psi_2(-b) = \psi_1(a) e^{-ik(a+b)}$$
(19)

$$\frac{d\psi_2}{dx}|_{n=-b} = \left(\frac{d\psi_1}{dx} \right)_{n=a} e^{-ik(a+b)}$$
(20)

Applying boundary conditions for equations (10) (11) (19) and (20) we get

$$A + B = C + D \quad \dots\dots\dots(21)$$

$$i \times (A - B) = \beta(C - D) \quad \dots\dots\dots(22)$$

$$C e^{-\beta b} + D e^{\beta b} = e^{-ik(a+b)} (A e^{i\alpha a} + B e^{-i\alpha a}) \quad \dots\dots\dots(23)$$

$$\beta c e^{-\beta b} + \beta D e^{\beta b} = i\alpha e^{-ik(a+b)} [A e^{i\alpha a} - B e^{-i\alpha a}] \quad \dots\dots\dots(24)$$

The above equation will have non-vanishing solutions if and only if the determinant of the coefficient A, B, C and D vanishes ie

$$\begin{vmatrix} 1 & 1 & -1 & -1 \\ i\alpha & -i\alpha & -\beta & \beta \\ -e^{-ik(a+b)+i\alpha a} & -e^{ik(a+b)-i\alpha a-\beta b} & e^{-\beta b} & e^{\beta b} \\ -i\alpha e^{ik(a+b)+i\alpha a} & i \times e^{-ik(a+b)-i\alpha a} & \beta e^{-\beta b} & -\beta e^{\beta b} \end{vmatrix}$$

On simplifying this determinant we get

$$\cos k(a+b) = \left(\frac{\beta^2 - \alpha^2}{2 \times \beta} \right) \sin \alpha a \sinh \beta b + \cos \alpha a \cosh \beta b \quad \dots\dots\dots(26)$$

In order to solve this equation further kroneig introduced the delta function ie as $b \rightarrow 0$ $V_0 \rightarrow \infty$ so that the product $V_0 b$ remains finite.

Under these assumptions as $b \rightarrow 0$

$$\sinh \beta b \rightarrow \beta b \quad \cosh \beta b \rightarrow 1$$

\therefore (26) because

$$\cos ks = \frac{\beta^2 - \alpha^2}{2 \times \beta} \beta b \sin \alpha a + \cos \alpha a \quad \dots\dots\dots(27)$$

$$\beta^2 - \alpha^2 = \frac{8 \pi^2 m}{h^2} (V_0 - E) - \frac{8 \pi^2 m E}{h^2} \quad \dots\dots\dots(28)$$

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

But $V_0 \gg E$

$$\beta^2 - \alpha^2 \approx \frac{8 \pi^2 m}{h^2} V_0 \quad \dots\dots\dots(29)$$

Thus eqn. (27) because

$$\cos ka = \frac{8 \pi^2 m V_0 \beta b}{2 \alpha \beta h^2} \sin \alpha a + \cos \alpha a \quad \dots\dots\dots(30)$$

$$\text{ie } \cos ka = \frac{4 \pi^2 m a}{h^2} V_0 b \frac{\sin \alpha a}{\alpha a} + \cos \alpha a \quad \dots\dots\dots(31)$$

$$\text{ie } \cos a = P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a \quad \dots\dots\dots(32)$$

$$\text{where } P = \frac{4 \pi^2 m a}{h^2} V_0 b$$

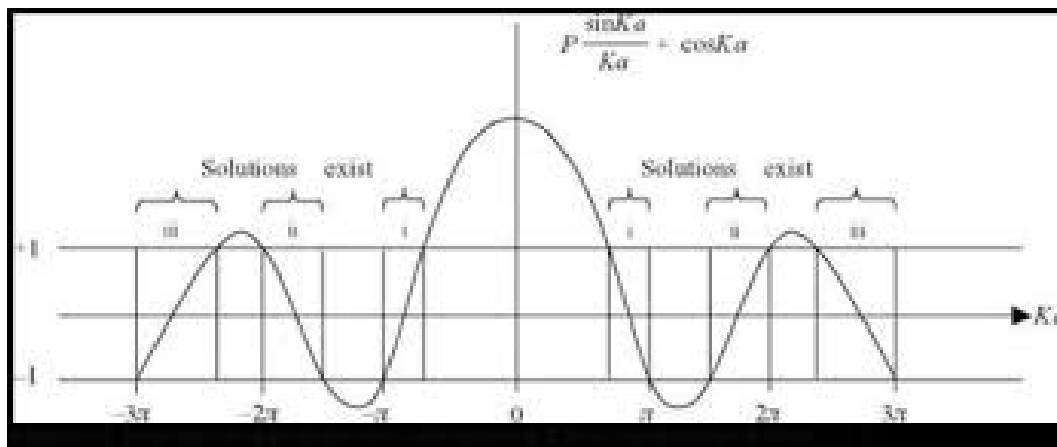


Fig-3

The LHS of equation (32) contains $\cos ka$ where values are restricted +1 to -1.

As a result of this restriction only certain values of $\alpha \left(\alpha = \frac{8\pi mE}{h^2} \right)$ and hence value

of E are allowed. For a specific value of E, $\cos ka$ can have only one value. Also $\cos ka$ is an even periodic function, it will have the same value whether ka is +ve or -ve or is increased by multiples of 2π . Thus total energy $E_{(a)}$ of the electron is an even periodic function of k with a period of $\frac{2\pi}{a}$

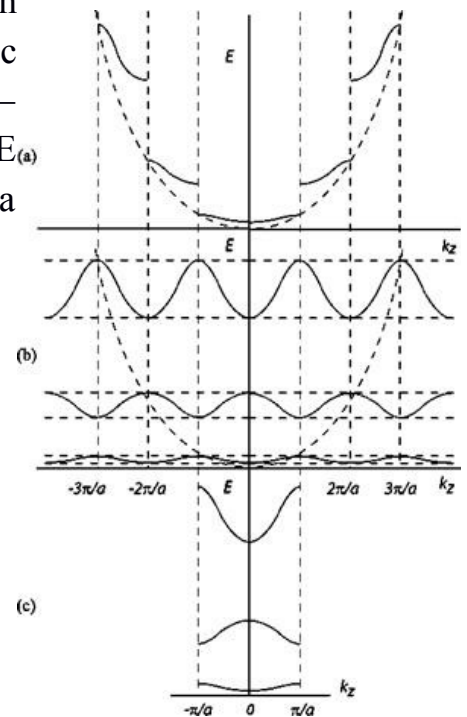


Fig-4

Inferences

1. The motion of electrons in a periodic lattice is characterized by allowed bands separated by forbidden regions.
2. As αa increases ie as Energy E increases the width of allowed band also increases and width of forbidden band decreases.
3. The quantity P is a measure of V_0b and it signifies the strength of the potential barrier. V_0b gives the area of the potential barrier. If P is large ie V_0b is large

the allowed bands became narrower and forbidden band became wider. The electron is trapped in the potential well affecting its energy values.

As $P \rightarrow \infty$ but $\cos ka \rightarrow \pm 1$ (Max. value)

Hence

$$\frac{\sin \alpha a}{\alpha a} \rightarrow 0$$

ie $\sin \alpha a = 0$

ie $\alpha a = \pm n\pi$

ie $\alpha^2 a^2 = n^2 \pi^2$

ie $\alpha^2 = \frac{n^2 \pi^2}{a^2}$

ie $\frac{8\pi^2 mE}{h^2} = \frac{n^2 \pi^2}{a^2}$

$\therefore E = \frac{n^2 h^2}{8ma^2}$

$n = 0, 1, 2, 3, \dots$

Thus the spectrum becomes discrete for high values of P.

If $P \rightarrow 0$ Then eqn. (32) yields

$\cos ka = \cos \alpha a$

$\alpha a = ka$

ie $\alpha^2 = k^2$

ie $\frac{8\pi^2 mE}{h^2} = k^2$

or $E = \frac{h^2 k^2}{8\pi^2 m}$

But $k = \frac{2\pi}{\lambda}$

$$E = \frac{h^2}{8\pi^2 m} \left(\frac{2\pi}{\lambda} \right)^2 = \frac{h^2}{8\pi^2 m} \cdot \frac{4\pi^2}{\lambda^2}$$

$$E = \frac{h^2}{2m} \cdot \frac{p^2}{h^2} = \frac{p^2}{2m}$$

$$p = \frac{h}{\lambda}$$

$$E = \frac{1}{2} mV^2$$

ie the electron behaves as a free particle having only kinetic energy.

Construction of Brillouin Zones

The Brillouin zones represent the permissible values of k of the electrons in one, two and three dimensions. This concept provides a way to understand the origin of allowed and forbidden bands.

Consider the motion of an electron through an one dimensional lattice. The periodicity of the lattice results in the energy spectrum of have allowed and forbidden bands.

From Kronig – Penny model theory

$$\cos ka = \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a$$

The maximum permitted values occur when

$$\cos ka = \pm 1$$

Ie $ka = \pm n\pi$ ie $k = \pm \frac{n\pi}{a}$

Where $n = 1, 2, 3, \dots$

At these values of k , a small increase in electron momentum will increase the energy so that it can jump from the top of one allowed band to the bottom of the next.

For one dimensional lattice the Brillouin zones are as shown in figure.

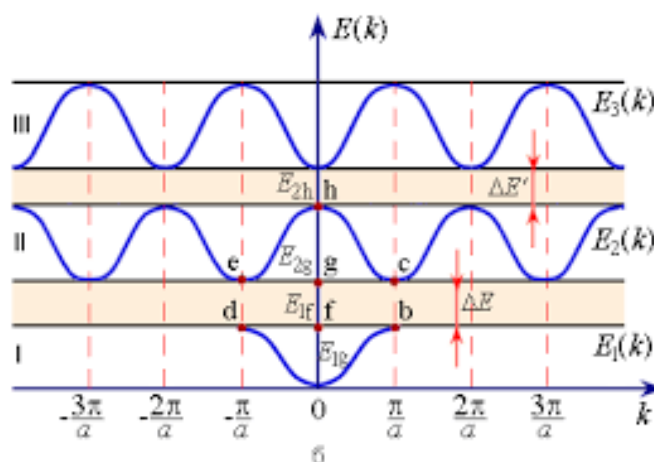


Fig-5

In the case of a two dimensional square lattice,

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

Low energy electrons have long wavelengths so that $\lambda \gg a$, the lattice spacing and travels freely through the crystal without getting diffracted. But electrons with sufficient energy i.e. the electrons near the Fermi surface, will have comparable wavelength with inter-atomic spacing i.e. $\lambda \approx a$ such electrons will get diffracted according to Bragg relation

$$n\lambda = 2a \sin \theta \quad n = 1, 2, 3, \dots$$

Where θ is the angle of diffraction.

For the 1st zone $k_x = \pm \frac{\pi}{a}$ and $k_y = \pm \frac{\pi}{a}$

$$k = k_x \hat{i} + k_y \hat{j}$$

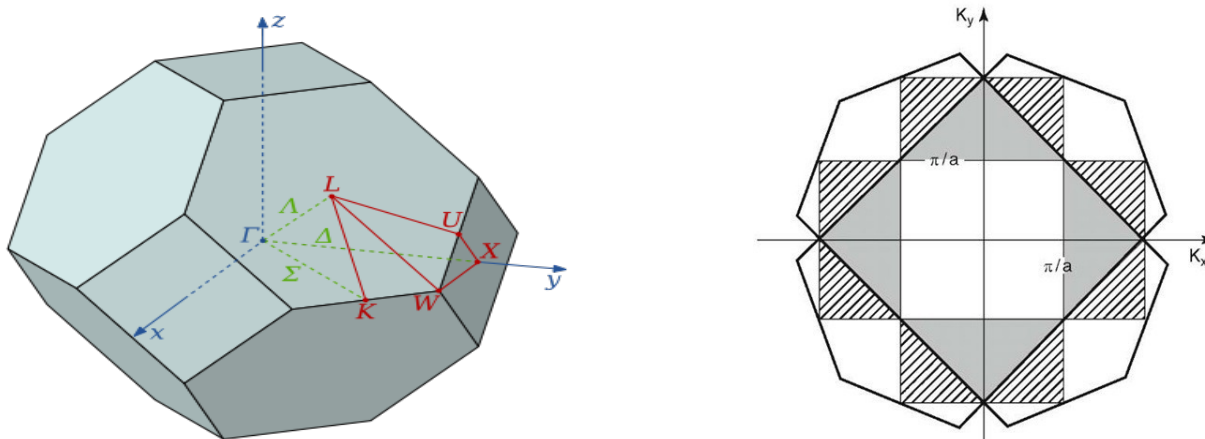


Fig-6

In three dimensions, the Brillouin zones can be evaluated using equation.

$$n_1 k_x + n_2 k_y + n_3 k_z = \frac{\pi}{a} (n_1^2 + n_2^2 + n_3^2)$$

In the case of simple cubic lattice, the first Brillouin zone is also a cube whose walls will intersect at the k_x , k_y and k_z axes at the points $\pm \frac{\pi}{a}$.

Conductors, semiconductors and Insulators

It is seen from the band theory that there are allowed and forbidden bands. The outer most filled band is called the valence band and the band above valence band is called conduction band.

According to the nature of band occupation by electrons, the solids can be grouped into two.

In the first group, there is a partially filled band immediately above the valence band. This is possible in two ways. In the first case valence band is partially filled or a completely filled valence band overlaps a partially filled conduction band. These solids act as metals which are very good conductors. Hence metals have partially filled or overlapping bands. Monovalent metals like Cu, Ag and Au have only one electron in the outermost shell and have partially filled bands. But in divalent metals such as Be, Mg, Ca have overlapping valence and conduction bands.

In the second group, there are empty bands lying above completely filled bands. These solids can be insulators or semi conductors depending on band gap. Solids with band gaps greater than 5eV behave as insulators while with an $E_g < 3\text{eV}$ they behave as semiconductors.

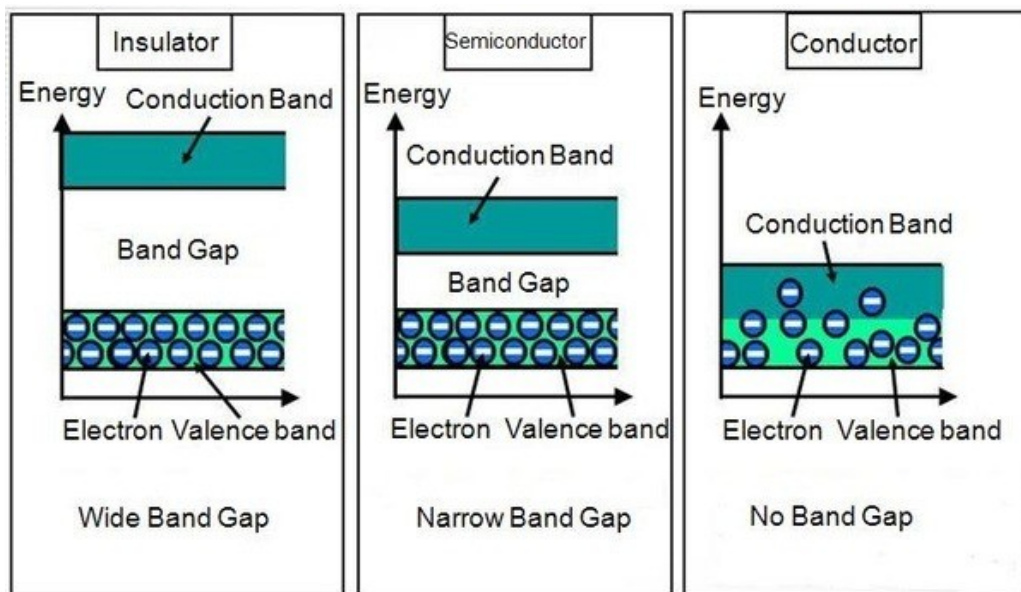


Fig-7

Magnetic properties of Materials

The Magnetic properties of materials have attracted the attention of physicists, Engineers and chemists for many years. These magnetic materials have wide ranging technological applications such as transformer cores, recording media in magnetic tapes etc.

Consider two charges $+q$ and $-q$ separated by a distance d . They form a magnetic dipole where moment is given by

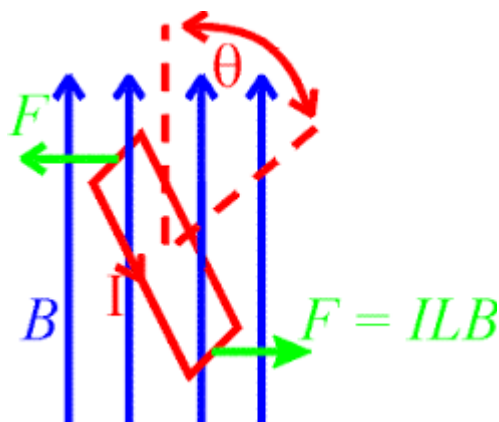


Fig-8

$$\mu_m = qd$$

Where d is a vector joining negative to +ve charge. If such a magnetic dipole is placed in a magnetic field of induction B it experiences a torque τ

$$\vec{\tau} = \vec{\mu}_m \times \vec{B}$$

The effect of the torque is to turn the dipole and align it with the field. Because of this torque the dipole has an orientation potential energy given by

$$V = \vec{\mu}_m \cdot \vec{B} = \mu_m B \cos \theta$$

Here minimum energy occurs at $\theta = 0$ where $V = -\mu_m B$ when the dipole lies along the field. The maximum comes when $\theta = 180^\circ$ where $V = \mu_m B$ as $\cos 180 = -1$ and the dipole is oriented opposite to the field.

All the known magnetic properties of matter are attributed to the rotation of electrical charges. An electric current loop acts like a magnetic dipole of dipole moment.

$$\mu_m = IA$$

Where I is the current and A is the area of the loop. The direction of $\vec{\mu}_m$ is normal to the plane of the loop.

The current loops in an atom are composed of rotating electrons.

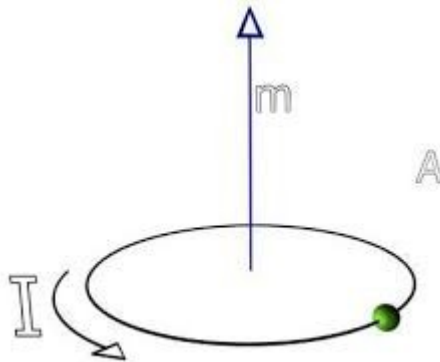


Fig-9

$$I = e \frac{w}{2\pi} \left[I = \frac{q}{t} T = \frac{2\pi}{w} \right]$$

$$A = \pi r^2 \quad L, \text{ angular momentum} = mr^2 w$$

$$\therefore \vec{\mu}_m = \left(\frac{-e}{2m} \right) \vec{L}$$

The -ve sign indicates that direction of \vec{L} is opposite to that of $\vec{\mu}_m$

The coefficient $(-e/2m)$ is called gyromagnetic ratio.

In addition to orbital motion electron also rotates about its own axis called spin. There is a magnetic moment associated with the spin motion. This moment is associated with spin angular momentum \vec{S} by the relation.

$$\vec{\mu}_m = \left(\frac{-e}{m} \right) \vec{S}$$

Thus the spin gyro-magnetic ratio is $-e/m$, twice the value obtained for orbital motion. This is a classical picture and does not apply to spin motion as it is entirely quantum nature.

Considering the motion of a dipole in a magnetic field, the eqn. of motion is

$$\frac{d\vec{L}}{dt} = \vec{\tau}$$

$$\tau = \mu_m \times B \quad \text{and} \quad L = \left(\frac{-2m}{e} \right) \vec{\mu}_m$$

We get

$$\frac{d\vec{\mu}}{dt} = \left(-\frac{e}{2m} \right) \vec{\mu} \times \vec{B}$$

This equation represents precessional motion of dipole with frequency

$$\omega_L = \frac{eB}{2m}$$

This frequency is called Larmor frequency and the precession is called Larmor precession. Thus the dipole precesses around the direction of the field always maintaining the same angle.

During this precession the dipole simply rotates around \vec{B} without ever getting closer to the field. In pure Larmor precession no alignment takes place. In practical situations, during this precession there will be numerous collisions, during which dipole loses energy. Then it gradually approaches to the direction of B and finally aligning with B . This process of gradual magnetization is called relaxation.

The potential energy of the dipole is

$$E = \frac{e}{2m} L_z B$$

Here B is taken to be in the Z direction and L_z is the z -component of angular momentum.

But according to quantum mechanics the component of L_z is quantized

$$\text{ie } L_z = m_l \hbar$$

Where m_l is an integer taking values such as $-l, -l+1, \dots, l-1, l$ where l is the orbital quantum number.

$$E = \frac{e\hbar}{2m} B m_L$$

The ratio $\frac{e\hbar}{2m} = \mu_B$ is called the Bohr magneton and has value $9.3 \times 10^{-24} \text{ Jm}^2/\text{wb}$

ie $E = \mu_B B m_L$

m_l takes $(2l + 1)$ values in the presence of a magnetic field. For $l = 1$ $m_L = 0, 1, -1$ and a single level splits into three in the presence of magnetic field.

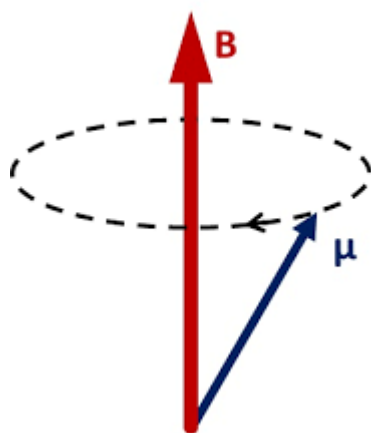


Fig-10

When $m_L = 0$

$$E_1 = 0$$

When $m_L = 1$

$$E = \mu_B B m_L \quad \therefore E_2 - E_1 = \mu_B B$$

This splitting of levels in the presence of magnetic field is referred to as Zeeman splitting. The separation between levels is given by

$$\Delta E = \mu_B B$$

At lowest level $m_L = -1$ \vec{L} is opposite to that of \vec{B} and $\vec{\mu}$ is parallel to \vec{B} .

In the case of spin motion

$$E = 2\mu_B B M_s$$

Where factor 2 arises from the fact that gyro-magnetic ratio for spin is twice the classical value.

For $S = \frac{1}{2}$ $M_s = -\frac{1}{2}$ and $+\frac{1}{2}$

Thus difference in energies are

$$\Delta E = 2 \mu_B B$$

Energy Levels for a Nucleus with Spin Quantum Number 1/2

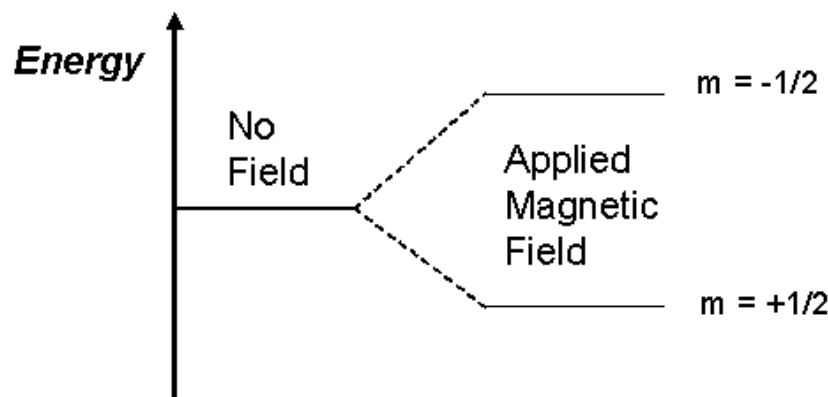


Fig-11

Thus the spin separation is double that of orbital separation.

In this case spin and orbital motion are treated separately. But actually there will be interaction between the two and they should be treated simultaneously.

References:

1. Simon L Altmann - Band theory of solids.
2. John Singleton - Band Theory and Electronic Properties of Solids.
3. MIT-Notes (https://www.google.co.in/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjvnlqxlcljaAhVLKY8KHfsgA4IQFggoMAA&url=https%3A%2F%2Focw.mit.edu%2Fcourses%2Fmaterials-science-and-engineering%2F3-091sc-introduction-to-solid-state-chemistry-fall-2010%2Felectronic-materials%2F13-band-theory-of-solids%2FMIT3_091SCF09_lec13.pdf&usg=AOvVaw3mNqFzPMt9FkWvEqNwXqRz)
4. MIT-Videos(<https://ocw.mit.edu/courses/materials-science-and-engineering/3-091sc-introduction-to-solid-state-chemistry-fall-2010/electronic-materials/13-band-theory-of-solids/>)

