CHAPTER-II

Theory of Plasmon Satellites in Solid
2.1 Introduction :-

In 1982 Langmuir [37] first time used the word plasma for a system composed of a very large number of positive and negative charges with total charge equal to zero. Examples of such system are ionosphere and hot gaseous discharges etc. Which are characterized by high temperature, low electron density (= $10^{12}$ cc) and obey Maxwell Boltzmann statistics. This is called as "classical plasma". Due to thermal fluctuation in the electron density, longitudinal oscillations are set up in the plasma. Langmuir [37] called these oscillations as plasma oscillations. Tonk and Langmuir [38] have derived the frequency of the plasma oscillation in 1929 as-

$$\omega_p = \left(\frac{4\pi ne^2}{m}\right)^{1/2}$$  \hspace{1cm} (2.1)

Where, $n$ is the average density of electrons for a typical gas discharge, $\omega_p$ is of the order of $10^{10}$ Hz.

Following definition of plasma by Langmuir [37], a metal can also be regarded as a plasma because a metal is a system of positive ions arranged on a crystal lattice, together with a valence of conduction electrons which are more or less free to travel throughout the lattice. The negative charge of the electrons gas is balanced by an equal concentration of positive charge of ion cores. In a metal the
electron density in very high of the order of $10^{22}$/cc, temperature is very low and obeys the quantum statistics. Thus metal is example of "Quantum Plasma". In a metal the plasma oscillations can be excited if a charge imbalanced is created by an incident electron or X-ray photon etc. The existence of plasma oscillations in a metal was first suggested by Steenbeck [39] in 1932 and by Kronig and Korringa [40] in 1943, who treated the energy losses of charged particles passing through metals from the point of view of plasma oscillations in a metal. The full significance of the plasma oscillation in metal was realized by Bohm and Pines [41-43].

2.2 Interaction of Electrons in metals:

Sommerfield [44] assumed that the electrons in a metal do not interact with each other and behave as a gas. This model has been very successful qualitatively and in many cases quantitatively in predicting metallic behavior. But there are some properties like cohesive energy etc., which can be explained only if we assume that the electrons do interact in metal. If we take account of the coulomb interaction between the electrons for calculating the cohesive energy, the agreement between the calculated and experienced values get worse. It was Bohm and Pines [41-43] who showed, for the first time that the various difficulties have their origin in the long range of the coulomb force between the electrons. In dividing point between the two ranges is the Debye length. For phenomena electrons show independent particle behavior which is equivalent to Sommerfield
free electron gas model. Bohm and Gross [45] have also shown that the static disturbance in a plasma could not be shielded out in a distance less than Debye length. Thus, the individual particle component represents the fluctuations, arising from randomly moving individual particles. This behavior is due to the short range screened coulomb force. They interact just like two body collision. For phenomena involving distances greater most suitably categorized by a set of harmonic oscillations, which represent the plasma oscillation. This behavior is due to the long-range part of the coulomb force, which is strong enough to influence the motion of many electrons simultaneously. That is, each particle interacts simultaneously with all other particles. Thus the electrons in a metal are capable of displaying both collective and independent particle behavior. This model of Bohm and Pines [41-43] has been very successful in explaining the cohesive energy of a metal. Thus experimental and theoretical investigation of the electrons in a metal show that they display a high degree of correlation their motion, so much so that in many regard the plasma behaves more like a liquid (called Fermi liquid or quantum liquid) than like a gas.

The existence of plasma oscillation in metals and its frequency can be derived by-

1. Classical method
2. Quantum mechanical method
3. Dielectric method
First of all a dielectric method is adopted as it is good for metals, dielectric and semiconductor etc., and then the quantum mechanical procedure is followed

2.3 Plasma Oscillations: Dielectric Theory:

The dielectric constant for solid is a measure of the interaction between incident electromagnetic radiations and the electrons of the solid. This interaction has a frequency dependency that varies in nature from solid to electrostatic screening of the coulomb interaction, and the dynamic response leads to the characteristic metallic reflection of light and to the excitation of plasma. Fermi [46], Budini [47-48] and Sternheimer [49-51] have given a simple model of a dielectric. Frohlich [52] have given a simple model of a dielectric and has considered the dielectric constants \( \varepsilon \) as a complex quantity.

\[
\varepsilon = \varepsilon_1 + \varepsilon_2
\]  

(2.2)

On the application of an electric field the electrons bound to the atom will be disturbed, thus the dielectric constant gives an idea how the incident electromagnetic waves will modify the system concerned. Now the equation of motion for an electron in a solid acted on by an electric field \( E(x, t) \) is given by Kittel [58], Slater and Frank [66].

\[
\frac{md^2x}{dt^2} + \gamma \frac{dx}{dt} = -e E(x, t)
\]  

(2.3)

Where, \( \gamma \) is the damping constant -

\[
\gamma = \frac{1}{\tau}
\]  

(2.4)
Here, $\tau$ is the life time of an excited state produced by an external force and also known as relaxation time. If the variation of $E$ and $x$ is as $e^{-i\omega \tau}$. Then the value will be-

$$x = \frac{eE}{m} \left( \frac{1}{\omega^2 + i\gamma \omega} \right)$$  \hspace{1cm} (2.5)

Now the dielectric constant is calculated as-

$$\epsilon(\omega) = \frac{D(\omega)}{E(\omega)} = \frac{E + 4\pi p}{E}$$  \hspace{1cm} (2.6)

Where, $P$ is the Polarisation for $n$ electrons per unit volume and is defined using equation (2.5) as -

$$P = -nex = -\frac{ne^2E}{m} \frac{1}{(\omega^2 + i\gamma \omega)}$$  \hspace{1cm} (2.7)

With the help of equation (2.7), equation (2.8) will become as

$$\epsilon(\omega) = 1 - \frac{4\pi ne^2}{m} \frac{1}{(\omega^2 + i\gamma \omega)} \hspace{1cm} or$$

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}$$  \hspace{1cm} (2.8)

Where, $\omega_p = \left(\frac{4\pi ne^2}{m}\right)^{1/2}$, the plasma frequency in terms of relaxation time and the equation (2.8) can be written as-

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\left(\frac{\omega^2 + i\omega}{\tau}\right)}$$

$$= -\frac{\omega_p^2\tau}{(\omega^2\tau + i\omega)}$$  \hspace{1cm} (2.9)
If \( n \) is refractive index and \( \beta \) is the excitation coefficient for absorption then, according to Savier [54] the dielectric constant is written as-

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2 = (n + i\beta)^2
\]

\[
= 1 - \frac{\omega_p^2\tau}{\omega^2\tau + i\omega}\quad (2.10)
\]

or

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2 = n^2 - \beta^2 + 2i\beta
\]

\[
= 1 - \frac{2\omega_p^2\tau^2}{1 + \omega^2\tau^2} + \frac{i\omega_p^2\tau}{\omega(1 + \omega^2\tau^2)}
\]

Separating the real and imaginary parts-

Real \( \varepsilon (\omega) = \varepsilon_1 = n^2 - \beta^2 \)

\[
= 1 - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2}\quad (2.11)
\]

 Imaginary \( \varepsilon (\omega) = \varepsilon_2 = 2i\beta \)

\[
= \frac{\omega_p^2\tau}{\omega(1 + \omega^2\tau^2)}\quad (2.12)
\]

In the case of bound electrons in solids such as semiconductors and insulators, one has to take account of the periodic potential of the crystal, as a result, energy band will exist in the solid. Thus, electrons transition may take place between filled and unfilled states of the same band (Intraband) or between two different bands (Interband).
Let us assume that a transition is taking place from a state 'g' in the band 'a' to a state 'f' in the band 'b', the energy of this transition will be-

$$h\omega_{a_g,b_f} = E(a_g) - E(b_f) \quad (2.13)$$

Where E's are the energies of a_g and b_f states as indicated in equation (2.13). Due to contribution of bound electrons, a term $$\delta \varepsilon^b(\omega)$$ will be added in the dielectric constant. Hence, equation (2.10) will become-

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2 \tau}{(\omega^2 + i\omega)} + \delta \varepsilon^b(\omega)$$

$$= 1 - \frac{\omega_p^2}{\omega}(\omega + \frac{i}{\tau})^{-1} + \delta \varepsilon^b(\omega) \quad (2.14)$$

or

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega)$$

$$= \varepsilon^f(\omega) + \delta \varepsilon^b(\omega) \quad (2.15)$$

Where, $$\varepsilon^f(\omega)$$ is the contribution of the free electron plasma $$\delta \varepsilon^b(\omega)$$ is due to the bound electrons and has the form-

$$\Delta \varepsilon^b(\omega) = -\frac{e^2}{m\pi^2} \int \sum_{a,b} \frac{f_a(g)f^\mu_{a,b}}{\left(\omega + \frac{i}{\tau_{a,b}}\right)^2 - \omega_{a,b}^2} \, dg \quad (2.16)$$

Where, $$f_a(g)$$ is the Fermi distribution function for state g in the band a, $$f^\mu_{a,b}$$ is the oscillator strength and $$\tau_{a,b}$$ is the interband relaxation time. With the help of equations (2.11) and (2.15) and neglecting $$\tau_{a,b}$$
the real part of the dielectric constant comes out to be-

\[ \varepsilon_1(\omega) = 1 - \frac{\omega_{p0}^2}{\omega^2} \]

\[ = 1 - \frac{\omega_{pf}^2}{\omega^2} + \delta \varepsilon^b_1(\omega) \]  \hspace{1cm} (2.17)

\( \omega_{p0} \) is the value of the frequency of volume plasma oscillations in dielectrics measured experimentally, and \( \omega_{pf} \) is the value of free electron plasma oscillation. But, Frohlich [52] and Kittel [58] have shown that the zeros of the dielectric function determines the frequency of the longitudinal optical modes, that is-

\[ \varepsilon_1(\omega) = 0 \]

Thus from equation (2.17), we have-

\[ \omega^2 = \omega_{p0}^2 = \frac{\omega_{pf}^2}{1 + \varepsilon^b_1(\omega)} \]

or

\[ \omega_{pf}^2 = \frac{\omega_{p0}^2}{1 - \delta \varepsilon^b_1(\omega)} \]  \hspace{1cm} (2.18)

In this equation (2.18) \( \delta \varepsilon_1(\omega) \) is regarded as a small correction by Srivastava et al. [59], and can be neglected to a first approximation, so-

\[ \omega_{pf}^2 = \omega_{p0}^2 \]  \hspace{1cm} (2.19)

Thus, the bound electrons in valence band also undergo a collective oscillations within the band and behave like free electrons.
Now, in the next section the case of plasma oscillations in solids in considered. Quantum mechanically, where no consideration of free or bound electrons is involved.

**2.4 PLASMA OSCILLATION : QUANTUM MECHANICAL THEORY :**

The model taken by Bohm and Pines [41-43] to describe plasma oscillations in solids is slightly different from Sommerfield [44] model. The periodic potential due to ions have been replaced by a uniform background of positive charges. Therefore the interacting electrons are supposed to be immersed in a uniform background of positive charges. The electron density is -

\[
\rho(\vec{r}) = \sum_n \delta(\vec{r} - \vec{r}_n) \tag{2.20}
\]

Where, \(\delta(\vec{r} - \vec{r}_n)\) is Dirac delta function. In a Fourier series expansion, equation (2.20) can be expanded as-

\[
\rho(\vec{r}) = \sum_k^n \rho_k e^{i\vec{k} \cdot \vec{r}}
\]

Where, the Fourier coefficient is-

\[
\rho_k = \sum_i^n e^{-i\vec{k} \cdot \vec{r}_i} \tag{2.21}
\]

Or

\[
\rho_{-k} = \sum_n \rho_k e^{+i\vec{k} \cdot \vec{r}} = \rho_k^* \tag{2.22}
\]

At \(k = 0\), \(\rho_0 = n\), which is the average electron density.
The Fourier coefficients of the electron density $\rho_k$ describes the fluctuation about the mean density $\rho_0$. Here $\mathbf{k}$ is the wave vector and $\mathbf{r}$ is the position vector of a given electron. The Hamiltonian of the interacting electrons is:

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$  \hspace{1cm} (2.23)

Hence, the first term of this equation represents the kinetic energy of the electrons, while the second term is the coulomb potential due to the interaction energy, it can be expressed in Fourier series as:

$$V(\mathbf{r}) = \frac{e^2}{r} = \sum_k v_k e^{i\mathbf{k} \cdot \mathbf{r}}$$  \hspace{1cm} (2.24)

Where, $V_k$ is the Fourier coefficient of $V(\mathbf{r})$ and can be written as:

$$V_k = \frac{2\pi e^2}{k} \int_0^\infty \sin(k r) dr$$  \hspace{1cm} (2.25)

Because this integral is divergent, so to evaluate this, let us make the approximation:

$$V(\mathbf{r}) = \lim_{\alpha \to 0} \frac{e^{-\alpha r}}{r}$$

With the help of this approximation equation (2.25) it becomes:

$$V_k = \lim_{\alpha \to 0} \frac{4\pi e^2}{k} \int_0^\infty e^{-\alpha r} \sin(k r) dr$$

$$= \lim_{\alpha \to 0} \frac{4\pi e^2}{k} \left[ k \frac{\alpha^2 + k^2}{} \right]$$


data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAAJAAAAAbCAYAAABwzLzYAAAAGXRFWHRTb2Z0d2FyZQBBZG9iZSBJbWFnZVJlYWR5ccllPAAAAy5 شي

\[ = \frac{4\pi e^2}{k} = m_k^2 \]

Where, \( m_k \) is the Fourier transform of coulomb integral. Hence, our Hamiltonian can be rewritten in the following form as:

\[
H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} m_k^2 e^{ik|\vec{r}_i - \vec{r}_j|} \quad (2.26)
\]

With the help of equation (2.22), equation (2.26) can be written as:

\[
H = \sum_i \frac{p_i^2}{2m} + \sum_k \frac{\rho_k^+ \rho_k - n}{2} \quad (2.27)
\]

Here, \( \Sigma' \) means the term \( k = 0 \) is excluded with corresponds to the ionic field.

Ionic field is a uniform background of positive charges, which is cancelled by an equal number of negative charges of electrons. Now, to obtain equation of motion of \( \rho_k \) starting from Heisenberg interaction picture as Mandl [60] -

\[
i\hbar \frac{d\rho_k}{dt} = [\rho_k, H]
\]

\[
= \left[ \rho_k, \sum_i \frac{p_i^2}{2m} \right] + \left[ \rho_k', \sum_k \frac{m_k^2}{2} (\rho_k^+ \cdot \rho_k - n) \right]
\]

\[
= \left[ \rho_k, \sum_i \frac{p_i^2}{2m} \right] + \text{zero} \quad (2.28)
\]
Using the relation by Schiff [61]-

\[
\frac{d\rho_k}{dt} = -i \sum_i \left( \frac{k \cdot \vec{p}_i}{m} + \frac{\hbar k^2}{2m} \right)^2 \rho_k
\]  

(2.29)

But

\[
\frac{d^2\rho_k}{dt^2} = -i \sum_i \left[ \left( \frac{k \cdot \vec{p}_i}{m} + \frac{\hbar k^2}{2m} \right)^2 \rho_k + \left( \frac{k \cdot \vec{p}_i}{m} \right) \rho_k \right]
\]  

(2.30)

The value of \( P_i \) is given by Bohm and Pines [41]-

\[
P_i = -4\pi e^2 \sum_q \alpha_q e^{iq |\vec{r}_i - \vec{r}_j|}
\]  

(2.31)

Using equation (2.31) we have-

\[
\frac{d^2\rho_k}{dt^2} = -\sum_{i,k} \left[ \left( \frac{k \cdot \vec{p}_i}{m} + \frac{\hbar k^2}{2m} \right)^2 e^{-ikr_i} - \frac{4\pi e^2}{m} \sum_{q} \frac{q}{q^2} \rho_{k \to q} \rho_q \right]
\]  

(2.32)

Separating the term \( k = q \) and \( k \neq q \), the value will be -

\[
\frac{d^2\rho_k}{dt^2} = -\sum_{i,k} \left[ \left( \frac{k \cdot \vec{p}_i}{m} + \frac{\hbar k^2}{2m} \right)^2 e^{-ik\vec{r}_i} - \frac{4\pi e^2}{m} \rho_k \right]
\]

\[
- \frac{4\pi e^2}{m} \sum_{k \neq q} \frac{q}{q^2} \rho_{k \to q} \rho_q
\]  

(2.33)
\[
\frac{d^2 \rho_k}{dt^2} + \omega_p^2 \rho_k = - \sum_{i,k} \left[ \left( \frac{k_i \overline{p}_i}{m} + \frac{\hbar k^2}{2m} \right)^2 e^{-i k_i r_i} \right] - \frac{4 \pi e^2}{m} \sum_{k \neq q} \frac{\overline{k} \cdot \overline{q}}{q^2} \rho_{k \rightarrow q} \rho_q \right] 
\]

(2.34)

Where, \[ \omega_p = \left( \frac{4 \pi e^2}{m} \right)^{1/2} \]

\( \omega_p \) is the plasma frequency, the second term in R.H.S. of equation (2.34) contains \( \exp \left[ -i (k - q) r_i \right] \), a phase factor. According to Bohm and Pines [41] this term will be averaged out to zero in random phase approximation. The bracketed in the R.H.S. of equation (2.34) is of the order of \( k^2 v_0^2 p_k \), where, \( v_0 \) is the velocity of electron at top of Fermi distribution. For long wavelength limit \( k \) is to small, the condition for collective oscillation, this term can be neglected, then equation (2.34) is reduced as -

\[
\frac{d^2 \rho_k}{dt^2} + \omega_p^2 \rho_k = 0 
\]

(2.35)

This is an equation of simple harmonic motion of \( \rho_k \) with frequency \( \omega_p \). From equation (2.35) it is clear that particles show a collective organized behavior due to the long range part of the coulomb interaction. Thus, the concept of plasma oscillation in solids is discussed that now it is possible even when no account has been
taken of free or bound electrons and how these plasma oscillations effect the X-ray emission and absorption spectra.

2.5 EFFECT OF PLASMA OSCILLATION ON X-RAY EMISSION AND ABSORPTION SPECTRA:

Ferrel [11], Nozieres and Pines [12] pointed out for the first time plasma oscillation in solids can complicate the structure of the X-ray emission and absorption spectra. In recent years, it has also been shown theoretically and experimentally by several workers [9, 10, 27, 62, 63] that the interpretation of X-ray emission and absorption spectra must include the contribution of the interaction between the suddenly created or annihilated core hole to the collective modes of conduction electrons. This interaction spectra which is displayed from the main peak by an energy (The plasmon energy).

In the X-ray absorption process an electron of core state is ejected and goes to the first unoccupied level above the Fermi level. According to Parratt [64] this electron is while traversing through the solid, interacts with the loosely bound valence electrons in such a way that collective oscillations are set up in the electron density. The energy of these oscillations is taken from the absorbed photon via kinetic energy of the ejected electron. This will give rise to the fine structure of the X-ray absorption edge separated by an energy equal to the plasma energy. This fine structure is called the X-ray plasmon structure [Srivastava et al. 18].
In the X-ray emission process the initial state consists of core vacancy, which is subsequently filled up by an outer shell electron with the emission of an X-ray photon. If the valence electrons, before filling the core vacancy, also excites a plasmon, then the energy needed for the excitation of these plasma oscillation is taken radiation will be deprived of an energy, and a low energy satellite will be emitted, whose separation from the main X-ray line will correspond to satellites and have been observed by a number of workers [9, 10, 65] in X-ray emission spectra. On the other hand, if plasmon pre-exists during the X-ray emission process, then on this decay it can give its energy to transiting valence electron, before it annihilated the core vacancy. Thus, the energy of the emitted X-ray photon will be higher than the main emission line by an amount, this emission line is known as high energy X-ray satellites.

After a brief discussion about theories in this chapter, review of various theories for both high and low energy satellites is given in the next chapter.