CHAPTER-IV

Mathematical Formulation and Calculation
Mathematical Formulation and Calculation

The involvement of plasma oscillation in the X-ray emission or absorption spectra of solids has been widely studied during the last few decades, and has been recognised that the electron-electron interaction has played an important role.

This chapter is devoted to derive an expression for the energy separation and the relative intensity of low and high energy X-ray plasmon satellites with respect to parent line. Firstly, the energy separation between the main line and plasmon satellite is calculated and secondly derived an expression for the relative intensity in both intrinsic processes that is (i) when number of slow electrons is not conserved and (ii) when the number of slow electrons are conserved respectively.

According to plasmon theory, it is discussed in previous chapter (Chapter-II), if the valence electron, before filling the core vacancy also excites a plasmon then the energy \( \hbar \omega_p \) needed for the excitation of plasma oscillation is taken from the transiting valence electron so that the emitted radiation will be deprived off an energy \( \hbar \omega_p \) and a low energy satellite will be emitted, whose separation from the main X-ray line will correspond to \( \hbar \omega_p \). On the other hand, if the plasmon pre-exists, during the X-ray emission process then, on its decay it can give its energy to the transiting valence electron before it annihilates the core vacancy.
Thus, the energy of emitted X-ray photon will be higher than the main emission line by an amount $\hbar\omega_p$, giving rise to high energy satellite.

Further, in order to confirm the involvement of plasmon in the emission of X-ray satellites the relative intensity of surface plasmon satellites must be calculated. In this chapter mathematical details of canonical transformation, carried out over the model Hamiltonian of the system is discussed. Thus the energy separation $\Delta E$ of the low and high energy plasmon satellite from the corresponding main line should be equal to the quantum of plasmon energy $\hbar\omega_p$ which is given by Morton et al. [114]-

$$\Delta E = \hbar\omega_p = 28.8 \left(\frac{Z\sigma}{W}\right)^{1/2} \text{ ev} \quad (4.1)$$

Where, $Z$ is effective number of electrons taking part in the plasmon oscillations, $\sigma$ is specific gravity and $W$ is the molecular weight.

This equation can be derived as -

From the classical consideration, the frequency of plasma oscillations is as-

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

Hence the amount of energy given to plasmon becomes-

$$\Delta E_p = \hbar\omega_p = \hbar \left(\frac{4\pi ne^2}{m}\right)^{1/2}$$
This may be written as -

\[ n = \frac{L \sigma Z}{W} \]

Where, \( \sigma, Z \) and \( W \) are defined above, and \( L \) is the Avogadro number. By putting the numerical value of constants, the plasmon energy is shown as-

\[ \hbar \omega_p = 28.8 \left( \frac{Z \sigma}{W} \right)^{1/2} \text{ ev} \quad (4.2) \]

and surface plasmon energy separation as

\[ \Delta E_s = \hbar \omega_s = 20.37 \left( \frac{Z \sigma}{W} \right)^{1/2} \text{ ev} \quad (4.2.1) \]

The calculated values of \( \Delta E \) have been compared with the Poonia and Soni [133], the experimental values of "X-ray satellite spectra in the L\( \alpha_4 \) region of 4d transition elements (Zr, Nb, Mo, Ru, Rh, and Rd)" and M. Aronmiemei et al. [144], the experimental values of "X-ray satellite spectra in core level 2p peaks of transition metal oxides (Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), Cr\(_2\)O\(_3\) and CrO\(_6\))". It can be explained by Table 1 & 2 –
Table-1 Energy separation $\Delta E$ at $1\alpha_1$ satellite of 4-d Transition elements

<table>
<thead>
<tr>
<th>S.No.</th>
<th>NAME</th>
<th>SYMBOL</th>
<th>Z</th>
<th>$w$</th>
<th>Sp. Gravity</th>
<th>Exper. Value [133]</th>
<th>Author Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZIRCONIUM</td>
<td>Zr(40)</td>
<td>1</td>
<td>91.224</td>
<td>6.51</td>
<td>6.54</td>
<td>5.44</td>
</tr>
<tr>
<td>2</td>
<td>NIBOLIUM</td>
<td>Nb(41)</td>
<td>1</td>
<td>92.906</td>
<td>8.58</td>
<td>6.51</td>
<td>6.19</td>
</tr>
<tr>
<td>3</td>
<td>MOLYBDENUM</td>
<td>Mo(42)</td>
<td>1</td>
<td>95.94</td>
<td>10.28</td>
<td>6.54</td>
<td>6.67</td>
</tr>
<tr>
<td>4</td>
<td>RUTHENIUM</td>
<td>Ru(44)</td>
<td>1</td>
<td>101.07</td>
<td>12.45</td>
<td>6.85</td>
<td>7.15</td>
</tr>
<tr>
<td>5</td>
<td>RHODIUM</td>
<td>Rh(45)</td>
<td>1</td>
<td>102.91</td>
<td>12.41</td>
<td>7.36</td>
<td>7.07</td>
</tr>
<tr>
<td>6</td>
<td>PALLADIUM</td>
<td>Pd(46)</td>
<td>1</td>
<td>106.42</td>
<td>12.02</td>
<td>7.59</td>
<td>6.84</td>
</tr>
</tbody>
</table>

Table-2 Energy separation $\Delta E$ Of transition metal oxides on their core level 2p peaks

<table>
<thead>
<tr>
<th>S.No.</th>
<th>COMPOUNDS</th>
<th>Z</th>
<th>$w$</th>
<th>Sp.Gravity</th>
<th>Exper. Value [133]</th>
<th>Author Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$_2$O$_3$</td>
<td>3</td>
<td>159.69</td>
<td>5.2</td>
<td>8.7</td>
<td>9.00</td>
</tr>
<tr>
<td>2</td>
<td>Fe$_3$O$_4$</td>
<td>2</td>
<td>231.53</td>
<td>5</td>
<td>5.7</td>
<td>5.99</td>
</tr>
<tr>
<td>3</td>
<td>Cr$_2$O$_3$</td>
<td>3</td>
<td>151.99</td>
<td>5.22</td>
<td>9.8</td>
<td>9.24</td>
</tr>
<tr>
<td>4</td>
<td>CrO$_3$</td>
<td>2</td>
<td>99.99</td>
<td>4.88</td>
<td>9.1</td>
<td>9.00</td>
</tr>
</tbody>
</table>

4.1 Model Hamiltonian:

To derive an expression for the relative intensity of the plasmon satellites the model is taken consisting of n valence electrons together with a hole at rest having an infinite mass and a +ve charge, which is responsible for X-ray transition. This X-ray transition is treated as a
hole-electron annihilation the model Hamiltonian in the presence of
electro-magnetic field is given by White [115], Pines [116] as –

\[ H = H_{el} + H_{el-el} + H_{el-vac} + H_{E.M} \]  \hspace{1cm} (4.3)

\[ H_{el} = \sum_i \frac{p_i^2}{2m}, \text{ the kinetic energy of valence electron} \]  \hspace{1cm} (4.4)

\[ H_{el-el} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]  \hspace{1cm} (4.5)

It is electron-electron coulomb interaction the energy of the
electron gas-

\[ H_{el-vac} = -\sum_i V(\vec{r}_i - \vec{R}) \]  \hspace{1cm} (4.6)

It is the interaction energy between the \( i \)th electron and vacancy
at \( \vec{R} \)

\[ H_{E.M} = \sum_i \left[ \frac{p_i - \frac{e}{c} \vec{A}(\vec{r}_i, t)}{2m} \right]^2 \]  \hspace{1cm} (4.7)

\( H_{E.M} \) is the interaction energy with the electromagnetic field.

Following Pines [116] the various terms in equation (4.3) can
be put in the second quantized forms as-

**First term of equation (4.3)**

\[ \sum_i \frac{p_i^2}{2m} = \int \psi^+(\vec{r}) \frac{\hbar^2 \nabla^2}{2m} \psi(\vec{r}) \, dr \]

\[ = \frac{\hbar^2}{2m} \int \nabla \psi^+(\vec{r}) \cdot \nabla \psi(\vec{r}) \, dr \]  \hspace{1cm} (4.8)
Where, the field operators \( \Psi(\vec{r}) \) and \( \Psi^+(\vec{r}) \) are defined as

\[
\Psi(\vec{r}) = \sum_p \phi_p(\vec{r}) c_p^\dagger
\]

\[
\Psi^+(\vec{r}) = \sum_p \phi_p(\vec{r}) c_p
\]

(4.9)

\( c_p^\dagger \) and \( c_p \) are the creation and annihilation operators for electron and obey the following anti commutation relations.

\[
[C_p, c_p^\dagger]_+ = [c_p^\dagger, c_p^\dagger] = 0
\]

(4.10)

\[
[C_p, c_q^\dagger]_+ = \delta_{pq}
\]

and

\[
[\phi_p(\vec{r}), \phi_{p'}(\vec{r}')] = \delta(\vec{r} - \vec{r}')
\]

(4.11)

\[
\phi_p(\vec{r}) = \frac{1}{\sqrt{3!}} e^{i\vec{p} \cdot \vec{r}}
\]

(4.12)

Hence, equation (4.9) can be written as:

\[
\sum_i \frac{p_i^2}{2m} = \sum_p E(p) c_p^\dagger c_p
\]

(4.13)

Where,

\[
E_p = \frac{\hbar^2 p^2}{2m}
\]

(8.14)

\( P \) is the momentum of electron and 'm' is its free mass.

**Second term of equation (4.3)**

The electron-electron interaction energy between the \( i^{th} \) and \( j^{th} \) electrons, whose position vectors are \( \vec{r}_i \) and \( \vec{r}_j \) respectively, is given as–
\[ H_{\text{el-\text{el}}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]  \hspace{1cm} (4.15)

The Fourier expansion of eqn (4.15) is given as –

\[ H_{\text{el-\text{el}}} = \frac{1}{2} \sum_{i \neq j} \frac{4\pi e^2}{k^2} e^{ik(\vec{r}_i - \vec{r}_j)} \]  \hspace{1cm} (4.16)

Which can be put in terms of density fluctuation operation and defined as –

\[ \rho(\vec{r}) = \sum_k \rho_k e^{i\vec{k}.\vec{r}} \]  \hspace{1cm} (4.17)

Multiplying both sides of equation (4.17) by \( e^{-i\vec{k}.\vec{r}} \) and integrating the right hand side as –

\[ \rho(\vec{r}) e^{-i\vec{k}.\vec{r}} = \int d\vec{r} \sum_k \rho_k e^{i(\vec{k} - \vec{k}').\vec{r}} \]

\[ = \sum_k \rho_k \Delta(\vec{k} - \vec{k}') \]

\[ = \rho_k \]

This shows that –

\[ \rho_k = \rho(\vec{r}) e^{-i\vec{k}.\vec{r}} \]  \hspace{1cm} (4.18)

Clearly \( \rho_k \) is the Fourier component of the electron density. Fluctuations about the average electron density \( \rho_0 = n \) considering electron to be a point charge.

Thus,

\[ \rho_k(\vec{r}) = \sum_{i=1}^{n} \delta(\vec{r} - \vec{r}_i) \]  \hspace{1cm} (4.19)
Using equation (4.18) and (4.19), it may be as –

\[
\rho_k = \sum_i^n \delta(\vec{r} - \vec{r}_i) \ e^{-i\vec{k}\cdot\vec{r}} \ dr \\
\rho_k = \sum_i e^{-i\vec{k}\cdot\vec{r}_i} 
\]

(4.20)

using the property of \(\rho(r)\), –

\[
\sum_{i,j} e^{i\vec{k}(\vec{r}_i - \vec{r}_j)} = \rho_k^+ \rho_k 
\]

(4.21)

Thus,

\[
H_{el-el} = \frac{1}{2} \sum_k m_k^2 (\rho_k^+ \rho_k - n) 
\]

(4.21)

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

(4.22)

Where, \(m_k^2\) is the Fourier transform of the coulomb interaction, \(\rho_k\) is the density fluctuation which fluctuates about \(\rho_0 = n\) (The average particle density). The prime on summation sign of equation (4.22) indicates that the \(k=0\) term is excluded, because author is dealing with a gas of electron immersed in a uniform background of positive charge, which means that the uniform distribution of negative charge of valence electrons in cancelled by the uniform distribution of positive charge of the ions.

Further, Pines [116]

\[
\rho_k = \sum C_{\vec{P} - \vec{K}}^+ C_{\vec{P}} 
\]
\[ \rho_k^+ = \sum_{\rho, \bar{\rho}, k} C_{\rho + \bar{\rho}}^+ C_{\bar{\rho}} \] (4.23)

Using equation (4.23) and equation (4.21), as –

\[ H_{el-el} = \frac{1}{2} \sum_{\rho, \bar{\rho}, k \neq 0} m_k^2 \left( C_{\rho + \bar{\rho}}^+ C_{\bar{\rho} - \rho}^+ C_{\rho} C_{\bar{\rho}} - n \right) \] (4.24)

Which obey the anti-commutation relations described in equation (4.10)

**Third Term of Equation (4.3)**

The interaction between the \( i \)th electron and the vacancy at \( R \) is shown as –

\[ H_{el-vac} = - \sum_i V(\bar{r}_i - \bar{R}) \] (4.25)

in the second quantized form it can be written as-

\[ H_{el-vac} = - \sum_{i < j k m} \langle V \rangle \langle k m | \langle i j \rangle \rangle \]

\[ = - \int \psi^+(\bar{r}) \psi^+(\bar{R}) V(\bar{r}) \psi(\bar{r}) \Psi(\bar{R}) \, d\bar{r} \, d\bar{R} \]

\[ = - \int \phi_i^+(\bar{r}) \phi_i^+(\bar{R}) V \phi_m(\bar{R}) C_{\rho + \bar{\rho}}^+ C_{\bar{\rho}} b^+(\bar{R}) b(\bar{R}) \, d\bar{r} \, d\bar{R} \]

\[ = - \int \psi C_{\rho + \bar{\rho}}^+ C_{\bar{\rho}} b^+(\bar{R}) b(\bar{R}) \]

\[ H_{el-vac} = - \sum_{i} m_k^2 C_{\rho + \bar{\rho}}^+ C_{\bar{\rho}} b^+(\bar{R}) b(\bar{R}) e^{-i\bar{R} \cdot \bar{r}} \] (4.26)

Where, the field operators for the vacancy at \( R \) are defined as-
\[ \Psi(\mathbf{R}) = \sum_j \phi_j b(\mathbf{R}) \]

\[ \Psi^+(\mathbf{R}) = \sum_j \phi_j^* b^+(\mathbf{R}) \quad (4.27) \]

and,

\[ \phi_j = e^{ik\cdot\mathbf{R}} \quad (4.28) \]

\( b^+ \) and \( b \) are the creation and annihilation operators for the vacancy and obey the following anti commutation rules.

\[ [b_i, b_j]_+ = [b_i^+, b_j^+] = 0 \]

\[ [b_i, b_j^+] = \delta_{ij} \quad (4.29) \]

Further, a number operator \( N(\mathbf{R}) \) is such that –

\[ b^+(\mathbf{R})b(\mathbf{R}) = N(\mathbf{R}) = \iota, \quad \text{if there is a vacancy} \]

\[ = 0, \quad \text{if there is no vacancy} \quad (4.30) \]

The value of the potential \( V \) has been evaluated by Fourier expansion as follows:

\[ V = \int V_k e^{-i \mathbf{K} \cdot \mathbf{r}} \, \text{d}r \]

\[ = \int \sum_k \frac{4\pi e^2}{K^2} e^{i \mathbf{K} \cdot (\mathbf{F} - \mathbf{R})} e^{-i \mathbf{K} \cdot \mathbf{r}} \, \text{d}r \quad (4.31) \]

\[ = \frac{4\pi e^2}{K^2} e^{-i \mathbf{K} \cdot \mathbf{r}} \]

\[ V = m_k^2 e^{-i \mathbf{K} \cdot \mathbf{r}} \quad (4.32) \]
Fourth term of equation (4.3)

The effective X-ray emission Hamiltonian which represents the interaction of photon with hole and the electron under transition can be written as-

$$H_{E,M} = \sum_i \left[ \frac{p_i - e}{c} \frac{A(\vec{r}, t)}{2m} \right]^2$$  \hspace{1cm} (4.33)

Where,

$$\vec{E} = -\frac{1}{c} \frac{\partial A}{\partial t}$$

and,

$$H = \vec{\nabla} \times \vec{A}$$  \hspace{1cm} (4.34)

Neglecting the periodic potential term, field energy term and $A^2$ term, the remaining term in equation (4.33) can be written as -

$$H_{E,M} = \frac{e}{2mc} \sum_i \left[ p_i A(\vec{r}, t) + A(\vec{r}_i, t), \vec{P}_i \right]$$  \hspace{1cm} (4.35)

Where, vector potential $\vec{A}(\vec{r}, t)$ is defined as-

$$\vec{A}(\vec{r}, t) = A(\vec{r})e^{-i\omega_k t}$$  \hspace{1cm} (4.36)

Expanding the $A(\vec{r})$ in a Fourier series in a cube of unit volume with periodic boundary conditions-

$$A(\vec{r}) = \sum_{k, \mu} (4\pi e^2)^{1/2} Q_{k\mu} \eta_{k\mu} e^{iK \cdot \vec{r}}$$  \hspace{1cm} (4.37)
The vacancy denotes the positive charge at R. $Q_{k\mu}$ is the amplitude of $K^{th}$ normal mode; $\eta_{k\mu}$ is the unit polarization vector, $\mu = 1$ or $2$ corresponding to 2 possible modes of polarization which are perpendicular to K, and $\omega_k$ is the angular frequency of photons.

The reality conditions for $A(\vec{r})$ are -

$$\eta_{k\mu} = \eta_{-k\mu}$$

$$Q_{k,\mu}^* = Q_{-k\mu}$$

(4.38)

In the transverse gauge the coulomb condition is-

$$\vec{\nabla} \cdot \vec{A} = 0$$

(4.39)

Thus equation (3.34) becomes-

$$H_{E,M} = \frac{e}{mc} \sum \limits_t P_t A(\vec{r}_t, t)$$

(4.40)

equation (4.40) in the following terms given by Pines [116]-

$$H_{E,M} = \frac{e}{2c} \int \text{d}r^3 A(\vec{r}, t) J(\vec{r})$$

(4.41)

Where, $J(\vec{r})$ is the electron current density, which is defined as-

$$J(\vec{r}) = \sum \frac{1}{2m} \left[ P_i \delta (\vec{r} - \vec{r}_i) + \delta (\vec{r} - \vec{r}_i) P_i \right]$$

(4.42)

The Fourier analysis equation (4.41) as-

$$H_{E,M} = \lim_{\delta \to 0} e \sum \limits_{k, \omega} \tilde{A}_{k,\omega} e^{-i\omega_k t} e^{-\delta t}$$

(4.43)

with ,
\[ \bar{J}_k = \sum \left( \frac{p_i}{m} + \frac{\hbar k}{2m} \right) e^{-i\hat{R}_i} \]  

(4.44)

In equation (4.43) the exponential factor \( e^{i\hat{R}_i} \) to turn on the interaction adiabatically is introduced, so that the response of the system to the electromagnetic wave will necessarily be casual. To quantize momentum the electromagnetic field, \( p_{k\mu} \) is the conjugate for \( Q_{k\mu} \) and equal time commutation relation is given as:

\[ [p_{k\mu}, Q_{k'\mu'}] = -i\hbar \delta_{kk'} \delta_{\mu\mu'} \]  

(4.45)

All the other commentators are zero, substituting the value of \( A_k \) in equation (4.43) from equation (4.37) as,

\[ H_{E.M} = \sum_{k,\mu} (4\pi e^2)^{1/2} \left( \eta_{k\mu}, \bar{J}_k \right) Q_{k\mu} \]  

(4.46)

Now introducing the photon creation \( \alpha_k^+ \) and annihilation \( \alpha_k \) operator as-

\[ Q_{k\mu} = \sqrt{\left( \frac{\hbar}{2\omega_p} \right)} \left( \alpha_k + \alpha_k^+ \right) \]  

(4.47)

Putting this value in equation (4.46) as-

\[ H_{E.M} = \sum_{k,\mu} (4\pi e^2)^{1/2} \left( \eta_{k\mu}, \bar{J}_k \right) (\alpha_k + \alpha_k^+) \]

For the emission of X-ray photons the above expression reduce to-

\[ H_{E.M} = \sum_{k,\mu} (4\pi e^2)^{1/2} \left( \eta_{k\mu}, \bar{J}_k \right) \left( \frac{\hbar}{2\omega_p} \right) \alpha_k^+ \]
In a simplified form this can be written as-

\[ H_{E.M} = \sum_l V(\bar{l}) C_l b(\bar{R}) \alpha^+ \]  \hspace{1cm} (4.48)

Where, \( C_l \) denotes the annihilation of an electron in the valence level \( V(l) \), \( b(\bar{R}) \) is the annihilation operator for the localized vacancy at position vector \( \bar{R} \) and \( V(\bar{l}) \) is the matrix element of the X-ray transition and \( \alpha^+ \) is the creation operation for X-ray photons.

Thus using equations (4.13), (4.25), (4.27) and (4.48) in equation (4.3) and after some simplification by Brousrs [36], the model Hamiltonian as-

\[ H = \sum_P E(P) C_P^+ C_P + \frac{1}{2} \sum_{P,Q \neq K} m_k^2 \left( C_{P+K}^+ C_{Q-Q}^+ C_Q C_P - n \right) \]

\[ - \sum_{P,K} m_k^2 \left( C_{P+K}^+ C_P b^+(\bar{R}) b(\bar{R}) e^{-i\bar{R} \bar{R}} \right) \]

\[ + \sum_l V(\bar{l}) C_l b(\bar{R}) \alpha^+ \]  \hspace{1cm} (4.49)

Where, \( V(l) \) is proportional to the matrix elements defined as -

\[ < K, R | M | l > = \int \Psi_K(X - R) \frac{\partial}{\partial x} \Psi_l(X) d\tau \]

or

\[ < K, R | M | l > = \int \Psi_L(X - R) \frac{\partial}{\partial x} \Psi_l(X) d\tau \]  \hspace{1cm} (4.50)
Corresponding to the transition of a valence electron with momentum $\hbar l$ to fill the vacancy in that K or L shell and $(X - R)$ is the distance of electron from the vacancy.

The $V(l)$ term together with $N(E_t)$ given the intensity of radiation in the emitted band. This intensity relation is given as-

$$I(E_p) \sim V^2(l)N(E_t) \quad (4.51)$$

Where, $N(E_t)$ is the number of energy levels in the energy range $E_t$ and $(E_t + dE)$, $E_t$ being the energy of the electron going from $l$ state to K or L state of the atom.

It $P_k$ and $Q_k$ are the canonically conjugate momentum and coordinate associate with an oscillator with wave vector $k$, there the set $P_k$ and $Q_k$ describes the longitudinal electro-magnetic field of the electrons which satisfy the following commutation relation by Pines [116] as-

$$[P_k, Q_{k'}] = -i\hbar \delta_{kk'} \quad (4.52)$$

Following Pines [23], addition of a term of a set of $P_k$ and simplicity, a set of $Q_k$ with $K < K_c$ in the Hamiltonian $H$ (4.49) i.e. the additional term as-

$$H' = \sum_{k,k<K_c} \left( \frac{1}{2} P_k P_k^+ + iM_k P_k \rho_k \right) \quad (4.53)$$

This $H'$ is the sum of field energy and electron field interaction energy. Thus, the model Hamiltonian of an assembly of an electrons embedded in a uniform distribution of positive charge plus field
oscillators with wave vectors $K < K_c$ integrating with the electron density fluctuation, written [Pines 23] as-

$$H'' = H + H'$$

$$H'' = \sum_P E(P) C_P^+ C_P + \frac{1}{2} \sum_{p,q,k} m_{k}^2 \left( C_{p+k}^+ C_{q-k}^+ C_q C_p - n \right)$$

$$+ \sum_{k < k_c} \left( \frac{P_k^+ P_k}{Z} + i m_k P_k C_{p-R}^+ C_P \right)$$

$$- \sum_{p,k} m_k^2 C_{p+R}^+ C_p b^+(R) b(R) e^{-i \cdot k \cdot R}$$

$$+ \sum_l V(l) C_l b(R) \alpha^+$$

(4.54)

Two more terms to the Hamiltonian are added-

(i) Coulomb interaction between ions and electron $H_{\text{ion-el}}$ and

(ii) Coupling between ion density fluctuation and the collective field $H_{\text{field-ion}}$.

The coulomb interaction energy between ions and electron is $-\frac{e^2}{(R-r_i)}$ and due to the fact that propagation vector for the ion is zero, the term $H_{\text{ion-el}}$ can be written as-

$$H_{\text{ion-el}} = -\sum_{p,k} m_k^2 C_{p-R}^+ C_p b^+(R) b(R)$$

(4.55)

Analogous to the third term of equation (4.54) the expression for the $H_{\text{field-ion}}$ can be written as-
\[ H_{\text{field-ion}} = i \sum_{k < k_c} m_k P_k b^+ (\bar{R}) b (\bar{R}) \]

Thus, the extended Hamiltonian for the system can be written as:

\[
H_t = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{p,q} m_k^2 \left( C_{p+K}^+ C_{q-K}^+ C_q C_p - n \right) - \sum_k m_k^2 \left( C_{p+K}^+ C_p b^+ (\bar{R}) b (\bar{R}) e^{-iK\bar{R}} \right) + \sum_l V(l) C_l b(\bar{R}) \alpha^+ + \sum_{k < k_c} \frac{P_k^+ P_k}{2} + i \sum_{k < k_c} m_k P_k C_{p-K}^+ C_p - \sum_k m_k^2 C_{p+K}^+ C_p b^+ (\bar{R}) b (\bar{R}) + i \sum_{k < k_c} m_k P_k b^+ (\bar{R}) b (\bar{R}) \]  

(4.56)

4.2 Canonical Transformation :-

Now, a canonical transformation are carried out, that is a transformation of operators, which leaves the eigen values of the Hamiltonian unaltered. The required canonical transformation is generated by an operator as:

\[ S_1 = -i \sum_{k < k_c} M_k Q_k C_{p-K}^+ C_p \]  

(4.57)

In the Hamiltonian denoted by equation (4.56) first, 4th, 5th, 6th and 8th terms are affected by the transformation. The transform Hamiltonian can be calculated with the aid of (4.52) and (4.57). It is easy to calculate following relations:

\[ [S_1, P_k] = \hbar m_k C_{p+K}^+ C_p \]
\[
[S_1, (S_1, P_k)] = 0
\]

where \( C_{\tilde{p}+K}^+ C_{\tilde{p}} = \rho_k \)

\[
[C_{\tilde{p}+K}^+ C_{\tilde{p}}, S_1] = 0
\]

\[
[C_{\tilde{p}-K}^+ C_{\tilde{p}}, S_1] = 0
\]

\[
[S_1, P_i] = i\hbar \sum_{k<k_c} m_k Q_k K e^{i\hat{K}_1}
\]

\[
[S_1[S_1, P_i]] = 0
\]

\[
[S_1, Q_k] = 0
\]

The relation between any old operator 0 and the corresponding new operator \( Q_{\text{new}} \) is given as -

\[
Q_{\text{new}} = e^{-iS_1/\hbar} O e^{iS_1/\hbar}
\]

\[
= 0 - \frac{1}{\hbar} [S_1, 0] - \frac{1}{2\hbar^2} [S_1[S_1, 0]]
\]  \hspace{1cm} (4.59)

Higher order term is neglected in equation (4.59), now using the commutation relation is (4.58), the relation between various old and new operator will be -

\[
(P_k)_{\text{new}} = P_k - i \sum_p m_k \rho_k^+
\]

\[
= P_k - i \sum_p m_k C_{\tilde{p}+K}^+ C_{\tilde{p}}
\]

\[
(Q_k)_{\text{new}} = Q_k
\]  \hspace{1cm} (4.60)
\[(P_i)_{\text{new}} = P_i - \sum_{k < k_c} m_k Q_k k e^{i\vec{k} \cdot \vec{r}_i}\]

and, \[(\rho_k)_{\text{new}} = \rho_k\]

or, \[\left( C_{\text{p+K}}^+ C_{\text{p}} \right)_{\text{new}} = C_{\text{p+K}}^+ C_{\text{p}}\]

Using the relations (4.60), various terms in equation (4.56) can be represented in terms of new variables. For the sake of simplicity, the suffix new has been dropped carrying the transformation term by term as -

**(i) First term of equation (4.56):**

\[
\left( \sum_i \frac{P_i^2}{2m} \right)_{\text{new}} = \sum_i \frac{1}{2m} \left( P_i - \sum_{k < k_c} m_k Q_k \vec{k} e^{i\vec{k} \cdot \vec{r}_i} \right)^2
\]

\[
= \left( \sum_i \frac{P_i^2}{2m} \right)
\]

\[- \sum_i \left[ \frac{1}{2m} P_i \sum_{k < k_c} m_k Q_k \vec{k} e^{i\vec{k} \cdot \vec{r}_i} + \frac{1}{2m} \sum_{k < k_c} m_k Q_k \vec{k} e^{i\vec{k} \cdot \vec{r}_i} P_i \right]
\]

\[+ \sum_{i,k,k'} m_k m_{k'} Q_k Q_{k'} \frac{\vec{K} \vec{K}'}{2m} e^{i(\vec{K} + \vec{K}') \cdot \vec{r}_i}
\]
\[
\begin{align*}
= & \sum_i \frac{P_i^2}{2m} + \sum_{i,k \leq k_c} \left( \frac{P_i \cdot \vec{k}}{m} - \frac{\hbar \vec{K}}{2m} \right) m_k Q_k e^{i\vec{k} \cdot \vec{r}_i} \\
+ & \sum_{i,k,k' \leq k_c} m_k m_{k'} Q_k Q_{k'} \frac{\vec{K} \cdot \vec{K}'}{2m} e^{i(\vec{k} + \vec{K}')} \vec{r}_i
\end{align*}
\] (4.61)

splitting the last term of the above equation in two parts. The part of which \(\vec{k} + \vec{K}' = 0\) is given as -

\[
\sum_{k < k_c} \frac{1}{2} m_k^2 Q_k Q_{-k} \frac{k^2}{2m} \cdot n = \frac{\omega_p^2}{2} \sum_{k < k_c} Q_k^+ Q_k^- \ 
\] (4.62)

Where, \(\omega_p\) is the Plasmon frequency given as -

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

**Second part :-**

When \(\vec{k} + \vec{K}' \neq 0\) and denoted by \(U\),

\[
U = \frac{2\pi e^2}{m} \sum_{p,k,k', k' \neq -k} Q_k^+ Q_{k'}^+ C_p^+ C_{p+k} C_{p-k'}^+ C_p^- \ 
\] (4.63)

The term \(U\), which has small numerical value, always depends on the electron position co-ordinates, Since electrons are randomly distributed in space, so there is a strong tendency for various terms entering in \(U\) to cancel out. This process was first suggested by Bohm and Pines [116] and is known as “Random Phase Approximation”. Hence, the first term of equation (4.56) becomes -
\[ \sum_i \frac{p_i^2}{2m} - \sum_{i,p,k \atop k < k_c} \left( \frac{\bar{p}_i \cdot \bar{K}}{m} - \frac{\hbar K^2}{2m} \right) m_k Q_k C_{p+\bar{K}}^+ C_{\bar{p}} + \frac{\omega_{\bar{p}}^2}{2} \sum_{k < k_c} Q_k^+ Q_k \] (4.64)

**Second term of equation (4.56):**

This term remain unaffected by the transformation. It may be separated out into two parts and demarcation limit is \( k = k_c \)

\[ \frac{1}{2} \sum_{k \neq 0} m_k^2 \left[ C_{p+\bar{K}}^+ C_{q-k}^+ C_{q} C_{\bar{p}} - n \right] \text{new} = \frac{1}{2} \sum_{k > k_c} m_k^2 \left[ C_{p+\bar{K}}^+ C_{q-k}^+ C_{q} C_{\bar{p}} - n \right] \]

(4.65)

**Third term of equation (4.56):**

\[ \left( - \sum_k m_k^2 C_{p+\bar{K}}^+ C_{\bar{p}} b^+(\bar{R}) b(\bar{R}) e^{-i\bar{K} \bar{R}} \right) \text{new} \]

\[ = - \sum_{k \neq 0} m_k^2 C_{p+\bar{K}}^+ C_{\bar{p}} b^+(\bar{R}) b(\bar{R}) e^{-i\bar{K} \bar{R}} \]

\[ - \frac{i}{\hbar} \left[ S_I, - \sum_{k \neq 0 \atop p} m_k^2 C_{p+\bar{K}}^+ C_{\bar{p}} b^+(\bar{R}) b(\bar{R}) e^{-i\bar{K} \bar{R}} \right] \]

\[ = - \sum_{k \neq 0 \atop p} m_k^2 C_{p+\bar{K}}^+ C_{\bar{p}} b^+(\bar{R}) b(\bar{R}) e^{-i\bar{K} \bar{R}} \]

That is the term remains unaffected.

**Fourth term of equation (4.56):**

This is the X-ray emission term and becomes -
\[
\left[ \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} \right]_{\text{new}} = e^{i s_l / \hbar} \left( \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} \right) e^{i s_l / \hbar} \\
= \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} - i \left[ S_{l}, \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} \right] \\
= \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} \\
- \frac{i}{\hbar} \left[ -i, \sum_{k<k_c} m_k Q_k C_{P_k}^+ C_{P}^+ \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} \right] \\
\text{(4.67)}
\]

Where, \( l \) varies from \((\vec{P} - \vec{K})\) to \((\vec{P} + \vec{K})\), first take the bracket of the equation (4.67), it can be written as -

\[
\frac{i}{\hbar} \sum_{\substack{p, k \in \vec{P} - \vec{K} \\left( k < k_c \right)}} i m_k V(\vec{P} + \vec{K}) C_{P_k}^+ C_{P}^+ \sum_{l} V(\vec{l}) C_{l} b(\vec{R}) \alpha^{+} Q_k \\
= \frac{i}{\hbar} \sum_{\substack{p, k \in \vec{P} - \vec{K} \\left( k < k_c \right)}} m_k V(\vec{P} + \vec{K}) \alpha^{+} Q_k C_{P} b(\vec{R}) \\
\text{(4.68)}
\]

Similarly, if it is considered \( l = |\vec{P} - \vec{K}| \), then commutator of equation (4.67) becomes -

\[
\frac{i}{\hbar} \sum_{\substack{p, k \in \vec{P} - \vec{K} \\left( k < k_c \right)}} m_k V(\vec{P} - \vec{K}) \alpha^{+} Q_k C_{P} b(\vec{R}) \\
\text{(4.69)}
\]

Now, it may be as -

\[
Q_k = \left( \frac{\hbar}{2 \omega} \right)^{1/2} (A_{k} - A_{-k})
\]
\[ P_k = i \left( \frac{\hbar \omega}{2} \right)^{1/2} (A_k^+ + A_{-k}) \]  

(4.70)

Where, \( A_k^+ \) and \( A_k \) are the plasmon creation and annihilation operators, then equation (4.68) becomes -

\[
\left( \frac{1}{2 \hbar \omega_p} \right)^{1/2} \sum_{p,k} \sum_{k < k_c} m_k V(\bar{\rho} + \bar{K}) \alpha^+ A_{k\bar{p}} b(\bar{R}) \\
- \sum_{k < k_c} \sum_{p,k} m_k V(\bar{\rho} + \bar{K}) \alpha^+ A_{-k\bar{p}}^+ C_{\bar{p}} b(\bar{R})
\]

Where, \( k < k_c; \ \omega \rightarrow \omega_p \)

The second term in the above expression has got no meaning, because creation of a plasmon in the negative state is not possible for the \((\bar{\rho} + \bar{K})\) level. Therefore, above expression takes the form of -

\[
\left( \frac{1}{2 \hbar \omega_p} \right)^{1/2} \sum_{p,k} \sum_{k < k_c} m_k V(\bar{\rho} + \bar{K}) \alpha^+ A_{k\bar{p}} b(\bar{R}) 
\]

(4.71)

Similarly, equation (4.69) takes the form by using equation (4.70) as -

\[
- \left( \frac{1}{2 \hbar \omega_p} \right)^{1/2} \sum_{k < k_c} \sum_{p,k} m_k V(\bar{\rho} - \bar{K}) \alpha^+ A_{k\bar{p}}^+ b(\bar{R})
\]

(4.72)

Thus putting the values, the fourth term in this new coordinate system becomes -
\[ \sum_{l} V(l) C_l b(\bar{R}) \alpha^+ + \left( \frac{1}{2 \hbar \omega_p} \right)^{1/2} \sum_{p,k, k<k_c} m_k V(\bar{P} + \bar{K}) \alpha^+ A_k C_p b(\bar{R}) \]

\[ - \left( \frac{1}{2 \hbar \omega_p} \right)^{1/2} \sum_{p,k, k<k_c} m_k V(\bar{P} - \bar{K}) \alpha^+ A_k b(\bar{R}) \]  

(4.73)

**Fifth term of equation (4.56):**

Substituting the value of \( P_k^+ \) and \( P_k \) in terms of new variables from relation (4.57) -

\[ \left[ \sum_{k<k_c} \frac{P_k^+ P_k}{2} \right]_{\text{new}} \]

\[ = \sum_{k<k_c} \frac{1}{2} \left[ \left( P_k^+ - i \sum_{p} m_k C_{\bar{P} - \bar{K}}^+ C_{\bar{P}} \right) \left( P_k + i \sum_{p} m_k C_{\bar{P} - \bar{K}}^+ C_{\bar{P}} \right) \right] \]

\[ = \sum_{k<k_c} \frac{P_k^+ P_k}{2} + i \sum_{p,k, k<k_c} (P_k + m_k C_{\bar{P} - \bar{K}}^+ C_{\bar{P}} - m_k C_{\bar{P} - \bar{K}}^+ C_{\bar{P}} P_k) \]

\[ + \frac{1}{2} \sum_{p,q,k, k<k_c} m_k^2 C_{\bar{P} + \bar{K}}^+ C_{\bar{q} - \bar{K}}^+ C_{\bar{P}} C_{\bar{q}} \]

Now using the relation \( P_k = -P_k^+ \) and replacing \(-k\) by \(k\) in the first part of the second term of above equation -

\[ \sum_{k<k_c} \frac{P_k^+ P_k}{2} + i \sum_{p,k} (P_k m_k C_{\bar{P} - \bar{K}}^+ C_{\bar{P}}) \]

\[ + \frac{1}{2} \sum_{p,q,k, k<k_c} m_k^2 C_{\bar{P} + \bar{K}}^+ C_{\bar{q} - \bar{K}}^+ C_{\bar{P}} C_{\bar{q}} \]  

(4.74)
Sixth term of equation (4.56):

\[
+i \sum_{k<k_c} m_k p_k C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}}^\dagger \]_{\text{new}} = i \sum_{p,k \atop k<k_c} m_k \left( p_k + i m_k C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}} \right) C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}}^\dagger
\]

\[
= \sum_{p,k \atop k<k_c} i m_k p_k C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}}^\dagger - m_k^2 C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{q}} C_{\bar{p}}
\]  \hspace{1cm} (4.75)

Seventh term of equation (4.56):

\[
- \sum_{k \neq 0 \atop p} m_k^2 C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}} \ b^+ (\bar{R}) b(\bar{R}) \]_{\text{new}}
\]

\[
= - \sum_{k \neq 0 \atop p} m_k^2 C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}} \ b^+ (\bar{R}) b(\bar{R})
\]

\[
- \frac{i}{\hbar} \left[ S_t - \sum_{k \neq 0 \atop p} m_k^2 C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}} \ b^+ (\bar{R}) b(\bar{R}) \right]
\]

\[
= - \sum_{k \neq 0 \atop p} m_k^2 C_{\bar{p} \rightarrow \bar{p}}^+ C_{\bar{p}} \ b^+ (\bar{R}) b(\bar{R})
\]  \hspace{1cm} (4.76)

So that this term remains unaffected

Eightth term of equation (4.56):
\[
\left[i \sum_{k<k_c} m_k p_k \, b^+ (\bar{R}) b(\bar{R}) \right]_{new} \\
= i \sum_{k<k_c} \left[ m_k p_k - i \sum_p m_k c_{\bar{p} + \bar{R}}^+ c_{\bar{p}} \right] b^+ (\bar{R}) b(\bar{R}) \\
= i \sum_{k<k_c} m_k p_k \, b^+ (\bar{R}) b(\bar{R}) \\
+ \sum_{p,k\atop k<k_c} m_k^2 c_{\bar{p} + \bar{R}}^+ c_{\bar{p}} \, b^+ (\bar{R}) b(\bar{R})
\]

(4.77)

Thus, putting all the eight term in equation (4.56) the new Hamiltonian becomes -
\[ H_2 = \sum_i \frac{p_i^2}{2m} + \sum_{i,p,k} \left( \frac{p_i \cdot \vec{k}}{m} - \frac{\hbar k^2}{2m} \right) m_k Q_k C_{\vec{p} + \vec{R}}^+ C_{\vec{p}}^+ + \sum_{l} V(\vec{l}) C_{\vec{l}} b(\vec{R}) \alpha^+ \]
\[ + \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} \sum_{p,k} m_k V(\vec{P} + \vec{R}) \alpha^+ A_k C_{\vec{p}} b(\vec{R}) \]
\[ - \sum_{p,k} m_k V(\vec{P} - \vec{R}) \alpha^+ A_k^+ C_{\vec{p}} b(\vec{R}) \]
\[ - \sum_{p,k} m_k^2 C_{\vec{p} + \vec{R}}^+ C_{\vec{p}}^+ b^+(\vec{R}) b(\vec{R}) e^{-i\vec{R} \cdot \vec{R}} \]
\[ + \sum_{k<k_c} \left( \frac{p_k^2}{2} + \frac{\omega_p^2}{2} Q_k^+ Q_k \right) - \sum_{p,k} m_k^2 C_{\vec{p} - \vec{R}}^+ C_{\vec{p}}^+ b^+(\vec{R}) b(\vec{R}) \]
\[ + i \sum_{k<k_c} m_k p_k b^+(\vec{R}) b(\vec{R}) \]

(4.78)

The first term of equation (4.78) is the kinetic energy of the electrons. The second term is the interaction between the Plasmon field and the individual quasi electrons and on using the relation (4.70) this becomes -

\[ H_{\text{int}} = \left( \frac{\hbar}{2\omega_p} \right)^{1/2} \sum_{k<k_c} \left( \frac{\vec{k} \cdot \vec{P}_i}{2} - \frac{\hbar k^2}{2} \right) m_k (A_k - A_{-k}^+) C_{\vec{p} + \vec{R}}^+ C_{\vec{p}}^+ \]

(4.79)
The third term is the short range coulomb interaction energy between the electrons; the forth term is the self energy of electrons which are under collective behavior; the fifth term represents the original X-ray emission line; first part of the sixth term represents the simultaneous emission of X-ray photon and the absorption of a plasmon with momentum $\hbar k$; while the second part describes the simultaneous emission of an X-ray photon and excitation of a plasmon with momentum $\hbar k$; The seventh term describes the presence of localized level vacancy and its interaction with the electron gas. The eighth term is the kinetic energy of the field oscillators, oscillating with frequency $\omega_p$; the ninth term represents the short range coulomb interaction between electrons and the ions; and the tenth term represents the coupling between the ion density fluctuations and the collective fields.

Thus, so far a general formalism for the involvement of plasmon oscillations in X-ray emission and absorption spectra has been developed. To deal a particular case one can modify the above as taken the total Hamiltonian of interacting electron gas coupled with the boson field of the plasmon as-

$$H_0 = \sum_i \frac{P_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{4\pi e^2}{k^2} e^{i\hbar \bar{r}_i - \bar{r}_j} \sum_{k < k_c} \frac{P_k^+ P_k}{2}$$

$$+ i \sum_{k < k_c} \left(\frac{4\pi e^2}{k^2}\right)^{1/2} P_k \rho_k$$

(4.80)
To change this Hamiltonian in the second quantization representation, first define $a_p^+$ and $a_p$ as the creation and annihilation operators respectively for an electron in the stat $|P>$ . The electrons, which are fermions obey the following anti-commutation rules for these operators -

$$[a_p, a_{p'}^+] = 0$$

$$[a_p^+, a_{p'}^+] = 0$$

$$[a_p, a_{p'}^+] = \delta_{p,p'}$$

If $b_q^+$ and $b_q$ are the creation and annihilation operators respectively of a plasmon in the state $q$, the plasmon being bosons, obeying following commutation rules.

$$[b_q, b_{q'}] = 0$$

$$[b_q^+, b_{q'}^+] = 0$$

$$[b_q, b_{q'}^+] = \delta_{q,q'}$$

Now, the procedure for changing any one particle operator, say $f_i(\vec{r}_i)$ in the second quantized representation is as follows-

The sum of these single particle operators is given as -

$$F_i = \sum_{i} f_i(\vec{r}_i)$$

And in the quantum mechanical form,
\[ F_i = \sum_{p,p'} \langle \Psi_p(\vec{r}_i)|f_1(\vec{r}_i)|\Psi_{p'}(\vec{r}_i) \rangle \]  

(4.81)

The wave function \( F_i \) can be written in the second quantized representation in terms of the creation and annihilation operator as:

\[ \Psi_p^*(\vec{r}_i) = \sum_p \phi_p^*(\vec{r}_i) a_p^+ \]

\[ = \sum_p \langle P|\alpha_p^+\Psi_{p'}(\vec{r}_i) = \sum_p \phi_{p'}(\vec{r}_i)a_{p'} = \sum_{p'} a_{p'} |p'\rangle \]  

(4.82)

where

\[ \phi_{p'}(\vec{r}_i) = e^{i\vec{p}\cdot\vec{r}_i} \]

and

\[ \phi_p(\vec{r}_i) = e^{-i\vec{p}\cdot\vec{r}_i} \]

(4.83)

Substituting this value in equation (4.81) as -

\[ F_i = \sum_{p,p'} \langle P|f_1(\vec{r}_i)|P'\rangle a_p^+ a_{p'} \]

(4.84)

**First term of equation (4.80):**

This is Kinetic energy of the electrons and is written as -

\[ F_i(\vec{r}_i) = \frac{p_i^2}{2m} \]

\[ F_i = \sum_i \frac{p_i^2}{2m} e^{-i\vec{p}\cdot\vec{r}_i} \left( \frac{p_i^2}{2m} \right) e^{i\vec{p}\cdot\vec{r}_i} a_p^+ a_{p'} dr_i = \sum_p \left( \frac{p_i^2}{2m} \right) \left[ \delta(P' - P)a_p^+ a_{p'} \right] \]

\[ = \sum_p E_p a_p^+ a_p \]

(4.85)

Where, \[ E_p = \frac{p_i^2}{2m} \]
(i) Third term of equation (4.80) :

In an exactly similar manner, the third term of the Hamiltonian equation (4.80), which represents the kinetic energy of the plasmon can be written in second quantized representation as-

$$\sum_{k<k_c} \frac{p_k^+ p_k}{2} = \sum \omega_q b_q^+ b_q$$ \hspace{1cm} (4.86)

Where, $\omega_q$ is the angular frequency of the plasmon state $|q$ the sum of two particle operators is -

$$F_2 = \sum_{i \neq j} f_2(\vec{r}_i, \vec{r}_j)$$

and in the quantum mechanical case

$$F_2 = \frac{1}{2} \sum_{\substack{p,p' \\
q,q'}} \langle \Psi_p(\vec{r}_i) \Psi_q(\vec{r}_j) |f_2(\vec{r}_i, \vec{r}_j) | \Psi_{p'}(\vec{r}_i) \Psi_{q'}(\vec{r}_j) \rangle$$

Using equation (4.82) -

$$F_2 = \frac{1}{2} \sum_{\substack{p,p' \\
q,q'}} \langle p,q | f_2 | p',q' \rangle a_p^+ a_q^+ a_{p'} a_{q'}$$ \hspace{1cm} (4.87)

(iii) Second term of equation (4.80) :

Applying equation (4.87), the second term of the Hamiltonian becomes -

$$F_2(\vec{r}_i, \vec{r}_j) = \frac{1}{2} \sum_{i \neq j} \frac{4\pi e^2}{k^2} e^{ik(\vec{r}_i-\vec{r}_j)}$$

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\[ F_2 = \frac{1}{2} \int \int e^{-i\bar{p} \cdot \bar{r}_i} e^{-i\bar{q} \cdot \bar{r}_j} \sum_k \frac{4\pi e^2}{k^2} e^{ik(\bar{r}_i - \bar{r}_j)} e^{i\bar{p}' \cdot \bar{r}_i} e^{i\bar{q}' \cdot \bar{r}_j} a_{p+q}^+ a_{p-q}^+ a_{p+q'} a_{p-q'} \, dr_i \, dr_j \]

\[ = \frac{1}{2} \sum_{p,p'} \sum_{q,q'} \left( \frac{4\pi e^2}{k^2} \right) \delta(-\bar{p} + \bar{k} + \bar{p}') + \delta(-\bar{q} - \bar{k} + \bar{q}) a_{p+q}^+ a_{p+q'}^+ a_{p+q} a_{p+q'} \]

\[ = \frac{1}{2} \sum_{p,p'} \sum_{q,q'} m_k^2 a_{p+q}^+ a_{p-q}^+ a_{p-k}^+ a_{p+k}^+ \quad (4.88) \]

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

**(iv) Fourth term of equation (4.80):**

This term represents the interaction between electrons and the plasmon field and its transformation is as follows. If \( Q_k \) and \( P_k \) are the boson field operator then in terms of the plasmon creation and annihilation operators \( b_k^+ \) and \( b_k \), they are given as:

\[ Q_k = \left( \frac{\hbar}{2\omega} \right)^{1/2} (b_k - b_k^+) \]

\[ P_k = i \left( \frac{\hbar \omega}{2} \right)^{1/2} (b_k + b_k^+) \quad (4.89) \]

Further,

\[ \sum_k \rho_k = e^{-i\bar{p} \cdot \bar{r}_i} e^{-i\bar{k} \cdot \bar{r}_i} e^{i\bar{p}' \cdot \bar{r}_i} a_{p+q}^+ a_{p}^+ \, dr_i = \delta(-p - k + p') a_{p+q}^+ a_{p+q'}^+ \]

\[ = a_{p}^+ a_{p+k} \quad (4.90) \]
using equation (4.89) and (4.90) the fourth term of Hamiltonian of equation (4.80) can be written as -

\[-i \sum_{k<k_c} \left[ \frac{4\pi e^2}{k^2} \right]^{1/2} i \left( \frac{\hbar \omega}{2} \right)^{1/2} (b_k^+ + b_k) a_p^+ a_{p+k} \]

According to Langreth [31], this can be written as -

\[ \sum_q a_p^+ a_{p+q} g_q (b_q^+ + b_q) \]  \hfill (4.91)

Here, \( g_q \) is the coupling constant which determines the extent of the interaction between electrons and plasmons; using equation (4.85), (4.87), (4.88) and (4.91) in the Hamiltonian (4.80) can now be written fully in the second quantized representation as -

\[ H = \sum_p E_p a_p^+ a_p + \sum_q \omega_q b_q^+ b_q + \frac{1}{2} \sum_{p,q} \sum_k m_k^2 a_p^+ a_q^+ a_{p-k} a_{q+k} + \sum_{q,p} a_p^+ a_{p+q} g_q (b_q^+ + b_q^+) \]  \hfill (4.92)

4.3 Determination of Expression for the relative intensity in the Intrinsic Process:

In the intrinsic process, the excitation of a plasmon takes place simultaneously with the creation of a hole. Bradshaw et al. [27] have divided core hole excitation into two classes.

(i) One where the number of show electrons are not conversed and

(ii) The other where the number of slow electrons are conserved.
The intensity in both the processes is found to be different, so there are two types of equations for the calculation of relative intensity. In this section the equations for relative intensity are derived in both the cases separately.

4.3 (i) Case 1: When the number of slow electrons are not conserved:

In this the probability for the occurrence of plasmon satellites in the three experiments XPS, SXAPS and $h\omega$ – APS have been calculated. The details of each process is as follows -

4.3 (i)(a): X-ray Photoelectron Spectroscopy (XPS):

In X-ray photoelectron spectroscopy, the final state is a core hole so that the transition operator $T_{XPS}$ will contain the annihilation operator for core electron, and is given as -

$$T_{XPS} = f_q a_p \tag{4.93}$$

Where, $f_q$ is the matrix element for the process and $a_p$ is the destruction operator for a core electron in the state $|P>$.

Now from equation (4.92), taking the terms which corresponds to the Hamiltonian with no core electrons as -

$$\tilde{H} = \sum_q \omega_q b_q^+ b_q + \sum_q a_p^+ a_{p+q} g_p (b_q^+ b_q^+) \tag{4.94}$$

Diagonalize this Hamiltonian performing a unitary transformation as -

$$\tilde{H} = U \tilde{H} U^+$$
where,

\[ U = \exp \left[ \sum_{q} f_q (b_q - b_q^+) \right] \]

\[ U \tilde{H} U^+ = \exp \left[ \sum_{q} f_q (b_q - b_q^+) \right] \cdot \tilde{H} \cdot \exp \left[ - \sum_{q} f_q (b_q - b_q^+) \right] \]

\[ = H + \left[ \sum_{q} f_q (b - b_q^+), H \right] \]

\[ = \sum_{q} \omega_q b_q^+ b_q + \sum_{q} a_q^+ a_{p+q} g_q (b_q - b_q^+) \]

\[ + \left[ \sum_{q} f_q (b_q - b_q^+), \sum_{q} \omega_q b_q^+ b_q + a_q^+ a_{p+q} g_q (b_p^+ + b_q^+) \right] \]

\[ = \sum_{q} \omega_p b_q^+ b_q + \sum_{q} f_q g_q \]

Here, commutation relation (4.30) for \( b_q \) & \( b_q^+ \). The matrix element \( f_q \) for XPS experiment is given by

\[ f_q = \frac{g_q}{\omega_q} \]

(4.96)

so

\[ U \tilde{H} U^+ = \sum_{q} \omega_q b_q^+ b_q + \sum_{q} \frac{g_q^2}{\omega_q} \]

Now transition probability per unit time per unit energy range at energy \( \omega \) is given as -
\[ P(\omega) = \sum_n |<\Psi_n|T|\Psi_0>|^2 \delta(\omega - E_n - E_0) \]  
(4.97)

Where, \( \Psi_0 \) denotes the initial state with energy \( E_0 \), \( \Psi_n \) the final state with energy \( E_n \) and \( T \) is transition operator. Equation (4.97) is rewritten in more convenient form as -

\[ P(\omega) = \frac{1}{2\pi} \int dt <\Psi_0|T^+T(t)|\Psi_0> e^{+i\omega t} \]  
(4.98)

where,

\[ T(t) = e^{iHt} \ T \ e^{-iHt} \]  
(4.99)

According to equation (4.93)-

\[ T^+ = f_q^+ a_p^+ \text{ and } T(t) = f_q a_p(t) \]  
(4.100)

while,

\[ a_p(t) = e^{iHt} \ a_p \ e^{-iHt} \]  
(4.101)

Transition probability is thus given as -

\[ P(\omega) = |f_q|^2 \int \frac{dt}{2\pi} <\Psi_0|a_p^+ a_p(t) e^{-iHt}|\Psi_0> e^{i\omega t} \]

\[ = |f_q|^2 \int \frac{dt}{2\pi} (\Psi_p|a_p^+ e^{iHt} a_p e^{-iHt}|\Psi_0)e^{i\omega t} \]

\[ = |f_q|^2 \frac{dt}{2\pi} <0|e^{iHt} |0> e^{i(\omega - \varepsilon_p)t} \]  
(4.102)

where, \( a_p|\Psi_0 >=|0> \)

Now from equation (4.96) -
\[ <0|e^{iHt}|0> = <0|U^+ \exp \left( i \sum_q \omega_q b_q^+ b_q t \right) U 0 > \exp \sum_q \frac{ig_q^2}{\omega_q} \] (4.103)

But from Lengreth [28] as -

\[
U(t) = \exp \left[ i \sum_q \omega_p b_q^+ b_q t \right] U \exp \left[ i \sum_q \omega_p b_q^+ b_q t \right] \\
= \exp \left[ i \sum_q \omega_q b_q^+ b_q t \right] \exp \left[ \sum_q f_q(b_q - b_q^+) \right] \\
- \sum_q f_q \left( b_q e^{-i\omega_q t} - b_q^+ e^{i\omega_q t} \right) \] (4.104)

Similarly,

\[
U^+(t) = \exp \left[ \sum_q f_q \left( b_q^+ e^{i\omega_q t} - b_q e^{-i\omega_q t} \right) \right]
\]

Thus,

\[
U^+(0) = \exp \left[ \sum_q f_q (b_q^+ - b_q) \right] \] (4.105)

Further for XPS experiments the coupling constants 'α' can be written as -

\[
\alpha = \sum_q \frac{g_q^2}{\omega_q^2} = \sum_q f_q^2 \] (4.106)
from equation (4.104 - 4.106) the equation (4.103) becomes as -

\[ < 0 | e^{iHt} | 0 > = < 0 | U^+(0) U(t) | 0 > e^{i\alpha \omega_q t} = \]

\[ < 0 | \exp \left( - \sum_q f_q^2 \right) \exp \left( \sum_q f_q^2 e^{i\omega_q t} \right) (e^{-i\omega_q t}) \]

\[ = e^{-\alpha} \exp(\alpha e^{i\omega_q t}) e^{-i\omega_q t} \]

(4.107)

But,

\[ \exp(\alpha e^{i\omega_q t}) = 1 + \alpha e^{i\omega_q t} + \frac{1}{2!} (\alpha e^{i\omega_q t})^2 + \ldots \]

\[ = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!} e^{i n \omega_q t} \]

Hence, equation (4.107) becomes -

\[ < 0 | \exp (iHt) | 0 > = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!} e^{i n \omega_q t} e^{-\alpha} e^{-i\omega_q t} \]

(4.108)

Now from equation (4.108) and equation (4.102) we can write

\[ P(\omega) = |f_q|^2 \int \frac{dt}{2\pi} \sum_n \frac{\alpha^n}{n!} e^{i n \omega_q t} e^{-\alpha} e^{-i\omega_q t} e^{i(\omega - \varepsilon_p)t} \]

\[ = |f_q|^2 \int \sum_n e^{-\alpha} \frac{\alpha^n}{n!} e^{i(\omega - \varepsilon_p - \omega_q + n \omega_q)t} \frac{dt}{2\pi} \]

To a first approximation \( \omega_q = \omega_p \). The plasmon frequency and the integral may be put in terms of Dirac delta Function as -
\[ P(\omega) = |f_q|^2 \sum_n e^{-\alpha \frac{\alpha^n}{n!}} \delta(\omega - \varepsilon_p - \alpha \omega_p + n\omega_q) \]  \hspace{1cm} (4.109)

### 4.3 (i) (b) : Soft X-ray Absorption Potential Spectroscopy (SXAPS)

In the SXAPS experiment, the final state consists of a core hole and two slow electrons at the fermi level. The transition operator \( T \) in this case contains the annihilation operator of a core electron, \( a_p^+ \) and the creation operator for two slow electrons \( a_h^+ \) and \( a_{h'}^+ \). Thus-

\[ T_{SXAPS} = \sum_{p,p'} |m_{p'p}\rangle, P|a_h^+a_{h'}^+a_p \]  \hspace{1cm} (4.110)

Where, \( m_{p'p} \) is the matrix element for the process, and -

\[ |p|, |p'| \approx K_F \]

In this case, the Hamiltonian is written as-

\[ H = \sum_p \varepsilon_p + \sum_q \omega_q b_q^+ b_q + \sum_q g_q (b_q - b_q^+) + \sum_q g_q^h a_h a_h^+ (b_q + b_q^+) \]

Where, \( g_q \) is the coupling constant of \( h \) core electron and \( g_q^h \) is that of a core hole proceeding in a manner similar to one for XPS, the transition probability comes out to be -

\[ P(\omega) = A \sum_n e^{-\alpha \frac{\alpha^n}{n!}} \delta(\omega - \varepsilon_p + 2\varepsilon_{k_F} - \alpha \omega_p + n\omega_p) \]  \hspace{1cm} (4.111)

where,

\[ A = 2 \sum_{p',p} |M_{p',p}|^2 \]  \hspace{1cm} (4.112)
and,

\[ \alpha = \sum \frac{(2g_q + g_q^h)^2}{\omega_p^2} \]

4.3 (i) (c) : Augger induced Appearance Potential Spectroscopy

\( (\hbar \omega - \text{APS}) \)

In this experiment, the final state consists of one core hole and
one slow electron at the fermi level, the transition operator (T)
contains one creation operator for the slow electron and one
annihilation operator for the core electron.

\[ T_{\hbar \omega - \text{APS}} = \sum_p m_p \alpha^+_p \alpha_n \quad (4.113) \]

Where, \(|P| = k_F\) and \(m_p\) is the oscillator strength. Analogous to
the case of XPS and SXAPS the transition probability comes out to be-

\[ P(\omega) = A \sum_n e^{-\alpha} \frac{\alpha^n}{n!} \left( \omega + \epsilon_{k_F} - \epsilon_p - \epsilon_{\omega_p} + n\omega_p \right) \quad (4.114) \]

Where

\[ A = \sum_p \left| m_p \right|^2 \]

and

\[ \alpha = \sum_q \frac{(g_q + g_q^h)}{\omega_p^2} \]

4.3 A Relative Intensity of Plasmon Satellite :

In equation (4.109) to (4.114) the weight factor \(e^{-\alpha} \frac{\alpha^n}{n!}\) denotes
the intensity of the nth plasmon satellite i.e. the main line. In the
present work first process is taken i.e., X-ray photoelectron
spectroscopy (XPS). Therefore, the intensity of the first order plasmon satellite relative to that of the main line is given as -

\[
i = \frac{I_1}{I_0} = \frac{e^{-\alpha} \alpha^1}{1!} \frac{e^{-\alpha} \alpha^0}{0!} = \frac{e^{-2\alpha} q_{\text{max}}}{\pi \hbar \omega_p} = 0.12 \, r_s
\]  

(4.115)

The coupling constant \( \alpha \) is given by Lengreth [28] as -

\[
\alpha = \frac{e^2 q_{\text{max}}}{\pi \hbar \omega_p} = 0.12 \, r_s
\]

Where, \( q_{\text{max}} \) is the plasmon cut off wave-vector and \( r_s \) is a dimensionless parameter given by Rooke [30] as -

\[
r_s = \left( \frac{47.11}{\hbar \omega_p} \right)^{2/3}
\]

Equation (4.115) gives -

\[
i = \frac{I_1}{I_0} = \alpha = 0.12 r_s
\]  

(4.116)

The coupling constant \( \alpha \) can be further modified by Lengreth [31], taking into account the effect of 'slow-fast' interference terms which produce the cancellation when slow charge is conserved. The effect of the interface term is to modify \( \alpha \) to a new coupling constant by Lengreth [31] as -

\[
\alpha' = \alpha - \left( \frac{e^2}{hv} \right) F
\]
Where, $F$ is a slowly varying function of velocity and has nearly unity. The value of $\left(\frac{e^2}{h\nu}\right)$ has been calculated to be of the order of 0.1 for incident energies of the order of $K_eV$ and so -

$$\alpha' = \alpha - \left(\frac{e^2}{h\nu}\right)F = 0.12\, r_s - 0.1$$

So that, the new equations for the relative intensity will becomes-

$$i_1 = \frac{l_1}{l_0} = 0.12\, r_s - 0.1 \quad (4.117)$$

The formula (4.117) derived for the relative intensity of first intrinsic process (i.e. When the number of slow electrons are not conserved) is same for both the low and high energy satellites. Using the above formula, the author has calculated the relative intensity of X-ray satellite spectra in core level 2p peaks of metal oxides ($\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, $\text{Cr}_2\text{O}_3$, and $\text{CrO}_3$).

4.3 (ii) Case II : When the number of slow electrons is conserved :

In order to derive the relative intensity in this case, the equation (4.78) is further modified. In this equation (4.78), its last term suppresses the collective behaviour of the system. So this term should be eliminated the Hamiltonian (4.78) does not have any term which can describes the plasmon loss. Therefore, the generator of a new canonical transformation is taken in such a way that the above two drawbacks can be overcome. That is the last term of equation (4.78)
which is eliminated and a new term for the plasmon loss is added simultaneously. A consideration for such a generator is:

\[ S_2 = i \sum_{k<k_c} m_k Q_k b^+(\bar{R})b(\bar{R}) \]  \hspace{1cm} (4.118)

Whether the above generator satisfies the object or not, for this the canonical transformation is applied on the first part of sixth term of the equation (4.78) or kinetic energy of field oscillators as:

\[ e^{-i\frac{s_2}{\hbar}} \sum_{k<k_c} \frac{p_k^+ p_k}{2} e^{i\frac{s_2}{\hbar}} = \sum_{k<k_c} \frac{p_k^+ p_k}{2} - i \sum_{k<k_c} m_k p_k b^+(\bar{R})b(\bar{R}) \]  \hspace{1cm} (4.119)

Putting the values of \( p_k \) from equation (4.70) then,

\[ \sum_{k<k_c} \frac{p_k^+ p_k}{2} - i \sum_{k<k_c} m_k p_k b^+(\bar{R})b(\bar{R}) \]

\[ = \sum_{k<k_c} \hbar \omega A_k^+ A_k - i \sum_{k<k_c} m_k p_k b^+(\bar{R})b(\bar{R}) \]  \hspace{1cm} (4.120)

The first term on the right hand side of equation (4.120) describes the collective loss value because \( \omega = \omega_p \) for \( k < k_c \). The second term with minus sign which neutralises the last term of equation (4.78). Hence, the generator \( S_2 \) for the canonical transformation is the right one which gives the desired results.

The effect of this canonical transformation generated by the operator \( S_2 \) on all other terms of equation (4.78), except first and second part of the sixth term of equation (4.78), gives second order effect and can be neglected. Only the first and second part of the sixth term (\( E.M_- \)) and (\( E.M_+ \)) respectively gives first order effect. Thus,
the effect of these two terms separately for new canonical transformation on these two terms separately are taken for study.

**First Part of Sixth term of equation (4.78):**

\[
(E\cdot M)_\text{new} = e^{-i\frac{s_2}{h}(E\cdot M)} e^{i\frac{s_2}{h}} \\
= (E\cdot M) \\
= \frac{i}{\\hbar} \left[ S_2 \left( \frac{1}{2\hbar\omega_p} \right) \right]^{1/2} \sum_{\substack{p, \ \kappa < \kappa_c}} m_k V(\overline{P} + \overline{K}) \alpha^+ \beta_{\kappa} \alpha A_k C_p b(\overline{R})
\]

up to first order -

\[
= (E\cdot M) - \frac{i}{\\hbar} \left[ i \sum_{\kappa < \kappa_c} m_k Q_k b^+ (\overline{R}) \left( \frac{1}{2\hbar\omega_p} \right) \right]^{1/2} \sum_{\substack{p, \ \kappa < \kappa_c}} m_k V(\overline{P}) \\
+ \overline{K} \alpha^+ \beta_{\kappa} \alpha A_k C_p b(\overline{R})
\]

\[
= \left( \frac{1}{2\hbar\omega_p} \right)^{1/2} \left[ \sum_{\substack{p, \ \kappa < \kappa_c}} m_k V(\overline{P}) \\
+ \overline{K} \alpha^+ \beta_{\kappa} \alpha A_k C_p b \left( i \sum_{\kappa < \kappa_c} m_k Q_k b^+ b \right) \right]
\]

(4.121)

The effect of the operator \( Q_k b^+ b \) on the X-ray emission term in the second term of equation (4.121) is zero, because they are in the same state, so equation (4.121) reduces to -
(E. M\(_-\))\(_{\text{new}}\) = E. M\(_-\) - \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} \left( \sum_{p,k<k_c} V(\bar{P} + \bar{K}) \alpha^+ C_p b \right) \\
\times \left( \hbar \sum_{k<k_c} m_k Q_k b^+ b \right) \tag{4.122}

in the right hand side of equation (4.122) the second term is summed over \( k < k_c \) twice, which may give rise to presence of virtual plasmons. In order to decouple the virtual plasmon form the real plasmons, author takes \( k = 0 \) in the matrix element \( V(\bar{P} + \bar{K}) \). Thus, the equation (4.122) becomes -

\[(E. M)_{\text{new}}\]
\[= E. M_- - \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} \left( \sum_{p,k<k_c} m_k V(\bar{P}) \alpha^+ A_k^+ C_p b (\bar{R}) \right) \tag{4.123}\]
\[= E. M_- + E. M'_- \tag{4.124}\]

Second Part of Sixth term of equation (4.78):

Proceeding as above, \((E. M_+)_\text{new}\) as-

\[(E. M_+)_\text{new}\]
\[= E. M_+ + \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} \left( \sum_{p,k<k_c} m_k V(\bar{P}) \alpha^+ A_k^+ C_p b (\bar{R}) \right) \tag{4.125}\]
\[= E. M_+ + E. M'_+ \tag{4.126}\]

Thus, the effect of new canonical transformation generated by operator (4.118) \( S_2 \) on the Hamiltonian is to produce two new terms \( E. M'_- \) and \( E. M'_+ \) are given by

\[\vdots\]
E. M'_- = \left( \frac{1}{2\hbar\omega_p} \right)^{1/2} \left( \sum_{p,k<k_c} m_k V(\overline{P}) \alpha^+ A_k C_p b(\overline{R}) \right) \quad (1.27)

E. M'_+ = \left( \frac{1}{2\hbar\omega_p} \right)^{1/2} \left( \sum_{p,k<k_c} m_k V(\overline{P}) \alpha^+ A_k^+ C_p b(\overline{R}) \right) \quad (1.28)

Thus, after making the canonical transformation generated by the operator $S_2$ on the Hamiltonian (4.78) but some of a new Hamiltonian as -

\[ H_3 = \sum_i \frac{p_i^2}{2m} + \sum_{k<k_c} \left( \frac{\overline{k} \cdot \overline{p}}{m} - \frac{\hbar k^2}{2m} \right) m_k Q_k C_{\overline{p}+\overline{R}} C_p \]

\[ + \frac{1}{2} \sum_{k<k_c} m_k^2 (C_{\overline{p}-\overline{R}} C_p C_{\overline{p}+\overline{R}} C_q - n) - \sum_{k<k_c} \left( \frac{2\pi e^2}{k^2} \right) \]

\[ + \sum_{l} V(l) C_p b \alpha^+ E. M_- + E. M_+ + E. M'_- + E. M'_+ \]

\[ - \sum_{p,k \neq 0} m_k^2 C_{\overline{p}} C_p b^+ b e^{-i \overline{R} \cdot \overline{R}} + \sum_{k<k_c} \frac{p_k^+ p_k}{2} - \sum_{p,k \neq 0} C_{\overline{p}+\overline{R}} C_p b^+ b \]

\[ + \sum_{k<k_c} \hbar \omega_p A_k^+ A_k \quad (4.129) \]

The second term of Hamiltonian (4.129) represents the interaction or coupling between the plasmon field and the individual quasi-electrons can be eliminated by a further canonical transformation generated by the operator $S_3$, given by Bohm and Pines [40] as -

\[ -: 108 :- \]
\[ S_3 = \left( -\frac{e_i}{m} \right) \sum_{i,k<k_c} \left( \frac{2\pi\hbar}{\omega} \right)^{1/2} \left[ \varepsilon_k \left( p_i - \frac{\hbar k}{2} \right) A_k^e e^{i\vec{k}\cdot\vec{r}_i} \right] \left( \omega - \frac{K.P_i}{m} + \frac{\hbar k^2}{2m} \right)^{-1/2} \] 

\[ - e^{-i\vec{k}\cdot\vec{r}_i} A_k^+ \varepsilon_k \left( p_i - \frac{\hbar k}{2} \right) \left( \omega - \frac{k.p_i}{m} + \frac{\hbar k^2}{2m} \right) \] 

(4.130)

The new Hamiltonian will be a function of new variables \( r_i', p_i' \), \( A_k' \), and \( A_k'^+ \), while the old Hamiltonian \( H_3 \) was a function of \( r_i, p_i, A_k \) and \( A_k^+ \). The new variables are related to old variables as follows -

\[
\begin{align*}
 p_i' &= (p_i')_{\text{new}} = p_i - \frac{i}{\hbar} [S_3, p_i] \\
r_i' &= (r_i')_{\text{new}} = r_i - \frac{i}{\hbar} [S_3, r_i] \\
A_k' &= (A_k')_{\text{new}} = A_k - \frac{i}{\hbar} [S_3, A_k]
\end{align*}
\]

(4.131)

and, \( S_3 \) satisfies the relation -

\[
- \left( \frac{i}{\hbar} \right) [S_3, H_a] = -H_{int}
\]

(4.132)

where,

\[
H_a = \sum_i \frac{p_i^2}{2m} + \sum_{k<k_c} \frac{\hbar \omega}{2} [A_k^+A_k + A_kA_k^+]
\]

(4.133)

Here, dropped the prime from the new variables is dropped, and further, equation (4.133) is the first and last term of equation (4.129).

Now, the effect of the canonical transformation is studied generated by \( S_3 \) operator on E.M._ and E.M._ terms of equation.
(4.127) and (4.128). Due to this transformation the plasmon frequency now depends on $k$

Due to this canonical transformation -

$$(E. M_-)_{\text{new}} = (E. M_-) - \frac{i}{\hbar} [S_3, E. M_-] \quad (4.134)$$

$$(E. M_+\text{)}_{\text{new}} = (E. M_+) - \frac{i}{\hbar} [S_3, E. M_+] \quad (4.135)$$

The new Hamiltonian will give two additional terms -

$$E. M'' = \sum_{p, k < k_c} V(\pmb{P} + \pmb{K}) \left( \frac{1}{2\hbar\omega_p} \right)^{1/2} m_k \left[ \frac{\frac{k \cdot \pmb{p}}{m} - \frac{\hbar k^2}{2m}}{\omega - \frac{\frac{k \cdot \pmb{p}}{m} + \frac{\hbar k^2}{2m}}{m}} \right] \alpha^+ A_k C_p b(\pmb{R}) \quad (4.136)$$

$$E. M'' = - \sum_{p, k < k_c} V(\pmb{P} - \pmb{K}) \left( \frac{1}{2\hbar\omega_p} \right)^{1/2} m_k \left[ \frac{\frac{k \cdot \pmb{p}}{m} + \frac{\hbar k^2}{2m}}{\omega - \frac{\frac{k \cdot \pmb{p}}{m} + \frac{\hbar k^2}{2m}}{m}} \right] \alpha^+ A_k^+ C_p b(\pmb{R}) \quad (4.137)$$

In these two term given by equation (4.136) and equation (4.137) respectively, first term gives the relative intensity of high energy plasmon satellite, while second term gives the relative intensity of low energy plasmon satellite. Since author is concerned only with the high energy plasmon satellites, hence the first term given by equation (4.136) is been used.

Again equation (4.136) provides the Hamiltonian for simultaneous absorption of plasmon and photon which may give rise to the absorption of high energy X-ray satellites. So that Hamiltonian (4.136) will give an expression for the intensity of second intrinsic absorption of high energy X-ray satellites.
4.3 (B) Relative Intensity of High Energy Single Satellite:

The Hamiltonian representing the absorption of plasmon with the emission of X-ray photon simultaneously. The initial state \( |i> \) is the localized vacancy in the inner shell of the atom together with the plasmon momentum \( \hbar k \). In the final state, there are hole in the valence band of the metal and X-ray photon. Since author is considering the collective excitation of electron gas, the short range effect is neglected. Then the matrix element of the equation (4.136) is given as:

\[
< f | E.M'' | i > = \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} V(\overline{p} + \overline{k}) m_k \left[ \frac{\hbar k.\overline{p} - \hbar k^2}{m} \frac{2m}{\omega_p - \frac{\hbar k.\overline{p}}{m} + \frac{\hbar k^2}{2m}} \right] \quad (4.138)
\]

The intensity of high energy plasmon satellite can be written as:

\[
I_{sat}(E_p) = \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} I_0(E_p) \sum_k m_k^2 \left[ \frac{\hbar k.\overline{p} - \hbar k^2}{m} \frac{2m}{\omega_p - \frac{\hbar k.\overline{p}}{m} + \frac{\hbar k^2}{2m}} \right] \quad (4.139)
\]

In the denominator the term \( -\frac{\hbar k.\overline{p}}{m} \) is due to a shift of the plasmon eigen field of the electron resulting from the relative velocity of the electron with respect to the ion and the term \( \frac{\hbar k^2}{2m} \) corresponds to recoil of the electron as it absorbs a plasmon. In the numerator the term \( \frac{\hbar k^2}{2m} \) comes from the non commutativity of the coordinator and the momentum of the electron. It is essentially a quantum defect.
In equation (4.139) author transform summation into an integration as -

\[ I_{\text{sat}}(E_p) = \left( \frac{1}{2\hbar \omega_p} \right)^{1/2} I_0(E_p) \frac{1}{(2\pi)^3} \]

\[ \int_0^{k_c} \int_{-1}^{+1} 2\pi k^2 dk \, d\theta (\cos \theta) \left[ \frac{\hbar k \cdot \vec{p}}{m} - \frac{\hbar k^2}{2m} \right] \]

(4.140)

As \( \cos \theta \) varies from \(-1\) to \(+1\), the value will be -

\[ \cos \theta = \mu \]

and

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

(4.141)

it becomes as -
\[ I_{\text{sat}}(E_p) = \left[ \frac{1}{2\hbar \omega_p} \right] I_0(E_p) \frac{1}{(2\pi)^3} 2\pi \times 4\pi e^2 \]

\[ \times \int_0^{k_c} \int_{-1}^{+1} \frac{1}{k^2} \, dk \, du \left[ \frac{\hbar \bar{p} - \hbar k^2}{m} \frac{\omega_p - \hbar k^2}{2m} \right]^2 \]

\[ = \left( \frac{e^2}{2\pi \hbar \omega_p} \right) I_0(E_p) \int_0^{k_c} \, dk \int_{-1}^{+1} \left[ \frac{\hbar \bar{p} - \hbar k^2}{m} \frac{\omega_p}{\omega_p - \hbar k^2/2m} - 1 \right]^2 \, d\mu \]

\[ = \frac{e^2 I_0(E_p)}{2\pi \hbar \omega_p} \int_0^{k_c} \, dk \int_{-1}^{+1} \left[ 1 + \frac{\omega_p^2}{(\omega_p - \hbar k^2/2m)^2} \right] \left( \frac{2\omega_p^2}{(\omega_p - \hbar k^2/2m)} \right)^2 \, d\mu \]  
(4.142)

First integral part of equation (4.142) is equal to -

\[ I_1 = \int_{-1}^{+1} \, d\mu = 2 \]  
(4.143)

Second integral is equal to -

\[ I_2 = \omega_p^2 \int_{-1}^{+1} \frac{1}{\left( \omega_p + \hbar k^2/2m \right)^2} \, d\mu \]
\[ = \frac{\omega_p^2}{\left(\omega_p + \frac{\hbar k^2}{2m} + \frac{\hbar \vec{p} \cdot \vec{\mu}}{m}\right)\left(\omega_p + \frac{\hbar k^2}{2m} - \frac{\hbar \vec{p}}{m}\right)} \]  

(4.144)

Third term is equal to

\[ I_3 = -2\omega_p \int_{-1}^{1} \frac{1}{\left(\omega_p - \frac{\hbar \vec{p} \cdot \vec{\mu}}{m} + \frac{\hbar k^2}{2m}\right)} d\mu \]

\[ = \frac{2\omega_p}{\hbar \vec{p}} \int_{-1}^{1} \frac{\left(-\frac{\hbar \vec{p}}{m}\right)}{\left(\omega_p - \frac{\hbar \vec{p} \cdot \vec{\mu}}{m} + \frac{\hbar k^2}{2m}\right)} d\mu \]

\[ = \frac{2\omega_p}{\hbar \vec{p}} \log_e \left(\frac{\omega_p - \frac{\hbar \vec{p}}{m} + \frac{\hbar k^2}{2m}}{\omega_p + \frac{\hbar \vec{p}}{m} + \frac{\hbar k^2}{2m}}\right) \]  

(4.145)

Substituting these values of \(I_1, I_2\) and \(I_3\) in equation (4.142) as -

\[ I_{\text{sat}}(E_p) = \frac{e^2}{\pi \hbar \omega_p} I_0(E_p) \int_0^{k_c} \frac{d\vec{p}}{2\pi} \left[ 1 + \frac{k_c}{\hbar \vec{p}} \log_e \left(\frac{\omega_p - \frac{\hbar \vec{p}}{m} + \frac{\hbar k^2}{2m}}{\omega_p + \frac{\hbar \vec{p}}{m} + \frac{\hbar k^2}{2m}}\right) \right. \]

\[ + \frac{\omega_p^2}{\left(\omega_p + \frac{\hbar k^2}{2m} + \frac{\hbar \vec{p}}{m}\right)\left(\omega_p + \frac{\hbar k^2}{2m} - \frac{\hbar \vec{p}}{m}\right)} d\vec{p} \]  

(4.146)

Where, \(k\) is a wave vectors of plasmon and \(\vec{p}\) is the momentum of electron it becomes further as -

\[ x = \frac{k}{k_F}, \quad y = \frac{p}{k_F}, \quad \beta = \frac{k_c}{k_F}, \quad \frac{\hbar \omega_p}{E_F} = 2\beta + \beta^2 \]

\[ dx = \frac{dk}{k_F}, \quad E_F = \left(\frac{\hbar k_F}{2m}\right)^2 \]  

(4.147)
Where, \( x \) varies from 0 to \( \beta \), \( k_F \) is the wave vector of Fermi energy from equation (4.147), the new expression for the intensity of the satellite in integral form is obtained as:

\[
I_{\text{sat}}(E_y) = \frac{e^2 k_F}{\pi \hbar \omega_p} I_0(E_y) \int_0^\beta \left[ 1 + \frac{2\beta + \beta^2}{2xy} \log_e \frac{2\beta + \beta^2 + x^2 - 2xy}{2\beta + \beta^2 + x^2 + 2xy} \right. \\
\left. + \frac{(2\beta + \beta^2)^2}{(2\beta + \beta^2 + x^2 - 2xy)(2\beta + \beta^2 + x^2 + 2xy)} \right] dx \quad (4.148)
\]

Now, to find out the values of various integrals of equation (4.148) -

\[
I_4 = \int_0^\beta dx = \beta 
\quad (4.149)
\]

\[
I_5 = \int_0^\beta \frac{2\beta + \beta^2}{2xy} \log_e \frac{2\beta + \beta^2 + x^2 - 2xy}{2\beta + \beta^2 + x^2 + 2xy} dx
\]

\[
= 2\beta \int_0^\beta \frac{1}{2xy} \log_e \left( 1 - \frac{4xy}{2\beta + \beta^2 + x^2 + 2xy} \right) dx
\]

\[
= 2\beta \sqrt{\frac{2}{\beta}} \tan^{-1} \frac{\beta}{2} 
\quad (4.150)
\]

\[
I_6 = \int_0^\beta \frac{(2\beta + \beta^2)^2}{(2\beta + \beta^2 + x^2 - 2xy)(2\beta + \beta^2 + x^2 + 2xy)} dx
\]

Let \( \beta^2 = 0, \quad y = 0 \)

Then,

\[
I_6 = (2\beta^2) \int_0^\beta \frac{1}{(x^2 + 2\beta^2)^2} dx
\]
\[ I_6 = \frac{1}{2} \frac{\beta}{\left(1 + \frac{\beta}{2}\right)} + \frac{1}{2} 2\beta \frac{1}{\sqrt{2\beta}} \tan^{-1} \frac{\beta}{2} \quad (4.151) \]

Substituting the values of \( I_4 \), \( I_5 \) and \( I_6 \) in equation (4.148) relative intensity of high energy plasmon satellites is obtained as -

\[ i_2 = \frac{I_{\text{sat}}(E_y)}{I_0(E_y)} = \frac{e^2 k_F}{\pi \hbar \omega_p} \left[ \beta - 2\beta \sqrt[2]{\beta} \tan^{-1} \frac{\beta}{2} + \frac{1}{2} \frac{\beta}{(1 + \frac{\beta}{2})} + \frac{\beta}{2} \sqrt[2]{\beta} \tan^{-1} \frac{\beta}{2} \right] \]

\[ i = \alpha \left[ 1 - \frac{3}{2} \sqrt[2]{\beta} \tan^{-1} \frac{\beta}{2} + \frac{1}{2} \frac{1}{(1 + \frac{\beta}{2})} \right] \quad (4.152) \]

Where,

\[ \alpha = \frac{e^2 k_c}{\pi \hbar \omega_p} = 0.166 r_s \]

\[ \beta = \frac{k_c}{k_F} = 0.814 r_s^{1/2} \quad (4.153) \]

Where \( r_s = \left( \frac{47.11}{\hbar \omega_p} \right)^{2/3} \) dimensionless parameter

It may be represented as a Table 3 -

\[ \text{116} \]
Table 3: Relative Intensity of transition metal oxides on their core level 2p peaks

<table>
<thead>
<tr>
<th>S. No.</th>
<th>COMPOUNDS</th>
<th>Author intensity</th>
<th>Exp. Intensity [133]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe₂O₃</td>
<td>0.36</td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>Fe₃O₄</td>
<td>0.47</td>
<td>0.52</td>
</tr>
<tr>
<td>3</td>
<td>Cr₂O₃</td>
<td>0.36</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>CrO₃</td>
<td>0.36</td>
<td>0.28</td>
</tr>
</tbody>
</table>

(4.4) (C) - Derivation of Expression for the Relative Intensity in the Intrinsic and Extrinsic Process:

The author has calculated the relative intensity of X-ray satellites using plasmon theory in new light. The physics of plasma excitation in photoemission is very interesting, because different processes contribute to its intensity. The sudden change in the potential due to formation of a core hole attracts the conduction electrons to screen the core-hole resulting in the intrinsic plasmon excitation [Tung & Ritchie 117]. On the other hand, the extrinsic plasmon excitation is created by the coulomb interaction of the conduction electrons with the photoelectron traversing through the solid form the photoemission site to the surface. The interference effect can also be visualizes as the interaction between localizes photohole (intrinsic) and the outgoing photoelectron (intrinsic) in which the virtual plasmon created by one is absorbed by the other. It
has been observed that both the contributions of both intrinsic and extrinsic plasmon excitations in photoemission spectrum overlap one another, so they are not be readily separable experimentally. Also the question whether the photoemission satellite spectra seen are intrinsic or extrinsic in nature has aroused much controversy. Thus, in order to analyse the spectrum a more detailed qualitative analysis is needed. Many theoretical studies have been performed to evaluate the contribution of the intrinsic and extrinsic processes and to understand their origin in photoemission. Lundqvist [118] suggested that over 50% of the loss spectrum is due to the intrinsic process, while a more recent semi-phenomenological analysis by Pardee et al. [119] indicated 10% or less for Al. Sunjic et al. [120-121] argued that photoemission is a many body process and thus the breakdown into intrinsic and extrinsic effects is artificial. Srivastava et al. [134] suggested that the intrinsic effect should always be of major importance for free electron like materials since the probability for electron-plasmon scattering in these materials is relatively high for almost any electron kinetic energy. Chang et al. [123] estimated that the intrinsic plasmon production associated with the core hole is quite small including the interferences between the core hole and outgoing electron. The analysis of the intensity profiles of the plasmon loss structure in XPS spectrum for Al indicates that the intrinsic effects contribute the major part. Feibelman [124] calculated the plasmon intensities as a function of depth and θ, assuming an infinite vector. Penn [126] calculated the plasmon line-shapes and estimated
the intrinsic bulk plasmon contribution to be 26% for Al, which was much lower than 50% intrinsic plasmon contribution suggested by Lundquist [118].

Iglesfield [127-128] studied the suppression of the plasmon intensities at low electron kinetic energy by calculating the plasmon line shapes as function of the kinetic energy and depth of photo emission site. Iglesfield [128] used the golden rule formalism of photoemission and considered plasmon depression as well as the interference effect. The interference between extrinsic and intrinsic plasmon was found to suppress the long wavelength plasmon excitations. Using a transition matrix approach, it has been calculated the line shape and intensity of the intrinsic, extrinsic and interference contributions to both bulk and surface plasmons as function of z, and their results are in good agreement with that of Iglesfield [128]. The theoretical calculations by different groups predict an asymmetric line-shape for both bulk and surface plasmon [126-128, 130, 27]. Although plasmon excitations in photoemission spectra of Al have been known for more than three decades and were studied by different groups in the late 1970s and early 1980s. Yet the explanation of satellite intensity remained unresolved. Now in the present study author has tried to tackle this long standing problem and incorporated both the processes i.e. the relative contribution of extrinsic process as well as intrinsic process. Intrinsic process is further divided into two categories [Srivastava et al. 131].
(a) When number of electrons is conserved; plasmon satellites are weak

(b) When number of electrons is not conserved; plasmon satellites are strong.

Relative intensity in both the cases with new modification in the light of Bradshaw [27] and Lengreth [122] is calculated, which explains that not only intrinsic process but extrinsic process and their relative contribution may also contribute in relative intensities. The combined effect of intrinsic and extrinsic plasmon excitation intensity variation was suggested by Lengreth [125, 134-139] as:

\[ i = \frac{I_s}{I_m} = \alpha^n \sum_{m=0}^{n} \left( \frac{\beta}{\alpha} \right)^m \frac{m!}{m!} \]  

(4.154)

The value of \( \beta \) is taken as \( \beta = 0.12 r_s \) which is purely intrinsic by Bohm and Gross [45].

\[ r_s = \left( \frac{47.11}{h \omega_s} \right)^{2/3} \] is dimensionless parameter [Rooke 30] and \( \alpha = 0.47 r_s^{1/2} \) [Lengreth 31] in the place of \( \alpha = (1 \frac{1}{L})^{-1} \) used by Pardee et al. [119] the equation (4.154) contains a series of terms. The first term of the equation is purely extrinsic, while a second term is purely intrinsic. The other terms are containing the relative contributions of both extrinsic and intrinsic. The speciality of this formula is that each term alone or simultaneously with other terms is able to give the relative intensity. This formula also includes both the categories mentioned by Bradshaw [27] and gives better results as
compared to traditional methods for calculation of the relative intensity. Using the values of $\alpha, \beta$ and $r_\alpha$ in equation (4.154), author has calculated the relative intensity of satellites using the formula (4.152). The author has calculated the relative intensity of $L_{\alpha 1}$ X-ray satellites for 4d transition metals Zr, Nb, Mo, Ru, Rh and Pd", and compared with the calculated values of Surendra Poonia & S. N. Soni [133] and found that the calculated values and estimated values are in agreement with the calculated values of Surendra Poonia & S. N. Soni [133]. It can be presented in table form –

**Table- 4 Relative Intensity of $L_{\alpha 1}$ satellite of 4-d Transition element**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of Metal</th>
<th>Surface Energy</th>
<th>Rs</th>
<th>Alpha</th>
<th>Beta</th>
<th>Author Intensity</th>
<th>Exp. Intensity [133]</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZIRCONIUM</td>
<td>5.44</td>
<td>4.22</td>
<td>0.97</td>
<td>0.51</td>
<td>0.78065</td>
<td>0.780012</td>
<td>$\beta + 0.1 + \beta^2 / 2\alpha$</td>
</tr>
<tr>
<td>2</td>
<td>NIBOLIUM</td>
<td>6.19</td>
<td>3.87</td>
<td>0.92</td>
<td>0.46</td>
<td>0.7780</td>
<td>0.770182</td>
<td>$\beta + 0.1 + \beta^2 / 2\alpha$</td>
</tr>
<tr>
<td>3</td>
<td>MOLYBDENUM</td>
<td>6.67</td>
<td>3.68</td>
<td>0.90</td>
<td>0.44</td>
<td>1.3530</td>
<td>1.36827</td>
<td>$2(\beta + 0.1 + \beta^2 / 2\alpha)$</td>
</tr>
<tr>
<td>4</td>
<td>RUTHENIUM</td>
<td>7.15</td>
<td>3.51</td>
<td>0.88</td>
<td>0.42</td>
<td>0.7834</td>
<td>0.7434</td>
<td>$2\beta - 0.1$</td>
</tr>
<tr>
<td>5</td>
<td>RHODIUM</td>
<td>7.07</td>
<td>3.54</td>
<td>0.88</td>
<td>0.42</td>
<td>0.8655</td>
<td>0.8498</td>
<td>$2\beta$</td>
</tr>
<tr>
<td>6</td>
<td>PALLADIUM</td>
<td>6.84</td>
<td>3.77</td>
<td>0.91</td>
<td>0.45</td>
<td>0.8623</td>
<td>0.9044</td>
<td>$2\beta$</td>
</tr>
</tbody>
</table>