Chapter 2

Theoretical aspects of inner shell ionization

2.1 Introduction

Inner-shell ionization by charged particles [1-2] has been extensively investigated in last three decades, mainly because of its importance for the particle induced x-ray emission (PIXE) in analytical studies. On the other hand, an accurate knowledge of the cross-sections for ionization induced by light and heavy ions over a wide energy and element ranges offers an experimental basis for developing and testing theoretical descriptions of both ionization [2-4] and inner-shell deexcitation [5-6] processes. Initially, most experiments [7-13] were performed for light-ion impact in case of the K and L shells. Following increased availability of heavy-ion beams, the inner-shell ionization measurements have been extended to heavier ions and the L and M shells [14-16]. Simultaneously with experimental studies, the main theoretical effort has been focused on the description of asymmetric collisions ($Z_1 \ll Z_2$), where $Z_1$ and $Z_2$ are the projectile and target atomic numbers, respectively. In such collisions, the inner-shell vacancies are produced predominantly by the direct Coulomb ionization process, which can be treated perturbatively using the first-order perturbation approaches, namely, the Plane-Wave Born Approximation (PWBA) [3] and the Semi Classical Approximation (SCA) [4]. Besides the quantum-mechanical treatment, the classical nonperturbative approach, known as the Binary-Encounter Approximation (BEA) [17], was developed for describing direct ionization. The standard PWBA [18-20] and SCA [21-23] approaches for direct ionization were further developed to include the hyperbolic trajectory of the projectile [24-26], the relativistic wave functions [25, 27-30], and the corrections for the "binding-polarization effect" [31-33]. The most advanced approach based on the PWBA, which goes beyond the first-order treatment to include corrections for the binding-polarization effects within the Perturbed Stationary States (PSS) approximation,
the projectile Energy loss \((E)\), and Coulomb deflection \((C)\) effects as well as the Relativistic \((R)\) description of inner-shell electrons, is known as the ECPSSR theory [34]. In this chapter, various theoretical aspects of inner shell ionization by charged particles are discussed.

### 2.2 General considerations and definitions

Consider a collision in which an incident projectile of energy \(E_1\), velocity \(v_1\), atomic number \(Z_1\) and mass \(M_1\) collides with a stationary atom of mass \(M_2\) and atomic number \(Z_2\) in some initial state \(i\), usually a ground state. The projectile imparts some of its energy \((\Delta E)\) to the target atom and leaves it in some arbitrary final state \(f\). If an inner shell is ionized in the collision, the final state will be described by a configuration in which the inner shell of the atom has a hole (with filled outer shells) plus an electron left in some excited state or emitted with finite kinetic energy into the continuum. In general the transferred energy \((\Delta E)\) can go into excitation of an electron from state \(n\) to state \(m\) and

\[
\Delta E = \hbar \omega_{nm}
\]  

(2.1)

where \(\omega_{nm}\) is the characteristic frequency associated with the excitation. For ionization

\[
\Delta E = \hbar \omega_{2s} = U_{2s} + E_e
\]  

(2.2)

Where \(U_{2s}\) is the electron binding energy in its initial states and \(E_e\) is the kinetic energy of the electron emitted.

The common assumption for all theoretical approaches is that the collision creating one or more inner shell vacancies takes place in a short time compared with the subsequent decay of the excited atom, which could be either the target atom or the projectile ion. In other words, the validity of a particular theoretical model depends on the relative velocity, which in turn is related to the characteristic time scales involved. The quantities to be compared are the collision
time \( t_c \) and the characteristic orbital time \( \tau \) for the electron in \( n \)th shell. These can be approximated as:

\[
t_c = \frac{a_{2s}}{v_1} \quad \text{and} \quad \tau = \frac{n \hbar}{2U_{2s}}
\]

where

\[
a_{2s} = \left( \frac{n^2}{Z_{2s}} \right) a_0
\] (2.4)

is the average electron shell radius. Here \( a_0 \) is the Bohr radius of the hydrogen atom. The ratio of \( \tau \) and \( t_c \) is an important parameter and its value determines the applicability of different theories for ion-atom collision. The screened charge of the projectile is denoted by \( Z_{2j} = Z_1 - S' \), where \( S' \) is the Slater screening constant for the shell having principal quantum number \( n \) and has a value 0.3 for the \( K \) shell and 4.15 for the \( L \) shell.

### 2.3 Direct Coulomb Ionization (DCI)

The major aspects of inner shell vacancy production by light projectiles can be understood from the proton and helium induced ionization data which are well characterized by the models in which the effects of these ions on atomic systems is considered to be a perturbation by a point charge. In the simplest model one makes a basic assumption that the production of an inner shell vacancy by charged particle impact occurs as a result of Direct Coulomb Ionization (DCI) of the incident charged particle with the bound electron. The DCI essentially involves the classical problem of direct transfer of momentum to the bound electrons of the target by the incident particle due to the Coulomb interaction between the projectile nucleus and the target electron to be ionized. The DCI is expected to be large for sufficiently fast collision and dominates over processes like charge transfer when the projectile atomic number is much smaller than the target atomic number, \( i.e., \ Z_1 \ll Z_2 \) so that the electron cloud is only slightly disturbed and the perturbation theory is still valid. There are three different models, viz., Binary encounter approximation (BEA), Semi-classical approximation (SCA) and the
Plane wane Born approximation (PWBA). These models are suitable to describe the contribution of DI.

2.3.1 Binary Encounter Approximation (BEA) theory

In the classical binary encounter approximation (BEA) [35], which is also known as impulse approximation, the dominant interaction producing the transition is assumed to be the result of direct energy exchange between the incident charged particle and the bound electron on the target. The remainder of the atom, i.e., the nucleus and the other electrons provide the momentum distribution of the active electron. To calculate total cross-section first a differential cross-section \( \frac{d\sigma}{d\Omega} \) is obtained for an exchange of energy \( \Delta E \) between two charged particles and then integrating over all energy exchanges from the binding energy of the electron to the total energy of the projectile, and average over the velocity distribution of the bound electron. These considerations imply a strict conservation of energy and momentum in the electron-projectile interaction. The final expression for the ionization cross-section, upon averaging over the speed distribution of the bound electron and summing over all the electrons in the subshell is given by

\[
\sigma(v_1) = N_s \int_{0}^{\infty} \sigma_i(v_1, v_2) f(v_2) dv_2
\]

(2.5)

Where \( f(v_2) \) represent the velocity distribution of bound electrons and \( N_s \) is the number of bound electrons having binding energy \( U_{2s} \). If hydrogenic velocity is used for \( f(v_2) \), scaling law for a given subshell in the parameterized form is given by Johansson et al. [36]

\[
\ln [\sigma_i(U_{2s})^2] = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x^5
\]

(2.6)

Where \( x = \ln \left( \frac{E}{\lambda U_{2s}} \right) \)

(2.7)

is the universal function and this universal character of ionization process is a major feature of BEA. The advantages of the BEA calculations are their simple
nature and the universal scaling laws that are the result of using appropriate hydrogenic wave function to obtain the desired shell electron velocity distribution.

2.3.2 Semi-Classical Approximation (SCA) theory

The Semi-Classical Approximation (SCA) theory was introduced by Bang and Hansteen [4] and developed with the aim to study the effects of projectile deflection and deceleration due to atomic Coulomb excitation during collision by incident ions \((Z_1 \ll Z_2)\) [21]. Here, \(Z_1\) and \(Z_2\) are the atomic numbers of the projectile and target atoms, respectively. The semi-classical approach (SCA) has been revived by Laegsgaard, Andersen and Lund [37]. The necessary condition for the ionization process to be treated classically is that the de-Broglie wavelength \((\lambda)\) of the moving ion is smaller than the distance of the closest approach \([38]\), \(i.e.,\)

\[
\frac{2d}{\lambda} = \frac{2Z_1Z_2e^2}{\hbar v_i} \gg 1
\]  

(2.8)

This ratio is called Coulomb parameter. Here \(d\) is the half distance of the closest approach in a head-on collision and is given by

\[
d = \frac{2Z_1Z_2e^2}{M_i v_i^2}
\]  

(2.9)

The straight line trajectory for the projectile ion used in the model is a reasonable approximation at high energy, but at lower energy the Coulomb deflection of the trajectory due to nuclear repulsion is important and reduces the ionization cross-section. This was first treated using the SCA model by assuming a hyperbolic trajectory. In this model, the ion path is taken to be the trajectory of a classical particle and the bound target electron was described quantum mechanically. The first order perturbation theory was used to calculate the ionization cross-section using the impact parameter formulation.

\[
\sigma = 2\pi \int_0^m b I(b) \, db
\]  

(2.10)
where $b$ is the impact parameter and $I(b)$ is related to the differential cross-section per unit final electron energy for the scattering of the electron by the projectile and is given by the following expression

$$ I(b) = \int_0^{\epsilon_{\text{ph}}} dE_f \frac{dI(b)}{dE_f} $$

(2.11)

where

$$ \frac{dI(b)}{dE_f} = |a_{E_f}(t \to \infty)| $$

(2.12)

Where $a_{E_f}$ is the amplitude for an electron transition from a bound state $|i\rangle$ to a final state $|f\rangle$ and is given by

$$ a_{E_f}(t \to \infty) = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle E_f | V(r,t) | i \rangle $$

(2.13)

where \( \omega = \frac{E_f - E_i}{\hbar} \) and $V(r,t)$ is the time-dependent Coulomb interaction field between the considered electron and the projectile,

$$ V(r,t) = \left| \frac{-Z e^2}{r-R_0(t)} \right| $$

(2.14)

2.3.3 Plane Wave Born Approximation (PWBA) theory

In order to consider the direct Coulomb repulsion between projectile and the screened atomic nucleus, the Coulomb wave functions are employed to describe the motion of the particle in the electrostatic field of the nucleus. In Born approximation, the projectile is described by a plane wave equation and the atoms plus ejected electrons are describes by anti-symmetrized self-consistent Hartee-Fock wave functions. Since the projectile wave function is a plane wave for both the incident and the elastically scattered particles, this approximation is known as the well-known Plane Wave Born Approximation (PWBA). The PWBA represents
a purely quantum mechanical approach to the problem of inner shell vacancy production. The interaction responsible for vacancy production is the Coulomb interaction between the bound electron and the incident particle. This model is valid only if the ionization probability is small and the projectile velocity is high and initial state of the target electrons in unperturbed. Generally these conditions are fulfilled for \[ Z_i << Z_2 \] and \[ \nu_i >> \nu_2 \]. In this approximation, the scattering amplitude for transition from state \( n \) to state \( m \) is given by

\[
f = \left< me^{iKR} | V | e^{iKR} n \right> \tag{2.15}
\]

where \( V \) is the Coulomb potential between the projectile and the electron, initially in state \( | n \rangle \). The quantities \( K \) and \( K' \) denote the initial and final relative momentum. The cross-section is given by

\[
\sigma \sim |f|^2 \sim Z_i^2 F(\eta_i, \theta_i) \tag{2.16}
\]

where, the function \( F(\eta_i, \theta_i) \) has been tabulated for the \( K \) shell by Khandelwal et al. [39]. The details can be found in the review article by Madison and Merzbacher [40].

### 2.3.4 Plane Wave Born Approximation with Binding energy and Coulomb correction (PWBA-BC) theory

The above discussed theories are appropriate for light projectiles like proton and helium. Additional complications arise when heavy ions are used as projectiles. In these cases it is found that the data for both the \( K \) and \( L \) shell ionization are no longer in agreement with the predictions of these theories for Direct Coulomb Ionization (DCI). The deviation from these theories can be associated with the following reasons

1. Corrections for the modification of the binding energy of the bound electrons in the target due to the presence of the projectile nucleus.

2. Coulomb deflection of the projectile due to the Coulomb interaction between projectile and the target nucleus.
iii. The electron transfer cross-section may become comparable or may exceed
the DCI cross-section

iv. Modification of the fluorescence yields from atomic values (neutral atom),
if multiple ionization is dominant.

The correction due to the increased binding energy is necessary for low energy
beams including light ions like H and He. In case of low velocity projectile ($v_1 \leq
v_{th}$), it is necessary to penetrate deep inside the $K$ shell of the atom in order to
transfer the necessary momentum for $K$ shell ionization [31]. Hence in such cases
since the projectile spends more time inside the s orbit ($\tau < t_c$), the bound target
electron in the shell gets enough time to adjust itself to the presence of the foreign
nucleus. The effective nuclear charge is increased with a corresponding increase in
the electron binding energy and decrease in the ionization cross-section
$\sigma_{K} \propto 1/U_{K}^2$), which is more prominent for heavier ions in particular $Z_1 \sim Z_2$. For
low velocity projectiles the ionization cross-sections are calculated using the
corrected binding energy as following

$$U_{2s} \frac{\theta_{2s}}{R_s} \left( Z_{2s} + Z_t \right)^2 = \frac{\theta_{2s}}{n^2} Z_{2s}^2 \left( 1 + \frac{2Z_1}{Z_{2s}} \right)$$

(2.17)

i.e., the binding energy increases by $2Z_1/Z_{2s}$, where $Z_1 << Z_{2s}$

Here $Z_{2s} = (Z_2 - 0.3)$ for the $K$ shell and $(Z_2 - 4.15)$ for the $L$ shell.

The modifications of $K$ shell binding energy of the target atom in presence of
light ions are described by Basbas et al. [31]. For calculation of $\sigma_{K}$, the reduced
binding energy $\theta_K$ is replaced by $\varepsilon_K \theta_K$, which is given by

$$\varepsilon_k \theta_k = \left[ 1 + \frac{2Z_1}{Z_{2s} \theta_k} g(\xi_k) \right] \theta_k$$

(2.18)

and

$$g(\xi_k) = \frac{(1+5\xi_k + 7.14\xi_k^2 + 4.27\xi_k^3 + 0.947\xi_k^4)}{(1+\xi_k)^4}$$

(2.19)
The limited value of \( g(\xi_k) \) for \( \xi_k \gg 1 \) is given by
\[
g(\xi_k) = \frac{0.95}{\xi_k} \tag{2.20}
\]

The binding energy correction is a low velocity effect and it can be seen easily that in high velocity limit, i.e., \( \xi_k \gg 1 \) (since \( \xi_k \propto V_i \)) \( g(\xi_k) \to 0 \) resulting \( \varepsilon_i \theta_i \to \theta_i \) as expected for uncorrected PWBA result in high velocity limit. So in the PWBA and PWBA-B (PWBA + binding energy correction), the ionization cross-sections can be expressed for the K shell as
\[
\sigma_{k}^{\text{PWBA}} = \frac{\sigma_{0k}}{\theta_i} f \left( \frac{\eta_i}{\theta_i^2} \right) \tag{2.21}
\]
and
\[
\sigma_{k}^{\text{PWBA-B}} = \frac{\sigma_{0k}}{\theta_i} f \left( \frac{\eta_i}{(\varepsilon_i \theta_i)^2} \right) \tag{2.22}
\]
where
\[
\sigma_{0k} = 8m_0 \frac{Z_1^2}{Z_2^2} \tag{2.23}
\]

Another low velocity effect that influences the inner shell ionization phenomenon is the Coulomb deflection correction and was first treated by Bang and Hansteen [4] in SCA. In high velocity limit, the SCA and the PWBA gives the same result for straight line trajectory. For low velocity collisions, a hyperbolic trajectory is to be considered instead of a straight line. The correction for Coulomb deflection effect [31] in PWBA is incorporated as
\[
\sigma_{i} = (n_i - 1) E_{n(i)} (\pi d q_{0i}) \sigma_{i}^{\text{PWBA}} \tag{2.24}
\]
where \( q_{0i} \) is the minimum moment transfer to an s shell electron from a particle of velocity \( V_i \) and \( n_i = 10 \) for \( s = K \) and \( L_1 \) and \( n_i = 12 \) for \( s = L_2 \) and \( L_3 \). The quantity \( d \) is half the distance of closest approach (equation 2.8). The function \( E_{n(i)} \) is the exponential integral of order \( n \) and is given by
\[
E_{n(i)} = \int_{0}^{\infty} t^{-n} e^{-t} dt \tag{2.25}
\]
It can be approximated according to Brandt and Lapicki [32] by

\[
(n_r-1) E_{n(\xi)}(x) = \left[ \frac{n_r-1}{n_r-1+x} \right] e^{-x} \tag{2.26}
\]

where \( x \) is the reduced variable and is given by \( x = b q_0 \), with \( b \) being the impact parameter. Including the effects due to increased binding energy (B) and Coulomb deflection (C) the expression for \( K \) shell ionization cross-section becomes

\[
\sigma_k^{PWBA-BC} = 9E_\beta (\pi d \theta \eta_k) \left( \frac{\sigma_{\theta k}}{\eta_k \theta_k} \right) F \left( \eta_k \theta_k \right) \tag{2.27}
\]

At high velocity where the large impact parameters contribute to the ionization process the binding energy becomes negligible and for impact parameters \( b \) larger than the shell radius \( a_{2s} \), the polarization correction becomes dominant as explained by Basbas et al. [41]. Qualitatively, due to the polarization of the atom by the moving ion the bound electrons are attracted towards the positive projectile. It results in decreasing the binding energy and effective impact parameter and increase the ionization cross-section. The corrections for energy loss (E) during the collision and the relativistic effect (R) are also incorporated in PWBA to give the more general ECPSSR formalism as described by Brandt and Lapicki [34].

2.3.5 ECPSSR theory

Brandt and Lapicki [33] modified the PWBA theory with hydrogenic wave functions, corrected for energy loss of the projectile during the collision (E), for de-acceleration and deflection of the projectile in the Coulomb field (C), for the perturbation of stationary target electron states by passing projectile (PSS), and for relativistic electron motion (R).

In the slow collision limit, the calculations of the first Born approximation (FBA) scales with

\[
\xi_r = \frac{2n_1}{v_2 \theta_2}, \quad \frac{\eta_j^{1/2}}{\theta_2} \tag{2.28}
\]
In the ECPSSR theory, $\xi_s$ is replaced by $\xi_s^R / \xi_s$ to correct the FBA for the relativistic and perturbed stationary state effects; $\xi_s$ is replaced with

$$\xi_s^R = \left[ m_s^R (\xi_s / \xi_s) \right]^{1/2} \xi_s$$

(2.29)

to simulate the relativistic effect and $\xi_s$ accounts for the perturbed stationary state (PSS) effect. Also, $\theta_i$ is replaced by $\xi_s \theta_i$, to include all effects in ionization cross-section. Where $m_s^R$ is the relativistic electron mass and is expressed in atomic units as

$$m_s^R (\xi_s) = (1 + 1.1 y^3)^{1/2} + y$$

(2.30)

with

$$y = \frac{0.4}{\xi_s} \left( \frac{Z_{sl}}{137} \right)^2$$

(2.31)

Hence, ECPSSR cross-section is expressed as

$$\sigma_s^{ECPSSR} = C_s \left( \frac{2 \pi d \theta_s \xi}{z (1 + z)} \right) f(z) \sigma_{PWBA} \left( \frac{\xi_s}{\xi_s}, \xi_s, \theta_s \right)$$

(2.32)

Where $C_s$ represents the correction for Coulomb deflection, $f(z)$ represents the energy loss correction, $q_{0s}$ represents the minimum momentum transfer and $d$ is the distance of closest approach.

The perturbed stationary state effects are described by

$$\xi_s = 1 + \frac{Z_l}{Z_{sl}} \left[ g (\xi_s) - h (\xi_s) \right]$$

(2.33)

The functions $g (\xi_s)$ and $h (\xi_s)$ are given by Brandt and Lapicki [33].

Part of the projectile energy loss during the collision is considered by the function $f(z)$ given by

$$f(z) = 1 - \left( \frac{45}{16} \right) \left[ (1 - z^2)^3 - (1 - z^2)^3 \right]$$

(2.34)
With
\[ z = 1 - \left( \frac{4}{M \xi_s \theta_s} \right) \left( \frac{\xi_s}{\xi_0} \right)^{3/2} \]  \hspace{1cm} (2.35)

where \( M \) is the reduced mass of the projectile and the target, in the atomic mass units.

### 2.3.6 United Atom approximation

In the ECPSSR, \( \theta_s \) is replaced by \( \zeta \theta_s \), where the PSS function as written in Equation (2.32), was derived in the separated atom (SA) picture as a first-order perturbation of the S-shell electron binding energy; the \( 0 < g_s(\xi_s) \) ≤ 1 accounts for increase in the binding that increases with decreasing \( \xi_s \) as the projectile penetrate deeper into the S-shell and \( h_s(\xi_s) \) accounts for decrease in the binding at intermediate \( \xi_s \) where the projectile polarizes the S-shell in its passage outside the S-shell. In the very slow collision limit of \( \xi_s \to 0 \) with \( h_s = 0 \) and \( g_s \to 1 \), \( \xi_s = 1 + 2 Z_1/Z_2 \theta_s \), the binding energy should have been the binding energy of the united atom (UA), \( \frac{1}{2} (Z_1 + Z_2)^2 \theta_s^{UA} / n^2 \) so that \( \zeta_s \) ought to be

\[ \zeta_s^{UA} = \left( 1 + Z_1/Z_2 \right)^2 \theta_s^{UA} / \theta_s \]  \hspace{1cm} (2.36)

Hence, \( \zeta_s^{UA} \) truncates the increase of the binding energy in the \( \xi_s \to 0 \) limit. Since the decrease in the binding energy yields greater cross sections, in that limit \( \sigma_{ECPSR} \) evaluated with \( \zeta_s^{UA} \) of eq. (2.36) is greater than \( \sigma_{ECPSR} \) of the ECPSSR.

Although various schemes had been suggested to bridge the united and separated atom treatments of the binding effect [42], Vigilante et al. [43] were the first to merge the UA and SA accounts for this effect within an ECPSSR approach. Hence, the ECPSSR is modified to ECUSAR via the \( \zeta_s \to \zeta_s^{UA} \) replacement where

\[
\sigma_{ECUSAR}^{UA} = \begin{cases} 
\zeta_s^{UA} & \text{when } \zeta_s^{UA} < \zeta_s \text{ for slow collisions} \\
\zeta_s & \text{when } \zeta_s \leq \zeta_s^{UA} \text{ for intermediate and fast collisions}
\end{cases} \]  \hspace{1cm} (2.37)
This joins the united and separated atom formulas as they are derived and valid in complementary collision regimes. This modification brings the theory to a closer agreement with the data. Although it lowers the kink by just a few percent for heavy targets but it cuts the difference between the data and the theory in half for the lightest target.
References


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