CHAPTER 3.0

THEORETICAL METHODS

(3.1) Introduction
The experimentally calculated values of ionization cross sections of molecules and atoms are very important in recent years. As these cross sections were very important in many applications but theoretical measurement of ionization cross sections have not made significant progress due to inherent complexity of such calculations.

A lot of approaches such as BED model, BEB model and Jain Khare approach, R-matrix method, semi-classical Deutsch-Mark (DM) formalism, Hamiltonian equation and Fourier method and time dependent calculations approach have been proposed.

Extensive comparison between experimental cross sections and their predictive theoretical cross section have been made for molecules and atoms [124-130].

(3.2) Binary-encounter-dipole/Bethe model (BED/BEB)

It is a theoretical model which is used for determination of single cross sections of atoms. It is used to determine single cross section of subshell by using kinetic energy and oscillator strength. The total cross section is directly related to energy of electron.

BED model can be used for measurement of total ionization cross section of target atom/molecule from ionization potential is several keV. When no high accuracy is required (10% or better), differential oscillator intensities calculated from the wave functions similar Hartree-Fock.

BEB theory is used for generation of singly ionized targets. According to this theory, our comparison is possible for singly ionized targets. The total ionization cross section of inner shell is contributed because of their large binding energies.

Ionizing collisions can be divided into two parts; soft and hard collisions. Soft collisions involve small momentum transfers from the incident to target bound electrons, and primarily generate slow ejected electrons.
Chapter 3.0 Theoretical Methods

Partial Differential Ionization Cross-Section Of Atoms and Molecules From Electron Impact By Plasma Processing

Hard collisions involve large momentum transfers and mostly generate fast ejected electrons. Most collision theories based on quantum mechanics address both types of collisions, a typical one being the Born approximation.

An exception is the Mott cross section, which is the exact solution for an idealized problem, namely, the interaction of two free electrons. This cross section does not include soft collisions arising from the electric dipole (El) collision between the incident and target electron, while Born approximation does.

The El interaction occurs only for bound electrons. The main hurdle in this approach is the fact that it is quantitatively difficult to isolate the part in the Born cross-section. This is the primary reason that existing theories of this type had to introduce empirical parameters.

The BEB model overcame this difficulty by requiring the asymptotic forms (high incident electron energy) of ionization cross section and stopping power is satisfy the correct forms obtained by the Born approximation.

When oscillator strength is not available, BEB model can be used [131].

(3.3) Jain Khare model

Collisions between atoms and electrons can be classified into two categories soft and hard collisions. The group of SP Khare and coworkers at Meerut University in India revisited this problem but with more success.

Khare et al calculated energy loss cross sections $d\sigma(E, w)/dw$ where $E$ is electron energy and $w$ is the energy loss in the ionizing collisions.

They were also able to calculate single differential ionization cross section $d\sigma(E, \epsilon)/d\epsilon$ for the production of secondary electrons. According to Ist Born approximation the single differential ionization cross section is given by

$$d\sigma(E, \epsilon)/d\epsilon = (4\pi a_0^2 R^2/Ew) \times \int (\delta f(w, K^2 a_0^2) / \delta w) d [\ln(K a_0)^2]$$

$a_0$ Denotes the Bohr’s radius,

R is the Rydberg Energy
**Chapter 3.0 Theoretical Methods**

Partial Differential Ionization Cross-Section Of Atoms and Molecules From Electron Impact By Plasma Processing

\( \mathbf{K}a_0 \) is the change in momentum vector

Nature of the energy transfer determines the nature of collision. The above equation can be reduced to Bethe term for soft collisions given by

\[
d\sigma (E, \varepsilon)/d\varepsilon \bigg|_B = (4\pi a_0^2 R^2 / Ew) \times \left( \frac{\delta f(w, 0)}{\delta w} \right) \ln(C\varepsilon)
\]

In the case of hard collisions differential cross section in form of Mott term is given by

\[
d\sigma (E, \varepsilon)/d\varepsilon \bigg|_M = (4\pi a_0^2 R^2 s) \times (1/ \varepsilon^2 - 1/(E-\varepsilon) \varepsilon + 1/(E - \varepsilon)^2E)
\]

Where \( s \) is number of electrons, 1st term in the bracket is the direct collision term, 2nd term represents interference between exchange term and direct term, 3rd term gives exchange effects.

Both the above mentioned equations are applicable in high electron energy.

Khare and coworkers extended the range of the validity at low incident energies by multiplying each cross section by arbitrary factors \( f_1 \) and \( f_2 \).

\[
d\sigma (E, \varepsilon)/d\varepsilon = f_1(d\sigma (E, \varepsilon)/d\varepsilon \bigg|_B) + f_2(d\sigma (E, \varepsilon)/d\varepsilon \bigg|_M)
\]

The total cross sections obtained by Khare et al using the above formalism after proper integration were found to have excellent agreement with experimental results [132].

**3.4 The ab inito Electrostatic Method**

The ab inito electrostatic model, developed at the University of Canterbury used an electrostatic approach for computed the ionization cross-sections [133-134].

The cross-section of target molecule having different orientations is calculated as a function of geometry of the electron and the target species.
After the total ionization cross-section, the average cross-section over the three Cartesian coordinates in both the positive and negative directions is taken. This model assumes that the critical impact parameter \( r_c \), corresponds to the division for which the Coulomb potential of the electron-molecule system is equivalent to the ionization potential of molecule. The ionization cross-section for the electron-molecule collision is then given by:

\[
\sigma = \pi r_c^2
\]

(1)

The energy of the system is determined at a series of \( T \) values using a systematic approach that converges on \( r_c \), with a Coulomb potential \( \phi \). This is determined using:

\[
T = E_n + \phi = E_n - E_0
\]

(2)

The vertical ionization energy \( E_0 \) is determined using geometry optimization of the neutral molecule in order to calculate \( E_n \). The zero point energy \( E_{zpe} \) is then determined and the neutral geometry of the molecule is then apply to positive ion for determination of energy of the positive ion, \( E_i \):

\[
E_0 = E_i - (E_n + E_{zpe})
\]

(3)

On one occasion the maximum ionization cross-section has been determined. This is achieved using a method that treats an electron as a de Broglie matter wave, and assumes that the maximum in the ionization energy.

It has been assumed that kinetic and potential energies are present in an orbital. The kinetic energy is basically given by classical orbital motion, and the potential energy, \( V \), is given by Coulomb potential among the electron charge and the effective nuclear charge, \( Z_{\text{eff}} \).

\[
E = V + E_k = \frac{Z_{\text{eff}} q}{4\pi\varepsilon_0 r} + \frac{1}{2}m_e r^2\omega^2
\]

(4)
With \( m_e \) as the mass of the electron, \( \omega \) as the angular velocity and \( r \) as the orbital radius. The frequency of the orbit is the angular velocity divided by \( 2\pi \).

\[
\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{2E}{m_e r^2}}
\]  

\( E_{\text{max}} \) corresponds to the point when the de Broglie frequency of the inbound electron matches the orbital frequency.

\[
E_{\text{max}} = h \nu = \frac{h}{2\pi} \sqrt{\frac{2E}{m_e r^2}}
\]  

The geometric optimization configurations are determined using a molecular orbital package [135]. This method might be readily applied to the inert gases.

It was found that increasing the level of theory only had a insignificant effect on the determined cross-section. In inert gases, the average difference between the calculated and measured results using this method was 14%.

This method has also been applied to molecules with a similar level of success, with the cross-section taken as the average over the Cartesian axes [136]. This model is unique in that, when applied to molecules the ionization cross-section is determined from six different approach geometries, hence an "ionization volume" can be calculated.

This enables steric effects on the ionization cross-section to be explored. The model is limited in that it can only find maximum cross-section. The calculations presume that the electron and the target species are static with respect to each other at the moment of ionization.
(3.5) Kim and Rudd model

This model uses the binary encounter approximation to replace the Mott cross section. The single differential cross section of subshell is given in BED model by

\[
\frac{d\sigma}{d\epsilon}(E, \epsilon) = 4\pi a_0^2 \left(\frac{R}{E_j}\right)^2 \frac{\xi}{E_j} (t + u + 1) \times \left\{ \left( [(N_i | \xi) - 2]/(t + 1) \right) \left[ (1 | w + 1) + 1/(t - w) \right] + [2 - (N_i | \xi)] \left[ (1 | w + 1) \right]^2 + 1/(t - w)^2 \right\} \\
\]

Where \( E_j \) is binding energy of ejected electron and \( \epsilon \) is the number of bounded electron.

By the integration of differential cross section, we can obtained total ionization cross-section is given by the following expression

\[
\sigma(E) = 4\pi a_0^2 \left(\frac{R}{E_j}\right)^2 \frac{\xi}{(t + u + 1)} \times \{ D(t) \ln(t) + [2 - (N_i | \xi)] \left[ (t - 1)/t - \ln(t)/(t + 1) \right] \}
\]

With

\[
D(t) = \xi^{-1} \int \left[ 1/(1 + w) \right] [df(w)/dw]dw
\]

The cross sections calculated above are only for a specific sub shell and the total cross section \( \sigma \) can be measured by the summation over all sub shell that contributes to the ionization [137].

(3.6) R-Matrix Method

In the year 1947, Wigner & Eisenud had introduced R-matrix method, related to the theory of nuclear reactions. The indispensable idea of the method is that configuration space describing the scattered particle and the target is bifurcated in two regions. In internal region, the interaction is many-body and strong and the collision process is hard
to determine.

In external region, the interaction is feeble and in many cases is accurately solvable in terms of plane waves or of Coulomb waves. In the internal region an absolute discrete set of state describing all the particles is defined by imposing logarithmic boundary conditions on the surface of this region. The $R$-matrix basis can then be used to develop the collision wave function at any energy and in particular to get the logarithmic derivative of this wave function on the boundary. Since this information and the known solution in the external region the $S$-matrix.

The theory described is accurate and is completely equivalent to solving the scattering problem accurately. In applications, though only a finite Eigen states can be retained in the internal region. Certainly in some applications in nuclear science only one state is retained, giving the so-called one-level formula which has been remarkably successful in describing reactions close to an isolated resonance. More recently consideration has been directed to using the $R$-matrix method as a scheme for determining resonant and non-resonant processes over an extended energy range. Nowadays the applications in electron atom scattering one might at first think that the Coulomb interaction would make the method improper.

If we are interested in transitions concerning a few low-lying states of the atom then an appropriate boundary is one which just envelops the charge distribution of these states. This ensures that the exchange interaction between target and scattered electron, which is the part of the problem to determine accurately, is only non-zero in the internal region.

On the other hand, in the external region the interaction reduces to long range local potentials behaving as inverse powers of the radius and as a result, the corresponding equations can be easily solved.

This choice of internal and external regions is also suitable for other applications in atomic science. If we consider the calculation of atomic frequency dependent polarizabilities then we are required to explain the atomic state perturbed by the oscillatory external electric field.
This perturbed state has the similar range as the unperturbed state and as a result it can be appropriately expanded in terms of $R$-matrix basis with a boundary chosen to just envelop the atom. If the frequency of the oscillation becomes high then the atom will ionize giving rise to the familiar photo ionization processes.

The resulting loss of flux through the boundary of the internal region can also be represented by the $R$-matrix basis states which do not disappear on the boundary. Other applications for which this expansion basis is suitable are the determination of Vander Waals coefficients and nonlinear optical coefficients.

One can describe the use of $R$-matrix theory as a method for calculating a broad range of atomic processes and an exact and economical way. We will not be concerned with applications which use the analytic properties of the $R$-matrix to develop multichannel effective range theories, nor with applications where the emphasis is on using the $R$-matrix as a method of parameterizing experimental data.

Consider a close coupled channel equation:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)}{2mr^2} - k^2 \right] u_i(r) = \sum_{j=1}^{n} V_{ij}(r) u_j(r)$$

Where $E = \frac{k^2}{2}$

General Definition of an $R$-Matrix:

$$u_i(x) = \sum_{j=1}^{n} R_{ij}(x, E) \left[ r \frac{du_j}{dr} - b u_j \right]_r=x$$

Where $b$ is arbitrary, normally take $b = 0$
Figure 3.1: Splitting of configuration in R-matrix model

Schroedinger Equation for finite volume becomes:

\[(H + L - E) \psi = \Lambda \psi\]

This has formal solution

\[\psi = (H + L - E)^{-1}\Lambda \psi\]

The boundary is chosen in such a way that the charge distribution of the target is restricted within the radius a. The correlation and exchange reactions are diminishing in the outer region and the trouble can be solved with a simpler estimate for a free electron moving in the potential of the target.

At the boundary both solutions (for the outer region and for the inner region) have to be steady. This is given by condition on the wave functions and their first derivatives which have been continuous in nature at the boundary.

**Why this is an R – Matrix?**

When the processes inside the sphere are unknown the parameterization scheme on surface of sphere is introduced.
The use of the R-matrix method for calculations of collision between an electron and an atom started in the early 70’s and is the method adopted by OP-IP team in a description that is continually acted upon from the initial non-relativistic code to the intermediate stage with the one-body Breit-Pauli terms to the present relativistic form (BPRM) and to future expansion with the inclusion of the relativistic 2-body terms.

The division of the configuration space in two parts known as the outer region (also called asymptotic) and the inner region make this method specific [138].

(3.7) **Plane Wave Born Approximation**

To determine cross section of different atoms, two easy scaling methods for first-order, plane-wave Born cross sections of excited neutral is not compared to experimental data (Bray & Stelbovics, 1995). The validity of scaling methods is only for dipole-allowed excitations. From exact wave functions these can be obtained [139-140].

Because scaled cross sections do not depends on the resonances. For applications such as in plasma processing and stellar atmosphere, these methods present quick finding of cross sections in numbers of atoms, mainly heavy atoms. Scaling methods is theoretical methods for measuring cross sections of molecules.

The PWB approximation is used as work for the reason that (a) at infinity; plane wave is the exact wave function when the electrons collide with atom and (b) it is the simple collision theory that uses target wave functions.

The cross sections $\sigma_{PWB}$ for first-order in a generic form is written as

$$\sigma_{PWB} = \frac{4\pi a_0^2 R}{T} F_{PWB}(T) \quad (7)$$

Where $R$ is the Rydberg energy, $a_0$ is the Bohr radius, $T$ is the incident electron energy and $F_{PWB}(T)$ is the strength of the collision. This approximation is not good for electron exchange effect with electrons of target.
(3.8) **The Close Coupling Hypothesis**

In the case of collisional effort, we attempt to uncover the wave function solution to the Schrodinger equation for a system with \((N+1)\) electrons describing the interaction of a free electron with what is known as the target (a nucleus with \(N\) electrons). The eigen states \(\Psi\), solutions of this equation, are generally developed in terms of the target and colliding electron wave functions.

\[
\Psi^\Gamma = \sum_i x_i^\Gamma (x_i, \ldots, x_{N+1}) \theta_i^\Gamma (x_{N+1})
\]  

where \(\Gamma \equiv \text{SLM}_1 M_\sigma \pi, x_i \equiv r \sigma \) represents the spin \((\sigma)\) and special \((r = (r, \theta, \varphi))\).

coordinates for electron \(l, x_i\) is the target ion wave function in a specific state \(S_l \pi_i\) or level \(J_l \pi_i\), and \(\theta_i\) is the wave function for the \((N+1)\)th electron in a channel labelled as \(S_l \pi_i \pi_i k_i^2 l_i (SL \pi_i [J \pi_i])\) and \(k_i^2\) is the electron energy associated to the channel \(i\). The sum includes all the feasible combinations of the target states and colliding electron wave function that offer the requisite symmetry \(\Gamma\) for \(\Psi_i^\Gamma (x_1, \ldots, x_{N+1})\) with the eigen energy \(E_i^\Gamma\) on behalf of the total energy.

For the ease we will skip the index \(\Gamma\). \(E = E_i + k_i^2\)

where \(E_i\) is the target energy. Depending on the value of \(k_i^2\), we have open channels when \(k_i^2 \leq 0\) and closed channels when \(k_i^2 \geq 0\).

In the coupled channel or close coupling (CC) approximation the wave function expansion \(\Psi\) is limited to contain only the channel \(i\) with strong coupling and limits the infinite sum to the number of channel \(n_{cc}\) which depends on the number of target states included in the calculation. The expansion becomes
Chapter 3.0  Theoretical Methods

Partial Differential Ionization Cross-Section Of Atoms and Molecules From Electron Impact By Plasma Processing

\[ \Psi(x_1, \ldots, x_{N+1}) = A \sum_{i}^{n_c} \chi_i(x_1, \ldots, x_N) \theta_i(x_{N+1}) + \sum_{j}^{n_c} c_j \phi_j(x_1, \ldots, x_{N+1}) \]  \hspace{1cm} (9)

where \( A \) is the antisymmetrisation operator and the second sum is introduced as:

(a) To compensate for the orthogonality conditions between the continuum and the bound orbitals of the target.

(b) To represent additional short-range correlations that is often of crucial significance in scattering and radiative CC calculations for all symmetry. The \( \phi_j \)'s are correlation wave functions also referred to as 'bound channels' as opposed to the 'free' channels \( n_{cc} \). The idea of 'free' channel refers to the radial function of the colliding electron that can liberally vary in order to resolve the Schrödinger equation for the system with \((N+I)\) electron.

We can merge the angular and spin part of the wave function \( \theta_i \) (Equation 8) for the \((N+I)\)th electron to the target wave function \( \chi_i \) which give \( \chi_i \) and

\[ \Psi(X) = A \sum_{i}^{n_c} \tilde{\chi}_i(\tilde{X}) \frac{1}{r_{N+1}} F_i(r_{N+1}) + \sum_{i}^{n_{bc}} c_i \phi_j(X) \]  \hspace{1cm} (10)

where \( X \) stands for \((x_1, \ldots, x_{N+1})\) and \( \tilde{\chi}_i \) corresponds to \((x_i, \ldots, x_N, \theta_{N+1}, \varphi_{N+1}, \sigma_{N+1})\) and \( F_i(r_{N+1}) \) is the reduced radial function of the colliding electron.

The Target

The first step in a collisional computation is to produce the target representation. The target wave function for a state \( i \) is developed in a configuration interaction (CI) expansion.
Chapter 3.0                                                                                   Theoretical Methods

Partial Differential Ionization Cross-Section Of Atoms and Molecules From Electron Impact By Plasma Processing

\[ \chi_i(x_1, \ldots, x_N) = \sum_j c_{ij} \phi_j(x_1, \ldots, x_N) \]  

(11)

The mixing coefficients \( c_{ij} \) are determined by diagonalization of the Hamiltonian and each configuration state is constructed as of the Slater orbitals. Using the Slater determinant, we have

\[ \psi_j(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} u_1(x_1) & \cdots & u_N(x_N) \\ \vdots & \ddots & \vdots \\ u_1(x_N) & \cdots & u_N(x_N) \end{pmatrix} \]  

(12)

where the Slater orbital \( u_i \) in the central field approximation can be constructed as the product of a radial function \( \frac{1}{r} P_{nl}(r) \), an orbital function (spherical harmonics) \( Y_{lm}^{m\ell}(\vartheta, \varphi) \) and a spin function \( \chi_{m\sigma}(\sigma) \).

\[ u_i(x) = u_i(r, \sigma) = \frac{1}{r} P_{nl}(r) Y_{lm}^{m\ell}(\vartheta, \varphi) \chi_{m\sigma}(\sigma) \]  

(13)

Since the orbital and spin functions are known mathematical functions, the difficulty consists in solving the radial Schrödinger equation for the \( P_{nl}(r) \)

\[ \left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V(\lambda_{ls}, r) + \epsilon_{nl} \right\} P_{nl}(r) = 0 \]  

(14)

where \( V(\lambda_{ls}, r) \) is the Thomas-Fermi-Dirac potential and the \( \lambda_{ls} \) are used as the variational parameters to optimize the potential in order to minimize a set of chosen
energies.

The structure code used by Eissner and Seaton were SUPERSTRUCTURE. The code SUPERSTRUCTURE includes relativistic corrections not only like those offered in equations except some two-body operators such as the spin-other-orbit term, the spin-spin term, the Two-body Darwin term and the spin-spin-contact term. They are usually incorporated in radiative calculations using SUPERSTRUCTURE, but in the case of collisional effort, in order to stay consistent only three terms from the Breit-Pauli approximation present in the R-MATRIX code are taken into account.

Once generated, the radial functions of the target are used in the R-MATRIX package to rebuilt the target and produce the \((N+1)\) bound states.

3.9 The Coupled Integro-Differential Equations

Providing a set of the target and bound channel wave functions the difficulty consists in solving the Schrödinger equations for the unidentified radial functions \(F_i\) of the colliding electron and the coefficients \(c_j\) (equation 9). These functions have to follow the boundary conditions which define the scattering matrix \(S\)

\[
\lim_{r \to 0} F_{ij}(r) = r^{l_{ij}}
\]

(15)

and

\[
\lim_{r \to \infty} F_{ij}(r) = k_i^{-1/2} \left( e^{i\theta_j(r)} \delta_{ij} - e^{-i\theta_j(r)} S_{ij} \right) \text{ for } k_i > 0, i = 1, \ldots, n_a
\]

(16)

\[0 \text{ for } k_i^2 < 0, i = n_a + 1, \ldots, n_{cc}\]

(17)

where \(l_i\) is the number of open channels, \(j = 1 \ldots n_a\) and the Coulomb phase \(\theta_i\) is...
\[
\theta_i = k_i r \left(1 - \frac{l_i}{2}\right) + \frac{Z - N}{k_i} \left(2 \ln(2k_i r) + \text{avg}(\Gamma) \left(l_i + 1 - \frac{Z - N}{k_i}\right)\right)
\]  

(18)

with \(l_i\) being the angular momentum in channel \(i\), \(Z\) being the nuclear charge and \(N\) being the number of electrons in the target. For numerical applications one defines the K-matrix such that real wave functions instead of complex ones are used. They assure the real boundary conditions.

\[
\lim_{r \to \infty} F_{ij}(r) = k_i^{-1/2} \left(\sin \theta_i(r) \delta_{ij} + \cos \theta_i(r) K_{ij}\right) \text{ for } k_i^2 > 0
\]

(19)

\[
0 \text{ for } k_i^2 < 0
\]

(20)

with the relation between the \(n_a \times n_a\) matrices \(S\) and \(K\) given by

\[
S = \frac{1 - iK}{1 + iK}
\]

(21)

The transmission matrix is then defined as

\[
T = 1 - S = -\frac{2}{1 + iK}
\]

(22)
Using the Kohn variational principle (Kohn, 1948) one derives the system of that the functions $F_i$ must satisfy.

\[
\left\{ \frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2z}{r} + k_i^2 \right\} F_i(r) = 2\sum_{j=1}^{n} (V_{ij}(r) + W_{ij}(r) + F_j(r) + \sum_{nl} \Lambda_{nl} P_{nl}(r) \delta_{nj} )
\]

which represents the so-called Coupled Integro-Differential equations.

The potential $V$ is the target potential together with the screening and the long distance component and $W$ represents the exchange interaction.

The last sum is included to require the orthogonality between the radial functions of the target $P_{nl}$ and of the colliding electron $F_i$.

At last the physical quantities of interest, the cross section $\sigma_{tot}$ and the collision strength $\Omega$ for a transition among an initial state $i$ and final state $j$ are defined in LS coupling as

\[
\sigma_{tot} (\gamma_i S_i \rightarrow \gamma_j S_j) = \frac{\pi a_0^2}{k_i^2} \sum_{LS} \sum_{L'S'} \frac{(2L+1)(2S+1)}{2(2L_i+1)(2S_i+1)} |T_{ij}^{LS\pi}|^2
\]

and

\[
\Omega (i,j) = \frac{(2L_i+1)(2S_i+1)k_i^2}{\pi} \sigma_{tot} (i \rightarrow j)
\]

(3.10) **Born-Oppenheimer Approximation**

Surface interaction of atoms/molecules with the most common form given by the Schrödinger equation as
\[ H \Psi \left( \{ R_m, r_n \} \right) = \varepsilon \Psi \left( \{ R_m, r_n \} \right) \]  

(26)

In this equation \( R_m \) = ionic coordinates.

and \( r_n \) = electronic coordinates.

For both ionic and electronic degrees of freedom it is very well-known that a complete analytical solution of the Schrödinger equation taking into concern is not sufficient apart from for easy cases. In the year 1998, the common approach is taken for granted as we know from the previous knowledge that there is a huge difference in the masses of nuclei and the electron as a result have to purse the nuclei motion and this is well-known Born-Oppenheimer approximation \([141-142]\). We have to check its validity carefully, since it is an approximation.

Electronically non-adiabatic process occurs on the surfaces having gas scattering. These are termed as chemiluminescence and exo-electron emission \([143]\). The velocity due to the electrons is quite more in contrast to the velocity due to atoms and this is considered in terms of strength of this approximation.

Electronic transitions are not important if the separations among energy levels are not well. Due to the quasi-continuum of electronic states, for metals the circumstances becomes more complex. One cannot calculate thoroughly the two important things, effective potentials and the coupling among the electronic states. If we find one thing the other will remain left.

(i) The efficiency of excitation due to electron gets reduced on the surface of metal as the excitation has short existence.

(ii) The surface interaction makes the molecular electronic levels more broad. An efficient quenching of electronic excitations takes place as short time period of excited state match with the broad levels.
Due to the band gap the situation in case of semiconductor and insulator surfaces is not same. For the time being, we just guess that the Born-Oppenheimer approximation is acceptable.

The Hamiltonian is written in the form as

\[
H_{el}(\{R_m\})|\Psi(\{r_n\}) = E(\{R_m\})|\Psi(\{r_n\})
\] (27)

The many-electron ground state energy \( E_0(\{R_m\}) \) then defines the potential for the nuclei. Once we get it, this can be blocked into the Schrödinger equation for the nuclei,

\[
\left( \sum_i \frac{-\hbar^2}{2m_i} \nabla^2_{R_i} + E_0(\{R_m\}) \right) \phi(\{R_m\}) = \varepsilon \phi(\{R_m\})
\] (28)

where the energy relevant for the dynamics of the nuclei is \( \varepsilon \), or, we can make use of this to solve the classical equations of motion.

\[
M_i \frac{\partial^2 R_i}{\partial t^2} = -\frac{\partial}{\partial R_i} E_0(\{R_m\})
\] (29)

For extended systems uncover the many-electron ground state energy \( E_0(\{R_m\}) \) from first principles is density functional theory [144-145] in grouping with the supercell concept.

In this approach the wave functions are extended and these are based on plane waves. By this one can get almost \textit{ab initio} potentials, but real-space [146-147] and Green function methods [148-149] have been planned as well.

The infinite substrate is modeled by a finite cluster [150] by the use of quantum chemical methods.

\textbf{(3.11) Scaling Methods}
(3.11.1) **BE scaling method**

BE scaling method, replaces the $T$ of Equation (7) by $T+B+E$, where $B$ is the binding energy and $E$ is the excitation energy.

$$\sigma_{BE} = \sigma_{PWB} T / [T + B + E]$$

(30)

The first scaling method (BE scaling) at low $T$ reduced cross-section magnitude and also shifts the peak to a higher $T$ keeping the high-$T$ validity of the PWB approximation intact.

Burgess considered orbital kinetic energy $U = (P^2)/2m$ as a substitute of $E$ in Equation (8). By the use of Burgess scaling along with others methods developed the binary-encounter-Bethe (BEB) and binary-encounter-dipole (BED) models for electron-impact ionization cross sections.

(3.11.2) **C scaling method**

Some examples on a few alkaline-earth elements evidently indicates that the experimental data works better by taking $B+E$ at inter-mediate and low $T$. Therefore in $C$ scaling a constant $C$ has placed in place of $B+E$ as under

$$\sigma_C = \sigma_{PWB} T / [T + C]$$

(31)

For getting better agreement with experimental data it is essential to establish $C$ greater than $B+E$ for alkaline-earth elements having resonance levels ns np$^1$P.

From this as the levels concerning $(n-1)$ $d$ electrons then $C$ may be bound with the polarizability of the target.

(3.11.3) **f scaling method**
As PWB cross section depends on two approximations:

(i) Using plane waves perturbation theory (first-order) for both incident and scattered electron.

(ii) For non-hydrogenic targets use of approximate wave functions.

The scaling methods $BE$ and $C$ rectify the discrepancies which were occurred in previously observed approximation. On the other hand, even at high $T$, the results will be unpredictable if we use poor target wave functions. Although by computational tools we can produce wave functions which will generate exact $f$ values and oscillator strengths, but it is not easy to use exact wave functions.

For a number of decades, there have been efforts for production of ionization cross-section to use accurate $f$ values. In the year 1979, Gaunt-factor method was introduced which is still a famous method. In this, for any desire transition $f$ values can be factored out, $F_{PWB}$ ($T$) in Equation (8) and then $F_{PWB}$ ($T$) as a result is customized [151].

In the $BE$ and $C$ scaling, the leading $T$ is variable and collision strength is fixed. By the use of other sources, the availability of $f$ values, $f$ scaling method is introduced. The $f$ scaling is given by:

$$\sigma_{PWB mc} = \left( \frac{f_{mc}}{f_{sc}} \right) \sigma_{PWB sc}$$

(32)

Where $\sigma_{PWB mc}$ shows PWB cross section (multi-configuration) with $f$ value as $f_{mc}$ and $\sigma_{PWB sc}$ shows for the PWB cross section (single configuration) with $f$ value as $f_{sc}$. We can apply successfully these scaling, wherever required. For afterward use, we can write them as under:

$$\sigma_{BE} = \sigma_{BE} \left( \frac{f_{mc}}{f_{sc}} \right)$$

(33)

And
\[ \sigma_{cf} = \sigma_c \left( \frac{f_{nc}}{f_{sc}} \right) \]  

(34)

The PWB approximation is not successful for electric dipole \( E1 \)- forbidden transitions than for \( E1 \)-allowed transitions. This is in \( E1 \)- forbidden transitions due to amplitude for the direct process in H-is small. The PWB cross sections are higher at intermediate \( T \) in contrast to the CCC cross sections for the 1\( s \)-2\( s \), 3\( s \) excitations of the hydrogen atom.

Due to two-step virtual transitions PWB cross sections near the threshold are lower than that of CCC cross sections for hydrogen atom above threshold region for the 1\( s \)-2\( s \), 3\( s \), and 4\( s \) excitations, the \( BE \) scaling described in Equation (8) works well.

(3.12) \textbf{Deutsch Mark (DM) formalism}

Deutsch and Mark devised a formalism to measure the ionization cross sections whose approach is completely different from the basic approach. The Deutsch Mark approach has also been applied and has been customized numerous times over the years. This approach was successful in both single and multiple ionization cross sections of different atoms. According to Gryzinski, ionization cross section \( \sigma \) is given by

\[ \sigma(E) = \sum_{n,l} 4 \pi a_0^2 \xi_n (R/E_{nl})^2 f(U) \]

With

\[ f(u) = d \left( \frac{1}{U} \right) \left( \frac{U-1}{U+1} \right)^a \times \left\{ b + c \left[ 1 - \left( \frac{1}{2U} \right) \right] \ln \left[ 2.7 + \left( U-1 \right)^{0.5} \right] \right\} \]

and \( a = 3/2, b = 1, c = 2/3 \) and \( d = 1 \)

\( \xi_n \) is the number of electrons in the \( n \)th atomic subshell and \( E_{nl} \) is the ionization energy in \( n \)th subshell, \( U \) is the reduced energy and \( E \) is the energy of incident electron. Deutsch and Mark replaced the Bohr’s radius \( a_0 \) with \( r_{nl} \) of the corresponding electronic subshell. Margreiter et al is used semi empirical formula for the determination of absolute electron impact ionization cross section \( \sigma \) on the basis of above substitution as:
\[ \sigma(E) = \sum_{n,l} g_{nl} \pi r_{nl}^2 \xi_{nl} f(U) \]

Straight forward extension of the DM formula of the above equation for molecular targets resulted in the following equation:

\[ \sigma(E) = \sum_{j} g_{j} \pi r_{j}^2 \xi_{j} f^{*}(U) \]

Where summation is now taken over the molecular orbital labeled ‘j’ are given as

1. Separate set of weighting factors are required for the groups having molecular symmetry, for this a separate set of weighting factors is to be calculated empirically or by other suitable method.

2. To define mean square radius \((r_{j})^2\) it is not obvious for different molecular orbital.

3. Calculation of an additional function \(f^{*}(U)\) is required which must have dependency of energy.
CHAPTER 4.0

OBJECTIVES OF RESEARCH WORK

There are many useful mathematical theories about ionization of molecules and atoms. There are several theoretical methods are used to find the ionization cross-section of atoms and molecules.

Outcomes of our Research work

A theoretical Semi-empirical model is used for dissociation of different molecules, the objectives and outcomes of our work are given by:

1. The Semi-empirical model is used to determine single, double, partial and total cross section of target molecules.
2. To develop and adapt existing codes that will include the effect of nuclear motion for finding ionization cross sections.
3. The ionization cross-section of target molecules can be calculated at different values of energy.
4. To calculate single, double partial and total differential cross-section of molecules in gas phase.
5. To compare such calculations and results with the available literature data.
CHAPTER-5.0

RESEARCH METHODOLOGY

Research Methodology

This formulation is used to calculate cross sections of molecules at different values of energy in collision process.

According to review of literature, some experimental and theoretical data is available for comparison of present calculations.

The semi empirical formalism is used for calculation which is developed by Jain-Khare.

The single ionization cross sections due to complete solid angle ($\Omega = 4\pi = \int 2\pi \sin \theta d\theta$), the production of ions by interaction of electron with molecule having energy $E$ is given by

$$Q_i(E, W, \theta) = \frac{a_0^2 R^2}{E} \int_0^{E-I_i} \frac{(E-W)}{E-I_i} \left( \frac{d f_i(W, K, \theta)}{d\theta} \right) \ln[1 + C_i(E - I_i)] +$$

$$E^{-\Omega} \left( c \cdot 0.3 + c \cdot 3 \right) x \cdot 2 E - c + c \cdot 2(E - c) 22 \pi \sin \theta d\theta$$

Where

$W = (\varepsilon + I_i)$ is energy loss

$I_i =$ Ionization Potential

$a_0 =$ Bohr radius,

$\varepsilon_0 =$ Energy parameter,

$C_i =$ Collision parameter,

$S_i =$ Number of ionized electrons,

$R =$ Rydberg constant and

$\theta =$ Scattering angle respectively.
Chapter 4.0

Objectives of Research work

The appearance potential depends on the photo ionization cross section [152-153].

The ionization potentials for various cations are given along with photo ionization determination.

The double differential cross sections were calculated by the differentiation of semi empirical formula due to the solid angle Ω is given by:

\[ Q_i^2 (E, W, θ) = \sum_i Q_i (E, W, θ) \]  \hspace{1cm} (2)

The double differential cross sections and oscillator is depends on angle. The angular oscillator strengths in angular-momentum-transfer k→ 0 is given by

\[ \frac{df_d(W, θ)}{dWdΩ} = \frac{1}{4\pi} \frac{df_d(W, θ)}{dW} \left[ 1 + \frac{β}{2} (3 \cos^2 θ - 1) \right] \]  \hspace{1cm} (3)

Where

β is energy dependent asymmetric parameter.

The integration of single differential we can calculate total ionization cross section due to energy loss is given by:

\[ Q_i (E) = \int Q_i (E, W) dW \]  \hspace{1cm} (4)

The total electron impact ionization cross section is given by

\[ Q_i^T (E, W) = \sum_i Q_i (E, W) \]  \hspace{1cm} (5)

In plasma, the ionization can be calculated by using this formula:

\[ R_i = \int_{-∞}^{∞} 4\pi \left( \frac{1}{2\pi mkT} \right)^{3/2} m^e (-eKT) Q_i (E)E de \]  \hspace{1cm} (6)

Where

K = Boltzmann constant
T= Temperature and
m= mass of the electron respectively.
By using Semi-empirical formula we can calculate single, double, partial and total differential cross section of molecules in gas phase. In case of a molecule, there is a hard prospect of dissociation into atom with ionized atoms.

On the theoretical side, Jain-Khare and semi empirical Approach exists to calculate the particle ionization-cross-section including direct dissociation and multiple ionization process for electron molecule scattering.

It has been seen in case of double, multiple ionization that there is some discrepancies among the experimental and theoretical value. [154-161].