Chapter 2

THEORETICAL FORMALISM FOR ELECTRON INDUCED MOLECULAR PROCESSES

This chapter presents the theoretical approaches that we have employed to estimate various total cross-sections for various atoms, molecules, and radicals. Total $(Q_{el} + Q_{inel})$ *cross sections are calculated using the Spherical Complex Optical Potential (SCOP) technique up to 5 keV in ionization energy. The Complex Scattering Potential-ionization Contribution (CSP-ic) formalism was used to determine the total ionization cross sections and total excitation cross sections. In addition, we developed the 2 Parameters – Semi empirical method (2P-SEM) to determine total and elastic cross sections, and we established a correlation between* Q_{ion}*(max) and dielectric constant. It will go through several approximations that are employed in this chapter's techniques.*

2.1 Introduction

The computation of the total elastic, ionization, and progressive excitation cross sections is the major goal of this work. Our team developed a mechanism for separating the ionization contribution from the total inelastic processes as a result of our work. We refer to it as the Complex Scattering Potential-ionization Contribution (CSP-ic) approach, as described in the portion of this chapter that follows. Our theoretical work starts with the creation of complicated phase shifts for the complex optical potential-based computation of the total elastic and total inelastic cross sections [1]. To compute preferred cross sections, let us think back to the association between cross sections as well as other quantum mechanical parameters.

2.2 Spherical Complex Optical Potential (SCOP) Method

Our goal is to create a simple estimation concept that will allow us to predict cross sections with reasonable accuracy. We are focused in electron scattering with atom-molecule (target) in its ground state with the current energy range (from ionization threshold to 5000eV), which leads to elastic scattering in the presence of cumulative inelastic scattering. Using the cross section computation, a notion of complicated phase shifts was established to incorporate "absorption" events in the context of absorption potential. This concept is directly related to the scattering potential concept. As a result, we are working with a complex potential, that is referred to as the "complex optical potential." This word refers to an analogy employed in the study of optics, notably the use of an optical model to investigate transmittance via a refractive medium. We created a complex optical potential model, which corresponds to the complex refractive index in the science of optics.

The system's complicated optical potential depicts the relationship among target and projectile,

$$V_{opt} = V_R + iV_I \tag{2.1}$$

The complex potential designates all of the primary impacts for the current molecules. In expression 2.1, the sum of the static potentials (V_{st}) represents the complex potential (V_R) the real component, exchange (V_{ex}), and polarisation (V_P) potentials, whereas the imaginary part (V_I) is the absorption potential (V_{abs}). These potentials govern the interactions of electrons (incoming particles) with the target.

2.2.1 Atomic charge density

It is hard to come up with an appropriate equation for charge density for heavy atoms. Consequently, we must use several approximation approaches. The amount of static charge is calculable via the Roothan-Hartree-Fock (RHF) wave functions presented in the form of Slater Type Orbitals (STOs), as detailed in Clementi and Roetti's research [2]. Bunge et al [3] catalogued very precise versions of RHF wave functions shortly thereafter. Its properties are typically determined by the elements contained in their ground state. R_{nl} represents RHF wave functions and may be extended as a limited combination of basic peripheral treatments as,

$$R_{nl} = \sum_{j} S_{jl} C_{jln} \tag{2.2}$$

The orbital expansion parameters are represented by C_{jln}, while the Slater Type orbitals being represented by S_{jl}:

$$S_{jl} = N_{jl} r^{n_{jl}-1} \exp\left(-Z_{jl} r\right) \tag{2.3}$$

With the normalization factor, N_{jl},

$$N_{jl} = \frac{\left(2Z_{jl}\right)^{\left[n_{jl}+\frac{1}{2}\right]}}{\sqrt{\left(2n_{jl}\right)!}} \tag{2.4}$$

The variables n_{jl}, Z_{jl}, and l represent the primary quantum number, orbital exponent, and azimuthal quantum number, respectively. Bunge et al [3] computed C_{jln}, and Z_{jl}, through which we may calculate electronic charge density. Now, using C_{jln}, and Z_{jl} parameters from Bunge et al [3], as an illustration, we calculate the oxygen atom's charge density. Let us now compute the charge density of an oxygen atom. For this, expressions 2.2, 2.3, and 2.4 are used to determine the radial wave functions for every single orbital of an electron R_{1s}, R_{2s}, R_{2p}, and R_{3s}. The total charge density of oxygen (Z= 8) may then be calculated.

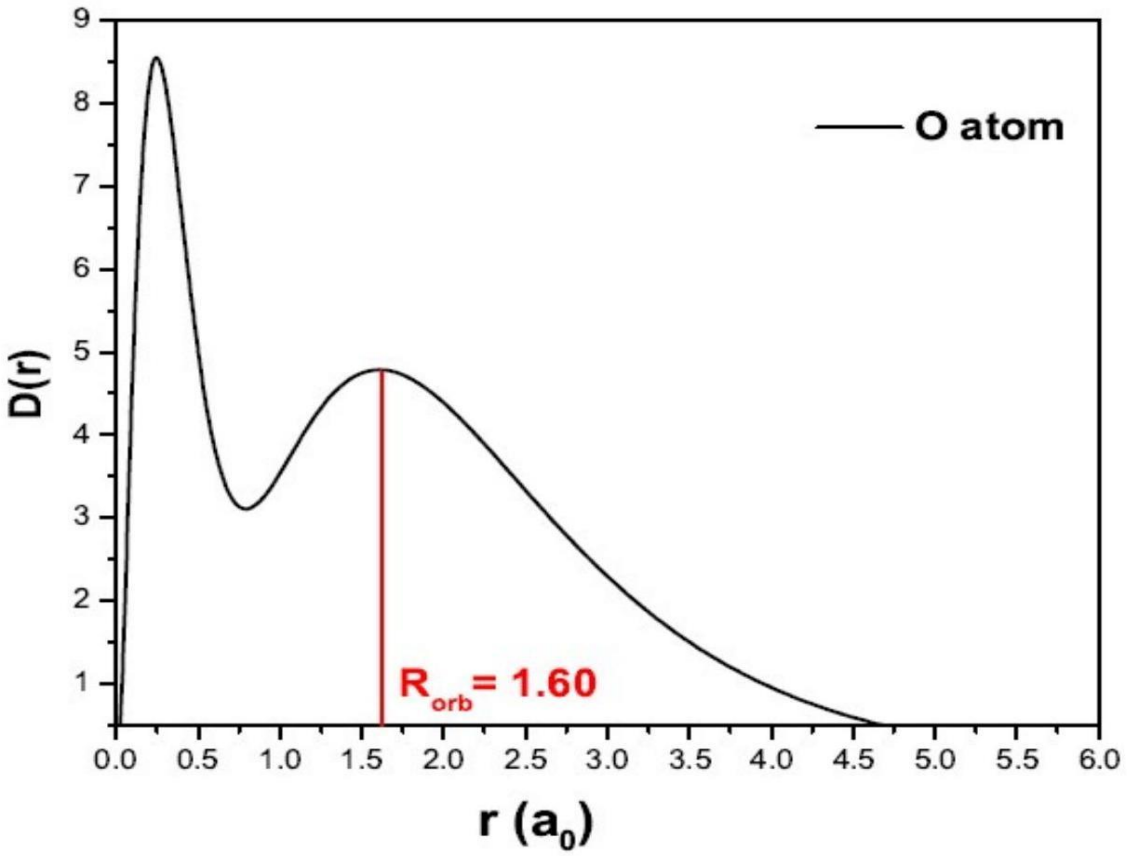

Figure 2.1 The distribution of the O atom's radial charge density is shown as a function of ' r ' (Swadia, 2017).

$$\rho(r) = \frac{1}{4\pi}\left(2|R_{1s}|^2 + 2|R_{2s}|^2 + 6\left|R_{2p}\right|^2\right) \tag{2.5}$$

In this context, $4\pi\int_0^\infty \rho(r)r^2dr = Z$ provides the total charge of all electrons. Figure 2.1 depicts the outcome of radial charge density $[D(r) = 4\pi r^2\rho(r)]$ for the oxygen atom. Figure 2.1 shows two distinct spikes, one for primary quantum number $n = 1$ and the other for principal quantum number $n = 2$. At $1.60a_0$, the outer orbital peak (R_{orb}) is detected. Where R_{orb} denotes the orbital radius of the O atom. The least square approach was used to fit the D(r) formula for the radial density of electrons in the well-known work of Cox and Bonham [5]. They provide a list of parameters for the atoms varying from total number of electrons Z=1 to 54. The charge density is calculated analytically as follows:

$$\rho(r) = \frac{Z}{4\pi r}\sum_{i=1}^{n} \gamma_i \lambda_i^2 \exp(-\lambda_i r) \qquad (2.6)$$

The Cox and Bonham parameters of several atoms that were applied to determine charge density are listed below.

Table 2.1 Hydrogen (Z=1)

γ_i	0.0524	5.0360	-4.0876
λ_i	1.9986	1.8954	2.1161

Table 2.2 Carbon (Z=6)

γ_i	1.2820	-0.0616	4.2766	6.7513	-3.9495	-7.3000
λ_i	1.9147	43.9979	5.3154	15.9205	4.1654	15.0304

Table 2.3 Flourine (Z=9)

γ_i	1.2644	-0.1763	3.0409	1.4796	-3.1755	-1.4335
λ_i	2.4893	21.5801	8.2525	13.0569	7.3313	12.2279

Table 2.4 Oxygen (Z=8)

γ_i	1.3017	-0.1670	2.6221	1.5881	-2.8644	-1.4804
λ_i	2.2491	19.5541	6.9101	10.7798	6.0560	9.9776

Table 2.5 Nitrogen (Z=7)

γ_i	1.3678	-0.2380	2.8625	1.9402	-3.0396	-1.8916
λ_i	2.0273	16.5256	5.9953	9.9313	5.0882	9.0839

The potential field parameters in this case are γ_i and λ_i.

2.2.2 Static effect

An incoming electron generates coulomb or electrostatic potential as it reaches an unaffected target charge cloud, which would be defined as static potential (V_{st}). The static potential $V_{st}(r)$ at distance'r'is described by [6], employing Poisson's equation.

$$V_{st}(r) = -\frac{Z}{r} + 4\pi\left[\frac{1}{r}\int_0^r \rho(r')r'^2dr' + \int_r^\infty \rho(r')r'dr'\right] \quad (2.7)$$

Thus, Z indicates the atomic number, in contrast, $\rho(r')$ denotes the electrical charge density of the atom/molecule. For the ground state of a hydrogen atom, we obtain an exact term for the wave function, which is $V_{st}(r)$.

$$V_{st}(r) = -\left(1 + \frac{1}{r}\right)e^{(-2r)} \quad (2.8)$$

According to equation 2.8, the static potential exists and has an impact only for small distances. It is hard to come up with suitable density of charge and V_{st} calculations for heavy atoms. As a result, we must rely on various estimation (accurate) techniques. The target atoms' static potential was stated theoretically as a Yukawa total components beginning alongside Hartree-Fock and all neutral atoms' subjective wave functions in the work of Cox and Bonham [5]. The following is the quantitative expression for static potential.

$$V_{st}(r) = -\frac{Z}{r}\sum_{i=1}^{n} \gamma_i \exp(-\lambda_i r) \tag{2.9}$$

Here γ_i and λ_i represents potential field parameters.

Salvat et al [7] created the Dirac-Hartree-Fock-Slater (DHFS) methodology, which is a revised form of the RHF technique that incorporates relativistic effects into account. The authors use this technique in an attempt to adapt the potential to an algebraic expression. In this case, estimation is determined by the values employing DHFS self-consistent data, which are calculated for the atomic screening function. The static potential's mathematical formula is,

$$V_{st}(r) = -\frac{Z}{r}\sum_{i=1}^{n} A_i \exp(-\alpha_i r) \tag{2.10}$$

Their scientific report [7] contains an inventory of the atomic screening variables A_i and α_i. The analytical formulas of Cox and Bonham [5] were employed in this investigation to calculate the electrostatic potentials and charge densities of ultralight targets.

2.2.3 Exchange effect

The exchange potential accounts for exchange of the incident electron with one of the target electrons. Hara [8] utilized the “free electron gas exchange model” to estimate the effects of exchange. Pauli's exclusion principle implies that the entire wave function is ant symmetrical when this occurs. he considers the electron gas to be a Fermi gas of quasi electrons. By adding all momentum phases up to and including the Fermi level E_f, the exchange energy is computed. The potential energy of the Hartree exchange is explained below.

$$V_{ex}(r,k) = -\frac{2}{\pi}k_F\left[\frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right] \tag{2.11}$$

Here k_F is known as Fermi wave vector.

$$k_F = \sqrt[3]{3\pi^2\rho(r)} \tag{2.12}$$

The target's radial charge density is represented by $\rho(r)$.

With

$$\eta = \frac{\sqrt{k^2 + k_F^2 + 2I}}{k_F} \tag{2.13}$$

This approximation is known as "Hara Free Electron Gas Exchange" (HFEGE) model. The ionization energy, denoted by the Hartree unit I, is the minimal energy needed to eject a bound state electron. For the majority of calculations involving atoms and molecules with open shells, we employ the potential of exchange effects from expression 2.11. Riley and Truhlar's [9] investigation also provides a hypothetical closed shell exchange in the investigation. These terms are used to describe this potential:

$$V_{ex}(r,k) = \frac{1}{2}\left[E_D - \sqrt{E_D^2 + 4\pi\rho(r)}\right] \tag{2.14}$$

where the kinetic energy is local,

$$E_D = \frac{1}{2}k_i^2 - V_{st} \tag{2.15}$$

2.2.4 Polarization effect

The impact of distortion of the atomic/molecule charged cloud system caused by incident electrons is substantial in elastic scattering of electrons by molecules or atoms. This transient distortion of the target is caused by the induced multipole moments and is inherently attractive in nature. This impact adds a new term to the polarization potential formula for potential energy. [1] represents an adiabatic formula of the asymptotic polarization potential.

$$V_{pol} = -\frac{\alpha_d}{2r^4} - \frac{\alpha_q}{2r^6} \tag{2.16}$$

The terms concerning higher-order multipoles have been neglected in this equation. For the target atom, α_d is static electric dipole polarizability and α_q is static electric quadrupole polarizability. At r → ∞, the potential is attractive and varies asymptotically as $\frac{1}{r^4}$. Singularity exists at $r = 0$. With' r_c ' as cutoff distance equation 2.16 can be written for dipole polarizability as,

$$V_{pol} = -\frac{\alpha_d}{2(r^2 + r_c^2)^2} \tag{2.17}$$

This is referred to as the 'Buckingham' polarization potential [10,11]. Target electrons are simply incapable of responding to a quick approaching electron. As a result, when energies are high, we need to adopt a dynamic or energy sensitive version of the polarization potential. As a result, Khare et al [12] proposed an energy dependent version of polarization potential.

$$V_{dp}(r,k) = -\frac{1}{2}\left[\frac{\alpha_d r^2}{(r^2 + r_c^2)^3} + \frac{\alpha_q r^4}{(r^2 + r_c^2)^5}\right] \tag{2.18}$$

r_c represents the energy dependent cut-off factor. It is feasible to demonstrate from Born approximation [1,13] that

$$r_c = \frac{3k}{8\Gamma} \tag{2.19}$$

The average atomic excitation energy is denoted by Γ in expression 2.19. The polarization potential described before is a long-range possibility. The straightforward r^{-4} response is invalid at shorter distances. We must thus take into account the implications of electron interaction for short distances [13].

2.2.5 Absorption effect

The complete amount of scattered energy lost into all permissible modes for ionization and electronic excitation is accounted for by the imaginary component (V_I) of the optical potential (V_{opt}), mainly composed of the absorption potential V_{abs}. Initially, the complex optical potential was brought up in relation to nuclear physics [14] before being used to describe electron-atom collisions. The e-atom scattering approach uses a number of absorption potential formulations, particularly the findings of [15–18], which are based on the local kinetic energy T_{loc} and the electronic charge density $\rho(r)$. It is a dynamic absorption potential (V_{abs}) represented in an angstrom unit that is non-empirical, quasifree, and Pauli blocking. Here, Pauli blocking corresponds to the ability of atoms to scatter light, making the gases more transparent and it is responsible for the stability of atoms.

$$V_{abs} = -\frac{1}{2}\rho(r)v_{loc}\sigma_{ee} \tag{2.20}$$

In this particular scenario, the incident electron's local speed is denoted by v_{loc}, and the typical total cross-section of the simultaneous impact among the target electron and the charged particles of the incoming beam is represented by σ_{ee}. A straightforward quasi-empirical calculation [18] as may be used to rewrite this.

$$\begin{aligned} V_{abs}(r, E_i) = \quad & -\rho(r)\left(\frac{T_{loc}}{2}\right)^{\frac{1}{2}} \\ & \times \left(\frac{8\pi}{10k_F^3 E_i}\right)\theta(p^2 - k_F^2 - 2\Delta)\cdot(A_1 + A_2 + A_3) \end{aligned} \tag{2.21}$$

The definition of the dynamical components A_1, A_2 and A_3 in the expression above is,

$$\begin{aligned} A_1 = \frac{5k_F^3}{2\Delta}; A_2 = \frac{k_F^3(5p^2 - 3k_F^2)}{(p^2 - k_F^2)^2};\ \text{and}\ A_3 \\ = 2\theta(2k_F^2 + 2\Delta - p^2)\frac{(2k_F^2 + 2\Delta - p^2)^{\frac{5}{2}}}{(p^2 - k_F^2)^2} \end{aligned} \tag{2.22}$$

T_{loc} is a representation of the incident electron's local kinetic energy.

$$T_{loc} = E_i - V_R = E_i - (V_{ex} + V_{st}) \tag{2.23}$$

The complex valued unit step-function is represented by $\theta(x)$, where $\theta(x) = 1$ for x ≥ 0, and $\theta(x) = 0$ or else. Since the absorption potential (V_{abs}) only affects short-range signals and is insensitive to distant signals, it is disregarded in T_{loc} equation 2.23. The absorption potential depends on the charge density of molecule, $\rho(r)$ and an energy dependant parameter Δ of the target. The Hartree expression for the term p^2 is $2\mathrm{E_i}$, that represents the energy of the incoming electron. The wave vector of Fermi is $k_F = \sqrt[3]{3\pi^2\rho(r)}$.

The energy value in the exclusive model [18] creates a threshold beyond which the inelastic channel, with absorption potential $V_{abs} = 0$, is energetically precluded. The first Staszeweska concept [18] Δ accounts for the target's ionization threshold for all incident energies. As a result, the contributions made by discrete excitations with lower incidence energy are effectively ignored. This was earlier recognized by Blanco and Garcia [19], and they talked about the need for Δ value. Following that, we adjusted the parameter to take into account the inelastic channel associated with excitations due to differing levels of E_i, which is equivalent to the target's (I) ionization threshold. A lowest value is assigned for Δ that steadily approaches to its highest value equal to (I). Therefore, Δ as a variable quantity that accounts for more of the absorption below the I as given by [19],

$$\Delta(\mathrm{E_i}) = \eta I + \beta(E_i - I) \tag{2.24}$$

The first component in expression 2.24 correlates to the lowest value of Δ at $E_i = I$ when the input originates from separate excitations. The element represents energy dependence before it achieved its extreme value I. The peak of the inelastic cross-sections occurs at the energy E_P. The parameter β is subsequently determined by using the criterion $\Delta = I$ at $E_i \geq E_P$.

The following equation can be used to explain the relationship between the sum of all discrete excitation channels and the integrate of all channels, comprising the entire continuum.

$$\eta = \frac{\sum_{n=1}^{n_\infty - 1} E_n}{\sum_{n=1}^{n_\infty} E_n} = \left(1 - \frac{\mathrm{I}}{\sum_{n=1}^{n_\infty} E_n}\right) \tag{2.25}$$

Where n_∞ refers to the continuum and E_n represents the n^{th} electronic level of energy. At 100eV, the beginning point of the attractive potential for an oxygen atom is $0.85a_0$ (figure 2.2).

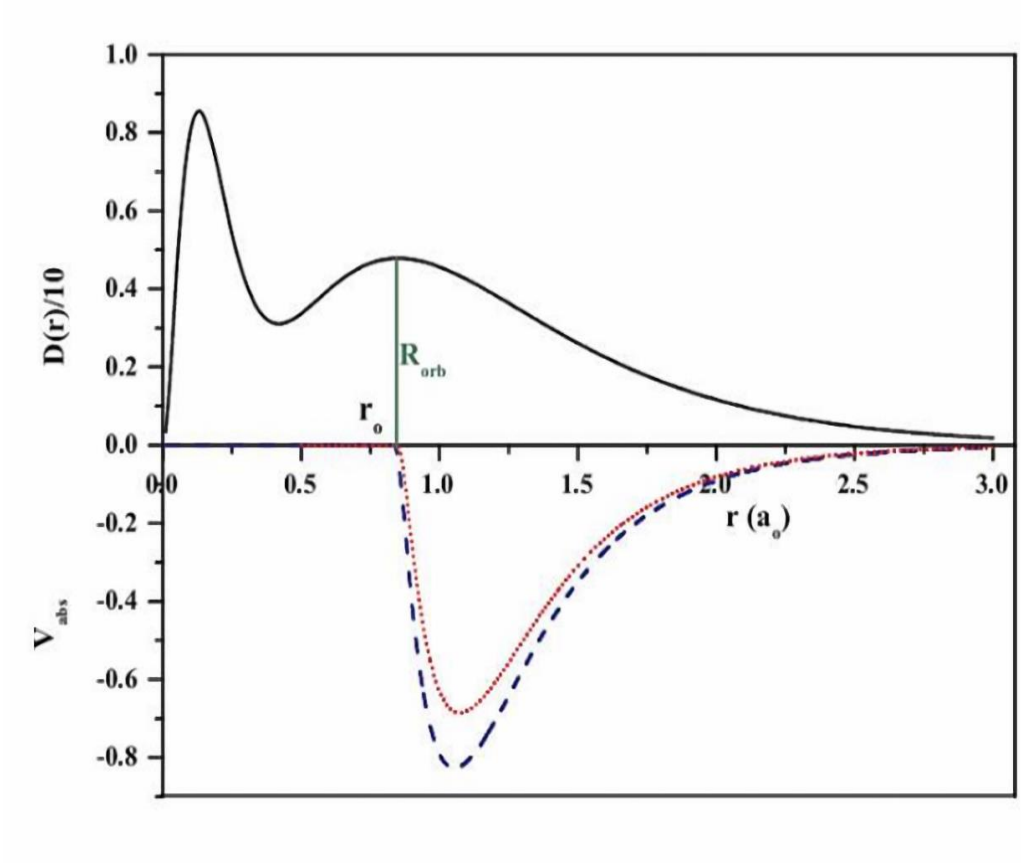

Figure 2.2 The radial charge density and absorption potential for oxygen atom at 100eV

Solid line: D(r)/10; Dashed line: V_{abs} with $\Delta = I = 13.6eV$; Dotted line: V_{abs} with $\Delta = I = 15.07eV$

Figure 2.2, depicts the charge distribution $D(r) = 4\pi r^2 \rho(r)$ for representative example. For 500eV, the point is set at $0.25a_0$ (not visible in figure 2.2). These levels represent an excessive loss of dispersed flux into inelastic effects, corresponding to larger values of $Q_{\text{inel.}}$ This is also due to the exclusion of finer elements in the V_{abs}, such as the varied probability of transitions for different states, and so on. The absorption potential V_{abs} also reaches the harder-to-

stimulate or becomes ionised inner electronic shells. However, because absorption potential has a great analytical capacity and a large prediction capability, it is required to employ it at medium energies to rectify it via $\Delta \geq I$. Consequently, we select this variable as a gradually changing function of E_i centred on the value of I. At greater energies, the potential V_{abs} and the Q_{inel} typically diminish.

In figure 2.2, we show an illustration of the $4\pi r^2 \rho(r)$, of the target V_{abs} for two mutual selections (a)$\Delta = I$, and (b) Δ as an ongoing variable centered on the I. Figure 2.2 depicts the dynamics of the previously outlined V_{abs}. In summary, preliminary calculations are conducted by a constant value $I = \Delta$, but as a variable compensates to assess the V_{abs} in the target charge cloud zone [19], and in many circumstances obtains more precision with experimental and non-experimental statistics. The modification in [20] was to assign an acceptable minimum value of $0.8 \cdot I$ to Δ and represent this variable as a function of E_i around I, as shown below.

$$\Delta(E_i) = 0.8 \cdot I + \beta(E_i - I) \tag{2.26}$$

This is also written as,

$$\Delta(E_i) = \Delta_{min} + \beta(E_i - \Delta_{max}) \tag{2.27}$$

The selection of the first component in equation 2.26, $0.8 \cdot I$, assures that the different excitation channels are open considerably, if not completely, at the threshold value $E_i = I$. At present, E_P is defined as the value of E_i at which our inelastic cross section (Q_{inel}) reaches its greatest value. The value of the variable β is derived in expression 2.26 by ensuring that $\Delta = I + 1(\text{eV})$ at $E_i = E_P$, beyond which Δ is maintained unchanged.

2.3 Potential Scattering

Take into account the procedure of non-relativistic electron scattering by atoms/molecules. Several physical events are conceivable based on on the distance among the input electrons and the destination electron cloud. These phenomena are generated by the potentials (fields) developed between the incident and target electrons. The atoms/molecules are much heavier than the incident electrons and hence can be treated as fixed centers of force. The non-

relativistic time-independent Schrodinger equation (TISE) for such a system in the position representation is [1].

$$-\frac{\hbar^2}{2m}\nabla_r^2\Psi(\vec{r}) + V(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{2.28}$$

$V(\vec{r})$ denotes the target's effective potential, while $\mathrm{E} = \frac{p^2}{2m}$ denotes incident kinetic energy. The electron momentum is denoted by $\mathrm{p} = \hbar\mathrm{k}$, where k is the wave vector. We suppose that the potential is spherically homogeneous and has a short range, so that $V(\vec{r}) \to 0$ as $r \to \infty$ is faster than any inverse factor of r. Equation 2.28 may be expressed without the non-spherical effects as,

$$[\nabla_r^2 + k^2]\Psi(\vec{r}) = \Psi(\vec{r})U(\vec{r}) \tag{2.29}$$

$$U(\vec{r}) = \frac{2m}{\hbar^2}V(\vec{r}) \tag{2.30}$$

In this case, $U(\vec{r})$ represents the "reduced potential," which approaches zero more quickly than 1/r for large $\mathrm{r}(\mathrm{r} \to \infty)$. The asymptotic boundaries requirement is satisfied by the $\Psi_{k_i}^{(+)}(\vec{r})$ outgoing stationary state wave function.

$$\Psi_{k_i}^{(+)}(\vec{r}) \to A\left[\mathrm{e}^{(ik_i\cdot r)} + f(\theta,\emptyset)\frac{\exp(ikr)}{r}\right] \text{ for large r} \tag{2.31}$$

Where A is a normalizing factor that is independent of $\vec{r}$ and angles θ and ϕ. $f(\theta, \phi)$ is an angular function that satisfies expression 2.31, whereas potential $V(\mathrm{r})$ is ignored at large r. The first term in equation 2.31 depicts the incoming plane waves, while the second term provides the outgoing spherical waves. At large distances, the static state scattering wave function $\Psi_{k_i}^{(+)}(\vec{r})$ is the superposition of an incoming plane wave of wave vector $\overrightarrow{k_l}$ and an outgoing spherical wave with magnitude dependent on θ and ϕ and inversely proportional to r. The scattering amplitude is given by the function $f(\theta, \phi)$ or $f(\Omega)$.

2.3.1 Partial wave analysis

The primary objective of our investigation is to solve the Schrodinger problem utilizing the spherical complex optical potential (SCOP). The partial wave analysis is employed to develop complex phase shifts [10], then applied in order to find total cross sections. Consider the example of a spherically symmetric or central potential that is dependent on the radial distance r in the partial wave analysis approach [1,10]. As a result, we must concentrate on the radial part of the Schrodinger equation (SE) 2.29. This approach is relies on an expanding of the wave function, according to eigen functions of angular momentum [1]. Phase shifts are determined for each orbital angular momentum quantum number, ' l ' (that is, $l = 0$ specifies the s orbital, $l = 1$ describes the p orbital, $l = 2$ determines the d orbital, and so on). It is simply an angular momentum expansion [10]. As seen below, we may expand the scattering wave function in partial waves of the quantum numbers l and m.

$$\Psi_{k_i}^{(+)}(k,r) = \sum_{l=0}^{\infty} \sum_{m=-1}^{+1} C_{lm}(k) R_{lm}(k,r) Y_{lm}(\theta,\phi) \tag{2.32}$$

The radial part of the wave function is represented by $R_{lm}(k,r)$. The radial Schrodinger equation is expressed by the expression,

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{l(l+1)}{r^2}\right] R_l(k,r) + V(r) R_l(k,r) = E R_l(k,r) \tag{2.33}$$

As a result, we may replace the "reduced potential" U(r) and $R_l(k,r) = \frac{u_l(k,r)}{r}$ with asymptotic Bessel and Neumann functions. As a result, we may derive,

$$u_l(k,r) \to A_l(k)\sin\left[kr - \frac{1}{2}l\pi + \delta_l(k)\right] \text{ for large } r \tag{2.34}$$

The term $\delta_l(k)$ for the l^{th} partial wave is referred as the phase shift, and it indicates how the interaction impacts the solution. We can understand from expression 2.34 that the interaction provides shift in the radial wave function's phase. The presence of potential at the scattering centre (target) causes a change in the angle. For repulsive potential, we assume the fact that the

radial wave function $u_l(k,r)$ is "pushed out" in relation to the incoming free radial wave [1]. In this occurrence of an attractive potential, the radial wave function $u_l(k,r)$ is "pulled in" in relation to the approaching free radial wave. As a result of calculating the amount $\delta_l(k)$, we may identify the many microscopic values necessary in our job.

To compute phase shifts quantitatively, use $rR_l(k,r) = u_l(k,r)$. Let us now proceed to solve the radial Formula 2.33 for internal region $(r < a)$. In this case, " a " represents the finite scattering potential range. When we implement the boundary condition, the role of radial waves R_l, its component $\frac{dR_l}{dr}$, and its log scale derivative $\mathrm{R}_l^{-1}\frac{dR_l}{dr}$ should be consistent at $r = a$.

As a result, at $r = a$, we obtain,

$$R_l(k,r) = \hat{A}_l(k)[j_l(k,r) - \tan\delta_l(k)\eta_l(k,r)]_{r=a} \tag{2.35}$$

Now let $\gamma_l = \left[\mathrm{R}_l^{-1}\frac{dR_l}{dr}\right]_{r=a}$ then we get,

$$\gamma_l(k) = \frac{k[j_l'(ka) - \tan\delta_l(k)\eta_l'(ka)]}{j_l(ka) - \tan\delta_l(k)\eta_l(ka)} \tag{2.36}$$

The symbols j_l and η_l stand for the Neumann functions and spherical Bessel. The term "prime" defines a derivation with regard to ' r ' Therefore,

$$\tan\delta_l(k) = \frac{kj_l'(ka) - \gamma_l(k)j_l(ka)}{k\eta_l'(ka) - \gamma_l(k)\eta_l(ka)} \tag{2.37}$$

Equation 2.37 can be applied to compute the phase shift, $\delta_l(k)$, The scattering amplitude can be determined independently of ϕ by comparing the factors of $e^{(ikr)}$ of the external spherical wave and then employing formulae 2.32 and 2.36. Thus

$$f(k,\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)[\exp\{2i\delta_l(k)\} - 1]P_l(\cos\theta) \tag{2.38}$$

Rewriting equation 2.38 as,

$$f(k,\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)[S_l(k)-1]P_l(\cos\theta) \tag{2.39}$$

Here, $S_l(k) = \exp\{(2i\delta_l(k)\}$ is the definition of the S-matrix (Scattering matrix) components. Thus the understanding of the phase shifts make possible to obtain the scattering amplitude. Equation 2.39 may be rearranged and written as

$$f(k,\theta) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\exp(i\delta_l)\sin\delta_l P_l(\cos\theta) \tag{2.40}$$

The equation of differential cross section is as follows;

$$\frac{d\sigma}{d\Omega}(k,\theta) = |f(k,\theta)|^2$$

Through the application of a spherical potential $V(\mathrm{r})$, we may obtain elastic scattering.

$$\frac{d\sigma}{d\Omega}(k,\theta) = \frac{1}{k^2}\sum_{l=0}^{\infty}\sum_{V=0}^{\infty}(2l+1)(2l'+1)\exp \mathrm{i}(\delta_l-\delta_V) \times \sin\delta_l\sin\delta_V P_l(\cos\theta)P_V(\cos\theta) \tag{2.41}$$

Total cross sections can be obtained by integrating (DCS) differential cross sections over all angles and applying the orthogonality criterion for Legendre coefficients.

$$\sigma_{tot}(k) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l(k) = \sum_{l=0}^{\infty}\sigma_l(k) \tag{2.42}$$

Here we can present each partial wave cross section $\sigma_l(k)$ is as,

$$\sigma_l(k) = \frac{4\pi}{k^2}(2l+1)\sin^2\delta_l(k) \tag{2.43}$$

It should be noted that the maximum contribution of each partial wave to the total cross section is provided by

$$\sigma_l^{\max}(k) = \frac{4\pi}{k^2}(2l+1) \tag{2.44}$$

When the $\sin^2\delta_l(k) = 1$ and

$$\delta_l(k) = \left(n + \frac{1}{2}\right)\pi \text{ with } n = 0, \pm 1, \pm 2 \ldots \tag{2.45}$$

Elastic scattering accompanies allowed with non-elastic effects over the threshold in scattering effects. In addition to the elastic, there can be a single, several or even an infinite number of open channels. In fact, inelastic effects like as excitation and ionization, which offer information about the target [1] to be studied, are significant in scientific disciplines. We must study the scattering wave function's asymptotic behaviour as a merger of the plane wave $e^{(-ikr)}$ and the scattered particles spherical wave $e^{(ikr)}$.

$$\begin{aligned}\Psi_{ki}^{(+)}(k,r) \underset{r\to\infty}{\longrightarrow} \quad & A(k)\sum_{l=0}^{\infty}(2l+1)i^l\frac{i}{2kr}\exp(i\delta_l) \\ & \times\left[(-1^l)e^{-ikr} - S_l e^{ikr}\right]P_l(\cos\theta)\end{aligned} \tag{2.46}$$

Here, $S_l = e^{(2i\delta_l)}$ .The phase shift δ_l is considered to be real in the instance of only elastic processes, and $|S_l| = 1$, yet we have to generalize the effects that include non-elastic occurrences. We must allow δ_l to be complex in order to obtain the elastic processes in the context of 'absorption' or quasi-elastic events. The reason for this is the amplitude of the transmitted radial wave might be reduced (if inelastic effects are involved) or stays constant (if just elastic scattering is there), which indicates that,

$$|S_l| \leq 1 \tag{2.47}$$

As a result, we introduce complex phase shift

$$\delta_l = R_e\delta_l + iI_m\delta_l \tag{2.48}$$

Consequently, the complex S-matrix is given by

$$S_l = \exp[2i(R_e\delta_l + iI_m\delta_l)] \tag{2.49}$$

This means that,

$$S_l = \eta_l \exp(2iR_e\delta_l) \tag{2.50}$$

Where $\eta_l = \exp(-2I_m\delta_l)$ is defined as "inelasticity" or "absorption factor". Here the disappearance of particles from the incident channel can be understood in the sense of the term "absorption". Because of $|S_l| \leq 1$, we have

$$0 \leq \eta_l \leq 1$$

and

$$I_m\delta_l \geq 0$$

We get purely elastic scattering (no absorption) for the special case $\eta_l = 1$ (i.e. $I_m\delta_l = 0$).

2.3.2 Elastic and inelastic cross-section (CS) effects

For a given absorption potential, we determine scattering probabilities for elastic and inelastic channels. This approach is identical to the one described previously for pure elastic scattering, but that the phase shift (δ_l) is not real due to the absorption potential [1] in expression 2.49. Equation 2.38 can be used to compute the elastic scattering amplitude for quasi-elastic processes.

$$f_{el} = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)[\exp(2i\delta_l) - 1]P_l(\cos\theta) \tag{2.51}$$

We may now rewrite the above equation using equation 2.50.

$$f_{el} = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)[\eta_l\exp(2iR_e\delta_l) - 1]P_l(\cos\theta) \tag{2.52}$$

The elastic differential cross sections are as follows:

$$\frac{d\sigma}{d\Omega} = |f_{el}|^2 \tag{2.53}$$

The total elastic cross section expression (Q_{el}) is defined as,

$$Q_{el}(k) = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)|\eta_l\exp(2iR_e\delta_l) - 1|^2 \tag{2.54}$$

We may determine total inelastic cross sections by considering the inelastic effects.

$$Q_{\text{inel}}(k) = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)(1-\eta_l^2) \tag{2.55}$$

2.4 Complex Scattering Potential-ionization contribution (CSP-ic) Method

The two primary cross-sections in electron-atom/molecule collision interactions are classified as

(1) Q_T (total cross section)

(2) Q_{ion} (total ionization cross section)

There is no perfect formula for calculating Q_{ion} from $Q_{\text{inel.}}$ Using a novel semi-empirical CSP-ic [21] technique, the TICS (total ionization cross sections) were derived from the total inelastic processes. The majority of standard theories, including Kim and Rudd's [22] Binary-Encounter-Bethe (BEB) formulation and the semi-classical Deutsch-Märk (DM) theory [23], use shell-wise quantification and addition to find the total ionization cross-section, which makes this method unique. Total inelastic cross-section includes total ionization cross-section, which is used in the present method. Another important component of this is that it generates the total electronic excitation cross-section put together ($\sum Q_{exc}$) as a consequence.

$$Q_{\text{inel}}(E_i) = \sum Q_{\text{exc}}(E_i) + Q_{\text{ion}}(E_i) \tag{2.56}$$

In expression 2.56, the first term reflects the sum of all excitation cross sections for all possible electronic transitions, whereas the second term reflects total cross sections due to all permissible electronic transitions to the continuum, i.e. ionization.

The first term arises mainly as a consequence of low-lying dipole-allowed transitions, where the cross-section decreases as energy increases. The first term in expression 2.56 becomes less relevant at the ionization threshold point [24].

The following equation depicts an important disparity that forms the basis of the CSP-ic technique.

$$Q_{\text{inel}}(E_i) \geq Q_{\text{ion}}(E_i) \tag{2.57}$$

Using the energy-dependent ratio $R(E_i)$, a semi-classical technique was used to calculate the impact of ionization in $Q_{\text{inel.}}$

$$R(E_i) = \frac{Q_{\text{ion}}\,(E_i)}{Q_{\text{inel}}\,(E_i)} \tag{2.58}$$

It is so,

$0 \leq R \leq 1$

We require $R = 0$ while $E_i \leq I$. The result can be found in a set of the following conditions, which are as below.

$$R(E_i)\begin{cases} = 0 & \text{for} \quad E_i \leq I \\ = R_P & \text{at} \quad E_i = E_P \\ \cong 1 & \text{for} \quad E_i > E_P \end{cases} \tag{2.59}$$

(2.60)

(2.61)

Where E_P denotes the incident energy that occurs when the estimated Q_{inel} reaches its peak value. The topmost point of Q_{inel} arises at the energy where (ΣQ_{exc}) begin to decrease and Q_{ion} begins to increase. As a consequence, the ratio should fall anywhere between 0.5 and 1. R_P denotes the value of R when $E_i = E_P$, and it had been discovered that at the peak of the Q_{inel}, the role in contributing for ionization is around $70 - 80\%$ [25] based on semi-empirical computations that excitation was less likely than ionization for gaseous water (H_2O) beyond 30eV. Although this is the overall trend across all molecules, we find that the ratio seems to be near 0.6 for smaller systems (based on our estimates and other studies). R_P increases ambiguity around the average value (0.75) even for heavier targets, although typical error rates from experiments are 10% to 15%. Ne, for example, has a high ionization potential (I = 21.56eV), [26] exhibit the maximum limit of the ratio of 80%. The majority of the targets examined in this study had ionization potentials vary between 8 to 14eV. Therefore, 70% was selected as the lowest limit. We highlight that the current choice maintains the generality of our technique [21]. The current value of R_p appears to be the fact that, above the ionization threshold value, transitions to continuum begin to dominate as of they relate to an infinite number of open scattering channels. An iterative procedure can be applied because the value of ratio R cannot be estimated precisely. To derive Q_{ion} from Q_{inel}, R as a function of energy is required $E_i \geq I$, therefore we show the ratio R as below.

$$R(E_i) = 1 - f(U) \tag{2.62}$$

$$R(E_i) = 1 - \mathrm{C}_1\left[\frac{C_2}{U+a} + \frac{\ln U}{U}\right] \tag{2.63}$$

The dimensionless quantity is denoted by $\mathrm{U} = \frac{E_i}{I}$.

The current CSP-ic technique is represented by equations 2.57 to 2.63. In the above equation 2.63, the following information is utilized to identify the function $f(U)$. When $\mathrm{E_i}$ increases over I, the ratio R also increases and approaches unity in many cases, as the ionization contribution increases and the discrete excitation term in equation 2.56 decreases. At higher energies, the discrete excitation effects, which are predominantly driven by dipole transitions, fall of as $\frac{\ln(U)}{U}$. The drop of the function $f(U)$ at large energy ranges must likewise be related to $\frac{\ln(U)}{U}$. In equation 2.63, $\mathrm{C}_1, \mathrm{C}_2$ and a are parameters without dimensions that describe target properties such as I and E_P. Moreover, E_P is affected by target properties such as ionization potential and molecule structure. As an outcome, we construct these characteristics by utilizing the three requirements listed below on the ratio R.

(1) $\mathrm{R} = 0$ when the ionization threshold is reached and below.

(2) At the peak of the E_P, R acts in accordance with expression 2.60.

(3) R equals to 1 asymptotically when E_i is adequately greater than E_P.

A method known as "Complex Scattering Potential-ionization contribution" can be used to figure the total Q_{ion}. In the following chapter, this approach will be effectively utilized to various compounds.

2.5 Various Approximation For Charge Density

Owing to its competence with atomic targets, we chose the SCOP approach for analyzing molecules. Because the SCOP approach was designed for atomic systems, it will need to be modified to work with molecules. Number of researchers [27,28] are collaborating to develop electron impact ionization and TCS for molecules. We generally focused on determining Q_{ion} and Q_T simultaneously using an equivalent method. For polyatomic compounds, we need to

develop certain approximation methods. Applying the basic additivity rule (AR) [20], we investigate e^-- molecule process of scattering. The additivity rule is a crude, higher-energy method that states that the TCS of a molecule/atom is just the addition of the TCS component atoms. The downside of this vague method is the lack of understanding of molecular bonding. It gave rise to a innovatory method called MAR (Modified Additivity Rules) in this case. Although MAR produces more results than AR, it is nevertheless not dependable. This rationale has prompted us to use a better method that is more reliable and simple to use. We will now talk about the following techniques.

2.5.1 Additivity rules

The approximate representation of the highly energetic independent atom model (IAM) was enlarged, which resulted in the development of the additivity rules (AR) [20,28,29]. IAM is based on two vital concepts,

(1) It is assumed that each atom in the molecule operates independent as scattering centres. The notion that each atom is associated to the molecule and that the incoming electron will experience the field of other molecule elements is ignored here.

(2) Scattering phenomenon does not exist in multiple ways. It indicates that after colliding with each atom, the electron avoids colliding with other atoms and proceeds straight to the detector.

Consequently, the peculiar atomic cross sections are calculated individually and then summed. in accordance with a few stated conditions under the additivity rules. Let $Q(A)$, $Q(B)$, and $Q(AB)$ be the corresponding cross sections of atoms A, B, and molecule AB.

$$Q(AB) = Q'(A) + Q'(B) \tag{2.64}$$

In the above equation a prime indicate a something more improvement performed in the computation of peculiar atomic cross sections.Typically, expression 2.64 for each molecule M turns into,

$$Q(M) = \sum_{i=1}^{n} Q'(A_i) \tag{2.65}$$

Here, $Q'(A_i)$ is the cross section for a single atom in the molecule, and n is the molecule's total number of atoms, modified to include some molecular property.

(A) Simple Additivity Rule (AR)

The simple additivity rule (AR) is used when Q' reflects only the total cross-section of an individual atom, as shown in expression 2.65.

$$Q(AB) = Q(A) + Q(B) \tag{2.66}$$

This appears to be valid for compounds with greater atomic spacing at medium and high energies. Although the outcome is relatively high at low energy.

(B) Modified Additivity Rule (MAR)

In the case of MAR, the individual cross sections are modified that contain some of the molecular properties. Various types of MAR are described in the available literature, depending on the molecular properties incorporated into the simple AR. The MAR technique is employed to compute molecule total Q_{ion} [30] is as follows:

Arguably, the most important aspect of molecule or atom target is its ionization potential. It is more important than other characteristics when computing the total Q_{ion} of the molecule. As a result, the individual atomic Q_{inel} are obtained by substituting the constituent atoms' ionization potentials with the molecule's ionization potential. This indicates that Q' in equation 2.64 represents the calculated atomic cross sections. In this case, the Q_T of an O_2 molecule calculated using the MAR technique. We guess the Q_{ion} in the MAR using the CSP-ic method. This method, which has high reliability, may allow us to predict Q_{ion} for larger biologically important molecules [31]. In brief, we integrate a CSP-ic method with MAR in our investigation [29,32,33].

2.5.2 Single Centre Approach (SCA)

The bonding between ingredient atoms and multiple scattering in the molecular target are ignored by additivity methods. It is a disadvantage in the instance of the above theories mentioned. This has evolved into what we refer to as the 'Single Centre Approach' (SC), in which bonding of atoms is included. Using this method, we can calculate the charge density

of any molecule, which is the key input to calculate the Q_{ion} and Q_T of the molecules. We assume that the molecule's charge density and V_{st} are expanded at a single center. Geometry, IP, and distribution of charges are taken into consideration in this process. To obtain a cross section of molecule is a main success of our research work. Now discuss about a few examples.

(A) Single center approach for diatomic molecules

We begin with an example of a diatomic molecule AB. We assume that the total charge density ρ_{AB} is approximately the same as the sum of the atomic density of charge ρ_A and ρ_B of free atom A and B respectively and then we proceed from Bader's explanation [34].

$$\rho_{AB} = \rho_A + \rho_B \tag{2.67}$$

This is a crude approximation. Overlapping and bonding are not considered in expression 2.67. A simple correction has been introduced to the above equation. In theoretical investigations, our research team has developed ρ_{AH} for the AH hydride molecule [20]. The density of charge of a hydrogen atom in a hydride AH with bond length R is expanded to atom A using simulations [20,35,36]. The charge density is given by,

$$\rho_H(r,R) = \left(\frac{\lambda e^{-\lambda R}}{16\pi r R}\right)\left[(1 - r\lambda + R\lambda)e^{\lambda r} - (1 + r\lambda + R\lambda)e^{-\lambda r}\right] \text{ for } r \leq R \tag{2.68}$$

and

$$\rho_H(r,R) = \left(\frac{\lambda e^{-\lambda r}}{16\pi R r}\right)\left[(1 - R\lambda + r\lambda)e^{\lambda R} - (1 + R\lambda + r\lambda)e^{-\lambda}\right] \text{ for } r > R \tag{2.69}$$

A charge density value generated from the above equation was employed in H_2 molecule computations [20,27]. While a covalent bond forms a diatomic molecule, partial migration of electrical charge across either atomic associates. It corresponds to the electronegativity of the two atoms. As an example, in the hydrogen fluoride (HF) molecule, the electron charge is partially shifted from the H atom to the F atom. If the shifted minute charge is $q(A)$, the

hydrogen atom loses $q(A)$, while the fluorine atom gains $q(A)$. Assume the case of a molecule AH, where the charge density ρ_{AH} is given as follows:

$$\rho_{AH}(r,R) = \left[\frac{N(A)+q(A)}{N(A)}\right]\rho_A(r) + \left[\frac{N(H)-q(A)}{N(H)}\right]\rho_H(r,R) \qquad (2.70)$$

In free atom $A, N(A)$ represents the number of electrons and in free atom H, $N(H)$ is equal to 1. Bader [34] calculated the bond charge $q(A)$ values for many hydrides. The bond charge magnitude $q(A) = -0.760$ au for the HF molecule. The bond charge $q(A) = -0.585$ au is shifted from the hydrogen atom to the oxygen atom, giving the hydrogen and oxygen atoms a partial positive and partial negative charge. Finally, we provide the following common statement for a diatomic molecule AB:

$$\rho_{AB}(r,R) = f_A\rho_A + f_B\rho_B \qquad (2.71)$$

Both f_A and f_B are modulating factors caused by partial charge shifting when it comes to covalent bonding. Although computational algorithms have been established for molecular wave functions to a higher order of accuracy, the method outlined above remains simple and gives relatively excellent single-centre charge densities. When the charge densities of atoms A and B are similar, the density of charge of each atom in the hetero-nuclear diatomic molecule AB may be extended from the system's centre of mass. For example, in the instance of the homo-nuclear diatomic molecule A_2, the density of charge at the Centre of mass may be expanded from the A_2 molecule's half-bond length, $\frac{1}{2}R_{AA}$.

(B) A single-center approach for polyatomic compounds

The concept of the SCA (Single Centre Approach) is conserved in the case of simple polyatomic molecules, and we followed similar trends as stated for diatomic atoms. The system's Centre of mass position must be determined by examining the molecule's geometry, such as bond angle, bond length, and so on. Each atom's charge density and static potential are then extended at the centres of mass of corresponding atoms. After adding these charge densities, we normalize the formula to yield the total quantity of electrons in a molecule. A spherical charge density and potential can be estimated in this way, which are imprecise and

depend on molecule characteristics. These densities and potential are utilized as inputs to our SCOP approach for scattering effect computations. Tetrahedral systems like SiH_4 and their radicals $SiH_x(X = 1 - 3)$ and other simple molecules like H_2O are examples of such molecules.

2.5.3 Multi Centre Approximation (MCA)

The various atomic charge densities and static potentials, which are expanded in the centre of the molecule, are linearly combined to produce the single-centre target charge density and V_{st}. Then it is once again renormalized while taking into consideration the molecule's covalent bonds and the total amount of electrons [37]. However, small molecules are the only ones that can undergo this type of expansion because they are more likely to contain a single centre that allows the charge density of each atom to increase over time. In this case, it may be assumed that every atom is located in the same region away from the mass centre. Clusters are an example of a large size, complex molecule to which this does not apply. A molecule is inherently a multi-centre system, thus to figure the density of charge, we need to account for more than one centre.

2.6 2 Parameters Semi Empirical Method (2p – SEM)

The impact energy dependence of the Q_T for the intermediate energy [38,39] and high energy [40,41] have been previously studied and the proposed formula was as follows,

$$Q_T = \frac{A}{E^B} \tag{2.72}$$

Where, parameter A is governed by the molecular characteristics such as size of the molecule and its polarizability. The value of B for the high energies, above 500 eV will be ~ 0.7, which is proposed by Joshipura [40] and Garcia [41] for smaller molecules i.e. for ten electrons (Z=10) and up to Z=22 electrons systems respectively. In the present work this formula has been derived for large molecules with 55 < Z < 95. Also, the dependence of Q_T on E_i is different for diverse energy regimes. In this work we have derived two different expressions for the intermediate (50 < E_i < 500 eV) and high energy regions ($E_i > 500\ eV$) for the complex and larger molecular systems with 55 < Z < 95.

In table 2.6, both the parameters A and B have been tabulated for the DNA bases and it is seen that the value of B is nearly same for all the molecules and is ~ 0.5. Our calculations reveal that the Q_T depends on energy [42] and the dependence on incident energy is similar as that of Nishimura and Tawara [38] for 50-500 eV as,

$$Q_T = \frac{A}{\sqrt{E}} \tag{2.73}$$

However, the value of A is different for each molecule, suggesting its dependency on the number of target electrons (n_e).

Table 2.6 Parameters A and B for 50 - 500 eV

Targets	Adenine	Guanine	Thymine	Cytosine	Uracil
A	46.53	54.79	43.66	34.68	34.56
B	0.58	0.56	0.57	0.56	0.53

To observe this relation we plotted the graph of A vs n_e as shown in figure 2.3 and 2.4 for $50 < E_i < 500\ eV$ and $E_i > 500\ eV$ respectively. The linear relationship observed in figure 2.3 is represented through the following equation,

$A(n_e) = n_e - 23.54$ (Correlation r = 99%)

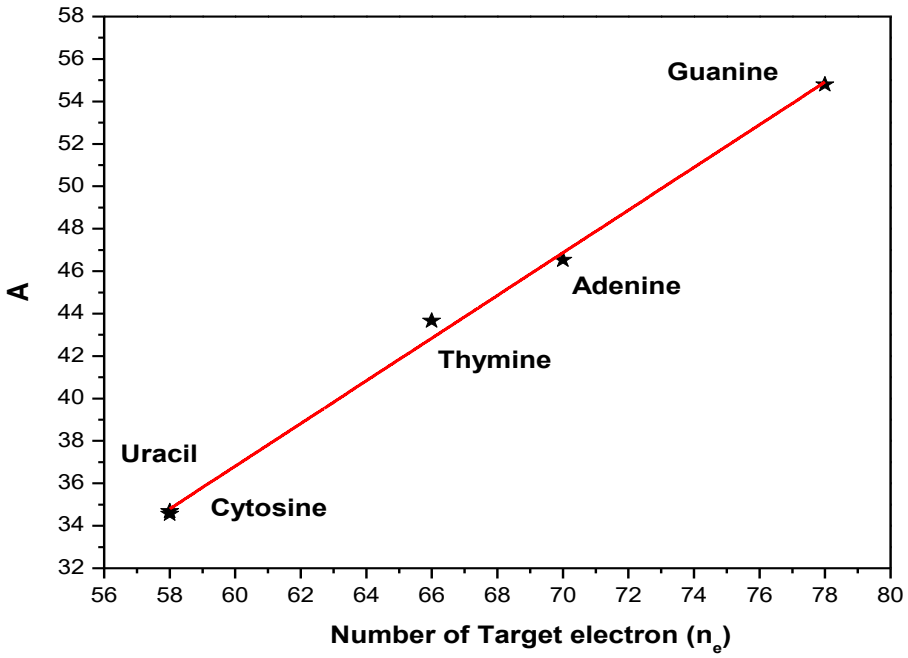

Figure 2.3 Parameter A vs n_e $50 < E_i < 500\ eV$

However, for a given n_e, the precision of this approximation can be enhanced by considering the difference between the actual values of 'A' (from table 2.6) and those derived from equation (2.73) for each molecule.

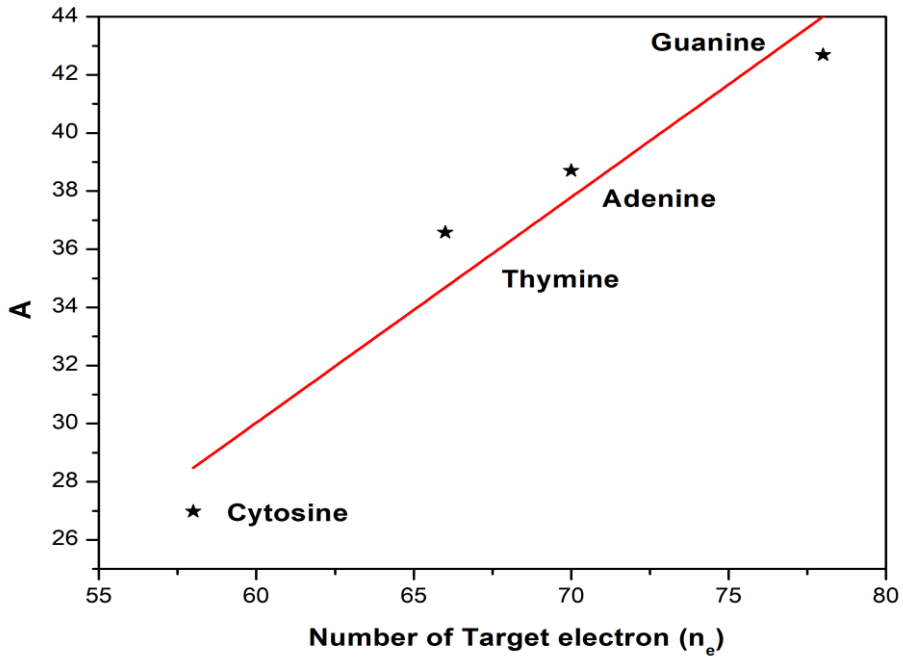

Figure 2.4 Parameter $A\ vs\ n_e$ ($E_i > 500\ eV$)

We have observed the dependency of this deviation (A - A(n_e)) on the molecular size through the polarizability (α). The linear relationship between them is,

$$A - A(n_e) = -0.003\alpha + 0.63 \tag{2.74}$$

Hence, from the equations (2.72), (2.73) and (2.74), a two-parameter expression for Q_T can be formulated for the energy range from 50-500 eV,

$$Q_T(n_e, \alpha) = \frac{n_e - 0.003\alpha - 22.91}{E^{0.56}} \tag{2.75}$$

Similar method has been followed to derive the two parameter expression of Q_T as a function of α and n_e for the energies above 500 eV.

$$Q_T(n_e, \alpha) = \frac{0.016\alpha + 0.776n_e - 17.88}{E^{0.77}} \tag{2.76}$$

We note the power of energy E is $E^{0.56}$ for lower side and $E^{0.77}$ for higher side of the incident energy.

The two equations (2.75) and (2.76) provide the two parameter expressions for Q_T for impact energy 50 eV < E_i < 500 eV and E_i >500 eV respectively allowing the estimation of Q_T for the entire energy range of current study.

2.7 Computation Of Dielectric Constant, ε

The dielectric constant for various molecules has many applications for the study of electrical energy storage, the structure of high-performance electrical insulation materials, the evolution of new electronic devices and other electrical properties.

The Clausius-Mossotti equation [43] yields,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} * N * \alpha \tag{2.77}$$

N is the number density of molecules in the material, and α is the molecular polarizability.

The number density can be calculated using the following equation [44]:

$$N = \frac{N_A * \rho}{M} \tag{2.78}$$

Where, ρ is the density of the substance, N_A is Avogadro number (6.022 x 10^{23}), N is the number density of target and M is the molar mass of the molecule.

$$Q_{ion(\mathrm{m})} = \frac{e}{4\varepsilon_o}\sqrt{\frac{\alpha}{\Delta}} \tag{2.79}$$

According to Harland's proposed qualitative dependency nature of the maximum ionization CSs, ($Q_{ion(m)}$) with its polarizability (α) [45],

The two expressions for dielectric constant (ε) have been derived in the present work using the dependency of the $Q_{ion(m)}$ on α and ε. The first proposed expression of dielectric constant as a function of $Q_{ion(m)}$, derived using the dependency of $Q_{ion(m)}$ with α (equation 2.79) and the Clausius-Mosotti (CM) equation,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \mathrm{C} \cdot (\mathrm{Q_{ion}(max)})^2 \mathrm{N}\Delta \tag{2.80}$$

Where, *C* is the constant = $\frac{64\pi}{3}\left(\frac{\varepsilon_o}{e}\right)^2$ and *N* is the number density of the molecule.

Secondly, the Onsager dielectric equation [46], which works well for the case of liquids is given by,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\alpha N + \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \tag{2.81}$$

This equation is thought to be more applicable in the present aqueous phase study, and again the equation of dielectric constant as a function of $Q_{ion(m)}$ is proposed as,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = C \cdot \left(Q_{ion(m)}\right)^2 N\Delta + \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \qquad (2.82)$$

Where, ε_∞ is the high frequency dielectric constant, which can be obtained from the CM equation.

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