Chapter 2

THEORETICAL PREREQUISITES AND FORMALISM USED FOR THE PRESENT STUDY

2.1 Introduction

This chapter builds the theoretical foundation of the thesis, which is devoted to the theoretical prerequisites, formalisms used for the scattering calculations for present study and other formalisms used by the theoreticians for electron scattering calculations. While considering electron collisions it is useful to divide the collision energies involved into three regimes. The easiest to treat theoretically is the high-energy region where the collisions are effectively impulsive and very simplified calculations based on perturbation theory or the impact approximations which neglect exchange interactions usually give reliable results [62]. Such approximations are not useful in the low-energy regime, the region below the ionization threshold of the target, and intermediate energy, which spans the target ionization threshold and the region directly above it. The physics involved with low-energy collisions is complicated with many subtle effects and many possible outcomes. It is perhaps not surprising that the prototypical processes such as elastic scattering, rotational excitations, vibrational excitations, dissociative attachment, electronic excitations etc. are mainly sensitive
to collisions in this energy regime. For the present study collision energy is divided into two parts in terms of formalism used for the calculations, low energy regime (0-20 eV) involving complex physics and intermediate to high energy regime (ionization threshold of the target to 5 keV) involving relatively simple Physics.

This chapter is a trio of segments namely theoretical prerequisites, R-matrix formalism [4,38] for low energy calculations and Spherical Optical Complex Potential (SCOP) formalism [39–41]. First section is attributed to the brief discussion of the prerequisites of the electron molecule scattering problem. The second of trio articulates the R - matrix formalism [4,38] used for the low energy calculation (0.01 eV - 20 eV) along with the calculation algorithm and modules used for the calculations. Detailed discussion of various scattering phenomena such as electronic excitation, resonances and Dissociative Electron Attachments (DEA) is also included in this part. Later and last segment of the chapter is dedicated to the Spherical Complex Optical Potential (SCOP) formalism [39–41] used for the high energy calculation (ionization threshold of the target to 5 keV) along with the molecular modeling prerequisites. Along with the theoretical foundations exact implementation of these theoretical approaches to the scattering problem using various numerical methods is also discussed briefly.

2.2 Prerequisites for scattering calculations

The equation of motion for the scattering process is the Schrödinger equation, but due to the size of the system involved often it cannot be solved analytically, even electron scattering by \( H_2 \) must be treated numerically. There are different models that may be used to solve the electron-molecule scattering problem as accurately as possible. In treating elastic scattering by electrons, we will discuss some of these models briefly [99].
2.2.1 Scattering Models

2.2.1.1 Static Model

This scattering model assumes incident electron beam to be a separate entity from the target electrons. Both exchange and polarization effects are neglected with an assumption that target charge remains unperturbed by approaching electron. Treating the problem at this level has the advantage that the equations are easily solved, but it has the disadvantage that the answers may be quantitatively and qualitatively incorrect, particularly at low collision energies.

2.2.1.2 Static Exchange (SE) model

In this model the target wave function is not allowed to relax, or polarize, in response to the incoming electron but, as the name implies, exchange between this electron and those of the target is explicitly included. The SE model cannot treat many physical processes such as, obviously, electron impact electronic excitation. It also cannot model Feshbach resonances since these also implicitly involve electronic excitation of the target. The SE approximation does give shape resonances, although these are usually too high in energy since their position is lowered by the inclusion of attractive target polarization effects.

The SE approximation must be regarded as fairly crude but it has a number of uses. At higher scattering energies, in particular at energies above the ionization threshold of the target, it avoids problems with pseudo-resonances which affect more sophisticated models. It can be used to identify shape resonances and, unlike most other models which are implementation dependent, it is a rigorously defined model which can be used to make cross comparisons between codes and methods.

2.2.1.3 Static Exchange plus Polarization (SEP) model

The logical advance on the SE approximation is to include target polarization effects giving the static exchange plus polarization (SEP) approximation. This can be done in number of ways, for example by use of an optical potential [42] or a local polarization potential [43, 44]. We discuss this model here in context of its implementation to the R-matrix method. In R matrix method it’s used via $L^2$ configuration to the
target wavefunction (Refer Section 2.3.3.2).

Under the framework of Hartree-Fock target wave function, this approach takes advantage of Brillouin’s theorem [45] which shows that configurations’ single excitations from a Hartree-Fock wave function do not interact with it. This means that it should be possible to include configurations involving single excitations of the target wave function without the risk of artificially improving the target. Polarization effects can therefore be included by promoting one electron from the target into a virtual orbital and also putting the scattering electron into a virtual orbital giving two particle, one hole or (2p, 1h), configurations.

The SEP approximation cannot explicitly describe electron impact electronic excitation but is now capable of resolving both shape and Feshbach resonances [46]. In this model Feshbach resonances arise from (2p, 1h) \( L^2 \) configurations (section 2.3.3.2) which correspond to target excitations. Besides these physical resonances, the SEP method is prone to display pseudo-resonances at higher energies. Furthermore models based on use of a Hartree-Fock target wave function suffer from the well-known problems with such wave functions at elongated bond lengths.

### 2.2.1.4 Close Coupling (CC) expansion

An obvious way to reduce problems with low-lying pseudo-resonances and at the same time to allow for electron impact electronic excitation is to include several target states in the wave function expansion. This approach is computationally more expensive than the SE and SEP approaches. However it has significant advantages over these methods; for instance Feshbach resonances are modelled in a straightforward fashion if the associated ”parent” state is included in the close-coupling expansion.

In this model the scattering wavefunction is expanded in terms of a complete set of unperturbed eigenstates of the isolated molecule \( \psi_i \) [47]:

\[
\Psi_\epsilon = \hat{A} \sum_i F_i(r_{N+1})\psi_i
\]  

(2.1)

where \( \hat{A} \) is the antisymmetrisation operator and \( r_{N+1} \) is the scattering electron position vector. Summation in Eq. 2.1 can include the continuum states of the molecule as well. The one-electron scattering function \( F_i(r_{N+1}) \) satisfies the set of coupled
equations

\[ [\nabla^2_{N+1} + k_n^2]F_i(r_{N+1}) = \sum_j [V_{ij} + W_{ij}]F_j(r_{N+1}) \tag{2.2} \]

where \( k_n \) is the channel linear momentum and \( \nabla^2_{N+1} \) is the Laplacian operator for the scattering electron. \( F_j(r_{N+1}) \) corresponds to a target state \( i \) that depends on the initial target state specified in the asymptotic boundary conditions

\[ \lim_{r \to \infty} \Psi_t \sim \Psi_{inc} + \Psi_{scat} \tag{2.3} \]

where for some initial target state \( \psi_0 \) and wave vector \( k_0 \)

\[ \Psi_{inc} = e^{i(k_0,r)}\psi \quad \text{and} \quad \Psi_{scat} = \frac{1}{r} \sum_j e^{ik_jr} f_{j0}(k_j, k_0)\psi_j \tag{2.4} \]

\( f_{j0}(k_j, k_0) \) is the scattering amplitude for a transition \( \theta \to j \). \( V_{ij} \) is the electron molecule scattering potential and \( W_{ij} \) is the exchange matrix. In this thesis, in outer region, the exchange is considered negligible so the antisymmetrisation operator \( \hat{A} \) is omitted and \( W_{ij} = 0 \).

\( F_i(r_{N+1}) \) may be expanded in terms of spherical harmonics \( Y_{lm}^m(\theta, \phi) \). Eq. 2.2 is then reduced to a set of coupled second order ordinary differential equations which has to be truncated in order to be solvable. The method is used in all the chapters presented here to account for electronic excitation channels, but it can also be used to account for the rotational and vibrational excitation channels.

In principle a CC expansion can give a complete treatment of the scattering process, and indeed this property has been exploited very successfully for atomic problems [48,49] for which it has been possible to derive complete basis sets. However, except in the special case of anions [50], there are always an infinite number of target states that should in principle be included in the CC expansion. This consideration limits standard CC treatments to energies below the target ionization threshold.

### 2.2.1.5 Dipole Born Approximation

In case of polar molecule potential contains the long-range potential leading to the singularity in the differential cross sections (DCS) in the forward direction and hence
at very low energy Total Cross Sections (TCS) diverges in the fixed nuclei approximation. Cross sections of dipole dominated processes converges slowly with the partial waves and hence number of partial waves required to converge the TCS is very high. Also to obtain the converged cross sections, the effect of rotation must be included with a large number of partial waves. Such system with requirement of higher partial wave is treated using the Dipole Born Approximation [51, 52]. Higher partial waves, those above a certain minimum \( l_0 \) say, are only weakly scattered and certainly can be treated using the Born approximation [51]. Those partial waves below \( l_0 \) can be treated using a scattering theory which models the short-range interactions more accurately. A Born correction accounting for the higher partial waves \((l > l_0)\) is calculated by computing first the Born cross section for all partial waves \((\sigma_B(E))\) and for the partial waves \(l \leq l_0\) \((\sigma_{B,l\leq l_0}(E))\).

\[
\delta \sigma(E) = \sigma_B(E) - \sigma_{B,l\leq l_0}(E)
\]  

(2.5)

Born corrections \((\delta \sigma(E))\) thus obtained is then added to the cross sections obtained for low partial waves \((l \leq l_0)\) obtained through the scattering theory (i.e. for short range interactions). In the present thesis scattering calculations are done using R-matrix theory in which short range interactions are taken care for the partial waves up to \(l=4\) (g waves) i.e. \(l_0 = 4\).

### 2.2.2 Hartree-Fock Approximation

The Hartree-Fock approximation is one of the simplest but powerful tool in quantum chemistry. It’s foundation stone for the accurate techniques to incorporate the electron electron correlations.

Hartree-fock theory is equated to single determinant theory [53] to obtain a set of spin-orbitals \(\chi_a\) such that the single determinant formed from these:

\[
|\Psi_0\rangle = |\chi_1\chi_2...\chi_a\chi_b...\chi_{N_e}\rangle
\]  

(2.6)
is the best possible representation for the ground state of an $N_e$-electron system described by a Hamiltonian, $H_{ele}$. By the variational principle, the best spin-orbital set is that which minimises the electronic energy functional,

$$E_0(\Psi_0) = \langle \Psi_0 | H_{elec} | \Psi_0 \rangle = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [\langle ii | jj \rangle - \langle ij | ji \rangle]$$

where

$$\langle ij | kl \rangle = \int d\tau_1 d\tau_2 \chi_i^*(x_1) \chi_j(x_1) r_{12}^{-1} \chi_k^*(x_2) \chi_l(x_2)$$

and the one-particle Hamiltonian is,

$$\hat{h}(1) = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}$$

with the constraint that the spin-orbitals be orthogonal:

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}$$

The spin-orbitals are then varied until $E_0$ is minimised. The equation for obtaining the best possible spin-orbitals set is the Hartree-Fock eigenvalue equation:

$$\left[ \hat{h}(1) + \sum_{b \neq a} \mathcal{J}_b(1) - \sum_{b \neq a} \mathcal{K}_b(1) \right] \chi_a(1) = \epsilon_a \chi_a(1)$$

and where the exchange and Coulomb operator are defined such that

$$\mathcal{K}_b(1) \chi_a(1) = \left[ \int d\tau_2 \chi_b(2)^* \frac{1}{r_{12}} \chi_a(2) \right] \chi_b(1)$$

$$\mathcal{J}_b(1) \chi_a(1) = \left[ \int d\tau_2 \chi_b(2)^* \frac{1}{r_{12}} \chi_b(2) \right] \chi_a(1)$$

respectively. From the restricted summation, the operator in the square brackets is different for every spin-orbital $\chi_a$. However, if one lets $b = a$ it is clear, from equations (2.12) and (2.13), that $[\mathcal{J}_b(1) - \mathcal{K}_b(1)] \chi_a(1) = 0$ and therefore it is quite possible to add this term to equation (2.11) with no major effect on the spin-orbitals. Now, we define a Fock operator $\hat{f}$,

$$\hat{f}(1) = \hat{1} + \sum_b \mathcal{J}_b(1) - \mathcal{K}_b(1)$$
The Hartree-Fock equation is simplified to

\[ \hat{f} |\chi_a\rangle = \epsilon_a \chi_a \]  

(2.15)

A full derivation of the Hartree-Fock (HF) equations is presented in the book by Szabo and Ostlund [53]. Normally, to solve these, basis functions are introduced in the expansion of the spin-orbitals and one then proceeds to solve a set of matrix equations.

### 2.2.2.1 Introduction of a Basis: The Roothan Equations

Spin orbitals can be represented in terms of Spatial and spin components as follow:

\[ \chi_i(X) = \begin{cases} \psi_i(r) |\alpha\rangle \\
\psi_i(r) |\beta\rangle \end{cases} \]

By eliminating spin, the calculation of the molecular orbitals is equivalent to solving the

\[ \hat{f}(r_i)\psi_i(r_i) = \epsilon_i \psi_i(r_i) \]  

(2.16)
eigenvalue equation [53]. By introducing a known spatial basis set [54] the equations (2.16) may be transformed to a set of algebraic equations which may be solved by techniques of linear algebra.

In solving for the spatial part of the spin-orbitals one expands the molecular orbitals as a linear combination of known (atomic) ones:

\[ \psi_i = \sum_{j=1}^{B} C_{ij} \phi_j \]  

(2.17)

If the basis set were complete then one would have the exact solution to the Fock eigenvalue equation, but this is not possible for computational reasons and one is restricted to a finite set with B basis function elements.

From equation 2.17 the problem of calculating the HF molecular orbitals reduces to the problem of solving for the expansion coefficients \( C_{ij} \). By substituting equation 2.17 into Eq. 2.16 one obtains the Roothan equations

\[ \text{FC} = \text{SC} \epsilon \]  

(2.18)
where $F$ is the Hermitian Fock matrix,

$$F_{ij} = H_{ij} + \sum_{a=1}^{N_e} \sum_{kl} C_{ka} C_{la}^* [2 \langle ij | kl \rangle - \langle ik | lj \rangle]$$

$$= H_{ij} + \sum_{kl} P_{kl} \left[ \langle ij | kl \rangle - \frac{1}{2} \langle ik | lj \rangle \right]$$

(2.19)

where $C$ is a $B \times B$ matrix of the expansion coefficients in equation 2.17 and $S$ is a Hermitian overlap matrix with elements,

$$S_{ij} = \int d\tau_1 \phi_i^* \phi_j$$

$$P_{ij} = 2 \sum_{a=1}^{N_e} C_{ia} C_{ja}$$

(2.20)

The matrix representations presented here are in the basis of atomic functions. The basis functions are not in general orthogonal so $S_{ij}$ will have small non-diagonal elements. But since it is Hermitian it is possible via a unitary transformation to obtain a diagonal representation of the same.

### 2.2.2.2 The Self-Consistent Field Optimization

Fig. 2.1 presents the steps to optimize the Self-Consistent Field (SCF). Step by step procedure to achieve the same is as follows:

1. specify a molecule (nuclear co-ordinates, proton numbers and electrons) and a basis set $\{ \phi_i \}_{i=1}^B$;

2. compute the required molecular integrals $S_{ij}$, $H_{ij}$ and $\langle ij | kl \rangle$;

3. diagonalise the overlap matrix and obtain the transition matrix $X$ such that

$$\varphi_i = \sum_j X_{ij} \phi_j$$

(2.21)

where $\{ \varphi_i \}_{i=1}^B$ is an orthonormal basis set;

4. obtain a guess for $P$, the matrix with elements as given in equation 2.20;
5. obtain the second summation term of equation 2.19 using the two-electron integrals and the P-matrix;

6. evaluate the Fock matrix;

7. calculate the transformed Fock matrix $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$;

8. diagonalise $\mathbf{F}'$ to obtain $\mathbf{C}'$ and $\epsilon$;

9. using the transition matrix $\mathbf{X}$ obtain $\mathbf{C}$;

10. using $\mathbf{C}$ calculate the new density matrix $\mathbf{P}$;

11. confirm whether the procedure has yielded convergence, namely, whether the new density matrix is the same as that in step 4 within a threshold. If not, then return to step 5 using the new density matrix;

12. if it has converged then this orbital set may be used elsewhere.
2.2.3 Basis sets

There are two types of orbitals namely Slater type of orbitals (STOs) [56] and Gaussian type of Orbitals [57] used for the representation of the basis sets \( \{ \phi_i \}_{i=1}^B \).

Slater type of Orbitals (GTO) [56] can be represented as,

\[
\phi_{n\ell m}^s = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} r_{\alpha}^{n-1} e^{-\zeta r_{\alpha}} Y_{\ell m}(\theta_{\alpha}, \phi_{\alpha})
\]  

(2.22)

with \( \zeta \) a constant and Gaussian-type orbitals (GTOs) [57] as

\[
\phi_{n\ell m}^g = N r_{\alpha}^{n-1} e^{-\zeta r_{\alpha}^2} Y_{\ell m}(\theta_{\alpha}, \phi_{\alpha})
\]  

(2.23)

where \( r_{\alpha} \) is the distance of the electron from a nuclear centre \( \alpha \), \( \zeta \) is again a constant and \( N \) is a normalisation constant.

Although with Slater-type orbitals one can obtain the best possible representation of the molecular orbitals \( \psi_i \) with the least number of expansion terms, Gaussian-type orbitals have the advantage that two-electron integrals can be evaluated very fast and very accurately. By using contracted Gaussian functions both these purposes can be achieved. A contraction has the form,

\[
\phi_{i}^{cg}(r_{\alpha}) = \sum_{p=1}^{L} d_{pi} g_p(\alpha_{pi}, r_p)
\]  

(2.24)

where \( \alpha_{pi} \) and \( d_{pi} \) are the contraction exponents and coefficients and \( L \) is the length of the contraction. Integrals involving such basis functions reduce to sums of integrals involving the primitive Gaussian functions \( g_p \). Although there may be many primitive integrals to be evaluated for each basis function, the basis function integrals will be rapidly calculated provided the method of computing primitive integrals is very fast [53]. A library of contracted GTO basis sets may be found in EMSL Gaussian Basis Set Order Form [58].

2.2.3 Configuration Interaction Method

Although Hartree-Fock (HF) method is a potent tool in Quantum Chemistry with a remarkable success, it has certain limitations. Dipole moment calculated using the HF
method often found to be inaccurate, internuclear distances go to infinity and results into very inaccurate dissociation energies. Beyond that HF approximation neglects the short-range correlation interaction with an assumption that each electron interacts with an averaged charge distribution due to the other electrons. These limitations are overcome by the Configuration Interaction (CI) method. CI method handles the electron-electron correlation with much more accuracy using the foundation laid by HF method. The underlying principle is to obtain a diagonalised representation of the \(N_e\) electron Hamiltonian operator in the basis of \(N_e\) - electron functions or Slater determinants. We wish to express the exact wavefunction as a linear combination of \(N_e\) - electron trial Slater determinants (more commonly referred to as configuration state functions or CSFs) by appealing to the principle of variation. Technically CI method can yield an exact solution to the \(N_e\) - electron problem but in practice one can only handle a finite set of \(N_e\) - electron trial functions so the method only provides upper bounds on the exact eigen energies. The determinant \(|\Psi_0\rangle\) of the \(N_e\) lowest energy spin orbitals can easily be formed, once the Hartree-Fock spin-orbitals are obtained using Self Consistent Field (SCF) optimization. In addition, a large number of other \(N_e\) - electron determinants may also be formed from all occupied as well as unoccupied orbitals. In describing these other \(N_e\) - electron determinants it is convenient to compare how they differ from \(|\Psi_0\rangle\), the reference determinant. Thus in addition to \(|\Psi_0\rangle\) we have singly excited determinants, \(|\Psi_a^r\rangle\), which differ by having spin orbital \(\chi_a\) being replaced by \(\chi_r\), doubly excited determinants \(|\Psi_{ab}^{rs}\rangle\) which differ from \(\Psi_0\) in that orbitals \(\chi_a\) and \(\chi_b\) are replaced by \(\chi_r\) and \(\chi_s\) etc., up to inclusion of n-tuply excited determinants. These determinants or CSFs may be used as a basis for the expansion of the exact wavefunction \(|\Phi_0\rangle\) expressed by Eq. 2.25 and similarly for electronically excited state wavefunctions.

\[
|\Phi_0\rangle = |\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \frac{1}{2!} \sum_{a<b,r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + ... \tag{2.25}
\]

\(c_a^r\) and \(C_{ab}^{rs}\) are variationally determined coefficients, and the summation pre-factor ensures that an excitation is counted only once. Hence Eq. 2.25 is the form of the full-CI (FCI) wavefunction, which provides the exact solution to the \(N_e\) - electron Hamiltonian eigenvalue problem. But the size of the Hamiltonian matrix expands with the number of determinants and the FCI method is only feasible for small molecules e.g.
\( H_2 \) and \( H_2^\dagger \).

By restricting the summation in Eq. 2.25 to include only singly and doubly excited CSFs, this elaborate method may be made feasible. Another possibility is to employ the complete active space CI (CAS-CI) method, used for the present low energy calculations throughout this thesis, where the spin-orbitals may be divided into a core, active and virtual orbitals space. The lowest energy core orbitals are fully occupied in all orbitals configurations, the highest-lying virtual orbitals remain unoccupied and the active orbitals vary in occupancy [59].

2.2.4 The Fixed-Nuclei Formulation

![Electronic coordinates in BODY frame](image)

**Figure 2.2:** Electronic coordinates in BODY frame

In fixed nuclei approximation as name suggest, nuclei of a molecule are assumed to be fixed in space i.e. Nuclear motions are assumed to be fixed (Nuclear motion relaxation). Then one need to deal with the eigenvalues and their eigenvectors correspond to the electronic Hamiltonian [47]. An appropriate co-ordinate frame may simplify the equations describing the collision process. Hence define two ref-
erence frames: the body (BODY) frame of reference (Fig. 2.2) and the laboratory (LAB) frame (Fig. 2.3) [47]. Here the BODY co-ordinate frame is defined such that the z-axis lies along the vector direction of the dipole moment while in the laboratory frame it lies along the momentum vector of the incident electron. In both the origin coincides with the centre of mass of the molecule.

Define \( \{ r_i \}_{i=1}^{N_e} \) and \( \{ R_A \}_{i=1}^{N_n} \) to be the position vectors of the electrons and nuclei of the molecule respectively and \( r_{N+1} \) the co-ordinates of the projectile electron in the BODY co-ordinate frame. The primed version of these are defined relative to the LAB frame. Hence the electron-molecule Hamiltonian operator is,

\[
\hat{H}_{N+1, \text{ele.}} = - \frac{1}{2} \nabla_i^2 N_{N+1} + \hat{H}_{N, \text{ele.}} + \hat{V}_{e-\text{mol}} \tag{2.26}
\]

where \( \nabla_i^2 N_{N+1} \) is the electron kinetic energy operator appropriate for the body frame, \( \hat{H}_{N, \text{ele.}} \) is the electronic target Hamiltonian and \( \hat{V}_{e-\text{mol}} \) is the electron-molecule interaction potential operator. For a molecule with \( N_e \) electrons and \( N_n \) electrons these may be written as,

\[
\hat{H}_{N, \text{ele.}} = - \sum_{j=1}^{N_e} \frac{1}{2} \nabla_j^2 - \sum_{i}^{N_e} \sum_{A=1}^{N_n} \frac{Z_A}{|r_i' - R_A|} + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{|r_i' - r_j'|} \tag{2.27}
\]

\[
\hat{V}_{e-\text{mol}} = - \sum_{A=1}^{N_n} \frac{Z_A}{|r_{N+1}' - R_A|} + \sum_{j=1}^{N_e} \frac{1}{|r_{N+1}' - r_j'|} \tag{2.28}
\]

The fixed-nuclei (FN) approximation is only valid when the collision time is very much shorter than the time of nuclear rotation or vibration and corresponds to a 'fast' collision. It is not however applicable to systems where scattering is dominated by a strong long-range interaction, such as electron scattering by a polar molecule, or when the incident electron energy is close to a narrow, long-lived resonance, where the collision time is long.

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The fixed-nuclei approximation may be combined with other methods to obtain reliable cross sections [47]. In the frame-transformation procedure [60,61] the FN approximation is only appropriate in the region close to the nuclei, where the BODY co-ordinate frame is used. Then, a boundary is chosen such that the nuclear Hamiltonian can be ignored, and where the exchange and electron-electron correlation interactions are dominant but can be ignored in the outer region. At this boundary the solutions are transformed to the LAB frame, the nuclear Hamiltonian is introduced and the new set of equations solved in the asymptotic region. The frame-transformation approach underlies the R-matrix method used here and which is described in the Section 2.3.

2.2.5 Adiabatic Nuclei Approximation

In some cases the inner region employed in the frame-transformation approach may be extended to infinity and the entire problem solved in this region. The actual frame transformation is carried out at the end of the calculation when the scattering quan-
tities (T-matrix etc.) have been computed. It is valid under the following conditions, i) the incident electron energy is away from threshold and ii) there are no resonances and absence of any significant long range interactions.

2.3 The ab-initio R-matrix method for low energy (0.01-20 eV) calculations

2.3.1 History and background of R-matrix formalism

The roots of the R-matrix theory are found to be in the work by Wigner [63–65] in the mid 40’s. R-matrix method is based on the division of space into an inner and outer region, and requires that the wave function of the target molecule is totally contained with this inner region. The formulation given by Wigner and Eisenbud [65] is particularly in general although, as noted in that work, it has similarities with work by Kapur and Peierls [66] done earlier in 1938. These studies were all aimed at addressing scattering problems in nuclear physics where the precise form of the short-range interaction between the particles involved was unknown.

2.3.2 Fundamentals of R-matrix theory

Figure 2.4: Division of the configuration space in Inner region building a r-matrix sphere with radius a contains the wave function of target molecule (AB) and outer region; c.m - centre of mass of molecule.
The R-matrix method is in widespread use in scattering theory. Prior to discussion of R-matrix methodology in details, let’s have a look at the basic principles of R-matrix method. Consider a radial scattering wave function, $F_i(r)$, where the subscript $i$ denotes the channel or the different, asymptotic quantum states of the colliding particles before and/or after the collision. In its simplest form the R-matrix links the radial wave function to its derivative. At some point, $r=a$, this can be written

$$F_i(a) = \sum_j R_{ij}(a, E) a \frac{dF_j}{dr} \bigg|_{r=a} \quad (2.29)$$

where the dependence of the R-matrix on both distance and energy has been made explicit. There is actually a degree of flexibility in the precise definition of the R-matrix which can be shown in matrix notation as,

$$F(a) = R(a, E) a \frac{dF}{dr} \bigg|_{r=a} \quad (2.30)$$

The R-matrix is actually used in two distinct but inter-related ways. For scattering problems, propagating the R-matrix itself is much more inherently stable than propagating either the wave function or its derivative [67]. This is because in numerical applications the functions themselves rapidly become contaminated by the exponential growth of noise from closed, that is energetically inaccessible, channels associated with the problem. The R-matrix element for such channels is simply a constant. This property has led to the widespread use of R-matrix propagation, and closely related procedures, for reactive scattering problems [68,69], but this not what is normally meant by R-matrix methods.

R-matrix methods count on the division of space into an inner and outer region (see Fig. 2.4). The inner region is defined as the volume of a sphere of radius 'a' centered at the center of mass (c.m) of the target molecule. This region is constructed so that the wave function of all but one of the particles is entirely contained within. This wave function is usually designated the target wave function and defined as containing $N$ electrons. Conversely only a single scattering particle can be found in the outer region. Here the Physics of the outer region is relatively simple as compared to the Physics involved in the inner region. Apparently, as all the $N+1$ electrons in the problem can exist in the inner region, the physics of this region is necessarily complicated. Implicitly this method assumes that the Pauli principle, which asserts that
all electrons are identical and many electron wave function must be anti-symmetric to interchange of these electrons, is only obeyed in the inner region. In the outer region it is assumed that one electron can be considered to be distinct. This electron therefore moves in a local potential arising from the long-range interaction between it and the target. In this procedure it is the R-matrix, whose expression in terms of inner region solutions is derived in the next section, which is used to provide the link between the inner and outer region. This R-matrix should be in a suitable form to propagate to larger distances is a convenient but not a necessary part of the method. The R-matrix method has a number of distinct advantages, i) Given basis sets that span the appropriate energy range, ii) the inner region problem needs to be solved only once and the energy dependence is obtained entirely from solution of the much simpler outer region problem. iii) The ability to generate solutions at a large number of energies at little extra computational cost.

### 2.3.3 Mathematical details of R-matrix method

#### 2.3.3.1 Equations and definition of the R-matrix method

First of all we will derive the R-matrix expression which links the inner region to the outer region:

For N+1 electrons (N target + 1 scattering electron) system Schrödinger equation under the framework of fixed nuclei approximation can be written as:

\[(H - E)w(E) = 0\] (2.31)

If one wants to consider this equation over a finite spherical volume which has a surface at \(r = a\) then one has to add an extra term, as derived by Bloch [70], to keep the operator Hermitian. The Bloch term, which is a one electron operator, takes the form:

\[L(b) = \sum_{i=1}^{N+1} \frac{\hbar^2}{2ma} \delta(r_i - a) \left( \frac{d}{dr_i} - \frac{b - 1}{r_i} \right)\] (2.32)

where \(m\) is the mass of an electron. Further atomic units are assumed and \(m\) and \(\hbar\) are set to unity and dropped from most equations. The constant \(b\) is arbitrary and
often taken as zero.

Including the Bloch term in the Schrödinger equation 2.31 yields,

\[(H + L - E)w = Lw\]  \hspace{1cm} (2.33)

which is the Schrödinger equation for the space contained within the sphere given by \(r \leq a\); and hereafter the operator \(H + L\) will be referred to as the inner region Hamiltonian. This equation has the formal solution,

\[w = (H + L - E)^{-1}Lw\]  \hspace{1cm} (2.34)

As Eq. 2.34 is for the finite region given by \(r \leq a\), it is only satisfied at discrete values of the energy, \(E\). Denoting the energy of each solution \(E_k\) and its associated wave function \(w_k\), these satisfy the equation,

\[\langle w_k | H + L | w_k' \rangle = \delta_{kk'}E_k\]  \hspace{1cm} (2.35)

where the integration implied by the Dirac brackets runs only over the finite volume defined by \(r \leq a\). The eigenfunctions of the inner region Hamiltonian \(w_k\), define a complete basis set inside the R-matrix sphere and the solution of the Schrödinger equation 2.31 can be expanded in this basis set:

\[w(E) = \sum_k A_k(E)w_k\]  \hspace{1cm} (2.36)

Using Eq. 2.35 in Eq. 2.34 we obtain,

\[w(E) = \sum_k \frac{|w_k\rangle \langle w_k | L | w\rangle}{(E_k - E)}\]  \hspace{1cm} (2.37)

where use has been made of the resolution of the identity given by \(\sum_k |w_k\rangle \langle w_k|\).

So, Eq. 2.37 can be re-written by explicitly substituting in for the Bloch operator using the definition 2.32 and projecting the inner region wave functions \(w_k\) onto the individual states of the target \((\Phi_i^N)\) as:

\[F_i(a) = \frac{1}{2} \sum_k \frac{w_{ik}(a)}{E_k - E} \sum_j w_{jk}(a) \left[ r \frac{dF_j}{dr} - bF_j \right]_{r=a}\]  \hspace{1cm} (2.38)

In Eq. 2.38, \(F_i(r)\) is the radial wave function in the outer region, i.e. \(r \geq a\), associated
with asymptotic channel ‘i’ and \( w_{ik}(a) \) are the amplitudes of the inner region functions at \( r = a \), known as the boundary amplitudes. Both \( F_i(r) \) and \( w_{ik}(a) \) will be discussed further. Eq. 2.38 can be re-written as,

\[
F_i(a) = \sum_j R_{ij}(a, E) \left[ r \frac{dF_j}{dr} - bF_j \right] \bigg|_{r=a}
\]

(2.39)

where

\[
R_{ij}(a, E) = \frac{1}{2} \sum_k \frac{w_{ik}(a) w_{jk}(a)}{E_k - E}
\]

(2.40)

Eq. 2.40 is the standard form of the R-matrix on the boundary. An alternative derivation of this expression, which avoids the need to explicitly define a 'Bloch term' is given by Burke et. al. [71]. It should be noted that the eigenenergies of the inner region problem \( E_k \), represent singularities in the R-matrix; for this reason these energies are usually referred to as R-matrix poles. It should be noted that condition 2.38 is valid regardless of \( w \) in the outer region. Finally, it should also be noted that the above derivation make no use of any boundary condition for \( r > a \). Eq. 2.40 serves as the inner boundary condition for the differential equations in the outer region and therefore can be used as the starting point to search bound states as well as to solve scattering problems.

The main task of the inner region calculation is to provide the necessary numerical values to construct the R-matrix of Eq. 2.40 on the boundary. The necessary information are the R-matrix pole positions, \( E_k \) and the associated surface amplitudes, \( w_{ik}(a) \), of the inner region wave functions as well as data on the target molecule itself. These parameters are all independent of the scattering energy which is why the inner region problem needs only be solved once for each total space-spin symmetry of the scattering problem.

### 2.3.3.2 R-matrix Inner Region

In the internal region the problem is very similar to a standard bound state calculation. The inner region wave function is constructed using the close-coupling approximation [72] (Refer Section 2.2.1.4). Within this framework the inner region
wave function is customarily expressed as,

$$\Psi_{N+1}^k = A \sum_i \Phi_i^N(x_1, ..., x_N) \sum_j \zeta_j(x_{N+1}) a_{ijk} + \sum_m \chi_m(x_1, ..., x_{N+1}) b_{mk} \quad (2.41)$$

where the target contains \( N \) electrons and functions are labelled as \( N \) or \( N+1 \) according to whether they refer to the target or the compound scattering system respectively. Eq. 2.41 contains most of the physics of the problem and considerable care is required in its construction. Each of the terms making up this equation is defined below.

In Eq. 2.41, \( \Phi_i^N \) is the wave function of \( i^{th} \) target state, \( \zeta_j \) are the extra orbitals introduced to represent the scattering electron while \( a_{ijk} \) and \( b_{mk} \) are the variational coefficients determined in the calculation. In first term for the continuum orbitals, \( \zeta_j \) sum also run over the target state index \( 'i' \) as it depends on the symmetry of the particular target state, since the two must couple together to give the correct overall spatial and spin symmetry of the total wave function \( \Psi_{N+1}^k \). Furthermore the electrons, whose space-spin coordinates are represent by \( x_i \), must obey the Pauli exclusion principle and are therefore anti-symmetrized by an operator \( A \). One must take care that while generating the configurations for first \( N \) electrons, target state must not be contaminated by the states with the same configuration but different space-spin symmetry. This can be achieved by imposing the special constraints over configuration generation.

The second summation in Eq. 2.41 runs over configurations \( \chi_m \), where all electrons are placed in target molecular orbitals. The number of these configurations varies considerably with the model employed. With the wave function given by Eq. 2.41, a static exchange calculation has a single Hartree-Fock target state in the first sum. The second term runs over the minimal number of configurations usually 3 or fewer. It involves configurations which have no amplitude on the R-matrix boundary (\( r=a \)) and where all electrons are placed in orbitals associated with the target. Since they are confined to a finite volume of space they will be referred to as \( L^2 \) configurations discussed further here. Such configurations, the choice of which is quite understated, are essential even in the simplest scattering model as they allow for relaxation of the orthogonalization between the continuum orbitals and those belonging to the target given that the continuum orbitals are forced to be orthogonal to the
target ones. In more sophisticated models, the $L^2$ configurations are also used to model the effects of target polarization. Thus, the present fully close-coupled system uses the lowest number of target states represented by a CI expansion in the first term and over a hundred configurations in the second. These configurations allow for both orthogonality relaxation and short-range polarization effects.

In order to match correctly with the asymptotic channels in the outer region, the continuum basis functions are written as a partial wave expansion using polar coordinates $(r, \theta, \phi)$:

$$
\psi_{ij}(r, \theta, \phi) = f_{ij}(r)Y_{l_i m_i}(\theta, \phi)\Xi_{1/2}^{1/2} (2.42)
$$

where the $(l_i, m_i)$ match with the asymptotic channel associated with the $i^{th}$ target state and these angular momentum quantum numbers. The function $\Xi_{1/2}$ is a one half electron spin function; since all calculations are non-relativistic the definition of this function can remain purely formal but it is necessary to ensure the correct spin coupling to the target state in expressions such as Eq. 2.41. Procedures, which largely concern orthogonalizing the continuum orbitals to the target orbitals, for turning continuum basis functions $\psi_{ij}$. The continuum basis set needs to be placed at the origin of the R-matrix sphere. It is usual for this origin to be the molecular center-of-mass although other choices are possible [73]. Although the center-of-charge and center-of-mass often coincide, there are situations when they do not which can introduce important physical effects.

A major reason for using the partial wave expansion for low-energy electron-molecule studies is its rapid convergence for most problems. This means that it is usually only necessary to consider a few partial waves in the expansion. For example all R-matrix calculations on electron collisions with polyatomic molecule have thus only considered up to g-waves, i.e. $1 \leq 4$, with little evidence for loss of accuracy. However, here is one case where such low-l expansions are insufficient and that is for collisions with species with a significant dipole moment. Methods which allow for the long-range, partial wave mixing effect of dipoles without the need to consider higher partial waves in the R-matrix inner region are well established [74,142] and will be discussed below in Section 2.3.4.
2.3.3.3 Boundary for the R-matrix configuration space

To construct the R-matrix on the boundary it is necessary to know the R-matrix pole positions, $E_k$, the boundary amplitude, $w_{ik}$, plus a Buttle or any other correction if needed. The pole positions come directly from diagonalizing the inner region Hamiltonian, but constructing the boundary amplitudes require some manipulation. The boundary amplitudes for channel $i$ are defined by the overlap integral,

$$w_{ik}(a) = \left\langle \Phi_N Y_{l_i m_i \Sigma_i} \left| \psi_{k}^{N+1} \right\rangle, \right.$$  \hspace{1cm} (2.43)

where $\psi_{k}^{N+1}$ is the wave function of the $k^{th}$ R-matrix pole, see Eq. 2.41 and $\Phi_N$ is the target wave function for channel $i$. The integral runs over all space-spin coordinate except the radial coordinate of the scattering electron, $r$; $\psi_{k}^{N+1}$ is evaluated at $r = a$. In practice this integral is not usually directly evaluated as the boundary amplitudes are computed from the continuum orbitals, $u_{ij}$ and the coefficients of the inner region wave function, $a_{ijk}$ see Eq. 2.41, using the expression

$$w_{ik}(a) = \sum_j u_{ij}(a) a_{ijk} \hspace{1cm} (2.44)$$

where $i$ labels asymptotic channels and $k$ numbers the inner regions solutions, $\psi_{k}^{N+1}$. So,

$$F_i(a) = \sum_k A_k(E) w_{ik}(a) \hspace{1cm} (2.45)$$

corresponds to the energy-dependent wave function of the projectile in the $i^{th}$ channel at the boundary.

The remaining information that is required to set-up the outer region problem concerns properties of the target. The target state energies relative to the ground state are needed as they give the energies of the asymptotic channels. The multipole moments associated with these target states are also required as they determine the outer region, long-range or asymptotic potential which is given by the multipole expansion:

$$V_{ij}(r) = \sum_{\lambda=0}^{\infty} \alpha_{ij}^{\lambda} r^{\lambda+1} \hspace{1cm} (2.46)$$

The asymptotic potential coefficients are defined as [76],

$$\alpha_{ij}^{\lambda} = \frac{2l_i + 1}{2l_j + 1} \frac{1}{2} C(l_i \lambda l_j; m_i m_j m_i) C(l_i \lambda l_j; 000) Q_{ij}^{(\lambda)} \hspace{1cm} (2.47)$$
where \( C(l_1 l_2 l_3; m_1 m_2 m_3) \) is a Clebsch-Gordan coefficient. \( Q^{\lambda}_{ij} \) is the target moment for which it usual to only consider dipoles, \( \lambda = 1 \) and quadrupoles, \( \lambda = 2 \) and, of course, for charged targets the Coulomb potential given by \( \lambda = 0 \). If \( i=j \), \( Q^{(\lambda)}_{ij} \) represents a permanent moment of the \( i^{th} \) target state, whereas if \( i \neq j \) it is a transition moment. These outer region potential coefficients provide the coupling between the channels in the outer region, (see Eq. 2.49).

2.3.3.4 R-matrix Outer Region

In the outer region the wave function can be written as [71]

\[
\psi^{N+1}(E) = \sum_{i=1}^{N} \Phi_i^N(x_1...x_N)F_i(r_{N+1}Y_{l_i,m_i}(\theta, \phi)\Xi_{l_i}^{\frac{1}{2}})
\]  

(2.48)

where the sum runs over the n-channels of the problem. For molecular problems, there are usually several channels associated with each target state, which means that even a one-state problem normally involves solving a multichannel outer region problem. Substituting the wave function of Eq. 2.48 into the Schrödinger equation of the problem and projecting on the target state wave functions yields the following system of n-coupled differential equations for the radial functions, \( F_i(r) \) [71]:

\[
\left[-\frac{d^2}{dr^2} + \frac{l_i(l_i + 1)}{r^2} - k_i^2\right]F_i(r) = 2\sum_{j=1}^{n} V_{ij}(r)F_j(r),
\]  

(2.49)

where \( V_{ij} \) represents the long-range potential constructed from the target properties and given by Eq. 2.47. In principle, the outer region consists of setting up and solving this set of differential equations. Having obtained the R-matrix on the boundary in the form of Eq. 2.40, the problem is how to obtain the final, energy dependent solutions to the scattering problem. The standard procedure for tackling the outer region problem uses two stages. First the R-matrix is propagated from the boundary given by \( r = a \) to some large \( r = r_f \) [77,78], where \( r_f \) is chosen such that the non-Coulombic potential can be neglected for asymptotic region defined by \( r > r_f \). To obtain the asymptotic solutions, Gailitis method of asymptotic expansion is the most commonly used procedure [79,80]. It should be noted that while the Gailitis procedure
gives the outer region wave function at \( r_f \), the use of R-matrix propagation avoids specifying this wave function in the region, \( a < r < r_f \).

In solving the outer region problem, asymptotic channel \( 'i' \) is defined by a state of the separated target molecule and a partial wave of the scattering electron, \((l_i, m_i)\).

If the target state associated with channel \( 'i' \) has energy \( E_i^N \), then the wavenumber of the scattering electron associated with this channel is given by,

\[
k_i^2 = 2(E - E_i^N)
\]

where \( E \) is the energy of the scattered electron and the energy of the lowest target state is taken to be zero by convention. A channel is said to be open if \( k_i^2 < 0 \) since it can be reached asymptotically and closed if \( k_i^2 \geq 0 \). For a standard scattering problem and energy normalization of the wave function, the outer region solutions go asymptotically, as denoted by the symbol \( \sim \), to

\[
F_{ij} \sim \frac{1}{\sqrt{k_i}}(\sin \theta_i \delta_{ij} + \cos \theta_i K_{ij})
\]

for open channels and \( F_{ij} \sim 0 \) for closed channels, ones for which \( E_i < 0 \).

For neutral targets the channel angle \( \theta_i \) is given by,

\[
\theta_i = k_i r - \frac{1}{2} l_i \pi
\]

while for collisions with a target of net charge \( Z - N \), it has the more complicated form

\[
\theta_i = k_i r - \frac{1}{2} l_i \pi - \eta_i \ln(2k_i r) + \sigma_i
\]

with \( \eta_i = \frac{Z - N}{k_i} \) and \( \sigma_i = \arg \Gamma(l_i + 1 + i\eta_i) \) where \( \sigma_i \) is sometimes referred to as the Coulomb phase.

The critical parameter in Eq. 25 is the \( K \)-matrix. \( K \)-matrix is a symmetric matrix whose dimension is the number of open channels. All the scattering observables can be obtained by starting from the \( K \)-matrix. The parameters of our interest for the scattering problem are \( S \)-matrix and the eigenphase sum. Where \( S \)-matrix is defined by,

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

The eigenphase sum, \( \delta \) is obtained from the sum of the eigenvalues of the \( K \)-matrix, \( K_{ii}^D \), as:

\[
\delta(E) = \sum_i \arctan(K_{ii}^D)
\]
Eigenphase sum provides with the useful resonance information. Resonance appears as a discontinuities in the eigenphases [91].

2.3.3.5 Resonance in low energy electron scattering by molecules

"The temporary trapping of an electron to form a quasibound or short-lived state is known as a resonance."

The formation and behaviour of resonances is the key to many processes in electron-molecule scattering. Resonances are generally characterized qualitatively by type and configuration, and quantitatively by their symmetry, position, $E^r$, and width, $\Gamma$, the latter of which arises from the Heisenberg Uncertainty Principle. Obtaining these parameters is a major objective of many calculations. Some processes such as dissociative attachment [81] and dissociative recombination [82,83] are thought to be entirely driven by resonances, although in practice there are occasional exceptions [84,193]. Other processes, notably electron impact vibrational excitation [81], can have their cross section hugely enhanced by the presence of resonances. Indeed cross sections for all processes can show features, usually enhancements, due to resonances. In their most basic form they appear as 'bumps' in the cross sections.

For a resonance to occur there must be some mechanism for binding the electrons temporarily to the target. Thus we can classify resonances according to the means by which the projectile is trapped. Primarily resonances can be classified in two types 1) Shape resonances 2) Feshbach resonances.

2.3.3.5.1 Shape resonances:

The simplest trapping mechanism is a potential barrier. Let us suppose that the incident particle experiences a region of attractive potential surrounded by a region of repulsive potential. If the particle enters the region of attractive potential its escape will be hindered by the potential barrier surrounding it. Resonances which are supported by potential barriers will be called shape resonances. The best-known
examples are the radioactive nuclei which decay by the emission of an α particle which has tunneled through the Coulomb barrier.

2.3.3.5.2 Core-excited shape resonances

In core excited shape resonances, the incident electron excites a target state whose energy is less than the resonant energy. The extra electron has sufficient energy to escape from the target leaving it in its excited state. If the potential experienced by the electron as it is moving in the field of the excited target contains a barrier then its escape will be hindered and the electron will become temporarily bound to the target. Shape resonances are often broad but there are narrow ones too [85].

2.3.3.5.3 Electron-excited Feshbach resonances

Feshbach resonances occur when the incident electron loses energy in exciting the target and finds itself with insufficient energy to escape while the target remains in its excited state. Before the electron can be emitted it must reabsorb energy from the target. The simplest situation would be that the incident electron excites only a single electronic target state for which the vibrational levels lie above the resonant energy. Feshbach resonances are nearly always narrow although for large nuclear separations some become broad.

2.3.3.5.4 Nuclear-excited Feshbach resonances

These are Feshbach resonances in which the kinetic energy of the incident electron is absorbed solely into the nuclear motion of the target. The collision does not involve excitation of the electronic motion in the target. Shape resonances and Feshbach resonances can be discussed within the Born-Oppenheimer separation of nuclear and electronic motion. In this third type the resonances are formed by an interchange of energy between these two modes, and thus the existence of the resonance is a consequence of the breakdown of the Born-Oppenheimer approximation. Thus inclusion of the nuclear motion is essential to the definition of these resonances. If the nuclei were kept fixed the resonances would become stable against electron emission.
2.3.3.5.5 Characterizing resonances

Despite the fact that resonances can be predicted by fitting to scattering cross sections, it’s not a good method for the prediction of the resonance parameter. However, there are quite a few other methods available for obtaining these parameters. These methods can be divided in two classes: those which can be used as part of any electron-molecule scattering procedure, and those which take specific advantage of the structure of the \( R \)-matrix [86–89]. It’s to be noticed that R-matrix methods, can be important for characterizing complicated resonance structures as it does owe an ability to repeat the collision calculation on a fine energy grid at little extra computational cost. This is particularly true for electron collisions with positively charged ions which have infinite series of resonances. One formal definition of a resonance is that it constitutes a pole in the \( S \)-matrix in the complex plane with the real part of the energy representing the resonance energy, \( E_r \) and the imaginary part its half-width, \( \frac{1}{2} \Gamma \). Resonances also manifest themselves as an increase in the value of the eigenphase sum (see Eq. 2.55 ) by \( \pi \). In practice eigenphases are arbitrary modulo \( \pi \) so resonances often actually appear as discontinuities in plots of the eigenphases sums.

The standard method for characterizing an isolated resonance is to represent the eigenphase sum in the region of the resonance using the Breit-Wigner form [90],

\[
\delta(E) = \delta_0(E) + \sum_{i=1}^{m} \tan^{-1} \frac{\Gamma_i}{2(E^r_i - E)}
\]  

(2.56)

Eq. 2.56 is written for ‘m’ resonances. Generally direct fits to the Breit-Wigner form are generally not reliable for ‘m’ greater than one, although several of the other procedures discussed below work well for the many resonance case. Tennyson and Noble implemented a recursive procedure for detecting and performing Breit-Wigner fits to resonances in program RESON [91] which relies of the ability to quickly generate new energy points. This procedure scans \( \delta(E) \) and marks those points where the numerically computed second derivative \( \frac{d^2E}{dE^2} \) changes signs from positive to negative. A new, usually finer, grid is constructed about each of these points which is then used as the input to a Breit-Wigner fit. In principle the method can fit pairs of nearby resonances but such fits are generally found to be less satisfactory. Because the slope
of the eigenphase can be discontinuous upon the opening of a new threshold, the procedure is restricted to scanning energy grids between thresholds.

### 2.3.4 Scattering from polar molecule

Scattering from a target molecule with a permanent dipole moment requires special treatment. This is because the dipole potential leads to strong coupling between channels which differ by one in \( l \) and the long-range nature of the dipole potential means that the partial wave expansion, Eq. 2.42, requires many more terms as it is necessary to extend the continuum basis to high \( l \). It should be noted that it is possible to match asymptotically to dipole functions specifically adapted to the dipole moment of the potential under consideration [92]. These functions are obtained by solving a Schrödinger equation which includes the dipole interaction term which therefore introduces couplings between channels with \( l \) and \( l \pm 1 \). The resulting functions have to be represented by a numerically determined linear combination of spherical harmonics. For strongly polar molecule to include higher partial waves where rotational motion is neglected, leads to an overestimation of cross section. This happens because rotational motion deteriorates the effect of asymptotic motion. Hence negation of rotational motion leads to unphysical cross sections which diverge at low energy. In practice instead of explicitly including large numbers partial waves in the expansion, procedures have been developed based on the use of a frame transformation [47] and the adiabatic nuclear rotation (ANR) approximation to account for the rotational motion, and the dipole Born approximation to account for the contribution from high partial waves [47,93,141,142].

The standard procedure for implementing this correction [94] is to perform a detailed, R-matrix or similar, calculations for the lowest few symmetries, add this to the dipole Born approximation results for the problem and then subtract the partial dipole Born results for the symmetries included in the original calculations (See Section 2.2.1.5). Studies have shown that this procedure is not necessary for rotational transitions with \( \Delta J \geq 2 \) as these are entirely determined by short-range interactions and can be satisfactorily converged by the original scattering calculations [95,96].
One aspect of the ANR approximation is that it assumes all channels are degenerate. This is clearly not a good approximation at collision energies close to the excitation threshold and can result in the unphysical excitation of closed rotational channels. One approach is to correct for this using simple kinematic scaling [97]; however a recent study showed that simply cutting the rates at the appropriate threshold gives surprisingly good agreement when compared with a full, energy-resolved treatment [98]. This is now the recommended procedure.

2.3.5 UK Molecular R-matrix Codes

In present section UK molecular R-matrix codes’ modules used for the present calculations are discussed briefly.

2.3.5.1 Inner region and target wave functions

Inner region R-matrix problem is treated numerically using the Quantum chemistry model which includes the generation of target wave function, target properties and electronic structure calculations. The UK polyatomic R-matrix code is built about the Sweden Molecule quantum chemistry package of Almlöf and Taylor [150,151]. Fig. 2.5 shows the steps that are taken to generate target wave functions and associated properties as a prelude to a full scattering run [99]. The first three modules, SWMOL3, SWORD and SWFJK perform the necessary integral evaluation, ordering and Fock-matrix building steps prior to the actual SCF calculation in SWSCF.

- **SWMOL3**: generates one and two-electron integrals from the given GTO basis set.
- **SWORD**: orders the atomic integrals evaluated by SWMOL3.
- **SWFJK**: forms combinations of Coulomb and exchange integrals for the Fock matrix.
Figure 2.5: R-matrix inner region flow chart for the target calculation

Figure 2.6: Flow chart of the inner region calculation. Inputs are target orbitals and CI vectors; outputs are the boundary amplitudes, the R-matrix poles and associated eigenvectors.

- **SWSCF**: performs the Hartree-Fock self consistent field (HF-SCF) optimisation to generate the target molecular orbitals from linear combinations of atomic ones. Here it employs the integrals obtained from the **SWFJK** code.
• **SWEDMOS**: constructs molecular orbitals and boundary amplitudes for the continuum and Gaussian-type orbital (GTO) target wave function. It applies Schmidt orthogonalisation to orthogonalise each continuum orbital to all the target ones and symmetric orthogonalisation to orthogonalise the continuum orbitals among themselves. A threshold (typically of order $10^{-7}$) is employed for orbital deletion. Those continuum orbitals with overlap matrix eigenvalues less than this threshold are deleted.

• **SWTRMO**: carries out the four-index transformation from atomic orbital to molecular orbital representation of the ordered integrals obtained from **SWMOL3**.

• **CONGEN**: generates the necessary configuration state functions with appropriate spin and symmetry couplings for performing a configuration interaction (CI) calculation. It generates prototype CSFs for the target molecule and for the $(N+1)$-electron system. **CONGEN** also solves phase factor problems that arise from the use of CI expansions [100].

• **SCATCI**: performs a CI calculation of the target molecular and the $(N+1)$-complex wavefunctions [101]. It employs the CSFs generated earlier by the **CONGEN** module. The Hamiltonian is diagonalised to obtain the CI expansion coefficients (eigenkets) and the corresponding eigenvalues. In the case of the $(N+1)$-complex these are the R-matrix poles of equation 2.40.

• **GAUSPROP**: generates the property integrals required by **DENPROP**.

• **DENPROP**: constructs the transition density matrix from the target eigenvectors obtained from the CI calculation. From this it then calculates the multipole transition moments required for solving the outer region coupled equations, the dipole spherical polarisability $\alpha_0$, and where possible the diagonalised tensor components $\alpha_{xx}$, $\alpha_{yy}$ and $\alpha_{zz}$. These are computed using second-order perturbation theory and the property integrals evaluated by **GAUSPROP**. Only multipole moments up to and including $l = 2$ are computed, and together with the target Hamiltonian eigenvalues (figure 2.5), they are saved to unit 24 (fort.24) for later use in **SWINTERF** (figure 3.4).
• **GAUSTAIL**: evaluates the contribution to each integral from outside the R-matrix sphere and adds matrix elements of the Bloch operator to the Hamiltonian ones [102].

As shown in Fig. 2.6, number of modules used in calculating the target wave functions are also used for the inner region calculations but with some subtle differences. Thus the integrals over atomic orbitals are again computed by SWMOL3 but those which are marked as involving a continuum orbital are adjusted for the finite dimension of the R-matrix sphere using GAUSTAIL [102].

### 2.3.5.2 Outer Region calculation modules

Unlike the inner regions codes the outer region is run as a single program with a driver routine which specifies which modules are needed for a particular run. Fig. 2.7 shows the main but by no means all the modules available in this code; other modules available include **POLYDCS** [103] or **DCS** [104] for calculating differential cross sections, **MCQD** for calculating multichannel quantum defects from the above threshold S-matrix [105], **ROTIONS** [95] for calculating rotational excitation of ions, **BORNCROS** for adding a dipole Born correction to both elastic and inelastic cross sections [106] and others.

• **SWINTERF**: interfaces the internal and outer regions. It requires the boundary amplitudes from **SWEDMOS**, the N +1 - system eigenvectors and their corresponding eigenvalues and the molecule’s multipole moments (figure 2.7). Its output provides for the target properties and other data necessary to rapidly construct the R-matrix initially at the interaction radius as a function of energy.

• **RSOLVE**: constructs the R-matrix at the interaction radius and uses **RPROP** [78] to propagate this R-matrix to the asymptotic region for matching to the boundary condition there by solving the coupled ordinary differential equations in an outer region which is divided into sectors. It then constructs the fixed-nuclei K-matrices using **CFASYM** [80]. The output of [306] **SWINTERF** is
Figure 2.7: The main modules used in the outer region of the polyatomic UK Molecular R-matrix codes [227] showing inputs and possible outputs.

- **EIGENP**: calculates the multichannel eigenphase sum in the manner discussed earlier, namely, by diagonalising the $K$-matrix and summing over channels (Eq. 2.55)

$$T = \frac{2iK}{1 - iK}$$

- **TMATRIX**: calculates the T-matrix from the K-matrix using Eq. 2.57. It uses the channel data in unit LUCHAN ('fort.10') and K-matrices in unit LUKMT ('fort.19');

- **IXSEC**: computes the integral cross sections from the T-matrices (unit LUTMT or ‘fort.10’);

- **RESON**: detects resonances and performs a least square fit of the eigenphase sums to a Breit-Wigner profile [91];
• **TMATSUB**: transforms the \( C_2v \) T-matrices to \( C_\infty v \) ones using the algorithm in table 3.1. The \( ^2A_1 \) T - matrix is used to obtain the \( ^2\Sigma^+ \), \( ^2\Delta \) and \( ^2\Gamma \) matrices, while the \( ^2B_1 \) T - matrix yields the \( ^2\Pi \) and \( ^2\Phi \) ones. This module is intended to be run independently of the outer region suite of codes;

• **ROTLIN**: using the ANR approximation it computes, from the \( C_\infty v \) T-matrices, the rotationally resolved integral cross sections. It computes and includes the Born correction for \(|\Delta J| = 1\). It was adapted from the existing **ROTIONS** code [95], which computes the same for cations, and invokes the Coulomb-Born approximation. Like **TMATSUB**, this module is also intended to be run independently of the outer region codes;

• **DCS**: an implementation of the Born completion formalism of Itikawa [107], this suite of codes is designed to treat linear molecules. It calculates the differential cross sections (DCSs) using fixed-nuclei \( C_\infty v \) T - matrices (calculated by **TMATSUB** for example). Additional information required includes the dipole and quadrupole moment, the rotational constant, spherical and non-spherical polarizabilities, the angular grid, \( J \) - transition and incident electron energy. This suite is entirely independent of the R-matrix codes.

• **POLYDCS**: the suite calculates the rotationally elastic and inelastic DCSs for electron (and positron) scattering by neutral polyatomic molecules of various symmetries (including \( C_{2v}, C_{3v}, T_d \) and \( C_\infty v \)) be they polar, weakly polar or non-polar. **POLYDCS** takes a number of inputs including the K-matrices, polarisabilities, dipole and quadrupole moments, incident electron energies and the desired rotational transition. This module is also independent of the R-matrix codes.

### 2.4 Spherical Complex Optical Potential (SCOP) formalism for high energy calculations

Present section is attributed to the Spherical Complex Optical Potential (SCOP) formalism used for the high energy calculations. In this section Potential used for the
electron scattering problem and their numerical counterparts are discussed briefly. In the framework of electron atom/molecular scattering problem SCOP formalism is used to obtain the Spherical Optical Potential which is further used to solve the Schrödinger equation numerically to generate the complex phase shifts using the method of ‘Partial Wave Analysis (PWA)’. Further complex phase shifts are used to obtain the various cross sections using the standard relations. Here I am avoiding discussion of the topics such as Potential scattering, Optical theorem, Partial Wave Analysis, Numerov method etc. as it’s widely discussed in our earlier publications [37,108]. Here we discuss the Complex Optical Potential used for the e - molecule scattering along with the scattering in the presence of Absorption. At the end we discuss about the derivation of various cross sections by means of analytical formulas using the complex phase shifts

2.4.1 Complex Optical Potential (COP)

To solve the Schrödinger equation, we require the total (complex optical) potential (COP) of the system. COP comprise of all the major physical effects involved in the e - molecule scattering process. COP can be expressed as,

\[ V_{opt} = V_R + iV_I \]  \hspace{1cm} (2.58)

The real part \( V_R \) of the complex potential \( V_{opt} \) is the sum of static \( V_{st} \), exchange \( V_{exc} \) and polarization \( V_{pol} \) potentials and the imaginary part \( V_I \) corresponds to the absorption potential, \( V_{abs} \). The interaction between electrons and the target is determined by these potentials. So we discuss these potentials in detail below.

The analogy "Optical Potential" comes from the field of optics, particularly from the application of optical model in the analysis of the propagation of light through a refractive medium. The complex optical potential introduced in our theory is equivalent to the complex refractive index in optics. We discuss the concept of these potentials and the method of formulation, in detail in the next section.
2.4.1.1 Target charge density and static potential

The static potential $V_{st}$ is the basic electrostatic and coulomb potential experienced by the projectile electron upon approaching a field of an unperturbed target charge cloud. The $V_{st}(r)$ at a distance $r$ is given through the Poisson’s equation by,

$$ V_{st}(r) = -\frac{Z}{r} + 4\pi \left[ \frac{1}{r} \int_{0}^{r} \rho(r') r'^2 dr' + \int_{r}^{\infty} \rho(r') r' dr' \right] $$

(2.59)

where $\rho(r')$ is the charge density which may be calculated from Roothan - Hartree Fock wave functions in terms of the Slater Type Orbitals (STOs) as given by Clementi & Roetti [109] and by Bunge et. al. [110].

In the work of Cox and Bonham [111], a fitting procedure was done by the least square method for the radial electron density function $D(r)$. The static potential of the target atoms was represented by an analytical expression (Eq. 2.60 ) involving a sum of Yukawa terms by starting with Hartree-Fock and the relativistic wave functions for all the neutral atoms.

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

(2.60)

where $\gamma_i$ and $\lambda_i$ are the potential field parameters. The analytical expression for the charge density is,

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

(2.61)

In the present work, the charge densities and electrostatic potentials are obtained using Cox and Bonham parameters [111] with the aid of Eq. 2.60 and Eq. 2.61. For molecular case Single Centre (SC) approach is incorporated to use the Cox & Bonham atomic parameters for the molecular potential and molecular charge density. Here basic idea of SC approximation is that whole molecule can be treated as a sphere (Of course not a perfect sphere in most of the cases but near to sphere with some approximations) in order to solve the Schrödinger equation numerically with spherical polar coordinate system. Most logical way of SC approximation is to expand the charge density of constituting atoms to the centre of charge of the molecule in order to obtain the spherical molecular charge density.
2.4.1.2 Exchange Potential

Effect arose due to the exchange of projectile electron with the target electron is taken care by the exchange potential. Hara [112] adopted the 'free electron gas exchange model' for exchange effect. He considered the electron gas as a Fermi gas of non-interacting electrons when the total wave function is anti-symmetrized in accordance with Pauli’s exclusion principle. It’s approximate but provides an effective exchange potential. The exchange energy is calculated by summing all momentum states up to Fermi level $E_F$. The problem is to compute the exchange correlation in the free-electron gas. In the treatment suggested by Slater [56] the local equation is obtained for the average potential energy term introduced by the exchange effect or the Pauli exclusion principle. This Hartree exchange potential can be expressed as,

$$V_{ex}(r, k) = -\frac{2}{\pi} k_F F(\eta)$$  \hspace{1cm} (2.62)

where the fermi wave vector

$$k_F = [3\pi^2 \rho(r)]^{\frac{1}{3}}$$  \hspace{1cm} (2.63)

The function $F(\eta)$ is given by

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right|$$  \hspace{1cm} (2.64)

where, $\eta = \frac{K(r)}{k_F}$ and K(r) is wave vector of the electron. Hara [112] adopted this model for the exchange of the scattering electron with one of the target electrons. The target electron being bound has a negative energy and the minimum energy required to make it zero is the ionisation potential energy. On the other hand, the scattering electron has positive energy $\frac{1}{2k^2}$ (a.u.). So as per Hara’s [112] model,

$$K^2(r) = k^2 + k_F^2 + 2I$$  \hspace{1cm} (2.65)

where I is the atomic ionisation potential energy in a.u. With this, the exchange potential given by Hara (1967) is same as in Eq. 2.62. This approximation is usually referred to as 'Hara Free Electron Gas Exchange' (HFEGE) model [112]. The target electron being bound has a negative energy and the minimum energy required to
make it zero is the ionization energy, which is denoted as I (in Hartree). Here the approximation of Eq. 2.65 implies that the electron kinetic energy is given by $E_i + I$ in the asymptotic region. This may not be a serious inconsistency since the correct exchange potential is very small at large r, but an obvious way to correct Eq. 2.65 for large - r behavior is to remove the ionization energy from it. This has led to the introduction of the ‘Asymptotically Adjusted Hara Free Electron Gas Exchange’ model (AAHFEGE) [113,114], which turned Eq. 2.65 to be:

$$K^2(r) = k^2 + k_f^2$$  \hspace{1cm} \text{(2.66)}

It’s well studied now that discrepancies observed between all the models is very marginal with no significant difference in exchange potential and consequently in scattering cross sections obtained from them. In the present case we have used the Hara’s HFEGE model [112].

2.4.1.3 Polarization potential

When the electron approaches the target atom or molecule, the electron cloud of target is distorted momentarily. Consequently there is a slight displacement of the electron cloud from the original unperturbed state. This distortion is due to induced multipole moments and is attractive in nature. It gives rise to polarisation potential. This polarisation effect can be treated by perturbation methods. The adiabatic asymptotic polarisation potential which can be expressed as [115,116]:

$$V_{pol} = -\frac{\alpha_d}{2r^4} - \frac{\alpha_q}{2r^6}$$  \hspace{1cm} \text{(2.67)}

where $\alpha_d$ and $\alpha_q$ are dipole and quadrupole static polarisabilities of the target atom. This potential varies asymptotically as $r^{-4}$ at $r \to \infty$ and is of long range. At $r = 0$ there is a singularity. In order to avoid this, a cut off parameter $'r'_c$ is introduced in the first term of Eq. 2.67 as expressed below:

$$V_{pol} = -\frac{\alpha_d}{2(r^2 + r'_c)^2}$$  \hspace{1cm} \text{(2.68)}

Eq. 2.68 is referred as Buckingham polarisation potential [5,117]. The above potential is not only asymptotic but also adiabatic suggesting that the external electron is
stationary. In reality, the external projectile electron moves past the target atom, so that the response of the atomic charge cloud (charge redistribution) depends also on the speed of the incident electron. Thus unless the incident electron is very slow, the polarisation effect is dynamic or energy dependent. Hence Khare and co-workers [118] proposed,

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

(2.69)

where \( r_c \) is the energy dependent cut off parameter. Using the Born-approximation we find that,

\[
r_c = \frac{3k}{8\Delta}
\]

(2.70)

where \( \Delta \) represents the average excitation energy of the atom.

The energy dependent cut-off parameter \( r_c \) (Eq. 2.70) is obtained through the Born approximation, hence this polarisation potential Eq. 2.69 fails at low energy, say below 50 eV [118]. Further, this potential does not provide a clear estimate of a cut-off distance for the long-range effects. On the other hand, the exact form of the short range part of the charge-cloud distortion is not known. The polarization potential mentioned above is a long range potential. The simple \( r^{-4} \) behavior does not hold at short distances. Therefore we have to consider the electron correlation effects at short distances.

2.4.1.3.1 Correlation polarization potential

As discussed earlier in Section 2.2.2, HF method doesn’t take care of electron-electron correlation, so there must be an alternative method to take care of e-e correlation. Correlation effect is produced, when an electron is far from the target, by the distribution of inner electrons and the nucleus, resulting in an induced dipole moment [119]. In the Hartree-Fock approach, electrons are moving in the average Self Consistent Field (SCF) created by other electrons. Here we have considered the coulomb energy and the Pauli exclusion principle. Correlation is the correction of this average interaction to allow electrons to avoid one another in every region of configuration space. For example, when an electron (bound or in continuum) is sufficiently far from the other electrons in the closed shell, correlation takes the form of an inner
electron (and nucleus) distribution, resulting in an induced dipole moment. Thus an approximated local density functional form of the short range (SR) correlation and the long range polarization potential is given by [120–122],

\[
V_{cp}(r) = V_{corr}^{SR}, \text{ at } r \leq r_o
\]

\[
= -\frac{\alpha_d}{2r^4}, \text{ at } r > r_o
\]

Here \( r_0 \) is the point of intersection between the short range correlation part \( V_{corr}^{SR} \) and the long range dipole part \( -\frac{\alpha_d}{2r^4} \). This value may be approximated as the atomic (or molecular) radius. The short range part of the potential in the above equation is known as PZ form of the potential, named after the authors Pedrew and Zunger [120]. It is given by,

\[
V_{corr}^{SR}(r) = 0.0311nrs - 0.0584 + 0.00133nrslns - 0.0084rs, \text{ at } r_s < 1
\]

\[
= \frac{\gamma(1 + \frac{7}{6}\beta_1r_s^4 + \frac{4}{3}\beta_2r_s)}{(1 + \beta_1r_s^2 - \beta_2r_s)^2}, \text{ at } r_s \geq 1
\]

where the constants are \( \gamma = -0.1423, \beta_1 = 1.0529 \) and \( \beta_2 = 0.3334 \) in au. \( r_s = \sqrt[3]{\frac{3}{4\pi\rho(r)}} \) is the density parameter, with \( \rho(r) \) as the electronic charge density of the target. As no single potential can describe the polarization effect adequately for all targets in a wide range of incident energy, the need for an alternate method was obvious. DeFazio et. al. [123] proposed a damped energy polarization potential having the form,

\[
V_{pol} = -D[\rho(r)]\frac{\alpha_d}{2r^4}
\]

with the damping factor \( D[\rho(r)] \) obtained through the charge density \( \rho(r) \) which brings the potential to zero at \( r = 0 \). Moreover Reid and Wadhera [124] represented the correlation potential as:

\[
V_{CP} = -\alpha_d r^2 - \alpha_q + \left(\frac{k^2}{2}\right)
\]

\[
\frac{2(r^3 + d_c^2)}{2(r^3 + d_c^2)^2}
\]

where \( \alpha_d, \alpha_q \) and \( Z \) are the electric dipole polarizability, quadrupole polarizability and atomic number of the target respectively. \( d_c \) is the cut-off parameter obtained through the matching of \( V_{CP} \) curve with \( V_{corr}^{SR} \) curve at the orbital radius of
the atom. As a concluding remarks what we can quote here is that ’for higher energies (say above 100 eV), the dynamic polarization potential $V_{dp}$ given in equation 2.69 is suitable, While, at intermediate energies (typically below 100 eV) the correlation potential shown in Eq. 2.67 is recommended.

### 2.4.1.4 Absorption Potential

The imaginary part of the complex optical potential ($V_{opt}$) of Eq. 2.58 refers to the absorption potential which corresponds to the loss of the scattered electron flux into the inelastic channels. The idea of complex optical potential was first introduced in nuclear physics [125] and later adopted to electron - atom/molecule collisions.

There are several absorption potential models employed in the electron - atom scattering theory from the literature, particularly the works of Reitan [126], Green et al [127] and Staszewska et. al. [128,133]. In the present work we have used the modified Staszewska absorption potential [134] of the original model potential, given by Staszewska et. al [128,133], which is a function of electronic charge density $\rho(r)$, and the local kinetic energy. It is a quasi-free, Pauli-blocking, dynamic absorption potential ($V_{abs}$) given in au, as:

$$V_{abs} = -\frac{1}{2} \rho(r) \nu_{loc} \sigma_{ee}$$  \hspace{1cm} (2.75)

Here, $\nu_{loc}$ is the local speed of the incident electron, and $\sigma_{ee}$ denotes the average total cross section of the binary collision of the incident electron with a target electron. Eq. 2.75 can be rewritten as non-empirical formula in terms of incident energy $E_i$ [133] as :

$$V_{abs}(r, E_i) = -\rho(r) \left[ \sqrt{\frac{T_{loc}}{2}} \left( \frac{8 \pi}{10 k_F^2 E_i} \right) \theta(p^2 - k_F^2 - 2\Delta).(A_1 + A_2 + A_3) \right]$$  \hspace{1cm} (2.76)

Where,

$k_F = \sqrt[3]{3\pi^2 \rho(r)}$ is the Fermi wave vector magnitude and $p^2 = 2E_i$
\[ A_1 = \frac{5k_F^3}{2\Delta} \]
\[ A_2 = -\frac{k_F^3(5p^2 - 3k_F^2)}{(p^2 - k_F^2)^2} \]
\[ A_3 = 2\theta(2k_F^2 + 2\Delta - p^2) \frac{(2k_F^2 + 2\Delta - p^2)^2}{(p^2 - k_F^2)^2} \] (2.77)

\( \Delta \) is the average electronic excitation energy of the target.

Here, \( \theta \) the step function or the Heaviside function, is defined as:

\[ \theta(x) = 1 \text{ for } x \geq 0 \]
\[ \theta(x) = 0 \text{ for } x < 0 \] (2.78)

The local kinetic energy of the incident electron is obtained from,

\[ T_{loc} = E_i - V_R(r, E_i) = E_i - (V_{st} + V_{ex} + V_p) \] (2.79)

At high energies only the first term of Eq.2.79 is important. The dynamic functions \( A_1, A_2 \) and \( A_3 \) given above depend differently on \( \rho(r), I, \) and \( E_i \). The parameter \( \Delta \) is assumed to be fixed in the original model and determines a threshold below which \( V_{abs} = 0 \), and the ionization or excitation is prevented energetically. Here we have modified \( \Delta \) such that at impact energies close to the ionization threshold \( I \), the excitations to the discrete states also take place, but as \( E_i \) increases valence ionization becomes dominant, together with the possibility of ionization of the inner electronic shells.

In order to include the excitations due to discrete levels at lower energy, we have considered \( \Delta \) as energy dependent parameter. So, \( \Delta \) as a variable accounts for more penetration of the absorption potential in the target charge-cloud region. Following the earlier works in this context by Blanco & Garcia [129,135], we express \( \Delta \) as a function of \( E_i \) around \( I \) as,

\[ \Delta(E_i) = 0.8I + \beta(E_i - I) \] (2.80)

where, \( \beta \) is deduced with the conditions that \( \Delta = I \) at \( E_i = E_p \), where \( E_p \) is the value of \( E_i \) at the peak of inelastic cross sections [130]. The choice of \( \Delta = I \) throughout the incident energy range would not allow even excitation at \( E_i \leq I \). On the other
hand, if parameter $\Delta$ is much less than the ionization threshold, then $V_{abs}$ becomes exceedingly high near the peak position. In the range of intermediate energies the $V_{abs}$ shows a rather excessive loss of flux into the inelastic channels i.e., into higher values of $Q_{inel}$. This is partly also due to neglect of finer aspects in the $V_{abs}$, like different transition probabilities for different states etc. The potential $V_{abs}$ also penetrates into the region of inner electronic shells, which are harder to be excited or ionized. This absorption potential has a very good analytical behaviour, and it does have a general predictive capacity, therefore, in order to employ this potential at medium energies it is necessary to rectify it through $\Delta$ and $I$. Hence we choose the $\Delta$ parameter to be a slowly varying function of $E_i$, around the value of $I$. At high energies of course the potential $V_{abs}$ and the cross section $Q_{inel}$ decreases in strength.

## 2.4.2 Scattering in presence of absorption

It is very clear now that during the scattering process, phenomena other than elastic scattering can also occur. At high enough energies there can be infinite number of open channels in addition to the elastic one. Indeed these inelastic processes have got immense importance in applied sciences and these processes, which include ionization and excitation essentially bring information about the target in question. So realistically, we now consider the non-elastic processes too.

Let us consider the asymptotic scattering wave function as a combination of incoming plane wave, $\exp(-ikz)$ and the outgoing spherical wave, $\exp(ikr)$,

$$
\psi^{(+)}_{k_i}(r \to \infty) \to A(k) \sum_{l=0}^{\infty} (2l + 1) i^l \exp(i\delta_l) \frac{i}{2kr} [(-1)^l \exp(-ikr) - S_l \exp(ikr)] P_l(\cos \theta)
$$

(2.81)

with $S_l = \exp(2i\delta_l)$. The coefficient $A_l(k)$ merely fixes the 'normalization' of the radial wave function and has no influence in scattering.

In case of pure elastic scattering, the phase shift $\delta_l$ is considered to be real so that $|S_l| = 1$, but we have to generalize the processes to include inelastic cases. Thus to get the elastic scattering cross section in the presence of inelastic or "absorption" processes we have to allow $\delta_l$ to be complex. This is because the amplitude of the outgoing radial wave may be either reduced (when inelastic processes occur) or left
unchanged (only elastic process), such that \(|S_l| \leq 1\). Here complex phase shifts are attributed to the loss of scattered flux in inelastic process. Complex phase shift can be written as:

\[
\delta_l = \text{Re} \, \delta_l + i \text{Im} \, \delta_l
\]  

(2.82)

thus the complex S-matrix is given by,

\[
S_l = \exp[2i(\text{Re} \, \delta_l + i \text{Im} \, \delta_l)]
\]  

(2.83)

That is,

\[
S_l = \eta_l \exp(2i \, \text{Re} \, \delta_l)
\]  

(2.84)

where \(\eta_l = \exp(-2i \text{Im} \, \delta_l)\) is called the ‘inelasticity’ or ‘absorption factor’. By ‘absorption’ we mean that the particles are removed from the incident channel, so that, \(0 \leq \eta_l \leq 1 \) and \(\text{Im} \delta_l \geq 0\). So when \(\text{Im} \delta_l = 0\) we get the pure elastic scattering.

### 2.4.2.1 Elastic and inelastic cross sections

Our next task is to calculate the elastic and inelastic scattering cross sections in presence of the absorption potential. The method is exactly similar to the one discussed above. The elastic scattering amplitude in the case of non-elastic processes as,

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

(2.85)

Now by using Eq. 2.84 we rewrite the above equation to get,

\[
f_{el} = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)[\eta_l \exp(2i \, \text{Re} \, \delta_l) - 1]P_l(\cos \theta)
\]  

(2.86)

Thus the elastic differential cross section is given by,

\[
\frac{d\sigma}{d\Omega} = |f_{el}|^2
\]  

(2.87)

And the total elastic cross section \((Q_{el})\) is given by [5]

\[
Q_{el}(k) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) |\eta_l \exp(2i \, \text{Re} \, \delta_l) - 1|^2
\]  

(2.88)

Considering the flux densities for reaction or inelastic processes, we can derive the total inelastic cross section as [5]

\[
Q_{inel}(k) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1)(1 - \eta_l^2)
\]  

(2.89)
2.4.2.2 Total (complete) cross sections

The Eq. 2.88 and Eq. 2.89 define the $Q_{el}$ and $Q_{inel}$ respectively. Now the total (complete) cross section ($Q_T$) can be obtained from the following relation:

$$Q_T = Q_{el} + Q_{inel}$$ (2.90)

Here, the first term is the total elastic cross section and the second term is the total inelastic cross section.

Therefore

$$Q_T(k) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l + 1)[1 - \eta_l \cos(2i \text{ Re } \delta_l)]$$ (2.91)

Using the above equations, we can form some other important relations [5]:

$$Q_{el}(k) \leq \sum_{l=0}^{\infty} \frac{4\pi}{k^2}(2l + 1)$$ (2.92)

$$Q_{inel}(k) \leq \sum_{l=0}^{\infty} \frac{\pi}{k^2}(2l + 1)$$ (2.93)

$$Q_T(k) \leq \sum_{l=0}^{\infty} \frac{4\pi}{k^2}(2l + 1)$$ (2.94)

So when $Q_{inel}$ is maximum, $\eta_l = 0$ and so,

$$Q_T(k) = 2 \sum_{l=0}^{\infty} \frac{\pi}{k^2}(2l + 1) = 2 \times Q_{inel}^{\text{max}}(k)$$ (2.95)

Thus at the maximum of inelastic cross section, the elastic and the inelastic contributions are equal.

While deriving the cross section in presence of the absorption potential, we have the complex phase shifts to account for the ‘absorption’ processes. This idea is directly related to the potential of the scattering system.

2.4.3 Complex Scattering Potential-ionization contribution (CSP-ic) method

The calculations we report here are carried out within the frame-work of complex potential comprising of well-known model potential terms (as described in the previous...
section 2.4.1). Here, total ionization cross section has to be derived from the total inelastic cross section. $Q_{inel}$ is the sum of total cross section for all allowed ionization processes and the sum over total excitation cross sections for all accessible electronic transitions. The latter arises mainly from the low-lying dipole allowed transitions for which the cross section decreases rapidly at higher energies. CSP-ic method is based on the fact that,

$$Q_{inel}(E_i) = Q_{ion}(E_i) + \sum Q_{exc}(E_i) \quad (2.96)$$

and

$$Q_{inel}(E_i) \geq Q_{ion}(E_i) \quad (2.97)$$

Based on the above facts, we have extracted the total ionization cross section from the total inelastic cross section. This method is named as 'Complex Scattering Potential-ionization contribution' or CSP-ic method, to find total ionization cross section out of total inelastic cross section. This method gives the summed total electronic excitation cross section as a by product. For the purpose of formulating this method, let us define the following quantity for $E_i \geq I$:

$$R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)} \quad (2.98)$$

such that, $0 \leq R \leq 1$. Here essentially $R = 0$ when $E_i \leq I$. The general experimental trend indicates that the ratio $R$ rises steadily as the energy increases above the threshold, and it is found that,

$$R(E_i) \begin{cases} = R_p, \quad \text{at} \quad E_i = E_p \\ \approx 1, \quad \text{for} \quad E_i \gg E_p \end{cases}$$

where, $E_p$ is the energy value at the peak of $Q_{inel}$. $R_p$ stands for the value of $R$ at $E_i = E_p$, and we choose $R_p \approx 0.7$. This choice follows from the general observation that at energies close to the peak of the ionization cross section the contribution of the atomic $Q_{ion}$ is about 70-80% of the total inelastic cross sections $Q_{inel}$. The value of ratio $R$ cannot be calculated in a rigorous manner. The quantum mechanical origin of the present value of $R_p$ seems to be based on the fact that gradually above the threshold the transitions to continuum start dominating, since they corresponds to an infinite number of open scattering channels.

For calculating the $Q_{ion}$ from $Q_{inel}$ we need $R$ as a continuous function of energy.
\( E_i \geq I \), hence we represent the ratio \( R \) in the following manner [131,132].

\[
R(E_i) = 1 - f(U) = 1 - C_1 \left[ \frac{C_2}{U + a} + \frac{\ln(U)}{U} \right]
\tag{2.99}
\]

Here \( U \) is the dimensionless variable defined through, \( U = \frac{E_i}{I} \). The Eq. 2.97 to 2.99 describes present CSP-ic (Complex Scattering Potential-ionization contribution) method. The functional form of \( f(U) \) in Eq. 2.99 is adopted from the fact that, as \( E_i \) increases above \( I \), the ratio \( R \) increases and approaches unity, since the ionization contribution rises and the discrete excitation term in Eq. 2.96 decreases. The discrete excitation cross sections, dominated by dipole transitions, fall off as \( \frac{\ln(U)}{U} \) at high energies. Accordingly the decrease of the function \( f(U) \) must also be proportional to \( \frac{\ln(U)}{U} \) in the high range of energy. However the two term representation of \( f(U) \) given in Eq. 2.99 is more appropriate since the first term in the square bracket ensures a better energy dependence at low and intermediate \( E_i \). Eq. 2.99 involves dimensionless parameters \( C_1, C_2 \) & \( a \), that reflect indirectly the target properties as we are considering the ionization energy, \( I \) and energy at the peak, \( E_p \) while determining the parameters. \( E_p \) depends upon the target properties like ionization potential and geometry of the molecule. To determine these parameters, we apply the following three conditions on the ratio \( R \).

1. It is zero at and below the ionization threshold.

2. It behaves in accordance with Eq. 2.99 at the peak position \( E_p \).

3. It approaches 1 asymptotically for \( E_i \) sufficiently larger than \( E_p \).

This method of finding the total ionization cross section discussed in this section and employed for many simple to complex molecular target earlier [146,147] is referred as ‘Complex Scattering Potential-ionization contribution’.