CHAPTER 1

ELECTRON IMPACT ATOMIC-MOLECULAR PROCESSES; OCCURRENCE & APPLICATIONS

1.1 Preamble and History

‘Ionization by moving electrified particles’- This was the title of a historic and perhaps the first ever theoretical paper on electron impact ionization of atoms, written by Sir J J Thompson. The paper published in Philosophical Magazine in 1912 marked the beginning of the classical era of electron-atom scattering theory almost a hundred years ago. It is also about a century now [1] since the experimental work on scattering of electrons by gaseous atoms and molecules was investigated first. That was the period when hardly anything was known about the detailed structures of atoms and molecules and the quantum era was yet to set in. Now we have a wealth of knowledge on electron induced processes with various atomic molecular targets and a lot of basic as well as applied work is being done both theoretically and experimentally, in India and abroad.
An atom or a molecule is a bound system in which the electrons and the nuclei are held together quantum mechanically. The first scattering experiment to understand the structure of atoms was done by Rutherford again a hundred years ago [2]. Earlier on the true beginning of atomic and molecular physics was marked by spectroscopic studies. The semi-quantal analysis of spectrum lines of hydrogen atoms was attempted by Bohr [3]. The study of spectra led to the birth of quantum mechanics, which is the language of atomic and molecular kingdom.

1.2 Introduction to Scattering processes

A different class of properties of atoms and molecules can be obtained by collision studies. Such experiments involve collisions between the projectile such as electron, ion or photon and an atomic or molecular system. During the collision, several processes such as elastic or inelastic scattering, dissociation, ionization etc. can occur. The probability of a particular process is measured by specifying the quantity known as cross section. For a certain type of event in a given collision, the cross section is defined as the ratio of the number of event of this type per unit time and per unit scatterer, to the flux of the incident particles with respect to the targets. The nature of this quantity depends on the energy of projectile and targets. This quantity can give many kinds of information about the atomic and molecular system, for example the strength of electron–electron and electron–nucleus interaction in bound state system can be obtained by collision experiment.

The other example is the global property of an atom or molecule such as the charge density that can be inferred from the cross sections for high energy electron scattering [4]. The study of electron–atom or molecular collision has also been strongly
motivated by the need of data for testing and developing suitable theories of the scattering and collision processes, and for providing a tool for obtaining details information on the structure of targets atoms or molecules [5,6].

1.3 Electron impact scattering phenomena - A brief review

The electron itself is a fundamental particle in physics, and electron collisions with molecules are not only of great interest from the pure quantum mechanical perspective, but they have a number of applications. Collisions of electrons with atoms and molecules provide a unique diagnostic probe of fundamental interactions of many-electron systems and are the basic physical processes that determine the behaviour of ionized gases, ranging from those created from plasma processing technologies to the plasma existing in the early universe after the first few seconds. Early experiments on electron impact collisions played a central role in the development of quantum mechanics. The demonstration of diffraction of beams by gases confirmed the quantum mechanical duality of waves and particles and measurements of the energy losses in electron collisions in gases established discrete nature of energy level structure of atoms and molecules.

Indeed the most fundamental of the discharge processes are collisions between electrons and atoms, radicals or molecules. So a quantitative understanding of the electron collision processes and rates is important and the availability of accurate data on such observables is key to the success of plasma processing technology [7]. In order to fully understand the processes listed above, the scientific community requires detailed knowledge of the electron-molecule interactions underlying these processes.

During a scattering process, where a free electron collides with an atom or
molecule, various kinetic processes may take place. All these processes fall into two categories: elastic and inelastic processes. In case of elastic scattering of an electron no energy is transferred to the internal motion of the molecule, while in inelastic scattering, the incoming electron loses a portion of its kinetic energy to the excitation of the target. Consider a mono-energetic, non-interacting and well collimated beam of particles A, incident on a target B as illustrated in figure 1.1. The energy of the incident electron will be denoted by $E_i$. The incident beam flux is just enough so that interaction between the incident particles A is very weak and neglected. The scatterer or the target B is a macroscopic sample and the source of incident particle is usually kept at a distance quite larger than the de Broglie wave length of the incident particles. The target is very thin and can be considered as a single particle B. Hence, our main focus is on the collision of a particle A with another particle B. The scattering is a single collision event. During a collision many processes are possible or channels are open and the outgoing particles

Figure 1.1 A schematic diagram of electron scattering
resulting from these collisions are collected and registered by the detector. The various processes that can occur are illustrated below.

1.3.1 Elastic Scattering

When two particles A and B are simply scattered without any change in their internal structure, and total kinetic energy and momentum are conserved. It is elastic scattering. Thus in a process like the following the total kinetic energy of the colliding system remains constant.

\[ A + B \rightarrow A + B \]

In principle, during elastic collisions the electrons lose part of their energy due to momentum transfer, but this energy loss is insignificantly smaller because it is proportional to the ratio of electron mass to molecular mass.

Example:

\[ e + H \ (1s) \rightarrow e + H \ (1s) \]

which occurs purely below the excitation threshold 10.2 eV of atomic hydrogen.

1.3.2 Inelastic Scattering; channels and processes

The two particles A and (or) B undergo a change of their internal quantum state during the collision process. Denoting by A' and B' these new internal states, we may have
\[
A + B \rightarrow A' + B \\
A + B \rightarrow A + B' \\
A + B \rightarrow A' + B'
\]

The processes involving the loss of kinetic energy by electrons are called inelastic collisions where the electrons lose kinetic energy owing to the excitation of the target molecule, ionization of the target atom/molecule, and other internal processes that occur in the molecule.

There are three major channels by which inelastic processes can occur:

**Excitation processes:**

The incident electron collides with the target and excites it from its ground state to the higher state. The probability of these processes depends on the energy of the incident electron as well as on the energy difference between the two states involved.

Examples:

* \(e + \text{H}_2\text{O} \rightarrow e + (\text{H}_2\text{O})^+ [\text{electronic excitation}]
* \(e + \text{H}_2\text{O}(J) \rightarrow e + \text{H}_2\text{O}(J') [\text{rotational excitation}]
* \(e + \text{H}_2\text{O}(\nu) \rightarrow e + \text{H}_2\text{O}(\nu') [\text{vibrational excitation}]

**Ionization processes**

In this process the incident electron ionizes the target directly. This process occurs at and after the ionization threshold energy of the target.

Example:

* \(e + \text{H}_2\text{O} \rightarrow e + \text{H}_2\text{O}^+ [\text{parent ionization}]

**Dissociative ionization and other channels**
The incident electron can dissociate the target molecules in different fragments depending upon their dissociation energy.

Also the properties of atoms, molecules and clusters change dramatically when an ‘extra’ electron is attached to them. The ‘extra’ electron in the anion is bound by the short range induced dipole potential and there is usually not more than one bound electronic state. The electronic states of anions are usually accessed by Dissociative Electron Attachment (DEA) where a general molecule, AB, combines with a free electron, e, to give a super-excited anion AB−* which dissociates to give molecular fragments, A− and B.

Examples:

\[
e + \text{H}_2\text{O} \rightarrow 2e + \text{OH}^+ + \text{H} \ [\text{dissociative ionization}]
\]
\[
e + \text{H}_2\text{O} \rightarrow 2e + \text{H}^+ + \text{OH} \ [\text{dissociative ionization}]
\]
\[
e + \text{H}_2\text{O} \rightarrow 2e + \text{O}^+ + \text{H}_2 \ [\text{dissociative ionization}]
\]
\[
e + \text{H}_2\text{O} \rightarrow 2e + \text{H}_2^+ + \text{O} \ [\text{dissociative ionization}]
\]
\[
e + \text{H}_2\text{O} \rightarrow 3e + \text{O}^{2+} + \text{H}_2 \ [\text{dissociative ionization}]
\]
\[
e + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^- \ [\text{electron attachment}]
\]
\[
e + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H} \ [\text{dissociative electron attachment}]
\]

1.3.3 Scattering Cross sections

A cross section is a measure of the occurrence of a particular event while scattering between two particles takes place.

**Differential cross sections**

We will now consider the elastic process from figure 1.1, where dN number of particles (A) are scattered elastically per unit time within a solid angle dΩ. Then, for a sufficiently thin target, the number of particles scattered per unit time per unit solid angle is proportional to incident flux (Φ_A) and the number of target scatterers (n_B) is,
\[ dN \propto \Phi_A n_b d\Omega \quad (1.1) \]

Equation 1.1 can also be written as,

\[ dN = \frac{d\sigma}{d\Omega}(\theta, \phi) \Phi_A n_b d\Omega \quad (1.2) \]

Where the proportionality factor \( \frac{d\sigma}{d\Omega}(\Omega) (\Omega = \theta, \phi) \) is called the differential cross section (DCS) for elastic scattering. DCS at a particular direction \((\theta, \phi)\) is defined as the number of particles scattered per unit solid angle, per unit incident flux and per unit time, where the polar angles are defined in figure 1.1. Thus from equation 1.2 we get,

\[ \frac{d\sigma}{d\Omega}(\Omega) = \frac{dN}{\Phi_A n_b d\Omega} \quad (1.3) \]

Further it is shown in Joachain [8] that we have the following standard result for elastic scattering,

\[ \frac{d\sigma}{d\Omega} = \left| f(\Omega) \right|^2 \quad (1.4) \]

**Total elastic cross section**

Total or integrated elastic cross section is obtained by integrating the differential
cross section over all the solid angles (dΩ), which can also be written as,

\[
\sigma_{el} = \int_0^\pi \int_0^{2\pi} \frac{d\sigma}{d\Omega}(\Omega) \sin \theta d\theta d\phi
\]  

(1.5)

This total elastic cross section is the purely elastic cross section without the presence of any inelastic channels. But realistically we have to consider inelastic channels while finding the total elastic cross section. The total elastic cross section in the presence of inelastic scattering is denoted by \( Q_{el} \), where \( Q \) comes from the German word ‘Querschnitt’ meaning cross section. We will use the abbreviation TCS for total cross section.

**Total inelastic cross section**

Besides the elastic process, there can be various inelastic processes that may occur in a scattering event. The total inelastic cross section is denoted by \( Q_{inel} \), which is actually a cumulative inelastic scattering cross section, and is divided into two parts,

\[
Q_{inel} = \sum_n Q_{ion}(A^{+n}) + \sum Q_{exc}
\]  

(1.6)

The first term in equation 1.6 accounts for the total of all total ionization cross sections for all energetically allowed states with \( A^{+n} \) as the charge state of the ion. The second term indicates the total excitation cross section for all allowed electronic transitions of the target by incident electrons. If ‘i’ is the initial (ground) state and ‘f’ is
the final state of electronic transition, and if \( Q[i \rightarrow f] \) is the total cross section of this transition then,

\[
\sum_{f} Q_{exc} = \sum_{f} Q[i \rightarrow f]
\]  

(1.7)

**Total (complete) cross section**

The sum of both total elastic and inelastic cross sections will give the total (complete) cross section, \( Q_T \). This corresponds to the effect of all the different channels that can be present in any scattering processes. The total cross section indicates the probability that an incident particle interacts with a target particle and has therefore been removed in some way from the incident beam. Thus,

\[
Q_T = Q_{el} + Q_{inel}
\]  

(1.8)

**Rotational excitation cross section**

The total (complete) cross section we have discussed up to now arises from spherical interactions only. The method we use to solve Schrodinger equation is the partial wave analysis with spherical potential. This is satisfactory for atoms as they do not have a permanent dipole moment, but in the case of molecules particularly those having a permanent dipole and/or quadrupole moments, the non-spherical potential and the resulting cross sections also need to be considered.

Throughout the thesis the most important non-spherical contribution is considered in the form of dipole rotational cross sections. These are more appreciable at low energies and are denoted by \( Q_{rot} \).
Grand total cross section

The total cross section $Q_T$ we have defined, is the spherical part of the grand total cross section, denoted by $Q_{TOT}$. For molecules with a permanent dipole moment, rotational excitation cross section is the most important non-spherical contribution. The $Q_{rot}$ can be added to the total cross sections $Q_T$. Here $Q_T$ is the spherical part and $Q_{rot}$ is the non-spherical part of the grand total cross section. Thus grand total cross section ($Q_{TOT}$) is defined as

$$Q_{TOT}(E_i) = Q_T(E_i) + Q_{rot}(E_i)$$

(1.9)

1.4 Significance of electron scattering in various fields

Such collisions are precursors of the ions and radicals which drive the etching, cleaning and deposition processes. Therefore To predict quantitatively the behaviour of ionized gases produced by electrical discharges in lighting systems and by lightning or created in fusion plasmas or found in astrophysical environments requires development of the theory of electron collisions and construction of mathematical methods that enable reliable calculations of the critical collision parameters identified by the theory. Despite the applications of electron-molecule collisions discussed above being important, little is known about their physics and chemistry.

Our interest in the present collision calculation arises in view of the applications of relevant cross section data in both pure and applied sciences. The targets selected presently find applications in atmospheric science, astrophysics, plasma physics/chemistry and radiation physics, semiconductors and gaseous electronics, mass
spectrometry etc. [9] Ionization of atmospheric atoms / molecules is produced basically by high energy radiation and to some extent by particles emitted from the Sun and the cosmic rays. Indeed some people suggest that these particles may play a role in cloud formation and climate change [9, 10], while more recently a link between ozone depletion and cosmic radiation has also been suggested. Therefore it is important to be able to determine the electron impact total and ionization cross sections of aeronomic species. Plasma etching, deposition and cleaning are indispensable fabrication techniques in the manufacture of microelectronics components. The plasma equipment for these processes use partially ionized plasmas to dissociate and ionize feedstock gases. The resulting radicals and ions interact with the semiconductor surface, either removing or adding material, to define the desired features. The high cost of developing the plasma equipment has led to modeling/simulation of these processes to speed the time to market and to reduce costs. The application of this modeling infrastructure to industrially relevant problems has been limited by the availability of fundamental data (e.g., electron impact cross sections). With the need to develop 'clearer technology' other chemistries and types of processes have recently come to prominence for which databases are also required. Particular emphasis has recently been placed upon the study of electron induced processes including measurement of ionization cross sections; electronic excitation (leading to observational fluorescence and dissociation of the parent molecule) and the role of negative ion formation. Both gas phase and surface studies have been investigated extensively and the different chemistry induced by electrons on a surface compared to the gas phase is emphasized [8].
Radiation therapy is one of the major cancer treatment techniques other than chemical and surgical therapy. During radiation therapy electrons are produced with a wide range of energies from the irradiated areas. The secondary electrons produced can collide with DNA molecules in human cells, causing damage that destroys the cancer cells. In modeling such processes there is a need for accurate knowledge of electron collision cross sections for relevant biological molecules [11].

These applications emphasize the need for developing rapid, computational techniques to produce cross sections on industrially relevant time scales. Due to the computational demands, however, most techniques are currently restricted to simple quasi-one and quasi-two electron atomic targets that can be described in a non-relativistic model. Extension of theoretical methods to more complex targets including radicals is therefore a priority. These issues underline the importance of the present study.

The scope of present theoretical approach lies in its quickness with reasonable reliability in producing cross section data on a wide range of targets from light atoms to heavy molecules. Since the volume of data required in the technologies is enormous, theories like ours can find importance to present day science. Other accurate or better theories have the limitations to energy range and also to the size of the target. For example the accurate R-matrix method can find cross section and even predict the resonances but only for small molecules, while the range of energy is low (10 eV). Such theories cannot handle complex molecules, either. Even for small molecules, the time consumed for computation is rather high. Collisions of electrons with atomic silicon and its compounds find applications in different fields of research and industry, e.g., plasma physics and surface studies.
Electron impact electronic excitation plays a crucial role in molecular plasmas for a number of reasons: it is the main route to electron impact dissociation, electronically excited states are chemically very active, and the process leads to electron cooling. In many cases part of the energy transmitted into excited states will be lost to the plasma by emission of photons. The ability to compute accurate electronic excitation cross sections for polyatomic molecules, in coupled-state calculations that employ accurate wave functions for a large number of target states, is an undertaking that will require a major future investment. The need to carry out such an undertaking is especially important since electronic excitation of polyatomic molecules has been largely neglected by experimental groups (see above) and therefore most of the recent theoretical calculations have little or no data with which to compare. Most likely, theory will be the major source for critically needed cross section data on electronic excitation of polyatomics for some time to come, so it is essential that the methods under development be reliable, accurate and benchmarked against the few existing experimental data. Electronic collisions with polyatomic molecules are of fundamental theoretical importance in this context, because with many different degrees of freedom and opportunities for interaction between excited electronic states, they offer a rich array of non-adiabatic processes which are still not completely understood [12]. Attempt has been made in this thesis to study electron scattering with plasma important molecules.

1.4.1 Astrophysics, Astro-chemistry and Atmospheric sciences

The importance of electron-molecule collisions in astrophysical environments has been a major motivation for a number of studies, including this thesis, on astro-physically important molecules. In this section we shall briefly review the role played by electron
collisions in C-type shocks, comets and planetary atmospheres, and some previous work carried out on molecules of astrophysical importance.

Electron-impact excitation plays a significant role in astrophysical environments where the electron fraction is higher, e.g. diffuse interstellar media, in shocks and comets. Electrons can dominate the excitation process because the electron-impact excitation rate coefficients can exceed those for neutrals by about five orders of magnitude: Modeling of the early stages of C-type shocks predicts that the ion and electron densities are enhanced by the magnetic precursor [13].

Electrons are known to have a profound effect in the rotational excitation of the polar water molecule. Xie and Mumma [14] observed that in the case of the 0→1 rotational transition, the e-H₂O collisional excitation rate exceeds that of neutral-neutral collisions at distances exceeding 3000 km from the cometary nucleus. Their conclusion was that the rotational temperature of water in the intermediate coma may be controlled by collisions with electrons rather than neutrals, and that they may affect the rotational population of the molecule in the intermediate and outer coma of an active comet such as Halley. Similar conclusions were drawn by [15] in the case of HCN, which is highly polar (~ 3 D [16]). Electron collisions might also contribute to the pumping of H₂O MASERs commonly observed in star forming regions or active galactic nuclei [17].

1.4.2 Plasma systems and mass spectrometry

Quantitative descriptions of fundamental collision processes in terms of cross sections are required to understand and model plasmas. The production and loss of electrons are the key processes that determine the formation, stability, and decay of the plasma. Electron impact cross sections, the appearance energies and the kinetic energy
release play an important role in this context, since they determine plasma-wall interactions and the ionization balance in the plasma. In fusion plasma studies there is a need to determine the lifetime of particular excited state of a specific ion or a molecule. Accurate electron scattering cross sections are essential in these determinations [18].

Plasma etching, deposition and cleaning are indispensable fabrication techniques in the manufacture of microelectronics components. The plasma equipment for these processes typically use partially ionized, low pressure plasmas to provide activation energy to dissociate and ionize feedstock gases. The resulting radicals and ions interact with the semiconductor surface, either removing or adding material, to define the desired features or modify the surface. The high cost of developing both the plasma equipment and processes has motivated development of less empirical methods, and modeling/simulation in particular, to speed the time to market and to reduce costs.

1.4.3 **Semiconductor physics and Biophysics**

Low-temperature plasmas are used in the semiconductor industry to etch features deposit materials and clean reaction chambers. Development of these applications requires a detailed understanding of the physical and chemical processes occurring in the plasmas themselves. Advances in this require knowledge of the basic processes taking place between species in the plasma.

Apart from these applications in life sciences, the role of electron-driven processes is being recognized as crucial to our understanding of radiation damage of cellular material. Radiation therapy is one of the major cancer treatment techniques other than chemical and surgery therapy. During radiation therapy electrons with a wide range of energies are produced from the irradiated areas. The secondary electrons produced can
collide with DNA molecules in human cells, causing damage that destroys the cancer cell. In modeling such processes there is a need for accurate knowledge of electron collision cross sections for relevant biological molecules.

1.5 Electron scattering theories; A bird-eye view

Consider a collision process of electron with an atom as shown in figure 1.1. Various physical consequences are possible depending on the incident energy and the distance between the incident electron and the electron cloud of target atom. The reason for this is the potential developed between the incident electron and the electron cloud plus nucleus. Even when the incident electron is far away from the target atom, the target cloud experiences an electric field which induces a dipole moment. This dipole moment in turn affects the kinetic motion of the incident electron. This gives rise to a long range potential is known as the polarization potential. As the incident electron approaches the target electron cloud, it becomes indistinguishable from the target electrons. At this stage the potentials which dominate the process are (a) static potential and (b) exchange potential. The cross sections that we obtain are total elastic and inelastic cross sections, total (complete) cross section and the grand total cross section respectively. In equation 1.6, the first term represents total ionization cross sections to all energetically allowed ion states. The dominant contribution comes from the first ionization state and the cross sections from successive ionization states are smaller in the present range of energy, i.e. from threshold to about 2000 eV. So equation 1.6 can be written as

\[ Q_{inel} = Q_{ion} + \sum_{f} Q_{exc} \]  

(1.10)
The first term in equation 1.10 accounts for the total ionization cross section and the second term indicate the total excitation cross section for all allowed electronic transitions of the target to various final states \( f \) (allowed by energy) by incident electrons. In our research group, we have proposed [10] a new way of extracting the ionization cross section from inelastic cross section. We call it “Complex Scattering Potential - ionization contribution” (CSP- ic) method, as discussed in the next chapter. Our main task is to find elastic and inelastic cross sections using a Complex Optical Potential by generating complex phase shifts [9] and then calculate total and ionization cross section from them. To begin with, we develop a relation between the cross sections and the quantum mechanical quantities which will enable us to calculate these total cross sections.

1.6 Literature survey of electron scattering processes

Let us briefly review the wide research in the 20\textsuperscript{th}-21\textsuperscript{st} century on the electron scattering processes in literature from both the theoretical and experimental point of view.

1.6.1 Theoretical Calculations

Total cross sections

Cross section calculations using a complex optical potential which is called Spherical complex optical potential, SCOP [19] are of great interest in view of the difficulty in experiments as well as the accurate theories like R-matrix. The SCOP has been successfully employed by many groups like, Jain and Baluja [20], Jiang and co-workers [21] and Lee and co-workers [22]. The present work is mostly dedicated to SCOP calculations, with our own modifications. Our version of the SCOP method will be
described in more details in later chapters. The Continuum multiple scattering method (CMS) is based on Slater's free-electron gas model of a metal [23]. In CMS method the configuration space is divided into several regions. The Schrödinger equation is then solved in each region and the total scattering wave function is derived by matching the wave functions at each boundary. In this work presented in [24] the non-spherical potentials are replaced by atomic potentials of the constituent atom in the molecule. Once the total wave function is known, we can easily extract the S-matrix and in turn the scattering cross sections.

The R-matrix theory [24] considers the dominant physics governing the behavior of incident electron in different regions of the configuration space. The configuration space is divided into two regions: an inner region and an outer region. The Schrödinger equation is solved in each region separately to obtain the total wave function by smoothly matching the solution at each boundary. In principle the R-matrix method is ab initio and has been applied to highly accurate calculations with impressive success. However, for larger molecules this method becomes increasingly complex and requires large computational efforts. Thus the R-matrix calculations have to date, been limited to small systems and low energy scattering, below 15 eV, i.e. below the ionization threshold, e.g. Savinder and Baluja [25] of India, have calculated ab-initio elastic scattering cross sections using R-matrix theory at low energies.

Ionization cross sections

The binary-encounter-Bethe (BEB) method of Kim and Rudd [26,27] and Deutsch-Maerk (DM) formalism [28, 29] are the other two most widely used semi-rigorous methods to calculate absolute (total single) electron-impact ionization cross sections for
molecules. Both methods were originally developed for the calculation of atomic ionization cross sections and were subsequently extended to neutral molecular targets. Later on, both the groups modified their theory to include molecular ions.

The Binary-Encounter-Bethe (BEB) model, a simplified version of Binary-Encounter-Dipole (BED) model combines the Mott cross section with the high incident energy behavior of the Bethe cross section. Here the Mott cross section formalism [30], which is a generalized Rutherford cross section taking into account electron exchange effects, describes the collision of two ‘free’ electrons, thus accounting well for hard collisions. While, Bethe cross section formula [31] for the dipole interaction involving fast incident electrons and thus accounting for soft collisions Kim and Rudd also introduced a simplified version of the BED model, called the Binary-Encounter-Bethe (BEB) [26, 27] model in which a simple expression for the optical-oscillator strength (OOS), based on the results from H, He, and H₂, is employed in the expression of the Bethe cross section. Both the BED and BEB models depend on quantities either determined using target and ion wave functions or from experiment. Calculations based on either model are generally in good agreement with experiment at incident energies from threshold to several keV. For many cases the deviation from experiment is within 5-15% at the peak, with the BED model performing somewhat better than the BEB model.

Later on, Khare et al [32, 33] introduced their version of the binary-encounter-dipole model in which once again the Bethe cross section was used to describe long-range dipole collisions.

The DM formalism as originally introduced by Deutsch and Maerk [34] was developed for the calculation of atomic ionization cross sections and has been modified
and extended several times, most notably including also the case of molecular ionization cross sections [28, 29]. The DM formula expresses the atomic ionization cross section as the sum over all partial ionization cross sections corresponding to the removal of a single electron from a given atomic sub-shell labeled by the quantum numbers $n$ and $l$ [28].

The DM formula can be easily extended to the case of molecular ionization cross section calculations provided one carries out the Mulliken or other molecular orbital population analysis, which expresses the molecular orbitals in terms of the atomic orbitals of the constituent atoms. Both BEB and DM formulations are known to have their own limitations.

1.6.2 Experimental highlights

The basic experimental apparatus used to study electron impact collision, usually consists of the following parts: (1) an electron gun as a source, which generates mono-energetic electrons having an energy selective beam, (2) a setup to generate the target gas and measure its number density, (3) an arrangement to pass the target gas into the collision chamber and electrons to start the scattering processes and (4) a detector assembly to monitor the outgoing electrons after scattering and analysis of the final strength of the target measures their angular distribution and the energy loss.

Literature on experimental methods and results can be found in many texts and articles e.g. by Christophorou [35], and Massey and Burhop [36] and Bransden and Joachain [37]. Electron collision experiments can broadly be classified into three categories:

1. Electron swarm experiments
2. Electron beam experiments, and
3. A suitable combination of both

The cross sections measured using the swarm experiments are, (1) momentum transfer cross sections, (2) inelastic cross sections and (3) electron attachment cross sections. The electron swarm experiments are suitable for low energy scattering at or below around 1 eV, while beam measurements are favorable from 1 eV to the very high energy. There are many groups worldwide performing the beam experiments. Let us mention below some of the European experimental groups, whose data have been included for comparison of our results in the present thesis.

Freund et al [38] measured absolute electron-impact cross sections in the energy range of 0 eV to 200 eV for single ionization of 16 atoms (Mg, Fe, Cu, Ag, Al, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se and Te) with an estimated accuracy of 10 % using the crossed-electron-beam-fast-atom-beam method. In addition to this the group has also measured double ionization of ten atoms and triple ionization of eight atoms [38].

Tarnovsky and co-workers in US and in Germany [39] performed electron scattering and ionization experiments in the energy range from threshold to around 200 eV. They have also measured the cross sections for many hydro and fluoro-carbon (and silicon) radicals.

**Total cross section $Q_{tot}$**

Zecca and co-workers [40] in Italy have used Ramsauer type spectrometer. They measured total cross sections for various molecules in the energy range ~ 100 to 3 keV. Kimura, Sueoka and co-workers [41, 42] in Japan have performed experiments at low and intermediate energies for total cross sections. They used a time-of-flight apparatus to find the cross sections. The Garcia group at Spain along with Mason and co-workers at
UK performed experiments [43, 44] to obtain total cross section for intermediate and high energies. Experiments of Szmytkowski and co-workers [45] at Gdansk Poland have reported cross sections at low to intermediate energies (1 eV to 250 eV) for absolute total cross sections. They measured the total cross sections for e - scattering by NH₃, SiH₄ and H₂S molecules in the intermediate range. They also reported total cross sections for electron scattering on SO₂, NO₂ and OCS molecules in the energy range 90 to 4000 eV.

**Ionization cross section**

Electron-molecule experiments are performed by Harland Group [46,47] on a modified External Fourier-transform mass spectrometer (FTMS). Nishimura in Japan working in collaboration with Y. K. Kim in US [48] measured total ionization cross section in the energy range from threshold to around 1000 eV. Stebbings and co-workers [49] in the US studied total and partial ionization cross section measurements. Ionization cross sections were also measured at intermediate and high energies by Mason and co-workers in UK [50] for molecules like O₃.

1.7 A brief review of atomic and molecular properties

Also let us now introduce the ‘atomic unit system’ which is followed throughout all the present calculations in this thesis, unless otherwise stated.

**Atomic unit system**

Atomic molecular physics deals with quantities much smaller than what we see in normal experiences, e.g. the order of magnitude of length is close to the magnitude of Bohr radius ‘a₀’ (most probable radius of hydrogen atom, \(a₀ = 0.529 \times 10^{-8}\) cm). So for simplifying the theoretical calculations we use the atomic unit (au) system in our calculations. The various quantities defined in a.u. are as follows:
Electron charge, $e = 1$; electron mass, $m_e = 1$; $h = 1$ ($h = h/2\pi$, where $h$ = Planck's constant); and $4 \pi \varepsilon_0 = 1$ ($\varepsilon_0$ = permittivity of free space); Velocity of light, $c = 1$; Using the $au$ system we can derive the units for other physical quantities required in our calculations. Thus, Linear momentum, $p = h k = k = 2\pi / \lambda$ ($\lambda = 1$) ($k$ = wave vector and $\lambda$ = wavelength); Energy, $E = h^2 k^2 / 2m = k^2 / 2(a_o^{-2})$; 1 $au$ of energy (Hartree) = 27.2114 eV; and 1 $au$ of energy (Rydberg) = 1/2 Hartree = 13.6057 eV; Differential cross section, DCS = $a_o^2$/Sr (Sr = Steradian); Total cross section, TCS and Momentum transfer cross sections, MTCS = $a_o^{-2}$. In this thesis we have used $\text{Å}^2$ or $10^{-16}$ cm$^2$ as the unit for cross sections unless otherwise specified.

Now it is also important to know the relevant properties of the atoms and molecules which appear as the basic inputs for calculation of various potentials. Let us define some of the important input parameters.

**First electronic excitation energy $\Delta_{gap}$**: It is the energy of the first excited state above the ground state of an atom / molecule.

**Average excitation energy $\Gamma$**: The average excitation energy is defined as

$$
\Gamma = \frac{2 \langle \Psi_0 | Z^2 | \Psi_0 \rangle}{\alpha_d}
$$

(1.11)

where $|\Psi\rangle$ is the ground state of the target atom, $\alpha_d$ is the static dipole polarizability of the atom.

**Orbital radius $R$**: It is the position of the peak of the charge density $\rho (r)$ of the outermost orbital in an atom, with reference to the plot of $4\pi r^2 \rho (r)$→$r$. 

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**Dipole polarizability $\alpha_d$:** In the presence of an electrostatic field $\vec{E}$, the charge distribution of an atom or a molecule is distorted. In a simple situation this amounts to an induced dipole moment $\vec{p}$ in the system such that

$$\frac{|\vec{p}|}{|\vec{E}|} = \alpha_d |\vec{E}|$$

(1.12)

Here, $\alpha_d$ defines static electric dipole polarizability. Polarizability is a measure of the ease with which an external electric field is able to distort the charge cloud of an atom or molecule. The external field can come from a nearby ion, or even from the polar end of a molecule that is electrically neutral but does not have its electron cloud distributed evenly. In general, polarizability is a tensor. It has the dimensions of volume and can be conveniently expressed in $a_0^3$. In the case of a molecule the average polarizability is denoted by $\alpha_0$.

**Ionization energy:** This term refers to the minimum work done in overcoming the electrostatic attraction between the electron and nucleus in order to remove the electron from the atom and to make a positive ion. A multi-electron atom has as many ionization energies as it has several electrons. Electrons are always easily removed from the highest-energy occupied orbital. Successive ionization energies of an atom increase rapidly due both to reduced electron-electron repulsion and the additional positive charge that binds the remaining electrons even more tightly. An examination of the successive ionization energies of the first ten elements provides experimental confirmation that the binding of the two innermost electrons (1s orbital) is significantly different from that of the n=2
Atoms

Atmospheric/astrophysical Molecules

Compounds of Boron

Compounds of Beryllium

Polar Molecules

<table>
<thead>
<tr>
<th>Atom</th>
<th>Molecules</th>
<th>Compounds</th>
<th>Compounds</th>
<th>Polar Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>N₂ &amp; N₂*</td>
<td>BH</td>
<td>BeH</td>
<td>SiO</td>
</tr>
<tr>
<td>P</td>
<td>O₂</td>
<td>BN</td>
<td>BeH₂</td>
<td>H₂O</td>
</tr>
<tr>
<td>As</td>
<td>H₂ &amp; H₂*</td>
<td>BF</td>
<td></td>
<td>OCS</td>
</tr>
<tr>
<td>Sb</td>
<td>HCN</td>
<td>BCl</td>
<td></td>
<td>LiH</td>
</tr>
<tr>
<td>Bi</td>
<td>CO</td>
<td>BH₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>CN</td>
<td>BF₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td></td>
<td>BCl₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: List of Atomic-Molecular targets studied for this thesis

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Atomic number (Z)</th>
<th>Atomic Atoms</th>
<th>Ionization Energy I (eV)</th>
<th>Dipole polarizability a₀(a₀³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>Be</td>
<td>9.32</td>
<td>5.6</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>B</td>
<td>8.29</td>
<td>3.03</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>N</td>
<td>14.53</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>P</td>
<td>10.48</td>
<td>3.63</td>
</tr>
<tr>
<td>5</td>
<td>33</td>
<td>As</td>
<td>9.87</td>
<td>4.31</td>
</tr>
<tr>
<td>6</td>
<td>51</td>
<td>Sb</td>
<td>8.06</td>
<td>6.6</td>
</tr>
<tr>
<td>7</td>
<td>83</td>
<td>Bi</td>
<td>7.28</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Table 1.2: Properties of atoms

the n=2 electrons.

In the present thesis we have reported electron impact collision calculations on atomic and molecular targets relevant to plasma and astrophysical systems. Total 28 targets listed in table 1.1, are neutral ground-state species. The important properties of
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Molecule (No. of electrons)</th>
<th>Bond Length (au)</th>
<th>Avg. Sph. Polarizability $a_0 (a_0^3)$</th>
<th>Ionization Potential $I$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N$_2$</td>
<td>N – N 2.07</td>
<td>11.88</td>
<td>15.58</td>
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<tr>
<td>2</td>
<td>O$_2$</td>
<td>O-O 2.29</td>
<td>10.81</td>
<td>12.07</td>
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<tr>
<td>3</td>
<td>H$_2$</td>
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<td>HCN</td>
<td>C-H 1.06</td>
<td>2.59</td>
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<td>5</td>
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<td>C-O 2.13</td>
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<td>C-N 1.17</td>
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<tr>
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<td>B-Cl 1.72</td>
<td>32.61</td>
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<td>8</td>
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<td>B-F 1.26</td>
<td>-</td>
<td>11.12</td>
</tr>
<tr>
<td>9</td>
<td>BN</td>
<td>B-N 1.28</td>
<td>-</td>
<td>11.92</td>
</tr>
<tr>
<td>10</td>
<td>BH</td>
<td>B-H 1.23</td>
<td>3.32</td>
<td>9.77</td>
</tr>
<tr>
<td>11</td>
<td>SiO</td>
<td>Si-O 1.51</td>
<td>-</td>
<td>11.49</td>
</tr>
<tr>
<td>12</td>
<td>H$_2$O</td>
<td>O-H 1.81</td>
<td>11.00</td>
<td>12.00</td>
</tr>
<tr>
<td>13</td>
<td>OCS</td>
<td>O-C 1.16</td>
<td>5.71</td>
<td>11.18</td>
</tr>
<tr>
<td>14</td>
<td>LiH</td>
<td>Li-H 1.60</td>
<td>3.84</td>
<td>7.7</td>
</tr>
<tr>
<td>15</td>
<td>BeH</td>
<td>Be-H 1.34</td>
<td>-</td>
<td>-</td>
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<tr>
<td>16</td>
<td>BeH$_2$</td>
<td>Be-H 1.34</td>
<td>4.34</td>
<td>11.82</td>
</tr>
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<td>BH$_2$</td>
<td>B-H 1.23</td>
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<td>8.10</td>
</tr>
<tr>
<td>18</td>
<td>BF$_2$</td>
<td>B-F 1.26</td>
<td>-</td>
<td>8.84</td>
</tr>
<tr>
<td>19</td>
<td>BCl$_2$</td>
<td>B-Cl 1.72</td>
<td>-</td>
<td>8.75</td>
</tr>
</tbody>
</table>

Table 1.3: Properties of molecules

Atoms are listed in Table 1.2 and properties of molecules are listed in Table 1.3.
1.8 Conclusions

In conclusion, this chapter describes the occurrence and applications of various electron scattering phenomena and highlights electrons as convenient and effective probes for investigation. Electron atomic/molecular scattering is a very well known field of experimental and theoretical research for almost a century now. A number of papers have been published on measured as well as calculated differential and total cross sections on various atomic-molecular systems. However, the fact is that experiments have their own difficulties and theories have their own limitations. The present scenario highlighted in this chapter not only provides motivation but also a challenge for yet another theoretical attempt. Our theoretical attempts are described in the chapters to follow.
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