Chapter 6

Thesis summary and future prospects

In the present thesis we have reported our broad theoretical method and necessary modifications therein, to calculate various total cross sections for electron impact on different atomic and molecular systems. The development and application of the modified SCOP and CSP-ic methods to find total and ionization cross sections for a wide range of atoms and molecules were outlined. The methodology has been discussed in detail in chapter 2 and our results are displayed and described in the following chapters. Here we conclude the thesis with the summary of work that has been done, a brief outline on merits and challenges in the theory and discussion on the future prospects of the present method with respect to its relevance from the application point of view. We will also give a brief note on the adaptability of our method to other systems and possible improvements to it.

6.1 Present work in a nutshell

The main purpose here was to introduce our recently established theory of electron impact with atoms and molecules to testify the theory for simple and stable targets and employ it to less studied targets or those species for which experiments
Table 6.1: Atomic and molecular targets studied in this work

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Target</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>He, Ne, Ar, Kr, Xe (Inert Gases)</td>
<td>[1,2]</td>
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<tr>
<td>2.</td>
<td>CH₄, SiH₄, GeH₄, CF₄, SiF₄, CCl₄, SiCl₄ (Tetrahedral molecules)</td>
<td>[3]</td>
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<tr>
<td>3.</td>
<td>C₂H₂, C₂H₄, C₂H₆, C₃H₄, C₃H₆, C₃H₈ (Hydrocarbons)</td>
<td>[4]</td>
</tr>
<tr>
<td>4.</td>
<td>F, Cl, Br, I, F₂, Cl₂, Br₂, I₂ (Halogen atoms and molecules)</td>
<td>[5]</td>
</tr>
<tr>
<td>5.</td>
<td>H₂O (Water in various phases)</td>
<td>[6]</td>
</tr>
<tr>
<td>6.</td>
<td>C, N, O, Al, Cu (Atoms of applied interest)</td>
<td>[7]</td>
</tr>
<tr>
<td>7.</td>
<td>OH, CHₓ (x=1-3) (Radicals)</td>
<td>[8]</td>
</tr>
<tr>
<td>8.</td>
<td>H₂O dimer and H₂CO (Exotic species)</td>
<td>[9,10]</td>
</tr>
</tbody>
</table>

are difficult or impossible to perform. Our main aim in this work was to develop a quick and reliable theoretical method to calculate total and ionization cross sections for such targets. Our purpose was also to develop a theoretical method that yields several important total cross sections within the same theoretical formalism. Usually the measurements of the total (complete) cross sections (TCS) for the total transmission are carried out by different groups or laboratories in their own experimental set ups corresponding to different energy ranges. Experimental total elastic cross sections Qₑ are obtained by integrating the measured differential cross section data. The sum total of the different experimental TCSs for different processes does not always agree well with the observed total (complete) cross sections for a given target [11]. Therefore we need a suitable theory to examine the relative importance or contributions of different TCSs to the Qₜ and to see how the relative contributions vary with respect to incident energy.
Keeping the goal as above in mind, we have presented a new, simple and effective method aimed at providing an estimate of both the total and ionization cross sections for electron scattering from atoms and molecules. The results of present calculations are compared with other calculations and experiments (where available). The results from our new methodology will provide a good guideline to the magnitude and behaviour of the cross section at intermediate and high incident energies (from threshold to 2keV). In particular, for targets like radicals and other chemically unstable and highly reactive species, wherein the experimental uncertainties could also be high. The targets studied in this work are tabulated in table 6.1.

6.2 Conclusions - pros and cons of the present methodology

Though the SCOP method employed here is basically a quantum mechanical approach, its an approximation. It has its constraints and merits, but not in isolation. They have to be looked with respect to the target in question and the applications need regarding the accuracy of the results of the relevant cross section. Let us summarize a few challenges and merits of the present theory in this context.

Since we employ spherical charge density of the target, and carry out the partial wave analysis, this method supports only the spherical part of the scattering problem. Hence the target potential is required to be a spherical potential. This approximation is justified since we aim to calculate TOTAL cross sections which are averaged over angular dependance. While this is good enough for atomic targets, it neglects the long range dipole and other anisotropic interactions in
molecules. However the dipole rotational excitation is dominant typically below 20 eV for polar molecules like H$_2$O. Vibrational excitations resulting from non spherical potentials are resonant in nature and are important usually below 10-20 eV. The absorption potential chosen in our theory is spherical and it depends on short range potentials through the local kinetic energy term. Let us note here that, since our aim is to calculate different TOTAL cross sections, the spherical charge density and potential are justified. The present energy range of interest is from threshold (≥10 eV) to 2000 eV allows us to ignore those effects. Of course, if one is interested in total (complete) cross sections then non spherical interactions must be considered [8]. Our methodology is successful in predicting all the different TCSs at medium and high energies.

We have developed and used a semi-empirical method called CSP-ic to calculate the $Q_{\text{ion}}$ from the $Q_{\text{inel}}$, and this involves the use of a ratio function $R(E_i)$. The present approximation was developed because of the lack of a direct or rigorous way to find the $Q_{\text{ion}}$ from $Q_{\text{inel}}$. The present $Q_{\text{inel}}$ is comprised of both $Q_{\text{ion}}$ and $\Sigma Q_{\text{exc}}$. To extract $Q_{\text{ion}}$ from $Q_{\text{inel}}$ we have developed the CSP-ic method, which is in itself a maiden attempt towards this goal. In this method we define a ratio, $R = \frac{Q_{\text{ion}}}{Q_{\text{inel}}}$, which has a value for $R_p$ at the peak of the $Q_{\text{inel}}$. The approximation $R_p \simeq 70-80\%$ may bring about an uncertainty of about 10 % as against the usual experimental uncertainties of 10-15 % and above. Also, this uncertainty in our method will be towards the positive side as our $Q_{\text{ion}}$ is extracted from $Q_{\text{inel}}$, which is the upper limit of $Q_{\text{ion}}$. The choice of $R_p$ in our method is semi empirical but it is required to draw out definite values of $Q_{\text{ion}}$ from complex potential calculations.

We have modified the absorption potential to allow excitations of valance shell
below the ionization threshold. The absorption potential depends crucially on $\Delta$. If we chose $\Delta = I$, ionization threshold, it would mean truncation of all excitation channels below that threshold. In the present work we have chosen to vary $\Delta$ - parameter from excitation to ionization threshold. This is not possible when the excitation threshold is very low. For example in atomic oxygen the low lying excited states are within 1 eV of the ground state. Now, $\Delta = 1$ eV will blow off the cross section to a large value. In fact, for $\Delta = 0$, $Q_{\text{inel}} = \infty$. Therefore we were compelled to strike a balance in between.

The most striking feature of our method is that it can give results on various TCS with the same frame-work of formalism. The two important cross sections required in applications are $Q_T$ and $Q_{\text{ion}}$. These two cross sections are obtained from $Q_{\text{el}}$ and $Q_{\text{inel}}$, which are the outcome of our single theoretical calculation – SCOP. The present theory can produce and predict results for a wide range of targets from atoms to molecules to clusters and even for radicals, where experiments are difficult to perform and other theories are inadequate presently. So under the same umbrella of the present method, we are capable of producing reliable various cross sections for targets from small atoms to complex polyatomic molecules. In this context the bar chart of different TCSs is important (see figure 4.3). The present method is computationally fast and found to be reasonably reliable. While deriving $Q_{\text{ion}}$ from $Q_{\text{inel}}$, we are also getting $\Sigma Q_{\text{exc}}$ as a by product [3]. Finally, we can see from our figures 3.8 and 4.8 for $He$ atom and $CH_4$ molecule that present theory can produce $Q_T/Q_{\text{TOT}}$, $Q_{\text{el}}$, $Q_{\text{inel}}$, $Q_{\text{ion}}$ and $\Sigma Q_{\text{exc}}$. This will help in determining the sum-checks of all the processes in an electron impact scattering processes [11]. This is a major advantage in our theory. Moreover our cross section calculations are obtained by making use of basic structure properties of
the molecular targets and are interpreted with reference to such target properties, adding to the validity of the theory. In a nutshell, we enlist major merits – demerits of the present theory.

Challenges:

1. Spherical approximation
2. Empirical method to find \( Q_{\text{ion}} \)
3. Lower energy limit

Advantages:

1. Quantum mechanical approach
2. Various cross sections under the same formalism
3. Simple and fast method
4. Maiden attempt to extract \( Q_{\text{ion}} \) from \( Q_{\text{inel}} \)

6.3 Future prospects

Let us think of the following opportunities in the present field and elaborate them. In chapter 2 we have presented the method of group additivity to include a large class of molecules such as the hydrocarbons. Some results are also presented in chapter 4. However there remains a vast regime of less studied molecules like aromatic hydrocarbons and larger biologically important molecules which are very relevant in the study of radiation physics and other fields. The case of fluorocarbons is similar. Extending the present method to include such groups by
our multi centre approximation may be an interesting area of work. In this area of work some of the outstanding problems and opportunities are related to the following aspects.

1. Overlapping or screening of atoms in larger molecules
2. Variable phase approach
3. Partial and dissociative ionization of molecules
4. Molecules in condensed phase and bulk properties
5. Larger biomolecules and fluorocarbons
6. Low energy regime – electronic excitations

Let us outline the above mentioned future prospects regarding the present work in detail.

1. Recently there have been theoretical attempts [12] to consider the overlap or screening of atoms or groups of atoms in larger molecules, with the aim of obtaining reliable consideration of the bonding. We are putting our own efforts in this direction.

2. The calculation presented in chapter 4 on hydrocarbons can be extended to other aromatic hydrocarbon systems and isomers which are yet to be explored. It can be used to investigate bigger molecules such as biomolecules which will prove useful in the field of medical therapies and biotechnology.

3. An alternate approach for cross section calculation is the variable phase approach. In this approach [13,14] one considers the phase shift as a function of \( r \) the target region. This method has the capacity to get reasonable phase...
shifts in the lower energy regime. Even though the basic formalism remains the same, such a method can of course improve present theory especially at lower energies.

4. Presently we have considered only the total ionization of the target molecule. Partial and dissociative ionization of molecules in other than gaseous phases are relatively difficult to handle experimentally. Our method cannot predict such individual channels, but can be extended through the consideration of the relative ratio of the individual partial fragments to its parent in the gaseous form of the same species. It will be useful to bifurcate total ionization cross section $Q_{\text{ion}}$ of a molecule into contributions from parent ionization and other dissociative products.

5. In the present work we have taken a step forward by extending our calculations to a molecule like H$_2$O in condensed phase (ice). It will be important again to be able to calculate electron collision cross sections in other condensed molecules like NH$_3$, CH$_4$, CO$_2$ (dry ice) etc. This will be quite useful in the astrophysical context. Even a first hand calculation would be welcome in this regard, since the experiments in condensed phase are likely to be very difficult.

6. Another major area that can be considered is the determination of Bulk scattering properties, like rate coefficients, macroscopic cross sections, mean free paths etc. No attempt has been made to study such properties in this thesis and we look forward more work in this direction.

As I come to the end of the thesis I feel that the best way to conclude is to pose a sweet confusion; is it really the end or the beginning of the work...?
"I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the sea-shore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me."

– Sir Isaac Newton (1642 - 1727)
Bibliography


