Chapter 4

Electron scattering at Low Energies – Theoretical Methodology

4.1 Introduction

Electron molecule interactions are important over all ranges of incident energy starting from very low impact energies (0.01 eV) to intermediate and high energies (10 keV). Perhaps Low energy collision processes are the most important processes to understand since they underpin the development of vibrant new technologies of the 21st century.

The inelastic collisions of low-energy electrons with molecules produce energetic species that are primarily driving forces for a wide variety of radiation-induced chemical reactions [1]. Low energy electrons in their impact with target molecule can produce longer-lived species like free radicals via dissociative electron attachment. Moreover, low-energy electrons are thought to contribute significantly to DNA damage. Capture of low-energy electrons via dissociative electron attachment induces specific bond cleavage [2]. Single molecule chemistry [3] and nanoscale synthesis [4] induced by low-energy electrons is demonstrated with the help of scanning tunneling microscopy. Control of chemical reactions can also be accomplished using electron-induced dissociation of molecules [5].

Thus, low-energy electron-induced reactions have significant implications in several diverse fields. So the present chapter aims to provide a theoretical framework of low energy electron impact studies.
4.2 The ab initio R-matrix Method

The R-matrix or ‘reaction’ matrix was first introduced by Wigner [5] in the 1940's to describe nuclear reactions and resonances. This method was then modified to include a wide range of atomic processes including electron-atom scattering [6] and later extended to treat scattering by diatomic molecules [7]. The R-matrix method was employed for e-LiH scattering by one of our research group members [9, 10], using the UK R-matrix diatomic code developed earlier [8].

In R-matrix method, the configuration space occupied by the incident electron is mainly divided into two regions: one is the inner region surrounding the nuclei or a sphere of radius $a$ around the target centre-of-mass, and an outer region as shown in figure 4.1. Basically R-matrix is a mathematical construct designed to communicate the necessary information between the two regions. A configuration interaction (CI) target molecular wave function $\Psi^N_I$ is expressed as a linear combination of configuration state functions (CSF) with the wave function’s symmetry in a CI expansion. The time independent Schrödinger equation for the scattering process is then given by

$$H_{N+1}\psi = E\psi \quad (4.2.1)$$

Where $H_{N+1}$ is the non-relativistic Hamiltonian for the $(N+1)$ electron system.

In the $R$-matrix theory, the internal region is chosen with radius ‘$a$’ such that the orbitals of the target molecule have negligible amplitudes at the boundary, and exchange effects may be neglected in the outer region. The $(N+1)$ electron collision complex behaves similar to a bound state in the internal region, solution of equation (4.2.1) can be written as

$$\psi = \sum_k \psi_k A_{Ek} \quad (4.2.2)$$
Figure 4.1: Partition of configuration space in fixed-nuclei $R$ – matrix theory. Radial coordinate of scattered originates at centre of mass of the molecule or centre of R-matrix sphere with $a$ radius.

In the inner region the total wave function for the system is written as [7],

$$\Psi_{k}^{N+1} = A \sum I \psi_{j}^{N}(x_{1}, ..., x_{N}) \sum j \xi_{j}(x_{N+1})a_{ijk} + \sum m \chi_{m}(x_{1}, ..., x_{N}, x_{N+1})b_{mk} \tag{4.2.3}$$

Where $A$ is the anti-symmetrization operator, $x_{n}$ is the spatial and spin coordinate of the $n^{th}$ electron, $\xi_{j}$ is a continuum orbital spin-coupled with the scattering electron and $a_{ijk}$ and $b_{mk}$ are variational coefficients determined in the calculation. The first summation ‘$j$’ runs over the target states used in the close-coupled expansion. The second summation ‘$m$’ runs over configurations $\chi_{m}$ in which all electrons are placed in the target molecular
orbitals, known as $L^2$ functions and are needed for relaxing the orthogonality imposed between the target and continuum orbitals.

The continuum orbitals are not restricted to special boundary conditions at $r = a$, so the surface or Bloch operator [11] is to be added to the Hamiltonian to make it Hermitian inside the $R$-matrix sphere. The Bloch operator is given as

$$L_{N+1} = \frac{1}{2} \sum_{i} \sum_{j} \langle \Psi_{j}^{N+1} Y_{l,m_{j}} (r_{i}) \rangle \cdot \delta(r - a) \left( \frac{d}{dr} - \frac{b-1}{r} \right) \langle \Psi_{j}^{N+1} Y_{l,m_{j}} (r_{i}) \rangle$$

(4.2.4)

And therefore the modified inner region Hamiltonian can be given by $H_{N+1} + L_{N+1}$.

Thus by diagonalizing this modified Hamiltonian, i.e

$$\langle \psi_{k} | H_{N+1} + L_{N+1} | \psi_{k} \rangle_{\text{int}} = E_{k} \delta_{kk}. \quad (4.2.5)$$

The inner region $(N+1)$ – electron eigen functions $\psi_{k}^{N+1}$ can be found. Thus in the internal region, equation 4.2.1 can be solved by rearranging it as

$$(H_{N+1} + L_{N+1} - E)\psi = L_{N+1} \psi \quad (4.2.6)$$

This has a standard solution

$$\psi = (H_{N+1} + L_{N+1} - E)^{-1} L_{N+1} \psi \quad (4.2.7)$$

Thus the inner region $\psi_{k}^{N+1}$ are eigen functions of the $(H_{N+1} + L_{N+1})$ Hamiltonian with eigen values $\varepsilon_{k}$, the inverse operator in above equation can be rewritten as an expansion to obtain

$$\psi = \sum_{k} \frac{\langle \psi_{k}^{N+1} | L_{N+1} | \psi \rangle}{(\varepsilon_{k} - E)} \psi_{k}^{N+1} \quad (4.2.8)$$

With

$$\langle \psi_{k}^{N+1} | L_{N+1} | \psi \rangle = \frac{1}{2} \sum_{j} F_{j}(r) \left( \frac{dF_{j}}{dr} - bF_{j}(r) \right)_{r=a} \quad (4.2.9)$$

Where $F_{j}(r)$ is reduced radial function computed on the $R$-matrix sphere and is given as
\[ F_i(r) = \sum_j R_{ij}(E) \left( a \frac{dF_j}{dr} - bF_j \right)_{r=a} \]  

(4.2.10)

and \( R_{ij}(E) \) is the \( R \)-matrix element given as

\[ R_{ij}(E) = \frac{1}{2a} \sum_k \frac{f_{ik}(a) f_{jk}(a)}{\varepsilon_k - E} \]  

(4.2.11)

The summation in 4.2.11 runs over the surface amplitudes \( f_{ik} \) and therefore, over the eigenfunctions \( \psi_i^{N+1} \). The surface amplitudes \( f_{ik} \) are given as

\[ f_{ik} = \left\langle \psi_i^N Y_{l,m} | \psi_k^{N+1} \right\rangle \]  

(4.2.12)

Here \( \left\langle \psi_i^N Y_{l,m} \right| \) represent channel wave functions. A channel pertains to all possible grouping of various particles involved in the scattering and is determined by a particular set of label \( l \) and \( m \).

In the outer region, the scattering electron moves under the influence long range multipole potential of the target. A single centre, no exchange, close-coupling expansion of the wave function [12] can be given as

\[ \psi = \sum_i \Phi_i \left( x_1, \ldots, x_N, \sigma_{N+1} \right) r_{N+1}^{-1} F_i(r_{N+1}) Y_{l,m} \left( \mathbf{r}_{N+1} \right) \]  

(4.2.13)

Where \( x_j = (r_j, \sigma_j) \) gives position and spin of the \( j \)th target electron \( \Phi_i \) are functions formed by the coupling of scattering electron spin \( \sigma_{N+1} \) with the target state \( \Phi_i \), and \( F_i \) are reduced radial wave functions.

On substituting equation (4.2.13) into Schrödinger equation (4.2.1) and projecting onto the channel functions \( \left\langle \psi_i Y_{l,m} \right| \), a set of coupled, second order differential equations satisfied by the reduced radial functions \( F_i \) can be written as

\[ \left( \frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} + k^2 I \right) F_i(r) = 2 \sum_j ij F_j(r) \]  

(4.2.14)
Where $V_{ij}$ is the potential matrix in the outer region and describes the coupling between channels $i$ and $j$.

$$k_i^2 = 2(E - \varepsilon_i) \quad (4.2.15)$$

Where $E$ is the total energy of the system, and $\varepsilon_i$ is the eigen energy of the target state $\Phi_i$. Equation (4.2.14) can be solved by propagating $R$ - matrix from boundary to sufficiently large distances where interaction between the scattering electron and target molecule can be assumed to be zero [13, 14]. Asymptotic expansion techniques are used to solve the outer region functions [15]. In the limit $r \to \infty$, equation (4.2.14) have linearly independent standing wave asymptotic solutions $j$ for each energetically open channel $i$.

$$F_{ij} \approx \frac{1}{\sqrt{k_i}} \left( \sin(k_i r - \frac{1}{2} l_i \pi) \delta_{ij} + \cos(k_i r - \frac{1}{2} l_i \pi) K_{ij} \right) \quad (4.2.16)$$

Where $K_{ij}$ are the coefficients which define a real, symmetric K matrix, from which the eigenphase sum $\delta$ can be extracted by diagonalizing the K matrix. Eigen phase sum is a quantity analogous to phase shift of potential scattering, which can also provide information of resonance phenomena and Ramsauer-Townsend minima. The eigen phase sum $\delta$, is given as

$$\delta = \sum_i \arctan(K_{ii}^D) \quad (4.2.17)$$

In equation (4.2.17) $K_{ii}^D$ is trace of K-matrix from which eigen phase sum $\delta$ is obtained. The sum in equation (4.2.17) runs over the open channels. The corresponding $S$- matrix is a transformation of the $K$ matrix,

$$S = \frac{1 + iK}{1 - iK} \quad (4.2.18)$$

The T – matrix can be derived from S-matrix from the equation $T = S - 1$, which provides observables like integral and differential cross sections. The integral cross section from state $i$ to $i'$ can be written as
\[
\sigma(i \rightarrow i') = \frac{\pi}{k_i} \sum_l \frac{(2S + 1)}{2(2S_i' + 1)} \sum_{i'i} |T_{li'i'}|^2
\] (4.2.19)

\(S_i\) is the spin angular momentum of the \(i^{th}\) target state, \(S\) is total spin angular momentum, \(\Gamma\) runs over all symmetries, \(l, l'\) are the orbital angular momentum quantum number of states \(i\) and \(i'\) respectively.

Applications of the R-matrix have come a long way since it was originally proposed as method. The most advanced and widely used R-matrix codes are UK molecular R-martix code introduced by Morgan et al [16] and developed over a period of about 30 years. The UK R-matrix codes are very flexible. Besides the computation of the basic scattering quantities and observables, the package has been adapted to locate (diffuse) bound states, molecular properties, resonance parameters, etc. as discussed in the proceeding section.

### 4.3 Quantemol – N Package:

Now a days, there is an increase in demand for computational procedures to obtain cross sections or aid to the interpretation of observations, as electron scattering process have many applications in different fields. So, one can think of accessing the UK molecular R-matrix code which is freely available from [17]. Despite the accuracy, only experienced scientists can use the code efficiently due to complex structure of the code. A beginner requires atleast six months to become familiar with the code in order to obtain accurate results. Also, de-bugging of the input files required by the code(s) is tantalizing. To address this problem Quantemol-N was developed by Tennyson and its group [18]. Quantemol-N is a software system that has been developed to provide graphical user interface to expert UK R-matrix code. Quantemol is linux based software package, and it consists of around 20 separate modules and is extremely complex tool to carry out low energy \textit{ab initio} electron molecule collision studies. Tutorial facility has been built into the application and some of the queries have been summoned, this proves to be a good guide for beginners.
4.3.1 UK molecular R-matrix code – The frame work of Quantemol N

Quantemol is java based user friendly software package for polyatomic version of UK molecular R-matrix code. The modules constituting the polyatomic R-matrix package code of Morgan et al. [16] makes use of the Sweden-Molecule suite of quantum chemistry codes developed by Almlof and Taylor [19] to generate target molecular orbitals and transformed integrals. The outer region modules were programmed and re-organized by Morgan. Flow chart for running a target inner and outer region calculation modules are shown in figure 4.2 to figure 4.4. A detailed description of inner and outer region modules are as follows:

Inner Region:
The flowchart in the figure 4.2 introduces systematic design for inner region module of the code. The role of each module is briefly described here.

- **SWMOL3**: generates one and two-electron integrals from the given GTO basis sets.
- **GAUSTAIL**: evaluates the contribution to each integral from outside the R-matrix sphere and adds matrix elements of the Bloch operator to the Hamiltonian as in Morgan et al. [20]
- **SWORD**: orders the atomic integrals evaluated by SWMOL3
- **SWFJK**: forms combinations of Coulomb and exchange integrals for the Fock matrix.
- **SWSCF**: performs the Hartree-Fock self consistent field (HF-SCF) optimization 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 wavefunction. It applies Schmidt orthogonalisation to orthogonalise each continuum orbital to all the target ones and then symmetric orthogonalisation to orthogonalise the continuum orbitals among themselves. The continuum orbitals that correspond to small eigenvalues of overlap matrix are deleted.
Figure 4.2: Inner region flow chart for the target calculation in UK molecular R-matrix code.

- **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 (Tennyson et al.[21]).
- **SCATCI**: designed to perform CI calculation of the target molecular and the (N+1)-complex wave functions (Tennyson et al.[22]). It employs the CSFs generated earlier by the CONGEN module. It constructs and diagonalise Hamiltonian matrix to obtain the CI expansion coefficients (eigenkets) and the corresponding eigenvalues.
Figure 4.3: R-matrix inner region flow chart for the calculation of (N+1) scattering eigenket.

- **GAUSPROP**: generates the property integrals required by DENPROP.
- **DENDROP**: constructs the transition density matrix from the target eigenvectors obtained from the CI calculation. Then it calculates the permanent dipole moment, multipole transition moments required for solving the outer region coupled equations, spherical dipole polarizability $\alpha_0$, and the diagonalised components of polarizability tensor.

**Outer Region:**

- **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. 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.

Figure 4.4: R-matrix outer region flow chart.

- **RSOLVE**: constructs the R-matrix at the interaction radius and uses RPROP 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. The output of SWINTERF is used as input.
- **EIGENP**: calculates the multichannel eigenphase sum in the manner discussed earlier, namely, by diagonalising the K-matrix and summing over channels.
- **RESON**: detects resonances and performs a least squares fit of the eigenphase sums to a Breit-Wigner profile.
- **TMATRIX**: The T-matrix is calculated from the K-matrix using standard equations.
- **IXSECS**: computes the integral cross sections from the T-matrices.
4.3.2 Necessary background knowledge/input for Quantemol

4.3.2.1 Molecular geometry

Molecular geometry or molecular structure is the three-dimensional arrangement of atoms within a molecule. The Cartesian coordinates for the distance of separation between the constituent atoms of the molecular target is doorstep for the calculations. It is important to predict and understand the molecular structure as many properties of a substance are determined by its geometry. The geometry can be obtained from sources like NIST [23], ccbd [24]

4.3.2.2 Symmetry and point group of the molecule

Symmetry operation is a movement of a body such that, after the movement has been carried out, every point of the body is coincident with an equivalent point of the body in its original orientation. Each molecule has a structure that corresponds to a symmetry operation. The full set of point symmetry operations that a particular molecule has is called a point group. There are symbols for each of the possible point groups. These symbols are often used to describe the symmetry of a molecule. Different Point groups for different molecular structures are shown in figure 4.5

Figure 4.5: Point group for different molecular structures.
4.3.2.3 Abelian group and correlation tables

Like the underlying R-matrix code, Quanemol N can handle only abelian groups, this means point groups like $C_{\infty v}$ and $D_{\alpha h}$ are not covered in the calculations. The highest allowed point group symmetry supported by the software is $C_{2h}$ and $D_{2h}$. Other permitted point groups are $D_2$, $C_s$, $C_2$ and $C_1$. So, in order to calculate the targets of high symmetry one has to convert point group to the accessible abelian group with the help of correlation tables.

4.3.2.4 Basis Sets

Basis sets in the present problem of quantum chemistry is a set of one-particle wave functions used to build the molecular orbitals. Basis set of a molecule is constructed from atomic orbitals (AO) of the constituent atoms. AO’s were constructed using Slatter Type orbitals (STOs) [25] were widely used in earlier days, Gaussian type orbitals [26] were also used for constructing basis sets, but now a days physicists prefers plane wave basis sets. Till date a huge number of basis sets are developed. Choosing basis set plays a vital role in abinitio R-matrix calculation set up as it depends on structure and bonding of the molecule. So it is most important input for the calculation. The best source for exploring basis set is an online library called EMSL Gaussian Basis Set order form [27]. There is many other basis set online libraries from which basis sets can be obtained very easily.

4.3.2.5 Resonances in scattering

A temporary trapping of an electron to form a quasi-bound or a short lived state is known as resonance. Resonances are generally characterized qualitatively by the type of resonance and quantitatively by their symmetry, position ($E^r$) and width ($\Gamma$). Obtaining these parameters is major issue of many theoretical methods. A resonance corresponds to a pole in S-matrix in the complex k-plane. Real part of the energy a parameter called resonance energy $E^r$ and the imaginary part associates another parameter called width $\Gamma$; the imaginary part is its half-width $1/2\Gamma$. A detailed discussion of this (and multichannel bound states) may be found in [28 - 29].
In the vicinity of this pole the eigenphase sum $\eta^\Delta$ undergoes a rapid increase by $\pi$ radians. The parameters of a resonance can be obtained by fitting to the Breit-Wigner formula [30].

$$\eta^\Delta (E) = \eta^\Delta_{bg} + \eta^\Delta_{res}$$

$$= \eta^\Delta_{bg} + \arctan \frac{\Gamma_r}{E - E_r}$$

(4.3.19)

Where $\eta_{bg} (E)$ is the background phase.

As resonance refers to a sharp increase in value of eigen phase sum, so it actually appears as discontinuities in the plot of the eigen phase sums. Many processes of electron scattering processes are described by the formation and behavior of resonances. Some processes such as electron attachment, dissociative recombination are thought to be entirely driven by resonances. Moreover, cross sections for all processes enhances due to resonances, in their most basic form they appear as ‘bumps’ or ‘peaks’ in the cross sections. There are different types of resonances whose modeling requires different theoretical treatments, they are as follows:

- **Shape Resonance:**

  Shape resonances have the molecular electronic ground state as their parents. They occur when the electron is trapped by the centrifugal barrier and the attractive polarisation of the molecule. The more chemical of shape resonance is that the incoming electron occupies the low-lying or lowest unoccupied molecular orbital, which is equivalent to that of electron trapping by centrifugal barrier. This has an additional constraint that the lowest orbital is not an s-orbital. Experimentally, shape resonances are seen as broad peaks in the cross section curves. Shape resonances are generally short-lived and appear as a broad features as a function of energy in the scattering observables. They provide most common route for dissociative electron attachment [31].
• **Feshbach Resonance**

Feshbach resonances are generally narrower than the shape ones, and are caused by simultaneous excitation of the target and trapping of the scattering electron, or in other words this resonance involves electronic excitation of the target which binds an extra electron. For example, an incoming electron excites He\(^+\) ion to an \(n=2\) state and if does not have enough energy, then it can be temporarily trapped in resonance state to form doubly exited He. Later on the two electrons will exchange the energy and one of them will be ejected. Thus, this resonance lies below its parent state and parent state is energetically inaccessible. These resonances provide general idea towards dissociative recombination [32].

• **Core Excited Shape resonance**

Core-excited shape resonance is combination of both shape and Feshbach resonance. Like feshbach, these resonances are associated with electronic excitation of the target, and the electron is trapped by a barrier potential as in the shape resonance. A core-excited shape resonance is associated with parents of negative electron affinity that is found lying above its parent state and can therefore decay back to its parent state or lower-lying ones.

4.3.3 **Results obtained from Quantemol**

After a successful run of Quantemol the results must be saved in order to retrieve the data, which is saved in a directory named ‘Result of calculation’ directory. The data is available as text files for analysis and use in models. A calculation file saves the physical model used for the target and other calculation details for future reference. The result can be analyzed from these files saved in the respective directories.

In this chapter we are addressing electron scattering with phosphine PH\(_3\) as a case study. This target has already been treated with high energy electron scattering in chapter 3. In low energy regime, very less work is published for the present target. Total cross sections for PH\(_3\) have been measured by Szmytkowski et al. (0.5–370 eV) [33] using the
linear transmission method. Munjal and Baluja [34] used R–matrix method to calculate the cross sections at energies (0.025–15 eV), and Bettega et al. [35] have considered energy range 1–10 eV. Recently, Vinodkumar et. al. [36] have calculated elastic cross sections \(Q_{el}\) across a wide energy range of 0.1 eV to 2000 eV. They have combine \(Q_{el}\) computed from Quanemol at low energy below ionization threshold with the cross sections produced by standard SCOP formalism in order to include the wide energy range.

It is important to precisely state the model employed in calculation so that the results may be re-produced later by other studies. Thus, during the Quanemol-N calculation, the key details of a theoretical model set up by the software are saved to a text file for the user’s information. For PH\(_3\), the software was instructed to employ the DZP basis set, the natural point group of the molecule is C\(_{3v}\) that has been reduced to its abelian C\(_3\) point group.

Ground state configuration of PH\(_3\) was specified as \(1a_1^2, 2a_2^2, 1a_2^2, 3a_1^2, 4a_1^2, 5a_1^2, 6a_1^2, 2a_2^2\) and \(7a_1^2\). From total 18 electrons, 10 electrons were frozen in the orbitals \(1a_1, 2a_1, 1a_2, 3a_1\) and \(4a_1\). Remaining electrons are allowed to move in the active space amongst the molecular orbitals \(5a_1, 6a_1, 7a_1, 8a_1, 9a_1, 2a_2, 3a_2\). The total number of generated CSF’s for the ground state is 260. The radius of the spherical boundary separating the inner and outer region was set to 10 a\(_0\) and for matching to the asymptotic boundary conditions, the R-matrix was propagated to a radial distance of 100.1 a\(_0\). The ground-state energy obtained is \(-342.47\) Hartree, and the dipole moment generated is 0.313 a.u.

We have listed in the ground-state energy, the dipole moment, Ionization potential and static dipole polarizability of the target obtained through the calculations, and these are compared with available theoretical and experimental data wherever possible. The present results for ground-state energy are in excellent agreement with the previous theoretical calculations. Our calculated Ionization potential and static dipole polarizability also agree well with the data in the literature. The present value of dipole
moment also compares fairly well with available data, as observed in Table 4.1. Vertical excitation energies for different electronic states are shown in Table 4.2.

<table>
<thead>
<tr>
<th>Ground state energy (hartree)</th>
<th>Dipole moment (a.u.)</th>
<th>Ionization energy (eV)</th>
<th>Polarizability (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>present</td>
<td>Theo</td>
<td>present</td>
<td>Theo</td>
</tr>
<tr>
<td>-342.4</td>
<td>0.313</td>
<td>0.311</td>
<td>0.225</td>
</tr>
<tr>
<td>[36]</td>
<td>[33]</td>
<td>[22]</td>
<td>[23]</td>
</tr>
</tbody>
</table>

In Fig. 4.6 we report the total cross sections for e-PH₃ scattering along with previous experimental data this molecule, and the only experimental data are that of Szmytkowski et al. [32]. A peak is observed in our data at 3.4 eV with a maximum value of cross section of around 47.0 Å². Whereas the experimental data of Szmytkowski et al. [32] shows a peak at 2.4 eV, and the peak value of cross section is 48.3 Å², which is close to present calculations. Experimental data show a strong second peak around 5 eV, but the present calculation does not exhibit such characteristics. This is a limitation of present Quanemol calculation with only 8 states.
Figure 4.6: TCS for e- PH₃ scattering.
Solid line – present TCS using Quantemol; dash line – theoretical calculations of Munjal and Baluja[33]; dash dot line – Bettega et al [34]; pentagon – experimental Szmytkowski et al.[32].

Resonances are automatically fitted to yield their parameters and these parameters can be cross checked from the available eigen phase sum data generated after the successful run. The shape resonances are detected in state 2A’ and 2A” at positions 3.23 eV and 3.02 eV respectively, as displayed in the table 4.3. This position of resonances can be verified from plots of eigen phase sum of both the states as presented in fig 4.8. The ionization potential of the molecule is 10.10 eV; therefore, we report all the excitation cross sections up to 10 eV. In Fig. 4.8 we show the inelastic or excitation cross sections from the ground state to the first five physical states whose vertical excitation thresholds are less than target ionization threshold i.e, 10 eV.
Figure 4.7: Eigen phase sum for $^{2}\text{A'}$ and $^{2}\text{A''}$ states of PH$_3$ molecule

Table 4.3: Resonance parameters and properties of PH$_3$

<table>
<thead>
<tr>
<th>State</th>
<th>Position (eV)</th>
<th>Width (eV)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{2}\text{A'}$</td>
<td>3.23</td>
<td>1.82</td>
<td>Shape</td>
</tr>
<tr>
<td>$^{2}\text{A''}$</td>
<td>3.02</td>
<td>1.90</td>
<td>Shape</td>
</tr>
</tbody>
</table>
Figure 4.8: Excitation cross sections from the ground state to other states of the PH$_3$ molecule.

Apart from low energy electron impact processes, Quantemol also produces BEB ionization cross section in energy from ionization threshold to 500 eV as a by-product of the UK R-matrix package. During the inner region calculation, Quantemol generates binding energies and kinetic energy for each occupied orbital in the molecule. Since, Binary-encounter-Bethe (BEB) formalism requires the binding energy and kinetic energy of each occupied orbital in a molecular structure for calculation of ionization cross sections. Thus, the output of inner regions is used by separate module of Quantemol to generate BEB cross sections. Figure 4.9 shows the electron-impact ionization cross section of PH$_3$ from threshold to 2,000 eV using the standard formalism of the BEB model. The ionization cross section as seen in figure 4.9, rises from threshold to a peak value of 4.32 Å$^2$ at 47.34 eV and then shows ln $E/E$ behavior as $E$ approaches greater
values. The present values are also compared with the experimental ionization cross sections reported by Mark et al [38], and we find very good matching of the present results with the measured values. The molecular orbital data used in the calculation of the BEB cross section is given in Table 4.4, which is generated at the SCF level.

![Graph](image)

**Figure 4.9:** Ionization cross section for e⁻-PH₃ scattering. Solid line – present Qₗₒₜ using Quantemol; dash line – cross sections by csp-ic method; triangle – experimentally measured cross sections by Mark et al [37].

In this section we have presented only some of the results supplied by the software Quantemol N. There are other outputs from the software which depends on target and results as required. Normally it is found that the cross section calculations are reported either in low incident energy regime or at high energy range, creating void between the two. It will be interesting to combine Quantemol and our standard SCOP method for bridging the gap of low and high energy of incident electron. The next chapter will be an attempt to fill the void and generate cross sections along a wide incident energy range and obtain the complete picture of electron interaction with few targets.
Table 4.4: Molecular orbital binding energy (B) and average kinetic energy (U) for PH$_3$ applying DZP basis set at equilibrium geometry.

<table>
<thead>
<tr>
<th>Molecular orbital</th>
<th>Binding Energy B (eV)</th>
<th>Kinetic Energy U (eV)</th>
<th>Occupation number N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A'</td>
<td>2175.47</td>
<td>2889.87</td>
<td>2</td>
</tr>
<tr>
<td>2A'</td>
<td>203.79</td>
<td>431.32</td>
<td>2</td>
</tr>
<tr>
<td>3A'</td>
<td>146.44</td>
<td>401.61</td>
<td>2</td>
</tr>
<tr>
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<td>401.61</td>
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<td>402.23</td>
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<tr>
<td>6A'</td>
<td>14.13</td>
<td>27.70</td>
<td>2</td>
</tr>
<tr>
<td>2A''</td>
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4.4 Conclusions

In this chapter we have examined electron scattering with PH$_3$ molecule at low incident energies (0.01 eV to 10 eV). Phosphine was particularly taken as it is stable and small and having even number of electrons with negligible dipole moment. It has closed shell configuration and the measurements of various cross sections of the molecule are available. The R-matrix method is one of the most successful methods for treating low energy electron collision with a variety of targets. In particular the UK molecular R-matrix code is widely used for low energy electron scattering calculation for molecules. Quantemol-N is an expert system developed to run these codes. Quantemol-N is designed so that abinitio electron molecule scattering calculations can be performed by a non specialist. The results for electron phosphine (PH$_3$) produced by Quantemol when compared with other existing results, shows a very good agreement. We also observe resonances in 2A' and 2A'' states while studying this target.
Bibliography


