Near-threshold electron impact
dissociation of molecular hydrogen

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Abstract

Electron impact dissociation of molecular hydrogen is considered to be a major route to molecular break-up in cool hydrogen plasmas. Such plasmas are found in a number of astrophysical environments and in the divertor region of tokamak fusion plasma.

At low energies, the major pathway for the electron impact dissociation of H$_2$ is through excitation to the b $^3\Sigma_u^+$ dissociative excited electronic state. The purpose of this work is to develop a theoretical formulation for this process for an arbitrary diatomic molecule, and to derive the formal expressions that describe the differential and total cross sections, which involve three fragments in the exit channel, and to study the electron impact dissociation of molecular hydrogen and its isotopomers at near-threshold energies.

Ab initio calculations of total cross sections, angular differential cross sections, energy differential cross sections and double differential cross sections are made for the $v = 0$ vibrational level of H$_2$. The effect of nuclear motion is then included in such calculations, with the dissociation taking place from the electronic ground state at different initial vibrational levels, dissociating into continuum states.

Studies of mixed isotopes are performed using the R-matrix method, and total cross sections, energy differential cross sections and rate coefficients for electron impact dissociation of H$_2$, D$_2$, T$_2$, HD, HT and DT as a function of the vibrational states are presented.

Finally, a scaling rule that describes integral cross sections as a function of the initial vibrational state, the reduced mass of the target molecule and the energy of the projectile electron is developed and compared against cross sections calculated accurately for the H$_2$ molecule and its isotopomers.
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Chapter 1

Introduction

1.1 Overview

In all phases of matter, in all areas of the universe, electrons are in great abundance and are highly reactive. The scattering of electrons from molecules is important in many natural processes in a variety of areas of physics and underlies the development of many new technologies.

Electron-molecule collision processes are important in determining the energy balance and transport properties of electrons in low-temperature gases and plasmas under a wide variety of conditions. Applied areas as diverse as plasma deposition and etching of semiconductors, gaseous high voltage switches and electrostatic precipitators for the processing of atmospheric pollutants, have all required a wide variety of electron-molecule cross section information for numerical modelling studies (Brunger & Buckman 2002).

In CO₂ and other molecular lasers, the energy necessary for population inversion is provided by indirect excitation of vibrational and rotational states of the CO₂ molecule through electron impact. Other molecules can also be included in the laser to tune its operating characteristics. A detailed knowledge of the electron vibronic collision cross sections for all the species involved is therefore required in order to optimize the laser performance (Demaria 1973).

Collisions of electrons with molecules and molecular ions play a crucial role in the physics
of the interstellar medium, as in the case of interstellar shocks (Hollenbach & McKee 1989) and X-ray irradiated dense clouds (Tiné et al. 1997), and in planetary atmospheres (Kim et al. 1997).

For example, electron rotational excitation of interstellar molecules is a significant mechanism in the cooling down of electrons. This mechanism will also establish the populations of rotational states and hence determine the intensities in the emission lines of the molecules. Electron collisions with molecules are also important in the aftermath of supernovae explosions (Yan & Dalgarno 1998). Other electron-molecule collision processes, like the dissociative attachment (DA) of electrons to hydrogen molecules and its inverse, the process of associative detachment (AD), play an essential role in many areas of physics and chemistry. In astrophysics, for example, it is assumed that the process of AD is responsible for the creation of the hydrogen molecule at early stages of the development of the Universe after the Big Bang. The occurrence of $\text{H}_2$ molecules leads to a very efficient cooling mechanism of the hot material which eventually leads to the creation of stars and galaxies (Houfek et al. 2002).

In the earth’s ionosphere, the electron impact resonant vibrational excitation of $\text{N}_2$ is similarly an important electron cooling mechanism. In the thermosphere of the outer planets, $\text{H}_2$ is in great abundance and a knowledge of electron collisions with $\text{H}_2$ is necessary to model the conductivity in order to study the interaction of the magnetosphere and the atmosphere (Strobel & Atreya 1983).

In the biological and life sciences, a knowledge of electron-molecule collisions is required to model the indirect effects of radiation on cells. When ionizing radiation passes through matter it will excite and liberate electrons. Along with damage caused directly by the radiation, these energetic electrons can themselves collide with molecules and cause damage to cells and may play a part in genetic mutation (Green 1997). Electron collision may also be important in the treatment of cancerous tumours through radiation therapy.

One of the processes involved in the electrical breakdown of air is the ionization of air molecules through electron impact (see, for example, Okada et al. 1996). An understanding of this process is required in the design of high voltage transmission systems. One of the byproducts of such a breakdown is ozone and this has been used as a method for generating ozone. However, collisions between electrons and ozone will limit the amount of ozone produced (Mason 1997).
Electron scattering is used in material science to probe the structure of materials such as molecular crystals (Dorset 1996). Electron collision cross section data is required for the design and optimisation of processes involving plasmas, such as plasma etching (Pearton & Ren 1994), magnetohydrodynamic power production (Spence & Phelps 1976), and thin film chemical vapour deposition techniques (Springer et al. 1997).

Electron-molecule collisions are of great importance in fusion plasmas. The electron impact dissociation of molecules, for instance, has been described as the most important electron impact cross section, as it determines the radical densities in the plasma (Kushner 1998). In detached divertor plasmas, vibrationally excited molecules increase plasma recombination due to dissociative attachment followed by mutual neutralization and ion conversion. Dissociative recombination, which then destroys the molecular ions present in these cold plasmas, has been found to be a dominant process (Fantz et al. 1999, Behringer & Fantz 2000, Fantz et al. 2001, Heger et al. 2001, Hey et al. 2000).

In many of the areas mentioned above, the data required for the models is not experimentally available. There is, therefore, a very practical reason for theoretical calculations of electron molecule scattering - to provide data where experiment cannot. More fundamentally, the electron molecule system with its many degrees of freedom provides a challenging test of current quantum mechanical methods and promotes the development of new techniques.

1.2 The electron-molecule scattering problem

When an electron collides with a neutral atom, there are only three likely outcomes: i) the electron scatters elastically off the atom leaving the atom in its original electronic state; ii) the electron excites the atomic electrons leaving the atom in an excited state; iii) the electron has sufficient energy to remove one or more electrons from the atom, leaving it positively ionized. Additionally, the electron can be captured by the atom to form a negative ion but this requires an extra process such as the emission of a photon.

When an electron collides with a neutral diatomic molecule, however, the story is far more complicated. Firstly, the molecule has vibrational and rotational degrees of freedom which can be excited with little energy. Any of the above outcomes of electron-atom collisions can occur
along with rotational and/or vibrational excitation of the molecule. Secondly, the interaction between electron and molecule is multicentred and non-local which leads to additional complications. Thirdly, the molecule can break up in a variety of different ways through dissociation, dissociative attachment and dissociative ionisation (see figure 1.1).

![Figure 1.1: The different possibilities for the break up of a diatomic molecule due to electron impact](image)

At electron impact energies below the molecular ionisation limit, the collision of electrons with a diatomic molecule $AB$ can lead to a number of possible processes, which include:

1. Elastic Scattering

   \[ AB + e^- \rightarrow AB + e^- \]

2. Rotational Excitation

   \[ AB(N'') + e^- \rightarrow AB(N') + e^- \]

3. Vibrational Excitation

   \[ AB(v'' = 0) + e^- \rightarrow AB(v') + e^- \]
4. Electronic Excitation

\[ AB + e^- \rightarrow AB^* + e^- \]

5. Dissociative attachment

\[ AB + e^- \rightarrow A^- + B \quad \text{or} \quad A + B^- \]

6. Impact dissociation

\[ AB + e^- \rightarrow A + B + e^- \]

Classical mechanics cannot describe anything more than the most basic elastic scattering process and the system must be treated quantum mechanically. This entails the solution of the Schrödinger equation, but because of the size of the system involved it is not possible to solve the equation exactly (even the smallest electron-molecule system, \( H_2 + e^- \), is already large enough to require an approximate approach). The different methods of electron-molecule scattering are characterized by the different approximations they make in their attempt to solve the problem as accurately as possible.

The physics behind low-energy electron molecule scattering and the different theories which can be implemented for its solution have been excellently reviewed by Morrison (1993). Details of modern computational methods used can be found in Huo & Gianturco (1995).

For the electron-molecule system, the Hamiltonian can be written in a coordinate system fixed in space as:

\[ \mathcal{H} = \mathcal{H}_N(\mathbf{x}) + \hat{T}_e(\gamma) + \hat{V}_{\text{int}}(\mathbf{x}, \gamma), \tag{1.1} \]

where \( \mathbf{x} = (\mathbf{r}, \mathbf{R}) \) includes both the electronic and nuclear coordinates of the molecule, and \( \gamma \) is the scattering electron coordinate. \( \mathcal{H}_N(\mathbf{x}) \) is the molecular Hamiltonian including all the kinetic and potential terms of the target electrons and the nuclei, \( \hat{T}_e(\gamma) \) is the kinetic energy operator of the scattering electron and \( \hat{V}_{\text{int}}(\mathbf{x}, \gamma) \) is the interaction energy between the scattering electron and the molecule. As a simplification, explicit spins have not been included.

The solution for a neutral molecular target, assuming no ionization nor dissociation, must satisfy the asymptotic boundary condition

\[ \psi(\mathbf{x}, \gamma) \sim \exp(i\mathbf{k}_0 \cdot \gamma)\psi_0(\mathbf{x}) + \frac{1}{\gamma} \sum_n \exp(i\mathbf{k}_n \cdot \gamma)f_{n0}(\mathbf{k}_n, \mathbf{k}_0)\psi_n(\mathbf{x}), \tag{1.2} \]
where $\psi_n$ is the wavefunction of the $n$th unperturbed target state, $k_0$ and $k_n$ are the initial and energetically allowed final momenta of the scattered electron and $f_{n0}$ is the scattering amplitude. The first term represents an initial plane wave incident on the ground state and the second consists of a superposition of outgoing waves associated with each of the energy accessible target states.

The interaction energy $V_{int}(x, \gamma)$ in equation 1.1 can be further split into two parts:

$$V_{int} = V_{nuc-elec} + V_{elec-elec}$$

where $V_{nuc-elec}$ is the potential between the nuclei and the scattering electron and $V_{elec-elec}$ is the repulsion between the target electrons and the scattering electron.

The potential $V_{nuc-elec}$ introduces a coupling between the nuclear and electronic motions which makes the resulting equations extremely difficult to solve. It is therefore usual to invoke the Born-Oppenheimer approximation (Born & Oppenheimer 1927, Morrison et al. 1977) which assumes that the electrons travel so quickly that they can react instantaneously to the motion of the nuclei. This makes the wavefunction separable into a nuclear part and an electronic part, which can be solved separately.

It has also been common practice to invoke the fixed-nuclei approximation where the nuclei are considered to remain stationary, simplifying the Hamiltonian even further. If required, it is often possible to approximate nuclear motion \textit{post facto} (Morrison 1993) given a series of fixed-nuclei calculations as a function of bond length.

Alternative theories of electron-molecule scattering, thus, reflect different approaches to the solution of the Schrödinger equation

$$(\mathcal{H} - \varepsilon)\Psi_\varepsilon(x, \gamma) = 0$$

for electron-molecule system eigenfunctions $\Psi_\varepsilon(x, \gamma)$ at total energies $\varepsilon$ of interest. The most natural approach would seem to be a "coupled-states" or "close-coupling" expansion in terms of the complete set of unperturbed states of the isolated molecule, viz.

$$\Psi_\varepsilon(x, \gamma) = A \sum_n F_n(\gamma) \psi_n(x),$$

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where, assuming proper spin couplings have been carried out, $A$ is the usual antisymmetrization operator. The summation in equation (1.5) includes continuum as well as bound states of the target. The one-electron "scattering functions" $F_n(\gamma)$ corresponding to bound target state $n$ play something of the role of continuum molecular orbitals, except that they depend on the initial target state specified in the boundary conditions given by equation (1.2); these functions satisfy a set of coupled equations very difficult to solve.

Some of the difficulties in the solution of the Schrödinger equation for electron-molecule scattering systems arise because the scattering particle is an electron. Since the electrons are indistinguishable, the Pauli exclusion principle requires that the total wavefunction be antisymmetric with respect to exchange of label. This requirement can be imagined as an 'exchange force' which prevents the electrons sharing the same space. In some methods it is modelled explicitly as an exchange potential $\tilde{V}_{\text{exch}}$ (Morrison 1993). Since this effect is non-local, it results in a coupling between states, and hence introduces a coupling between equations which complicates their solution for certain methods. Close-coupling methods treat exchange implicitly by forcing each of the components of the (N+1) wavefunction to be antisymmetric.

Additionally, because the scattering electron is a charged particle, polarization and correlation effects arise from the distortion of the target molecule charge cloud due to its electric field. Quantum mechanically, polarization and correlation effects arise through virtual excitation into energetically inaccessible excited electronic states. In some methods, such as those using a single centred expansion (Gianturco et al. 1995), polarization/correlation is treated explicitly by the use of a model potential. In close-coupling methods it is treated implicitly by including so-called $L^2$ configurations in the (N+1) wavefunction for which all electrons are placed in target molecular orbitals.

The scattering problem can be treated at different levels, depending on which, and to what extent, these effects are to be included in the calculation. The different levels used by electronically elastic calculations are as follows:

- **Static**

  At this level, the scattering electron is deemed to be a separate entity from the target molecule. The exchange is neglected and it is assumed that the target itself remains
undistorted by the approaching electron, i.e. the polarization is also neglected. Treating the problem at this level has the advantage that the equations are easily solved. It has the disadvantage that the answers will be wrong quantitatively and, more often than not, even qualitatively, particularly at low collision energies.

- **Static exchange (SE)**

  In this approximation, exchange is included either implicitly or explicitly. However, the target molecule is not allowed to be perturbed, assuming again that the polarization is zero. Since polarization is the major cause of Feshbach resonances, any resonant region will not be well modelled.

- **Static exchange plus polarization (SEP)**

  In this case, along with exchange, the target is allowed to be perturbed through the inclusion of polarization and correlation effects.

For electronically inelastic calculations, close-coupling methods (of which the R-matrix method is one) are used. These involve the expansion of the \((N+1)\) wave function over configurations made of target eigenfunctions multiplied by one-particle scattering functions. Such calculations will be at the SE or SEP level since, as mentioned previously, exchange is included implicitly by forcing the configurations to be antisymmetric. Polarization can be included through the addition of \(L^2\) terms as mentioned above.

### 1.3 Previous work on \(e-H_2\) scattering

#### 1.3.1 Theoretical work

Since \(H_2\) is the simplest neutral molecule, there have been a very large number of calculations of \(e-H_2\) collisions over many years. All calculations pre-1980 were extensively reviewed by Lane (1980) and this has been complemented by the review by Domcke (1991). Early calculations, performed at the static exchange level, did not see Feshbach resonances. This is understandable as polarization effects are the major contributor to the potential that traps the scattering electron in a quasi-bound state (a state of virtual excitation).
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The electronic transition between the ground state $X^1\Sigma_g^+$ and the b $^3\Pi_u$ excited state is spin forbidden and the states are only coupled through the exchange force. The transition thus provides an excellent test of different scattering methods. Three studies of this transition performed at the equilibrium fixed nuclear separation were reported simultaneously in 1985 (Schneider & Collins 1985, Lima et al. 1985, Baluja et al. 1985). All three calculations are 2-state calculations using self-consistent field (SCF) level target wavefunctions. The (N+1) wavefunctions contained $L^2$ or 'correlation' terms (all three electrons in target molecular orbitals - see equation (3.10)) which allow for the relaxation of orthogonality conditions and polarization.

Schneider & Collins (1985) used the linear algebra method. This employs the Feshbach (1958) projection operator description to formulate the separable optical potential form of the scattering equations. The resultant equations can be reduced to a set of radial, coupled integro-differential equations which are solved by means of the linear algebraic technique (Schneider & Collins 1981). Lima et al. (1985) used the Schwinger multichannel variational method (a close-coupling SEP method), which also employs the projection operator formalism. This method, developed by Takatsuka & McKoy (1981) and based on the Schwinger variational method (Schwinger 1947), incorporates the correct boundary condition automatically by using Green's functions, and so can use an $L^2$ basis without the need to tailor it for particular boundary conditions. The multichannel method was explicitly designed to treat the multicentre nature of the scattering problem. It has the advantage that by choosing Gaussian functions for the $L^2$ basis and plane waves for the incoming electron, all two-electron integrals can be calculated analytically. Another advantage is that the variational trial function does not have to be asymptotically correct and need only be a good approximation to the exact function in the region where the potential is effective. The usual approach is to introduce a partial wave expansion, where the scattering wavefunction is expressed as a sum over radial functions to take advantage of the spherical nature of the problem in the region far from the molecule:

$$F_n(\gamma) = \sum_l C_l R_{lm}(\gamma) Y_{lm}(\theta, \phi),$$

where $Y_{lm}(\theta, \phi)$ are spherical harmonics, $R_{lm}(\gamma)$ is a radial continuum function (e.g. Bessel or Coulomb functions) and $l, m$ are the usual orbital angular momentum and magnetic quantum
numbers, respectively.

As the multichannel method uses plane waves to represent the incoming electron instead of the usual partial wave expansion, it produces T-matrices using a linear momentum instead of an angular momentum representation. Baluja et al. (1985) used the R-matrix method in a similar formulation to that used in this work.

All three calculation produced very similar cross sections with those of Lima et al. (1985) particularly close to those of Schneider & Collins (1985). This is not surprising given the similarity of the (N+1) wavefunction for all three and the similarity of the methods of the latter two. There was good qualitative agreement with experimental integral cross sections.

Parker et al. (1991) employed the complex Kohn variational method (Miller & Jansen op de Haar 1987, McCurdy, Rescigno & Schneider 1987) in a four-state calculation to generate integral and differential cross sections for excitation from the ground $\chi \Sigma_g^+$ to the $b \Sigma_u^+$, $a \Sigma_g^+$ and $c \Pi_u$ states. This method was developed from the Kohn variational method (Collins & Robb 1980) in an attempt to avoid anomalous singularities in the K-matrices suffered by that method. It uses a close-coupling expansion, similar to that used in other methods, and employs Feshbach partitioning to define an effective Hamiltonian. T-matrices are calculated from the matrix elements of this effective Hamiltonian to produce integral and differential cross sections.

Rescigno & Schneider (1988) calculated the electron impact excitation of the $b^3 \Sigma_u^+$ state of $H_2$ using the complex Kohn method, with similar accuracy to the R-matrix method at near threshold energies. They performed a series of two-state, fixed nuclei calculations to find R-dependent T-matrices which they averaged using an initial vibrational function and a $\delta$-function approximation to a final continuum function. However, they made no allowance for the variation in the vertical excitation energy with the internuclear separations, $R$, and took no account of energy partitioning between the outgoing atoms and the exciting electron. This prevents their method from being used near the effective Franck-Condon threshold. Furthermore, the expression they quote for the differential cross sections gives no dependence on the isotopic mass. The effect of using the $\delta$-function approximation instead of fully calculated final continuum functions for the $v = 0$ vibrational state is discussed in chapter 6.

Branchett et al. (1990, 1991) performed ab initio R-matrix scattering calculations for electron-
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H\textsubscript{2} collisions for electronic excitation from the electronic ground state \(X^1\Sigma_g^+\) to the lowest six excited electronic states, \(3\Sigma_u^+, \Sigma_g^+, 3\Pi_u, B^1\Sigma_u^+, E, F^1\Sigma_g^+, \) and \(C^1\Pi_u, \) for all total symmetries up to and including \(2\Phi_g\) for a single \(H_2\) geometry (1.4 \(a_o\)). Total electronic excitation cross sections, as well as resonances and other eigenphase sum features were calculated to energies up to 25 eV, with good agreement with the observed electronic excitation cross sections for all the processes considered. Both resonant and non-resonant differential cross sections were presented for scattering energies of up to 20 eV, with excellent agreement with available experimental data for the elastic differential cross sections and only moderate agreement for inelastic differential cross sections.

Stibbe & Tennyson (1997a, 1998a) made a detailed study of low-energy electron-\(H_2\) collision resonances using the R-matrix method for eight total symmetries: \(2\Sigma_g^+, 2\Sigma_u^+, 2\Pi_u, 2\Pi_g, 2\Delta_g, 2\Delta_u, 2\Phi_u, 2\Phi_g, \) over a range of bond lengths from 0.8 to 4.0 \(a_o\). Resonances were fitted where possible, and positions and widths tabulated. Potential curves of individual resonant states were derived and used for nuclear motion calculations. An excellent agreement with experiment allowed them to assign all resonances below 13 eV. They also made \textit{ab initio} calculations of vibrationally resolved resonances in electron collisions with \(H_2, HD\) and \(D_2\) (Stibbe & Tennyson 1997b). The T-matrices calculated in these investigations were later used by the authors to study the near-threshold electron impact dissociation of \(H_2\) within the adiabatic nuclei approximation (Stibbe & Tennyson 1998b). They made \textit{ab initio} calculations of the rate of dissociation of \(H_2\) from its electronic ground state, \(X^1\Sigma_g^+, \) to its first excited (repulsive) state, \(3\Sigma_u^+, \) as a function of initial vibrational level. They found that near-threshold rates depend strongly on the initial vibrational level. The same T-matrices form the basis for the work presented here.

Celiberto & Rescigno (1993) used the impact-parameter method to look at excitation cross sections from the ground state to the \(B^1\Sigma_u^+\) and \(C^1\Pi_u\) states. They studied both \(H_2\) and \(D_2\) molecules and found cross sections as a function of vibrational quantum number from threshold energies to 200 eV. Celiberto et al. (1996), employing the same method and energy range, reported a scaling rule for the electronic excitation cross sections of vibrationally excited diatomic molecules using \(H_2\) and \(D_2\) as examples. The impact-parameter method is useful in the higher energy regime but cannot be used for accurate determination of cross section in the highly resonant region studied in this work.
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An extensive database of cross sections for inelastic electron-impact processes of vibrationally excited hydrogen and its isotopes has been compiled by Celiberto et al (2001). Cross sections reported for the singlet-triplet transition $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ were obtained using a semi-classical method (Celiberto et al. 1989, Bauer & Bartky 1965) for $\text{H}_2$ and $\text{D}_2$. This method should give satisfactory results at high impact electron energies and hence temperatures, but is not reliable in the near-threshold (low temperature) regime where subtle quantum effects must be correctly modelled. No data involving this transition is reported for isotopomers other than $\text{H}_2$ and $\text{D}_2$.

Celiberto et al (2001) also give analytical fits of the numerical cross section data and provide scaling relationships for the electronic excitation $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ and $X^1\Sigma_g^+ \rightarrow C^1\Pi_u$ transitions, and the processes of dissociative ionization and dissociative electron attachment. They did not extend their work onto the singlet-triplet transition under study here. Nevertheless, Celiberto et al. (1999) presented electron-molecule cross sections for excitation of vibrationally excited $\text{H}_2$ and $\text{D}_2$ molecules to electronic Rydberg states ($X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$, $B^1\Sigma_u^+$, $D^1\Pi_u$, $D^1\Pi_u$). They used the quantum mechanical impact-parameter method to obtain cross sections for the excitation to the first Rydberg states as a function of the initial vibrational levels, covering incident energies from threshold to thousands of eV. Resonant effects, however, which affect the cross section near threshold, are not accounted for, so the low energy results are probably less reliable. Within the same study, Celiberto et al. presented vibrational and mass scaling relations capable of reproducing their calculated cross sections. In particular, they introduced a mass scaling factor that accounts for an “isotopic effect” that appears when cross sections are plotted against vibrational quantum numbers. Such effect disappeared when cross sections are plotted against energy eigenvalues, relative to the ground electronic state vibrational levels. However, in the 3-body dissociative case there is a significant isotope effect that arises due to the density of final states in the outgoing dissociation channel, as will be seen in chapter 5.

1.3.2 Experimental work

Molecular hydrogen, as the most fundamental of all electron-diatomic molecule scattering systems, has been the subject of numerous experimental studies. Trajmar et al. (1983) published
a compilation and critical assessment of available cross sections for electron molecule scattering. A specific review article on H$_2$ was written by McConkey et al. (1988) dealing mostly with excitation cross sections, and the paper by Morrison et al. (1987) provides a summary of the comparisons between experiment and theory at low energies. Cross sections for elastic and inelastic processes have also been given by Tawara et al. (1990).

Recently, experimental techniques and cross section data for electron scattering of diatomic molecules were extensively reviewed by Brunger & Buckman (2002). The article updates the data compilation of Trajmar et al. (1983), accounting for differential and integral cross section measurements for elastic scattering, rotational, vibrational and electronic excitation. They also discuss experimental techniques, with particular emphasis on new developments in measurements of absolute scattering cross sections since the paper of Trajmar et al.

Brunger & Buckman compiled a great number of elastic and inelastic electron-H$_2$ scattering cross sections measurements, and compared them with theoretical calculations. At the time of the Trajmar review, there were only fragmentary measurements of absolute cross sections for the electronic excitation of molecular hydrogen by electron impact. Some of these were actual measurements of scattered electron intensities whilst most consisted of measurements of optical excitation functions. The main drawback of the latter technique is the unknown role that cascade contributions from higher lying states can make to the intensity of a given optical line.

Hall & Andrić (1984) measured near threshold angular differential cross sections (DCS) for the $b^3\Sigma_u^+$ state; Khakoo & Trajmar (1986) measured DCS for the $a^3\Sigma_g^+$, $B^1\Sigma_u^+$, c$^3\Pi_u$, and C$^1\Pi_u$ states; Nishimura & Danjo (1986) measured the DCS for the excitation of the $b^3\Sigma_u^+$ state as did Khakoo et al. (1987) and Khakoo & Segura (1994). Finally, the total excitation cross section for the $c^3\Pi_u$ state was measured by Mason & Newell (1986).

As will be seen in the remaining sections of this chapter, one of the main dissociation pathways for the H$_2$ molecule is via excitation of the lowest lying, repulsive, $b^3\Sigma_u^+$ state ("b-state") which consists of a broad continuum occupying the excitation energy interval between about 6 and 15 eV. It is the electron impact excitation of molecular hydrogen to this repulsive state that will be studied in this work, and the experimental measurements covered in the discussion that follows will refer to such case.
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Prior to the Trajmar et al. review there was only one study of absolute excitation cross sections for this state, by Weingartshofer et al. (1970) and these values have been tabulated by Trajmar et al. Since that time, there have been several other studies which have yielded absolute scattering cross sections. Hall & Andrić (1984) measured the near-threshold cross section for the b-state channel with a view to investigating the role of resonances in this scattering channel. They measured DCS at four energies, 10.5, 11.0, 11.6 and 12.0 eV and also derived integral cross sections at each of these energies. Unfortunately, they do not provide tabulated cross sections. Nishimura & Danjo (1986) measured DCS for the b-state at incident energies between 12 and 60 eV and at scattering angles from 10° and 130°. Their technique involved integrating the scattered electron signal over the energy loss range from 7 to 10.38 eV and absolute values were obtained by normalizing to the elastic electron signal, the absolute cross section for which had been obtained by normalizing to the helium cross section using the relative flow technique. Khakoo et al. (1987) also measured DCS in the 20-100 eV energy range and fitted the profile of the \( b^3 \Sigma_u^+ \) state, extrapolating the fitted Franck-Condon envelope to an energy loss value of 15 eV. Their measurements cover the angular range of 15-120°. Khakoo & Segura (1994) then extended the earlier measurements of Khakoo & Trajmar to energies below 20 eV.

Surprisingly, there have been very few measurements of cross sections for isotopomers like HD and D\(_2\). Becker & McConkey (1984) measured optical emission cross sections for the Lyman and Werner bands in D\(_2\) and found no significant isotopic effect. Buckman & Phelps (1985) published cross sections for D\(_2\) based on a Boltzmann equation analysis of their own infra-red excitation coefficients and previously published transport, excitation and ionisation coefficients. These authors also list the source of several previous cross sections sets for D\(_2\). Petrovic & Crompton (1989) derived a momentum transfer cross section for D\(_2\) based on an analysis of new measurements of the transverse diffusion coefficient and drift velocity. Their initial reference cross section was that of Buckman & Phelps; however they found that slight modifications were needed to obtain better self-consistency between calculated and measured swarm parameters.
1.4 Electron impact dissociation of H\textsubscript{2}

In order to understand the role of collision processes in plasmas and their effects on plasma properties and dynamics, it is essential to have an in-depth knowledge of the physics of these processes and detailed information on their quantitative characteristics (transition rates, cross sections, reaction rate coefficients, etc.). Modelling of cool plasmas requires the knowledge of a large number of cross sections involving electron-molecule interactions (electronic excitation, dissociation, and ionisation). As mentioned in the previous section, a lot of information, both experimental and theoretical, has been obtained to this end. Experimentally, many cross sections have been obtained from investigations of electron-molecule interactions in cross-beams experiments (Ehrhardt 1990), as well as by deconvolution of transport properties by a Boltzmann analysis of swarm data (Hayashi 1990). Theoretically, many quantum mechanical methods including resonance theories, close-coupling methods, distorted-wave approximations, and variational methods, have been developed (Bardsley 1990, Burke 1993). Most of these data, however, refer to the various processes involving the ground vibrational state of H\textsubscript{2} and D\textsubscript{2} molecules so that their use is limited to very cool plasmas in which the presence of vibrationally excited molecules can be neglected.

Under many circumstances, such as multicusp magnetic plasmas or fusion edge plasmas, the vibrational excitation of H\textsubscript{2}, D\textsubscript{2} and T\textsubscript{2} cannot be neglected, so that complete sets of cross sections involving the whole vibrational manifold of the diatoms should be known (Capitelli & Celiberto 1995). Indeed, subtle effects in the detailed physics can have consequences for the plasma. For example, the origin of many low energy H atoms observed in tokamak plasmas (Mertens et al. 2001, Tanaka et al. 2000, Hey et al. 1996, Hey et al. 2000) is believed to be the dissociation of vibrationally excited molecules (Pospieszczyk et al. 1999).

Dissociation of molecular hydrogen and deuterium has been extensively studied experimentally in the plasma physics environment (Hey et al. 1996, Hey et al. 1999, Hey et al. 2000, Mertens et al. 2001) and in electron-molecular collision experiments in gases (Ogawa et al. 1992). Those studies revealed the existence of cold atoms presumably produced by electron impact induced molecular dissociation. However, detection of the cold atoms required that one of the atomic dissociation products be released into the plasma in an excited state, so it could be observed spectroscopically before appreciable collisional heating by plasma ions.
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This means that the incident energies studied lie appreciably above the range covered by the present calculations.

Electron impact dissociation of molecular hydrogen is considered to be a major route to molecular break-up in cool hydrogen plasmas (Kushner 1998, Fantz et al. 1999). Such plasmas are found in a number of astrophysical environments and in the divertor region of tokamak fusion plasma. In all cases, it is the rate of electron impact dissociation in the near-threshold region which is the important physical quantity.

Experimentally it is difficult to measure cross sections (or rates) for electron impact dissociation of a neutral species into neutral fragments. Only limited experimental data is available for the electron impact dissociation of molecular hydrogen (Corrigan 1965, Khakoo & Segura 1994, Nishimura & Danjo 1986, Hall & Andrić 1984), all of it for H$_2$ in its $v = 0$ vibrational ground state. However, calculations by Stibbe and Tennyson (1998b, 1999) have shown that the rate of near threshold electron impact dissociation is strongly dependent on the initial vibrational state of H$_2$. The information about cross sections involving vibrationally excited states comes from theoretical considerations.

Although velocity distributions of final states within the context of dissociative autoionisation of H$_2$ and D$_2$ have been studied classically (Hazi 1974, Hazi & Wiemers 1977), up until now there has been no theoretical work on differential cross sections for electron impact dissociation. Differential cross sections are of interest for two reasons. Most of the near threshold experimental measurements of the dissociation cross sections actually measured angular differential cross sections over a limited range of angles. A more rigorous test of any theory is therefore given by a direct comparison at the angular differential cross section level, rather than by comparing with integral cross sections which are only determined experimentally with large uncertainties.

A break-up process, such as electron impact dissociation, also has an energy differential cross section. Although the energy with which the H atoms are created is of considerable interest for models of cool hydrogen plasmas (Kushner 1998, Tawara et al. 1987, Matveyev & Silakov 1995, Silakov et al. 1996), there appears to have been no previous work, either experimental or theoretical, on the energy differential cross section for the electron impact dissociation of H$_2$. Indeed, there appears not even to be a proper theoretical formulation for this pro-
cess, although related processes in nuclear physics have been studied (Ohlsen 1965, Tostevin et al. 1998). The outlines of a general theory which accounts for all the possible excitations of the molecule by electron impact but excludes break-up (ionisation or dissociation) have also been presented (Shugard & Hazi 1975)

1.5 Objectives

In an attempt towards an improved theoretical model of near-threshold electron impact dissociation of molecular hydrogen and its isotopomers, the objectives of this work are as follows:

- To develop the theoretical formulation and derive the formal expressions needed for the calculation of differential and integral electron-molecule dissociation cross sections.
- To develop and adapt existing codes that will include the effect of nuclear motion in the calculation of cross sections and dissociation rate coefficients.
- To run R-matrix calculations to determine how the mass polarization dipole of mixed isotopomers (HD, HT and DT) will affect the original H$_2$ electron scattering T-matrices and cross sections.
- To calculate differential and integral dissociation cross sections of molecular hydrogen and its isotopomers as a function of the initial vibrational state of the molecule and the energy of the incoming electron, and to compare such calculations with the available data.
- To calculate dissociation rate coefficients of molecular hydrogen and its isotopomers.
- To see if there is a scaling rule that will satisfactorily describe integral cross sections as a function of the initial vibrational state, the reduced mass of the target molecule, and of the energy of the incoming electron.
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1.6 Method

Throughout this work, the adiabatic nuclei approximation and the energy balance model of Stibbe & Tennyson (1998) is used to obtain the appropriate energy-dependent T-matrices. This model assumes that the dissociation of H$_2$ for energies below around 12 eV proceeds exclusively via electronic excitation to the first excited state of H$_2$:

$$e + H_2(^1\Sigma_g^+) \rightarrow H_2(^3\Sigma_u^+) + e \rightarrow H(1s) + H(1s) + e.$$  \hspace{1cm} (1.7)

Although most molecules have a forest of electronically excited states some 6–12 eV above their electronic ground states, at energies below around 12 eV and at the internuclear distances (or bondlengths) of interest here (between 0.8 and 4.0 \(a_0\)), only direct excitation is pertinent for H$_2$, as can be seen in figure 1.2 which illustrates the potential curves of H$_2$. Above that energy, the molecule can be excited to higher states from which it can dissociate directly or cascade down to the repulsive state. Another possibility above 12 eV is the excitation of an H$_2$ resonance state which can then decay into the \(^3\Sigma_u^+\) state. The adiabatic model used is not valid for these long-lived resonances and will not take into account the additional dissociation pathways above 12 eV.

Calculations are performed starting from the electronic ground state, at different initial vibrational states of the target molecule, dissociating into continuum states. Explanation of the methods developed and employed, together with calculational details will be given in the chapters to follow.

1.7 Layout of the thesis

Chapter 2 describes the theoretical background of the electron-molecule collision process studied. The Born-Oppenheimer approximation, fixed-nuclei formulation and the adiabatic nuclei approximation are introduced.

In chapter 3, the adiabatic molecular R-matrix theory of electron-molecule scattering is introduced. The computer codes used to implement the theory are described.

Chapter 4 describes the utilisation of the codes for the system under consideration here,
Figure 1.2: Potential curves of the first seven states of H₂ taken from the following quantum chemistry structure calculations: X ¹Σ⁺, b ³Σ⁺ from Kolos & Wolniewicz (1965a); B ¹Σ⁺, C ¹Π_u from Wolniewicz & Dressler (1988); E,F ¹Σ⁺ from Wolniewicz & Dressler (1985); c ³Π_u from Kolos & Rychlewski (1977); a ³Σ⁺ from Kolos & Rychlewski (1995).
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electron–H₂ scattering. The calculations are considerably complicated by the fact that they must be performed over a range of bond lengths, and the various tests and optimizations and other adjustments that this necessitates are outlined.

In chapter 5, the theoretical formulation behind the dissociation process, which involves three fragments in the exit channel, is developed. The δ-function approximation and the standard formulae for the calculation of rate coefficients are introduced and discussed.

Chapter 6 describes the calculation method employed. Results for the vibrational ground state of H₂ are presented, compared against available data and discussed.

Chapters 7 and 8 extend calculations to higher vibrational states and other isotopomers. Integral and differential cross sections, and dissociation rate coefficients are presented and discussed.

In chapter 9, a scaling rule to describe integral cross sections as a function of the initial vibrational state and the reduced mass of the target molecule and of the energy of the incoming electron, is derived. Scaled cross sections are compared against fully calculated ones.

In the conclusion (chapter 10), the results are summarised and suggestions for improvements to the calculation are given. Possible future directions for the work are described.
Chapter 2

Theoretical background

This chapter describes some of the powerful approximations invoked in order to solve the electron-molecule scattering problem outlined in the introduction. They rest on the separation of the electronic and nuclear variables due to the large difference between the masses of the electrons and nuclei.

2.1 The Born-Oppenheimer approximation

In this and future sections it will be necessary to distinguish between electronic and nuclear coordinates within the molecule. As before, \( r \) and \( R \) represent the electronic and nuclear coordinates of the molecule, and \( \gamma \) is the scattering electron coordinate. Primed coordinates refer to the molecular or BODY frame and unprimed coordinates to the laboratory or LAB frame. Both frames are coordinate systems having a common origin at the centre of mass of the system. The LAB frame has a space-fixed \( z \) axis (often chosen along the initial momentum \( k_o \)), whereas that of the BODY frame is directed along a symmetry axis of the molecule.

Atomic units will be used throughout this chapter, where \( e = \hbar = m_e = 1 \), and length, mass, charge, and energy are given in units of \( a_o \approx 5.29 \times 10^{-11} \text{ m} \), \( m_e \approx 9.110 \times 10^{-31} \text{ kg} \), \( e \approx 1.602 \times 10^{-19} \text{ C} \) and 2 Ry \( \approx 27.2 \text{ eV} \), respectively.

Using the coordinate system employed by Lane (1980), the molecular Hamiltonian in equation (1.1) can be written as
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\[ H_N(r, R') = H_N^{(e)}(r, R') + H_N^{(n)}(R') \]  
(2.1)

with the electronic contribution given by

\[ H_N^{(e)}(r, R') = -\frac{1}{2} \sum_{j=1}^{N_e} \nabla_j^2 - \sum_{\alpha=1}^{N_n} \sum_{j=1}^{N_e} \frac{Z_\alpha}{|r_j - R'_\alpha|} + \sum_{i=1}^{N_n} \sum_{j > i}^{N_n} \frac{1}{|r_i - r_j|} \]  
(2.2)

and the nuclear contribution by

\[ H_N^{(n)}(R') = -\frac{1}{2} \sum_{\alpha=1}^{N_n} \frac{1}{M_\alpha} \nabla_\alpha^2 + \sum_{\alpha=1}^{N_n} \sum_{\beta > \alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|R'_\alpha - R'_\beta|} \]  
(2.3)

for a molecule containing \( N_e \) electrons and \( N_n \) nuclei with charges and masses \( Z_\alpha \) and \( M_\alpha \), respectively. The interaction potential energy is

\[ \hat{V}_{\text{int}}(\gamma, r, R') = -\sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|\gamma - R'_\alpha|} + \sum_{j=1}^{N_n} \frac{1}{|\gamma - r_j|} \]  
(2.4)

The Born-Oppenheimer approximation permits a separation of nuclear and electronic variables so that one can first solve the electronic problem with the nuclei fixed, obtaining electronic wavefunctions and energies that depend parametrically on the nuclear coordinates. The nuclei are then assumed to move in response to the adiabatic potential energy corresponding to the stationary electronic state. The wavefunction is written as a product of electronic and nuclear functions. Perturbation theory may then be used to correct for the “break-down” of the Born-Oppenheimer approximation. These corrections are found to be important for highly excited vibrational states (large nuclear speeds), high-Rydberg electronic states (small electron speeds), or “curve crossings” where two or more electronic energy curves (or surfaces) cross or come very close to one another.

In the electron-molecule scattering problem, continuum (scattering) states will have positive total energy with respect to the ground state of the target molecule. A product form for the wavefunction such that the fixed-nuclei (FN) electronic wavefunction, \( \Psi_{\epsilon}^{FN} \), depends only parametrically on \( R' \) is required,

\[ \Psi_{\epsilon}(\gamma', r', R') = \Psi_{\epsilon}^{FN}(\gamma', r'; R') \chi(R') \]  
(2.5)
Chapter 2: Theoretical background

The most convenient electronic coordinates here are those referred to the BODY frame. The approximate form given in equation (2.5) is valid in two limiting cases. When the electronic wavefunction $\psi^{FN}_e$ is highly localized in the vicinity of the molecule, as in the case of narrow (long-lived) resonances, the nuclei respond adiabatically to the potential energy of the "negative-molecule-ion complex", and well-defined rotational-vibrational states, described by resonant wavefunctions $\chi$, are established. At the other extreme is the "impulse limit", appropriate for non-resonant scattering at energies sufficiently high that the velocities of the incident and outgoing electrons are considerably larger than those of the nuclei. In this limiting case, the nuclear wavefunction $\chi$ is simply the unperturbed nuclear wavefunction for the molecule. When neither the adiabatic nor the impulse limits apply, it is necessary to treat the nuclei and the electrons on a more equal footing. This can be accomplished by a full coupled-state (LAB-frame) approach, in which the system wavefunction is expanded in terms of unperturbed target wavefunctions as in equation (1.5), or more efficiently by some type of frame-transformation procedure wherein one takes full advantage of the (Born-Oppenheimer) separation of electronic and nuclear variables when the electron is near the molecule, but relaxes this assumption at larger electron-molecule separations. When the scattering is dominated by a resonance, a "decaying electronic state" formalism is appropriate. The electronic state is represented as a bound state immersed (and decaying into) an adjacent continuum. In the Born-Oppenheimer separation of equation (2.5), $\psi^{FN}_e$ represents the decaying (nonstationary) state, and the nuclear wavefunction, $\chi$, is determined by a complex nuclear potential energy.

2.2 Fixed-nuclei formulation

If the nuclei are held fixed, only the electronic Hamiltonian for the electron-molecule system needs to be considered:

$$H^{(e)}_{N+1} = -\frac{1}{2} \nabla_\gamma^2 + H^{(e)}_N + \hat{V}_{int}$$  \hspace{1cm} (2.6)

where $\nabla_\gamma^2$ is the Laplacian in terms of BODY-frame coordinates $\gamma$, and where the target contribution and the electron-molecule interaction potential energy are given by equations (2.2) and (2.4), respectively. For the sake of simplicity, the interaction potential between nuclei (sec-
Chapter 2: Theoretical background

The second term in equation (2.3) is now included in $H^{(e)}_N$. Also, the development of the formalism will be restricted to diatomic target molecules. It is convenient to refer all electronic coordinates to the BODY frame, where the polar axis is taken along the internuclear line, i.e., $\hat{z} = \hat{R}$. The electronic states of the target molecule are represented by the functions $\psi^{(e)}_{\alpha}(r'; R')$, with $r' = (r'_1, r'_2, ..., r'_{N_e})$ representing all the target-electron coordinates collectively (spin is implicit); $\alpha$ stands for all electronic quantum numbers. These $N_e$-electron wavefunctions satisfy the target electronic Schrödinger equation

$$[H^{(e)}_N - E^{(e)}_{\alpha}(R')]\psi^{(e)}_{\alpha}(r'; R') = 0 \quad (2.7)$$

where the eigenvalues $E^{(e)}_{\alpha}(R')$ are the electronic "curves" for the molecular states.

In the electron-molecule scattering problem, one seeks for solutions of the $N_e+1$ electron Schrödinger equation

$$\left( H^{(e)}_{N+1} - \epsilon \right) \Psi^{FN}_{\epsilon}(\gamma', r'; R') = 0 \quad (2.8)$$

where $(\gamma', r') = (\gamma', r'_1, r'_2, ..., r'_{N_e})$ denotes all $N_e+1$ electron coordinates, collectively. In equation (2.8) the entire nuclear Hamiltonian is omitted. This fixed nuclei approximation is expected to be valid in "fast collision" conditions, i.e., provided that the collision time, $\tau_c$, is much less than the periods for nuclear rotation, $\tau_R \geq 10^{-12} s$, or vibration, $\tau_v \approx 10^{-14} s$. If the fixed nuclei approximation is valid, then rotational and vibrational excitation cross sections can be obtained by carrying out fixed-nuclei calculations for a sufficiently large number of different internuclear separations and then calculating the matrix element of the transition operator between the appropriate rotational and vibrational eigenfunctions

$$T_{nuj,n'j'} = \langle nj' | T_{nu}(\mathbf{x}) | nj \rangle \quad (2.9)$$

where $\mathbf{x}$ denotes the totality of inter-nuclear coordinates, and $n, v, j$ and $n', v', j'$ denote the electronic, vibrational and rotational quantum numbers respectively.

If the energy of the incident electron is of the same order as the rotational or vibrational energy levels splittings, then equation (2.9), which assumes that all these levels are degenerate, is invalid. If the collision energy is close to a narrow resonance where the time of the collision
becomes long, the fixed nuclei approximation breaks down. This causes particular difficulties in the case of vibrational excitation, since the transfer of energy between the motion of the incident electron and the vibrational motion of the target is most efficient in resonance regions. The approach also breaks down when strong long range interactions are present, as in the case of electron scattering by polar molecules (again the time of collision becomes long).

Nevertheless, fixed-nuclei calculations can still be used as the initial step in the calculation of reliable cross sections even in the above circumstances (Lane 1980, Temkin 1976). Among them, the frame transformation approach of Chang & Fano (1972) sub-divides configuration space into a number of regions, depending on the distance of the scattered electron from the target molecule. The fixed-nuclei approximation is then used only in the inner region where electron exchange and detailed electron-electron correlation are strong, but where the scattered electron spends only a small part of the total collision time. Calculations in the proximity of the nuclei are performed with electronic coordinates referred to the BODY frame of the molecule. At some carefully chosen boundary, one transforms the solution to the LAB frame, and introducing the nuclear Hamiltonian, continues solution of the resulting equations into the asymptotic region. The idea is to find a transformation radius such that \( H_N^{(n)} \) can be safely ignored in the inner region and complicated exchange interactions (always short range) can be ignored in the outer region. This is the concept behind the R-matrix method that will be used in this work and described in chapter 3.

### 2.3 Adiabatic nuclei approximation

Regardless of how the fixed-nuclei problem is solved, it is still not complete; the motion of the nuclei must be incorporated. As outlined above, this is properly done by means of a frame transformation from the BODY frame (with fixed nuclei) to LAB frame (with moving nuclei). However, there are many circumstances under which the inner region can be extended to infinity, i.e., the entire problem can be solved to a very good approximation in the BODY frame, ignoring \( H_N^{(n)} \) entirely. The frame transformation then reduces to a single step at the end of the calculation. This procedure is formally equivalent to the adiabatic approximation applied to the nuclear motion. It is generally valid when the incident electron energy is well above threshold,
the scattering amplitude is not dominated by strong long-range interactions, and the scattering
is non-resonant.

From a classical point of view, a "fast collision" should be well represented by a fixed nuclei
approximation. The "fast collision" is alternatively described as the "impulse" and "adiabatic
nuclei" limit by different authors. Indeed, it is appropriate to say that the nuclei experience
an impulse due to the collision. On the other hand, the electron adiabatically responds to the
instantaneous position of the nuclei, and therefore is not sensitive to the instantaneous momenta
of the nuclei. The Born-Oppenheimer approximation is valid and the total (electronic and
nuclear) wavefunction may be approximated by equation (2.5), rewritten for the diatomic case
(suppressing spin coordinates) as

$$\psi_{\alpha o \nu o}(\gamma', r', R') \equiv \psi_{\alpha o \nu o}^{FN}(\gamma', r'; R') \chi_{\alpha o \nu o}(R') \tag{2.10}$$

where $\chi_{\alpha o \nu o}$ is the unperturbed initial nuclear-state wavefunction of the target, and $\nu o$
represents vibrational and rotational quantum numbers for this state. Taking the overlap of the
asymptotic form of equation (2.10) with an arbitrary final nuclear-state wavefunction $\chi_{\alpha\nu}(R')$,
the adiabatic nuclei (AN) approximate scattering amplitude for a transition $\alpha o \nu o \rightarrow \alpha \nu$ is
obtained

$$f_{\alpha \nu, \alpha o \nu o}(k_{\alpha}, k_{o}) = \langle \chi_{\alpha\nu}(R') | f_{\alpha \nu, \alpha o \nu o}^{FN}(k_{\alpha}, k_{o}; R') | \chi_{\alpha o \nu o}(R') \rangle \tag{2.11}$$

where $f_{\alpha \nu, \alpha o \nu o}^{FN}$ is the fixed-nuclei (FN) scattering amplitude corresponding to an electronic tran-
sition $\alpha o \rightarrow \alpha$. The non-primed $k_{\alpha}$ and $k_{o}$ denote LAB-frame momenta. The integration over
molecular orientation $R$ requires that $f_{\alpha o \nu o}$ be calculated only once for a particular value of $R$,
most conveniently on the BODY frame. A simple application of the rotation operation effects
the transformation to the LAB frame. The integration over $R$ requires that $f_{\alpha \nu, \alpha o \nu o}^{FN}$ be computed
for several values of $R$ and that a numerical quadrature be performed.

As will be described in the chapters that follow, the present work will only account for
vibrational excitation, assuming an isotropic rotational distribution.
Chapter 3

Molecular R-matrix theory and implementation

In the first half of this chapter, the theory behind the molecular R-matrix method is introduced. In the second, the UK molecular R-matrix group computer codes developed to utilize the method are described.

3.1 Overview

R-matrix theory is based on the division of configuration space into two regions by a spherical R-matrix boundary at $r = a$ centred at the molecular centre of mass (figure 3.1). The boundary is placed so that the inner region contains the electronic charge distribution of the target molecule. The contributions which dominate the Hamiltonian are different in the two regions. In the inner region ($r < a$), the scattered electron lies within the molecular charge cloud and short-range interactions, such as exchange, polarization and correlation must be taken into account. The target molecule plus scattering electron behave analogously to a bound state, and rigorous quantum chemistry methods can be used to find the wavefunctions. In the outer region ($r > a$), where exchange and detailed electron-electron correlation are negligible, the scattering electron moves in the long-range multipole potential of the target and a single-centre
expansion of the wavefunction can be used.

In the inner region, a set of scattering energy-independent eigenfunctions and eigenvalues are found for the (N+1) system using a close-coupling expansion. The final inner region wavefunction is a linear combination of these with the coefficients found by matching with the computed outer region functions at the boundary using the R-matrix. This is a sum over quantities related to the overlap integrals of the internal and external wavefunctions evaluated at the surface of the sphere and the eigenenergies of the internal states (Burke et al. 1977).

The R-matrix basis at the boundary is then propagated outwardly (Morgan 1984) until it can be matched with asymptotic solutions. Asymptotic expansion techniques (Noble & Nesbet 1984) are used to find the K-matrix (related to the asymptotic solutions of equation (1.2) and described later) from which eigenphase sums can be calculated. Physical observables such as cross sections can be derived from the T-matrix which is found trivially from the K-matrix.

The development of the R-matrix approach to electron atom and electron molecule scattering is well documented by Burke & Berrington (1993). The discussion that follows refers to diatomic molecules only, since polyatomic molecules are better tackled with different bases and modules.

3.2 The inner region

In the inner region, scattering energy-independent target plus scattering electron (N+1) eigenfunctions are found by diagonalizing the inner region Hamiltonian using Configuration State Functions (CSFs) as the basis in a close-coupling expansion. The CSFs are composed of linear combinations of Slater determinants; these determinants involve spin orbitals with the spatial part of these being linear combinations of functions defined on the nuclei and on the centre of gravity of the molecule.
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Figure 3.1: Splitting of configuration space in the R-matrix model
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3.2.1 Target molecular orbitals

The target molecular orbitals use a basis set of Slater-type atomic orbitals (STOs) (Slater 1960). These are of the form:

$$\rho_{ik}(n, l, m, \zeta_i, r_k) = \sqrt{\frac{(2\zeta_i)^{2n+1}}{(2n)!}} r_k^{n-\frac{1}{2}} e^{-\zeta_i r_k} Y_{lm}(\hat{r}_k)$$

(3.1)

where \(i\) is the orbital index, \(k\) is the nuclear centre index and \(r_k\) is the distance from the nuclear centre \(k\). \(n, l\) and \(m\) have their usual meanings, \(\zeta_i\), the orbital exponent, can be varied to provide optimum representation, and the \(Y_{lm}\) are complex spherical harmonic functions.

The target molecular orbitals, \(\gamma_l\), are linear combinations of these atomic orbitals (LCAO),

$$\gamma_l = \sum_{ik} D_{lik} \rho_{ik},$$

(3.2)

with the coefficients \(D_{lik}\) found through a self-consistent field (SCF) or Hartree-Fock calculation (see, for example, Bransden & Joachain 1983), or by some other method.

The electrons are placed in certain combinations of these target molecular orbitals multiplied by spin functions to produce configuration state functions (CSFs) \(\phi_i^N\) of different total symmetries. In the case of \(H_2\), as it is a few-electron molecule, all possible combinations can be used. For larger molecules, the number of configurations is too great for all of them to be considered and only certain combinations are chosen. The target molecular wavefunctions \(\psi_i^N\) are linear combinations of all the CSFs of the wavefunction’s symmetry in a configuration interaction (CI) expansion

$$\psi_i^N = \sum_i c_{ii} \phi_i^N.$$  

(3.3)

The coefficients \(c_{ii}\) are found by diagonalizing the \(N\)-electron target Hamiltonian matrix given by

$$< \phi_i^N | H_N | \phi_i^N >,$$

(3.4)

using the configuration state functions as a basis.

3.2.2 Continuum molecular orbitals

The target molecular orbitals are supplemented with a set of continuum orbitals which describe the scattering electron in a partial wave expansion (Salvini & Burke 1984). These are centred
on the centre of mass of the molecule and take the form:

\[ \eta_{il}(r_G) = \frac{1}{r_G} u_{il}(r_G) Y_{lm}(\hat{r}_G) \]  

(3.5)

where the \( Y_{lm} \) are complex spherical harmonics and the \( u_{il} \) are effective atomic orbitals found by solving the model, single channel scattering problem:

\[ \left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V_0(r) + k_I^2 \right] u_{il}(r) = 0 \]  

(3.6)

subject to the boundary condition

\[ u_{il}(0) = 0 \]  

(3.7)

and the logarithmic boundary condition

\[ \frac{1}{u_{il}} \frac{du_{il}}{dr} \bigg|_{r=a} = b. \]  

(3.8)

In equation (3.6), \( k_I^2 \) are the eigenenergies in Rydbergs, \( V_0 \) is an arbitrary potential and \( b \) is an arbitrary constant, both taken to be zero in this work.

Since only a finite number of terms can be used in the expansion of the R-matrix, the artificial boundary condition (3.8) necessitates a correction to the R-matrix known as the Buttle correction which is added to the diagonal elements of the matrix (Buttle 1967). It is discussed further in section 3.2.4.

The continuum functions may be Lagrange orthogonalized to several of the target molecular orbitals (Tennyson et al. 1987) and then all the orbitals are Schmidt orthogonalized. The final continuum orbitals are therefore of the form:

\[ \xi_j(r_G) = \sum_i \frac{1}{r_G} u_{ij}(r_G) Y_{im}(\hat{r}_G) + \sum_i \rho_i^A B_{ij} + \sum_i \rho_i^B C_{ij} \]  

(3.9)

where \( A \) and \( B \) are the two nuclear centres.

### 3.2.3 Inner region (N+1) eigenfunctions

The inner region scattering energy-independent eigenfunctions of the target molecule plus scattering electron system are represented by:

\[ \psi_k^{N+1} = A \sum_l \psi_l^{N}(X_1, ..., X_N) \sum_j \xi_j(X_{N+1}) a_{lj} + \sum_m \chi_m(X_1, ..., X_N, X_{N+1}) b_{mk}. \]  

(3.10)
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where \( \mathcal{A} \) is the anti-symmetrization operator, \( \chi_n = (r_n, \sigma_n) \) with \( r_n \) the spatial coordinate and \( \sigma_n \) the spin state of the \( n^{th} \) electron. \( \bar{\xi}_j \) is a continuum molecular orbital spin-coupled with the scattering electron.

The first term summation runs over CI target states. It accounts for one electron in a continuum state with the remaining electrons in a target state, known as a 'target+continuum' configuration.

The second term summation runs over configurations \( \chi_m \) in which all the electrons are placed in target molecular orbitals and are known as \( L^2 \) functions. This provides a relaxation of orthogonality conditions introduced by the orthogonalization of the continuum orbitals to the target orbitals and accounts for polarization and correlation. Scattering calculations with larger molecules cannot use full CI due to computational limitations. This complicates the situation for the \( L^2 \) functions in these cases and there are different types of \( L^2 \) functions depending on whether the electron is placed in unoccupied virtual orbitals or in occupied orbitals (Gillan et al. 1995).

The coefficients \( a_{ijk} \) and \( b_{mk} \) are found through diagonalization of the relevant Hamiltonian matrix. This is constructed by first finding the individual matrix elements appropriate to the target configurations \( \phi_i^N \) of which the CI target states \( \psi_i^N \) are a summation (equation (3.3)). These are then combined together using the coefficients of the target configurations \( c_{ij} \) calculated in the CI calculation, in a step known as the CI contraction. In this way, the size of the Hamiltonian matrix to be diagonalized can be reduced.

The Hamiltonian matrix elements can be divided into three groups: i) elements between two target+continuum configurations, ii) elements between a target+continuum configuration and an \( L^2 \) configuration and iii) elements between two \( L^2 \) configurations. It can be shown that no reduction in matrix size will be made by the CI contraction for case iii), but considerable savings are made for i) with smaller savings for ii) (Tennyson 1996).

In early R-matrix calculations (such as those of Branchett & Tennyson 1990, Branchett et al. 1990, Gillan et al. 1988), a problem arose at this point due to inconsistencies in the phase of CI coefficients. The signs of each of the coefficients of the target CI expansion (the \( c_{ij} \) in equation (3.3)) obtained explicitly when generating the target \( \psi_i^N \) can differ from those.
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obtained implicitly when generating the (N+1) eigenfunctions \( \psi_k^{N+1} \) (Tennyson 1997). The reason for this is the ordering of spin-orbitals within a configuration. The ALCHEMY configuration generator (Liu & Yoshimine 1981), adapted for use in the UK R-matrix codes and used here, orders by symmetry and index. For \( \text{H}_2 \) (D\(_{\infty h}\) symmetry) this ordering is \( 1\sigma_g, 2\sigma_g, ..., 1\sigma_u, 2\sigma_u, ..., 1\pi_u, 2\pi_u, ..., 1\pi_g, 2\pi_g, ... \) etc.

Tennyson (1997) considered an \( \text{H}_2 \) target of \( ^1\Pi_u \) symmetry of which two typical configurations are \( 1\sigma_g 1\pi_u \) and \( 1\sigma_u 1\pi_g \). If the total (N+1) symmetry is \( ^2\Sigma_g^+ \), the appropriate (N+1) configurations would be \( 1\sigma_g 1\pi_u 1\pi_u \) and \( 1\sigma_u 1\pi_g 1\pi_u \) with \( j \) denoting the index of a continuum orbital. The first configuration is in the correct spin-orbital ordering but the second needs to be rewritten as \( 1\sigma_u 1\pi_u 1\pi_g \). This interchange causes a change of sign in the Slater determinant and hence an inconsistency with the target CI coefficient.

This problem was tackled by using a dummy continuum electron in an (N+1) calculation immediately following the target CI calculation. All integrals related to this electron were set to zero so that the (N+1) calculation simply reproduced the target CI vectors but with the necessary sign changes to particular coefficients that would make them consistent with the real (N+1) calculation (Gillan 1994, Orel et al. 1991).

However, this method is inefficient as it requires a repeat diagonalization of the target Hamiltonian. It also does not ensure that the sign of off-diagonal transition moments in the outer region is the same as the implicit sign in the internal region which can lead to problems (Tennyson 1997). A new solution has been realized by Tennyson (1997) which is based on the analysis of configurations. When an (N+1) configuration is generated, a phase factor is calculated for that configuration by finding the number of swaps required to reorder the spin-orbitals correctly. This is then multiplied by the relevant coefficients. This is the method used for the calculations reported here.

Since the target molecular functions are considered zero at the distance of the R-matrix boundary, the logarithmic boundary condition on the continuum functions (equation (3.8)) also holds for the (N+1) total wavefunction, i.e.:

\[
\frac{1}{\psi^{N+1}} \frac{d\psi^{N+1}}{dr} \bigg|_{r=a} = b
\]  

(3.11)

This logarithmic boundary condition has the effect of making the Hamiltonian Hermitian by
cancelling out surface terms which arise from the scattering electron kinetic energy operator (Oberoi & Nesbet 1973, Oberoi & Nesbet 1975).

As an alternative, the Hamiltonian can be made Hermitian through the use of the Bloch operator, \( L_{N+1} \), (Bloch 1957) which can be added to the Hamiltonian and which cancels the surface terms. The Bloch operator is of the form:

\[
L_{N+1} = \frac{1}{2} \sum_{i=1}^{N+1} \sum_{j} \left| \psi_{i}^{N+1} Y_{l} m_{j}(r_{i}) \right> \delta(r_{i} - a) \left( \frac{d}{dr_{i}} - \frac{b}{r_{i}} \right) \left< \psi_{i}^{N+1} Y_{l} m_{j}(r_{i}) \right|
\]

The coefficients in (3.10) are found by diagonalization of the modified inner region (N+1) Hamiltonian,

\[
< \Omega_{N+1}^{p} | H_{N+1} + L_{N+1} | \Omega_{N+1}^{p} >
\]

where the \( \Omega_{N+1}^{p} \) are the basis configurations, to obtain the inner region (N+1) eigenfunctions \( \psi_{k}^{N+1} \).

### 3.2.4 Generation of the R-matrix

Once the energy-independent inner region eigenfunctions have been found, it is necessary to find the energy-dependent R-matrix in order to match the inner and outer region wavefunctions.

The general Schrödinger equation for the system is

\[
H_{N+1} | \Psi > = E | \Psi >
\]

where \( \Psi \) is the total (N+1) wavefunction and \( E \) is the total energy of the system, incorporating the scattering energy. By adding and subtracting the operator \( L_{N+1} \) and rearranging this becomes:

\[
(H_{N+1} + L_{N+1} - E) | \Psi > = L_{N+1} | \Psi >
\]

By multiplying each side by the inverse of the left hand side operator this becomes:

\[
| \Psi > = (H_{N+1} + L_{N+1} - E)^{-1} L_{N+1} | \Psi >
\]

Remembering that the inner region \( \psi_{k}^{N+1} \) are eigenfunctions of the \( (H_{N+1} + L_{N+1}) \) Hamiltonian with eigenvalues \( e_{k} \), the inverse operator can be rewritten as an expansion over these
functions to obtain
\[ |\Psi> = \sum_k |\psi_k^{N+1}> <\psi_k^{N+1}|L_{N+1}|\Psi> (e_k - E). \] (3.17)

The reduced radial functions \( F_i(r) \) and the surface amplitudes \( f_{ik}(r) \) are defined as:
\[ F_i(r) = <\psi_i^NY_{l_i m_i} | \Psi> \] (3.18)
\[ f_{ik}(r) = <\psi_i^NY_{l_i m_i} | \psi_k^{N+1}> \] (3.19)

where \( <\psi_i^NY_{l_i m_i} | \) are channel functions. By substituting in the Bloch operator (equation (3.12)), it can be shown that at the R-matrix boundary (Gillan et al. 1995):
\[ F_i(a) = \sum R_{ij}(E) \left( a \frac{dF_j}{dr} - bF_j \right)_{r=a} \] (3.20)

in which the R-matrix is defined as
\[ R_{ij}(E) = \frac{1}{2a} \sum f_{ik}(a) f_{jk}(a) \] (3.21)

The summation in equation (3.21) is over the surface amplitudes \( f_{ik} \) and hence in turn over the \((N+1)\) eigenfunctions \( \psi_k^{N+1} \). Clearly it is necessary to truncate this expansion at some point to include only a finite number of terms \( N_{ll} \) for each value of \( l \). The error from this truncation is exacerbated by the boundary conditions at the R-matrix sphere given in equations (3.7) and (3.8) and is known as the Gibbs phenomenon (Gillan et al. 1995). As mentioned previously, in order to correct at least partially for this, a ‘Buttle correction’ (Buttle 1967, Shimamura 1978) is added to the diagonal terms of the R-matrix and takes the form:
\[ B_{ll}(E) = \frac{1}{2a} \sum_{i=N_{l_i l_i + 1}}^{\infty} \frac{|u_{l_i}(a)|^2}{\frac{1}{2} k_{l_i}^2 - E} \] (3.22)

where \( k_{l_i}^2 = 2e_{l_i} \) with \( u_{l_i} \) and \( e_{l_i} \) the eigenvector and eigenvalues respectively of equation (3.6). The Buttle correction is evaluated as part of the continuum numerical function generation.
3.3 Inner region program modules

The UK Molecular R-matrix scattering package has been developed over many years by a variety of people. The inner region code was originally based on the quantum chemistry package ALCHEMY (McLean 1971) developed by IBM in the 1970s with many modifications to make it suitable for the scattering problem (Noble 1982b).

The flow diagram for the inner region calculation of the target is shown in figure 3.2 and for the (N+1) calculation in figure 3.3

**INTS** is the integral generator that produces 1-electron, 2-electron and property integrals. It has been modified to restrict the range of the radial coordinate to within the R-matrix boundary (Noble 1982b). Its first task is in providing the necessary integrals to be used by the SCF module in setting up the target. It is later used to provide the integrals for the (N+1) calculation.

**SCF** performs a self consistent field (Hartree-Fock) calculation to produce target orbitals $\gamma_i$ (equation (3.2)), from linear combinations of atomic orbitals.

The module **NUMBAS** (Salvini & Burke 1984) generates continuum orbitals of the form of equation (3.5) in accordance with equations (3.6), (3.7) and (3.8). It is possible to specify different potentials $V_0$ either by inputting a potential or by allowing the module to work out a potential from the SCF vectors. The Buttle correction (equation (3.22)) is also calculated by this module although for file handling reasons it is passed down to be outputted by **MOS**.

The module **MOS** initially takes as its input the target orbitals from SCF or elsewhere, to output molecular orbitals used in the target CI calculation. In the scattering calculation it takes both the target orbitals and the continuum orbitals from **NUMBAS** and outputs orthogonalized molecular orbitals. It has options to Schmidt orthogonalize all the orbitals and to Lagrange orthogonalize the continuum orbitals to a specified number of target orbitals (Tennyson et al. 1987). The purpose of the latter is to eliminate linear dependence between the continuum and the target orbitals. Each time a Lagrange orthogonalization is performed, the linear combinations of continuum orbitals most linearly dependent on a target orbital are removed. **MOS** also computes the amplitudes of the continuum orbitals on the R-matrix boundary.

Module **TRANS** takes atomic integrals produced by **INTS** and multiplies them by combi-
Figure 3.2: Flow diagram of the inner region target state calculation. Red arrows indicate input required by the scattering calculation, green arrows indicate input required by the outer region codes.
Figure 3.3: Flow diagram of the inner region (N+1) scattering calculation. Green arrows indicate input required by the outer region codes.
nations of molecular orbital coefficients to transform them into molecular integrals which are required for the construction of the Hamiltonian.

The module CONGEN generates configuration state functions (CSFs) with appropriate spin and symmetry couplings. The molecular orbitals to be included are hand picked by the user. It is used initially to produce CSFs for the target and then later for the target plus scattering electron (N+1) system. When a CSF is generated, the module also computes a phase factor to keep the phases between the target and (N+1) system consistent (Tennyson 1997). CONGEN has been adapted for scattering calculations to allow explicit coupling of the continuum electron to individual target states (Noble 1982a).

SCATCI (Tennyson 1996) performs the configuration interaction calculation first for the target and then for the (N+1) system. It takes the configurations generated by CONGEN and the molecular integrals supplied by TRANS to build up the Hamiltonian matrix. In the case of the (N+1) system, the matrix is first contracted using the target eigenstate vectors. For both the target and (N+1) system, the matrix is then diagonalized to find all the eigenvectors and eigenvalues.

The module DENPROP (Gillan 1992) calculates dipole and quadrupole moments of the target from the target CI vectors produced by CI and the property integrals produced by INTS. The moments are used in the outer region calculation.

3.4 The outer region

As mentioned in the overview, in the outer region, exchange and detailed electron-electron correlation between the scattering electron and the target electrons are ignored. The wavefunction is expanded in a single-centre close-coupling expansion over target states (Gillan et al. 1995):

$$\Psi = \sum_i \tilde{\phi}_i (\vec{x}_1 \ldots \vec{x}_N, \sigma_{N+1}) \tau_{N+1}^{-1} F_i (\tau_{N+1}) Y_{l m_i} (\vec{r}_{N+1}),$$  \hspace{1cm} (3.23)

where \(x_j=(\vec{r}_j, \sigma_j)\), the position and spin of the \(j\)th target electron, the functions \(\tilde{\phi}_i\) are formed by coupling the scattering electron spin \(\sigma_{N+1}\) with the target state \(\phi_i\), and the \(F_i\) are reduced radial wavefunctions.

Substituting this equation into the Schrödinger equation and projecting onto the channel
Chapter 3: Molecular R-matrix theory and implementation

functions \( \psi_i Y_{l_i m_i} \) in a similar procedure to that used in the inner region, gives a set of coupled, homogeneous differential equations for \( F_i \):  
\[
\left( \frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2 \right) F_i(r) = 2 \sum_j V_{ij}(r) F_j(r),
\]
(3.24)

where \( V_{ij} \) is the potential matrix in the outer region which describes the coupling between the channels \( i \) and \( j \) and

\[
k_i^2 = 2(E - \epsilon_i),
\]
(3.25)

with \( \epsilon_i \) the eigenenergy of target state \( \phi_i \) and \( E \) the total energy of the system.

For a neutral molecule, the reduced radial functions \( F_i \) of equation (3.23) in the limit \( r \to \infty \) have asymptotic solutions \( j \) for each open channel \( i \) of the form:

\[
F_{ij} \sim \frac{1}{\sqrt{k_i}} \left( (\sin(k_i r - \frac{1}{2} l_i \pi) \delta_{ij} + \cos(k_i r - \frac{1}{2} l_i \pi) K_{ij} \right)
\]
(3.26)

and \( F_{ij} \sim 0 \) for closed channels. Equation (3.26) defines the K-matrix elements \( K_{ij} \), which contain all the scattering information.

Equation (3.24) is solved by first propagating the R-matrix (Baluja et al. 1982, Morgan 1984) from the boundary to the asymptotic region (in this work taken as \( r = 150 \ a_0 \)). Gailitis (1976) asymptotic expansion techniques are then used to solve for the outer region functions (Noble & Nesbet 1984).

The eigenphase sum, \( \delta \), which can be used for the detection and parametrization of resonances can be found directly from the diagonalized K-matrix \( K_{ii}^{DK} \):

\[
\delta = \sum_i \arctan(K_{ii}^{DK}),
\]
(3.27)

where the sum is over the open channels.

The scattering matrix \( S \) is a transformation of the K-matrix,

\[
S = (1 + iK)(1 - iK)^{-1}.
\]
(3.28)

The T-matrix which is formed trivially from the S matrix, \( T = S - 1 \), can be used to derive physical observables such as integral and differential cross sections. For example, the integral cross section for excitation from state \( i \) to \( i' \) is (Burke 1982b):

\[
\sigma(i \to i') = \frac{\pi}{k_i^2} \sum_S \frac{(2S + 1)}{2(2S_i + 1)} \sum_{M_L} |T_{ii'j'}^{AS}|^2,
\]
(3.29)
where $S_i$ is the spin angular momentum of the $i_{th}$ target state, $S$ is the total spin angular momentum and $\Lambda$ is the total electronic angular momentum projected onto the molecular axis.

### 3.5 Outer region program modules

A flow diagram for the outer region codes used in this work and some of the other available modules is shown in figure 3.4. Unless otherwise stated, the codes have been developed by Morgan.

**INTERF** provides the interface between the inner and outer regions. It takes the boundary amplitudes and CI vectors generated in the inner region to construct the surface amplitudes $f_{ik}$ of equation (3.19) and adds the Buttle correction to the diagonal of the R-matrix. It also passes on target and channel data.

**RSOLVE** takes the output of **INTERF** and uses subroutines RPROP (Baluja et al. 1982, Morgan 1984) to propagate the R-matrix to the asymptotic region and CFASYM (Noble & Nesbet 1984) to solve the wavefunctions in this region and hence to calculate K-matrices.

**EIGENP** takes the K-matrices and produces eigenphase sums using equation (3.27). A standard Breit-Wigner (1936) form can then be fitted to the eigenphase sum by **RESON** (Tennyson & Noble 1984) which is a program for automatically detecting and parameterizing resonances. Difficult resonances can be parametrized using **TIMEDEL** and **FITLOR** (Stibbe 1997).

**TMATRIX** transforms K-matrices into T-matrices. For adiabatic vibrational calculations, it has the option to average a set of T-matrices at different bond lengths over vibrational functions which are inputted separately, although this has not been used in the present work.

The T-matrices (vibrationally averaged or otherwise) can then be used by modules such as **IXSECS** and **DCS** (Malegat 1990) which calculate integral and differential cross sections respectively.

Other modules, such as **MQDT**, which calculates multichannel quantum defects, and **RATES**, which gives the integration of collision strengths over a Maxwellian temperature distribution, are also available.
Figure 3.4: Flow diagram of the outer region scattering calculation. Other modules are also available (see text for details).
Electron–H$_2$ calculations over a range of bond lengths

In this chapter, the general methods of the previous chapter are discussed for the specific case of the electron–H$_2$ collision calculations performed over a range of bond lengths. Various optimizations and tests undertaken by Stibbe & Tennyson (1998a) to allow the most accurate calculation given limited computing power are described, as are the difficulties encountered and overcome in the implementation of their calculation.

4.1 Introduction

The previous chapter gave an overview of the theory and implementation of a general scattering calculation using the R-matrix method. As will be seen in the following chapters, the T-matrices used in the dissociation cross sections and rates calculations were originally calculated in an investigation of H$_2^-$ resonances as a function of the internuclear distance $R$ by Stibbe & Tennyson (1998a). Such resonances are known to be associated with the low-lying H$_2$ target states and in this calculation, the first seven states are explicitly considered: $X^{1\Sigma_g^+}$, $b^{3\Sigma_u^+}$, $a^{3\Sigma_g^+}$, $c^{3\Pi_u}$, $B^{1\Sigma_u^+}$, $E,F^{1\Sigma_g^+}$, $C^{1\Pi_u}$. In order to include a reasonable number of vibrational levels, calculations were performed over a range of bond lengths from 0.8 to 4.0 a$_0$ on a grid.
Extending calculations from a single bond length to a range of bond lengths complicates matters considerably. The basis functions that represent the target and continuum orbitals may work well at one particular bond length but might be very poor at another. The phases of the molecular orbital vectors are arbitrary and can jump around from bond length to bond length. Their ordering can also change with bond length as their energies cross. Additionally, at different bond lengths, the effects of higher target states not considered in the calculation might be significant.

To ensure continuity of the quality of the calculations across bond length, detailed testing and optimizing of the calculation for the range of geometries and energies considered needs to be performed.

### 4.2 Choice of basis STOs

The quality of the calculation rests to a large part on the quality of the target, and hence on the quality of the basis set used to represent it. Given a basis set, it is possible to determine the errors in target state energy as a function of bond length by comparing the energies obtained using that basis with 'exact' energies. These 'exact' energies are taken from the following quantum chemistry structure calculations which used very large basis sets: $X^{1\Sigma^+_g}$, $b^{3\Sigma^+_u}$ from Kolos & Wolniewicz (1965a); $B^{1\Sigma^+_g}$, $C^{1\Pi_u}$ from Wolniewicz & Dressler (1988); $E,F^{1\Sigma^+_g}$ from Wolniewicz & Dressler (1985); $c^{3\Pi_u}$ from Kolos & Rychlewski (1977); $a^{3\Sigma^+_g}$ from Kolos & Rychlewski (1995).

The basis used in this calculation is a set of Slater-type orbitals (STOs) of the form shown in equation (3.1). The criteria determining the choice of the STOs are that the basis be small enough to be manageable but flexible enough to be able to represent the target sufficiently at all the bond lengths used. The set taken by Stibbe & Tennyson as a starting point was that used by Branchett et al. (1991) which has 13 STOs and had been optimized at the SCF level for the lowest seven target states at the single equilibrium geometry of $R = 1.4$ $\text{a}_0$. The task of optimization here is a more complicated one, and requires the optimization of
Chapter 4: Electron–H₂ calculations over a range of bond lengths

the energy at the CI level over a range of 33 bond lengths for all seven target states.

Any rigorous mathematical method for optimizing the 13 exponents of the basis set for all the different target symmetries over all the internuclear separations would be impossible if the ζ variables are taken as coupled. The first assumption was thus that each ζ exponent can be optimized independently of the rest. Even assuming this, changing the value can improve the representation at certain bond lengths but worsen it at others. A degree of arbitrariness is also therefore required in deciding the optimum value.

Taking each STO in turn, Stibbe & Tennyson performed a series of target CI calculations, varying the ζ exponent of the STO about its original value and the internuclear separation over the range under consideration. The target threshold energies from these calculations were compared with the ‘exact’ values to give an energy error of the target thresholds for every value of ζ at each internuclear separation. These were then plotted for all the target symmetries. From each graph, the ζ which best minimises the energy for that symmetry can be found.

In most cases, changing a particular ζ affected only one target state strongly, and so the best value for that target state could be taken. However, there were problems with interdependency between states. Some of the difficulties encountered, as well as the approach made to overcome them, are described in Stibbe (1997).

The final basis set used by Stibbe & Tennyson is given in table 4.1. The errors in the target state energies using the final basis are shown in figure 4.1.

<table>
<thead>
<tr>
<th>Orbital Exponent</th>
<th>Orbital Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1sσ₉</td>
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</tr>
<tr>
<td>2sσ₉</td>
<td>1.176</td>
</tr>
<tr>
<td>2σ₉</td>
<td>0.500</td>
</tr>
<tr>
<td>2pσ₉</td>
<td>1.300</td>
</tr>
<tr>
<td>2pπₚ</td>
<td>0.574</td>
</tr>
<tr>
<td>3pπₚ</td>
<td>0.636</td>
</tr>
<tr>
<td>3dπₚ</td>
<td>1.511</td>
</tr>
</tbody>
</table>

Table 4.1: The ζ exponents of the STOs used by Stibbe & Tennyson (1998a). The orbitals are denoted g or u to show the symmetry of the two-centred orbitals they are used to create.
Figure 4.1: Error in the target state energies as a function of bond length using the basis set optimized and used by Stibbe & Tennyson (1998a)
4.3 Continuum molecular orbitals

In previous, fixed-nuclei, calculations, the arbitrary potential $V_0$ used in the calculation of the continuum orbitals (equation (3.6)) has often been taken as an expansion of the isotropic parts of the SCF wavefunction potential (e.g. Branchett et al. 1990, Gillan et al. 1987). However, in Stibbe & Tennyson's calculation, $V_0$ was taken as zero, resulting in bond length-independent continuum functions. At the equilibrium bond length of 1.4 Å, there was a negligible difference in the results of calculations using the different orbital sets suggesting that the numerical flexibility of the functions was, in this case, sufficient to cope with the reduced physicality of the model.

The effect of changing the number of continuum functions was also tested. Increasing the maximum eigenenergy of the orbitals increases the number of possible continuum functions, the number of available channels and hence the size of the calculation. When this energy was increased from 5 Ryd to 8 Ryd there was a large increase in the total number of continuum orbitals from around 270 to 370, although only a subset of these orbitals is used for each total symmetry. The increased number of orbitals only had a very small effect on the final eigenphase sum (see figure 4.2).

In order to test the effect of increasing the maximum allowed eigenenergy to a region in which there is resonance activity, two-state calculations ($X \ ^1\Sigma^+_g + B \ ^1\Sigma^+_u$) with maximum values of 6 Ryd and 12 Ryd were performed. Figure 4.3 shows that increasing the maximum value makes very little difference to the eigenphase sum even in a resonance region (there is a resonance of $^2\Sigma^+_g$ symmetry at around 10 eV).

A maximum energy of 6 Ryd (with 307 orbitals made up of $58 \sigma_g$, $42 \sigma_u$, $42 \pi_u$, $42 \pi_g$, $42 \delta_g$, $27 \delta_u$, $27 \phi_u$ and $27\phi_g$ orbitals) was taken as a compromise.

The continuum orbitals are initially Lagrange orthogonalized to several target molecular orbitals to alleviate linear dependence problems. This procedure in effect removes continuum orbitals that are too similar to target molecular orbitals. In this calculation the continuum orbitals were orthogonalized to the lowest two $\sigma_g$, one $\sigma_u$, two $\pi_u$ and one $\pi_g$ target orbitals.
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Figure 4.2: Effect of increasing the maximum allowed eigenenergy (and hence the number) of the continuum orbitals from 5 (solid) to 8 Ryd (dashed) (Stibbe 1997).

Figure 4.3: Effect of increasing the maximum allowed eigenenergy (and hence the number) of the continuum orbitals from 6 (solid) to 12 Ryd (dashed) in a resonance region (Stibbe 1997).
Chapter 4: Electron-$H_2$ calculations over a range of bond lengths

4.4 Effect of increasing the number of target states

Earlier coupled state calculations (Fliflet & McKoy 1980, Baluja et al. 1985, Schneider & Collins 1985, Lima et al. 1985, Parker et al. 1991, Branchett et al. 1990) were performed only at the $H_2$ equilibrium bond length. At this bond length there is a gap in energy between the first seven and the next highest energy level of around 1.6 eV. However, at the extremes of the bond lengths considered by Stibbe & Tennyson, the higher target states are much nearer in energy. They therefore decided to determine the effects of increasing the number of target states included in the calculation to thirteen. It was found that going up in energy, the representation of the target states became more and more unphysical. This can be put down to the fact that the STO basis set is very compact and has been optimized for the first seven states. To model the higher states properly, a larger basis set including more diffuse functions would be required. These diffuse functions would be likely to leak out of the R-matrix sphere and require such an increase in its size to contain the functions that many of the efficiencies gained from using the R-matrix method would be lost.

The effect of increasing the number of target states to 13 on the $^2\Sigma_g^+$ symmetry eigenphase sum up to 13.5 eV can be seen in figure 4.4. At the equilibrium bond length of 1.4 $\text{a}_0$, as expected, the additional states made very little difference. At a bond length of 4.0 $\text{a}_0$, it began to make a difference at energies over around 10 eV. Given the unphysicality of the extra states and since the energy region at the bond length where the effect is important is not sampled, they decided to leave the extra states out of the calculation.

4.5 Final model

The T-matrices finally used in this work are those calculated in the investigation of $H_2^-$ resonances mentioned above as a function of the internuclear distance, $R$ (Stibbe & Tennyson 1997a, 1997b, 1998a). Calculations were performed for $R$ ranging from 0.8 $\text{a}_0$ to 4.0 $\text{a}_0$ in steps of 0.1 $\text{a}_0$ using the UK Molecular R-matrix suite of programs (Gillan et al. 1995). Target wavefunctions were represented using a full configuration interaction (CI) within a basis set of $4\sigma_g$, $3\sigma_u$, $3\pi_u$ and $3\pi_g$ Slater-type orbitals (STOs) which have been energy optimized (Stibbe
Chapter 4: Electron–\(H_2\) calculations over a range of bond lengths

Figure 4.4: Effect of increasing the number of target states in the calculation from 7 (blue) to 13 (red) for a) the equilibrium bond length \(R = 1.4\; a_0\) and b) the most extreme bond length used in this calculation, \(R = 4.0\; a_0\) (Stibbe 1997).
& Tennyson 1998a) for the lowest seven target states \((X^1\Sigma_g^+, b^3\Sigma_u^+, a^3\Sigma_g^+, B^1\Sigma_u^+, C^1\Pi_u, c^3\Pi_u, E,F^1\Sigma_g^+)\), those retained in the close-coupling expansion. Numerical functions were used to represent the continuum electron in a truncated \((l \leq 6, m \leq 3)\) partial wave expansion. Such calculations yielded full T-matrices linking all the (open) target states included in the calculation; in this particular case only the off-diagonal portion of the matrix which links the \(X^1\Sigma_g^+\) and \(b^3\Sigma_u^+\) states is of interest. Full details can be found in Stibbe & Tennyson (1998a).

Calculations performed by Stibbe & Tennyson and described in this chapter have proven to be extremely successful in tracking resonances where previous methods have failed. The complicated structure revealed by their study showed even more resonance activity than had previously been suspected (Stibbe & Tennyson 1998a). Furthermore, calculations for vibrationally resolved resonances were presented and compared with experimental studies for \(e\)-\(H_2\), \(e\)-\(D_2\) and \(e\)-\(HD\), with excellent agreement (Stibbe & Tennyson 1997b). This supports the reliability of the data obtained by their method and opens a wide range of possibilities for its use in other calculations such as adiabatic vibrational calculations, among which the electron impact dissociation of molecular hydrogen can be included, and non-adiabatic calculations. Details of further applications can be found in Stibbe (1997).
At low energies, the major pathway for the electron impact dissociation of H₂ is through excitation to the b ³Σ⁺. In this chapter, the equations that describe the electron impact dissociation process within the adiabatic nuclei approximation, which involves three fragments in the exit channel, are derived. These equations are then used to derive the commonly used δ-function approximation. Finally, the necessary equations to calculate the dissociation rates are stated.

5.1 Theory behind the dissociation process

Consider the electron impact dissociation of a molecule XY,

\[ XY + e \rightarrow X + Y + e \]  \hspace{1cm} (5.1)

To describe the three particles in the final state of this break-up process, Jacobi coordinates, illustrated in figure 5.1, are adopted.

Parameters that refer to the outgoing electron are labelled with subscript e and, for the purpose of generality, those denoting the outgoing atoms with subscripts X and Y. Let the three particles have masses \( m_e, m_X, m_Y \) and position vectors \( \mathbf{r}_e, \mathbf{r}_X \) and \( \mathbf{r}_Y \) (which are referred
Figure 5.1: Jacobi coordinates.
to an arbitrary fixed or uniformly moving origin). The following coordinates are defined:

\[ s = m_e r_e + m_x r_x + m_y r_y \]  \hspace{1cm} (5.2)

\[ s_{e-XY} = r_e - \frac{m_x r_x + m_y r_y}{m_X + m_Y} \]  \hspace{1cm} (5.3)

\[ s_{X-Y} = r_X - r_Y \]  \hspace{1cm} (5.4)

and reduced masses:

\[ \mu_{e-XY} = \frac{m_e(m_X + m_Y)}{M} \]  \hspace{1cm} (5.5)

\[ \mu_{X-Y} = \frac{m_X m_Y}{m_X + m_Y} \]  \hspace{1cm} (5.6)

\[ M = m_e + m_X + m_Y \]  \hspace{1cm} (5.7)

The associated momenta \( \mathbf{P}, \mathbf{p}_{e-XY} \) and \( \mathbf{p}_{X-Y} \) may be written in terms of the momenta

\[ \mathbf{p}_i = m_i \frac{d}{dt}(\mathbf{r}_i)(i = e, X, Y) \]  \hspace{1cm} (5.8)

as follows:

\[ \mathbf{P} = \mathbf{p}_e + \mathbf{p}_X + \mathbf{p}_Y \]  \hspace{1cm} (5.9)

\[ \mathbf{p}_{e-XY} = \frac{\mu_{e-XY}}{m_e} \mathbf{p}_e - \frac{\mu_{e-XY}}{m_X + m_Y}(\mathbf{p}_X + \mathbf{p}_Y) \]  \hspace{1cm} (5.10)

\[ \mathbf{p}_{X-Y} = \frac{\mu_{X-Y}}{m_X} \mathbf{p}_X - \frac{\mu_{X-Y}}{m_Y} \mathbf{p}_Y \]  \hspace{1cm} (5.11)

The total kinetic energy \( E_{tot} \) in this arbitrary coordinate system is

\[ E_{tot} = \frac{p_{e-XY}^2}{2\mu_{e-XY}} + \frac{p_{X-Y}^2}{2\mu_{X-Y}} + \frac{p^2}{2M} = E_{e-XY} + E_{X-Y} \]  \hspace{1cm} (5.12)

since \( \mathbf{P} = 0 \) in the centre of mass system.

According to the previous definitions (Ohlsen 1965, Tostevin et al. 1998), the differential cross section for the break-up in Jacobi coordinates may be written as
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\[ \frac{d^2 \sigma}{d \Omega_{e-XY} dE_{e-XY}} = \frac{2\pi \mu_{e-XY}}{\hbar^2 k_e} |T_{\nu \rightarrow c}(E_{tot}, E_{e-XY})|^2 \rho(E_{e-XY}) \]  

(5.13)

with \( h k_e \) the relative momentum of the electron and XY target. \( \rho \) is referred to as the "phase space factor" or as the "density of final states". \( T_{\nu \rightarrow c} \) represents the T-matrices associated with the transition from bound state \( \nu \) to the continuous state \( c \) of XY.

Starting from a constant cross section in the phase space of the six independent variables involved, the density of final states will be proportional to the total number of "states" available to the three final particles which is given by Fuchs (1982) as

\[ dN = h^{-6} p_{e-XY} dE_{e-XY} d\Omega_{e-XY} d\Omega_{X-Y}(E_{tot} - A) \]  

(5.14)

where \( E_{tot} \) is fixed at a value \( A \). The only constraint assumed so far is the total available kinetic energy. This constraint introduces a relation between \( E_{e-XY} \) and \( E_{X-Y} \) and allows \( E_{X-Y} \) to be eliminated by integration over \( E_{X-Y} \), leaving only five independent variables (\( E_{e-XY} \) and four angles). Using the coordinate transformations given in table 1 of Fuchs, we can write equation (5.14) as

\[ dN = h^{-6} p_{e-XY}^2 p_{X-Y} d\Omega_{e-XY} d\Omega_{X-Y} d\Omega_{X-Y} d\Omega_{X-Y} d\Omega_{X-Y}(E_{tot} - A) \]

\[ = h^{-6} p_{e-XY} \mu_{e-XY} dE_{e-XY} d\Omega_{e-XY} p_{X-Y} \mu_{X-Y} dE_{X-Y} d\Omega_{X-Y} \delta(E_{tot} - A) \]

\[ = h^{-6} p_{e-XY} \mu_{e-XY} p_{X-Y} \mu_{X-Y} dE_{e-XY} d\Omega_{e-XY} d\Omega_{X-Y} dE_{X-Y} d\Omega_{X-Y} \delta(E_{tot} - A) \]  

(5.15)

Following Ohlsen (1965) and Fuchs (1982),

\[ \rho(E_{e-XY}) = \frac{dN}{d \Omega_{e-XY} dE_{e-XY}} \]

\[ = \int \frac{dN}{d \Omega_{e-XY} dE_{e-XY} d\Omega_{X-Y} dE_{X-Y}} dE_{X-Y} d\Omega_{X-Y} \]

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\[ = 4\pi h^{-6} \int p_{e-XY} \mu_{e-XY} p_{X-Y} \mu_{X-Y} \delta(E_{tot} - A) dE_{X-Y} \]

\[ = 4\pi h^{-6} \int p_{e-XY} \mu_{e-XY} p_{X-Y} \mu_{X-Y} \delta(E_{tot} - A) \frac{dE_{tot}}{\partial E_{tot} / \partial E_{X-Y}} \]

\[ = 4\pi h^{-6} \mu_{e-XY} \mu_{X-Y} \left[ \frac{p_{e-XY} p_{X-Y}}{\partial E_{tot} / \partial E_{X-Y}} \right]_{E_{tot}=A} \] (5.16)

But

\[ \frac{\partial E_{tot}}{\partial E_{X-Y}} = \frac{\partial E_{tot}}{\partial p_{X-Y}} \frac{\partial p_{X-Y}}{\partial E_{X-Y}} \] (5.17)

Thus, using equation (5.12),

\[ \frac{\partial E_{tot}}{\partial E_{X-Y}} = p_{X-Y} (2\mu_{X-Y} E_{X-Y})^{-1/2} = p_{X-Y} p_{X-Y}^{-1} = 1 \]

one finally obtains

\[ \rho(E_{e-XY}) = 4\pi h^{-6} \mu_{e-XY} \mu_{X-Y} p_{e-XY} p_{X-Y} \] (5.18)

In terms of energy,

\[ \rho(E_{e-XY}) = 2^{-3} (\pi)^{-5} (h)^{-6} (\mu_{e-XY} \mu_{X-Y})^{3/2} (E_{e-XY} E_{X-Y})^{1/2} \] (5.19)

or

\[ \rho(E_{e-XY}) = 2^{-3} (\pi)^{-5} (h)^{-6} \left( \frac{m_e m_X m_Y}{M} \right)^{3/2} [E_{e-XY} (E_{tot} - E_{e-XY})]^{1/2} \] (5.20)

This expression for \( \rho \) can now be used in the expression for the double differential cross sections, equation (5.13) to obtain a general, double differential, break-up cross section in terms of T-matrices:

\[ \frac{d^2 \sigma}{d\Omega_{e-XY} dE_{e-XY}} = \frac{\mu_{e-XY}}{4\pi^4 h^8 k_e} \left( \frac{m_e m_X m_Y}{M} \right)^{3/2} [E_{e-XY} (E_{tot} - E_{e-XY})]^{1/2} \]
Recasting this general break-up expression into the notation used by Stibbe & Tennyson (1998b) for the electron impact dissociation of H₂, \( E_{e-XY} = E_{out} \) represents the energy of the scattered electron; \( E_{tot} = E_{in} - D_v \), where \( E_{in} \) is the energy of the incoming electron and \( D_v \) the vibrational state dependent dissociation energy; \( E_{X-Y} = E_{ke} \), where \( E_{ke} \) is the kinetic energy of the dissociating atoms. Finally, \( m_X = m_Y = m_H \), with \( m_e \) and \( m_H \) the masses of the electron and hydrogen atom, respectively.

\( \hbar k_e \), the relative momentum of the electron and XY target, can be approximated by \( p_e \), assuming the standard Born-Oppenheimer approximation based on \( (m_X + m_Y) \gg m_e \). With this, the double differential cross section can be expressed as

\[
\frac{d^2\sigma}{d\Omega dE_{out}} = \frac{m_e^2 m_H^{3/2} E_{out}^{1/2} (E_{in} - D_v - E_{out})^{1/2}}{16\pi^4 \hbar^7 E_{in}^{1/2}} | T_{\nu \rightarrow e}(E_{in}, E_{out}) |^2
\]

(5.22)

or, in terms of the scattering amplitude, \( f_{\nu \rightarrow e} \),

\[
\frac{d^2\sigma}{d\Omega dE_{out}} = \frac{m_H^{3/2} E_{out}^{1/2} (E_{in} - D_v - E_{out})^{1/2}}{64\pi^6 \hbar^3 E_{in}^{1/2}} | f_{\nu \rightarrow e}(E_{in}, E_{out}) |^2
\]

(5.23)

where use has been made of the following relation between T-matrices and scattering amplitudes (Morrison & Sun 1995):

\[
T_{ij} = \frac{i\hbar^2}{2\pi m_e} f_{ij}
\]

(5.24)

Equation (5.24) depends upon the normalization used and upon the choice of relationships between the scattering matrices \( S \) and transition matrices \( T \), \( T = S - 1 \) and unit normalization are used. For a further discussion on this topic, see Morrison & Sun (1995).

Stibbe & Tennyson (1998b) proposed an energy balance model which generalised the adiabatic nuclei approximation to the break up problem of electron impact dissociation. Within their model, T-matrices for transitions to the continuum are obtained from fixed nuclei inelastic (off-shell) T-matrices by
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Figure 5.2: Distribution of incoming electron energy, $E_{in}$, from a particular initial vibrational level, $v$ in the energy balance model. The lower curve is the $X^1Σ_g^+$ and the upper one is the dissociative $b^3Σ_u^+$. $D_v$ is the conventional dissociation threshold, $E_{in}$ the energy of the incoming electron, $E_{ke}$ the asymptotic kinetic energy of the dissociating atoms, $E_{out}$ the energy of the scattered electron and $E_{extra}$ the energy available after dissociation. $\epsilon(R)$ is the fixed-nuclei or vertical target electronic excitation energy. The dotted curve represents the $v=0$ nuclear wavefunction.

\[ T_{\nu\rightarrow c}(E_{in}, E_{out}) = \langle \Xi_c(E_{ke}, R)|T_{ij}(\epsilon(R) + E_{out}, E_{out}, R)|\Xi_\nu(R) \rangle \]  

(5.25)

where $R$ represents the internuclear distance or bondlength, and $\epsilon(R)$ is the fixed-nuclei or vertical target electronic excitation energy. $\Xi_\nu$ represent bound nuclear wavefunctions and $\Xi_c$ represent continuum nuclear wavefunctions. Figure 5.2 illustrates the distribution of incoming electron energy, $E_{in}$, from a particular initial vibrational level, $v$ in the energy balance model. Within this model, a particular $E_{in}$ will determine, for each vibrational state, the energy available after the dissociation process has taken place, $E_{extra}$. But the energy of the scattered electron, $E_{out}$, and of the dissociating atoms, $E_{ke}$, can be varied in any proportion and are swept from their minimum to their maximum values.
Stibbe and Tennyson used energy normalized continuum functions (in atomic units),

\[
\Xi_c(R \to \infty) \sim \left( \frac{2\mu}{\pi \hbar^2 k} \right)^{1/2} \sin(kR + \delta)
\]  

But in order to be consistent with the expressions derived above for the double differential cross sections and angular differential cross sections formulae discussed below, \(\Xi_c\) needs to be momentum-normalized. Thus, when using \(\Xi_c\) from Stibbe and Tennyson, a correction factor, \(\xi^2\), needs to be included such that

\[
\xi^2 = 2\hbar \left( \frac{E_{ke}}{m_H} \right)^{1/2}
\]

which implies a momentum normalization such that the wavefunction’s asymptotic behaviour is \(\left( \frac{2}{\pi} \right)^{1/2} \sin(kR + \delta)\). The standard energy-normalized asymptotic form of the wavefunction for an electron incident upon a neutral molecule was used, which can be found, for instance, in Burke (1982a), equation (5) or Malegat (1990), equation (1) and is consistent with treatment given by Friedrich (1990).

The brackets in equation (5.25) also introduce a \(4\pi\) factor, because of the implied integration over 3-D space. With that, equation (5.23) becomes

\[
\frac{d^2\sigma}{d\Omega dE_{\text{out}}} = \frac{m_H^{3/2} E_{\text{out}}^{1/2} (E_{\text{in}} - D_v - E_{\text{out}})^{1/2}}{4\pi^4 \hbar^3 E_{\text{in}}^{1/2}} \left| f_{\nu \rightarrow c}(E_{\text{in}}, E_{\text{out}}) \right|^2
\]

The relation between the scattering amplitudes, \(f_{ij}\) and the transition matrices, \(T_{ij}\) has been derived by Burke (1982a) and is used by Malegat (1990). Malegat developed a computational code that calculates, among other things, angular differential cross sections, \(\frac{d\sigma}{d\Omega}\), for elastic and inelastic scattering for diatomic molecules. According to Malegat’s expressions (6) and (7), we can write

\[
\left| f_{ij} \right|^2 = \frac{k_i}{k_j} \sum_i A_{ij}^t P_t(\cos \theta)
\]

where \(i, j\) label the initial and final electronic states of the molecule, respectively and \(A_{ij}^t\) are coefficients given by Malegat’s equation (8):
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\[ A_{ij}^t = \frac{(-1)^{\lambda_i + \lambda_j}}{8(2t + 1)(2S_i + 1)k_i^2} \sum_{\lambda' \nu'} \frac{(\mathbf{i}_i - \mathbf{i}_j - \mathbf{i}_j + \mathbf{i}_j)}{\mathbf{i}_i \mathbf{i}_j} \]

\[ \times \left[ (2\mathbf{i}_i + 1)(2\mathbf{i}_j + 1)(2\mathbf{i}_j + 1)(2\mathbf{i}_j + 1) \right]^{1/2} \]

\[ \times \left( \mathbf{i}_i \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \right) \]

\[ \times \left( \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \mathbf{i}_j \right) \]

where the indicies i, j stand for all quantum numbers needed to specify the electronic state i, j of the molecule, respectively. \( \lambda \) is the projection of the total electronic angular momentum on the internuclear axis; \( i, j \) stand for \((\Lambda_i, S_i, \nu_i)\) and \((\Lambda_j, S_j, \nu_j)\), and \( i, j \) run over values satisfying \((-1)^{\nu_i} = \nu; (-1)^{\nu_j} = \nu; S \) represents the total spin and \( \nu \) labels the gerade or ungerade symmetry in homonuclear molecules. Primed coordinates refer to the molecular frame (MF), with the z'-axis along the interatomic axis and unprimed coordinates to the laboratory frame (LF), with the z-axis along the incident beam. The 3-j coefficients are those of Messiah (1960). Thus,

\[ |f_{\nu \rightarrow c}(E_{in}, E_{out})|^2 = \frac{E_{in}^{1/2}}{E_{out}^{1/2}} \sum_t A_{ij}^t(E_{in}, E_{out}) P_t(\cos \theta) \]  \hspace{1cm} (5.31)

Substituting (5.27) and (5.31) into (5.28), we obtain

\[ \frac{d^2\sigma}{d\Omega dE_{out}} = \frac{m_H}{2\pi^4 \hbar^3} (E_{in} - D_v - E_{out}) \sum_t A_{ij}^t(E_{in}, E_{out}) P_t(\cos \theta) \]  \hspace{1cm} (5.32)

Alternatively, if the continuum wavefunctions have been momentum-normalized,

\[ \frac{d^2\sigma}{d\Omega dE_{out}} = \frac{m_H^{3/2}}{4\pi^4 \hbar^3} (E_{in} - D_v - E_{out}) \sum_t A_{ij}^t(E_{in}, E_{out}) P_t(\cos \theta) \]  \hspace{1cm} (5.33)
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Integrating (5.32) over solid angle \( d\Omega \) gives

\[
\frac{d\sigma}{dE_{\text{out}}} = \frac{m_H}{2\pi^4 \hbar^2} (E_{\text{in}} - D_v - E_{\text{out}}) 4\pi A_{ij}^0 (E_{\text{in}}, E_{\text{out}})
\]

or, in terms of the kinetic energy of the dissociating H atoms,

\[
\frac{d\sigma}{dE_{\text{ke}}} = \frac{m_H}{8\pi^3 m_e} \frac{E_{\text{ke}}}{E_{\text{in}}} \sum_{\Lambda \nu \lambda l, j S} (2S + 1) \left| T_{\nu \rightarrow c}(E_{\text{in}}, E_{\text{ke}}) \right|^2
\]

Generalizing equation (5.35) as a function of the reduced mass, \( \mu \), of the molecular target,

\[
\frac{d\sigma}{dE_{\text{ke}}} = \frac{\mu}{4\pi^3 m_e} \frac{E_{\text{ke}}}{E_{\text{in}}} \sum_{\Lambda \nu \lambda l, j S} (2S + 1) \left| T_{\nu \rightarrow c}(E_{\text{in}}, E_{\text{ke}}) \right|^2
\]

Malegat's expression (7) is now used for the angular differential cross sections:

\[
\frac{d\sigma}{d\Omega} = \sum_{t} A_{ij}^t (E_{\text{in}}) P_t (\cos \theta)
\]

where

\[
A_{ij}^t (E_{\text{in}}) = \frac{\mu}{\pi^4 \hbar^2} \int_0^{E_{\text{in}} - D_v} (E_{\text{in}} - D_v - E_{\text{out}}) A_{ij}^t (E_{\text{in}}, E_{\text{out}}) dE_{\text{out}}
\]

Finally, for the integral cross sections,

\[
\sigma(E_{\text{in}}) = \int_0^{E_{\text{in}} - D_v} \frac{d\sigma}{dE_{\text{out}}} dE_{\text{out}}
\]

At the same time,

\[
\sigma(E_{\text{in}}) = A_{ij}^0 (E_{\text{in}})
\]

Integral cross sections have been calculated by both methods as a numerical check of this procedure.

In the particular case of dissociation of molecular hydrogen or its isotopomers from \( X^1\Sigma_g^+ \) ground state, only S=1/2 will survive, and this will reduce equation (5.36) to

\[
\frac{d\sigma}{dE_{\text{ke}}} = \frac{\mu}{2\pi^3 m_e} \frac{E_{\text{ke}}}{E_{\text{in}}} \sum_{\Lambda \nu \lambda l} \left| T_{\nu \rightarrow c}(E_{\text{in}}, E_{\text{out}}) \right|^2
\]
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When calculating energy differential cross sections, Stibbe & Tennyson (1998b) used an expression that did not consider the density of final states and, thus, did not model the dissociation process, which involves three fragments in the exit channel, properly. The density of final states introduces a mass dependence in all dissociation processes which is important for the present work. This reformulation, thus, gives results which differ somewhat both in magnitude and energy dependence from the earlier results of Stibbe and Tennyson (1998b, 1999).

5.2 Nuclear motion with the δ-function approximation

In the δ-function approximation, the final continuum vibrational function is replaced by

$$\left| \frac{dV}{dR} \right|^{-1/2} \delta(R - R_0^k)$$

(5.42)

where \(R_0^k\) is the classical turning point on the upper state potential curve \(V\). Within this approximation, \(E = V(R_0^k)\) and

$$dE = \left| \frac{dV}{dR} \right|_{R=R_0^k} dR_0^k$$

(5.43)

The physical assumption behind this approximation is that the electronic jump takes place so rapidly that the position and velocity of the nuclei are expected to remain unchanged during the transition (Franck-Condon principle). Suppose A and B in figure 5.3 are the two potential curves of a target molecule and that the initial vibrational level is \(v_a\). In the classical vibration, the velocity of the nuclear motion vanishes at the turning points, so that the probability of finding the internuclear distance within a unit range of \(R\) has maxima at both ends of the classically allowed range. When the molecule is near the inner turning point \(R_1\), the transition to the electronic state B is likely to produce the molecule in the vibrational level \(v_c\), since this is the vibrational state where the nuclear motion has nearly the zero velocity at the position \(R_1\). Similarly, when \(R \sim R_2\), it is likely that the vibrational level \(v_b\) is produced. Quantum mechanically, the Franck-Condon factor, which is the squared overlap integral of the initial and final vibrational wavefunctions, contains approximately the information of the vibrational level distribution in the final state. Except for the few lowest vibrational levels, the vibrational
wavefunction oscillates many times within the classically allowed region, while it decays exponentially to zero in the classically forbidden region. The wavefunction has a large amplitude and a large local wavelength in the neighbourhood of the turning points of classical motion. In the intermediate bondlength region, on the other hand, both amplitude and wavelength are small. The product of a vibrational wavefunction with another function, therefore, generally oscillates in the intermediate region and will only lead to a small contribution to the integral. From these considerations, the Franck-Condon factor is expected to be small unless the two vibrational states involved in the transition have the classical turning points at nearly the same internuclear distance. A detailed derivation of the $\delta$-function approximation can be found in McCulloh (1967).

In many circumstances, and in the lack of more accurate wavefunctions, the $\delta$-function approximation is used to describe the final continuum state. In order to establish a comparison, this approximation was introduced into the equations derived previously. From equation (5.25) we have
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\[ T_{\nu \rightarrow c}(E_{in}, E_{out}) = < \Xi_c(E_{ke}, R) | T_{ij}(\epsilon(R) + E_{out}, E_{out}, R) | \Xi_\nu(R) > \]

\[ = 4\pi \int \Xi_c(E_{ke}, R) T_{ij}(\epsilon(R) + E_{out}, E_{out}, R) \Xi_\nu(R) dR \]  
\[ (5.44) \]

The \(4\pi\) arises from the integration over solid angle. Replacing \(\Xi_c\) by \(|d\nu/d\Omega|^{-1/2}\delta(R - R^k_0)\) we get

\[ T_{\nu \rightarrow c}(E_{in}, E_{out}) = 4\pi \int T_{ij}(\epsilon(R) + E_{out}, E_{out}, R) \Xi_\nu(R) \left| \frac{dV}{dR} \right|^{-1/2} \delta(R - R^k_0) dR \]

\[ = 4\pi T_{ij}(\epsilon(R) + E_{out}, E_{out}, R) \Xi_\nu(R) \left| \frac{dV}{dR} \right|^{1/2} \delta(R - R^k_0) \]
\[ (5.45) \]

Introducing equation (5.45) in equation (5.41):

\[ \frac{d\sigma}{dE_{out}} = \frac{\mu}{2\pi^3 m_e} \frac{V(R^k_0)}{E_{in}} \Xi_\nu(R^k_0)^2 \left| \frac{dV}{dR} \right|^{-1/2} \sum_{\nu_{i j} k l j} \left| T^{\nu}_{i j \nu_{i j} k l j}(E_{in}, E_{out}) \right|^2 \]
\[ (5.46) \]

Thus,

\[ \sigma = \frac{\mu}{2\pi^3 m_e} \frac{1}{E_{in}} \int \frac{V(R) \Xi_\nu(R)^2}{\sum_{\nu_{i j} k l j}} \left| T^{\nu}_{i j \nu_{i j} k l j}(E_{in}, E_{out}) \right|^2 dR \]
\[ (5.47) \]

having used equation (5.43) and changing name of variable \(R^k_0\) to \(R\).

Rescigno & Schneider (1988) used the following expression for the differential cross sections at a particular incident energy \(E_\nu\):

\[ \sigma_{\nu \rightarrow k}(E_\nu, \theta, \phi) = \int | \int \chi_{i\nu}(R) T(E_\nu, \theta, \phi; R, \Omega) \chi_{k\nu}(R) dR |^2 \frac{d\Omega}{4\pi} \]
\[ (5.48) \]

where \(\chi_{i\nu}\) and \(\chi_{k\nu}\) are the initial (discrete) and final (continuous) vibrational wavefunctions. This equation is quoted without derivation or citation. It is unclear how it deals with the issue of the density of dissociating states. By introducing equation (5.42), equation (5.48) takes the form:

\[ \sigma_{\nu \rightarrow k}(E_\nu, \theta, \phi) = \int | \int \chi_{i\nu}(R) T(E_\nu, \theta, \phi; R, \Omega) \left| \frac{dV}{dR} \right|^{-1/2} \delta(R - R^k_0) dR |^2 \frac{d\Omega}{4\pi} \]
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\[
\sigma(E_o) = \int \sigma_{\nu \rightarrow k_i}(E_o) dE
\]  
(5.51)

Thus, by introducing (5.43) in (5.51):

\[
\sigma(E_o) = \int \chi^2_{\nu \omega}(R_e^k) | T(E_o, \theta, \phi; R_e^k) |^2 \left| \frac{dV}{dR} \right|_{R=R_e^k}^{-1} dR
\]

\[
= \int \chi^2_{\nu \omega}(R) | T(E_o, \theta, \phi; R) |^2 dR
\]

\[
= \frac{1}{k^2} \sum_{l'm} \int \chi^2_{\nu \omega}(R) | T_{l'm} |^2 dR
\]  
(5.52)

using a partial wave expansion for the T-matrix.

Equations (5.47) and (5.52) have different dependence on isotopic mass and the dissociating state potential.

5.3 Dissociation rate coefficients

The rate of electron impact dissociation of the diatom in vibrational state \( \nu \) as a function of electron temperature \( T_e \) can be calculated from the relevant cross sections using the standard formula

\[
q_{\nu}(T_e) = \frac{8\pi}{m_e^{1/2}} \left( \frac{1}{2\pi k T_e} \right)^{3/2} \int_0^\infty \sigma_{\nu}(E) e^{-E/k T_e} E dE
\]  
(5.53)

where \( k \) is the Boltzmann constant and \( m_e \) is the electron mass. For relatively low temperatures (up to 15,000 K), the threshold region of dissociation provides the dominant contribution to the total rate.
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At local thermal equilibrium (LTE), the molecules and the electrons each have a Maxwellian distribution associated with the same temperature $T$. The LTE rate, $q_{LTE}$, can be found from the thermally averaged cross section $\bar{\sigma}(E)$,

$$q_{LTE}(T) = \frac{8\pi}{m_e} \left( \frac{1}{2\pi kT} \right)^{3/2} \int_0^\infty \bar{\sigma}(E) e^{-E/kT} EdE \quad (5.54)$$

where

$$\bar{\sigma}(E) = \frac{1}{z} \sum_{v=0} \sigma_v(E) e^{-\gamma(v)/kT} \quad (5.55)$$

with $z$ the partition function, $z = \sum_{v=0} e^{-\gamma(v)/kT}$, and $\gamma(v)$, the vibrational energy levels, with the sums running over the finite number of vibrational states. Alternatively, the rates themselves can be thermally averaged:

$$q_{LTE}(T) = \frac{1}{z} \sum_{v=0} q_v(T) e^{-\gamma(v)/kT} \quad (5.56)$$

Throughout this treatment, an isotropic rotational distribution has been assumed.

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This chapter describes the calculation methods employed in obtaining electron impact double differential dissociation cross sections and rates for H\(_2\). Ab initio results for the vibrational ground state, \(v = 0\), are presented and discussed. Comparisons with available data are made.

### 6.1 Calculation method

As outlined in chapter 1, the results presented in this chapter employ the adiabatic nuclei approximation and the energy balance model of Stibbe & Tennyson (1998b) to obtain the appropriate energy-dependent T-matrices. This model assumes that the dissociation of H\(_2\) for energies below around 12 eV proceeds exclusively via electronic excitation to the first excited state of H\(_2\):

\[
e + H_2(X^1\Sigma_g^+) \rightarrow H_2^*(b^3\Sigma_u^+) + e \rightarrow H(1s) + H(1s) + e.\quad (6.1)
\]

Figure 6.1 illustrates this electron impact dissociation process, beginning at the electronic ground state, \(X^1\Sigma_g^+\) and dissociating into the continuum. Also shown are the ground \(v = 0\) nuclear wavefunction (black broken curve) and continuum wavefunctions (full curves from red
**Figure 6.1:** Electron impact dissociation of \( \text{H}_2 \) near threshold energies. The molecule is excited from the electronic ground state, \( \Sigma_g^+ \) (black full curve) to the first repulsive excited state, \( \Sigma_u^+ \) (blue full curve). Also shown are the ground \( v = 0 \) nuclear wavefunction (black broken curve) and continuum wavefunctions (full curves from red to blue) for different asymptotic kinetic energies of the dissociating molecule, \( E_{ke} \).

The formal expressions needed for such calculations were derived in chapter 5. To generate differential cross sections it was necessary to rederive the expressions for all cross sections from first principles because of problems with Stibbe and Tennyson's formula for the cross sections which arose from not having considered the density of final states. This term introduces a mass dependence in all dissociation processes which is important for the present investigation. This reformulation, thus, gives results which differ somewhat both in magnitude and energy dependence from the earlier results of Stibbe and Tennyson (1998b, 1999).

The calculation of the T-matrices used in this work was described in chapter 4, section 4.5.
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6.1.1 Symmetry convergence

As the excitation is from a singlet to a triplet state, it is exchange dominated and rapidly convergent with total symmetry. Only the lowest four total symmetries, $^2\Sigma^+_g$, $^2\Pi_u$, and $^2\Pi_g$, were included by Stibbe and Tennyson, who found higher symmetries gave a negligible contribution to the total cross section, in agreement with previous calculations (Baluja et al. 1985, Branchett et al. 1991). Nevertheless, a symmetry convergence check over a range of energies for the incoming electron was performed in order to analyse how much the inclusion of four further symmetries would affect angular differential cross sections. After performing calculations of angular differential cross sections with a total of four and then eight total symmetries and having found that differences between these calculations were within an acceptable range, the decision to include only the lowest four symmetries when analysing angular information was justified.

Figures 6.2, 6.3 and 6.4 illustrate elastic scattering angular differential cross sections at an incoming electron energy of 10 eV, 12 eV and 15 eV, respectively. The full curves represent...
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Figure 6.3: Elastic differential cross sections at an incoming electron energy, $E_{\text{in}}$, of 12 eV. The full curve represents differential cross sections that include the lowest eight symmetries in the calculation; the broken curve includes only the lowest four.

Figure 6.4: Elastic differential cross sections at an incoming electron energy, $E_{\text{in}}$, of 15 eV. The full curve represents differential cross sections that include the lowest eight symmetries in the calculation; the broken curve includes only the lowest four.
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**Figure 6.5**: Inelastic differential cross sections at an incoming electron energy, $E_{\text{in}}$, of 12 eV. The full curve represents differential cross sections that include the lowest eight symmetries in the calculation; the broken curve includes only the lowest four.

Differential cross sections that include the lowest eight symmetries in the calculation. Broken curves represent differential cross sections calculated by including a total of four lowest symmetries only.

Similarly, figures 6.5, 6.6 and 6.7 represent inelastic electronic excitation scattering differential cross sections at an incoming electron energy of 12 eV, 13 eV and 15 eV, respectively. Just as before, full curves are calculations which include a total of eight symmetries, whereas broken curves represent calculations with only the four lowest symmetries. Both curves overlap at 12 eV (figure 6.5) and lower energies. The largest difference between both curves can be seen in figure 6.4, where at small scattering angles the maximum difference reaches 17%. At lower energies for the incoming electron and larger scattering angles, the difference between these curves decreases rapidly.

This behaviour can be explained taking into account that, at small scattering angles, the many partial waves involved create an interference pattern that will be sensitive to the total number of symmetries included in the calculation. At higher angles, however, only a few partial waves are dominant. Hence, less interference is produced and differential cross section
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**Figure 6.6:** Inelastic differential cross sections at an incoming electron energy, $E_{\text{in}}$, of 13 eV. The full curve represents differential cross sections that include the lowest eight symmetries in the calculation; the broken curve includes only the lowest four.

**Figure 6.7:** Inelastic differential cross sections at an incoming electron energy, $E_{\text{in}}$, of 15 eV. The full curve represents differential cross sections that include the lowest eight symmetries in the calculation; the broken curve includes only the lowest four.
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curves for different number of symmetries are closer to each other.

6.1.2 Calculation of nuclear wavefunctions

Nuclear continuum wavefunctions, \( \Xi_c(E_{ke}, R) \), were calculated by directly solving the Schrödinger equation for the dissociating potential, and energy normalized according to the asymptotic condition stated in eq. (5.26). The exact potential of Kolos and Wolniewicz (1965) was used in place of that implicit in the T-matrix calculations, which is (\( \sim 0.1 \) eV) less accurate. The initial vibrational wavefunctions and energies were found with the program LEVEL (LeRoy 1996) also using the exact potential. For each value of \( E_{\text{out}} \), the appropriate fixed nuclei T-matrices were interpolated over 1000 points between \( R = 0.8 \) and \( 4.0 \alpha_0 \) prior to numerical integration to account for the rapid oscillations of the continuum functions.

6.2 Dissociation cross sections

6.2.1 Integral dissociation cross sections

Figure 6.8 shows the dissociation cross sections for \( \text{H}_2 (v = 0) \) as a function of incoming electron energy. Although cross sections are shown up to 14.5 eV, the present calculations, represented by the full curve, are expected to be accurate only up to around 12 eV. Above that energy, as mentioned in chapter 1, the molecule can be excited to higher states from which it can dissociate directly or cascade down to the repulsive state. Alternatively, it can reach an \( \text{H}_2 \) resonance state which can then decay into the \( 3 \Sigma_u^+ \) state. The adiabatic model used is not valid for these long-lived resonances and will not take into account the additional dissociation pathways above 12 eV.

In the region where this model is valid, there are few available experimental results. Those that are available have very wide error bars. The agreement with the measurements of Khakoo and Segura (1994) is good considering the large experimental uncertainties, with errors ranging from 22% to 31%. The agreement with the cross sections of Nishimura and Danjo (1986), with estimated errors of about \( \pm 37\% \), is also good, although their results are in energy ranges just above the region of validity of this model (12 eV). As expected at higher energies, the present
calculations underestimate experimental values, due to the additional dissociation pathways that are not being considered.

As discussed in chapter 5, the present work employs an expression for the dissociation cross sections that takes into account the density of final states and is different from that of Stibbe & Tennyson (1998). In practice this results in total cross sections about 10% higher than those obtained previously by Stibbe and Tennyson using the same, bondlength-dependent T-matrix data.

Also shown in the figure are calculations performed using the fixed nuclei model at the equilibrium bond length for molecular hydrogen (R=1.4 \( a_0 \)), represented by a broken curve. Note that the dissociation cross section drops to zero below its vertical target electronic excitation energy of 10.5 eV. This model gives no dissociation cross sections below that threshold. Above around 11 eV, however, the fixed-nuclei approximation is in good agreement with experimental data, its structure due to resonances in that impact energy region. Within the present model, much of that structure appears to be “washed out” due to the inclusion of nuclear motion.

Most previous calculations (Fliflet & McKoy 1980, Baluja et al. 1985, Schneider & Collins 1985, Lima et al. 1985, Parker et al. 1991, Branchett et al. 1990) were performed at the \( H_2 \) equilibrium bond length and do not take into account the nuclear motion. As mentioned in chapter 1, Rescigno and Schneider (1988) performed a series of two-state, fixed nuclei calculations using the Kohn variational method to find R-dependent T-matrices which they averaged using an initial vibrational and a \( \delta \)-function approximation to a final continuum function. However, they made no allowance for the variation in the vertical excitation energy with R, and took no account of energy partitioning between the outgoing atoms and the exiting electron. This prevents their method from being used near the effective Franck-Condon threshold.

Celiberto et al. used the semiclassical Gryzinski approximation to look at the dissociation of \( H_2 \) (Celiberto et al. 1989) and \( D_2 \) (Celiberto et al. 2001), again using a \( \delta \)-function approximation for the continuum, which they suggest should be useful for qualitative comparison. Gorse et al. (1992) also used the Gryzinski approximation and by adjusting parameters within that approximation gained good agreement with experiment at higher energies. The method they used for the nuclear dynamics is not well documented, making it difficult to judge the ac-
Figure 6.8: Electron impact dissociation cross sections for H$_2$(v = 0) as a function of the incoming electron energy, $E_{in}$. Round points with error bars are measurements of Khakoo and Segura (1994). Squares with error bars are measurements of Nishimura and Danjo (1986). The full curve represents present calculations and the broken curve represents the fixed nuclei model. The chain curve represents total cross sections using the classical $\delta$-function approximation for the final continuum vibrational function.

The accuracy of their near-threshold results. For comparison purposes, total cross sections using the classical $\delta$-function approximation for the final continuum vibrational function were included in figure 6.8, and are represented by the chain curve. This approximation appears to significantly underestimate the total cross sections, suggesting that the approximate treatment of the continuum nuclear wavefunction is inappropriate for a light system near threshold. Interestingly, however, the $\delta$-function approximation, as given by the formulation developed in this work and represented by equation (5.52), does reproduce the correct near-threshold behaviour.

The vertical target electronic excitation energy (or fixed nuclei energy) at the outer classical turning point for the vibrational ground state of H$_2$ using the exact potential curves is 8.7 eV.
Within the present model, this means that any dissociation found at electron energies below this arises via tunneling, for which this model explicitly allows. The effective Franck-Condon threshold region has not been well characterized experimentally, although there are indications in the results of both Nishimura and Danjo (1986) and Khakoo and Segura (1994) that it lies below 8.7 eV.

### 6.2.2 Angular differential cross sections

As mentioned in chapter 4, T-matrices obtained by R-matrix calculations can be then used by modules as IXSECS and DCS (Malegat 1990) which calculate integral and differential cross sections respectively. Nevertheless, such codes have been developed to operate at one specific bond length at a time, as the original T-matrices will depend on the particular internuclear distance at which the calculations were chosen to be performed, and on the energy of the scattering electron.

Unlike elastic scattering and other inelastic scattering processes, the electron impact dissociation of a diatomic molecule has three fragments in the output channel. Furthermore, the excess energy available above the dissociation energy can be split between the outgoing electron and the dissociating atoms in any proportion. In their work on H$_2$, Stibbe & Tennyson (1998) did not look into calculating angular differential cross sections. To do this required, therefore, the writing of a code that would output the original T-matrices not only as a function of the bond length and energy of the projectile electron, $E_{in}$, but also as a function of the energy of the outgoing electron, $E_{out}$, or of the centre of mass of the dissociating atoms, $E_{ke}$.

Malegat’s DCS code was created to compute differential cross sections for elastic and inelastic electron impact scattering of diatomic molecules from the corresponding fixed-nuclei T-matrices. Thus, it had to be modified as well, both to read in the outgoing electron energy-dependent T-matrices and to perform the calculations needed for this work and described in chapter 5.

Figures 6.9 to 6.14 illustrate angular differential cross sections for different values of incoming electron energy. The full curve represents present calculations; the broken curve represents the fixed nuclei model. Points with error bars represent available experimental values. At
energies below 10.5 eV the fixed nuclei model cannot predict dissociation cross sections. As expected, above 12 eV present results do not model experimental results properly.

6.2.3 Energy differential cross sections

Figure 6.15 shows energy differential cross sections for H₂(ν = 0) as a function of the energy of the dissociating atoms for different values of incoming electron energies. At low energies (below 12 eV), most of the available energy above dissociation is carried away by the dissociating hydrogen atoms. This suggests that electron impact dissociation of ν = 0 H₂ is unlikely to be the source of anomalously cold H atoms which have been found in a number of hydrogen plasmas (Hey et al. 2000, Hey et al. 1999, Hey et al. 1996, Mertens & Silz 1997). In chapters 7 and 8, however, it will be shown that at higher initial vibrational states, energy differential cross sections will follow the structure of the vibrational level involved. At lower projectile energies,
Figure 6.10: Angular differential cross sections for impact dissociation of $H_2(v = 0)$ by an incoming electron energy of 10.2 eV. The full curve represents the present model, which includes nuclear motion. Round points with error bars represent experimental values of Khakoo and Segura (1994).

Figure 6.11: Angular differential cross sections for impact dissociation of $H_2(v = 0)$ by an incoming electron energy of 12 eV. The full curve represents the present model, which includes nuclear motion. The chain curve illustrates cross sections calculated after doubling the $^2S_u^+$ contribution. The broken curve represents the fixed nuclei model. Squares with error bars represent experimental values of Nishimura and Danjo (1986).
Chapter 6: Near-threshold electron impact dissociation of $H_2 (v = 0)$

Figure 6.12: Angular differential cross sections for impact dissociation of $H_2(v = 0)$ by an incoming electron energy of 12.2 eV. The full curve represents the present model, which includes nuclear motion. The broken curve represents the fixed nuclei model. Round points with error bars represent experimental values of Khakoo and Segura (1994).

Figure 6.13: Angular differential cross sections for impact dissociation of $H_2(v = 0)$ by an incoming electron energy of 13 eV. The full curve represents the present model, which includes nuclear motion. The broken curve represents the fixed nuclei model. Squares with error bars represent experimental values of Nishimura and Danjo (1986).
Figure 6.14: Angular differential cross sections for impact dissociation of H$_2$ ($v = 0$) by an incoming electron energy of 15 eV. The full curve represents the present model, which includes nuclear motion. The broken curve represents the fixed nuclei model. Squares with error bars represent experimental values of Nishimura and Danjo (1986).
the excess energy will continue to be carried away by the H atoms. But as the projectile energy increases, the population of H atoms carrying away most of the excess energy decreases and slower H atoms appear.

6.3 Resonances

Aterns & Wadehra (1993) studied the resonant dissociation of H₂ by low-energy electron impact by a semi-empirical analysis of the contributions of the two lowest resonant states, \( ^2Σ^+_u \) and \( ^2Σ^+_g \). They used models based both on \textit{ab initio} calculations and on fits to experimental data. The authors presented theoretical cross sections for the dissociation of H₂ via these two resonances and compared them with other theoretical calculations obtained by non-resonant
methods. They also studied the effect of initial vibrational excitation, \( v \), on the dissociation cross section, finding the \( ^2\Sigma_g^+ \) resonance contribution to be significant to the total dissociation cross section for all values of \( v \) for incident energies between 12 eV and 18 eV (which lie beyond the energy range relevant to the present work), and found that the effect of \( ^2\Sigma_u^+ \) becomes appreciable only for values of \( v > 5 \). Their overall conclusions support the earlier results that the resonant contributions to dissociation, for incident energies in the 10-18 eV range, are much smaller than those of direct excitation of the \( ^3\Sigma_u^+ \) electronic state of \( \text{H}_2 \).

Later, Stibbe & Tennyson (1998a) made an extensive study of electron-\( \text{H}_2 \) scattering resonances as a function of bond length of the eight total symmetries: \( ^2\Sigma_g^+ \), \( ^2\Pi_u \), \( ^2\Pi_g \), \( ^2\Delta_g \), \( ^2\Delta_u \), \( ^2\Phi_u \), \( ^2\Phi_g \), as discussed in chapter 1. The method they used proved to be extremely successful in tracking resonances where previous methods had failed and they found even more resonance activity than had previously been suspected. Table 6.1 compares the partial widths of the lowest \( ^2\Sigma_g^+ \) resonance calculated by Stibbe & Tennyson (1998a) against calculations using the models of Atems & Wadehra (1993) for a few bond lengths relevant to this work. The probability that this resonance decays to the \( ^3\Sigma_u^+ \) electronic state, which is the concern of the present investigation, is in Stibbe & Tennyson’s more accurate calculations up to two orders of magnitude smaller than that presented by Atems & Wadehra.

Xu et al. (2001) give electron impact dissociation cross sections for different vibrational states of \( \text{H}_2 \) through the \( ^2\Sigma_u^+ \) shape resonance. Their cross sections for the vibrationally excited states \( v=3,6,9 \) agree well with the results of Atems & Wadehra but are about an order of magnitude larger for the ground state. Nevertheless, the non-resonant model cross sections calculated in this work are approximately two orders of magnitude greater than the maximum values obtained by Xu et al. The resonance mechanism is therefore disregarded below, except for its possible contribution to the angular differential cross sections.

In Stibbe and Tennyson’s energy balance model, therefore, the low lying \( ^2\Sigma_u^+ \) shape resonance does not contribute non-adiabatically, but that omission is not expected to make a significant difference (Atems & Wadehra 1993). Due to its short lifetime (\( \Gamma \sim 1 \text{ eV} \)), the adiabatic treatment of the \( ^2\Sigma_g^+ \) \( \text{H}_2^- \) resonance associated with the \( ^3\Sigma_u^+ \) dissociative state should be sufficient. In practice, the largest contribution comes from the non-resonant \( ^2\Sigma_u^+ \) symmetry in line with previous calculations (Rescigno & Schneider 1988, Atems & Wadehra 1993). Never-
Chapter 6: Near-threshold electron impact dissociation of $H_2$ ($v = 0$)


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<th>$R$ (a.u.)</th>
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Table 6.1: $^2\Sigma_u^+$ resonance energy positions above ground state, $E_o$, and partial widths, $\Gamma$, as a function of bond length $R$. Bond lengths are in atomic units, a.u. Energy positions and widths are given in Hartrees.

theless, the poor agreement of the angular differential cross sections with experiment reopens the issue of the contribution of resonances to this process in the near-threshold region, as was recently highlighted by Xu et al. (2000, 2001). Tests using these results showed that doubling the $^2\Sigma_u^+$ contribution to the differential cross sections gave differential cross sections significantly closer in form to experiment, but somewhat too high. Figures 6.9 and 6.11 illustrate angular differential cross sections at an incoming electron energy of 9.2 eV and 12 eV, respectively. The full curves represent the present model, which includes nuclear motion. The chain curves are the cross sections calculated after doubling the $^2\Sigma_u^+$ contribution. The broken curve in figure 6.11 represents the fixed nuclei model. Such model will predict zero cross sections at incoming electron energies below approximately 10.5 eV for $v = 0$. Round points and squares with error bars represent available experimental data.
Chapter 7

Near-threshold electron impact
dissociation of H$_2$, D$_2$ and T$_2$: higher
vibrational states

This chapter describes the calculations and ab initio results obtained for the electron impact
dissociation of molecular hydrogen, deuterium and tritium at higher vibrational states. Integral cross
sections, energy differential cross sections and rate coefficients are presented, compared against the
limited data available, and discussed.

7.1 Calculation method

As described in chapter 6, the results presented in this chapter employ the adiabatic nuclei approxima-
tion and the energy balance model of Stibbe & Tennyson (1998b) to obtain the appropriate energy-dependent T-matrices. The formal expressions needed for such calculations were derived in chapter 5. Integral and differential cross sections for the electronic ground state vibrational level $v = 0$ of H$_2$ were presented in chapter 6.

Cross section calculations of chapter 6 are now extended to the $v = 0-4$ H$_2$, $v = 0-6$ D$_2$
and $v = 0-7$ T$_2$ vibrational states and rate coefficients for such vibrational states are produced.
The extrapolation procedure of Stibbe & Tennyson (1999) to approximate the rate coefficients
for all of the higher vibrational levels is then adapted to calculate the LTE rate coefficients.

7.2 Integral and differential cross sections

The T-matrices used, described in chapter 5, were averaged between the different initial vibrational wavefunctions of the ground electronic state and the nuclear continuum wavefunctions with appropriate energy to represent the dissociating state. This generalization of the adiabatic nuclei approximation to electron impact dissociation is discussed in detail by Stibbe & Tennyson (1998b). The formal expressions needed for the calculation of differential and integral cross sections were developed in chapter 5. The energy differential cross sections are described by equation (5.41). As mentioned previously, the mass dependence in equation (5.41) comes from considering the density of final states for a three body problem in the output channel. Because its derivation is independent of any particular electronic state, the same scaling of cross sections for all dissociation processes as a function of the isotopic mass is expected.

As in the case with H$_2$ ($v = 0$) and described in chapter 6, nuclear continuum wavefunctions, $\Xi_c(E_{ke}, R)$, were calculated by directly solving the Schrödinger equation for the dissociating potential, and energy normalized. The potential of Kolos and Wolniewicz (1965) was used in place of that implicit in the T-matrix calculations, which is ($\sim 0.1$ eV) less accurate. The initial vibrational wavefunctions, $\Xi_v(R)$, and energies were found with the program LEVEL (LeRoy 1996) also using the former potential.

Integral cross sections are given by equation (5.39). No allowance is made for the possible effect of rotational motion of the diatoms.

7.2.1 Integral cross sections

Figures 7.1 to 7.3 show the dissociation cross sections for H$_2$($v$), D$_2$($v$) and T$_2$($v$) as a function of incoming electron energy. Although cross sections are shown up to values of $E_{in}$ that go beyond 12 eV, these calculations are expected to be accurate only up to around that value.

Comparison of Celiberto et al.'s (2001) results with the present calculations for H$_2$ and D$_2$ is shown in figures 7.1 and 7.2, respectively, where integral cross sections are plotted against
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Figure 7.1: Electron impact dissociation cross sections of H₂ as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level, $v$, obtained from full T-matrix calculations.

Figure 7.2: Electron impact dissociation cross sections of D₂ as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level, $v$, obtained from full T-matrix calculations.
Figure 7.3: Electron impact dissociation cross sections of $T_2$ as a function of the incoming electron energy, $E_{in}$, and initial vibrational level, $v$, obtained from full T-matrix calculations.
the energy of the incoming electron for all the vibrational states that can be fully calculated. Cross sections calculated by Celiberto et al. appear to be lower than the ones obtained by the present calculation, with a more noticeable effect in the case of D_2. This effect is almost certainly due to them not having a mass factor in their cross section equation (they do not give the explicit expression used).

Because of the finite range of internuclear separations (R = 0.8 - 4.0 \textit{a}_0) for which T-matrices are available, full calculations are only possible for \( v \leq 4 \) in H_2(v), \( v \leq 6 \) in D_2(v) and \( v \leq 7 \) in T_2(v). In order to obtain accurate cross sections for higher vibrational states, T-matrices need to be calculated over a much wider range of bond length. The present calculation cannot be easily extended to provide these T-matrices because of basis set limitations and because, at long bond length, the target electronic wave function will leak out of the R-matrix boundary, as discussed above.

### 7.2.2 Energy differential cross sections

Figures 7.4 to 7.6 illustrate energy differential cross section contour plots for the different isotopes and for each of the initial bound vibrational wavefunction for which the T-matrices used were able to support full calculations. The energy of the dissociating atoms, \( E_{ke} \), is plotted against the electron impact energy, \( E_{in} \); values for a single atom can be obtained by halving \( E_{ke} \). At low energies for the incoming electron (below 12 eV), contour plots for the \( v = 0 \) vibrational state show that most of the available energy above dissociation is carried away by the dissociating atoms. As mentioned in chapter 6, this suggests that the electron impact dissociation from that vibrational state is unlikely to be the source of anomalously cold H atoms which have been found in a number of hydrogen plasmas (Hey \textit{et al.} 1996, 1999, 2000, Mertens and Silz 1997). Nevertheless, these contour plots also show that, for dissociation from higher vibrational states, the heavy particles’ energy, \( E_{ke} \), is only weakly dependent on \( E_{in} \). The distribution of \( E_{ke} \) becomes narrower, and its mean value becomes lower for dissociation from excited vibrational levels. This finding is in accordance with the suggestion that low energy dissociation is predominantly from the outer turning point of the H_2 ground state potential, in contrast with the conventional Franck-Condon behaviour assumed (which predicts that the probability for excitation is highest near either of the classical turning points).
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and could explain the presence of cold atoms which originate from electron impact dissociation from higher vibrational states.

The need for vibrational excitation as a pre-requisite for cold atoms in plasmas had already been pointed out by Pospieszczyk et al. (1999). However, their work considered relatively high (> 18 eV) electron impact energies. At such energies, both the inner and the outer classical turning points are important (see figure 5.3). At the near threshold energies (< 12 eV) which concern us here, it is only the outer classical turning point which is important (Stibbe & Tennyson 1998a).

There have been Doppler and laser measurements of velocity distributions of H and D atoms in the edge of fusion plasmas which have revealed the existence of cold atoms (Mertens et al. 2001, Tanaka et al. 2000, Hey et al. 2000). These spectroscopic measurements of low-$n$ Balmer line profiles of atomic hydrogen and deuterium require the atoms to be in an excited state. The electron impact dissociation of vibrationally excited molecules is a possible source of such atoms. Energy differential cross section peaks can be used to model and predict the distribution of atomic velocities providing, thus, a possible explanation regarding the origin of these low energy atoms. They can also be used to compute plasma momentum transfer by neutral particles arising from the electron impact dissociation of $H_2$ and its isotopomers for different initial vibrational states.

7.3 Dissociation rate coefficients

The rate coefficients of electron impact dissociation of the diatom in vibrational state $v$ as a function of electron temperature $T_e$ are calculated from the cross sections using equation (5.53):

$$q_v(T_e) = \frac{8\pi}{m_e^{1/2}} \left(\frac{1}{2\pi k T_e}\right)^{3/2} \int_0^{\infty} \sigma_v(E) e^{-E/kT_e} E dE$$

(7.1)

where $k$ is the Boltzmann constant and $m_e$ is the electron mass. For the temperatures under consideration here (up to 15,000 K), the threshold region of dissociation provides by far the largest contribution to the total rate. The upper limit for the integral in equation (7.1) of 15 eV
Figure 7.4: Energy differential cross section electron impact dissociation of H$_2$ contour plots for vibrational states $v = 0 - 4$ in atomic units. The energy of the dissociating atoms, $E_{ke}$, is plotted against the different values of incoming electron energies, $E_{in}$. The structure of the bound vibrational wavefunction can be seen as $v$ increases from $v = 0$ to $v = 4$ (left to right and top to bottom).
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should give an accurate rate at temperatures below 15,000 K.

Stibbe & Tennyson (1999) found a strong dependence of $H_2$ rate coefficients on the initial vibrational state. They proposed an extrapolation procedure to approximate the rate coefficients for all the vibrational levels above the ones provided by full T-matrix calculations. In this procedure, the fixed nuclei T-matrices used in the full calculation of the nuclear motion averaged T-matrices are replaced by a constant obtained by fitting Franck-Condon results for the cross sections of the lower vibrational states to those of the full calculation as closely as possible in the threshold region (see Stibbe and Tennyson, 1999, figure 1). For higher vibrational states, such Franck-Condon calculations can be used to model the cross sections near threshold without the need for further fixed nuclei T-matrix calculations.

This approximation should be useful, because the contribution from a $v = n$ level will be most significant in the region near its threshold. Beyond that region, the contribution due to the next lower vibrational state should predominate. Stibbe and Tennyson (1999) assumed that the contribution of a particular vibrational state to the total dissociation rate should be negligible beyond the threshold region, and used the Franck-Condon fitted results directly in the calculation of rate coefficients of the higher vibrational states. Away from threshold, the estimated cross sections are always lower than the ones obtained by full calculations, so the rate coefficients calculated using this approximation will consistently underestimate the true values.

In order to test the validity of this extrapolation procedure, a value for the estimated cross sections beyond which the actual cross sections should have a small contribution to the calculation of rate coefficients was chosen. This value was chosen above the threshold for the $v = n - 1$ state such that it would make the contribution of the cross sections of the $v = n$ vibrational state negligible. In this way, each vibrational state determines the point at which its previous (higher) vibrational state contributes significantly for the $v = n$ state. Beyond that point, the estimated values obtained by the present Franck-Condon calculations were doubled and the dissociation rate coefficients were recalculated. The results shown in figures 7.7 to 7.9 are those obtained by performing calculations at a mid-point between the original Franck-Condon fits and the ones produced after doubling the estimated cross section “tails”. The maximum differences found by this procedure were of about 25%. At temperatures below
10,000 K, the differences, which are temperature dependent, vary between approximately 0% and 20%. This relaxes the initial assumption of Stibbe and Tennyson (1999) and establishes an error estimation for it. This analysis also serves to emphasize the point that the reliability of the rate coefficients calculated in this work drops with temperature.

Following this procedure, thermal rate coefficients for the higher vibrational levels $5 \leq v \leq 14$ in $H_2(v)$, $7 \leq v \leq 20$ in $D_2(v)$ and $8 \leq v \leq 25$ in $T_2(v)$ were estimated by extrapolation. Figures 7.7 to 7.9 show both the calculated (full curves) and extrapolated (broken curves) rate coefficients and the local thermal equilibrium rate coefficients (chain curve). For $H_2$, the rate coefficients calculated in this work are lower than those calculated by Stibbe and Tennyson (1999), with differences increasing with $v$: rate coefficients practically coincide for $v = 0$, but get progressively smaller as $v$ increases. The local thermal equilibrium (LTE) rate coefficients obtained here are almost an order of magnitude lower than the LTE rate coefficients calculated by Stibbe and Tennyson. The reason for this is that, although the same T-matrices were used, the formulation derived in chapter 6 led to a significantly different expression for the energy differential cross sections. The resulting total cross sections were approximately 10% higher than those obtained by Stibbe and Tennyson for $H_2 v = 0$, but reach lower maximum values for higher vibrational states. Nevertheless, the dependence on the initial vibrational level was found to be strong. This is significant when considering total rate coefficients for a particular distribution of molecules among its vibrational levels. The $v = 0$ value for rate coefficients is often used to approximate the total dissociation rate coefficients. However, the $v$ dependence is so critical that this is unlikely to be a good approximation in many situations.

The rate coefficients (in cm$^3$s$^{-1}$) are parametrized to the form

$$ q(T) = aT^b \exp \left( -\frac{c}{T} \right) \times 10^{-9} $$  (7.2)

and the parameters are given in Table 7.1. Although a formal statistical deviation for these fits was not performed, the difference tolerance is guaranteed to be below 0.01%.

The Franck-Condon cross sections were calculated using the $H_2$ potential curve of Kolos and Wolniewicz (1965) for all of the vibrational states. Rate coefficients were calculated using equation (7.1) with cross sections obtained from full T-matrix calculations and from the Franck-
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Condon factor cross sections for those states for which full calculations are not possible; they are illustrated in figures 7.7 to 7.9. These rate coefficients were put into eq. (5.56) to find the LTE rate coefficients for each molecule. The LTE rate coefficients are also illustrated in figures 7.7 to 7.9 and parametrized in Table 1.

The cross sections depend on the isotope's mass and, hence, calculated rate coefficients will also be sensitive to the specific diatom considered. Nevertheless, because of the Boltzmann distribution assumed among the vibrational levels, this mass effect will be less noticeable when calculating dissociation rate coefficients than in the actual dissociation cross sections.
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Figure 7.5: Energy differential cross section electron impact dissociation of D\textsubscript{2} contour plots for vibrational states \(v = 0 - 6\) in atomic units. The energy of the dissociating atoms, \(E_{ke}\), is plotted against the different values of incoming electron energies, \(E_{im}\). The structure of the bound vibrational wavefunction can be seen as \(v\) increases from \(v = 0\) to \(v = 6\) (left to right and top to bottom).
Figure 7.6: Energy differential cross section electron impact dissociation of $T_2$ contour plots for vibrational states $v = 0 - 7$ in atomic units. The energy of the dissociating atoms, $E_{k_e}$, is plotted against the different values of incoming electron energies, $E_{in}$. The structure of the bound vibrational wavefunction can be seen as $v$ increases from $v = 0$ to $v = 7$ (left to right and top to bottom).
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**Figure 7.7:** Electron impact dissociation rate coefficients as a function of initial $H_2$ vibrational state, $v$. Full curves from the bottom are the rate coefficients for $v = 0 - 4$, obtained from full T-matrix calculations. Broken curves from the bottom are the rate coefficients for $v = 5 - 14$. The chain curve represents the LTE rate coefficients.

**Figure 7.8:** Electron impact dissociation rate coefficients as a function of initial $D_2$ vibrational state, $v$. Full curves from the bottom are the rate coefficients for $v = 0 - 6$, obtained from full T-matrix calculations. Broken curves from the bottom are the rate coefficients for $v = 7 - 20$. The chain curve represents the LTE rate coefficients.
Figure 7.9: Electron impact dissociation rate coefficients as a function of initial \( T_2 \) vibrational state, \( v \). Full curves from the bottom are the rate coefficients for \( v = 0 \) – 7, obtained from full T-matrix calculations. Broken curves from the bottom are the rate coefficients for \( v = 8 \) – 25. The chain curve represents the LTE rate coefficients.
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**Table 7.1:** Parameters for the fit formula of the electron impact dissociation rate coefficients in $\text{cm}^3\text{s}^{-1}$ for $v \leq 4$ in $H_2(v)$, $v \leq 6$ in $D_2(v)$ and $v \leq 7$ in $T_2(v)$ assuming a thermal electron distribution, and for the local thermal equilibrium (LTE) rate coefficients for each diatom. $T_{\text{min}}$ is the cutoff temperature below which each rate coefficient is under $10^{-14} \text{cm}^3\text{s}^{-1}$ and effectively zero.
Near-threshold electron impact
dissociation of HD, HT and DT: higher vibrational states

This chapter describes the calculations and ab initio results obtained for the electron impact
dissociation of the mixed isotopomers HD, HT and DT at higher vibrational states. Total cross
sections, energy differential cross sections and rate coefficients are presented and discussed.

8.1 Calculation method

Just as for the calculations presented in chapter 7, the adiabatic nuclei approximation and the
energy balance model of Stibbe & Tennyson (1998b) are used to obtain the appropriate energy-
dependent T-matrices. Once again, the formal expressions needed for such calculations are
those derived in chapter 5.

Mixed isotopomers have lower symmetry than H\textsubscript{2} and their centre-of-mass does not co-
incide with the geometric centre of the molecule. These changes could affect the electron
scattering T-matrices and cross sections. A series of C\textsubscript{2v} symmetry R-matrix calculations
centred on the HT centre-of-mass were therefore performed to evaluate these effects. Such
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calculations gave results that differed negligibly from the corresponding calculations on H₂, thus concluding that the T-matrices originally computed for H₂ could be used for the mixed isotopomers without significant loss of accuracy.

Integral cross sections and energy differential cross sections at threshold energies as a function of vibrational states \( v = 0 - 5 \) for HD, \( v = 0 - 5 \) for HT and \( v = 0 - 7 \) for DT are calculated for the electron impact dissociation through excitation to the \( b^3 \Sigma_u^+ \) excited electronic state, which is the dominant dissociation process at such energies. The rate coefficients of dissociation as a function of electron temperature for each state are parametrized. For the higher vibrational levels, the rate coefficients are extrapolated following the procedure discussed in chapter 7, and are then used to calculate the LTE rate coefficients.

8.1.1 R-matrix calculations

To evaluate how the mass polarization dipole of mixed isotopomers would affect the electron scattering T-matrices, R-matrix calculations were performed at the equilibrium bond length of H₂, namely, \( R = 1.4a_0 \).

As a preliminary test, all the original inputs for the H₂ molecule (symmetry \( D_{ooh} \)) were changed to the lower symmetry of \( C_{oov} \). Because only the four lower symmetries were found to contribute significantly to the results (see chapter 6, section 6.1.1), only \( \Sigma \) and \( \Pi \) scattering symmetries were included in the calculations. The calculation details are those described in chapter 4.

Calculations were therefore performed for the \( ^2 \Sigma_g^+, ^2 \Sigma_u^+, ^2 \Pi_u \) and \( ^2 \Pi_g \) symmetries of \( D_{ooh} \) H₂, so as to compare them against \( \Sigma \) and \( \Pi \) symmetries of \( C_{oov} \) H₂. Target properties and continuum basis were calculated and compared. At the stage of the inner region (N+1) scattering calculations (see figure 3.3), calculations for the \( \Sigma \) symmetry were performed smoothly for both \( D_{ooh} \) and \( C_{oov} \) setups, as well as for \( ^2 \Pi_u \) and \( ^2 \Pi_g \) symmetries of \( D_{ooh} \) H₂. But the inclusion of all the basis functions used in the \( D_{ooh} \) arrangement for the \( \Pi \) symmetry of \( C_{oov} \) H₂ was not possible, as its total number exceeded the code limitation of 225 basis functions. Therefore, comparisons were made by analyzing the \( \Sigma \) symmetries only.

Once the inner region (N+1) scattering calculations were attained, the outer region calcula-
Chapter 8: Electron impact dissociation of HD, HT and DT

Figure 8.1: Electron impact integral cross section comparison curves of H₂ and HT as a function of the incoming electron energy, $E_{in}$. The full curve represents R-matrix calculations performed for HT, whereas the chain curve describes H₂. Both curves appear overlapped.

The last stage, then, was to run these diatomic R-matrix calculations for HT, which is the isotopomer with the largest mass polarization dipole, so as to compare its results against H₂. Integral cross section curves coincided exactly, and elastic differential cross sections overlapped almost perfectly as well, as can be seen in figures 8.1 to 8.3. Inelastic differential cross sections also gave curves very similar to each other, as illustrated in figures 8.4 to 8.7, including in the $E_{in}=12$ eV resonance region. With this, it was concluded that the mass polarization dipole of the mixed isotopomers did not affect the results significantly and the original T-matrices calculated by Stibbe & Tennyson could be used safely for all the diatoms studied in this work.
Figure 8.2: Electron impact elastic differential cross section comparison curves of H₂ and HT at $E_{in}$ energies of 9 eV, 9.5 eV, 10 eV and 10.5 eV. Full curves represent R-matrix calculations performed for HT, whereas chain curves describe H₂. Curves appear overlapped.
Figure 8.3: Electron impact elastic differential cross section comparison curves of H$_2$ and HT at $E_{\text{in}}$ energies of 11 eV, 11.5 eV, 12 eV and 12.5 eV. Full curves represent R-matrix calculations performed for HT, whereas chain curves describe H$_2$. Curves appear overlapped.

Figure 8.4: Electron impact inelastic differential cross section comparison curves of H$_2$ and HT at $E_{\text{in}}$ energies of 10.8 eV, 11 eV, 11.2 eV and 11.4 eV. Full curves represent R-matrix calculations performed for HT, whereas chain curves describe H$_2$. 
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Figure 8.5: Electron impact inelastic differential cross section comparison curves of H$_2$ and HT at $E_{in}$ energies of 11.6 eV, 11.8 eV, 12 eV and 12.2 eV. Full curves represent R-matrix calculations performed for HT, whereas chain curves describe H$_2$.

Figure 8.6: Electron impact inelastic differential cross section comparison curves of H$_2$ and HT at $E_{in}$ energies of 12.4 eV, 12.6 eV, 12.8 eV and 13 eV. Full curves represent R-matrix calculations performed for HT, whereas chain curves describe H$_2$. 
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Figure 8.7: Electron impact inelastic differential cross section comparison curves of H$_2$ and HT at $E_{in}$ energies of 13.2 eV and 13.4 eV. Full curves represent R-matrix calculations performed for HT, whereas chain curves describe H$_2$. 
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8.2 Integral and differential cross sections

Just as with the homonuclear molecules discussed in the previous chapter, the T-matrices described in chapter 6 were averaged between the different initial vibrational wavefunctions of the ground electronic state and the nuclear continuum wavefunctions with appropriate energy to represent the dissociating state. The formal expressions needed for the calculation of differential and total cross sections were developed in chapter 5 and the energy differential cross sections are described by equation (5.41).

As before, nuclear continuum wavefunctions were calculated by directly solving the Schrödinger equation for the dissociating potential, and energy normalized. Again, the potential of Kolos and Wolniewicz (1965) was used in place of that implicit in the T-matrix calculations, which is (~ 0.1 eV) less accurate. The initial vibrational wavefunctions, $\Xi_v(R)$, and energies were found with the program LEVEL (LeRoy 1996) also using the former potential.

Integral cross sections were obtained using equation (5.39).

8.2.1 Integral cross sections

Figures 8.8 to 8.10 show the dissociation cross sections for HD, HT and DT as a function of incoming electron energy. As before, the present calculations are only expected to be accurate up to $E_{in}$ values below around 12 eV.

Because of the finite range of internuclear separations ($R = 0.8-4.0 \, a_o$) for which T-matrices are available, full calculations are only possible for $v \leq 5$ in HD($v$), $v \leq 5$ in HT($v$) and $v \leq 7$ in DT($v$). In order to obtain accurate cross sections for higher vibrational states, T-matrices must be calculated over a much wider range of bond length. As explained in earlier chapters, the present calculation cannot be extended easily to provide these T-matrices because of basis set limitations and because, at long bond length, the target electronic wave function will leak out of the R-matrix boundary.
Chapter 8: Electron impact dissociation of HD, HT and DT

Figure 8.8: Electron impact dissociation cross sections of HD as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level, $v$, obtained from full T-matrix calculations.

Figure 8.9: Electron impact dissociation cross sections of HT as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level, $v$, obtained from full T-matrix calculations.
Chapter 8: Electron impact dissociation of HD, HT and DT

Figure 8.10: Electron impact dissociation cross sections of DT as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level, $v$, obtained from full T-matrix calculations.
8.2.2 Energy differential cross sections

Figures 8.11 to 8.13 illustrate energy differential cross section contour plots for the different isotopomers and for each of the initial bound vibrational wavefunction for which the T-matrices used were able to support full calculations. The energy of the dissociating atoms, \( E_{ke} \), is plotted against the electron impact energy, \( E_{in} \). These energy differential cross sections are qualitatively similar to those of \( \text{H}_2 \), \( \text{D}_2 \) and \( \text{T}_2 \) presented in the previous chapter. Again, they support the predictions that low energy dissociation takes place predominantly from the outer turning point of the \( \text{H}_2 \) ground state potential and could explain the presence of cold atoms which originate from electron impact dissociation from higher vibrational states.

8.3 Dissociation rate coefficients

Just as before, the rate coefficients of electron impact dissociation of the diatom in vibrational state \( v \) as a function of electron temperature \( T_e \) are calculated from the cross sections using equation (5.53):

\[
q_v(T_e) = \frac{8\pi}{m_e^{1/2}} \left( \frac{1}{2\pi kT_e} \right)^{3/2} \int_0^\infty \sigma_v(E)e^{-E/kT_e}EdE
\]  

(8.1)

where \( k \) is the Boltzmann constant and \( m_e \) is the electron mass. For the temperatures under consideration here (up to 15,000 K), the threshold region of dissociation provides by far the largest contribution to the total rate. The upper limit for the integral in equation (8.1) of 15 eV should give accurate rate coefficients at temperatures below 15,000 K.

Following the extrapolation procedure discussed in detail in chapter 7, thermal rate coefficients were estimated for the higher vibrational levels \( 6 \leq v \leq 16 \) in HD, \( 6 \leq v \leq 17 \) in HT and \( 8 \leq v \leq 22 \) in DT. Figures 8.14 to 8.16 show both the calculated (full curves) and extrapolated (broken curves) rate coefficients and the local thermal equilibrium rate coefficients (chain curve). As with the calculations made for \( \text{H}_2 \), \( \text{D}_2 \), and \( \text{T}_2 \), the rate coefficients dependence on the initial vibrational level was found to be strong, with the LTE rate coefficients for each isotopomer being an order of magnitude greater than the \( v = 0 \) rate. This is significant when considering total rate coefficients for a particular distribution of molecules among its vibra-
Figure 8.11: Energy differential cross section electron impact dissociation of HD contour plots for vibrational states $v = 0 - 5$ in atomic units. The energy of the dissociating atoms, $E_{ke}$, is plotted against the different values of incoming electron energies, $E_{in}$. The structure of the bound vibrational wavefunction can be seen as $v$ increases from $v = 0$ to $v = 5$ (left to right and top to bottom).
Chapter 8: Electron impact dissociation of HD, HT and DT

Figure 8.12: Energy differential cross section electron impact dissociation of HT contour plots for vibrational states $v = 0 - 5$ in atomic units. The energy of the dissociating atoms, $E_{ke}$, is plotted against the different values of incoming electron energies, $E_{in}$. The structure of the bound vibrational wavefunction can be seen as $v$ increases from $v = 0$ to $v = 5$ (left to right and top to bottom).
tional levels. The $v = 0$ value for the rate coefficients is often used to approximate the total dissociation rate coefficients. However, the $v$ dependence is so critical that this is unlikely to be a good approximation in many situations.

The rate coefficients (in cm$^3$s$^{-1}$) are parametrized to the form

$$q(T) = aT^b \exp\left(-\frac{c}{T}\right) \times 10^{-9}$$ (8.2)

and the parameters are given in Table 8.1. Although a formal statistical deviation for these fits was not performed, the difference tolerance is guaranteed to be below 0.01%.

The Franck-Condon cross sections were calculated using the H$_2$ potential curve of Kolos and Wolniewicz (1965) for all of the vibrational states. Rate coefficients were calculated using equation (8.2) with cross sections obtained from our full T-matrix calculations and from the Franck-Condon factor cross sections for those states for which full calculations are not possible; they are illustrated in figures 8.14 to 8.16. These rate coefficients were used to find the LTE rate coefficients for each molecule. The LTE rate coefficients are also illustrated in figures 8.14 to 8.16 and parametrized in Table 8.1.

Figure 8.17 compares the LTE rate coefficients of all the isotopomers studied. Although less noticeable than with the dissociation cross sections, the rate coefficients are sensitive to the mass of the particular molecule analyzed, with rate coefficients increasing with the reduced mass of the diatom. This is a direct consequence of the mass factor in equation (5.41) and shows that even at low temperatures, this factor is more important than the more favoured tunnelling of the lighter species.
Figure 8.13: Energy differential cross section electron impact dissociation of DT contour plots for vibrational states $v = 0 - 7$ in atomic units. The energy of the dissociating atoms, $E_{ke}$, is plotted against the different values of incoming electron energies, $E_{in}$. The structure of the bound vibrational wavefunction can be seen as $v$ increases from $v = 0$ to $v = 7$ (left to right and top to bottom).
Chapter 8: Electron impact dissociation of HD, HT and DT

Figure 8.14: Electron impact dissociation rate coefficients as a function of initial HD vibrational state \( v \). Full curves from the bottom are the rate coefficients for \( v = 0 - 5 \), obtained from full \( T \)-matrix calculations. Broken curves from the bottom are the rate coefficients for \( v = 6 - 16 \). The chain curve represents the LTE rate coefficients.

Figure 8.15: Electron impact dissociation rate coefficients as a function of initial HT vibrational state \( v \). Full curves from the bottom are the rate coefficients for \( v = 0 - 5 \), obtained from full \( T \)-matrix calculations. Broken curves from the bottom are the rate coefficients for \( v = 6 - 17 \). The chain curve represents the LTE rate coefficients.
Chapter 8: Electron impact dissociation of HD, HT and DT

Figure 8.16: Electron impact dissociation rate coefficients as a function of initial DT vibrational state $v$. Full curves from the bottom are the rate coefficients for $v = 0 - 7$, obtained from full T-matrix calculations. Broken curves from the bottom are the rate coefficients for $v = 8 - 22$. The chain curve represents the LTE rate coefficients.

Figure 8.17: Comparison between the local thermal equilibrium (LTE) rate coefficients of the different isotopomers studied. The rate coefficients increase with the reduced mass of the diatom.
Chapter 8: Electron impact dissociation of HD, HT and DT

<table>
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<th>c</th>
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Table 8.1: Parameters for the fit formula of the electron impact dissociation rate coefficients in cm$^3$s$^{-1}$ for $v \leq 5$ in HD($v$), $v \leq 5$ in HT($v$) and $v \leq 7$ in DT($v$) assuming a thermal electron distribution, and for the local thermal equilibrium (LTE) rate coefficients for each diatom. $T_{\text{min}}$ is the cutoff temperature below which each rate coefficient is under $10^{-14}$ cm$^3$s$^{-1}$ and effectively zero.
Scaling of electron impact dissociation of vibrationally excited diatomic molecules

This chapter describes the derivation of a scaling rule for the electron impact dissociation cross sections of vibrationally excited $\text{H}_2$ and its isotopomers. Cross sections from this scaling rule are then compared against those obtained through full calculation.

9.1 Physical considerations

The presence of molecules in vibrationally excited states in molecular plasmas can assume considerable importance. The modelling of these kinds of plasmas requires the collision cross section information as a function of the vibrational state of the molecule.

In order to provide plasma modellers with a simple way to obtain cross section data for vibrationally excited $\text{H}_2$ and its isotopomers, a scaling rule for the electron impact dissociation for the singlet-triplet transition $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ was derived. In doing so, a number of properties have been used:

- The threshold energy decrease with increasing $v$ is related to the rapid decrease of the vertical target excitation (or fixed nuclei) energy at larger internuclear separations. This threshold is largely determined by the vertical excitation at the vibrationally-dependent
outer turning point of the potential. Such variation has a significant role when including nuclear motion. At the same time, low energy dissociation is predicted to occur predominantly from the outer classical turning point, thus determining the energy shifts, \( \Delta E_{\mu}(v) \), to use for the different vibrational states in this scaling rule. These values arise from the energy difference between the \( b^3\Sigma_u^+ \) and the \( X^1\Sigma_g^+ \) potential curves of \( H_2(v) \) (vertical target excitation energy) at the outer classical turning point for each vibrational state.

- At high energy, the isotopomer dependence of the cross section is simply proportional to the isotopomer's reduced mass, \( \mu \).

- Cross sections decrease as the vibrational state increases.

- The \( \tanh \) (or “switch”) function satisfactorily reproduces the shape of the \( H_2(0) \) cross section curve at the relevant incoming electron energies.

### 9.2 Scaling rule

Taking the above mentioned properties into account, a simple scaling rule applicable to every isotopomer was derived from parametrizing the following expression to the \( v = 0 \) vibrational state for \( H_2(v) \):

\[
\sigma = 2\mu \left( 1 - \frac{v}{v_{\text{max}}} \right) c_0 \tanh(c_1(E_{\text{in}} + \Delta E_{\mu}(v)) + c_2) + c_3 \tag{9.1}
\]

where \( \mu \) is the reduced mass of the isotopomer in atomic units, \( v \) the vibrational state considered, \( v_{\text{max}} \) the highest vibrational state for which full calculations can be performed in each case, and \( c_0 \) to \( c_3 \) are coefficients that arise from the parametrization. As before, \( E_{\text{in}} \) is the energy of the incoming electron in eV. \( \Delta E_{\mu}(v) \) is the shift in the threshold energy for each vibrational state and each isotopomer, also in eV. The parametrization coefficients, and the energy shifts and \( v_{\text{max}} \) values for the different isotopomers are given in Table 9.1 and Table 9.2, respectively. Cross sections are in \( a_0^2 \).

The \( \tanh \) function in equation (9.1) tends to unity at high values of \( E_{\text{in}} \) and to -1 at small \( E_{\text{in}} \) values. To follow the \( H_2(0) \) cross section curve satisfactorily above the threshold region,
it needs to be shifted upwards, which is done by the parameter $c_3$. The multiplying factor, $c_0$, of $\tanh$ in equation (9.1) is negative, and adjusts the point of inflection in the curve to the correct energy. This means, however, that for sub-threshold values of $E_{in}$, equation (9.1) will give negative cross sections. In this case, the cross section should simply be set to zero, i.e. $\sigma = \max(\sigma, 0)$. At high $E_{in}$ values, this scaling rule gives flat curves; calculations in the present work do not give information on this region.

<table>
<thead>
<tr>
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<th>$c_1$</th>
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<td>17.6080</td>
<td>0.8504</td>
</tr>
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</table>

**Table 9.1:** Parameters for scaled electron impact dissociation cross sections. Cross sections are in $a_0^2$ for energies in eV and reduced mass in atomic units.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$H_2$</th>
<th>HD</th>
<th>HT</th>
<th>$D_2$</th>
<th>DT</th>
<th>$T_2$</th>
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<tr>
<td>0</td>
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<td>8.87</td>
<td>8.87</td>
<td>9.01</td>
<td>9.08</td>
<td>9.22</td>
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<td>1</td>
<td>7.07</td>
<td>7.32</td>
<td>7.50</td>
<td>7.69</td>
<td>7.82</td>
<td>8.00</td>
</tr>
<tr>
<td>2</td>
<td>5.93</td>
<td>6.26</td>
<td>6.43</td>
<td>6.78</td>
<td>6.89</td>
<td>7.14</td>
</tr>
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<td>3</td>
<td>4.92</td>
<td>5.36</td>
<td>5.51</td>
<td>5.93</td>
<td>6.15</td>
<td>6.43</td>
</tr>
<tr>
<td>4</td>
<td>4.08</td>
<td>4.55</td>
<td>4.74</td>
<td>5.21</td>
<td>5.46</td>
<td>5.77</td>
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<td>4.87</td>
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<tr>
<td>6</td>
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<td>4.00</td>
<td>4.33</td>
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<td>6</td>
<td>7</td>
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**Table 9.2:** Energy shifts, $\Delta E_{\nu}(v)$, for each vibrational state and each isotopomer in eV, and highest vibrational state, $v_{max}$, for which full cross section calculations can be performed for each isotopomer.

### 9.3 Results

Figures 9.1 to 9.6 illustrate the dissociation cross sections calculated fully and the scaled dissociation cross sections for the different initial vibrational states of $H_2(v)$, HD($v$), HT($v$), $D_2(v)$, DT($v$) and $T_2(v)$ as a function of incoming electron energy.
Figure 9.1: Electron impact dissociation cross sections for $\text{H}_2$ as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level $v$. Full curves from right to left are the cross sections obtained from full T-matrix calculations. Chained curves from right to left illustrate the curves obtained by applying the present scaling rule to each of the vibrational states described.

Figure 9.2: Electron impact dissociation cross sections for $\text{HD}$ as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level $v$. Full curves from right to left are the cross sections obtained from full T-matrix calculations. Chained curves from right to left illustrate the curves obtained by applying the present scaling rule to each of the vibrational states described.
Chapter 9: Scaling of electron impact dissociation of molecules

Figure 9.3: Electron impact dissociation cross sections for HT as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level $v$. Full curves from right to left are the cross sections obtained from full T-matrix calculations. Chained curves from right to left illustrate the curves obtained by applying the present scaling rule to each of the vibrational states described.

Figure 9.4: Electron impact dissociation cross sections for $D_2$ as a function of the incoming electron energy, $E_{\text{in}}$, and initial vibrational level $v$. Full curves from right to left are the cross sections obtained from full T-matrix calculations. Chained curves from right to left illustrate the curves obtained by applying the present scaling rule to each of the vibrational states described.
Chapter 9: Scaling of electron impact dissociation of molecules

**Figure 9.5:** Electron impact dissociation cross sections for DT as a function of the incoming electron energy, $E_{in}$, and initial vibrational level $v$. Full curves from right to left are the cross sections obtained from full T-matrix calculations. Chained curves from right to left illustrate the curves obtained by applying the present scaling rule to each of the vibrational states described.

**Figure 9.6:** Electron impact dissociation cross sections for $T_2$ as a function of the incoming electron energy, $E_{in}$, and initial vibrational level $v$. Full curves from right to left are the cross sections obtained from full T-matrix calculations. Chained curves from right to left illustrate the curves obtained by applying the present scaling rule to each of the vibrational states described.
Table 9.3 gives the mean values of the dissociation cross section curves calculated fully and the standard deviations of the difference between the calculated dissociation cross sections and those obtained by this scaling rule for each of the vibrational states involved. It shows that the typical error is about 15%, similar to that achieved by Celiberto et al. (1996, 1999), who derived a scaling rule for the electron impact electronic excitation cross sections of vibrationally excited diatomic molecules. They considered non-dissociative excitation and excitation to dissociation states with two fragments in the exit channel (dissociative attachment), hence, a simpler process. As can be observed in figures 9.1 to 9.6, calculated cross sections will be described rather satisfactorily at energies up to approximately 2eV above the threshold value of each vibrational state. Extrapolations to regions above $E_{in}=12eV$ and to vibrational states with $v > v_{max}$ can be performed, but should be handled with caution.
### Chapter 9: Scaling of electron impact dissociation of molecules

Table 9.3: Mean value of fully calculated dissociation cross sections and standard deviations of the difference between the calculated dissociation cross sections and those obtained by the scaling rule derived, for each vibrational state and each isotopomer. Cross sections are in $\sigma_0^2$

<table>
<thead>
<tr>
<th>$v$</th>
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<th>DT</th>
<th>$T_2$</th>
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<tbody>
<tr>
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<tr>
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<td>0.34</td>
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<tr>
<td>Std. dev.</td>
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Conclusions

10.1 Summary of results

The electron impact dissociation of molecular hydrogen and its isotopomers has been studied at near-threshold energies. The dissociation process has been modelled with the target molecule initially at the electronic ground state, $X^1\Sigma_g^+$, dissociating into continuum states through excitation to the $b^3\Sigma_u^+$, which is the major pathway for the electron impact dissociation at such low energies of about around 12 eV.

The theoretical formulation for this dissociation process, which involves three fragments in the exit channel, and the expressions needed for such study, were derived.

The R-matrix method and the energy balance method have been used to produce geometry dependent T-matrices, and nuclear motion was included in the calculations by averaging these T-matrices with initial bound and final continuum wavefunctions. Calculations of integral and differential cross sections were made for $\text{H}_2$ and its isotopomers at different initial vibrational states.

Up until now, models for the electron impact dissociation of molecular hydrogen found it difficult to predict experimental cross sections near threshold energies. The calculations made in this work provide a better agreement with experiment than former models at electron energies below 12 eV.
Chapter 10: Conclusions

Integral cross sections were found to give a good agreement with experimental results. Dissociation at electron energies below the classical turning point value was modelled as well, by taking into account the effects of tunnelling. The poorer angular differential cross sections of H\(_2(v = 0)\) reopen the issue of the contribution of resonances to this process in the near-threshold region.

There are very limited data available for the low energy electron impact dissociation from vibrationally excited states of H\(_2\) and D\(_2\), and none for HD, HT, DT nor T\(_2\). The dissociation rate coefficients for \(v \leq 4\) in H\(_2(v)\), \(v \leq 5\) in HD\((v)\), \(v \leq 5\) in HT\((v)\), \(v \leq 6\) in D\(_2(v)\), \(v \leq 7\) in DT\((v)\) and \(v \leq 7\) in T\(_2(v)\) was calculated accurately. Having found that the rate coefficients increase so dramatically with \(v\), all of the initial vibrational levels must be included in a calculation of the rate coefficients at local thermal equilibrium (LTE).

From the results of the vibrational states for which full calculations can be performed, the rate coefficients of dissociation from the remaining vibrational levels, \(5 \leq v \leq 14\) in H\(_2(v)\), \(6 \leq v \leq 16\) in HD\((v)\), \(6 \leq v \leq 17\) in HT\((v)\), \(7 \leq v \leq 20\) in D\(_2(v)\), \(8 \leq v \leq 22\) in DT\((v)\) and \(8 \leq v \leq 25\) in T\(_2(v)\) were estimated. The LTE rate coefficients for each molecule were calculated from these rate coefficients and found to be at least an order of magnitude greater than the \(v = 0\) rates. The fact that the LTE rate coefficients are so much higher than the \(v = 0\) rate coefficients is important given that, with the lack of any alternative, the \(v = 0\) rate coefficients are likely to be used as approximations to the LTE rates.

The cross sections depend on the isotopomer's mass and, hence, calculated rate coefficients will also be sensitive to the specific diatom considered. Nevertheless, because of the Boltzmann distribution assumed among the vibrational levels, the mass effect will be less noticeable when calculating dissociation rate coefficients than in the actual dissociation cross sections.

Energy differential cross sections for the different isotopomers and for each of the initial bound vibrational wavefunction for which the T-matrices used in this work were able to support full calculations, were calculated. Contour plots of the energy of the dissociating atoms, \(E_{ke}\), against the electron impact energy, \(E_{in}\), were produced. Such figures show that, for dissociation from higher vibrational states, the heavy particles' energy \(E_{ke}\) is only weakly dependent on \(E_{in}\). The distribution of \(E_{ke}\) becomes narrower, and its mean value becomes lower for dissociation from excited vibrational levels. This finding is in accordance with predictions that
low energy dissociation is predominantly from the outer turning point of the \( \text{H}_2 \) ground state potential. It could explain the presence of cold atoms which originate from electron impact dissociation from higher vibrational states.

Finally, a scaling rule that describes integral cross sections as a function of the initial vibrational state, the reduced mass of the target molecule, and the energy of the projectile electron was derived and compared against cross sections calculated accurately for the \( \text{H}_2 \) molecule and its isotopomers. Calculated cross sections will be described rather satisfactorily at energies up to approximately 2 eV above the threshold value of each vibrational state. Extrapolations to regions above \( E_{\text{th}}=12 \) eV and to higher vibrational states can be performed, but should be handled with caution. This scaling rule therefore provides modellers with a simple way to obtain cross section data for the studied dissociation process. Also, in calculating thermal electron impact dissociation rates, a Maxwellian electron energy distribution is assumed. However, in non-equilibrium plasmas, the electron energy distribution function may be far from a Maxwellian one (Capitelli et al. 1999). In such cases, this general scaling relationship offers a convenient method of computing the dissociation rate coefficients for an arbitrary (low) energy electron distribution.

### 10.2 Limitations and outstanding problems

In modelling this near-threshold electron impact dissociation process, it was assumed that the dissociation proceeds exclusively through direct excitation of the target molecule to the first excited electronic state, \( b \, \Sigma_u^+ \), which is repulsive. Calculations made in this work are expected to be accurate only up to around 12 eV. Above that energy, the molecule can be excited to higher states from which it can dissociate directly or cascade down to the repulsive state. Another possibility above 12 eV is the excitation of an \( \text{H}_2 \) resonance state which can then decay into the \( b \, \Sigma_u^+ \) state. The adiabatic model we use is not valid for these long-lived resonances and the additional dissociation pathways above 12 eV are not included in this model.

Although the lowest seven target states were included in the original T-matrix calculations, much of them are needed to account for polarization and detailed electron-electron correlation effects. Therefore, the inclusion of a greater number of target states is necessary if the excitation
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to higher electronic states is pursued.

Also, because of the finite range of internuclear separations \((R = 0.8-4.0 \, a_o)\) for which T-matrices were calculated, full cross section calculations are only possible for a limited number of vibrational states for each molecule. In order to obtain accurate cross sections for higher vibrational states, T-matrices must be calculated over a much wider range of bond length. The calculation performed in this work cannot be extended easily to provide these T-matrices because of basis set limitations and because, at long bond lengths, the target electronic wave function will leak out of the R-matrix boundary.

10.3 Future work prospects

The theoretical formulation for the three-body dissociation process developed in this work and the energy balance method can be used to study other diatomic and polyatomic molecules. Gorfinkiel et al. (2002) employed the energy balance method and expressions derived as part of the present study to calculate electron impact dissociative excitation cross sections for the four lowest-lying electronically excited states of \(\text{H}_2\text{O}\) in the energy range of 5-15 eV. They treated the nuclear dynamics of water as a pseudo-diatomic molecule, investigating the dissociation of \(\text{H}_2\text{O}\) into \(\text{H} + \text{OH} + e\) under the assumption that it will take place via stretching of a single OH bond. Therefore, they fixed one of the O-H bonds and the angle between both bonds and varied the other bond length in the range between 1.3 and 2.6 \(a_o\). In this way, they performed the first calculations taking into account the nuclear motion in electron impact dissociation of a polyatomic molecule.

The calculation of energy differential cross sections has opened up a wide range of possibilities for future calculations. Data has already been supplied to collaborators looking at velocity distributions of H and D atoms in the edge of fusion plasmas. The calculations performed in this work can be used to model and predict the distribution of atomic velocities providing, thus, a possible explanation regarding the origin of these low energy atoms. They can also be used to compute plasma momentum transfer by neutral particles arising from the electron impact dissociation of \(\text{H}_2\) and its isotopomers for different initial vibrational states.

Calculations performed throughout this work are expected to describe the electron molecule
dissociation process satisfactorily only at energies below around 12 eV. Methods that use the Born approximation, such as the perturbation methods outlined in the introduction, will only be accurate at energies above 50 eV. It is therefore possible to use the differential cross sections obtained in this study to extrapolate cross sections for the region of intermediate energies, which neither method will describe properly. Other possible future calculations include the following:

10.3.1 Adiabatic vibrational calculations

In the adiabatic-nuclei model employed in this work, cross sections for excitation from an initial state $i$ to a final state $f$ have been approximated by vibrationally averaging the fixed-nuclei T-matrices over the nuclear wave functions of the two states:

$$T_{vi \rightarrow vf} = \langle \Xi_{vf} | T | \Xi_{vi} \rangle.$$  \hspace{1cm} (10.1)

with the nuclear wavefunctions $\Xi$ found by solving the Schrödinger equation for the potential curves.

Using this approximation, the following can, for example, be calculated:

- Electronically elastic, vibrational excitation cross sections $v = 0 \rightarrow 1, 2, 3$ etc.
- Electronic and vibrational excitation cross sections
- Dissociative attachment cross sections through excitation to the $B \, ^2 \Sigma^+_g \text{H}_2^-$ resonance

10.3.2 Non-adiabatic calculations

In non-adiabatic R-matrix theory, configuration space is split by a hypersphere defined by $0 < r < a$, where $r$ is the electron-centre of mass distance, and $A_{in} \leq R \leq A_{out}$ (see figure 10.1). $A_{in}$ is chosen so as just to exclude the singularity in the potential at the nuclei and $A_{out}$ such that the target vibrational states have negligible amplitude for $R > A_{out}$.

In this model, configuration space can be split into three distinct regions depending on the outcome of the collision. $r > a$, with the bond length $R$ remaining within the boundary, is
Figure 10.1: Splitting of configuration space in the non-adiabatic model. $R$ is the bond length and $r$ the electron-molecular centre of mass distance.
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equivalent to the electron simply scattering from the molecule. \( r \) remaining within the boundary but \( R > A_{out} \) is characterized by dissociative attachment. With both \( r > a \) and \( R > A_{out} \), the molecule dissociates.

The non-adiabatic model includes vibrational functions in the close-coupling expansion. The functions are derived from the potential curves of the R-matrix poles which are tracked as a function of bond length in a series of adiabatic fixed-nuclei calculations. However, in order to calculate the vibrational functions, the diabatic potential of each R-matrix pole (i.e. the potential without avoided crossings) is required. Therefore, if there are avoided crossings between poles, the pole energies need to be reordered, a process which is currently performed by hand.

Nevertheless, there can be a bunching of R-matrix poles around target states and the high bond length area is riddled with avoided crossings which makes it virtually impossible to reorder the pole energies in this region. Until a better reordering procedure is introduced, this limits the adiabatic calculations in this case to areas where there are few avoided crossings, such as vibrational excitation of the ground state.

Applications of the non-adiabatic approximation (Schneider et al. 1979) to nuclear vibration and dissociative attachment have been studied for several diatomic and polyatomic molecules (see Morgan 1995 and references therein). Sarpal et al. (1994) presented a theory for calculations of dissociative recombination and dissociative attachment cross sections applicable for systems with or without curve crossings. The theory uses the R-matrix method to build up \( N+1 \) electron "curves" in an inner region which can be coupled in a full non-adiabatic treatment. The authors employed it to calculate low-energy dissociative recombination cross sections for HeH\(^+\), obtaining a good agreement with measurements. Non-adiabatic calculations of NO Rydberg states above several ionisation thresholds have also been made (Rabadán et al. 1998).
Bibliography


Bloch C 1957 Nucl. Phys. 4, 503.


BIBLIOGRAPHY


Friedrich H 1990 *Theoretical Atomic Physics* Springer-Verlag.


BIBLIOGRAPHY


Lane N F 1980 Rev. Mod. Phys. 52, 29.


BIBLIOGRAPHY


Noble C J 1982b The ALCHEMY Linear Molecule Integral Generator, Daresbury Laboratory Technical Memorandum, DL/SCI/TM33T.


