Theoretical studies of chemical dynamics on excited states, driven by non-adiabatic effects

Charge recombination reactions

Sifiso Musa Nkambule

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Abstract

This thesis is based on theoretical studies of molecular collisions occurring at relatively low to intermediate collision energies. The collisions are called dissociative recombination (DR) and mutual neutralization (MN). In a molecular quantum mechanical picture, both reactions involve many highly excited molecular electronic states that are interacting by non-adiabatic couplings with each other. The molecular complexes involved in the collisions are relatively (diatomic or triatomic systems) composed of relative light atoms. This allows for accurate quantum chemistry calculations and a quantum mechanical description of the nuclear motions. The reactions studied here are the MN reaction in collisions of \( \text{H}^+ + \text{H}^- \), \( \text{Li}^+ + \text{F}^- \), and \( \text{He}^+ + \text{H}^- \) and the DR reaction of \( \text{H}_2\text{O}^+ \). Rotational couplings are investigated in the study of MN reaction for \( \text{He}^+ + \text{H} \). For some reactions, the electronic resonant states have to be considered. These are not bound states, but are states interacting with the ionization continuum. Electronic structure calculations are combined with electron scattering calculations to accurately compute potential energy curves for the resonant states involved in the DR of \( \text{H}_2\text{O}^+ \) and the MN of \( \text{He}^+ + \text{H} \). From these calculations, the autoionization widths of the resonant states are also obtained. Once the potential energy curves are computed for the systems, the nuclear dynamics are studied either semi-classically, using the Landau-Zener method or quantum mechanically, employing the time-independent and time-dependant Schrödinger equations. Reaction cross section and final states distribution are computed for all the reactions, showing significantly large cross section at low to intermediate collision energies. For the MN processes, studied here, not only total cross sections are calculated but differential cross sections as well. Where possible, comparisons with previous experimental and theoretical results are performed.

Keywords: Mutual neutralization, Dissociative recombination, electronic structure, non-adiabatic.

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Abstract

This thesis is based on theoretical studies of molecular collisions occurring at relatively low to intermediate collision energies. The collisions are called dissociative recombination (DR) and mutual neutralization (MN).

In a molecular quantum mechanical picture, both reactions involve many highly excited molecular electronic states that are interacting by non-adiabatic couplings with each other. The molecular complexes involved in the collisions are relatively (diatomic or triatomic systems) composed of relative light atoms. This allows for accurate quantum chemistry calculations and a quantum mechanical description of the nuclear motions.

The reactions studied here are the MN reaction in collisions of of H\(^+\) + H\(^-\), Li\(^+\) + F\(^-\) and He\(^+\) + H\(^-\), and the DR reaction of H\(_2\)O\(^+\). Rotational couplings are investigated in the study of MN reaction for He\(^+\) + H\(^-\). For some reactions, the electronic resonant states have to be considered. These are not bound states, but are states interacting with the ionization continuum. Electronic structure calculations are combined with electron scattering calculations to accurately compute potential energy curves for the resonant states involved in the DR of H\(_2\)O\(^+\) and the MN of He\(^+\) + H\(^-\). From these calculations, the autoionization widths of the resonant states are also obtained.

Once the potential energy curves are computed for the systems, the nuclear dynamics are studied either semi-classically, using the Landau-Zener method or quantum mechanically, employing the time-independent and time-dependant Schrödinger equations. Reaction cross section and final states distribution are computed for all the reactions, showing significantly large cross section at low to intermediate collision energies. For the MN processes, studied here, not only total cross sections are calculated but differential cross sections as well. Where possible, comparisons with previous experimental and theoretical results are performed.
This thesis is dedicated to my children
Thandelwethu and Neo.
List of Papers

The following papers, referred to in the text by their Roman numerals, are included in this thesis.

PAPER I: **Landau-Zener studies of mutual neutralization in collisions of** $H^+ + H^-$ **and Be$^+ + H^-$.**


PAPER II: **Mutual neutralization in collisions of** $Li^+ + F^-$.  

PAPER III: **Studies of HeH: DR, RIP, VE, DE, PI, MN,...**


PAPER IV: **A theoretical study of mutual neutralization in** $He^+ + H^-$ **collisions.**

Å. Larson, S. M. Nkambule and A. E. Orel, *in manuscript*.

PAPER V: **Differential and total cross sections of mutual neutralization in low-energy collisions isotopes of** $H^+ + H^-$.  

PAPER VI: **Theoretical study of the mechanism of** $H_2O^+$ **dissociative recombination.**
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Author’s contribution

My contributions to the papers, included in the thesis, are as follows:

- **Paper I**: I calculated the electronic couplings that are extracted from *ab initio* data (the so called “APS” and “ATD” electronic couplings) and performed the strict diabatisation of the adiabatic potential energy curves used in the Landau-Zener study. I participated in discussions about the other electronic coupling elements and discussions about the paper.

- **Paper II**: I carried out the diabatic transformation calculations and performed the nuclear dynamics calculations. I also took part in all discussions on writing the article.

- **Paper III**: I performed the transformation of the $^2\Sigma^+$ states and took part in paper discussions.

- **Paper IV**: I participated in discussion on how to include autoionization and the rotational couplings into the nuclear dynamics models. I performed the diabatic transformation on the states relevant for the MN process and carried out all the nuclear dynamics calculations. I also took part in paper writing discussions.

- **Paper V**: I participated in deriving the formulas relevant to the MN total and differential cross section calculations for the different hydrogen isotopes. I also carried out the nuclear scattering calculations and analysed the results. I also wrote the first draft of the article.

- **Paper VI**: I participated in analysing the electronic structure data for the relevant resonant states. I computed autoionization widths for some of the electronic states and performed the wave packet nuclear dynamics calculations and analysis. I also participated in the discussions about the paper.
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Sammanfattning

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## Abbreviations

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<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>CAP</td>
<td>Complex absorbing potential</td>
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<tr>
<td>CASSCF</td>
<td>Complete active space self-consistent field</td>
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<tr>
<td>CI</td>
<td>Configuration interaction</td>
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<tr>
<td>CIS</td>
<td>Configuration interaction singles</td>
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<tr>
<td>CISD</td>
<td>Configuration interaction singles and doubles</td>
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<td>CSF</td>
<td>Configuration state function</td>
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<td>DR</td>
<td>Dissociative recombination</td>
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<td>FCI</td>
<td>Full configuration interaction</td>
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<tr>
<td>GTO</td>
<td>Gaussian type orbitals</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree Fock</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear combination of atomic orbitals</td>
</tr>
<tr>
<td>LZ</td>
<td>Landau-Zener</td>
</tr>
<tr>
<td>MCSCF</td>
<td>Multi-configurational self-consistent field</td>
</tr>
<tr>
<td>MCTDH</td>
<td>Multi-configuration time-dependent Hartree</td>
</tr>
<tr>
<td>MN</td>
<td>Mutual neutralization</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbitals</td>
</tr>
<tr>
<td>MRCI</td>
<td>Multi-reference configuration interaction</td>
</tr>
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<td>MRCIS</td>
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<tr>
<td>SCF</td>
<td>Self-consistent field</td>
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<tr>
<td>STO</td>
<td>Slater type orbitals</td>
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Declaration

Portions of this work has been taken from my licentiate degree thesis. With few modifications, sections 1.1, 1.2, 2.1 are extracted from my licentiate thesis. With some minor edits, chapter 4 was taken from section 2.3 of the licentiate thesis.
1. Introduction

What causes chemical bonds to break or form? What mechanism drives a particular chemical reaction? This work is mainly concerned with the understanding of underlying mechanisms in chemical processes involving small molecular systems, where highly excited electronic states are involved. In this thesis, I have studied the reactions in which oppositely charged ions collide and neutralize as well as the process where an electron is captured by a molecular cation, causing it to neutralize and then break up. Here the processes are theoretically studied at low to intermediate collision energies (< 100 eV). The reactions are important for understanding cold plasma environments, such as primordial and pre-galactic gas reactions, interstellar gas clouds chemistry, planetary ionosphere chemistry and laboratory plasmas. In the reactions studied here, oppositely charged particles collide and thus the Coulomb attraction is involved, which causes the reactants to collide, even at very low energies.

The evolution of molecular gases is important for understanding the early universe. For example, H$_2$ is believed to have played an important role as a dominant coolant in the collapsing primordial clouds in the formation of the first stars and galaxies. Thus the chemical evolution of gases at the early epochs is crucial if one needs to understand the competing processes in the formation of H$_2$ [26; 37; 42–44; 66; 75; 87]. One such process is the mutual neutralization reaction of H$^+$ + H$, which I have studied. Several molecular ions have been detected in space, in regions such as the interstellar medium, the planetary ionospheres, dense and diffuse molecular clouds [50; 52; 79; 80]. These environments are also rich in free electrons and the molecular ions are often destroyed by dissociative recombination with low energy electrons [80]. A strong motivation for this research has been to get a better understanding of how molecular ions involved in these reactions are destroyed and the kind of new fragments that are formed.

In an attempt to theoretically study such molecular processes, one encounters the mammoth task of solving the Schrödinger equation for a many-body system (two or more nuclei and many electrons). An exact solution to this problem is still unknown. However it is often customary to circumvent the problem by employing the Born-Oppenheimer approximation [15]. In this approach, the total wave function is expressed as a product of the nuclear and electronic wave functions. This approximation is primarily based on observa-
tions since it is not rigorously possible to separate the total molecular Hamiltonian [72]. Even for the lightest molecule, $\text{H}_2^+$, the ratio of nuclear reduced mass to electron mass is about 1000, and in the Born-Oppenheimer approximation [57] it is assumed that the motions of the electrons can be treated as uncoupled to the nuclei motion, that is the electrons will instantaneously adjust to any changes in nuclear coordinates. A detailed theoretical background on this approach is outlined in chapter 2. Thus when one studies the electronic motion at fixed nuclear distance, the eigenvalue (known as potential energy) is obtained and if obtained for several internuclear distances, a potential energy curve (in case of a diatomic system) or a potential energy surface (in case of a polyatomic system) can be obtained. This is known as the adiabatic picture [72] and it forms the basis of most models aimed at describing chemical phenomena at microscopic level [117].

The Born-Oppenheimer approximation, is applicable, to a good approximation, for processes that involve electronic states well separated in energy. This includes, in general, reactions occurring in the ground electronic state [96; 116]. On the other hand, reactions involving excited electronic states do not fall in this category. For processes driven by the dynamics on highly excited electronic states, the Born-Oppenheimer approximation can often not be applied. These electronic states can lie close to each other in energy. As a result, non-adiabatic transitions from one electronic state to another may occur [19].

In studying non-adiabatic processes, where the states are coupled together, it is advantageous, for numerical purposes, to transform the adiabatic states (coupled by non-adiabatic couplings) to diabatic states (coupled by electronic couplings). This is further discussed in chapter 4.

The reactions studied here entail dynamics taking place in more than one electronic state and involve non-adiabatic transitions between electronic states. They are mutual neutralization (MN$^1$) and dissociative recombination (DR), both of which involve two or more electronic states. The mutual neutralization process is further discussed in section 1.1, while dissociative recombination is discussed in section 1.2. In chapter 2, the theoretical description of the molecular system is outlined, while in chapter 3 the methods for computing electronic molecular states are discussed and methods for transforming the states from adiabatic to diabatic states are discussed. Non-adiabatic couplings amongst the adiabatic states are also computed. In chapter 4 the electron scattering method is outlined, which is used to compute energies of resonant states and autoionization widths. Once the potential energy surfaces, couplings and autoionization widths are obtained, the nuclear dynamics are studied and this is described in chapter 5. Chapter 6 discusses the results contained in the attached papers.

$^1$For all abbreviations see the glossary on page xiii.
The conclusion and outlook are given in chapter 7.

1.1 Mutual neutralization

A mutual neutralization process involves two oppositely charged atomic or molecular ions, that collide and exchange an electron to form neutral separated fragments. Schematically, for collisions of atomic ions, the process can be written as

\[ A^+ + B^- \rightarrow A^{(*)} + B^{(*)}. \]  \hspace{1cm} (1.1)

Here the asterisk (\( ^* \)) denotes the fact that A and/or B may be electronically excited. Fig. 1.1 illustrates possible pathways on adiabatic potential energy curves (see section 2.2) in which the reaction can take place. The reaction

![Figure 1.1: Schematic illustrations of the adiabatic potential energy curves involved in the mutual neutralization process. In the present system there are five possible pathways that can lead to neutralization as shown by the red and blue arrows forming products in different quantum states A(\( n \)) + B and A(\( n' \)) + B.](image)

starts, at large internuclear distances, in the ion-pair state, which in general is a highly excited electronic state. The system moves towards smaller internuclear distances, as illustrated in Fig 1.1. The blue and red arrows show different pathways for formation of products in various final states. The process is non-adiabatic since to pass from the reactants to the product side, two or more electronic states have to be crossed. Only two covalent states are shown in the figure, but in reality there can be many states with energies lying close
to each other. At specific internuclear distances the curves can get close to
each other. In this region where the transition between the states occurs, non-
adiabatic coupling is significantly large. It is customary to transform the states
to a diabatic representation where the potential energy curves cross each other.
This is further discussed in chapter 3.

Due to the Coulomb attraction between the oppositely charged ions, at low
collision energies, the cross section for the reaction is expected to be large. At
low collision energy, the cross section is found to be inversely proportional to
the energy ($\sigma \propto E^{-1}$), according to the Wigner’s threshold law [125].

The merged beam facility, named DESIREE, located in AlbaNova university centre, in Stockholm, is aimed at studying low energy molecular reactions
[111; 113]. In this facility, oppositely charged atomic and molecular ions are
stored separately in the doubly electrostatic ion storage rings which are kept
at very low and well controlled center-of-mass energies (down to a few meV)
and at very low temperatures (down to 10 K). The two ion beams are merged
in a section where the neutral fragments formed in reactions, such as the MN
reaction, are detected.

In fusion plasmas, like the ITER [1] facility, there is a possibility of having
oppositely charged ions and it is of interest to understand how these species are
formed and destroyed. Thus at the divertor section of the plasma facility there
is a possibility of inelastic scattering collision [30; 31; 64]. The presence of
anions and cations in space renders the possibility of MN reaction, with high
rate constant, a dominant reaction in space plasmas [70; 71].

In the thesis, I have studied the following mutual neutralization reactions;

- $\text{H}^+ + \text{H}^- \rightarrow \text{H}_2^+ \rightarrow \text{H} + \text{H}$ (in Paper V)
- $\text{He}^+ + \text{H}^- \rightarrow \text{HeH}^+ \rightarrow \text{H} + \text{He}$ (in Paper IV)
- $\text{Li}^+ + \text{F}^- \rightarrow \text{LiF}^+ \rightarrow \text{F} + \text{Li}$ (in Paper II)
- $\text{Be}^+ + \text{H}^- \rightarrow \text{BeH}^+ \rightarrow \text{H} + \text{Be}$ (in Paper I).

Not only can the ions collide with each other, but there is also a possibility
of ions colliding with free electrons. A process of cation-electron collision
studied here is dissociative recombination and is discussed below.

1.2 Dissociative recombination

Dissociative recombination (DR) is a process in which a molecular cation cap-
tures a low energy electron to form a neutral molecule that then dissociates
to separated fragments. The most fascinating question to ask is how a low
energy electron can cause a molecule, which has a huge mass in comparison

4
and a dissociation energy of several eV, to dissociate. However, the electron can temporarily attach to the molecule to form a repulsive state that drives the dissociation. The neutral intermediate state formed is called a resonant state and it is not stable in a traditional sense since, at short internuclear distances, the electron can be re-emitted and detach from the molecule. The probability for the electron detachment is given by the autoionization width, which is inversely proportional to the autoionization lifetime of the resonant state.

There are two different mechanisms in which the DR process can take place; a direct and an indirect mechanism. In the direct mechanism, the cation $AB^+$ captures the electron to a resonant state $AB^{**}$, as illustrated in reaction (1.2) for a diatomic molecule:

$$AB^+ + e^- \rightarrow AB^{**} \rightarrow A + B.$$ (1.2)

The resonant state has a repulsive potential energy curve and the system dissociates into neutral fragments. The relevant potential energy curves are schematically shown for a diatomic molecule in Fig. 1.2.

![Figure 1.2: Schematic illustration of the potential energy curves involved in the direct dissociative recombination process. The ion $AB^+$ captures an electron to a doubly excited neutral state, $AB^{**}$, followed by dissociation.](image-url)

Before the potential energy curves of the resonant state and the ion cross, there is a possibility of re-emitting the captured electron, the process known as
autoionization. Once the potential curve of the ion has been crossed, autoionization is no longer possible and the system continues to dissociate into neutral fragments, A and B. These fragments might be excited.

Due to the Coulomb attraction between the molecular cation and the electron, the low energy DR cross section follows the same Wigner threshold law [125] as found in low energy MN reactions.

It was a study by Bates [9] in 1950, which revealed that DR in molecular gases was the most dominant process for ionization decay. This study provided the first explanation of the direct dissociative recombination mechanism and it was discussed that dissociative recombination involves a single radiationless transition and that the rate for recombination of electrons and molecular ions is several magnitudes larger than the rate for recombination of electrons and atomic ions.

In the indirect mechanism, the ion captures an electron to a ro-vibrationally excited Rydberg state, AB*, which then couples to a state open for dissociation, as described by reaction (1.3)

\[
AB^+ + e^- \rightarrow AB^* \rightarrow AB^{**} \rightarrow A + B.
\]  

(1.3)

Fig. 1.3 shows the pathway for the indirect DR mechanism.

The indirect mechanism was first independently discussed by Bardsley [7; 8] and Chen and Mittleman [21] who suggested that the molecular ion might capture a thermal electron which can give up its energy to the rotational or vibrational motions of the molecule. Thus a molecule can be temporarily formed whose electronic configuration is that of a highly excited Rydberg state with the initial ionic electronic configuration in its core [41].

There is an infinite number of Rydberg states that converge to the ground state of the ion. The indirect process will in general manifest itself as resonant structures in the low energy DR cross section. The two DR mechanisms, as can be seen from the figures, can take place at the same time, and they need to be considered coherently as discussed by Giusti [41].

DR of e.g. HeH+ [77] and H3+ [65] is not driven by capture into a resonant state. Instead the electron capture goes entirely through the Rydberg states, referred to as the tunnelling mechanism. Recent studies indicate that this is the case for DR of many polyatomic ions [27].

The DR process studied in this work is for the water cation, and it is described in Paper IV. The process is

\[
H_2O^+ + e^- \rightarrow H_2O^* \rightarrow \begin{cases} H + H + O \\ H_2 + O \\ OH + H. \end{cases}
\]
Figure 1.3: Schematic illustration of the potential energy curves involved in the indirect dissociative recombination process. The ion AB$^+$ captures an electron to an excited Rydberg state, AB*, which then couples to a doubly excited resonant state, AB**, which results in dissociation.
The goal of Paper IV was to implement simplified models of the dissociation dynamics to determine the mechanism of DR of the H$_2$O$^+$ ion.

In studying the two processes discussed above (MN and DR), a series of calculations have been carried out. The computation scheme is outlined in the next section.

1.3 Overview of computation scheme

In carrying out the study of the processes described above, we have carried out computations that can be categorised as follows:

- **Quantum chemistry calculations**: The electronic potential energy curves (surfaces) are obtained using either the full configuration interaction method, the multireference configuration interaction method or the complete active space self-consistent field. These quantum chemistry methods are discussed in chapter 3. In general highly excited states of both the neutral molecular system as well as the ionic system have to be computed.

- **Electron scattering calculations**: More precise energy positions of the resonant states relative to the ion potential energy surface are computed as well as the autoionization widths of the resonant states. This method is described in chapter 4.

- **Diabatization**: Here different approaches are employed to transform the adiabatic states to a new set of states called diabatic states. These diabatic states makes some ease in the numerical evaluation of the nuclear Schrödinger equation and the diabatization methods are discussed in chapter 3.

- **Molecular dynamics**: The time-dependent or time-independent Schrödinger equations for the nuclear motion are solved for coupled states to evaluate quantities of interest such as the total and differential cross sections and branching ratios. A semi-classical method where transition probabilities are calculated using the Landau-Zener model is also employed. The nuclear dynamics methods implemented here are detailed in chapter 5.

Now we proceed in chapter 2 by discussing the theoretical background of the quantum mechanical molecular system.
2. Theoretical molecular description

In order to facilitate the discussion in the subsequent chapters and for a better understanding of the results in Papers I-VI, a theoretical background is given in this chapter. The relevant quantum mechanical equations are outlined. These equations are applied to molecular systems and the concepts of adiabatic states, non-adiabatic couplings and potential energy surfaces are also introduced. Throughout the thesis atomic units are used, i.e., $\hbar = k_e = m_e = e = 1$, where $\hbar = \frac{h}{2\pi}$, $h$ is the Planck constant, $k_e$ is the Coulomb constant, while $m_e$ and $e$ are the electron mass and the elementary charge, respectively.

2.1 Quantum molecular description

The non-relativistic molecular Hamiltonian, $H_{\text{mol}}$, that describes an isolated molecular system is of the form;

$$H_{\text{mol}} = T_{\text{N}}(R) + T_{\text{e}}(r) + V(R,r).$$  \hspace{1cm} (2.1)

Here $R$ denotes nuclear positions and $r$ denotes all electronic coordinates for a $N$ nuclei (each of mass $M_i$, $i = 1, \ldots N$) and $n$ electrons system. $T_{\text{N}}$ is the nuclear kinetic energy operator;

$$T_{\text{N}} = -\sum_{i=1}^{N} \frac{1}{2M_i} \nabla^2_{R_i}. \hspace{1cm} (2.2)$$

$T_{\text{e}}$ is the electronic kinetic energy operator, given by

$$T_{\text{e}} = -\sum_{j=1}^{n} \frac{1}{2} \nabla^2_{r_j}. \hspace{1cm} (2.3)$$

For the electronic kinetic energy operator, we have neglected the mass polarisation term. For a diatomic system this term is of the form

$$\frac{1}{2(M_1 + M_2)} \sum_{i,j} \nabla_{r_i} \cdot \nabla_{r_j}. \hspace{1cm} (2.4)$$
and it has been shown to have a very small contribution, even for H$_2$ [18].

$V(R, r)$ is the electrostatic potential energy term for the nuclei and electrons. It can be separated into the electron-electron repulsion term, $V_{ee}$, electron-nuclei attraction term, $V_{eN}$, and nuclear repulsion term, $V_{NN}$:

$$V_{NN} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{Z_i Z_j}{|R_i - R_j|}, \quad (2.5)$$

$$V_{eN} = -\sum_{i=1}^{n} \sum_{j=1}^{N} \frac{Z_j}{|r_i - R_j|}, \quad (2.6)$$

$$V_{ee} = \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|r_i - r_j|}. \quad (2.7)$$

$Z_k$ denotes the nuclear charge for the $k^{th}$ nucleus.

The complete many-body time-independent Schrödinger equation has the form

$$H_{mol} \Psi(R, r) = E \Psi(R, r), \quad (2.8)$$

with $\Psi(R, r)$ representing the total molecular wave function. This equation is, in principle, impossible to solve analytically. Thus approximations are employed. The most common approximation is to express the total wave function as a product of the nuclear wave function and the electronic wave function. This approximation is based on the desired energy expression, which should be a sum of the electronic energy, vibrational energy and rotational energy [72]. This product is known as the Born-Oppenheimer product,

$$\Psi^{BO}(R, r) = \Phi(R, r) \tilde{\chi}_N(R). \quad (2.9)$$

Consequences of applying the Born-Oppenheimer approximation and adiabatic representation are further discussed in section 2.2 below.

### 2.2 Born-Oppenheimer approximation and the adiabatic representation

As pointed out in the above section, in an attempt to solve eq. (2.8), the molecular Hamiltonian is separated as;

$$H_{mol} = T_N + H_{el}, \quad (2.10)$$

where $T_N$ contains the vibrational and rotational part of the nuclear kinetic energy operator. Section 2.3 expands on the importance of the rotational motion.
$H_{el}$ is known as the electronic Hamiltonian and the electronic Schrödinger equation can be expressed in the form

$$H_{el} \phi^a_i (R, r) = \varepsilon^a_i (R) \phi^a_i (R, r). \quad (2.11)$$

By solving eq. (2.11), at fixed nuclear distances, the electronic energies, $\varepsilon^a_i (R)$, which depend parametrically on the nuclear separation are obtained. The electronic wave function, $\phi^a_i (R, r)$ now depends parametrically on the nuclear coordinates. If the electronic energies are obtained for various $R$, a potential energy surface (or a potential energy curve in case of a diatomic molecule) is obtained. These potential energy surfaces (curves) are called adiabatic, hence the superscript “$a$”, since it is assumed that electrons respond instantly to the nuclear motion. For diatomic systems, adiabatic potential energy curves of electronic states with the same symmetry are not allowed to cross [121].

Once the electronic problem has been solved, and a complete set of orthonormal electronic states, $\phi^a_i$, has been obtained for all possible nuclear configurations, the full molecular wave function, $\Psi (R, r)$, can be expanded as

$$\Psi (R, r) = \sum_{i=1}^{\infty} \tilde{\chi}^a_i (R) \phi^a_i (R, r). \quad (2.12)$$

If we insert eq. (2.12) in eq. (2.8), we obtain

$$(T_N + H_{el}) \sum_{i=1}^{\infty} \tilde{\chi}^a_i (R) \phi^a_i (R, r) = E \sum_{i=1}^{\infty} \tilde{\chi}^a_i (R) \phi^a_i (R, r). \quad (2.13)$$

Without any loss of generality, a diatomic case of nuclear masses $M_1$ and $M_2$, with reduced mass $\mu = \frac{M_1 M_2}{M_1 + M_2}$ is considered, in the centre of mass frame [12]. The nuclear wave function can be conveniently written as a product of a radial and angular wave function, $\tilde{\chi}^a_i (R) = \frac{\chi^a_i (R)}{R} Y(\theta, \phi)$. The kinetic energy operator, $T_N(R)$, for the radial nuclear wave function, $\chi^a_i (R)$, is

$$T_N(R) = -\frac{1}{2\mu} \frac{d^2}{dR^2}, \quad (2.14)$$

with the centre of mass translational and rotational motions transformed away [12].

If eq. (2.13) is multiplied from the left by $\phi^a_j^* (r, R)$, then integrated over the electronic co-ordinates and with the use the orthonormality of the electronic states, a set of coupled time-independent differential equations for the nuclear vibrational motion is obtained;
\[-\frac{1}{2\mu} \frac{d^2}{dR^2} \chi_i^a (R) + \left[ \epsilon_i^a (R) + \frac{\ell (\ell + 1)}{2\mu R^2} - E \right] \chi_i^a (R) - \sum_{j=1}^{\infty} \left[ \frac{1}{\mu} F_{ij} \frac{d}{dR} + \frac{1}{2\mu} G_{ij} \right] \chi_j^a (R) = 0, \tag{2.15} \]

where the term $\frac{\ell (\ell + 1)}{2\mu R^2}$ is the centrifugal barrier term, usually added to the potential energy. It originates from the separation of the rotational and vibrational motion. $F_{ij}^a$ is a matrix that contains the first derivative non-adiabatic coupling elements, defined as

$$F_{ij}^a (R) = \langle \phi_i^a | \frac{\partial}{\partial R} | \phi_j^a \rangle, \tag{2.16}$$

and $G_{ij}^a$ is the matrix with second derivative non-adiabatic coupling elements, defined as

$$G_{ij}^a (R) = \langle \phi_i^a | \frac{\partial^2}{\partial R^2} | \phi_j^a \rangle. \tag{2.17}$$

$F_{ij}$ contains only off-diagonal elements, while $G_{ij}$ also has diagonal terms, which are referred to as adiabatic corrections. If the electronic wave functions are real, $F_{ij}^a$ is an anti-symmetric matrix. Eq. (2.15) can be compactly written in matrix form as

$$- \frac{1}{2\mu} \frac{d}{dR} \chi^a + \left[ \epsilon^a_{\text{eff}} - E \right] \chi^a - \frac{1}{2\mu} \left[ 2F^a \frac{d}{dR} + G^a \right] \chi^a = 0, \tag{2.18}$$

where all the $\chi_i^a$ are collected in column vector $\chi^a$. $\epsilon^a_{\text{eff}}$ contains elements of the adiabatic electronic potential energies, $\epsilon_i^a$, and the centrifugal barrier term, $\frac{\ell (\ell + 1)}{2\mu R^2}$.

In practice, the off-diagonal contributions from $G_{ij}^a$ are smaller than the contribution from $F_{ij}$ and they can sometimes be neglected [85]. Starting from eq. (2.11), it is possible to derive, from the off-diagonal Hellmann-Feynman theorem [20; 33; 63], the following expression

$$\langle \phi_i | \frac{\partial H_{\text{el}}}{\partial R} | \phi_j \rangle = (\epsilon_j^a - \epsilon_i^a) \langle \phi_i | \frac{\partial}{\partial R} | \phi_j \rangle. \tag{2.19}$$

Thus, the first derivative non-adiabatic coupling element can be written as

$$F_{ij}^a (R) = \frac{\langle \phi_i^a | \frac{\partial H_{\text{el}}}{\partial R} | \phi_j^a \rangle}{\epsilon_j^a - \epsilon_i^a}. \tag{2.20}$$

Unless it vanishes by symmetry, the right hand side numerator of eq. (2.20) is finite whilst the denominator will depend on the energy separation of the $i$-th and the $j$-th adiabatic electronic states. It is thus evident that $F_{ij}^a$ is very
significant in the regions where the electronic states lie very close in energy. Neumann and Wigner [122] proved that for diatomic molecules, the potential energy curves for states of the same electronic symmetry will not cross, and the adiabatic potential energy curves will have avoided crossings where the non-adiabatic coupling elements are large.

Polyatomic molecules do not possess the non-crossing rule. Instead potential energy surfaces may become degenerate and at the point (or seam) of degeneracy a conical intersection may exist [126]. The non-adiabatic coupling between these states may then become infinite.

Non-adiabatic effects are driving processes such as dissociative recombination, mutual neutralization, and photochemical reactions, therefore it is imperative to go beyond the Born-Oppenheimer approximation when studying such reactions, which is further discussed in chapter 4.

2.3 Rotational motion

As highlighted in section 2.2, the nuclear kinetic energy operator term contains terms describing both vibrational and rotational motions. For a diatomic molecule it can be expanded as

$$T_N(R, \theta, \phi) = T_N(R) + H_{\text{rot}}(R, \theta, \phi).$$

(2.21)

The off-diagonal elements of $T_N(R)$, as discussed above, give rise to the non-adiabatic interactions between electronic states of same symmetry. The rotational part of the nuclear kinetic energy operator is given as [72]

$$H_{\text{rot}}(R, \theta, \phi) = \frac{1}{2\mu R^2}\Pi^2.$$  

(2.22)

$\Pi$ here is the nuclear rotational angular momentum operator, such that

$$\Pi^2 = \Pi_x^2 + \Pi_y^2,$$

(2.23)

where the molecular rotation is necessarily assumed to be in a plane containing the internuclear axis, and here chosen as the z-axis, thus $\Pi_z = 0$. The total angular momentum operator, $J$, can be expressed as $J = \Pi + L + S$, where $L$ is the total orbital angular momentum operator and $S$ is the total spin momentum operator. If we introduce the ladder operators, such that

$$J_\pm = J_x \pm iJ_y$$
$$L_\pm = L_x \pm iL_y$$
$$S_\pm = S_x \pm iS_y,$$
then eq. (2.22) can be expanded as

\[ H_{\text{rot}} = \frac{1}{2\mu R^2} \left[ (J^2 - J_z^2) + (L^2 - L_z^2) + (S^2 - S_z^2) \right] + \frac{1}{2\mu R^2} \left[ (L+S_+ + L_- S_+) - (J+S_+ + J_- S_+) - (J+L_+ + J_- L_+) \right]. \] (2.24)

The first three terms of eq. (2.24) have diagonal matrix elements. The last three terms couple the orbital, spin and total angular momenta and they are responsible for rotational couplings between different electronic states. They are classified as the spin-electronic homogeneous coupling term, the \( L \)-uncoupling term and the \( S \)-uncoupling term. If the projection of quantum numbers \( J \), \( L \) and \( S \) on the molecular axis is denoted by the well-known \( \Omega \), \( \Lambda \) and \( \Sigma \), respectively, the selection rules for the three terms are as tabulated in table 2.1.

<table>
<thead>
<tr>
<th>Term</th>
<th>Coupling type</th>
<th>Selection rules; ( \Delta J = 0 )</th>
<th>( \Delta \Omega )</th>
<th>( \Delta \Lambda )</th>
<th>( \Delta \Sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \frac{1}{2\mu R^2} [L+S_- + L_- S_+] ]</td>
<td>Spin-electronic</td>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>( \mp 1 )</td>
</tr>
<tr>
<td>[ \frac{1}{2\mu R^2} [J+L_- + J_- L_+] ]</td>
<td>( L )-uncoupling</td>
<td>0</td>
<td>( \pm 1 )</td>
<td>0</td>
<td>( \pm 1 )</td>
</tr>
<tr>
<td>[ \frac{1}{2\mu R^2} [J+S_- + J_- S_+] ]</td>
<td>( S )-uncoupling</td>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>( \pm 1 )</td>
</tr>
</tbody>
</table>

**Table 2.1:** Properties of off-diagonal rotational coupling terms

Thus for the basis \( |J, S, \Omega, \Lambda, \Sigma\rangle \), we can obtain the following matrix elements for the rotational Hamiltonian, where the \( S \)-uncoupling term gives,

\[ -\frac{1}{2\mu R^2} \langle J, S, \Omega \pm 1, \Lambda, \Sigma \pm 1 | J \pm S \pm | J, S, \Omega, \Lambda, \Sigma \rangle \] (2.25)

\[ = -\frac{1}{2\mu R^2} \left[ (J+1) - \Omega \pm 1 \right] \frac{1}{2} \left[ S(S+1) - \Sigma \pm 1 \right] \],

and the \( L \)-uncoupling terms gives,

\[ -\frac{1}{2\mu R^2} \langle J, S, \Omega \pm 1, \Lambda, \Sigma \pm 1 | J \pm L \pm | J, S, \Omega, \Lambda, \Sigma \rangle \] (2.26)

\[ = -\frac{1}{2\mu R^2} \left[ (J+1) - \Omega \pm 1 \right] \frac{1}{2} \langle J, S, \Omega \pm 1, \Lambda, \Sigma \pm 1 | L \pm | J, S, \Omega, \Lambda, \Sigma \rangle , \]

while the spin-electronic coupling terms gives

\[ -\frac{1}{2\mu R^2} \langle J, S, \Omega \pm 1, \Lambda, \Sigma \pm 1 | L \pm S \pm | J, S, \Omega, \Lambda, \Sigma \rangle \] (2.27)

\[ = -\frac{1}{2\mu R^2} \left[ S(S+1) - \Sigma \mp 1 \right] \frac{1}{2} \langle J, S, \Omega, \Lambda \pm 1, \Sigma \mp 1 | L \pm | J, S, \Omega, \Lambda, \Sigma \rangle . \]
In Paper IV, rotational couplings that are responsible for coupling the states of $^2\Sigma$ and $^2\Pi$ symmetry in the HeH system are considered. This will be further discussed in section 6.3.

In order to obtain the potential energy surfaces (curves), electronic structure calculations have been carried out. A brief descriptions of the quantum chemistry methods applied here are given in chapter 3.
3. Potential energy surfaces, couplings and transformation

The potential energy surfaces and the non-adiabatic couplings, discussed in the previous chapter, are the most important quantities that enter the nuclear Schrödinger equation for a molecular system. Thus it is important that they are computed reliably. In this chapter, the electronic structure methods performed to obtain the potential energy surfaces and the non-adiabatic couplings are discussed in section 3.1. Once the adiabatic potential energy surfaces are obtained, they are then transformed to the diabatic representation, with diabatic potential energies and electronic couplings as discussed in section 3.2. If resonant states are involved, electron scattering calculations are carried out to determine the energy positions of these states. This is outlined in chapter 4.

3.1 Quantum chemistry calculations

This section deals with a computational technique aimed at a detailed description of the electronic wave-function, thus there is no substitute to quantum mechanics, a background of which has been described in chapter 2. The difficulty in solving the problem, arises from the fact that for any system (atom or molecule) with more than one electron, an exact analytical solution to the Schrödinger equation is still unknown. One of the methods to try and approach the problem *ab initio* was developed by Hartree in 1928 [51] and formalized by Fock in 1930 [34]. The approach here is to describe each electron in a molecular system by a function, which is constructed in such a way that it takes care of the spatial and the spin distribution, using an independent-particle approximation. The Hartree-Fock (HF) [57; 95] method, is an approach in which the wavefunction for a system is constructed by a Slater determinant and it is further discussed in the section 3.1.1 below. Further improvement methods, built on the HF method, have been applied here to accurately describe the molecular states involved here and these methods are discussed in subsections 3.1.2 and 3.1.3.
3.1.1 Hartree-Fock method

The standard approach for describing electrons in a molecule is by using a set of one-particle functions. These one-particle functions, called molecular orbitals, are constructed in such a way that they take care of the electronic spatial and spin distributions (so-called spin orbitals). The total wave function of a molecule is expressed as a product of the spin orbitals. For electrons, which are fermions, the total wave function must be antisymmetric with respect to the interchange of two electronic coordinates, as a requisite of the Pauli principle. This is achieved by expressing the total electronic wave function in a form of a Slater determinant [4],

\[
\phi_{HF} = \frac{1}{\sqrt{n!}} \left| \begin{array}{cccc}
\zeta_1(1) & \zeta_2(1) & \cdots & \zeta_n(1) \\
\zeta_1(2) & \zeta_2(2) & \cdots & \zeta_n(2) \\
\vdots & \vdots & \ddots & \vdots \\
\zeta_1(n) & \zeta_2(n) & \cdots & \zeta_n(n)
\end{array} \right|,
\]  

(3.1)

where \( \zeta_i(j) \) denotes the molecular spin orbital \( i \) for electron \( j \) in an \( n \) electron system. The \( \zeta \) functions are constructed in such a way that they are orthonormal to one another. This trial wave function will now consist of a single Slater determinant. By making such an approximation, where the electron-electron repulsion is only added as an average effect, the implication is that electron correlation is not well taken care of. Each electron is considered to move in an electrostatic field represented by the average positions of all other electrons.

If we now define a one-electron operator, \( h_i \), as the sum of the kinetic energy and the electron-nuclei interaction of electron \( i \);

\[
h_i = -\frac{1}{2} \nabla_i^2 - \sum_{j=1}^{N} \frac{Z_j}{|r_i - R_j|},
\]  

(3.2)

and a two-electron operator, \( g_{ij} \), for the electron-electron repulsion as

\[
g_{ij} = \frac{1}{|r_i - r_j|},
\]  

(3.3)

The electronic Hamiltonian can now be simply expressed as

\[
H_{el} = \sum_{i=1}^{n} h_i + \sum_{i=1}^{n} \sum_{j>i} g_{ij} + V_{NN}.
\]  

(3.4)

The term \( V_{NN} \) is the same as in eq. 2.5. The energy of this Slater-type wavefunction is given by [57]

\[
E_{HF} = \langle \phi_{HF}|H_{el}|\phi_{HF} \rangle = \sum_{i=1}^{n} h_i + \sum_{i=1}^{n} \sum_{j>i} (J_{ij} - K_{ij}) + V_{NN},
\]  

(3.5)
where
\[ h_i = \langle \zeta_i | h_1 | \zeta_i \rangle, \]  
\[ J_{ij} = \langle \zeta_i | \zeta_j (2) | g_{12} | \zeta_i (2) \rangle, \]  
\[ K_{ij} = \langle \zeta_i | \zeta_j (2) | g_{12} | \zeta_i (1) \zeta_j (2) \rangle. \]  

The term \( h_i \) is called a one-electron integral and it represents the energy of an electron occupying orbital \( i \), in the field of all nuclei. \( J_{ij} \) is the Coulomb integral and it represents the electrostatic repulsion between two electron clouds, due to, say, electron 1 in orbital \( \zeta_i \) and electron 2 in orbital \( \zeta_j \). \( K_{ij} \) is the exchange integral which mathematically arises from the Slater determinant expansion terms that differ only in exchange of electrons. The exchange integral arises due to the antisymmetry requirement of the wave function.

In the Hartree-Fock (HF) method \([57; 95]\), the molecular orbitals are determined by applying the variational principle, which minimizes the energy. If we define a Coulomb \( (J_i) \) and an exchange \( (K_i) \) operator, defined by their action on a spin orbital, such that
\[ J_i | \zeta_j (2) \rangle = \langle \zeta_i (1) | g_{12} | \zeta_i (1) \rangle | \zeta_j (2) \rangle, \]  
\[ K_i | \zeta_j (2) \rangle = \langle \zeta_i (1) | g_{12} | \zeta_i (1) \rangle | \zeta_i (2) \rangle, \]  

The energy can now be expressed as
\[ E_{HF} = \sum_{i=1}^{n} \langle \zeta_i | h_i | \zeta_i \rangle + \sum_{i=1}^{n} \sum_{j>i}^{n} \left( \langle \zeta_j | J_i | \zeta_j \rangle - \langle \zeta_j | K_i | \zeta_j \rangle \right) + V_{NN}. \]  

We now define a one-electron operator, \( F_i \), that describes the electron kinetic energy, attraction to all nuclei and electron repulsion with all other electrons as the Fock operator,
\[ F_i = h_i + \sum_{j=1}^{n} \left( J_j - K_j \right). \]  

The Fock operator can be inserted in eq. (3.8) and by applying the Lagrange energy minimisation technique \([57]\), we arrive at the Hartree-Fock equation;
\[ F_i \zeta_i = \epsilon_i \zeta_i, \]  

where \( \epsilon_i \) has the interpretation of orbital energy.

Eq. (3.10) is a pseudo-eigenvalue equation, since the Fock operator depends on all occupied molecular orbitals, as can be clearly seen from the dependence of the operator on the exchange and Coulomb operators.

In our calculation, eq. (3.10) is solved by expanding each of the molecular orbitals in some predefined \( M \) basis set of atomic orbitals,
\[
\zeta_i = \sum_{k=1}^{M} C_{ki} \xi_k
\]

(3.11)

where \(C_{ki}\) are the expansion coefficients. This expansion can now be inserted into the Hartree-Fock equation and after multiplying on the left by \(\xi_v\) and integrating results into the Roothaan-Hall equations [4; 57]. For a closed-shell system the equations can be expressed as

\[
\sum_{k=1}^{M} F_{vk} C_{ki} = \epsilon_i \sum_{k=1}^{M} S_{vk} C_{ki},
\]

(3.12)

where

\[
S_{vk} = \langle \xi_v | \xi_k \rangle,
\]

(3.13)

\[
F_{vk} = \langle \xi_v | F | \xi_k \rangle.
\]

(3.14)

Eq. (3.12) can be written compactly in matrix form,

\[
FC = SC\epsilon.
\]

(3.14)

Eq. (3.14) is an eigenvalue equation, except for the overlap matrix \(S\). It has a non-trivial solution only if the secular equation is satisfied;

\[
|F - S\epsilon| = 0.
\]

(3.15)

By requiring that the basis is orthogonal, \(S\) is replaced by a unitary operator. This equation cannot be solved directly because the matrix elements \(F_{ij}\) involve integrals over the Coulomb integral and exchange terms which themselves depend on the spatial wave functions. Thus, a self-consistent field (SCF) approach is employed, obtaining with each iteration a new set of coefficients \(C_{ki}\) and continuing until a convergence criterion has been reached.

With the HF method, the ground state wave function and molecular orbitals are obtained. However, electron correlation effects are not accurately included and hence there is a need to incorporate correlation effects, especially when performing a calculation that involves excited states, like the electronic states involved in the processes studied in this thesis.

In the HF method, the molecular orbitals (MO) are optimised. These are usually constructed using an expansion in a basis of known functions, often as a linear combination of atomic orbitals (LCAO). In most quantum chemistry calculations the atomic orbitals are approximated by an expansion of a basis set of known exponential functions of the form (motivated by the known hydrogen orbitals);

\[
\phi_{orb}(r) = p(x,y,z)e^{-(\beta r^n)},
\]

(3.16)
where $p(x,y,z)$ is a polynomial and $\beta$ is a parameter defining the range of the orbital. If $n = 1$, such a basis is said to be made of Slater type orbitals (STO) and for $n = 2$, they are referred to as Gaussian type orbitals (GTO) [78]. Some of the most used basis sets are those developed by Dunning [62] whose advantage is the computational cost. These are correlation consistent basis sets and are widely used in post-Hartree-Fock methods. They are usually denoted "cc-pVNZ", where N (N=D,T,Q,5,6...) stands for double, triple, quintuple, etc, zeta functions. The "cc-pV" denotes that they are correlation consistent, polarized and valence only basis sets. Additional core or diffuse functions can be augmented for calculating specific properties, such as nuclear properties or electronic excited states properties, and such basis sets are denoted "aug-cc-pVNZ". These basis sets have been employed to compute the potential energy surfaces of the systems studied here.

3.1.2 Configuration interaction

The configuration interaction (CI) method [57] is one of the most straightforward method for including electron correlation effects. It is built as an improvement of the Hartree-Fock solution. In the CI equation, the electronic wave function is constructed as

$$\phi_{CI} = a_0\phi_{HF} + \sum_i a_i\phi_i,$$

(3.17)

where $\phi_{HF}$ is the initial single-determinant Hartree-Fock wave function, the $a_i$'s are the CI expansion coefficients, and the $\phi_i$'s are the Slater determinants that are obtained by distributing the electrons between the occupied and unoccupied (virtual) spin orbitals as illustrated by Fig. 3.1. Applying the variational principle to eq. (3.17) leads to the secular equation for the CI expansion coefficients,

$$Ha = Ea$$

(3.18)

where the diagonal matrix $E$ contains the CI energy, $\langle \phi_i | H | \phi_i \rangle$, $a$ contains the CI coefficients $a_i$ and $H$ is the Hamiltonian matrix

$$H_{ij} = \langle \phi_i | H_{el} | \phi_j \rangle.$$  

(3.19)

Eq. (3.18) has as many solutions as there are configurations in the CI wave function, with the lowest energy solution corresponding to the ground state, the second lowest to the first excited state, etc.
Figure 3.1: Model illustrating the configuration in a multi-reference calculation, where more than one Slater determinant is used in the expansion. The system’s orbitals are presented here in two spaces, labelled the frozen (always doubly occupied and inactive) and the active space orbitals formed by distributing the remaining electrons. A linear combination of these configurations is used to form the CI wavefunction.

The size of the CI expansion of eq. (3.17) scales by the number of basis functions included in the calculation as well as electron excitations that are allowed outside the HF wave function. In CI singles (CIS), only single excitations are allowed, while in CI singles and doubles (CISD) single and double excitations are allowed. If all possible excitations are included, the approach is called full CI (FCI). The FCI method scales exponentially with the number of electrons and orbitals and hence it is computationally feasible only for systems with few electrons [57]. In the thesis, the FCI method has been applied to the study of Paper III, IV, and VI for the H\(_2\) and HeH molecular systems.

In larger electronic systems there is a need to truncate the FCI expansion. One convenient approach is taking a linear combination of dominant configurations, depending on the molecular properties of interest in the calculation. Some multi-configuration methods that have been employed in this work are the multi-reference configuration interaction (MRCI) and the multi-configurational self-consistent field (MCSCF) methods [124] described in section 3.1.3 below.

In the multi-reference CI (MRCI) method [57], terms that have an insignificant contribution to the total energy of the system are truncated, while capturing a significant amount of the electron correlation. In truncating the configuration space, it is important to distinguish between static correlation, which is associated with electrons avoiding each other on a permanent basis, like those occupying different spatial orbitals, and dynamic correlation which is the “instant” correlation between electrons, like those occupying the same spatial orbital. By retaining the dominant configurations of the FCI expansion, static correlation is treated and these configurations are referred to as the reference configuration of the CI wave function. By including all configurations in the...
reference space as well as those generated by excitations out of the reference space, the MRCI wave function is created.

In the MRCI calculation, not only the single Slater orbitals can be combined to form an MRCI wave function, but a symmetry-adapted linear combination of Slater determinants can also be used. Such functions are known as configuration state functions (CSF). The expansion coefficients are then optimised in an MRCI calculation and further excitation out of the active space can be implemented, such as single excitations (MRCIS), single and double excitations (MRCISD), etc.

A typical approach in reducing the computational time for the CI calculation to achieve faster convergence is by using orbitals that diagonalize the density matrix of orbitals obtained in a CI calculation. The corresponding eigenvectors of the diagonal matrix are called natural orbitals (NOs). A multi-configurational calculation that is carried out with such orbitals is compact and suitable to be implemented in an electron scattering calculation as detailed in chapter 4. The MRCI method has been applied in the studies of Papers II (for the LiF system) and VI (for the H$_2$O system).

### 3.1.3 Multi-configurational self-consistent field methods

In the MCSCF method, not only the expansion coefficients of the MRCI wave function are optimised, but also the orbitals are optimised. Thus the orbitals are not fixed, but are modified in such a way that the total energy is as low as possible. This is sometimes efficient in systems describing processes, such as dissociation [78], where there is a need to sufficiently describe the system when the bond is being broken and thus the CI expansion coefficients have a significant contribution to the wave function. The MCSCF optimization procedure is also iterative, like the SCF procedure, and the number of iterations needed to achieve convergence tends to increase with the number of configurations included. Thus in general the size of an MCSCF wave function that can be treated is somewhat smaller than the wave function in CI methods. If all possible configurations of the active space are used in a MCSCF calculation, it is referred to as a complete active space self-consistent field (CASSCF) method. In some calculations, the CASSCF calculation is first used to compute the CSF optimized orbitals which are then used in a subsequent MRCI calculation. This method is applied in the study of LiF in Paper II, where state-averaged molecular orbitals for the two lowest $^1\Sigma^+$ states are computed.

### 3.1.4 Non-adiabatic couplings

From the quantum chemistry calculation, not only the potential energy surfaces can be obtained, but also the radial non-adiabatic couplings are obtained. The
radial couplings can be non-zero for states of the same symmetry and zero for states of different symmetry [72]. The first derivative radial couplings, defined by

$$F_{ij}^a(R) = \langle \phi^a_i | \frac{\partial}{\partial R} | \phi^a_j \rangle,$$  \hspace{1cm} (3.20)

are computed from the electronic wave function, and thus they are very sensitive to the quality of the electronic structure calculation. As such their computation is non-trivial [81]. In this work, the finite difference method [81; 102] has been employed to compute the radial couplings in papers I, II and V. In addition to finite difference, the coupling elements of Papers III, and V are computed analytically using the MESA [100] code.

The potential energy surfaces and the non-adiabatic couplings are then used to transform the electronic states in a manner discussed in section 3.2.

### 3.2 Adiabatic to diabatic transformation

The non-adiabatic couplings that depend on the internuclear distance, $R$, can become very large (even infinite in polyatomic systems) in a region where two states come close to each other. The Schrödinger differential equation, for the nuclear motion, contains both first and second order derivatives whose numerical evaluation is non-trivial [5; 126].

A basic approach is to transform the electronic basis into the diabatic basis. In the diabatic basis, the off-diagonal elements of the nuclear kinetic energy operator are equal to zero or very small,

$$F_{ij}^d(R) = \langle \phi^d_i | \frac{\partial}{\partial R} | \phi^d_j \rangle \approx 0.$$  \hspace{1cm} (3.21)

By performing this transformation, the diabatic states no longer become eigenstates of the electronic Hamiltonian. Thus the diabatic potential energy curves do not obey the non-crossing rule and therefore when one follows the character of a diabatic state through an avoided crossing, the character of the state will be preserved as illustrated, for a diatomic case, in Fig. 3.2. However, in performing such a transformation, one obtains diabatic states that are not eigenfunctions of $H_{el}$ and thus there are non-zero elements of the form

$$\langle \phi^d_i | H_{el} | \phi^d_j \rangle = V_{ij}^d(R),$$  \hspace{1cm} (3.22)

where the diagonal elements are called diabatic potential energies and the off-diagonal elements are called electronic couplings.

The adiabatic potential energy matrix which contains elements of the form

$$\langle \phi^a_i | H_{el} | \phi^a_j \rangle = V_{ij}^a(R)\delta_{ij},$$  \hspace{1cm} (3.23)
will contain only diagonal matrix elements, unless rotational couplings are considered, which is the case in the study of paper IV.

Landau [68] and Zener [127] were the first to independently study the two-state crossing of potential energy curves. However, in reality there might be more than two states (often infinite) involved and hence there are many approaches developed to perform the transformation. They can be loosely categorised into strict diabatic and quasidiabatic transformation and they are further discussed below.

![Schematic diagram of potential energy curves in the vicinity of an avoided crossing point \( R_x \). The black (solid) lines are the adiabatic potential energy curves for two states (\( \phi_1^a \) and \( \phi_2^a \)) and the red (dashed) lines are the diabatic potential energy curves for two states (\( \phi_1^d \) and \( \phi_2^d \)).](image)

**Figure 3.2:** Schematic diagram of potential energy curves in the vicinity of an avoided crossing point \( R_x \). The black (solid) lines are the adiabatic potential energy curves for two states (\( \phi_1^a \) and \( \phi_2^a \)) and the red (dashed) lines are the diabatic potential energy curves for two states (\( \phi_1^d \) and \( \phi_2^d \)).

### 3.2.1 Quasidiabatisation

In the quasidiabatic representation, only part of the non-adiabatic coupling is removed. The method used in the thesis is to perform diabatisation by configurational tracking, where the electronic diabatic state is followed before and after the avoided crossing by examining the CI-coefficients of the adiabatic
states. In this approach, it is assumed that the molecular orbital does not significantly change when the nuclear coordinates are varied.

In the DR study of H$_2$O$^+$, studied in Paper VI, this method is applied. There are an infinite number of Rydberg states that converge to the ground ionic state. The Rydberg states have the ionic state configuration, with an additional electron in an excited state; [ion]($n\lambda$)$_1^1$ (where $n\lambda$ is a diffuse orbital and [ion] represents the ionic state configuration). Since this is a polyatomic system, a strict diabatisation cannot be achieved [86]. A quasi-diabatisation is performed by removing states dominated by the configuration of the form of Rydberg states as illustrated in fig. 3.3. The figure show potential energy curves for states in the $^1A'$ irreducible representation of the $C_s$ symmetry of the water molecule. Below the potential energy curve of the ground state of the ion, the electronic structure calculation computes bound states which are either Rydberg states or more compact valence states. Above the ionic ground state, a mixture of states which are trying to “mimic” the ionization continuum and resonant states are obtained.

![Figure 3.3](image-url)

**Figure 3.3:** Figure illustrating results of the quasidiabatic scheme applied to the $^1A'$ states of the H$_2$O system. The ground and first excited states of H$_2$O$^+$ is shown in solid black lines while the broken green lines show the bound and continuum states with mixed character (Rydberg states and resonant states). The red dotted lines are the quasi-diabatised resonant states.
3.2.2 Strict diabatisation

Strict diabatisation is only possible for a finite number of coupled states of diatomic systems [85; 86], such that if we assume $M$ states to be coupled, then

$$F_{ij}^a = 0 \quad \text{for} \quad i \leq M, j > M. \quad (3.24)$$

The adiabatic states, $\phi_i^a$, are then transformed to diabatic states, $\phi_i^d$, using

$$\phi_i^d = \sum_{j=1}^{M} \phi_j^a T_{ij}^T (R), \quad (3.25)$$

where $T_{ij}$ is an element of the orthogonal transformation matrix, $T$, which satisfies [86]

$$1 \frac{\partial}{\partial R} T + F^a = 0, \quad (3.26)$$

with the boundary condition

$$\lim_{R \to \infty} T(R) = I. \quad (3.27)$$

A similar transformation is performed for the nuclear wavefunction

$$\chi_i^d (R) = \sum_{j=1}^{M} \chi_j^a (R) T_{ij}^T (R), \quad (3.28)$$

in order to preserve the total wavefunction. By inserting the diabatic nuclear wave function (3.28) in the Schrödinger equation for the nuclear motion, (2.18), we obtain the coupled Schrödinger equation in the strictly diabatic basis as

$$-\frac{1}{2\mu} \frac{d^2}{dR^2} \chi^d + \left( V^d - \frac{\ell(\ell+1)}{2\mu R^2} \right) \chi^d = E \chi^d, \quad (3.29)$$

where the diabatic potential energy matrix is obtained from

$$V^d = T^T V^a T. \quad (3.30)$$

The diabatic matrix elements are

$$V_{ij}^d = \langle \phi_i^d | H_{el} | \phi_j^d \rangle, \quad (3.31)$$

which in contrast to the adiabatic potential matrix elements, contain off-diagonal elements. The diagonal elements are the diabatic potential energy curves, similar to the ones shown in Fig. 3.2, and these curves can cross each other, even for states of the same symmetry. The off-diagonal elements are called the electronic couplings and compared to the non-adiabatic couplings, they
vary smoothly with $R$. This is the approach employed in the study of MN of $\text{H}^+ + \text{H}^-$ and $\text{He}^+ + \text{H}^-$ of Papers I and IV, respectively.

If we assume that only two states are coupled together in the crossing region, a two-by-two strict transformation can also be performed. Here the transformation matrix, $T$, is

$$T = \begin{pmatrix}
\cos[\gamma(R)] & \sin[\gamma(R)] \\
-\sin[\gamma(R)] & \cos[\gamma(R)]
\end{pmatrix}. \quad (3.32)$$

The rotational angle, $\gamma(R)$, is obtained from integrating the first derivative coupling element [85]

$$\gamma(R) = \int_{R}^{\infty} F_{ij}(R')dR'. \quad (3.33)$$

One of the rotational angles obtained in the study of MN in collisions of $\text{Li}^+$ and $\text{F}^-$, in Paper II, is shown in fig. 3.4. For a system with more than two states interacting near an avoided crossing, as is the case in the $\text{H}_2$ system studied in papers I and IV, the non-adiabatic couplings do not have a perfect Lorentzian shape. To ensure that there is a complete “switch” at the avoided crossing, the non-adiabatic coupling elements are scaled such that

$$\tilde{F}_{ij}(R) = \frac{\pi F_{ij}(R)}{2\int_{R}^{\infty} F_{ij}(R')dR'}, \quad (3.34)$$

ensuring that before the avoided crossing $\gamma(R) \approx \frac{\pi}{2}$. 

Figure 3.4: Rotational angle obtained from the couplings of the two states in the LiF system.
To ensure that far away from the crossing region the diabatic and adiabatic states are the same, a scaling factor is imposed, such that

\[ T = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, R \ll R_x, \]  

(3.35)

and

\[ T = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, R \gg R_x. \]  

(3.36)

Mead and Truhlar [85] have pointed out that a strict diabatic representation, in the sense discussed above, is only possible for a diatomic molecule. In the studies carried out in this thesis a strict diabatisation is performed in the MN studies of H\(^+\) + H\(^-\), Li\(^+\) + F\(^-\) and He\(^+\) + H\(^-\). A Landau-Zener [68; 127] semiclassical analysis is also carried out for MN of H\(^+\) + H\(^-\) and Li\(^+\) + F\(^-\) where a two-by-two transformation is performed.

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4. Electron scattering

When resonant states are involved in the chemical reaction, the quantum chemical calculations are usually not sufficient to accurately locate such states. There is a need to perform electron scattering calculations. This is the case in the HeH system (studied in papers III and V) and the H$_2$O system (studied in Paper IV). The fixed-nuclei electron scattering calculations were carried out using an algebraic variational method known as the Complex Kohn variational method [97]. The basic concepts, in the case of one-particle elastic scattering, are illustrated in section 4.2, and then application to a more realistic case, like an electron-molecular ion scattering, is also briefly discussed. First, in section 4.1, we discuss the basic scattering process by a spherically symmetric short-range potential and how potential energies and autoionisation widths of the resonant states are determined.

4.1 Scattering theory

Reactions, similar to the ones studied in this thesis can be classified as scattering processes, and as such, we can analyse the initial system (reactants), which is related to the asymptotic wave function $\Psi_{in}$ and the final system (products), which is related to the asymptotic wave function $\Psi_{out}$. The outgoing system is related to the incoming system by the $S$-operator [109],

$$\Psi_{out} = S\Psi_{in}. \quad (4.1)$$

Theoretically, the $S$-operator contains all information about the reaction, hence the expectation value of $S$ can help compute observables of the reaction. $S$ can also be expressed in terms of the transition operator, $T$,

$$S = 1 - iT. \quad (4.2)$$

The first term in eq. (4.2) is for the case when there is no scattering taking place and the second term is the transition operator, $T$. The matrix elements of $T$ are related to the scattering amplitude, $f(k, k')$, for an incoming state with momentum $k$ and scattered state with momentum $k'$ [109],

$$f(k, k') = -\frac{(2\pi)^2}{\mu} \langle k' | T | k \rangle, \quad (4.3)$$
where $\mu$ is the mass of the system.

The mathematical basis for defining the scattering process is discussed for the case of a simple potential, $V(q)$, which is spherically symmetric, such that the scattering in each partial wave, $\ell$, can be considered separately. Here $q$ is the separation distance between incoming particle and the target. We additionally assume the potential to be short range (i.e. $qV(q) \to 0$ as $q \to \infty$). For such a potential, the Hamiltonian operator, $H = -\frac{1}{2\mu} \nabla^2 + V(q)$, will commute with the operators $L^2$ and $L_z$ [16]. Thus, the Schrödinger equation (2.8) is separable in spherical coordinates. The symmetry about the incident direction (taken along the $z$-axis) makes the total wavefunction, $\Psi(q, \theta)$, to be independent of the azimuthal angle $\varphi$. For a short-range potential, the solutions are sought from the Schrödinger equation, subject to the boundary conditions:

$$\Psi(q, \theta)_{q \to \infty} \sim e^{ikz} + f(E, \theta) \frac{e^{ikq}}{q}, \quad (4.4)$$

where $f(E, \theta) = f(k, k')$ (achieved by choosing the momentum $k$ along the $z$-axis) is the scattering amplitude and the dependence on the azimuthal angle, $\varphi$, has been omitted due the cylindrical symmetry of the potential. The wave function can be expanded as,

$$\Psi(q, \theta) = \frac{1}{q} \sum_{\ell=0}^{\infty} A_\ell \psi_\ell(q) P_\ell(\cos \theta), \quad (4.5)$$

where the constant $A_\ell$ is the expansion coefficient. Here $P_\ell(\cos \theta)$ are the well known Legendre polynomials [3] and $\psi_\ell(q)$ is the radial wave function which satisfies the radial Schrödinger equation [38],

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dq^2} + \frac{\ell(\ell+1)}{2\mu q^2} + V(q) \right] \psi_\ell(q) = E \psi_\ell(q). \quad (4.6)$$

A power series expansion of $\psi_\ell(q)$ will show that there are two kinds of solutions. One that is regular at the origin, and behaves like $\psi_\ell(q) \to q^{\ell+1}$, as $q \to 0$ and an irregular solution that behaves like $\psi_\ell(q) \to q^{-\ell}$, as $q \to 0$ [16]. Subject to the boundary condition $\psi_\ell(0) = 0$, the solution to eq. (4.6) has the asymptotic form [23; 104],

$$\psi_\ell(q) \to \alpha_\ell(q) - S_\ell(E) \beta_\ell(q) \quad (4.7)$$

where $\alpha_\ell(q)$ and $\beta_\ell(q)$ are solutions of the incoming and outgoing waves, respectively. $S_\ell(E)$ is the partial wave scattering matrix (S-matrix) and it can be interpreted as the eigenvalue to the $S$-operator [109]. Since $S$ is unitary, each
of the eigenvalues will have modulus one and can be written as an exponent of an imaginary number,

\[ S_\ell(E) = e^{2i\eta_\ell(E)}, \]

(4.8)

where \( \eta_\ell(E) \) is the phase shift [23].

For a totally elastic collision, where incident and outgoing electron have the same wave number \( k \), the cross section is

\[ \sigma(E) = \sum_{\ell=0}^{\infty} \sigma_\ell(E), \]

(4.9)

where

\[ \sigma_\ell(E) = \frac{\pi}{k^2} (2\ell + 1) |1 - S_\ell(E)|^2. \]

(4.10)

In the electron scattering process, the electron can be temporarily captured by the molecular ion into a short-lived (resonant) excited neutral state. This happens at certain energies, known as resonant energies, \( E_{\text{res}} \). The energy can be expressed as a complex energy eigenvalue [23],

\[ E = E_{\text{res}} - \frac{i\Gamma}{2}, \]

(4.11)

where \( \Gamma \) is the autoionization width. By analysing the time evolution factor for the wave function at the energy given by eq. (4.11), it can be shown that \( \Gamma \) is related to the lifetime, \( \tau \), of a resonant state by

\[ \tau = \frac{1}{\Gamma}. \]

(4.12)

Based on the complex nature of the energy of the system, the S-matrix is usually expressed as [23]

\[ S_\ell(E) = \left\{ \begin{array}{c} E - E_{\text{res}} - \frac{i\Gamma}{2} \\ E - E_{\text{res}} + \frac{i\Gamma}{2} \end{array} \right\} e^{2i\eta_\ell^{(0)}(E)}, \]

(4.13)

where \( \eta_\ell^{(0)} \) is the background phase shift. At \( E = E_{\text{res}} \), the S-matrix will have a pole, which causes the sharp variation in the elastic cross section. Thus the phase shift can be expressed in the Breit-Wigner form [17]

\[ \eta_\ell(E) = \eta_\ell^{(0)}(E) + \tan^{-1}\left[ \frac{\Gamma}{2(E_{\text{res}} - E)} \right]. \]

(4.14)

This implies that the phase shift will increase by \( \pi \) when energy is passing through a resonance energy, at \( E = E_{\text{res}} - \frac{i\Gamma}{2} \), and how fast the “jump” occurs is determined by \( \Gamma \).
In a system with more than one state interacting, the existence of a quantum resonant state (often referred to as a quasi-bound state) is often depicted by observing distortion of the continuum due to the interaction with an otherwise bound state. If the wave function for the bound state and the continuum state belong to the same internal state of the system, it is referred to as a shape resonance, while if the two states belong to different internal states of the system it is called a Feshbach resonance. The two types of resonances are illustrated in Figs. 4.1(a) and 4.1(b). In a shape resonance the driving mechanism is quantum tunnelling through the potential barrier, while for a Feshbach resonance the breakup is driven by the coupling of the two states.

![Figure 4.1: Schematic illustration of (a) Shape resonance and (b) Feshbach resonance.](image)

A resonance structure is illustrated in Fig. 4.2 (a), which shows elastic scat-
tering eigenphase sum for an electron colliding with the water cation ($\text{H}_2\text{O}^+ + \text{e}^-$) at fixed nuclear coordinates. The shape of the elastic cross section thus depends on the local value of $\eta^{(0)}(E)$, with sharp variation at a resonance energy. The elastic cross section of reaction $\text{H}_2\text{O}^+ + \text{e}^-$ is shown in Fig. 4.2 (b), where different resonance profiles (so-called Beutler-Fano line-shapes [24]) can be noticed.

![Graph](image.png)

**Figure 4.2:** The elastic scattering of $\text{H}_2\text{O}^+ + \text{e}^-$ in $^1\text{A'}$ symmetry, at fixed nuclear coordinates. In (a) the eigenphase sum is displayed as a function of energy and in (b) the corresponding elastic cross section is shown.
4.2 Complex Kohn variational method

The basic concepts of the method are easily described for a case of scattering of a spinless particle by a short-range, spherically symmetric potential $V(r)$ (N.B.: The separation distance between incoming particle and target is now denoted by $r$). The partial wave radial Schrödinger equation can be written as

$$L \psi_\ell(r) = 0, \quad (4.15)$$

where the operator $L$ is defined as

$$L = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{2r^2} + \frac{Z}{r} + V(r) - \frac{k^2}{2}. \quad (4.16)$$

The term $Z/r$ is included to generalize to the scattering by either neutral ($Z = 0$) or ionic ($Z \neq 0$) targets. A Kohn functional $I$, used to minimize the variational parameters, is defined as

$$I[\psi_\ell(r)] = \langle \psi_\ell(r) | L | \psi_\ell(r) \rangle = \int_0^\infty \psi_\ell(r) L \psi_\ell(r) dr. \quad (4.17)$$

This functional is defined such that $I[\phi_\ell(r)] = 0$ if $\phi_\ell(r)$ represents the exact solution. The boundary conditions built into the basis functions, $\psi_\ell(r)$ are

$$\psi_\ell(0) = 0 \quad (4.18)$$

$$\psi_\ell(r \to \infty) \sim F_\ell(kr) + \lambda G_\ell(kr), \quad (4.19)$$

where $F_\ell$ and $G_\ell$ are two linearly independent solutions of eq. (4.15), for the case when $V(r) = 0$ and $\lambda$ is a variational linear parameter. If, in eq. (4.16), $Z \neq 0$, $F_\ell(r)$ and $G_\ell(r)$ are the incoming and outgoing Coulomb functions, respectively. If a trial wave function, $\phi_\ell'(r) \neq \phi_\ell(r)$ is used instead, then $L \phi_\ell'(r) \neq 0$. We define the residual between the exact wave function and the trial wave function as

$$\delta \phi_\ell(r) = \phi_\ell(r) - \phi_\ell'(r), \quad (4.20)$$

and the following boundary conditions are assumed:

$$\delta \phi_\ell(0) = 0 \quad (4.21)$$

$$\delta \phi_\ell(r \to \infty) = \delta \lambda G_\ell(kr). \quad (4.22)$$

$\delta \lambda = \lambda - \lambda'$, and $\lambda'$ is the variational parameter. Inserting the trial wave function into eq. (4.17) yields

$$I[\phi_\ell'(r)] = I[\phi_\ell(r) + \delta \phi_\ell(r)] = \int_0^\infty \phi_\ell(r) L \delta \phi_\ell(r) dr \quad (4.23)$$

$$+ \int_0^\infty \delta \phi_\ell(r) L \phi_\ell(r) dr + \int_0^\infty \phi_\ell(r) L \phi_\ell(r) dr + \int_0^\infty \delta \phi_\ell(r) L \phi_\ell(r) dr.$$
The last two terms of eq. (4.24) will vanish due to the fact that \( L \phi_{\ell}(r) = 0 \). Integrating the first term by parts, and by matching the exact solution, \( \phi_{\ell}(r) \), and the trial function, \( \phi_{\ell}^t(r) \) at \( r = 0 \) and \( r = \infty \) we arrive at

\[
\int_0^{\infty} \phi_{\ell}(r)L\delta \phi_{\ell}(r)dr = \frac{k}{2} W \delta \lambda, \tag{4.24}
\]

where \( W \) is the Wronskian, defined as

\[
W = F_{\ell}(r) \frac{d}{dr} G_{\ell}(r) - G_{\ell}(r) \frac{d}{dr} F_{\ell}(r). \tag{4.25}
\]

By inserting the trial wave function, eq. (4.24) can now be written as

\[
\lambda = \lambda' + \frac{2}{kW} \int_0^{\infty} \phi_{\ell}^t(r)L\phi_{\ell}^t(r)dr - \int_0^{\infty} \delta \phi_{\ell}^t(r)L\delta \phi_{\ell}^t(r)dr. \tag{4.26}
\]

Eq. (4.26) is known as the Kato’s identity and it provides a stationary principle for approximating \( \lambda \) in the following way, where we have kept only first order terms of eq. (4.26),

\[
\lambda^s = \lambda' + \frac{2}{kW} \int_0^{\infty} \phi_{\ell}^t(r)L\phi_{\ell}^t(r)dr. \tag{4.27}
\]

If we choose a trial wave function, that contains only linear trial coefficients, eq. (4.27) can be solved explicitly. The trial wave function can have the form

\[
\phi_{\ell}^t(r) = f_{\ell}(r) + \lambda' g_{\ell}(r) + \sum_{i=1}^{m} c_i \phi_i(r) \tag{4.28}
\]

where \( c_0 = \lambda' \), \( \phi_0(r) = g_{\ell}(r) \), \( c_{m+1} = 1 \), \( \phi_{m+1}(r) = f_{\ell}(r) \). \tag{4.29}

Here the set \( \phi_i \), with \( i \in [1, m] \), are square integrable \((L^2)\) functions and

\[
f_{\ell}(r \to \infty) \sim F_{\ell}(kr) \tag{4.30}
\]

\[
g_{\ell}(r \to \infty) \sim G_{\ell}(kr). \tag{4.31}
\]

The coefficients \( \lambda' \) and \( c_i \) are determined by applying the following variational conditions;

\[
\frac{\partial \lambda^s}{\partial c_i} = \frac{\partial \lambda^s}{\partial \lambda'} = 0. \tag{4.32}
\]

Substituting the trial wave function of eq. (4.28) into eq. (4.27) and taking the derivative with respect to the \( c_i \) coefficients gives

\[
\int_0^{\infty} \phi_i(r)L\phi_i^t(r)dr = 0, \quad i = 1, \ldots, m. \tag{4.33}
\]
Taking the derivative with respect to $\lambda^i$ instead gives,

$$
\int_0^{\infty} g_\ell(r) \mathbf{L} \phi_i(r) dr = 0, \quad i = 1, \ldots, m. \tag{4.34}
$$

By defining all the $c_i$'s by a vector $\mathbf{c}$, eq. (4.33) and eq. (4.34) can be expressed in compact form

$$
\mathbf{c} = -\mathbf{M}^{-1} \mathbf{s}, \tag{4.35}
$$

where the matrix $\mathbf{M}$ contains the elements

$$
M_{ij} = \int_0^{\infty} \phi_i(r) \mathbf{L} \phi_j(r) dr, \quad i, j = 0, \ldots, m, \tag{4.36}
$$

and $\mathbf{s}$ is a vector containing the elements

$$
s_i = \int_0^{\infty} \phi_j(r) \mathbf{L} f_\ell(r) dr, \quad i = 0, \ldots, m. \tag{4.37}
$$

By substituting eq. (4.35) into eq. (4.27), the stationary value of $\lambda^s$ can be obtained

$$
\lambda^s = \frac{2}{kW} \left[ \int_0^{\infty} f_\ell(r) \mathbf{L} f_\ell(r) - \mathbf{s} \mathbf{M}^{-1} \mathbf{s} \right]. \tag{4.38}
$$

In order to avoid the matrix $\mathbf{M}$ from being singular at real energies, $g_\ell(r)$ is chosen to be an outgoing complex valued function, $h_\ell^+(r)$, defined as

$$
h_\ell^+(r) = \frac{i [F_\ell(kr) - iG_\ell(kr)]}{\sqrt{k}}, \tag{4.39}
$$

then the Wronskian simplifies to $W = \frac{-1}{\sqrt{k}}$. Eq. (4.38) reduces to an expression for the T-matrix, $\lambda = T_\ell = e^{i \delta_\ell} \sin \delta_\ell$ [109]

$$
T_\ell^s = -2 \left[ \int_0^{\infty} f_\ell(r) \mathbf{L} f_\ell(r) - \mathbf{s} \mathbf{M}^{-1} \mathbf{s} \right]. \tag{4.40}
$$

The matrix $\mathbf{M}$, whose inverse is generally non-singular at real energies [54], is now symmetric and complex, hence the method is called the complex Kohn variational method.

4.2.1 Generalization to electron molecular ion scattering

The electron- molecular ion scattering calculations are performed in the framework of the fixed nuclei approximation [101]. The trial wave function has to be appropriately chosen in this case, since the interaction potential is non-spherical. Such a wave function has to be suitable for describing both the interaction region and asymptotically. Usually, in scattering calculations, the
boundary conditions imposed are such that a wave function is finite-valued at
the origin and behaves like an outgoing wave asymptotically.

For a multi channel electron-molecular ion scattering, the trial wave function is expressed as [97]

$$
\Phi_a = \sum_{a'} A \{ \phi_{a'} F_{a'a} \} + \Theta_a,
$$

(4.41)

where the summation in the RHS is running over all the energetically open
$n$-electron target states. $\phi_{a'}$ is the target state function and $F_{a'a}$ is the wavefunction of the scattered electron. The operator $A$ antisymmetrizes product $\phi_{a'} F_{a'a}$. The subscripts $(a', a)$ refer to the (final, incident) channels. The second term contains a set of square integrable $(n + 1)$-electron functions that are used to represent polarization and correlation effects which are not included in the first term. It can be expanded as

$$
\Theta_a = \sum_{\mu} d_a^\mu \Theta_{\mu},
$$

(4.42)

where $\Theta_{\mu}$ are the $n + 1$ configuration state functions (CSFs).

The channel continuum functions, $F_{a'a}$, are further expanded as [97]

$$
F_{a'a} = \sum_{\ell m} [f_{\ell}(k_{a'}r) \delta_{\ell\ell_0} \delta_{m0} \delta_{a'a} + T_{a'a}^{d'a} g_{\ell}(k_{a'}r)] \frac{Y_{\ell m}(r)}{r} + \sum_i c_i^{d'a} \phi_i(r),
$$

(4.43)

where $f_{\ell}$ and $g_{\ell}$ are the continuum wave functions representing the incoming and outgoing wave for the scattering electron, $Y_{\ell m}$ is the normalized spherical harmonic, while the $\phi_i$'s are a set of square integrable functions. By energy conservation, the channel momenta, $k_{a'}$, are determined as

$$
k_{a'}^2 = 2(E - E_{a'}),
$$

(4.44)

where $E$ is the total energy and $E_{a'}$ is the energy of the target molecular ion corresponding to the state $\chi_{a'}$. The coefficients $T_{a'a}^{d'a}$ are the T-matrix elements and are the fundamental dynamical quantities of interest, from which quantities like the eigenphase sum and the scattering cross section can be calculated.

In a realistic electron-molecular ion collision event, the interaction potential is not necessarily spherical and thus the S-matrix (or T-matrix) will have both the $\ell$ and $m$ indices as shown by eq. (4.43). The T-matrix, thus described above, is related to the scattering matrix, S-matrix by the simple relation

$$
T_{a'a}^{d'a} = 1 - iS_{a'a}^{d'a},
$$

(4.45)

39
By diagonalizing the scattering matrix, the eigenphase sum can be calculated at a fixed internuclear coordinate, \( R \), as

\[
\eta(E; R) = \sum_i \eta_i(E; R),
\]

(4.46)

where the index “\( i \)” here represents eigen-channel index. To obtain the autoionization width, \( \Gamma(R) \) and the energy position, \( E_{\text{res}}(R) \) of a resonant state at the internuclear distance \( R \), the eigenphase sum is fitted to a Breit-Wigner formula [17]

\[
\eta(E; R) = \eta_{\text{res}}(E; R) + \eta^{(0)}(E; R) = \tan^{-1}\left( \frac{\Gamma}{2(E - E_{\text{res}})} \right) + a + bE + cE^2,
\]

(4.47)

where the parameters \( E_{\text{res}}, \Gamma, a, b, \) and \( c \), are optimized in the fit. The potential energy of the resonant state is then obtained by adding the resonant energy to the potential energy of the ion,

\[
V_{\text{res}}(R) = V_{\text{ion}}(R) + E_{\text{res}}(R)
\]

(4.48)

Fig. 4.2 shows the eigenphase sum and elastic scattering cross section for \( \text{H}_2\text{O}^+ \) in \( 1\text{A}' \) symmetry. Here the internuclear distances between the first and second H atoms and the O are 1.8 \( a_0 \) and 2.0 \( a_0 \), respectively, while the angle \( \angle \text{HOH} \) is 108.8°. In Fig. 4.2 (a) the eigenphase sum shows a sudden shift of \( \pi \) whenever the energy hits a resonance. The electron scattering cross section is shown in Fig. 4.2 (b) and it is also showing a sudden structure whenever it reaches a resonance. In the neighbourhood of such a resonance the eigenphase sum is fitted to eq. (4.47) to obtain \( E_{\text{res}}(R) \) and \( \Gamma(R) \).

The resonant state energies thus obtained for several internuclear distances can be plotted as energy positions above the potential energy of the ionic ground state as shown in Fig. 4.3.
Figure 4.3: Figure illustrating results from the electron scattering calculation in $^1A'$ symmetry of the H$_2$O system. Lines show potential energies obtained in quantum chemistry (MRCI) calculations. The ground state of H$_2$O$^+$ is shown in solid black line while the broken green lines show the bound and continuum states with mixed character (Rydberg states and resonant states). The red dots show the energy positions of resonant states from the scattering calculation.
5. Nuclear dynamics

This chapter describes the models used to study the nuclear dynamics of the systems studied in the thesis. In the previous chapter, details of how the relevant potential energy surfaces and couplings are calculated were discussed. These parameters are used as input for modelling the nuclear motion. The cross section for the molecular collision process is then calculated after solving the nuclear Schrödinger equation. For the DR process of H$_2$O$^+$ studied in Paper VI, a wave packet method, based on the time-dependent Schrödinger equation is employed. For the MN studies of Papers II, IV and V the time-independent Schrödinger equation is used. The semi-classical Landua-Zener model has also been used to carry out the investigation of MN for H$^+ + $H$^-$ and Be$^+ + $H$^-$ in Paper I and the MN study of Li$^+ + $F$^-$ in Paper III.

5.1 Landau-Zener semi-clasical approach

In a Landau-Zener (LZ) [68; 127] model, the nuclear dynamics is studied semi-classically. It is assumed that only two states are interacting. The Hamiltonian is expressed in the form

$$\hat{H} = \begin{pmatrix} \hat{T} + U_{11}(R) & U_{12}(R) \\ U_{21}(R) & \hat{T} + U_{22}(R) \end{pmatrix},$$

where $U_{11}(R)$ and $U_{22}(R)$ are the diabatic potential energy curves, while $U_{12}(R)$ and $U_{21}(R)$ are the off-diagonal elements that correspond to the electronic coupling.

In the model, it is assumed that $U_{11}(R) - U_{22}(R) = kR$, where $k$ is a constant, i.e. the difference between the two diabatic states is a linear function of the internuclear separation. The electronic coupling is assumed to be constant,

$$U_{12}(R) = U_{21}(R) = H_{12}. \quad (5.2)$$

In the LZ model, it is assumed that the transition region is small and only the characteristics of the region are of importance. The probability, $p_\ell$, of making a non-adiabatic transition (or following a state diabatically) is given by [68; 127]

$$p_\ell = \exp \left( -\frac{2\pi H_{12}^2}{\nu_1 k} \right),$$

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Figure 5.1: Schematic diagram illustrating the potential energy curves for an ion-pair (red) and a covalent state (purple). The solid lines show the potential energy when the centrifugal term is not added ($\ell = 0$), while the dashed lines are the potential energy curves when the centrifugal barrier is added ($\ell \neq 0$). For the MN reaction to occur the purple and the red dashed lines have to coincide at $R_x$, for $\ell = \ell_{\text{max}}$.

where $v_x^\ell$ is the radial velocity at the curve crossing, for a given angular momentum quantum number $\ell$. For a MN system, illustrated by Fig. 5.1, the classical turning point will depend on the centrifugal barrier term, hence on $\ell$.

Here we assume that the covalent states are constant as a function of the internuclear separation, while the ion-pair state will have the form

$$V_{\text{ion-pair}}(R) = V_{\text{asy}} - \frac{1}{R} - \frac{\alpha_p(A^+) + \alpha_p(B^-)}{2R^4},$$

(5.4)

where $V_{\text{asy}}$ denotes the asymptotic value of the potential energy of the ion-pair state and $\alpha_p$ is the polarizability of the ion.

For a fixed $\ell$, the centrifugal barrier is $\frac{\ell(\ell + 1)}{2\mu R^2}$, where $\mu$ is the reduced mass of the system. If we assume that the kinetic energy at the crossing point is given by

$$E_k = \frac{\mu(v_x^\ell)^2}{2},$$

(5.5)
then the total energy of the system can be equated to the kinetic energy,
\[ E + \Delta E - \frac{\ell (\ell + 1)}{2 \mu R^2} = \frac{\mu (v^\ell)^2}{2} \quad (5.6) \]

The radial velocity can thus be obtained as
\[ v^\ell = \sqrt{\frac{2}{\mu} \left[ E + \Delta E - \frac{\ell (\ell + 1)}{2 \mu R^2} \right]} \quad (5.7) \]

Here \( E \) is the collision energy of the system and energy difference between covalent and the ion-pair potential curves is \( \Delta E \), as illustrated in Fig. 5.1. Thus for the system to reach \( R_x \), the centrifugal barrier has to be smaller than the kinetic energy of the system. For a system to at least reach the point \( R_x \) and be reflected, the kinetic energy at \( R_x \) has to be larger or equal to the centrifugal barrier. Thus for a given \( E \),
\[ E + \Delta E \approx \frac{\ell_{\text{max}} (\ell_{\text{max}} + 1)}{2 \mu R_x^2} \quad (5.8) \]

where \( \ell_{\text{max}} \) is the maximum angular momentum reachable, at which the system is reflected before reaching smaller internuclear distances,
\[ \ell_{\text{max}} = 2 \sqrt{\mu (E + \Delta E) R_x} \quad (5.9) \]

To compute the electronic coupling, \( H_{12} \), \textit{ab initio} is challenging since the curve crossings driving MN process are occurring at large internuclear distances and involve highly excited states. However, there are several empirical methods that have been applied in trying to approximate electronic couplings and some of them are discussed and applied in Paper I. One of the systems studied here is the MN of \( \text{H}^+ + \text{H}^- \), where in the adiabatic representation there are two covalent states converging to the \( n = 2 \) limit and three converging to the \( n = 3 \) limit in \( 1\Sigma_g^+ \) symmetry [104]. According to Lewis [76], in the crossing region only two states are involved in the change of character from ionic to covalent. Using the energy difference of the adiabatic states, at the avoided crossing, \( R_x \), the electronic couplings, \( H_{12} \), can be approximated by [10]
\[ H_{12} = \frac{1}{2} \sqrt{\sum_i \left[ V_i^a(R_x) - V_{i-1}^a(R_x) \right]^2} \quad (5.10) \]

where \( V_i^a \) are the adiabatic potential energy curves obtained by \textit{ab initio} methods as outlined in Fig. 5.2, with the solid lines. Here, the diabatic potential energy curves (shown as broken lines) are crossing each other at \( R_x \). Also a
Figure 5.2: Adiabatic \((V_i^{a})\) and diabatic \((V_i^{d})\) potential energy curves for the H\(_2\) system. Here the potential energy curves for only the effective state converging to the \(n = 2\) asymptotic limit and the potential energy converging to the ion-pair limit are shown.

two-by-two strict diabatisation using the transformation matrix (3.32) has been performed and the electronic couplings are the off-diagonal elements of the diabatic potential energy matrix (3.30). These two methods of obtaining the electronic couplings have been applied to obtain the so-called “APS” and “ATD” couplings of paper I. In the MN of Li\(^{+} + F^{-}\) study (Paper II), there are only two electronic states relevant for the process that are of interest and hence the LZ approach is easily applied here to compute the transition probability. The electronic coupling was obtained by a two-by-two strict diabatization (ATD method). The collision cross section is evaluated by [90]

\[
\sigma(E) = \frac{\pi}{k^2_i} \sum_{\ell} (2l + 1) P_\ell(E),
\]  

(5.11)

where \(P_\ell(E)\) is the multi-state LZ probability [10] and in the case of two states interacting is,

\[
P_\ell(E) = 2p_\ell(1 - p_\ell).
\]

(5.12)

When several states interact with the ion-pair state, the LZ probabilities for all pathways to a given limit have to be combined and the expressions for the multi-state LZ probability become more complex. This is the case in paper I for the MN study of H\(^{+} + H^{-}\) and this is further discussed in section 6.1.
5.2 Time-independent nuclear dynamics

The nuclear dynamics of the MN quantum mechanical studies are carried out using the time-independent version of the Schrödinger equation. This method is applied to study the MN reaction of $\text{H}^+ + \text{H}^-$ in papers I and V and $\text{He}^+ + \text{H}^-$ in paper IV. Here we study multi-channel scattering. The asymptotic form of the wave function is similar to Eq. (4.4). The nuclear wave function is expanded into radial wave functions and Legendre polynomials

\[
\chi_{\ell}(R) = \frac{1}{R} \sum_{\ell=0}^{\infty} A_{\ell} \psi_{\ell, \ell}(R) P_{\ell}(\cos \theta),
\]  

where $A_{\ell}$ is a constant that is chosen to satisfy the boundary condition, $P_{\ell}(\cos \theta)$ are the well known Legendre polynomials and $\psi_{\ell, \ell}(R)$ is the radial wavefunction, satisfying the equation

\[
\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{\ell(\ell+1)}{2\mu R^2} \right] \psi_{\ell, \ell}(R) + \sum_{j=1}^{M} V_{ij}^d \psi_{j, \ell}(R) = E \psi_{\ell, \ell}(R).
\]  

The terms $\psi_{\ell, \ell}(R)$ can all be collected to a square matrix $\psi_{\ell}(R)$. At large internuclear distances ($R \geq R_p$), the electronic potential matrix, $V^d$, is assumed to be diagonal and then [61],

\[
\psi_{\ell}(R) = \alpha_{\ell}(R) + \beta_{\ell}(R) S_{\ell},
\]  

where $S_{\ell}$ is the scattering matrix [108] and $\alpha_{\ell}$ and $\beta_{\ell}$ are the regular and irregular solutions, respectively.

In order to numerically integrate the radial equation, the log derivative is introduced,

\[
y_{\ell} = \psi_{\ell}^\dagger(R) \psi_{\ell}^{-1}(R).
\]  

Using this expression, the radial Schrödinger equation (5.14) is transformed to a more numerically stable matrix Riccati equation [60]

\[
y_{\ell}' + Q_{\ell} + y_{\ell}^2 = 0,
\]  

where

\[
Q_{\ell} = 2\mu (E 1 - V^d) - \frac{\ell(\ell+1)}{R^2} 1.
\]  

The Riccati equation is integrated using the Johnson algorithm [60] out to the point where the diabatic potential energy curves have reached their asymptotic form, where $S_{ij, \ell}$ is evaluated. The asymptotic limit, $R_{\text{asy}}$, depends on the locations of the avoided crossings. For the reactions studied here, the asymptotic
limit is set at $50a_0$ for the $H^+ + H^-$ reaction, $40a_0$ for the $He^+ + H^-$ reaction and $20a_0$ for the $Li^+ + F^-$ reaction. The scattering amplitude can then be computed from the scattering matrix using the well known multi-channel formula [108]

$$f_{ij}(\theta, E) = \frac{1}{2i\sqrt{k_ik_j}} \sum_{\ell} (2\ell + 1) \left( S_{ij,\ell} - \delta_{ij} \right) P_{\ell} (\cos \theta)$$  \hspace{1cm} (5.19)

Here $k_i$ and $k_j$ are the wave numbers of the final and initial states (channels), respectively, and $S_{ij,\ell}$ is the scattering matrix for scattering from $j$ to $i$ for a fixed angular momentum, $\ell$. The partial cross section can also be obtained as

$$\sigma_{ij,\ell} = \frac{\pi}{k_j^2} (2\ell + 1) |\delta_{ij} - S_{ij,\ell}|^2,$$

and the total cross section for a given channel as

$$\sigma_{ij} = \sum_{\ell=0}^{\infty} \sigma_{ij,\ell}$$  \hspace{1cm} (5.21)

The differential cross section is obtained from the scattering amplitude as [108]

$$\frac{d\sigma_{ij}}{d\Omega} = \frac{k_i}{k_j} |f_{ij}(\theta, E)|^2.$$  \hspace{1cm} (5.22)

By integrating the differential cross section over a unit sphere, the total cross section [Eq. (5.21)] is regained.

### 5.3 Time-dependent nuclear dynamics

A wave packet is a superposition of stationary eigenstates, such that it is localized and normalizable [48]. The advantages of using time-dependant wave packets are that it can be used for any system, whether free or bound, the time evolution of the process can be followed carefully and details can be analysed at any given time, and thus we can intuitively follow the collision process in time. Using the wave packet approach the reaction is not studied at a specific energy, rather information about all energy components contained in the wave packet can be obtained from a single propagation. The time-dependent wave packets are all based on solving the time-dependant Schrödinger equation,

$$\frac{\partial}{\partial t} \Psi = H\Psi.$$  \hspace{1cm} (5.23)

A simplified model study for the DR process of $H_2O^+$ in Paper VI has been carried out to investigate the mechanism responsible for the DR process. Here
we have used the internal degrees of freedom; $R_1$ and $R_2$ for the two hydrogen-oxygen bond distances and $\theta$ for the H-O-H angle, as schematically shown in Fig 5.3. The study is systematically carried out by first fixing two coordinates at equilibrium, $R_2 = 1.9086 \ a_0$ and $\theta = 108.9^\circ$ and varying $R_1$ (asymmetric stretch). Another study is performed, where both radial distances are allowed to change, equidistantly, while the angle is frozen (symmetric stretch).

By direct integration of the time-dependent Schrödinger equation, a wave packet is propagated with local complex potentials [84]. The equation is of the form

$$i \frac{\partial \Psi(R,t)}{\partial t} = \left( T + V(R) - \frac{1}{2} \Gamma(R) \right) \Psi(R,t),$$

(5.24)

with the assumption that autoionization into a complete set of vibrational states is possible, hence the local boomerang model is employed. Here $T$ is the nuclear kinetic energy operator, $V(R)$ and $\Gamma(R)$ are the potential energy and autoionization width of the resonant state. The initial condition of the wave packet is given by [84]

$$\Psi(R,t = 0) = \sqrt{\frac{\Gamma(R)}{2\pi}} \chi_0(R),$$

(5.25)

where $\chi_0(R)$ is the initial vibrational wave function of the ion, calculated by numerically solving the time-independent Schrödinger equation of the ion using finite difference method [115]. Here the ion potential energy and wavefunction are defined on a grid of the coordinate $R$, such that

$$R(j) = R(0) + \Delta R(j - 1), \ j = 1 \ldots, n.$$  

(5.26)
where $R_i(n)$ is at the end of the grid. Then the second-order derivative to the vibrational wave function is approximated as

$$\frac{d^2}{dR^2} \chi(R(j)) \approx \frac{1}{(\Delta R)^2} \left\{ \chi(R(j+1)) - 2\chi(R(j)) + \chi(R(j-1)) \right\}. \tag{5.27}$$

The time-independent Schrödinger equation for the nuclear vibrational motion of the ion then becomes a tri-diagonal eigenvalue problem that can be solved.

Given the wave packet at $t = t_0$, the wave packet at later time $t$ can be expressed as

$$\Psi(R, t) = e^{-i(t-t_0)\mathbf{H}}\Psi(R, t_0) = e^{-i\Delta t\mathbf{H}}\Psi(R, t_0). \tag{5.28}$$

The factor $e^{-i(t-t_0)\mathbf{H}}$ operating on the wave packet in Eq. (5.28) is known as the evolution operator. There are several numerical approximations designed to evaluate this operator. In this work the Cranck-Nicholson propagator [45] is used to propagate wave packets in one dimension. In this approach, the evolution operator is approximated by the Cayley form;

$$e^{-i\Delta t\mathbf{H}} \approx \frac{1 - i\frac{1}{2} \Delta t\mathbf{H}}{1 + i\frac{1}{2} \Delta t\mathbf{H}}. \tag{5.29}$$

From this equation we then get

$$\left[ 1 + i\frac{1}{2} \Delta t\mathbf{H} \right] \Psi(R, t) = \left[ 1 - i\frac{1}{2} \Delta t\mathbf{H} \right] \Psi(R, t_0), \tag{5.30}$$

which is the propagation equation used and the Hamiltonian is replaced by the finite difference approximation. Although this is a first order approximation, it is a stable and unitary approximation [46].

The wave packet is propagated on the resonant state potential energy curve. Fig. 5.5 shows the probability density of the wave packet propagated on the first resonant state of the H$_2$O molecule in the “asymmetric” stretch mode, for the $^1A'$ symmetry. As can be seen from the figure, the wave packet spreads out in $R$ as the time increases; at $t = 0$ it is located near the point where the initial vibrational state of the ion couples to the resonant state and this is near the minimum of the potential energy curve (shown in Fig 5.4). The irregular shape of wave packet density is due to the fact that the potential curve is anharmonic in shape. The density also decreases with time as the wave packet spreads out due to loss of flux to autoionization. A complex absorbing potential (CAP) is placed at $R_c$ to avoid the wave function from being reflected back and this decreases the density with time. The flux is evaluated at $R_{stop}$.  


Figure 5.4: Potential energy curve for the lowest resonant state of H₂O, in "asymmetric" stretch mode, for \(^1A_1\) symmetry, showing the position where the CAP is placed (\(R_c\)) and where the flux is evaluated (\(R_{\text{stop}}\)).

Figure 5.5: Wave packet propagation on the lowest resonant state of H₂O in "asymmetric" stretch mode, \(^1A_1\) symmetry, for different times in atomic units. After a long enough time, \(t = 15000\) the wave packet dies out in the asymptotic region due to the complex absorbing potential.

After a sufficiently long propagation time (about 15000 a.u) the wave packet dies out in the asymptotic region because of the CAP. Its is only localised at small internuclear distances, due to the shape of the potential.

For calculating the total cross section, the transition amplitude is evaluated
by the Fourier transform method [40]. In this method, the transition amplitude
is calculated by a half-Fourier transform of the asymptotic wave packet,

\[ T_j(E) = \lim_{t_{\text{final}} \to \infty} \int_0^{t_{\text{final}}} \left\{ \sqrt{\frac{k_j}{2\pi\mu}} \Psi_j(R_{\text{stop}}, t) e^{iEt} \right\} dt, \quad (5.31) \]

where \( k_j \) is the wave number of the dissociating fragments in channel \( j \). From
the transition amplitude, the cross section for dissociating along a single state
is given by [67; 84]

\[ \sigma_j(E) = \frac{2\pi^3}{E} g_j |T_j(E)|^2, \quad (5.32) \]

where \( g_j \) is the multiplicity ratio of the neutral and the ionization continuum. To
obtain the total cross section a summation over all contributing states is
performed. To achieve convergence, the total cross section is evaluated for
different propagation times.
6. Discussion of attached papers

6.1 Paper I: Landau-Zener studies of mutual neutralization in collisions of $\text{H}^+ + \text{H}^-$ and $\text{Be}^+ + \text{H}^-$. 

At the ITER fusion reactor [1], a $\text{H}^-$ or $\text{D}^-$ ion source is used to produce the neutral heating beam [30; 31]. Collisional radiative modelling of the $\text{H}_\alpha/\text{H}_\beta$ line ratio has been found to be very sensitive to the MN reaction of these ions [32]. Beryllium ions will be present in the ITER fusion reactor, since the first plasma-facing wall will be based on beryllium [64]. Experimental studies on beryllium, however, are a challenge to obtain due to its toxicity, hence there is a need for theoretical calculations on cross sections for the reactions that might be important for the fusion plasma [1; 53]. One such reaction is the MN reaction $\text{Be}^+$ and $\text{H}^-$. 

In Paper I, a Landau-Zener study of the MN process is carried out, to understand the dominance of low energy collisions of $\text{Be}^+$ or $\text{H}^+$ with $\text{H}^-$. For the $\text{H}^+ + \text{H}^-$ system, the electronic structure data used here is that obtained by Stenrup et al. [104]. To carry out the study, the $^1\Sigma_g^+$ states of $\text{H}_2$, obtained by the FCI method, were considered. Here only states that were thought to be important for the $n = 2$ and $n = 3$ asymptotic limits are considered. In the Landau-Zener multi-state model, we assume that only two states are successively coupled at each avoided crossing distance [76] (one has covalent character and the other has ionic character). In all figures of this section, the labels $n = 2$ and $n = 3$ are placed at the avoided crossing distances where the ion pair and covalent states interact forming the fragments $\text{H}(1) + \text{H}(n = 2, 3)$, respectively. Fig. 6.1 shows the relevant adiabatic potential energy curves converging to the $n = 2$ and $n = 3$ asymptotic limit. The covalent state converging to the $n = 2$ asymptotic limit is characterised by the avoided crossing near $R = 12 \, \text{a}_0$ while the covalent state converging to the $n = 3$ asymptotic limit is characterised by the avoided crossing near $R = 36 \, \text{a}_0$.

Using a three-point finite difference method, Stenrup et al. [104] have obtained the radial couplings between the electronic states. Fig. 6.2 shows the non-adiabatic couplings between the electronic states considered for the Landau-Zener study. Note, from Fig. 6.2, that the couplings are large near the avoided crossing and they approximately have a Lorentzian form [6]. The
Figure 6.1: The potential energy curves of the $^1\Sigma^+_g$ adiabatic states interacting at each avoided crossing for the $n = 2$ and $n = 3$ in $\text{H}_2$.

non-adiabatic couplings are non-zero, not only in the vicinity of the avoided crossing. Using the adiabatic potential energies for the electronic states, as shown in Fig. 6.1, and the non-adiabatic couplings computed by Stenrup $et$ $al.$ [104], a two-by two adiabatic to diabatic transformation [see eq. (3.32)] has been carried out for the $^1\Sigma^+_g$ states that converge to the $n = 2$ and $n = 3$ asymptotic limit. The state converging to $n = 1$ contribute with a ratio of $10^{-6}$ to the total cross section, hence is is neglected. The non-adiabatic couplings for the $^1\Sigma^+_g$, displayed in Fig. 6.2, are then numerically integrated to obtain the rotational angle, $\gamma(R)$ [see eq (3.33)], which is then utilised in the transformation matrix, to obtain the diabatic electronic states and the electronic couplings [eq. (3.30)]. This method of obtaining the electronic coupling is termed “ATD” in the paper.

Another method to obtain the electronic coupling, at the curve crossing, is by using eq. (5.10). Here the values of the adiabatic potential energies at the curve crossing, $R_x$, are used. The electronic coupling obtained using this method is termed “APS” in the paper.

The quality of the electronic couplings, at the curve crossing, is very important in a Landau-Zener model and this is manifested by the magnitude of the cross section obtained in Paper I, when using the different coupling elements.

When working out the Landau-Zener probabilities, we follow the various pathways that can lead to the MN process, as shown by the arrows in Fig. 6.3. We follow the same formalism as discussed by Bates and Lewis [10], and if we assign the ion-pair state as 1 and the covalent state associated with the $n = 2$
Figure 6.2: Radial couplings among the states converging to $n = 2$ and $n = 3$ for the $^1\Sigma_g^+$ adiabatic states of H$_2$.

Asymptotic limit as 2 and the covalent state going to the $n = 3$ asymptotic limit as 3, we can obtain the total probabilities for the different cases as:

$$P_\ell(1,2) = 2p_2(1 - p_2)p_3, \quad \ell < \ell_2$$
$$P_\ell(1,2) = 0, \quad \ell > \ell_2$$
$$P_\ell(1,3) = 2(1 - p_2 + p_2^2)(1 - p_3)p_3, \quad \ell < \ell_2$$
$$P_\ell(1,3) = 2p_3(1 - p_3), \quad \ell_2 < \ell < \ell_3$$
$$P_\ell(1,3) = 0, \quad \ell > \ell_3,$$

where $p_2$ and $p_3$ are the probabilities of making a non-adiabatic transition at the $n = 2$ and $n = 3$ crossings, respectively. $\ell$ is the angular momentum of the system, while $\ell_2$ and $\ell_3$ are the maximum angular momenta [eq. (5.9)] allowed to reach crossings for $n = 2$ and $n = 3$, respectively.

Using eq. (5.11), for calculating the MN cross section in the Landau-Zener model, the total cross section, and states distribution are computed. The total cross section and the contribution of the $n = 2$ and $n = 3$ states are shown in Fig. 6.4. As observed previously [104], the $n = 2$ asymptotic limit starts to make a significant contribution above 1 eV collision energy. At low collision energies, the cross section is large and it agrees quite well with the total cross section computed ab initio.

In the study of the Be$^+ + \text{H}^-$ MN reaction, the ab initio data for the states relevant for MN does not have information about the avoided crossing of the adiabatic states at large internuclear distance. Thus no electronic couplings
from *ab initio* data were computed. However, using the one-electron asymptotic approximation method, proposed by Janev [56], which gives reliable results for the $\text{H}^+ + \text{H}^-$ reaction, the electron coupling was estimated and a total MN cross section larger than that of $\text{H}^+ + \text{H}^-$ was obtained.

**Figure 6.3:** Diabatic potential energy curves for states of the $\text{H}_2$ system converging to the $n = 2$ and $n = 3$ asymptotic limits. Arrows show the pathways included in a Landau-Zener model.

**Figure 6.4:** Cross section for MN in collisions of $\text{H}^+$ and $\text{H}^-$ calculated by the Landau-Zener model. Here the total cross section is compared with a full quantum *ab initio* study by Stenrup *et al.* [104]. The contributions for the $n = 2$ and $n = 3$ asymptotic limits are also shown.
6.2 Paper II: Mutual neutralization of Li$^+$ + F$^-$

Employing both the semi-classical Landau-Zener and fully quantum \textit{ab initio} methods, the MN in Li$^+$ + F$^-$ collision is studied to compute the total and differential cross sections at low to intermediate energies ($E < 100$ eV). This system has been of interest due to the fact that there are only two states that are relevant for the MN process at low collision energies. Thus a “good” theoretical study can be carried out.

First, quantum chemistry calculations are performed to compute the potential energy curves of the relevant states (one covalent and one ionic). Here the Dunning [62] correlation consistent basis sets are used. The aug-cc-pVXZ basis set is used on fluorine and the cc-pVXZ on lithium. X denotes either, D for double, T for triple, Q for quadruple and 5 for quintuple zeta functions. First a state-averaged CASSCF calculation is used to generate the molecular orbitals, which are subsequently used in a MRCI calculation. The reference configurations are generated by distributing six electrons among six or seven orbitals. For the MRCI calculation, single and double excitations out of the reference configurations are included. The adiabatic potential energy curves, where seven active orbitals are used, are shown in Fig. 6.5. The potential energy of the ion-pair state gets lower as the basis used gets larger as can be seen in the insert of Fig. 6.5.

![Figure 6.5: Adiabatic potential energy curves of the lowest two adiabatic potential energy curves of $^1\Sigma^+$ symmetry of LiF.](image)

The radial couplings, $f_{ij}(R)$, are obtained using a three-point finite difference method, with a step size of $dR = 0.01$ $a_0$. The non-adiabatic couplings obtained for all eight different basis sets are then integrated to obtain the ro-
tational angle for the transformation matrix and it is displayed in Fig. 6.6. An adiabatic to diabatic transformation is performed, using a transformation matrix and the nuclear dynamics relevant for the MN process is studied, by the Landau-Zener and quantum *ab initio* method. From both methods the total cross section is obtained, and additionally from the quantum *ab initio* calculation, the differential cross section is evaluated.

![Figure 6.6](image)

**Figure 6.6:** Rotation angles evaluated from the coupling elements between the ionic and covalent states in the different basis sets. The results with six active orbitals shown in (a) and for seven active orbitals in (b).

Fig. 6.7 shows the total MN cross section, from the electronic states computed using 7 orbitals, and quintuple zeta functions (V5Z). Here the cross section is compared with another calculation by Beinstock and Dalgarno [11] and there is a notable difference in magnitude, while they both show a similar shape. In addition, the Landau-Zener and quantum *ab initio* studies agree quite well for the entire energy range. Worth noting is the fact that Beinstock and Dalgarno claimed to have used the adiabatic potential energy curves and non-adiabatic couplings computed by Werner et al. [123]. However, the electronic coupling reported by Beinstock and Dalgarno [in Fig. 2 of ref [11]] did not agree with the one reported by Werner et al. Moreover, the total cross section we obtained, when using the data from Werner et al., was similar to the ones obtained in our methods.

In the quantum *ab initio* study the differential cross section can also be evaluated from the scattering amplitude, as described by eq. (5.22). Here it is evaluated at 0.1 eV and displayed in Fig. 6.8, showing a dominance of forward scattering, with an oscillatory behaviour that can be attributed to contributions from higher angular momenta, \( \ell \).
Figure 6.7: Total cross section for MN collisions of the Li$^+$ + F$^-$ system. Here the fully quantum model is compared with a previous calculation by Beinstock and Dalgarno [11] and a model based on a Landau-Zener study.

Figure 6.8: Differential cross section of MN of the Li$^+$ + F$^-$ system at 0.1 eV.

6.3  Paper III-IV: Study of the HeH system

6.3.1  Introduction

The HeH$^+$ molecular ion is inherently an appealing system for a theoretical study due to its size and charge composition. It is composed of the two most abundant elements in the universe, and is of interest in astrophysics. In the gas
evolution of the early universe, the HeH$^+$ ion is believed to have played a crucial role in gas cooling [75] and the chemistry of interstellar plasmas [13; 105]. There was difficulty in detecting the ion in the interstellar medium [55] and this seemed to contradict the predictions that HeH$^+$ could be abundant [98]. However, the predictions were neglecting the destruction of HeH$^+$ by DR [49]. In the interstellar environments, the HeH$^+$ ion is expected to participate in a large variety of other processes, such as the spontaneous emission of low energy photons from the ion and this process has been suggested as an important factor in primordial star formation [74].

Dissociative photoionization by extreme ultraviolet or x-ray radiation,

$$\text{HeH}^+ + h\nu \rightarrow \begin{cases} \text{He}^+ + \text{H}^+ \\ \text{He}_2^+ + \text{H} \end{cases}$$

is another process that is believed to control the abundance of HeH$^+$ in the interstellar medium [99]. As discussed in papers I and V, H$^-$ is also believed to be present in this environment and this renders the collision of He$^+$ and H$^-$ a possibility. One such reaction, studied here is the MN reaction involving He$^+$ + H$^-$. This is also a relatively small system and it has been previously studied both experimentally [36; 92; 94] and theoretically [22; 29].

In paper IV, the MN reaction involving He$^+$ and H$^-$ is studied. To carry out this study, first the potential energy curves relevant for the MN process are computed. The nuclear dynamics is performed on these potential energy curves using the time-independent quantum mechanical method. Here two effects are taken into consideration; The possibility that the resonant covalent states could autoionize, at short internuclear distances and the possibility of states of different symmetries interacting by rotational couplings to each other. The details on how this is done are discussed in the following subsections below.

6.3.2 Potential energy curves and couplings

A FCI method is implemented within the MESA [100] code to obtain the potential energy curves for the HeH system. Fig. 1 of paper III shows all states of $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ symmetries and Fig. 6.9 shows the potential energy curves that are relevant for the MN reaction. Note that these are electronic states with potential energy curves situated above the ground state of the ion, hence they are all electronic resonant states. At short internuclear distances (where the autoionization widths are non-zero) the potential energy curves are computed using the electronic scattering calculations based on the complex-Kohn variational method. For the MN process, potential energy curves of electronic states
Figure 6.9: Potential energy curves for the $^2\Sigma$ states (black), $^2\Pi$ states (red) and $^2\Delta$ states (green) for the HeH system.

of $^2\Sigma^+$ symmetry that are interacting with the ion-pair state are relevant and these are shown in Fig. 6.10(a).

For the $^2\Sigma^+$ states, non-adiabatic couplings between them are calculated first analytically [73] using the MESA code [100]. At short internuclear distances, these states are close to each other and hence the non-adiabatic couplings between the electronic states will be large. The couplings at all distances are as shown in Fig. 6.10(b). The couplings that are important for the MN process occur at large internuclear distances and they are shown in Fig. 6.11.

6.3.3 Rotational couplings

The rotational couplings are considered for the different states relevant for the MN process of He$^+$ + H$^-$. These are the $^2\Sigma^+$ states where $|\Lambda| = 0$, the $^2\Pi$ states where $|\Lambda| = 1$ and $^2\Delta$ states, where $|\Lambda| = 2$. The potential energy curves for these relevant states are shown in Fig. 6.9. We shall denote the electronic wavefunctions for the $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ states as $\phi_\Sigma$, $\phi_\Pi$ and $\phi_\Delta$, respectively. The MN process begins in the ion-pair state, which has $^2\Sigma^+$ symmetry, thus we shall investigate rotational couplings of $\phi_\Pi$ and $\phi_\Delta$ to $\phi_\Sigma$.

In section 2.3, we discussed the rotational couplings for a diatomic system. Specifically, the L-uncouplings will here be included using Eq. (2.27) for the specific HeH system. The allowed $\Lambda$ difference between any two states is $\pm 1$, thus coupling of $\phi_\Delta$ to $\phi_\Sigma$ is zero. Here we consider the L-uncoupling. The
Figure 6.10: Potential energy curves for the eleven $^2\Sigma^+$ states considered in the MN study shown in (a) and the non-adiabatic couplings in (b). The couplings shown here are between states that are lying close to each other with respect to the potential energies, where the color of the coupling elements are the same as the color of the potential energy curve of the lower state.
rotational couplings between $\phi_\Sigma$ and $\phi_\Pi$ states are

\[-\frac{[\ell(\ell+1)]^{1/2}}{2\mu R^2} \langle \phi_\Pi | L_+ | \phi_\Sigma \rangle, \tag{6.1}\]

where we have neglected $\Omega(\Omega+1)$ in eq. (2.27), since this term will be very small ($\frac{1}{4}$) compared to $\ell(\ell+1)$. To evaluate the bracket in eq. (6.1), we examine the character of the states. For the dominant electronic configuration for the covalent states associated with the same asymptotic limit, we have

\[\langle \phi_\Pi | L_+ | \phi_\Sigma \rangle = \langle (1\sigma)^1 (2\sigma)^1 (np\pi)^1 | L_+ | (1\sigma)^1 (2\sigma)^1 (np\sigma)^1 \rangle. \tag{6.2}\]

If $L_+$ is decomposed into one-electron operators, $\ell_{i+}$, such that $L_+ = \sum \ell_{i+}$, where

\[\ell_+ | n, \ell, \lambda \rangle = \sqrt{\ell(\ell+1) - \lambda(\lambda+1)} | n, \ell, \lambda + 1 \rangle, \tag{6.3}\]

then eq. (6.2) simplifies to

\[\langle \phi_\Pi | L_+ | \phi_\Sigma \rangle = \langle (np\pi)^1 | \ell_+ | (np\sigma)^1 \rangle. \tag{6.4}\]

To evaluate the matrix elements we employ the pure precision approximation [120], and eq. (6.3) gives

\[\langle \phi_\Pi | L_+ | \phi_\Sigma \rangle = \sqrt{2}. \tag{6.5}\]

Likewise for rotational couplings to the ion-pair state of covalent states associated with different asymptotic limits we obtain

\[\langle \phi_\Pi | L_+ | \phi_\Sigma \rangle = 0. \tag{6.6}\]

**Figure 6.11:** A zoom in of the potential energy curves of $^2\Sigma^+$ symmetry, in (a), and corresponding non-adiabatic couplings, in (b), at larger internuclear distances.
Thus, instead of having a diagonal adiabatic potential energy matrix, as discussed in section 3.2, now the potential matrix has some off-diagonal elements of the form

\[
V_{\Pi,\Sigma}(R) = -\sqrt{\frac{2\ell(\ell+1)}{2\mu R^2}}.
\]  

(6.7)

6.3.4 Autoionization

Autoionization is taken into account using the local “boomerang model” [2; 46], such that the adiabatic potential matrix contains elements of the form

\[
\mathcal{V}_{ij}^a(R) = V_{ij}^a(R)\delta_{ij} + i\frac{\sqrt{\Gamma_i\Gamma_j}}{2},
\]

(6.8)

where \(V_{ij}^a(R)\) is the adiabatic potential as discussed in section 3.2 and \(\Gamma_k\) is the autoionization width for adiabatic electronic state \(k\). The autoionization widths for the \(2\Sigma^+\) resonant states are obtained from the electron scattering calculation and are shown in Fig. 6.12. The off-diagonal elements of eq. (6.8) contains terms that are describing how two states are coupling each other via the ionization continuum.
6.3.5 Results

The nuclear dynamics are carried out for collisions between the isotopes $^4\text{He}^+$ or $^4\text{He}^+$ with $\text{H}^-$ or $\text{D}^-$. First the effect of autoionization on the total MN cross section is investigated for collisions of $^4\text{He}^+$ and $\text{H}^-$, and it is compared with the total cross section when autoionization is not taken into consideration. The effect is shown in Fig. 6.14, where autoionization seems to have a negligible effect. This is due to the fact that autoionization is significant at very short distances, where $\Gamma(R) \neq 0$, whereas MN is driven by couplings at large distances.

![Figure 6.13: Total cross section for the MN reaction of $^4\text{He}^+$ and $\text{H}^-$. Here the total cross section has been computed without taking autoionization effects into account (red solid line) compared to when autoionization is considered (dashed blue line). The effect of autoionization is negligible.](image)

The total cross sections for the collisions of isotopes helium and hydrogen are calculated, pointing to a larger cross section for systems with heavier reduced mass at energies lower than approximately 200 eV and above this collision energy, the isotopes with a lighter reduced mass have a larger cross section, as shown in Fig. 6.14. The total cross section is also computed when the rotational couplings of the $6^2\Pi$ states to the $11^2\Sigma^+$ states are taken into account. The rotational couplings cause the total cross section to increase above 1 eV. At such intermediate energies, a high number of rotational quantum numbers, $\ell$, starts to be important. In Fig. 6.14(a) the total cross section for different isotopes, without taking rotational couplings into account is plotted and in Fig. 6.14(b), the total cross section for the different isotopes, when rotational
couplings are taken into account is shown.

![Graph](image)

**Figure 6.14:** Total cross section for the MN reaction of different isotopes of He$^+$ and H$^-$. Heavier species tend to have a large cross section at energies \( \lesssim \) 200 eV. In (a) the rotational couplings are not taken into account and in (b) the rotational couplings are included.

To compare the effect of the rotational couplings, we investigate their contributions to the species with the heaviest mass (\(^4\text{He}^+ + \text{D}^-\)) and the lightest reduced mass (\(^3\text{He}^+ + \text{H}^-\)). Fig. 6.15(a) shows the comparison. The rotational couplings increase the MN cross section and the effect is largest for
isotopologues with a heavier reduced mass. In Fig. 6.15(b) a comparison of the total cross section calculated here for MN of $^4\text{He}^+ + \text{H}^-$ and t$^4\text{He}^+ + \text{D}^-$ collisions are compared with other measured and previously calculated results. The measurement by Olamba et al [92] is on the collisions of $^4\text{He}^+ + \text{D}^-$ while the measurements by Peart et al [94] and Gaily et al [36] are for collisions of $^4\text{He}^+ + \text{H}^-$. The theoretical calculations by Chibisov et al [22] are for collisions of $^4\text{He}^+ + \text{H}^-$. The final states distribution (also known as branching ratios) for the different isotopes shows dominance of the state converging to the He$(1s3s~^3S) + \text{H}$ asymptotic limit. The branching ratios for the different isotopes are displayed in Fig. 6.16. At low energies, the lightest isotope of helium ($^3\text{He}^+ + \text{H}^- / \text{D}^-$) has the highest ratio of the dominant channel. A preliminary measurement by the group of Xavier Urbain, in UC Louvain, Belgium has given the branching ratios for the MN reaction of $^4\text{He}^+ + \text{D}^-$ at 0.00876 eV [118]. The branching ratios are compared with our calculated ratios in fig. 6.17. Here only states going to the $n = 3$ limit are shown and the experimental measurement also confirms the dominance of the $^3S$ channel.

The differential cross sections are computed for all isotopes, showing a similar trend in terms of angular and energy dependence for collisions of various isotopes of hydrogen and helium ions. At all energies, the forward scattering is dominant. The differential cross sections for collisions at 0.1 eV, for all isotopes, are shown in Fig. 6.18.
Figure 6.15: Total cross section for MN of $\text{He}^+ + \text{H}^-$ collisions. Solid lines show the total cross section when the rotational couplings are taken into account and the dashed lines show the total cross section when the rotational couplings are not considered. In (a) a comparison of the heaviest reduced mass $^4\text{He}^+ + \text{D}^-$ and lightest $^3\text{He}^+ + \text{H}^-$ is made showing a larger contribution of the rotational couplings to the heavier reduced mass isotopes, compared with the lightest reduced mass. In (b) the total cross sections for $^4\text{He}^+ + \text{H}^-$ and $^4\text{He}^+ + \text{D}^-$ are compared with experimental results [36; 92; 94] and a theoretical result [22].
Figure 6.16: Branching ratios for all isotopes. (a) $^4\text{He}^+ + \text{D}^-$. (b) $^3\text{He}^+ + \text{D}^-$. (c) $^4\text{He}^+ + \text{H}^-$. (d) $^3\text{He}^+ + \text{H}^-$. 

Figure 6.17: Branching ratios for MN reaction of $^4\text{He}^+ + \text{D}^-$, showing calculated results (lines) compared with a preliminary experimental measurement (points).
6.4 Paper V: Differential and total cross sections of mutual neutralization in low-energy collisions of isotopes of \( \text{H}^+ + \text{H}^- \)

6.4.1 Introduction

The reaction of \( \text{H}^+ + \text{H}^- \) has served as a benchmark for MN studies, due to the small number of electrons involved. The first theoretical study was carried out by Bates and Lewis [10] using a semi-classical Landau-Zener model [68; 127]. Since then more refined theoretical approaches have been employed [28; 35; 104] and also experimental studies have been done, mainly at higher collision energies [88; 94; 108]. The only experimental measurement below 3 eV has been performed by Moseley et al. [88] and Urbain et al. [118; 119].

At the ITER [1] facility, for example, a \( \text{H}^- \) ion source is used for the neutral beam heating [30; 31]. To probe the low temperature plasma ion source, a diagnostic technique has been suggested to model the density of \( \text{H}^- \), based on measuring the \( \text{H}_\alpha/\text{H}_\beta \) line ratio [31; 32]. It has been shown, from collisional
radiative modelling, that the MN rate coefficient has a significant influence on the line ratio.

Employing a fully quantum mechanical ab initio model, the collisions of all isotopes of hydrogen cat- and anions have been studied. Here the differential cross section, total cross section and final state distributions are computed. Additionally, by the group of X. Urbain at U. C. de Louvain, Belgium [91], a merged beam experimental study is carried out for collisions of H\(^+\) and H\(^-\) and the final states distribution for the reaction are obtained and compared with calculated ones.

My focus has been to carry out the theoretical calculations, and here I proceed to discuss the derivations of the important expressions to consider for the collisions of different particles.

6.4.2 Scattering particles’ symmetry consideration

The collisions of the different particles, can be viewed, in a centre of mass frame, as shown in Fig. 6.19.

The electronic states of the colliding particles have inversion symmetry and they are labelled with gerade (\(g\)) or ungerade (\(u\)). If the masses of the nuclei, for the colliding ions are different we can assume that they can either be experimentally distinguished [case 1(i)] or they can not be distinguished [case 1(ii)]. When ions with identical mass are involved, depending on the spin of the nuclei, the total wavefunction of the collision complex could either be antisymmetric [case 2(i)] for fermions or symmetric [case 2(ii)] for bosons. The scattering amplitude, as discussed in section 5.2, is given by

\[
 f_{ij}(\theta, E) = \frac{1}{2i\sqrt{k_k j}} \sum_{\ell} (2\ell + 1) (S_{ij,\ell} - \delta_{ij}) P_{\ell}(\cos \theta). \tag{6.9}
\]

Here we follow the ideas of Masnou-Seeuws and Salin [82] where a symmetric \([f_{ij}^+(E, \theta)]\) and an antisymmetric \([f_{ij}^-(E, \theta)]\) amplitudes are formed as

\[
 f_{ij}^{+/−}(E, \theta) = f_{ij}^{di}(E, \theta) \pm f_{ij}^{ex}(E, \pi - \theta). \tag{6.10}
\]

The direct and exchange scattering amplitudes (illustrated in Fig. 6.19) are [82]

\[
 f_{ij}^{di}(E, \theta) = \frac{1}{2} \left[ f_{ij}^g(E, \theta) + f_{ij}^u(E, \theta) \right], \quad \text{and} \tag{6.11}
\]

\[
 f_{ij}^{ex}(E, \theta) = \frac{1}{2} \left[ f_{ij}^g(E, \theta) - f_{ij}^u(E, \theta) \right], \quad \text{respectively}. \tag{6.12}
\]

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Figure 6.19: Particle trajectory for (a) direct scattering at angle $\theta$, and (b) exchange scattering at angle $\pi - \theta$. The red small lines depict the movement of an electron, while the thick broken blue lines depicts the movement of the nuclei. Relative to the negatively (red) charged ion, scattering at the angle $\theta$ is described as the direct scattering and scattering at the angle $\pi - \theta$ is an exchange scattering.
Case 1

For hydrogen ions with non-identical nuclei (such as $T^+ + D^-$, $T^+ + H^-$, $D^+ + H^-$, etc) we consider scenarios where they are either not experimentally distinguishable (i) or they are distinguishable (ii).

(i): In this case the differential cross section will be an incoherent sum of the direct and indirect differential cross sections:

$$
\frac{d\sigma_{ij}}{d\Omega}(E, \theta) = \frac{k_i}{k_j} \left\{ |f_{ij}^{di}(E, \theta)|^2 + |f_{ij}^{ex}(E, \pi - \theta)|^2 \right\}
$$

$$
= \frac{k_i}{4k_j} |f_{ij}^{g}(E, \theta) + f_{ij}^{u}(E, \theta)|^2 + \frac{k_i}{4k_j} |f_{ij}^{g}(E, \pi - \theta) - f_{ij}^{u}(E, \pi - \theta)|^2
$$

(6.13)

(ii): If the particles are distinguishable, such that one can detect the mass of the red or blue particle, in Fig. 6.19, at angle $\theta$ then the differential cross section is either

$$
\frac{d\sigma_{ij}}{d\Omega}(E, \theta) = \frac{k_i}{4k_j} |f_{ij}^{g}(E, \theta) + f_{ij}^{u}(E, \theta)|^2,
$$

(6.14)

or

$$
\frac{d\sigma_{ij}}{d\Omega}(E, \pi - \theta) = \frac{k_i}{4k_j} |f_{ij}^{g}(E, \pi - \theta) - f_{ij}^{u}(E, \pi - \theta)|^2,
$$

(6.15)

depending on the experimental set-up.

Case 2

If the particles are identical, the appropriate nuclear spin factor has to be combined with the right spatial amplitude, so as to make the total wave function symmetric or antisymmetric. Particles studied here have either nuclear spin $\frac{1}{2}$ (H and T) or nuclear spin 1 (D). For spin $\frac{1}{2}$ particles, the overall spin for a molecular system, like $H_2$ (or $T_2$), is $S = |s_1 - s_2|, \ldots, |s_1 + s_2| = 0, 1$ where $s_1$ and $s_2$ denote the spin for nuclei 1 and 2, respectively. The spin multiplicities are $2S + 1 = 3, 1$, implying a $\frac{3}{4}$ probability for symmetric spin and $\frac{1}{4}$ probability for antisymmetric spin. For the spin 1 nuclei (like $D_2$), $S = 0, 1, 2$ and the multiplicities are $2S + 1 = 1, 3, 5$. This implies a $\frac{2}{3}$ probability for symmetric spin and $\frac{1}{3}$ probability for antisymmetric spin.

(i): For like fermions such as collisions of $H^+$ and $H^-$ or $T^+$ and $T^-$, the total wave function has to be antisymmetric. Thus the probability for having a symmetric spin part ($\frac{3}{4}$) will be combined with the antisymmetric scattering
amplitude and the probability for antisymmetric spin part \(\frac{1}{3}\) will be combined with the symmetric scattering amplitude;

\[
\frac{d\sigma_{ij}(E, \theta)}{d\Omega} = \frac{k_i}{4k_j} |f_{ij}^{\ell}(E, \theta)|^2 + \frac{3k_i}{4k_j} |f_{ij}^{\ell}(E, \theta)|^2
\]

\[
= \frac{k_i}{4k_j} |f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \pi - \theta)|^2
\]

\[
+ \frac{3k_i}{4k_j} |f_{ij}^{\ell}(E, \theta) - f_{ij}^{\ell}(E, \pi - \theta)|^2
\]

\[
= \frac{k_i}{16k_j} |f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \pi - \theta) - f_{ij}^{\ell}(E, \pi - \theta)|^2
\]

\[
+ \frac{3k_i}{16k_j} |f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \theta) - f_{ij}^{\ell}(E, \pi - \theta) + f_{ij}^{\ell}(E, \pi - \theta)|^2.
\]

If the expression for the scattering amplitude \([eq. (6.9)]\) is inserted into eq. (6.16) and by employing the properties of Legendre polynomials \([P_\ell(\cos \theta) = P_\ell(\cos \theta)]\) if \(\ell\) is even, \(P_\ell(-\cos \theta) = -P_\ell(\cos \theta)\) if \(\ell\) is odd \([3]\), the differential cross section becomes

\[
\frac{d\sigma_{ij}(E, \theta)}{d\Omega} = \frac{3k_i}{4k_j} |f_{ij}^{g, odd}(\theta, E) + f_{ij}^{u, even}(\theta, E)|^2
\]

\[
+ \frac{1k_i}{4k_j} |f_{ij}^{g, even}(\theta, E) + f_{ij}^{u, odd}(\theta, E)|^2, \tag{6.17}
\]

where \(f_{ij}^{g/u, even/odd}\) denote the angular momentum summation over odd or even \(\ell\).

(ii): For collisions of \(D^+\) and \(D^-\), the probability for having a symmetric spin \(\left(\frac{1}{3}\right)\) will be combined with the symmetric scattering amplitude and the probability for antisymmetric spin \(\left(\frac{1}{3}\right)\) will be combined with the antisymmetric scattering amplitude;

\[
\frac{d\sigma_{ij}(E, \theta)}{d\Omega} = \frac{2k_i}{3k_j} |f_{ij}^{\ell}(E, \theta)|^2 + \frac{1k_i}{3k_j} |f_{ij}^{\ell}(E, \theta)|^2
\]

\[
= \frac{2k_i}{3k_j} |f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \pi - \theta)|^2
\]

\[
+ \frac{1k_i}{3k_j} |f_{ij}^{\ell}(E, \theta) - f_{ij}^{\ell}(E, \pi - \theta)|^2
\]

\[
= \frac{k_i}{6k_j} |f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \pi - \theta) - f_{ij}^{\ell}(E, \pi - \theta)|^2
\]

\[
+ \frac{k_i}{12k_j} |f_{ij}^{\ell}(E, \theta) + f_{ij}^{\ell}(E, \theta) - f_{ij}^{\ell}(E, \pi - \theta) + f_{ij}^{\ell}(E, \pi - \theta)|^2.
\]
If eq. (6.9) is inserted in the above expression and the Legendre polynomial property applied, eq. (6.18) simplifies to

\[
\frac{d\sigma_{ij}}{d\Omega}(E, \theta) = \frac{k_i}{3k_j} |f_{ij}^{g,odd}(E, \theta) + f_{ij}^{u,even}(E, \theta)|^2 \\
+ \frac{2k_i}{3k_j} |f_{ij}^{g,even}(E, \theta) + f_{ij}^{u,odd}(E, \theta)|^2. \tag{6.19}
\]

The total cross section is obtained by integrating the expressions above over the unit sphere,

\[
\sigma_{ij}(E, \theta) = 2\pi \int_0^\pi \frac{d\sigma_{ij}}{d\Omega}(E, \theta) \sin \theta d\theta. \tag{6.20}
\]

### 6.4.3 Results

The differential cross section obtained for all different isotopes is displayed in Fig. 6.20, showing a dominance of backward scattering in all cases. In all the computations performed here we assume that the reaction products are not distinguished, and thus case 1(ii) is not considered. In order to understand the dominance of the backward scattering for all isotopes, each term of the scattering amplitude is analysed. For collisions of non-identical nuclei, eq (6.13) shows that the differential cross section is composed of direct and exchange terms that consists of linear combinations of the amplitudes of the gerade and...
ungerade manifolds of states. In Fig. 6.21 the amplitudes are plotted in a complex plane showing the change in phase and magnitude between $f^{di}_{ij}$ and $f^{ei}_{ij}$ at small angles ($\theta = 30^\circ$) and large angles ($\theta = 150^\circ$). Here the lowest $n = 3$ channel is plotted since it is the most dominant channel. From Fig. 6.21, it is clear that the phase difference between $f^{g}_{ij}$ and $f^{u}_{ij}$ causes the difference to

![Diagram](image_url)

**Figure 6.21:** Scattering amplitudes, for gerade and ungerade symmetries, including terms for direct scattering and indirect scattering at 0.1 eV collision energy. In (a) the amplitudes are plotted at $30^\circ$ while in (b) they are plotted for $150^\circ$ for the lowest state going to the $n = 3$ limit.
be larger than the sum, resulting in the exchange amplitude being dominant at large angles, as shown in Fig. 6.22, where the differential cross sections from the direct and exchange amplitudes are compared with the total differential cross section. The analysis is done for the lowest state converging to the $n = 3$ limit, at 0.1 eV for mutual neutralization reaction of $T^+$ and $D^-$. Moreover the difference between the sum and difference is much bigger at large angles.

Figure 6.22: Direct and exchange differential cross section for collisions of $T^+$ and $D^-$ at 0.1 eV. The difference between the direct and exchange is much more pronounced at larger angles.
6.5 Paper VI: Theoretical study of the mechanism of H$_2$O$^+$ dissociative recombination.

The H$_2$O$^+$ ion is also believed to be a precursor to the formation of the H$_3$O$^+$ ion, which is of interest in ionosphere chemistry [14; 89] and dense molecular clouds regions [103; 107] and in interstellar medium [110; 112]. The H$_3$O$^+$ ion is known to be formed in both the diffuse and dense interstellar clouds via a chain of ion-molecule reactions, initiated by ionization of H$_2$. The sequence of reactions can be outlined as in Fig. 6.23 [80; 83]. Thus the DR of H$_2$O$^+$ will remove this ion from the chain of reactions and thus the cross section for this reaction may influence the results of H$_3$O$^+$ formation and this has to be taken into consideration in chemical models of interstellar clouds.

![Figure 6.23: The ion molecule chemical reactions series, depicting the relevance of the H$_2$O$^+$ ion, reproduced from McCall [83].](image)

The reaction

$$\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_2\text{O}^+ + \text{H}, \quad (6.21)$$

in the atmosphere of Saturn has been proposed as a viable mechanism [25] for the formation of H$_2$O$^+$. Although the claim is that the water cation reacts quickly with molecular H$_2$, its destruction through DR is also plausible [80].
DR of \( \text{H}_2\text{O}^+ \) has been experimentally studied over the years \([59; 89; 114]\), where the DR cross section has been measured as well as the branching ratios and final state distributions. It has been observed that at low collision energies, the three-body breakup dominates with almost 60\% \([58; 114]\). A similar multi-bond fragmentation is found in other polyatomic ions \([58; 69]\).

The main goal of paper VI is to take a first step towards a theoretical understanding of the DR mechanism of \( \text{H}_2\text{O}^+ \). What is the main driving mechanism for the reaction, is it the direct or indirect mechanism? Using simplified models for both the direct and indirect mechanism, the contributions to the DR total cross section are computed. My main focus has been to study the direct mechanism.

To obtain the relevant potential energy curves the MRCI method is used to compute the electronic bound states of the ion and the neutral molecule.

This study is carried out to investigate the role of the direct mechanism in DR of \( \text{H}_2\text{O}^+ \). Here time-dependent wave packets are propagated on the complex potential energy surfaces of the resonant states relevant to the process. To form the complex potential, the local “boomerang model” \([2; 46]\), where the quasidiabatic part of the potential is combined with an imaginary term to account for autoionization,

\[
V_{\text{res},i}(R) = V_i(R) - i \frac{1}{2} \Gamma_i(R),
\]

where \( V_i(R) \) is the quasidiabatic potential energy for state \( i \) and \( \Gamma_i(R) \) is the autoionization width. Such a model is justified for resonant states with high enough energy, such that autoionization into a complete sets of vibrational states is possible \([2; 84; 93]\).

In carrying out the study, first a one-dimensional “asymmetric stretch” of one of the O-H bonds is studied. The other O-H bond is fixed at \( R = 1.9082a_0 \) and the H-O-H angle is fixed at \( \theta = 108.9^\circ \). We also consider a “symmetric stretch” in which both the O-H bonds are varied simultaneously, with the angle frozen at \( \theta = 108.9^\circ \). In \( C_s \) symmetry, there are electronic states of \( ^1\text{A'} \), \( ^1\text{A''} \), \( ^3\text{A'} \) and \( ^3\text{A''} \) irreducible representation. In \( C_{2v} \) symmetry, there are electronic states of \( ^1\text{A}_1, ^1\text{A}_2, ^3\text{A}_1, ^3\text{A}_2, ^1\text{B}_1, ^1\text{B}_2, ^3\text{B}_1, ^3\text{B}_2 \) symmetries. To compute the energy positions of the resonant states above the ground ionic state and also the autoionization widths, electron scattering calculations have been performed. The widths and resonant states for the “symmetric stretch” in both \( C_s \) and \( C_{2v} \) symmetries are obtained while in “asymmetric stretch” are obtained in the \( C_s \) symmetry.
6.5.1 Potential energy surface slices and autoionization widths

The potential energy curves are obtained for both H$_2$O and H$_2$O$^+$. Fig. 6.24 shows the potential energy curves obtained for the ground and excited state of H$_2$O$^+$ and the adiabatic states of H$_2$O. The broken lines (in Fig. 6.24) represents bound states, below the ground state of the ion and continuum state, above the ground state of the ion. The bound states are a mix of Rydberg states that have an electronic configuration of $(1a')^2(2a')^2(3a')^2(4a')^2(1d'')^1(n\lambda)^1$ in $C_s$ symmetry, where $n\lambda$ denotes a molecular orbital. Above the ion the roots obtained from the electronic structure calculations are a mix of states that are trying to represent the ionization continuum and the more compact resonant states. To obtain the states relevant to describe DR, we perform a configuration-tracking quasidiabatization. In the ionization continuum, electron scattering calculations have been carried out to determine the energy positions and autoionization widths of the resonant states.

![Figure 6.24: Slices of the potential energy surface for H$_2$O (broken lines) and the ground and excited state of H$_2$O$^+$ (solid lines) for the “asymmetric stretch” mode in $^1A'$ irreducible representation.](image)

The results from the electron scattering calculations, showing positions of resonant states, above the ground state of the ion are shown in Fig. 6.25, with red dots.

To follow the resonant states, below the potential energy surface of the ground state of the ion, a quasidiabatization, as discussed in Section 3.2.1, is performed. The resonant states obtained are shown with brown lines in Fig. 6.26.

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Figure 6.25: Slices of the potential energy surface for the “asymmetric stretch” mode in $^1A'$ irreducible representation, showing the energy positions of the resonant states (dots) obtained with the electron scattering calculations.

Figure 6.26: Slices of potential energy surfaces for the $^1A'$ irreducible representation for the “asymmetric stretch” mode, showing the resonant states potential energy surfaces obtained from the diabatisation.

In the symmetric stretch mode, the calculation can be done in either $C_s$ or $C_{2v}$ symmetry. In both symmetries, the potential energy surfaces will be
asymptotically similar. Fig 6.27 displays a slice of the potential energy surface for the “asymmetric stretch” mode, for electronic states in the $^1A'$ irreducible representation and they are displayed with the states of $C_{2v}$ that have the same asymptotic limit.

![Potential energy curves](image)

**Figure 6.27:** Potential energy curves in the “symmetric stretch” mode in $C_s$ (broken lines) and $C_{2v}$ symmetry (solid lines). Note that they have the same asymptotic limits.

6.5.2 Results

A wave propagation study is done for both the “asymmetric” and “symmetric” stretch modes. The total cross section for the symmetric stretch in both symmetries ($C_s$ and $C_{2v}$) and the asymmetric stretch mode are plotted in Fig 6.28. Here, it is compared with the indirect cross section from the simplified model and some experimental results from ion-storage rings [59; 114] and merged beam apparatus [89]. At lower energy, it is evident that the direct DR mechanism is not the main electron capture mechanism. Here the driving mechanism is mainly the indirect process. The indirect process has been studied using a simplified model, commonly employed to study DR of symmetric ions and linear polyatomic ions [27]. At low energy, the cross section obtained is higher than the experimental results. However in the model for the indirect mechanism, autoionization is not included. The cross section for the indirect DR mechanism only includes contributions from vibrational excitations of the ionic core from $\nu = 0$ to $\nu = 1$ and $\nu = 2$ for each normal mode coordinate. At
the opening of the vibrationally excited state mode, the cross section drops and thus it is zero at the opening of the highest vibrational state mode for $\nu = 2$ of the target ion.

**Figure 6.28:** Total cross section for direct and indirect DR, compared with experimental results measured by ASTRID [(a)] [59], a merged beam study [ref(b)] [89] and CRYRING [(c)] [114]. The direct DR cross section for the “asymmetric stretch” mode has a threshold energy of about 2 eV.
7. Conclusion and outlook

Cross sections for mutual neutralization and dissociative recombination have been computed both quantum mechanically and semi-classically. Not only total cross sections have been computed, but also differential cross sections and final state distributions.

The study of mutual neutralization of \( \text{H}^+ + \text{H}^- \) has been a continuation of a study carried out earlier [104], where the total cross section and final state distributions were computed. We have now calculated the differential cross section as well and considered collisions of different isotopes of hydrogen ions. The dependence of the MN cross section on the scattering angle is dependent on whether the colliding particles have electronic inversion symmetry or not. With increasing energy, the scattering differential cross section gets larger at \( \theta \rightarrow 0^\circ \) and \( \theta \rightarrow 180^\circ \). At low collision energies, the backward scattering dominates due to the phase difference of the scattering amplitudes for the gerade and ungerade symmetry terms. Isotope effects have also been studied and at low energies (< 10 eV) the heavier isotopologue has the largest cross section, while at higher energies, the order is reversed. This is somehow understood from looking at the branching ratios, where the significance of the \( n = 2 \) channel is greater for lighter isotopes. There are still some limitations, however, of the theoretical models applied. The number of states included in the model is finite, rotational couplings and autoionization are not considered. It may be interesting in this study to include higher electronic states which may be significant at higher energies. Autoionization and rotational couplings may also have an effect on the total cross section.

The MN reaction for \( \text{He}^+ + \text{H}^- \) shows that although autoionization may be negligible for this system, rotational couplings have some contributions at intermediate to high energies (above \( \approx 10 \) eV). The small effect of autoionization is due to the fact that the autoionization widths are non-zero only at short internuclear distances, as opposed to the non-adiabatic couplings driving the MN reaction which are at large internuclear distances. As the collision energy increases, the number of \( \ell \) contributing to the cross section also increases and this will also increase the contribution from the rotational couplings. Since the system does not have inversion symmetry and the scattering particles are distinguishable, the differential cross section is peaked in the forward direction for all energies.
A Landau-Zener study, carried out for the MN process of \( H^+ + H^- \) and \( Li^+ + F^- \), shows to be reliable, subject to “good” electronic couplings employed in the Landau-Zener formula. The total cross sections obtained for the two systems are comparable to ones obtained using a fully quantum mechanical approach.

The dissociative recombination reaction of the \( H_2O^+ \) cation has been studied, so far, using simplified one-dimensional models. However, even with such a simplified model, there is a significant contribution to the cross section from the direct mechanism and the simplified model for the indirect mechanism gives a larger cross section than the experiments. The methods used for the indirect mechanism have not included autoionization and it estimates the cross section by a frame-transformation of the elements of the calculated scattering matrix. Here harmonic oscillator wave functions are used for the vibrational wave functions for each normal mode co-ordinate. A further investigation of the indirect mechanism, using a model which somehow accounts for autoionization is proposed for future studies. Also, the next goal on this project is to study two-body and three-body breakup. Here the Multi-Configuration Time-Dependent Hartree (MCTDH) method can be employed to implement the multi-dimensional wave propagation. Furthermore, since in all the calculations done, the states have been treated as uncoupled to each other, a further study, including coupled states, where a complete description of both the direct and indirect mechanism is applied is the final goal.

The computations of the potential energy surfaces involved in all the systems studied here have limitations. At a given internuclear geometry, the potential energy of an electronic state may change, subject to the basis used and the number of configurations included in the CI wave function. This is clearly seen in the computation of the potential energy of the LiF system. Here the potential energy of the ion-pair state, gets lower as the basis used in the calculation gets larger. The reactions studied here will very much depend on the exact positions of avoided crossings for different sets of states. Thus it is important to have a consistent description of the different types of states included. It may be important to compare the electronic structure methods employed here with other methods, like the valence-bond methods [39].

The MN and DR processes studied here are somehow related. They both involve resonant states that at short internuclear distances may autoionize, and for all distances, are coupled to other states. Employing a multichannel quantum defect theory [47], at small distances, combined with methods where the coupled Schrödinger equation is used for the nuclear dynamics, at large distances, may be a better way to study the dynamics. Often there is an infinite number of Rydberg states involved in the processes studied here. However, in the theoretical models employed, only a finite number of states are included.
and that is obviously an approximation.

The studies, carried out here, have a very close relation with experimental work. The DESIERE storage rings facility [113], located in the department of physics, at Stockholm University is aimed at studying MN reaction collisions. Here, there is a possibility of the MN reactions studied to be measured experimentally. Ion storage rings, like the Cryogenic Storage Ring CSR [112], currently under construction in Heidelberg, are capable of experimentally studying molecular ion-electron collisions at low (<15k) temperatures. Some of the work presented here for MN of collisions of H\(^+\) + H\(^-\) and He\(^+\) + H\(^-\), have been a collaboration with the group of Professor Xavier Urbain at Université catholique de Louvain, in Belgium where a merged beam facility is used to study the MN reaction. It is important to have a complement of theory and experimental work.
Sammanfattning

Avhandlingen beskriver teoretiska studier av molekylära kollisioner som sker vid relativt låga kollisionsenergier. Två olika typer av reaktioner har studerats. Vid dissociativ rekombination fångar en positivt laddad molekylär jon in en fri elektron, och skapar därmed ett neutralt tillstånd som inte är stabilt utan molekylen faller isär i neutrala fragment. Den andra reaktionen är ömsesidig neutralisering, där två motsatt laddade joner kolliderar och en elektron förs över från den negativt laddade jonen till den positivt laddade så att neutrala fragment bildas.


Avhandlingen beskriver studier av ömsesidig neutralisering då H\(^-\) kolliderar med H\(^+\), Be\(^+\) och He\(^+\). Även neutralisering vid kollisioner av F\(^+\) och Li\(^+\) har studerats. Relevanta adiabatiska potentialkurvor har tagits fram med kvantkemi beräkningar. Även icke-adiabatiska kopplingselement mellan de olika elektroniska tillstånden har beräknats. Reaktionerna drivs här av de icke-adiabatiska kopplingarna mellan joniska och kovalenta tillstånd som är betydelsefulla vid stora kärnavstånd. I vissa system är tillstånden inte elektroniskt bundna. Potentialkurvor kan då inte beräknas med kvantkemi metoder utan elektronspridningsmetoder måsta tillämpas. Dessa beräkningar utförs vid fixa kärnavstånd och ger inte bara information om energin hos det resonanta tillståndet utan även den så-kallade autojonisationsbredden. När kurvorerna och kopplingarna är beräknade transformeras tillstånden till en diabetisk representation där kopplingen inte kommer från kärnornas kinetiska energioperator ut-
från den elektroniska delen av Hamiltonianen. Fördelen är att dessa kopplingsar är på potentialform. När denna transformation väl är gjord kan tvärsnitt beräknas genom att lösa den kopplade Schrödinger ekvationen för den radiella delen av kärnornas vågfunktion. Dessa kvantmekaniska beräkningar ger inte bara information om det totala tvärsnittet utan även det differentiella tvärsnittet erhålls samt information om tillstånden hos de neutrala atomer som bildas vid reaktionen. Även semi-klassiska Landau-Zener beräkningar har utförts och beräknade tvärsnitt stämmer bra med de som färs från kvantmekaniska beräkningar om kopplingselementen mellan tillstånden är de rätta. Dessa kopplingselement är inte triviala att beräkna \textit{ab initio}. I studien av kollisioner mellan He\(^+\) och H\(^-\) har autojonisation inkluderats i form av en imaginär potentialmatris som adderas till den adiabatiska potential matrisen. Elementen i den imaginär potentialmatrisen ges av beräknade autojonisationsbredder för nå de resonanta tillstånden. Dessa autojonisationsbredder är skilda från noll endast vid små kärnavstånd och beräkningarna visar att autojonisation inte har någon betydelse i denna reaktion. I samma system har även rotationskopplingar som sammankopplar elektroniska tillstånd med olika symmetrier tagits med i modellen. Dessa kopplingar har betydelse vid högre kollisionsenergier.

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Landau–Zener studies of mutual neutralization in collisions of H\textsuperscript{+} + H\textsuperscript{−} and Be\textsuperscript{+} + H\textsuperscript{−}

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Abstract

Semi-classical Landau–Zener studies of mutual neutralization reactions in low-energy H\textsuperscript{+} + H\textsuperscript{−} and Be\textsuperscript{+} + H\textsuperscript{−} collisions are performed. Avoided crossings between ionic and covalent states occurring at large internuclear distances are considered, and electronic couplings between these states are estimated using different semi-empirical and \textit{ab initio} methods and tested on the H\textsuperscript{+} + H\textsuperscript{−} reaction. The method is then applied to compute the cross sections and final state distributions for mutual neutralization in collisions of H\textsuperscript{−} with Be\textsuperscript{+}. These are reactions that might be important for the modeling of the fusion edge plasma of the divertor of ITER.

Keywords: mutual neutralization, Landau–Zener, semi-classical, charged transfer

1. Introduction

Dating back to the original work by Landau [1] and Zener [2], charge transfer processes have been studied using the semi-classical Landau–Zener model. One such process is mutual neutralization (MN), where oppositely charged ions collide and an electron transfer results in formation of neutral fragments. In 1955, Bates and Lewis [3] applied the Landau–Zener model to study MN in collisions of H\textsuperscript{+} and H\textsuperscript{−}. The MN reaction is driven by non-adiabatic couplings occurring at large internuclear distances (R). The system enters on the attractive ion-pair state. At large internuclear distances, the quasidiabatic ion-pair state crosses the more or less R-independent potential energy curves of the covalent states dissociating into neutral fragments. In an adiabatic representation, the curve-crossings between ionic and covalent states will manifest themselves as avoided crossings; and in the vicinity of the avoided crossings non-adiabatic couplings will be large. The Landau–Zener model is a two-state model assuming diabatic potential energy curves that vary linearly with R and R-independent electronic couplings [1, 2]. Due to the attractive Coulomb interaction of the ion-pair, even a small collision energy will provide large radial velocities at the curve crossing distances and a semi-classical treatment is justified. Furthermore, since in general, very high angular momenta contribute, any interference effects or resonant structures are usually averaged out. Provided the curve-crossings are well separated a multi-state Landau–Zener model may work surprisingly well describing charge-transfer processes such as MN. One dilemma, however, is the estimate of the coupling elements that enter the Landau–Zener formula. The computed cross section and final state distributions will critically depend on the magnitudes of the coupling elements. In the literature, there are numerous semi-empirical formulas for coupling elements. There are also methods to estimate the coupling elements \textit{ab initio}.

Some of us have previously carried out fully quantum mechanical \textit{ab initio} study on MN in low-energy H\textsuperscript{+} + H\textsuperscript{−} collisions [4]. We therefore first test the Landau–Zener model and the various coupling elements on this system. We compare the computed cross section and final state distributions with the quantum results. We then apply the semi-classical Landau–Zener model to study MN in collisions of Be\textsuperscript{+} and H\textsuperscript{−}.

The MN processes here studied might be of importance when modeling the fusion plasma of the divertor of ITER [5]. At ITER, neutral beam heating is based on an H\textsuperscript{−} ion source [6, 7]. By measuring the H\textsubscript{α}/H\textsubscript{β} Balmer line ratio, a new
diagnostic technique has been suggested to model the H\(^-\) density in the low temperature plasma of the ion source [7–9]. Collisional radiative modeling shows that the measured line ratio is very sensitive to the H\(^+\) + H\(^-\) MN cross section [8]. Beryllium will be used as a plasma facing material in the first wall of the ITER fusion reactor [5, 10]. The beryllium will enter the cooler plasma of the diverter where it will be ionized. In detached plasmas of the divertor, hydrogen anions (H\(^-\)), are produced by dissociative attachment of vibrationally excited H\(_2\) molecules. The hydrogen molecules get vibrationally excited by inelastic electron collisions. This is described in [11, 12] and modelled in [13] using a divertor simulator. The cross section and final state distributions for MN in collisions of Be\(^+\) and H\(^-\) might then be relevant to include when modeling the fusion plasma. Due to the toxicity of beryllium, experimental study of this reaction is not possible. Unless otherwise mentioned, atomic units are used throughout the article.

2. Landau–Zener calculation

The Landau–Zener model developed independently of Landau [1] and Zener [2] in 1932 is a two state model that can be applied to studies of crossings of molecular potential energy curves. It is based on a Hamiltonian of the form

\[
\hat{H} = \left( \hat{T} + V_1(\mathbf{R}) \right) H_{12}(\mathbf{R}) \left( \hat{T} + V_2(\mathbf{R}) \right),
\]

where the difference of the diabatic potential energy curves are assumed to vary linearly with the internuclear distance \( R \), i.e. \( V_1(\mathbf{R}) - V_2(\mathbf{R}) = a R \) and the electronic coupling is constant \( H_{12}(\mathbf{R}) = H_{12} \). The Landau–Zener diabatic transition probability \( p \) [1, 2] is given by

\[
p = \exp \left( -\frac{2\pi H_{12}^2}{v_x a} \right),
\]

where \( v_x \) is the radial velocity at the curve crossing (see below). At different crossing distances, \( R \), the potential of the ionic state associated with the ion-pair limit at large distances crosses several of the potential energy curves of the covalent states. By applying the Landau–Zener model for these types of processes, the transition regions where the Hamiltonian can be approximated with the Landau–Zener form (1) are regarded as small and well separated from each other. The distance of the Landau–Zener region (measured from the curve crossing point) can be estimated with \( R_0 = \frac{2\hbar \omega}{\pi a} \) [14], and this distance must be smaller than the internuclear distance between two neighboring curve crossings to treat the curve crossings as separable.

In the H\(_2\) system, there is one electronic state of both \( ^1\Sigma_g^+ \) and \( ^3\Sigma_u^+ \) symmetries associated with the ion-pair limit H\(^+\) + H\(^-\). At large internuclear distances the gerade and ungerade potential energy curves have very similar form [4] and there are avoided crossings around \( R = 11 \, a_0 \) and \( R = 35.6 \, a_0 \) between the ionic and covalent \( n = 2 \) and \( n = 3 \) states, respectively. In figure 1, the adiabatic potential energy curves of \(^3\Sigma_u^+\) symmetry are shown with black solid curves [4]. In the model, only the curve-crossings occurring at large internuclear distances are considered. There are two covalent states associated with the \( n = 2 \) limit and three states associated with the \( n = 3 \) limit. According to Lewis [15], only two adiabatic states are active in each curve crossing, changing characters from ionic to covalent form in the crossing region. Thus, it is enough to only include two effective states for each of the curve crossings and the coupling strength is obtained as [15]

\[
H_{12} = \sqrt{\sum_i \hat{H}_{1i}^2}.
\]

Here the summation goes over the diabatic states involved in the curve crossing.

The corresponding quasidiabatic potential energy curves of the ion-pair state and the effective Rydberg state are shown with the red dashed lines in figure 1. We assume that the attractive ion-pair potential has the form \( V_1(\mathbf{R}) = V_{1\text{asy}} - \frac{\alpha}{\sqrt{2\mathbf{R}}} \), where \( \alpha = 216 \) a.u. is the polarizability of H\(^+\) [16] and \( V_{1\text{asy}} \) is the asymptotic energy of the ion-pair. The covalent states are assumed to have constant potential energy curves \( V_c(\mathbf{R}) = V_{c\text{asy}} \). Following the early study by Bates and Lewis [3] on MN in H\(^+\) and H\(^-\) collisions, the cross section is given by

\[
\sigma(E) = \frac{\pi}{k_i^2} \sum_l (2l + 1) P_l(E).
\]

Here \( P_l(E) \) is the multi-state Landau–Zener probability that the reacting ion-pair results in neutral fragments after passing by the crossings between ionic covalent states both on the way in and out [3]. This probability depends on the angular momentum \( l \) of the molecular system. For a given angular momentum the centrifugal barrier \( \frac{\pi^2 (l + 1)^2}{2\mu R^2} \) is added to the diagonal terms of the Hamiltonian. For high enough angular momentum, the centrifugal barrier will screen the system.
from reaching small internuclear distances. The largest angular momentum, $\ell_{\text{max}}$, where the crossing point $R_x$ is reached is given by
\[
\ell_{\text{max}} = \frac{-1}{2} + \frac{1}{4} + \mu^2 \gamma^2 R_x,
\]
where $\mu$ is the reduced mass of the system. The radial velocity at the curve crossing depends on the collision energy $E$ and the angular momentum $l$, and it is given by
\[
v_r = \sqrt{\frac{2}{\mu}} \left( E + \frac{1}{R_x} + \frac{\alpha_p}{2R_x^2} \left( l(l+1) - 2\mu \right) \right).
\]

When calculating the multi-state Landau–Zener probabilities, the multiple pathways to a given set of fragments have to be considered. Here, the contributions from these different pathways are added incoherently and quantum interference effects (Stückelberg oscillations) are not considered.

The validity of the Landau–Zener model for describing processes such as MN has previously been questioned [18, 19]. As discussed above, there are several states coupled in the same region of internuclear distances and these multi-state curve crossings have to be described by two effective states interacting. Additionally, it has been pointed out by Kiera and co-workers [19] that the avoided crossings between ionic and covalent states may be better described using the Nikitin model, where the electronic coupling element is modeled using an exponential function [20, 21]. To accurately describe these processes at low collision energies, an ab initio quantum study should be performed. Today there are several such studies, not only on $\text{H}^+ + \text{H}$ [4, 22], but also on other systems such as $\text{H}^+ + \text{H}^+$ MN [4, 22, 24] and $\text{Mg}^+$ [25]. Also studies of collisions of $\text{F}$ with $\text{H}^+$ [26] and Li$^+$ [27] have been performed. To perform such ab initio study, non-adiabatic interactions arising from the avoided crossing among highly excited states occurring at large internuclear distances where the ionic and covalent states cross, have to be computed. These ab initio studies are far from trivial. Instead simple models such as the Landau–Zener model are very often applied. In the present study we do not want to test the Landau–Zener model. Rather, we want to test the different methods to estimate the ionic-covalent electronic couplings and show how sensitive the Landau–Zener cross sections and the final state distributions might be with small changes in coupling elements. Even though the model is simple and sometimes might work it can not be used as a ‘black box’.

3. Ionic-covalent coupling elements

The outcome from a semi-classical Landau–Zener study is very sensitive to the electronic coupling parameter, $H_{12}$, used in the Landau–Zener formula (2). It is not straightforward to compute the electronic couplings between the quasidiabatic electronic states used in the model. Here, several different methods discussed in the literature are summarized and tested on the $\text{H}^+ + \text{H}^+$ system.

3.1. Semi-empirical methods

During the 1970s, Olson and co-workers, published a number of semi-empirical methods to describe the electronic couplings in one-electron charge-transfer systems [28–31]. They gathered data from both experimental and theoretical studies and examined how the coupling strength depends on the crossing point $R_x$ and the energy of the reactants and products. For the MN reaction $A^* + B^* \rightarrow A^* + B$, we define $I_1 = \alpha^2/2$ as the electron affinity of $B$ and $I_2 = \gamma^2/2$ as the effective ionization energy of the transferred electron in the product state $A^*$. In the first study by Olson et al [28], they fitted the coupling data to the following form
\[
H_{12} = \alpha^2 \left[ 8.0 \exp(-0.91aR_x) - 7.5 \exp(-0.99aR_x) \right].
\]

This formula was a year later modified [29] to also include the effective ionization potential of the electron in the product state, $I_2$. The coupling parameters were then fitted to the following form
\[
H_{12} = A \exp \left( -\frac{R_x}{c} \right),
\]
with
\[
c = \frac{2}{\alpha + \gamma}, \quad A = \sqrt{\hbar K c}.
\]

This formula was soon modified [30] by introducing scaled coupling elements and crossing points
\[
H_{12} = 1.044R^* \exp \left( -0.857R^* \right),
\]
where
\[
H_{12} = \frac{H_{12}}{\sqrt{\hbar K c}}, \quad R^* = \frac{\alpha + \gamma}{2} R_x.
\]

Equations (7), (8) and (9) are below referred to as Olson1, Olson2 and Olson3, respectively.

3.2. One-electron asymptotic methods

The asymptotic expression for the exchange interaction can be derived using an one-electron approximation for the charge-transfer reaction ($A^* + e^- + B$). At large enough internuclear distances, the electron interacts with the ionic ($A^*$) and neutral (B) atomic cores and an one-particle Hamiltonian can be formulated [32–34]
\[
\hat{H}_d = -\frac{1}{2} \nabla^2 + V_A(r) + V_B(r).
\]

The electronic coupling between ionic and covalent states is given by $\langle \Phi_1 | \hat{H}_d | \Phi_2 \rangle$, where $\Phi_1, \Phi_2$ are the diabatic electronic wave functions describing the electron localized either close to the neutral atom (ionic state $A^* + B^*$) or the cation (covalent state $A^* + B$). These diabatic wavefunctions are represented as linear combinations of the adiabatic electronic wave functions. The basic idea of the Landau–Herring method [32] is to obtain the coupling strength from a surface integral over a hypersurface $S$ that separates the regions of
influence of the potentials \( V_A \) and \( V_B \) in the configuration space of the electronic coordinate
\[
H_{12} \propto \int \left( \Phi_i^{1} \nabla \Phi_j^{2} - \Phi_i^{2} \nabla \Phi_j^{1} \right) \times dS. \quad (11)
\]

Using this method and asymptotic electronic wave functions of the ionic and covalent states, Smirnov [35, 36] derived the following expression of the electronic coupling element
\[
H_{12}^{\text{II}} = \gamma^2 A^2 \left\{ 2 R_x^2 \right\}^{-1} 4^{1/2} \exp(-\gamma R_x) \Gamma^2 (2 l + 1) \times \Gamma (1/\gamma + l + 1) \Gamma (1/\gamma - l) \times \exp(\gamma R_x). \quad (12)
\]
Here \( A \) is a normalization factor and \( l \) is the angular momentum of the electron in the final state. In the case of \( \text{H}^+ \), \( A^2 = 2.65 \) [35, 36].

Using the same one-electron asymptotic method, Janev obtained a slightly different expression [34] for the electronic couplings
\[
H_{12}^{\text{II}} = \frac{1}{2} A_i A_j D R_v^{1/2} \exp(-\gamma R_x). \quad (13)
\]
Here, \( A_i \) and \( A_j \) are normalization constants of the asymptotic radial wave functions of the active electron in the initial and final states, respectively and \( D = [(2l + 1)(2S + 1)]^{1/2} \) is a factor originating from the coupling of the adiabatic and final angular and spin momenta of the electron [34, 37, 38]. In the case of \( \text{H}^+ \), \( A_i = 1.12 \) [37]. Furthermore, we have
\[
A_i = \gamma [2\gamma]^{1/2} \Gamma (1/\gamma + l + 1) \Gamma (1/\gamma - l)^{-1/2}. \quad (14)
\]

### 3.3. Ab initio methods

By calculating the adiabatic potential energy curves of the excited molecular states at large internuclear distances where the curve crossings occur, the electronic couplings can be estimated from \textit{ab initio} data. In the case of a two state crossing, the electronic coupling can be approximated with half the energy separation of the corresponding adiabatic potential energy curves at the curve crossing
\[
H_{12} = \frac{1}{2} \left[ V_{12}^{\text{id}}(R_i) - V_{12}^{\text{id}}(R_f) \right]. \quad (15)
\]

When several states are involved in the curve crossing (as in the case of \( \text{H}_2 \)), the electronic coupling is obtained from the square root of the sums of the corresponding potential energy differences squared [3]
\[
H_{12} = \frac{1}{2} \left[ \sum_{\delta}^{\text{id}} \left( V_{12}^{\text{id}}(R_i) - V_{12}^{\text{id}}(R_f) \right) \right]^{1/2}. \quad (16)
\]

From structure calculations, the non-adiabatic coupling elements, \( \tilde{J}_{ij}(R) = \left( \Phi_i^{\text{id}} \partial \Phi_j^{\text{ad}} / \partial R \right) \Phi_j^{\text{ad}} \) between adiabatic states can be computed. The electronic coupling elements between the ‘active’ states involved in the curve crossing can then be obtained by a unitary two-by-two transformation of the corresponding ‘active’ adiabatic states. Here the transformation matrix is
\[
T = \begin{pmatrix} \cos(\phi(R)) & \sin(\phi(R)) \\ -\sin(\phi(R)) & \cos(\phi(R)) \end{pmatrix}. \quad (17)
\]

The transformation of the adiabatic potential energy matrix \( V \) to the corresponding diabatic potential energy matrix \( U \) is given by
\[
U = T^{-1} V T, \quad (18)
\]
where the electronic coupling element is the off-diagonal element of the diabatic potential energy matrix. For a strict two-by-two diabatization, the rotational angle of the transformation matrix is obtained by [39]
\[
\phi(R) = \int_{R}^{\infty} \tilde{J}_{ij}(R) dR. \quad (19)
\]

### 4. \( \text{H}^+ + \text{H}^+ \)

As mentioned in the introduction, the cross section and final state distributions computed using the Landau–Zener method using the different set of coupling elements will be compared with results from the fully quantum study [4]. This calculation produces a total cross section that agrees well with measured cross sections at higher collision energies [4]. It also reproduces recent measurements of the energy dependence of the final state distributions [40].

In the Landau–Zener model the electronic couplings between the ionic and \( n = 2 \) and \( n = 3 \) covalent states at large internuclear distances are included. In table 1, the crossing points and the coupling elements obtained using the different methods described above are summarized. The potential energy curves of the \( n = 4 \) states cross the ion-pair potential at internuclear distances around 280 a₀. At such large distances, the motion is highly diabatic and thus the \( n = 4 \) states do not significantly contribute to the MN reaction [3, 41]. For the semi-empirical methods and the one-electron asymptotic methods, the crossing distances were calculated from the curve crossing of the attractive quasidiabatic ion-pair potential with the constant potential of the covalent state. ‘APS’ in table 1 refer to the coupling elements calculated using the energy difference of the computed adiabatic potential energy curves [4] and ‘ADT’ refer to the couplings obtained using the two-by-two diabatic transformation. Here the crossing distances are obtained from the \textit{ab initio} data.
Figure 2 shows the calculated cross sections for MN in H⁺ + H⁻ collisions in the energy range 0.01 eV to 100 eV using the different coupling elements discussed above. We compare with the cross section calculated ab initio [4].

As can be seen, the LZ cross sections do depend upon the coupling parameters used in the model. At low energy the Olson1 coupling parameters provide a MN cross section almost an order of magnitude smaller than the one obtained using the Smirnov coupling elements. The cross sections computed using the Olson2, Janev and ATD coupling elements have similar magnitudes as the quantum result. At larger energies (E > 10 eV) the cross section deviates from the E⁻¹ energy dependence. The cross sections obtained with Janev and ATD coupling parameters do show similar trends, while the Olson2 cross section continues to decay with increasing energy.

A more sensitive set of data to analyze than the total cross section is the final state distributions. Here we analyze the H(n = 2) + H and H(n = 3) + H branching ratios. These are channels included in both the ab initio quantum calculation [4] as well as the Landau–Zener studies. According to the quantum study, at low energy the n = 3 channel completely dominates, while at higher collision energies the n = 2 channel starts to contribute. Furthermore, the n = 1 channel can be neglected over the whole energy range. Figure 3 displays calculated ratio of the n = 3 channel. The quantum result is the black solid curve.

The LZ calculations using the Olson2 coupling erroneously predicts the n = 2 channel to completely dominate, contrary to the Smirnov coupling elements that show a dominance of the n = 3 channel over the whole energy range. The Olson1, Olson3, Janev, APS and ATD coupling elements all produce final state distributions that show that the dominance of the n = 3 channel reduces with increasing energy. All models, however, predict that this decrease occurs at lower energies than what is found in [4].

To summarize the study on H⁺ + H⁻ MN, both the ATD and the Janev couplings provide cross sections and final state distributions that are in good agreement with the ab initio study. For the ATD method, the non-adiabatic couplings at the avoided curve crossings have to be computed. For molecular systems with more electrons these non-adiabatic coupling elements are not straight forward to accurately determine. For the BeH systems studied below, the Landau–Zener model will be applied using coupling elements derived with the formula (13) by Janev.

### Table 1. Crossing distances and coupling strengths tested on the H⁺ + H⁻ mutual neutralization reaction.

<table>
<thead>
<tr>
<th>Method</th>
<th>Rx (a₀)</th>
<th>H₁₂ (eV)</th>
<th>Rx (a₀)</th>
<th>H₁₂ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olson1, equation (7)</td>
<td>11.099</td>
<td>2.6786 × 10⁻¹</td>
<td>36.043</td>
<td>2.8051 × 10⁻³</td>
</tr>
<tr>
<td>Olson2, equation (8)</td>
<td>11.099</td>
<td>1.1041 × 10⁻¹</td>
<td>36.043</td>
<td>3.8741 × 10⁻⁴</td>
</tr>
<tr>
<td>Olson3, equation (9)</td>
<td>11.099</td>
<td>2.9241 × 10⁻¹</td>
<td>36.043</td>
<td>3.7181 × 10⁻³</td>
</tr>
<tr>
<td>Smirnov, equation (12)</td>
<td>11.099</td>
<td>8.0935 × 10⁻¹</td>
<td>36.043</td>
<td>9.8105 × 10⁻³</td>
</tr>
<tr>
<td>Janev, equation (13)</td>
<td>11.099</td>
<td>3.2948 × 10⁻¹</td>
<td>36.043</td>
<td>5.9364 × 10⁻³</td>
</tr>
<tr>
<td>APS, equation (15)</td>
<td>11.600</td>
<td>2.7898 × 10⁻¹</td>
<td>35.900</td>
<td>3.4452 × 10⁻³</td>
</tr>
<tr>
<td>ADT, equation (17)</td>
<td>12.250</td>
<td>3.2697 × 10⁻¹</td>
<td>35.896</td>
<td>5.1996 × 10⁻³</td>
</tr>
</tbody>
</table>

Figure 2. H⁺ - H⁻ mutual neutralization cross sections calculated using the Landau–Zener method with different set of coupling parameters are compared with the cross section calculated ab initio [4].

Figure 3. Branching ratio to the H(n = 3) + H channel in H⁺ - H⁻ mutual neutralization calculated using the Landau–Zener method with different set of coupling parameters. The figure also displays the n = 3 ratio calculated ab initio [4].
5. H\textsuperscript{−}+Be\textsuperscript{+}

The ion-pair state of the BeH system has $^2\Sigma^+$ symmetry. It crosses several of the covalent states associated with the Be\textsuperscript{+} + H\textsuperscript{−} limits at large internuclear distances. Some of the relevant potential energy curves of BeH have been computed \textit{ab initio} [42, 43], but the avoided crossings at large internuclear distances have not been examined. In table 2, the relevant covalent states are listed. We present the Q-value defined as the energy difference between the asymptotic ion-pair and covalent states (excitation energies are obtained from [44] and electron affinity of H from [45]), together with curve crossing distance $R_c$, and the electronic coupling element estimated using the Janev formula (13). In present model nine covalent states are included. There are several higher lying states with curve crossing distances $R_c > 95$ a\textsubscript{0}. We assume that the electronic couplings to these states can be neglected. The electronic states associated with Be(2s3d $^3$D) + H and Be (2s4s $^3$S) + H are here treated as one effective state with an ionic-covalent electronic coupling obtained using the root of the squared coupling elements according to equation (3).

In figure 4, the total MN cross section is displayed. We compute the cross section for collisions of Be\textsuperscript{+} with H\textsuperscript{−}, D\textsuperscript{−} and T\textsuperscript{−}. There is a very small isotope-dependence in the MN cross section. We have also calculated the Be\textsuperscript{+} + H\textsuperscript{−} MN cross section using other set of coupling elements such as the Olson2, Olson3 and Smirnov couplings. We find that at low energies (<10 eV), the cross sections calculated using the various coupling elements differ with less than a factor of two. Additionally, the isotope effect in the total cross section remains vanishingly small when calculated with coupling elements estimated using the other methods.

In most cases, when the reaction is driven by avoided crossings at large internuclear distances a small isotope effect in the total cross section is observed. A similar behaviour is observed in an \textit{ab initio} quantum study of H\textsuperscript{+} + H\textsuperscript{−} MN [46]. If instead the reaction is driven by couplings at small internuclear distances, such as in H\textsuperscript{+} + F\textsuperscript{−} [26], a dramatic isotope dependence can be observed. However, in the case of Li\textsuperscript{+} + H\textsuperscript{−} [23] a significant isotope effect was observed even though the reaction was driven by avoided crossings at large internuclear distances.

By comparing the total MN cross sections for the two systems calculated with the Janev couplings (see figure 4), we note that the one of Be\textsuperscript{+} + H\textsuperscript{−} is a factor of 3–7 larger than the one of H\textsuperscript{+} + H\textsuperscript{−}. This can be explained by the fact that the BeH system has more ionic-covalent curve crossings in the region 20 a\textsubscript{0} < R < 40 a\textsubscript{0} where the so-called reaction windows [47] for these systems have their maxima.

From the Landau–Zener calculation, the final state distribution can be computed. Using the Janev coupling elements, at low collision energies (<10 eV), the Be(2s3p $^1$P) + H and Be(2s3d $^1$D) + H channels are most important with ratios of about 53% and 43%, respectively at an collision energy of 1 meV. At higher energies other channels with curve crossings occurring at smaller internuclear distances such as the Be(2s3p $^3$P) + H channel start to contribute. It should be noted, however, that even though the total Be\textsuperscript{+} + H\textsuperscript{−} MN cross section was relative insensitive to the coupling elements used, the final state distribution changes when other set of couplings are applied.

We note that at low energies (<10 eV), the Be(2s3p $^1$P) + H and Be(2s3d $^3$D) + H channels are important while at higher energies other channels with curve crossings occurring at smaller internuclear distances such as the Be(2s3p $^3$P) + H channel start to contribute.

6. Concluding remarks

Using the Landau–Zener model, MN in H\textsuperscript{+} + H\textsuperscript{−} and Be\textsuperscript{+} + H\textsuperscript{−} collisions have been studied. For the H\textsuperscript{+} + H\textsuperscript{−} reaction, the cross section and final state distributions depend critically upon the choice of electronic couplings. By comparing the semiclassical results with data obtained \textit{ab initio} quantum mechanically on H\textsuperscript{+} + H\textsuperscript{−}, we conclude that coupling elements obtained using formula derived by Janev (13) produce reliable results. These are the coupling elements used to study
MN in Be$^+$ + H$^-$ collisions and to compute total neutralization cross section and final state distributions.

Acknowledgments

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Mutual neutralization in collisions of Li$^+$ and F$^-$

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1. Introduction

Diatomic molecules of alkali halides possess avoided crossings between lower lying adiabatic states due to mixing between ionic and covalent configurations. These systems provide illustrative examples of the Born–Oppenheimer break-down and they have been the subjects of numerous theoretical studies [1–3]. One such system is the LiF molecule, where the ionic state crosses the covalent state associated with the ground state fragments, Li$(2\Sigma^+)+F$(2$P$), at an internuclear distance, $R_c$ of 13.7 a$_0$. Just below the ion-pair threshold, there is another covalent limit, Li$(2\pi)+F$(2$P$), with a very large crossing distance (around 190 a$_0$) and hence the corresponding electronic coupling can be neglected [4]. Asymptotically, the ion-pair potential can be described by the Rittner potential, $V_{ip}(R) = E_F + \frac{1}{2} \frac{\alpha^2}{R^2}$, with the polarizabilities given by $\alpha(L^+) = 0.193$ a$_0^2$ and $\alpha(F^-) = 13.5$ a$_0^2$ [1].

The avoided crossing between the two lowest $^1\Sigma^+$ states of LiF have been extensively studied by ab initio methods. One of the first studies was performed in 1974 by Kahn et al. [5], using a multi-reference configuration interaction (MRCI) approach, where single and double external excitations were included from a 12-configuration reference wave function. The calculated adiabatic states were diabatized using an orthogonal two-by-two transformation and by assuming the ion-pair state has the above mentioned Rittner form. The calculated crossing distance was found to be about 11.3 a$_0$. In 1981, Werner and Meyer [1] performed state-averaged multi-configuration self-consistent field (MCSCF) calculation on the two lowest $^1\Sigma^+$ states of LiF. The states were diabatized by performing an orthogonal transformation of the adiabatic dipole matrix into a diagonal diabatic one. This approach gave a crossing distance of 13.3 a$_0$. This was followed by a theoretical study of Bauschlicher and Langhoff [6], where MRCI calculation using state-averaged complete active space self-consistent field (CASSCF) orbitals were compared with configuration interaction calculations where the lowest three molecular orbitals $[F(1s), Li(1s)\text{ and } F(2s)]$ were kept doubly occupied, and all excitations among the remaining valence electrons were included. They found a curve crossing distance of 12.6 a$_0$. This is significantly shorter than the one expected due to the use of a small basis set. Again the states were diabatized by assuming a Rittner form of the diabatic ion-pair state. The ion-pair potential energy curve was shifted in energy to obtain a correct crossing distance. The fourfold way methodology for direct diabatization [7] has been illustrated for the LiF system using multiconfiguration quasidegenerate perturbation theory calculations and a crossing distance of 12.5 a$_0$ was obtained [8].

To mention some of the more recent quantum chemistry calculations on the LiF system, we have an extensive study by Varandas [9] in 2009 using the MRCI technique with a sequence of correlation consistent basis sets. The calculated energies were extrapolated to the complete one-electron basis set limit. The computed non-adiabatic coupling element was fitted to analytical forms and the obtained parameters were used to perform an adiabatic to diabatic transformation [9,10]. The extrapolated crossing distance was found to be 13.86 a$_0$, which is in very good agreement with the predicted one. The explicitly correlated multi-reference configuration interaction method, MRCI-F12, has been tested on the LiF system [11] using the same set of basis sets as the ones used by Varandas. It was demonstrated that with a given basis set and active space, the calculated curve crossing distance get significantly closer to the one expected when the MRCI-F12 scheme is used.
To theoretically study the mutual neutralization reaction, the electronic coupling between the ionic and covalent states has to be known. Rather than using \textit{ab initio} data, the coupling can be estimated semi-empirically. In 1974, Grice and Herschbach [12] used a simple model for the atomic orbitals of the transferred electron for approximating the coupling element with an exponential function. A few years later, Janev and Rudolovic [13] applied the one-electron Landau–Herring method [14] to estimate the magnitude of the ionic-covalent coupling element. The coupling element was used to perform a Landau–Zener calculation [15,16] on the mutual neutralization cross section.

In 1983, Bienstock and Dalgarno [17] performed an \textit{ab initio} quantum study of the chemi-ionization and mutual neutralization reactions for the LiF system. They used the diabatic potential energy curves and coupling calculated by Werner and Meyer [1] and numerically solved the Schrödinger equation for the nuclear motion. The goal of the present study is not to perform the “best” quantum chemistry calculation on the two lowest \(1\Sigma^+\) states of LiF. Rather, the intention is to find a relatively simple approach to study the mutual neutralization reaction \textit{ab initio} and quantum mechanically. Here, we systematically perform a number of MRCI calculations on the two lowest \(1\Sigma^+\) states of LiF based on state-averaged CASSCF orbitals. Different active spaces and sets of correlation-consistent basis functions are tested. We examine how the non-adiabatic coupling element depends on the level of the structure calculation. A strict two-by-two diabatization is performed and “scaling method” is proposed to obtain the expected ionic-covalent curve crossing distance.

Section 2 outlines the structure calculations, together with a description of the diabatization scheme and a brief discussion on the computations the mutual neutralization cross section. The results are presented in Section 3. We show that the non-adiabatic coupling can be fitted to a Lorentzian function with a width that decays with increasing crossing distance. This is used to obtain a set of “scaled” diabatic potentials and coupling. The electronic coupling element is compared with those obtained in previous studies. With the calculated diabatic potential energy matrix, the total and differential cross sections for mutual neutralization are calculated. The quantum mechanical cross section is compared with the one obtained using the Landau–Zener model and previously calculated cross section. Atomic units are used throughout.

2. Computational details

2.1. Structure details

The quantum chemistry calculations are carried out with the MOLPRO program package [18]. In the present study, results from series of calculations are presented using the correlation-consistent basis set cc-pVXZ for lithium and aug-cc-pVXZ for the fluorine atom, where X = D,T,Q,S [19]. Molecular orbitals are generated using CASSCF calculations, where the active space consists of six electrons distributed among seven (or six) orbitals. The lowest three \(\sigma\) orbitals [corresponding to F(1s), Li(1s) and F(2s)] are kept doubly occupied and the following three \(\sigma\) and two pairs of \(\pi\) orbitals are active in the case of seven active orbitals. Test calculations with six active orbitals are carried out, where the outer \(\sigma\) orbital is excluded from the active space. State-averaged molecular orbitals are computed, where the two lowest \(1\Sigma^+\) states of LiF are optimized with equal weights. The molecular orbitals are then used in the subsequent MRCI calculation where the reference configurations are generated by allowing for excitations of the six valence electrons among the same set of seven (or six) active orbitals. Additional single and double external excitations out of the reference configurations are included. These sets of calculations will be labeled “7 orb/VXZ” or “6 orb/VXZ” depending on whether seven or six active orbitals have been included in the CASSCF and MRCI calculations with the cc-pVXZ and aug-cc-pVXZ basis sets for Li and F, respectively. The adiabatic potential energy curves of the two lowest \(1\Sigma^+\) states of LiF are computed for internuclear distances ranging from 2.0 to 20.0 \(a_0\).

The non-adiabatic first-derivative coupling element, \(f_{12}(R) = \langle \Phi_i | i | \Phi_2 \rangle\), between the two lowest \(1\Sigma^+\) states of LiF is computed at the MRCI level using three-point finite difference with a step-size of \(dR = 0.01 \ a_0\).

2.2. Diabatization

Instead of using an adiabatic representation with adiabatic states coupled by non-adiabatic interactions, it is customary to perform an orthogonal transformation to a diabatic representation. The diabatic states are not eigenstates to the electronic Hamiltonian, but are coupled by electronic couplings. However, in the diabatic representation the coupling elements arising from the nuclear kinetic energy operator will vanish [20,21]. Assuming only two electronic states are coupled, the diabatic-to-diabatic transformation matrix becomes

\[
T(R) = \begin{pmatrix}
\cos(\alpha) & \sin(\alpha) \\
-\sin(\alpha) & \cos(\alpha)
\end{pmatrix},
\]

where the rotational angle is obtained by integrating the non-adiabatic coupling element [21]

\[
\alpha(R) = \int_R^\infty f_{12}(\hat{R}) \, d\hat{R}.
\]

Using the orthogonal transformation \(U = T^T V\), where \(V\) is a two-by-two diagonal matrix containing the two adiabatic potential energy curves, the elements of the diabatic potential energy matrix \(U\) become

\[
U_{11}(R) = V_{11}(R) \sin^2 \alpha + V_{12}(R) \cos^2 \alpha
\]

\[
U_{12}(R) = V_{11}(R) \cos^2 \alpha + V_{12}(R) \sin^2 \alpha
\]

\[
U_{22}(R) = \frac{1}{2} [V_{12}(R) - V_{11}(R)] \sin(2\alpha).
\]

2.3. Nuclear scattering calculations

The nuclear scattering matrix element, \(S_{ij}\), is computed at fixed collision energy from the asymptotic solution of the coupled equation for the radial nuclear wave function in the diabatic representation. The coupled differential equation is numerically solved using Johnson’s log-derivative method [22,23] and the cross section for mutual neutralization is computed with

\[
\sigma(E) = \frac{\pi}{k^2} \sum_s (2s + 1) |S_{ij} - \delta_{ij}|^2.
\]

Here \(k/2\mu = E\), where \(E\) is the collision energy (assuming zero threshold energy for the incoming channel) and \(\mu\) is the molecular reduced mass and \(\iota\) is the angular momentum quantum number. More details on the numerical scheme can be found in [24].

Using the scattering matrix elements not only the total, but also the differential cross section can be computed using

\[
\frac{d\sigma}{d\Omega} = \frac{k^2}{4\pi} |f_{ij}(E, \theta)|^2.
\]

Here, the scattering amplitude is given by
\[ f_i(E, \theta) = \frac{1}{2i\sqrt{kk_i}} \sum_{x} (2l + 1) P_l(\cos \theta), \]  

where \( P_l \) are the Legendre polynomials.

Additionally, instead of a quantum mechanical description of the nuclear motion, a semi-classical approach can be applied, where the cross section is calculated using the Landau–Zener model [15,16]. The cross section for neutralization is then given by [25]

\[ \sigma_{\text{L-Z}}(E) = \frac{\pi}{k_i^2} \sum_{x} (2l + 1) P_l(1 - \Gamma), \]

where \( \Gamma \) is the Landau–Zener probability for making a transition between the diabatic states.

3. Results

3.1. Structure calculations

As described in Section 2.1, the quantum chemistry calculations are carried out with the MRCI method using CASSCF orbitals with 6 or 7 active orbitals and the cc-pVXZ/aug-cc-pVXZ basis sets for Li and F, where \( X = D,T,Q,5 \). We compute the adiabatic potential energy curves of the two lowest 1\(^{\Sigma}\) states of LiF. From these calculations the obtained crossing distance, \( R_c \), ranges from 12.497 \( a_0 \) in the 6 orb/VDZ calculation to 13.587 \( a_0 \) at the 7 orb/V5Z level. In Fig. 1, the calculated adiabatic potential energy curves from the 7 orb/V5Z scheme are compared with those of Werner and Meyer [1] and the data obtained by Varandas by applying the extrapolation scheme towards a complete basis [9]. Our potentials agree very well with those obtained by Varandas, also in the region of the avoided crossing, as can be seen in the inset of the figure.

The non-adiabatic first-derivative coupling element, \( f_{12}(R) \), is computed for the different sets of calculations. Fig. 2 shows the results from the calculations using seven active orbitals for the various basis sets. The symbols show the results from the quantum chemistry calculations, while the lines show fits of the coupling elements to a Lorentzian function of the form

\[ f_{12}(R) = \frac{\Gamma}{4(R - R_c)^2 + \Gamma^2}. \]

The \textit{ab initio} coupling element can be well described by this function. This can be explained by the fact that in the vicinity of the avoided crossing only two electronic states interact [26]. It can be shown [27] that for a two state diabatic Hamiltonian, where the difference between the two diabatic potential energy curves vary linearly with \( R \) and the electronic coupling is constant [a Landau–Zener Hamiltonian (15,16)], the non-adiabatic coupling will have the above mentioned Lorentzian form. The parameter \( \Gamma \) will be proportional to the electronic coupling at the curve crossing. This analytical form of the non-adiabatic coupling element was also discussed in the study of Varandas [9].

Fig. 3 displays the width, \( \Gamma \), of the non-adiabatic coupling element as a function of the fitted crossing distance, \( R_c \). As can be seen, the width of the coupling element becomes smaller as the crossing distance increases. It is well known that the dominant factor for the magnitude of the ionic-covalent electronic coupling element decays approximately exponentially with the crossing distance [28,29]. This is due to the overlap between the asymptotic diabatic wave functions. Since the parameter \( \Gamma \) is proportional to the electronic coupling, also the length of the region where the two states interact will decay exponentially with the crossing distance. By fitting the calculated widths to an exponential decaying function (blue dotted line), the width can be extrapolated to the expected crossing distance of \( R_c = 13.7 \ a_0 \). The value...
\( C = 0.46415 \text{ au} \) is then obtained. The thick black curve in Fig. 2 shows the non-adiabatic coupling element scaled to the expected crossing distance.

The different sets of adiabatic states are diabatized as described in Section 2.2. We then obtain crossing diabatic potential energy curves, as shown in Fig. 4. The inset of Fig. 4 shows the diabatic potential energy curves near the curve crossing region. The potential energy of the covalent state does not significantly change in the different set of calculations. Rather, the ion-pair state gets lowered in energy compared to the covalent state for calculations with larger basis sets. We assume the diabatic ion-pair state can be "scaled" by subtracting a constant energy from the ion-pair state to obtain a curve crossing at the expected distance, \( R_\times = 13.7 \text{ au} \). The scaled diabatic potentials are displayed with the thick black lines in Fig. 4.

The electronic coupling element, \( U_{12}(R) \), obtained with seven active orbitals and the different basis sets is displayed in Fig. 5. At small distances, the electronic coupling element changes when different basis sets are used. However, in the vicinity of the curve-crossing region, the coupling element does not significantly depend on the basis set.

In Fig. 6, we compare our calculated electronic coupling at the 7 orb/V5Z level of theory with some previous reported results. As described in the introduction above, different diabatization schemes have been applied in earlier studies. In the vicinity of the curve crossing, we obtain similar magnitude of the coupling element as all previous studies did. This is the region that is important for the mutual neutralization reaction. At smaller distances, our coupling element becomes negative.

To obtain the "scaled" diabatic potentials, the diabatic potential energy matrix from the 7 orb/V5Z calculation, with the ion-pair potential shifted down in energy, is diagonalized. The obtained adiabatic potential energy curves will have the avoided crossing at the expected crossing distance \( R_\times = 13.7 \text{ au} \). It is assumed that the non-adiabatic coupling element is given by the scaled Lorentzian function. (At small distances, the non-adiabatic couplings are not zero and here the result from the 7 orb/ASZ calculation is used). Finally the scaled adiabatic states are diabatized.

### 3.2. Mutual neutralization cross section

The cross section for mutual neutralization is computed for the different models using Eq. (4) at collision energies ranging from

[Fig. 4. Diabatic potential energy curves of the two lowest \( ^1\Sigma^- \) states of LiF calculated with seven active orbitals.]

[Fig. 5. Electronic coupling between the lowest two \( ^1\Sigma^- \) diabatic states of LiF calculated with seven active orbitals.]

[Fig. 6. Electronic coupling calculated at the 7 orb/V5Z level is compared with coupling elements from Kahn et al. [5], Werner and Meyer [1], Bauschlicher and Langhoff [6], Varandas [10], Grice and Herschbach [12], as well as Janev and Radulovic [13].]

[Fig. 7. Total \( \text{Li}^+ + \text{F}^- \) mutual neutralization cross section computed both quantum mechanically and using the Landau–Zener model with diabatic states obtained using seven active orbitals. The cross section computed by Bienstock and Dalgarno [17] is displayed. We have also used the diabatic potential energy matrix given by Werner and Meyer [1] to compute the cross section.]
1 meV to 100 eV. In Fig. 7, we show the results from the calculations with seven active orbitals together with the cross section calculated with “scaled” potentials. As the calculation improves, the curve crossing distance increases and the magnitude of the cross section decreases. Also the semi-classical Landau–Zener model [Eq. (7)] is applied to compute the cross section for the scaled potentials. We obtain similar cross sections with the quantum and semi-classical calculations. Notably, the cross section given by Bienstock and Dalgarno [17] is significantly smaller than the cross section computed here. In [17] the diabatic potential energy matrix computed by Werner and Meyer [1] is used. However, the electronic coupling element tabulated by Werner and Meyer [1]. Furthermore, using in our quantum mechanical nuclear scattering code the diabatic potential energy curves and electronic coupling obtained by Werner and Meyer, a cross section similar to the ones we compute with a smaller basis set is obtained. This is shown with the dashed (brown online) line in Fig. 7.

A quantum mechanical description of the nuclear motion allows not only for computation of the total cross section, but also the differential cross section. We are grateful to Prof. N. Elander for support. We acknowledge the Swedish Research Council (Grant No. 2014-4164) and the Carl-Trygger Foundation for financial support.

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References


4. Conclusion

Ab initio quantum mechanical calculations on mutual neutralization in collisions of Li+ and F− ions have been performed. The total and differential cross sections have been computed based on strictly diabatic states calculated using the MRCI method. Due to the low threshold energy of the ion-pair limit, only two coupled electronic states have to be considered. By performing quantum chemistry calculations with a number of correlation-consistent basis sets, we obtain non-adiabatic coupling elements well described by a Lorentzian function with a width that decreases exponentially with the calculated crossing distance. Similar mutual neutralization cross sections are computed when the nuclear motion is described both quantum mechanically and semi-classically using the Landau–Zener model. A significantly larger cross section than the one computed by Bienstock and Dalgarno [17] is obtained. The reason for this discrepancy is not clear.

Conflict of interest

No conflict of interest.
Studies of HeH: DR, RIP, VE, DE, PI, MN, . . .

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Abstract. The resonant states of HeH are computed by combining structure calculations at a full configuration interaction level with electron scattering calculations carried out using the Complex-Kohn variational method. We obtain the potential energy curves, autoionization widths, as well as non-adiabatic couplings among the resonant states. Using the non-adiabatic couplings, the adiabatic to diabatic transformation matrix can be obtained. A strict diabatization of the resonant states will be used to study various scattering processes where the resonant states are involved. These processes involve high energy dissociative recombination (DR) and ion-pair formation (RIP), resonant and direct dissociative excitation (DE), penning ionization (PI) as well as mutual neutralization (MN).

1. Introduction

When an electron collides with a molecular ion, such as HeH⁺, a number of processes can occur. There is, of course, elastic scattering

\[ \text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{HeH}^+(v_i, J_i) + e^- , \]

where only the momentum of the electron has changed. There are inelastic processes, such as vibrational and rotational excitation, where some energy is exchanged

\[ \text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{HeH}^+(v_f, J_f) + e^- . \]

At higher energies, electron-impact excitation to a dissociative electronic state can result in direct dissociative excitation (direct DE). In this case, the incident electron causes a transition to a dissociative excited state of the target ion with enough internal energy to cause fragmentation [1–3]

\[ \text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{He}^+ + \text{H} + e^- . \]

In addition, there are a number of resonant processes. Every state of the ion can serve as a parent ion for a series of neutral states. Below the ground state, these are a Rydberg series of neutral states converging

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to the ion. Electron capture to these Rydberg states via non-adiabatic interactions drives the dissociative recombination (DR) process at low collision energies [4–7]

\[
\text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{He} + \text{H},
\]

where the H fragment becomes excited.

However, if the parent state is an excited state of the ion, the neutral Rydberg states are doubly excited (Feshbach) resonances that lie below the direct dissociation threshold, and are formed when an incoming electron excites the target ion and attaches to a Rydberg orbital. Capture into these states can initiate a number of resonant processes. As the neutral molecule evolves in time, the system can autoionize, meaning the electron can be re-emitted, returning the molecule to its original electronic state. If the system returns to a bound ro-vibrational state of the ion, the process is resonant vibrational excitation (resonant VE) (or de-excitation)

\[
\text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{HeH}^* \rightarrow \text{HeH}^+(v_f, J_f) + e^-.
\]

If the system has enough energy to dissociate to products, the process provides an efficient path to dissociation at energies below the direct excitation level and the reaction is resonant dissociative excitation (resonant DE) [3, 8]

\[
\text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{HeH}^* \rightarrow \text{He} + \text{H}^+ + e^-.
\]

If, while evolving in time, the neutral fragments reach an internuclear separation beyond which autoionization is no longer possible, the states are considered electronically bound and the result is again dissociative recombination

\[
\text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{HeH}^* \rightarrow \text{He} + \text{H}.
\]

The resonant states of HeH produce a peak in the DR cross section around 18 eV [9, 10] and in this process the He fragment becomes excited. At collision energies above 12.07 eV (with target ions in ro-vibrational groundstate), the energy of system is enough for dissociation into the ion-pair. The resonant ion-pair formation (RIP)

\[
\text{HeH}^+(v_i, J_i) + e^- \rightarrow \text{HeH}^* \rightarrow \text{He}^+ + \text{H}^-
\]

is a processes competing with the high-energy DR [10]. The study of these processes requires both the accurate treatment of the electron scattering processes, but must also include a consistent description of the neutral electronic states for all internuclear distances that are probed during the processes. This includes not only the adiabatic potential energy curves of the resonant states, but also the couplings. Both the couplings between the resonant states and the scattering continuum (the autoionization widths) and the non-adiabatic couplings among the resonant states are needed to completely describe the processes and to compute cross section including the branching ratios into final states.

The same curves and couplings mediate another series of collision processes. These include Penning Ionization (PI) [11–14]

\[
\text{He}^+ + \text{H} \rightarrow \text{HeH}^+ \rightarrow \text{He}^+ + \text{H}^+ + e^-.
\]

Associative Ionization (AI) [15, 16]

\[
\text{He}^+ + \text{H} \rightarrow \text{HeH}^+ \rightarrow \text{HeH}^+(v_f, J_f) + e^-,
\]

and Mutual Neutralization (MN) [17–19]

\[
\text{He}^+ + \text{H}^- \rightarrow \text{HeH}^* \rightarrow \text{He}^* + \text{H}.
\]

Our work in this area has been to develop methods to obtain these curves and couplings and next we will use them to study the above mentioned processes. In the next section we will outline our computational
approach both for the quantum chemistry calculations of the adiabatic potential energy curves and non-adiabatic couplings as well as the electron scattering calculations. This is followed by a section describing the diabatization procedure needed. We will then discuss our methods that will be applied to study some of the above mentioned processes and some preliminary results are presented.

2. Computational approach

The goal is to obtain an accurate and consistent set of curves and couplings that can be used in the study of these processes. Our computational approach to this problem combines quantum chemistry and electron scattering techniques carried out with the MESA program [20]. We use standard quantum chemistry methods to obtain the bound electronic states and the non-adiabatic coupling between those states. We then carry out electron scattering calculations to obtain the positions of the resonant states and the autoionization widths. It is important that these calculations are done accurately and consistently to obtain the potential energy curves and couplings. When the potential energies and autoionization widths of the resonant states as well as the non-adiabatic interactions between them are obtained, a strict diabatization procedure is followed.

2.1 Structure calculations

For HeH, there are two distinct sets of neutral electronic states. First there are the low lying electronic states that can be described as Rydberg states with an ionic core in the electronic ground state ($X^1\Sigma^+$). These states drive the low-energy dissociative recombination of HeH$^+$ through non-adiabatic interactions. The second set of states are higher lying electronic states that are the Rydberg states with an excited (either $a^3\Sigma^+$ or $A^1\Sigma^+$) ionic cores. These resonant states are important for high-energy dissociative recombination, resonant pair formation resonant dissociative and vibrational excitation, penning ionization and mutual neutralization. The present article focuses on these states.

To obtain the bound adiabatic potential energy curves, we carried out a full Configuration Interaction (CI) calculation with an aug-cc-pVQZ He basis [21] set and an aug-cc-pVTZ basis set for H [22]. Extra diffuse functions were added to describe the 3d states. This resulted in 106 basis functions. This reproduced the asymptotic limits of resonant states to $\sim 200$ cm$^{-1}$ with an accuracy for the relative energies of $\sim 5$ cm$^{-1}$.

Below the ion, all states have configurations of $(1\sigma)^2(n\ell)^1$, which are a series of Rydberg states converging to the ground state of the ion and are bound electronically. In Fig. 1, the potential energies of the ground state ($X^1\Sigma^+$) of the HeH$^+$ ion and the first two excited states ($a^3\Sigma^+$ and $A^1\Sigma^+$) are displayed with the thick black curves. The bound Rydberg states of $2\Sigma^+$ and $3\Pi$ symmetries are shown with the thin dotted black and red curves, respectively.

Above the ion, states with configurations $(1\sigma)^2(n\ell)^1$, are background states, representing a discretized ionization continuum. However, there exists electronic states with configurations $(1\sigma)^1(2\sigma)^1(n\ell)^1$ that are members of Rydberg series converging to excited states of the ion (either $a^3\Sigma^+$ or $A^1\Sigma^+$). Eleven resonant states of $2\Sigma^+$ symmetry, six states of $3\Pi$ symmetry and two $2\Delta$ states were obtained. The potential energies of these states can be extracted from the structure calculation by examining the configurations of the wave functions. As long as the autoionization width of the resonant state is small and there is no strong mixing of the resonant and background configurations, the structure calculations can provide reliable energy positions of the resonant states. In Fig. 1 the HeH resonant states of $2\Sigma^+$ (thin black curves), $2\Pi$ (thin green curves) and $2\Delta$ (thin black curves) are displayed.

We first focus on the resonant states of $2\Sigma^+$ symmetry. One of these states asymptotically correlates with the ion-pair He$^+$ + H$^-$ limit. When the attractive ion-pair state interacts with the covalent Rydberg states avoided crossings occur at large internuclear distances. The eleven resonant states of $2\Sigma^+$ symmetry include all resonant states with avoided crossings at distances smaller than 100 a$_0$. The
Figure 1. Thick black curves show the potential energies of the ground and first two excited states of HeH+. The thin dotted curves show bound Rydberg states, while thin solid curves are the potential energies of the resonant states of $^2\Sigma^+$ symmetry (black), $^2\Pi$ symmetry (red) and $^2\Delta$ symmetry (green).

Figure 2. Potential energies of HeH resonant states of $^3\Sigma^+$ symmetry.

Potential energies of the adiabatic resonant states of $^3\Sigma^+$ symmetry are displayed in Fig. 2. The thin lines at $R > 40 a_0$ show experimental dissociation limits relative to the ground state fragments. There are clear signs of avoided crossings occurring when the attractive ion-pair state interact with the Rydberg states at large distances. For Rydberg states dissociating into the He($n = 2$) + H, these avoided crossings occur...
Non-adiabatic coupling elements between neighboring adiabatic states involved in the He($n = 3$) + H – ion pair avoided crossings.

Figure 3. Non-adiabatic coupling elements between neighboring adiabatic states involved in the He($n = 3$) + H – ion pair avoided crossings.

around 10 \text{a}_0. For the He($n = 3$) + H states there are avoided crossings ranging from 24 to 37 \text{a}_0. The avoided crossings are accurate to within a few tenths of \text{a}_0.

The non-adiabatic couplings, $f_{ij}(R) = \langle \Phi^i_{\text{ad}} \mid \frac{\partial}{\partial R} \mid \Phi^j_{\text{adj}} \rangle$, were calculated analytically using the MESA code. These calculations could not be carried out at the full-CI level. They employed the same basis, but a Multi-Configuration Self Consistent Field (MCSCF) calculation was used to generate the orbitals. An active space of ten natural orbitals was used, with full CI in the active space and double external excitations. This resulted in the same energies as the full CI calculation. The resonance states were identified by configurations and the couplings between them were computed. The approach is straightforward at large internuclear distances where the autoionization widths of the resonant states are negligible. However, at small distances ($R < 5 \text{a}_0$) there is strong mixing between the ionization continuum and the resonant states. Work is presently in progress to extract coupling elements when each resonant state can be described as a superposition of roots from the structure calculation.

There are arbitrary signs of the adiabatic electronic wavefunctions. To correct for this sign-flipping, a minimization program is written where the signs of the states are determined by minimizing the sum of the differences of all coupling elements at neighboring grid points. Our preliminary results of some of the coupling elements involved in the He($n = 3$) + H and He$^+ + \text{H}^-$ avoided crossings are shown in Fig. 3. The couplings are peaked at the vicinity of the avoided crossings.

2.2 Electron scattering calculations

The electron scattering calculations could not be carried out at the full-CI level. These calculations, using the complex Kohn variational method [23], employed the same basis. Natural orbitals were obtained a full-CI level. An active space of ten natural orbitals was used, with full CI in the active space and single external excitations. By fitting the eigenphase sum of the fixed nuclei elastic scattering matrix to a Breit-Wigner form, the resonance energy position (relative to the target ion) and the autoionization width can
be obtained. This resulted in shifted energies, but when referenced relative to the ion, resulted in the same results. The results are shown in Fig. 4.

2.3 Diabatization procedure

We include 11 resonant states of $\Sigma^+$ symmetry. We assume these states interact with the ionization continuum [through the autoionization width $r_i$], and they interact with each other [through the non-adiabatic couplings $f_{ij}(R)$]. We do not include interactions to higher lying resonant states or between states of different symmetry. Usually the transformation between the adiabatic and diabatic representations are approximate. In the case of a diatomic, where the curves and non-adiabatic couplings are known, it is possible to use the exact “strict diabatization”. Further information can be found in paper [24]. In this case, the adiabatic resonant states can be transformed to a diabatic representation using the orthogonal transformation matrix $T$ obtained by integrating the equation

$$\left[1 - \frac{d}{dR} + f\right]T = 0,$$

where the off-diagonal anti-symmetric $f$-matrix contains the non-adiabatic coupling elements. We apply the boundary condition that asymptotically the adiabatic and diabatic states are identical. Once the transformation matrix is obtained, the diagonal complex adiabatic potential matrix $V^{\text{ad}}$ with elements $V_{\text{adi}}^{\text{ad}}(R) = V_i(R) - i\Gamma_i(R)$, can be transformed to a diabatic potential matrix $V^d = T V^{\text{ad}} T$. We use a local complex model for the autoionization [25], which is known to be valid for high-energy resonant states. The resulting real part of the diagonal elements of the diabatic potential matrix are displayed in Fig. 5. It should be noted that using a “strict diabatic” representation, the diagonal potentials do not remind of the more familiar shape of the “quasi-diabatic potentials” with an attractive ion-pair potential crossing the repulsive Rydberg states.

Figure 4. a) Comparison of the energies of the $\Sigma^+$ resonant states obtained from structure calculations (lines) and electron scattering calculations (symbols). b) Autoionization widths of the $\Sigma^+$ resonant states obtained from electron scattering calculations.
2.4 Nuclear dynamics

Once the potential energy curves, couplings and autoionization widths of the HeH resonant states are
determined, the reactions discussed in the introduction can be studied. The nuclear dynamics are studied
quantum mechanically by numerically solving either the time-dependent [26] or time-independent
driven Schrödinger equation [27]. For some processes, such as dissociative recombination, ion-pair
formation and dissociative excitation, the rotational motion of the system will be neglected. Studies
of reactions involving collisions of atoms or ions (such as penning ionization, associative ionization
and mutual neutralization) require inclusion of angular momentum. A partial wave decomposition is
performed and the coupled radial Schrödinger equation will be solved for fixed angular momenta [28].
The total cross section for the reaction is obtained by summarizing contributions from partial waves.

3. Results

We report some preliminary results from the studies of direct and resonant dissociative excitation
processes. These calculations can be seen as a test of the accuracy of the electron scattering calculations
upon which the present model is based.

3.1 Direct dissociative excitation

In direct dissociative excitation, inelastic electron scattering causes an excitation of the HeH\(^{+}\) ion to one
of the lowest two excited states (a\(^1\Sigma^{+}\) or A\(^1\Sigma^{+}\)), followed by a direct dissociation to He\(^{+}\) + H. Within
the adiabatic-nuclei approximation [29, 30], the energy-normalized nuclear continuum function of the
excited target state is approximated with a Dirac-delta function. Then the cross section can be written
[2, 31]

\[
\sigma_{n'\ell'}^{(n)}(E) = \int_{R_c}^{\infty} \hat{\sigma}_{n'\ell'}^{(n)}(E, R) \left[ I_{\ell'}(R) \right]^2 dR.
\]
where the fixed-nuclei inelastic electron scattering cross section, $\tilde{\sigma}_{NN}^{+}(E, R)$ obtained from the Complex-Kohn calculations, is averaged over the square of the vibrational wave function of the HeH$^+$ ion in the initial vibrational state $v_0$. The fixed-nuclei inelastic cross section has sharp, narrow resonances on a smooth and relative energy-independent background. The sharp resonances arise from capture into Feshbach resonances and to obtain only the direct contribution these were manually removed. In Fig. 6, the calculated cross section (red curve) is compared with the measured cross section using an ion-storage
ring [3]. We also compare with the computed cross section (blue curve) by Orel and Kulander [2] that was based on the same delta-function approximation, but with a smaller electron scattering calculation and assuming that the fixed nuclei cross section simply shifts with the threshold energies when the internuclear distance is changed. We have begun to explore methods that go beyond the delta-function approximation and that include the nuclear dynamics in the description of the process [31].

3.2 Resonant dissociative excitation

In the resonant dissociative excitation process, the electron is temporarily captured into the resonant states. Autoionization back to the ground ionic state may cause dissociation if the kinetic energy of the $\text{He} + \text{H}^+$ fragments is high enough. As a model to test the scattering calculation, we have only included the contribution from the lowest resonant state of $^2\Sigma^+$ symmetry. We do not include non-adiabatic couplings to higher resonant states. As can be seen in Fig. 7, the computed cross section [32] agrees well with the measured cross section from CRYRING [3]. At higher collision energies ($E > 14 \text{ eV}$), higher lying resonant states contribute to the cross section. Next, the process will be studied by including all resonant states as well as the couplings between them.

4. Conclusion

We have carried out combined structure/electron scattering calculations on HeH to obtain accurate energies, non-adiabatic couplings as well as autoionization widths of resonant states. These electronic states are important for many reactive collisional processes such as high-energy dissociative recombination, ion-pair formation, vibrational and dissociative excitation, associative ionization, penning ionization as well as mutual neutralization. Using a strict diabatic representation of the resonant states, consistent studies of these processes will be performed.

References

A theoretical study of mutual neutralization in $\text{He}^+ + \text{H}^-$ collisions

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Total and differential cross sections for mutual neutralization in low energy (0.001 eV -100 eV) $\text{He}^+$ and $\text{H}^-$ collisions are calculated ab initio and fully quantum mechanically. Atomic final state distributions and isotope effects are investigated. The theoretical model includes dynamics on eleven coupled states of $^2\Sigma^+$ symmetry where autoionization is incorporated. The potential energy curves, autoionization widths and non-adiabatic couplings of electronic resonant states of $\text{HeH}$ are computed by combining structure calculations with electron scattering calculations. The nuclear dynamics is studied using a strict diabatic representation of the resonant states. Effects of rotational couplings between $^2\Sigma^+$ and $^2\Pi$ electronic states are investigated in the pure precession approximation.

I. INTRODUCTION

In mutual neutralization, oppositely charged ions collide and driven by non-adiabatic couplings, an electron is transferred resulting in formation of neutral fragments. An ab initio description of the reaction is challenging since dynamics on highly excited electronic states has to be considered and the reaction is induced by non-adiabatic couplings between ionic and covalent states, often occurring at large internuclear distances. In the past there has been numerous semi-classical studies [1–3] of the process using e.g. the Landau-Zener model [4, 5] or similar approaches. Currently, there are just a handful of fully quantum mechanical ab initio studies of the MN reaction and all are limited to collisions between atomic ions [6–13].

Here, mutual neutralization in collisions of $\text{He}^+$ with $\text{H}^-$ is theoretically studied, i.e.

$$\text{He}^+ + \text{H}^- \rightarrow \text{HeH}^+ \rightarrow \text{He}^+ + \text{H}.$$  (1)

The calculation is performed ab initio and fully quantum mechanically. Potential energy curves and non-adiabatic interactions are computed using the configuration interaction method. The electronic states of the $\text{HeH}$ complex formed in the reaction are autoionizing states (they have potential energy curves and autoionization widths) since they have potential energies larger than the energy of the ground state of $\text{HeH}^+$. The present model includes autoionization using local complex potentials. With the complex-Kohn variational method [14], fixed nuclei electron scattering calculations are carried out and the autoionization widths are computed. The adiabatic resonant states are diabatized and the nuclear dynamics are studied using Johnson’s log-derivative method [15, 16].

The $\text{He}^+ + \text{H}^-$ mutual neutralization reaction is an ideal reaction for testing theory. The reaction forms a molecular complex simple enough for accurate quantum chemistry and electron scattering calculations. However, the reaction is also challenging to theoretical model since it involves very highly excited electronic states that couple to the ionization continuum. To accurately describe the process, a manifold of avoided crossings occurring at internuclear distances ranging from 7-37 a₀, have to be considered.

Using crossed and merged beam experiments, the cross section for mutual neutralization in collisions of $^3\text{He}^+$ with $\text{H}^-$ has been measured, for energies ranging from a few eV to several keV [17–21]. Additionally, measurements on the cross section for neutralization in $^4\text{He}^+ + \text{D}^-$ collisions have been performed [2, 21].

The $\text{He}^+ + \text{H}^-$ mutual neutralization reaction was first theoretically studied using the semi-classical Landau-Zener model including ten coupled states [2]. It was found that the cross section depends on the ionic-covalent coupling parameters used in the model. By applying coupling elements developed by Olson et al. [2], good agreement with measured cross section below 2 keV was obtained. In 1992, Ermolaev [22] calculated the neutralization cross section at higher collision energies using a one-active-electron model. In the theoretical study by Chibisov et al. [23], all three electrons were included. The nuclear motion was described classically and autoionization was not included. The total cross section as well as the final state distributions were calculated for collision energies ranging between 40 to 4000 eV.

The present study presents a theoretical ab initio investigation of the mutual neutralization reaction where all degrees of freedom are described quantum mechanically and autoionization is incorporated. Section II describes how the relevant electronic potential energy curves and autoionization widths of the resonant states are obtained by combining electron scattering and structure calculations. We additionally compute the non-adiabatic couplings that drive the reaction. Below, we formulate the coupled nuclear Schrödinger equation for the resonant states and describe the diabatization procedure and how the resulting coupled equation is solved using the log-derivative method. In section III, we present not only the total neutralization cross section, but also the final state distributions, differential cross section as well as an
analysis of isotopic substitution. Unless otherwise mentioned, atomic units are used.

II. THEORY

A. Electronic structure and scattering calculations

The $X^1\Sigma^+$ electronic ground state of HeH$^+$ has the dominant configuration (1$s^2$). This state is associated with the He + H$^+$ fragments at large internuclear distances. The lowest two excited electronic states of the ion are the $\alpha^3\Sigma^+$ and $\alpha^1\Sigma^+$ states with dominant configurations corresponding to triplet and singlet coupled (1$s^2$)(2$s\sigma^2$), respectively. These states have repulsive potential energy curves dissociating into He$^+ + H$. The $X^2\Sigma^+$ electronic ground state of the HeH system has a repulsive potential. However, below the potential of the ionic ground state of HeH$^+$ there are manifolds of Rydberg states converging to the excited ionic cores. These states have potential energy curves situated in the ionization continuum of the ground ionic state and through electronic interactions they will interact with the continuum to become electronic resonant states. These states dissociate into He$^+ + H$. The ion-pair fragments He$^+ + H$ form a molecular state of $\Sigma^+$ symmetry. At large internuclear distances the potential of the ion-pair state is described by an attractive Coulomb potential and it will cross many of the covalent resonant states dissociating into He$^+ + H$.

The present study includes eleven electronic resonant states of HeH of $\Sigma^+$ symmetry. These are the electronic states associated with He[H(1$s^1$)($n\ell\sigma$)]+$H^+$ limits, where $n = 2$ and $n = 3$. Also the $n = 4$ states are energetically below the ion-pair limit, but the avoided crossing distances induced by the ionic-covalent interactions are anticipated to be larger than 100 a$_0$ and these states are therefore neglected [7].

The electronic scattering and structure calculations are carried out using the MESA program [24]. To calculate potential energy curves of the HeH$^+$ and HeH systems, the full configuration interaction (CI) method was used with the aug-cc-pVTZ basis set for He [25] and the aug-cc-pVTZ basis set for H [26]. Extra diffuse functions were added on He to accurately describe the 3$d$-orbitals.

The electron scattering calculations could not be carried out at the full CI level. Instead by employing the complex-Kohn variational method [14], the same basis were used to construct natural orbitals of the ground state of HeH at the full-CI level. This was followed by a multi-reference configuration interaction (MRCI) calculation where the reference configurations were obtained by allowing for excitations of the three electrons among ten natural orbitals. Single external excitations were then added. By minimizing the complex-Kohn functional [14], unknown parameters of the scattering trial wave function can be optimized. This allows for determination of the scattering matrix and the corresponding eigenphase sum. We then extract fixed nuclei energy positions and autoionization widths of the resonant state by fitting the eigenphase sum to a Breit-Wigner form [27].

The radial first-derivative non-adiabatic coupling elements, $f_{ij}(R) = (\langle \Phi_i | \frac{\partial}{\partial R} | \Phi_j \rangle)^2$, were calculated analytically [28] using the MESA program. These calculations could not be performed at the full CI level. Instead, using the same basis set, the Multi-Configuration Self Consistent Field (MCSCF) method was used with an active space including all three electrons and ten orbitals. This was followed by a MRCI calculation where the reference configurations were generated by allowing for excitations of the three electrons among ten orbitals. Up to double external excitations were then included. These calculations were carried out in no symmetry. The resonant states were identified by analyzing the dominant configurations of the CI wave function. Since the sign of the electronic wave function is arbitrary, there are ambiguities in the signs of the coupling elements. The signs of these couplings were set by an optimization procedure where all signs of the electronic wave functions were optimized such that the difference between the sums of all coupling elements with previous calculated point was minimized.

It should be noted that at small internuclear distances ($R < 5$ a$_0$), the autoionization widths of the resonant states are non-zero. This is the region where these states become resonant states and will couple to the ionization continuum. When the non-adiabatic coupling elements were computed, the continuum part of the wave function of the resonant states were not included. The resonant states were treated as bound states and this is an approximation. To accurately compute non-adiabatic couplings among electronic resonant states is an interesting and challenging project beyond the goal of present work. Additionally, as will be seen below, the non-adiabatic couplings among the resonant states occurring at small internuclear distances are not significant for the mutual neutralization reaction studied here.

To confirm the non-adiabatic couplings, they have also been computed at the full CI level using a three-point finite difference method with a step-size of 0.1 a$_0$. Present FCI calculation is using molecular orbitals optimized at large internuclear distances. The atomic orbital coefficients are thus $R$-independent, and we assume all derivatives in the electronic wave functions originate from derivatives in the CI-coefficients. The non-adiabatic coupling elements computed using finite difference and the analytical method are similar in magnitude and shape.

B. Nuclear Schrödinger equation for the resonant states

Following the P- and Q- projection operator formalism [29, 30] and by applying a partial wave expansion of the nuclear wave function, the radial Schrödinger equation for the dynamics on the adiabatic resonant states can
be derived. For fixed angular momentum $\ell$, the equation is given by

$$\left[ \frac{1}{2\mu} \frac{d^2}{dr^2} + V_i + \ell (\ell + 1) \frac{1}{2r^2} \right] u_i,\ell + \sum_j \left[ W_{ij} - \frac{1}{\mu} f_{ij} \frac{d}{dr} - \frac{1}{2\mu} g_{ij} \right] u_j,\ell = Eu_i,\ell. \quad (2)$$

Here, the electronic states are approximate eigenstates of the electronic Hamiltonian $\langle \Phi_i, H_{el} \Phi_j \rangle = V_i(R) \delta_{ij}$ coupled by the non-adiabatic coupling elements $f_{ij}(R) = \langle \Phi_i | \frac{\partial}{\partial R} | \Phi_j \rangle$ and $g_{ij}(R) = \langle \Phi_i | \frac{\partial^2}{\partial R^2} | \Phi_j \rangle$. Autoionization is included through the complex matrix elements $W_{ij}$. For electronic resonant states with high enough energy, the “local Boomerang approximation” [31, 32] is justified, where it is assumed that autoionization into a complete set of vibrational eigenstates is possible. We then neglect the energy-shift of the resonant states and the $W_{ij}$ elements becomes purely imaginary of the form [30, 33]

$$W_{ij}(R) = -i \frac{\sqrt{1 - (R/R_j)^2}}{2}. \quad (3)$$

The diagonal elements $W_{ii} = -i\Gamma_i/2$ account for the autoionization, while the off-diagonal elements cause indirect electronic couplings between the resonant states through the ionization continuum. By combining the electronic structure with the electron scattering calculations described above, the potential energies of the adiabatic resonant states $V_i(R)$, non-adiabatic coupling elements $f_{ij}(R)$ and autoionization widths $\Gamma_i(R)$ are computed.

### C. Diabatization

We assume a finite number ($N = 11$), adiabatic electronic HeH states of $2\Sigma^+$ symmetry are coupled by non-adiabatic couplings. By applying an orthogonal transformation, the adiabatic states may be transformed to a "strict diabatic" representation [34]. The transformation matrix, $T$, can be obtained by integrating the equation

$$\left( 1 \frac{d}{dr} + f \right) T = 0. \quad (4)$$

Here $f$ is an anti-symmetric matrix containing the first-derivative non-adiabatic coupling elements. The boundary condition of the transformation matrix is given by the unit matrix at large internuclear distances. We thus assume that asymptotically, the adiabatic and diabatic states are identical and any non-zero asymptotic non-adiabatic couplings are hence neglected. Once the transformation matrix is computed, we transform the adiabatic nuclear Schrödinger equation (2) to the corresponding diabatic one

$$\left[ \frac{1}{2\mu} \frac{d^2}{dr^2} + \ell (\ell + 1) \frac{1}{2r^2} \right] \tilde{u}_{i,\ell} + \sum_j \left[ \tilde{V}_{ij} + \tilde{W}_{ij} \right] \tilde{u}_{j,\ell} = E\tilde{u}_{i,\ell},$$

where $\tilde{V} = T^T V T$ and $\tilde{W} = T^T W T$.

### D. Log-derivative method

Instead of directly solving the coupled nuclear Schrödinger equation (5) in the diabatic representation, the logarithmic derivative of the radial wave function $(y_\ell = \sqrt{\mu} u_\ell \phi_\ell)$ is introduced and the radial Schrödinger equation is transformed to a matrix Riccati equation. The physical boundary condition for the logarithmic derivative at origin becomes a diagonal matrix with very large (approximately infinite) diagonal elements. Using a numerical procedure developed by Johnson [15, 16, 35], the matrix Ricatti equation is integrated out to a region where the potentials have reached their asymptotic form. In the present study $R_f = 50 \ a_0$ is used.

By combining the asymptotic value of logarithmic derivative with the correct regular and irregular solutions of the asymptotic states, the reactance matrix can be calculated [10]. The elements of the scattering matrix $[S_{ij,\ell}(\mu)]$ are obtained as a Cayley transformation between the open partitions of the reactance matrix. Finally the cross section for mutual neutralization can be computed from the scattering matrix elements

$$\sigma_{ij}(\mu) = \frac{k_j \mu}{k_i} \sum_{\ell = 0}^\infty (2\ell + 1) |S_{ij,\ell} - \delta_{ij}|^2, \quad (6)$$

where $k_j = \sqrt{2\mu (E - E_{th}^j)}$ is the asymptotic wave number of the incoming channel and $E_{th}^j$ is the asymptotic energy of state $j$. The summation of partial waves is terminated when the ratios of partial cross section to accumulated total cross section are less than $10^{-4}$ for 25 terms in succession. The total neutralization cross section is obtained by summarizing the contributions from all covalent states.

By calculating the scattering amplitude

$$f_{ij}(\theta, \mu) = \frac{1}{2i k_i k_j} \sum_{\ell = 0}^\infty (2\ell + 1) (S_{ij,\ell} - \delta_{ij}) P_\ell (\cos \theta), \quad (7)$$

where $P_\ell$ are the Legendre polynomials, the differential cross section is obtained from

$$\frac{d\sigma_{ij}}{d\Omega} = \frac{k_i}{k_j} |f_{ij}(\theta, \mu)|^2. \quad (8)$$

The formalism outlined above are usually applied to study nuclear dynamics on electronically bound states. However, the method can also be used to calculate cross section when autoionization is added to the model using local complex potentials [11, 36, 37].
III. RESULTS AND DISCUSSION

We start by presenting the potential energy curves, autoionization widths and non-adiabatic coupling elements important for the description of the $\text{He}^+ + \text{H}^- \rightarrow \text{He} + \text{H}^-$ mutual neutralization reaction. This is followed by an analysis of the total neutralization cross section, where we investigate the role of the autoionization widths and rotational couplings. The reaction is studied for collisions of various hydrogen and helium isotopes. Finally, the final state distributions and differential cross sections are presented.

A. Molecular data of the resonant states

Potential energy curves of electronic resonant HeH states are computed using the FCI method described above. At the same level of theory also the lowest three electronic states of the cation are computed. As can be seen in Fig. 1, the potential energy curves of the resonant states have energies larger than the ground state energy of the ion. In the figure, we show potential energy curves of 11 resonant states of $2\Sigma^+$ symmetry and 6 $2\Pi$ resonant states. We also obtain the resonance positions from the electron scattering calculations carried out with the MRCI method. These scattering calculations are carried out for internuclear distances smaller than 5.0 $a_0$. As can be seen in Fig. 1, the energy positions obtained using the FCI structure and MRCI scattering calculations agree well.

From the electron scattering calculations not only the energy positions of the resonant states are obtained, but also the corresponding autoionization widths displayed in Fig. 2 for resonant states of $2\Sigma^+$ symmetry. The two lowest resonant states have the largest widths. All widths become negligible at internuclear distances larger than 5.0 $a_0$.

Fig. 3 shows the potential energy curves of the electronic resonant states of $2\Sigma^+$ symmetry. At large internuclear distances there are avoided crossings occurring due to the interactions between the ion-pair and covalent states. For distances larger than 20 $a_0$, there are sharp avoided crossings among the ion-pair state and the covalent states associated with $\text{He}(1s)^2(nl)^1+\text{H}^-$ limits, where $n = 3$, as shown in Fig. 4 (a). As will be seen, non-adiabatic first-derivative coupling elements $f_{ij}(R)$ among theses states are the interactions driving the $\text{He}^+ + \text{H}^- \rightarrow \text{He} + \text{H}^-$ reaction. These couplings are displayed in Fig. 4 (b). The non-adiabatic coupling elements are large in the vicinity of the avoided crossings and they have approximately Lorentzian profiles. The large coupling at 26 $a_0$ is not originating from an interaction between ionic and covalent states, but due to an avoided crossing between state 9 and 10. The avoided crossing due to interactions between the ion-pair state and the $n = 2$ covalent states occurring around 7-15 $a_0$ are not
as sharp and hence the corresponding coupling elements are smaller than the $n = 3$ coupling elements.

In Fig 5, all coupling elements between all neighboring states are displayed for internuclear distances ranging from 0.5 to 10 a₀. For internuclear distances smaller than 5 a₀, there are huge non-adiabatic coupling elements due to avoided crossing among the resonant states that are Rydberg states converging to different excited ionic cores. This is the region where autoionization widths are non-zero. The resonant states are therefore interacting with the ionization continuum. The approach to compute the non-adiabatic coupling elements using standard structure calculations and identifying the resonant states by analyzing the configurations of the wave function, is an approximation that in this region breaks down. However, as will be shown, for the mutual neutralization reaction the exact magnitudes of the non-adiabatic coupling elements at small internuclear distances ($< 5$ a₀) are not significant. To calculate the non-adiabatic couplings among resonant states and to incorporate the effects of the interactions to the continuum is an interesting and challenging project beyond the scope of present study.

B. Total cross section and isotope effects

The total mutual neutralization cross sections are calculated for collision energies ranging between 1 meV to 600 eV. In Fig. 6, our $^4\text{He}^+ + \text{H}^-$ cross section is compared with measured ones [17, 20, 21] and previous theoretical predictions [22, 23]. At large energies, the cross section connects smoothly to the measured and previous calculated ones. However, at lower energies the calculated cross section is larger than the one measured using a merged-beam apparatus by Peart and Hayton [20]. The measured cross section does not display the same low-energy $E^{-1}$ behavior as observed in the calculation.
and which is predicted by Wigner’s threshold law [39].

The role of autoionization can be investigated by turning on and off the imaginary term \( W_{ij} \) as described by equations (2) and (3). In Fig. 7, the total mutual neutralization cross sections in collisions of \(^4\text{He}^+ + \text{H}^-\) are displayed both when autoionization is included and when it is not considered. As can be seen, the effect of autoionization is negligible. This is due to the fact that the autoionization widths are non-zero only at small internuclear distances (\( R \leq 5 \ a_0 \)). At low energies, the centrifugal barrier added the potentials will prevent the system to reach these small distances.

The cross sections for mutual neutralization have been calculated for collisions of different isotopes of the hydrogen and helium ions. For the different isotopologues, we assume the adiabatic potential energy curves and non-adiabatic coupling elements are the same, but the reduced mass of the molecular system is changed. In Fig. 7, we compare the calculated cross sections for collisions of \(^4\text{He}^+\) or \(^4\text{He}^+\) with \(\text{H}^-\) or \(\text{D}^-\). As can be seen the cross sections for the heavier isotopologues have a smaller magnitude than the lighter ones. At large collision energies \((E > 200 \text{ eV})\), the orders of the cross sections are reversed. A similar isotope effect was found in mutual neutralization in collisions of \(\text{H}^+\) with \(\text{H}^-\) [38].

As described above in section IIIA, there are very large non-adiabatic couplings among the resonant states at small internuclear distances. This is the region where autoionization widths are non-zero and our approach to compute the coupling elements using structure methods is approximate. We investigate the effects of these non-adiabatic couplings at small distances by running calculations on the mutual neutralization reaction when all coupling elements smoothly are turned to zero for distances smaller than 5.0 \( a_0 \). At low energies, the calculated total cross section will then decrease by a few percent (1–5 % for \(E < 10 \text{ eV}\)) while at energies larger than 100 eV, the reduction increases to 18 %. Thus, the small \( R \) non-adiabatic couplings have no significant effect on the mutual neutralization cross section.

Previous quantum mechanical studies on mutual neutralization reactions have neglected rotational couplings [6–13]. However, in the review on recombination processes written in 1982, Bardsley pointed out that rotational couplings could be important in mutual neutralization reactions and should be considered [40]. The rotational couplings originate from correlation between the rotational motion of the nuclei and the electronic motions and it will give rise to different diagonal and off-diagonal terms that should be added to the Hamiltonian. The L-uncoupling terms will induce interactions between the resonant states of \(^2\Sigma^+\) and \(^2\Pi\) symmetry that approximately have the form [41]

\[
-\frac{\sqrt{\ell (\ell + 1)}}{2\mu R^2} \left( \Phi_{\Pi}^i \mid L_\pm \mid \Phi_{\Sigma}^j \right).
\] (9)

Due to the factor \( R^{-2} \), these rotational couplings are localized at small internuclear distances. However, the factor \( \sqrt{\ell (\ell + 1)} \) will make the rotational couplings large when high angular momenta quantum numbers contribute. This is the case in the mutual neutralization reaction presently studied. The rotational couplings are not calculated \textit{ab initio}, but are here approximated using a pure precession approximation. The dominant configurations of the adiabatic states have been identified and for the \(^2\Sigma^+\) and \(^2\Pi\) states associated with the same asymptotic limit they only differ by the highest occupied molecular orbital and we have

\[
\left( \Phi_{\Pi}^i \mid L_\pm \mid \Phi_{\Sigma}^j \right) \approx \left( (n_{\text{per}})^3 \mid L_\pm \mid (n_{\text{per}})^3 \right) \approx \sqrt{2}.
\] (10)

For \(^2\Sigma^+\) and \(^2\Pi\) states not associated with the same asymptotic limits, the rotational couplings are approximated with 0. In the diabatization procedure, the rotational couplings are transformed with a transformation matrix of the form

\[
\hat{T} = \begin{pmatrix}
T & 0 & \cdots \\
0 & 1 & \cdots \\
\vdots & \vdots & \ddots
\end{pmatrix},
\] (11)
where $T$ is the orthogonal transformation matrix for the $^3\Sigma^+$ resonant states computed by numerically solving eq. (4) above. No non-adiabatic interactions among the $^3$H states are considered.

The total mutual neutralization cross sections are calculated for collisions of all isotopes of hydrogen and helium ions, with and without the inclusion of the rotational couplings as displayed in Fig. 9 with solid and dashed lines, respectively for the $^3$He$^+ + \text{H}^-$ and $^4$He$^+ + \text{D}^-$ collisions. These are the isotopologues where the rotational couplings have the largest and smallest effects. As can be seen, the rotational couplings will at large collision energies ($E > 10$ eV) increase the neutralization cross section. The effect is largest for the system, where most partial waves contribute.

**C. Final state distributions**

From the scattering matrix elements, not only the total cross section can be computed, but also the final state distributions. Fig. 10 shows calculated branching ratios for collisions of $^3$He$^+ + \text{H}^-$ in (a) and $^4$He$^+ + \text{D}^-$ in (b) both with (solid lines) and without (dashed lines) the inclusion of rotational couplings.

The dominant channels are all associated with the He$[^1s^1(3s)^1]+\text{H}$ limits and these are the covalent states with avoided crossings due to interactions with the ion-pair state at internuclear distances ranging from 20-40 $a_0$ as displayed in Fig. 4. Most important is the state associated with the $1s3s\ ^3S$ limit, which has the lowest potential energy curve of the $n = 3$ states shown in Fig. 4 (a). Note that although the isotope effect in the total cross section is very small, there are some isotope-dependence in the final state distributions.

**D. Differential cross section**

The differential cross section is calculated from the scattering amplitude as described by eq. (8). In Fig. 11, the total differential cross section (summed over all channels) is displayed for selected collision energies for collisions of $^3$He$^+$ with $\text{H}^-$. As can be seen, the differential cross section is peaked at small scattering angles (forward
The differential cross sections are computed for collisions of various isotopes of hydrogen and helium ions. They all show similar behavior of differential cross sections, although the exact positions of the oscillations may vary. As an example, the differential cross sections for mutual neutralization in collisions of $^4\text{He}^+ + \text{H}^-$ and $^4\text{He}^+ + \text{D}^-$ at 0.1 eV collision energy are displayed in Fig. 12.

**IV. CONCLUSION**

Mutual neutralization in collisions of $\text{He}^+$ and $\text{H}^-$ is studied *ab initio*, where the nuclear motion is described quantum mechanically. The reaction involves electronic resonant states of $\text{HeH}$ of $^4\Sigma^+$ symmetry that have been computed by combining electron scattering calculations with structure calculations at the FCI and MRCI level of theory. Non-adiabatic couplings are computed analytically. Total and differential cross sections are computed as well as final state distributions. The reaction is studied for collisions of various isotopes of hydrogen and helium ions. The total cross section is in agreement with measurements and previous theoretical studies at higher energies, but is larger than the cross section measured using a merged beam apparatus [20] at relative low energies. At low collision energies, the autoionization and the rotational couplings between the $^3\Sigma^+$ and $^2\Sigma^+$ states, estimated using a pure precession approximation, are found to have a small effect on the outcome of the reaction. The mutual neutralization reaction will be dominated by formation of $\text{He}(1s8s\ ^3S)+\text{H}$ followed by $\text{He}(1s3p\ ^3P)+\text{H}$ with ratios of approximately 50% and 30%, respectively, at low collision energies. The calculated differential cross section shows a peak in the forward direction.

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Differential and total cross sections of mutual neutralization in low-energy collisions of isotopes of \( \text{H}^+ + \text{H}^- \)

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Mutual neutralization in the collisions of \( \text{H}^+ \) and \( \text{H}^- \) is studied both theoretically and experimentally. The quantum-mechanical ab initio model includes covalent states associated with the \( \text{H}(1)+\text{H}(n \leq 3) \) limits and the collision energy ranges from 1 meV to 100 eV. The reaction is theoretically studied for collisions between different isotopes of the hydrogen ions. From the partial wave scattering amplitude, the differential and total cross sections are computed. The differential cross section is analyzed in terms of forward- and backward-scattering events, showing a dominance of backward scattering which can be understood by examining the phase of the scattering amplitudes for the gerade and ungerade set of states. The isotope dependence of the total cross section is compared with the one obtained using a semiclassical multistate Landau-Zener model. The final state distribution analysis emphasizes the dominance of the \( n = 3 \) channel for collisions below 10 eV, while at higher collision energies, the \( n = 2 \) channel starts to become important. For collisions of ions forming a molecular system with a larger reduced mass, the \( n = 2 \) channel starts to dominate at lower energies. Using a merged ion-beam apparatus, the branching ratios for mutual neutralization in \( \text{H}^+ \) and \( \text{H}^- \) collisions in the energy range from 11 to 185 eV are measured with position- and time-sensitive particle detectors. The measured and calculated branching ratios satisfyingly agree with respect to state contributions.

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1. Introduction

When positive and negative hydrogen ions collide, charge transfer may occur, resulting in formation of neutral atoms:

\[ \text{H}^- + \text{H}^+ \rightarrow \text{H}(1) + \text{H}(n), \]

where, at low collision energies, only one of the hydrogen atoms can be excited. This process is called mutual neutralization (MN), and it is driven by nonadiabatic interactions of electronic states, occurring at large internuclear distances. Several studies have pointed out that such a reaction will have a large cross section at low collision energies [1–10].

In the study of the formation of pregalactic clouds in the early universe, \( \text{H}_2 \) acts as a coolant [11]. Through associative detachment [12], the hydrogen anion, \( \text{H}^- \), has been found to play a crucial role in the formation of primordial \( \text{H}_2 \) [12–18]. The MN process (1) is a competing reaction that removes \( \text{H}^- \). Thus, for the modeling of the early universe, it is important to have reliable data with respect to the MN rate coefficient and final state distributions [15,16], which helps in determining the share of \( \text{H}^- \) that ends up forming \( \text{H}_2 \).

At the international ITER fusion experiment [19,20], neutral beam heating is based on an \( \text{H}^- \) (or \( \text{D}^- \)) ion source [21,22]. There is a need for modeling of the hydrogen anion density of the source. A new diagnostic technique has been suggested based on measuring the \( \text{H}_	ext{a}/\text{H}_	ext{b} \) Balmer line ratio [21–24]. Collisional radiative modeling shows that the measured line ratio is very sensitive to the MN rate coefficient. The MN reaction has to be studied, even for deuterium ions, since either \( \text{H}^- \) or \( \text{D}^- \) ions are produced in the ion source [20,22,25].

The first theoretical study on the MN reaction in collisions of \( \text{H}^+ \) and \( \text{H}^- \) was carried out in 1955 by Bates and Lewis [1] using a semiclassical Landau-Zener model [26,27]. Several other semiclassical studies [2,5,28–31] have followed and they all agree on a relatively large cross section that is inversely proportional to the energy and a dominance of the \( \text{H}(1)+\text{H}(3) \) channel at low collision energies. Fussen and Kubach [3] performed a quantum-mechanical study of the process using a close-coupling one-electron model. More recently, some of us [4] carried out an \( \text{ab initio} \) quantum-mechanical study, where the adiabatic potential energy curves and the nonadiabatic interactions were calculated using the full configuration interaction method. The coupled radial Schrödinger equation for the nuclear motion was then solved using the log-derivative method of Johnson [32].

The first experiment on this reaction was carried out by Moseley et al. [6] using a merged beam technique, where the total cross section was measured for relative collision energies below 3 eV. This is so far the only published measurement of the total cross section at low collision energies. At higher collision energies, however, there are other measurements of the cross section [7–10] and they more or less agree with each other and the theoretical predictions. The measured cross section by Moseley et al. is about a factor of 3 larger than many theoretical results and it has been debated whether the experimental cross section might be overestimated [7–10]. We have here performed measurements on MN for collisions of \( \text{H}^+ \) and \( \text{H}^- \) at intermediate energies (11–185 eV) using a
merged-beam technique. The total cross section has not been determined, but rather the final state distributions.

For the theoretical calculations, we are using the same ab initio quantum model for studying the process as the one by Stenrup et al. [4]. Electronic states of $\Sigma_u^+$ and $\Sigma_u^+$ symmetries, associated with the H(1)+H(n ≤ 3) asymptotic limits, are considered. The nonadiabatic couplings among the states, computed ab initio by a three-point finite difference method, are used to perform an adiabatic-to-diabatic transformation. By solving the coupled Schrödinger equation for the different partial waves, the scattering matrix elements are computed. From the matrix elements, not only the total cross section but also the differential cross section can be obtained. The total and differential cross sections as well as the final state distributions for collisions between all possible isotopes of positive and negative hydrogen ions are calculated by using the appropriate reduced mass of the system. The reaction is studied for all possible isotopes of hydrogen ions and the symmetry effects due identical nuclei and inversion symmetries are discussed.

The paper is arranged as follows. Section II discusses the formulas for the total and differential cross sections for collisions of different isotopes of hydrogen ions. In Sec. III, the merged-beam measurements are described, while in Sec. IV we present the computed differential and total cross sections as well as the comparison between measured and calculated final state distributions. A conclusion on the results can be found in Sec. V.

II. SCATTERING THEORY

Employing the full configuration interaction method with a basis set consisting of (11s,8p,7d,2f) primitive Gaussian basis functions contracted to (9s,8p,7d,2f), the potential energy curves and nonadiabatic interactions of the seven lowest states of $\Sigma_u^+$ symmetry and six lowest states of $\Sigma_u^+$ symmetry have been computed [4]. These are the states associated asymptotically with the H(1)+H(n ≤ 3) and the ion-pair, H$^+$+H$^-$, limits. Using the radial first derivative nonadiabatic coupling elements, a strict adiabatic-to-diabatic transformation is performed [33]. Instead of directly solving the coupled radial Schrödinger equation, the matrix Riccati equation is solved for the logarithmic derivative of the radial wave function [32,34,35]. From the asymptotic value of the logarithmic derivative, the partial wave scattering matrix ($S_{ij}$) is obtained for both the gerade and ungerade manifold of states. (For more details see Ref. [4].)

For scattering of nonidentical particles (where there is no electron-inversion symmetry), the scattering amplitude is calculated from the scattering matrix as [36]

$$f_{ij}(\theta,E) = \frac{1}{2i k_i k_f} \sum_{\ell} (2\ell + 1)(S_{ij,\ell} - \delta_{ij})P_{\ell}(\cos \theta). \quad (2)$$

Here $k_i$ and $k_f$ are the wave numbers of the final and initial states (channels), respectively, $\ell$ is the angular momentum quantum number, and $P_{\ell}(x)$ is the Legendre polynomial of degree $\ell$. The differential cross section is obtained from the scattering amplitude as [36]

$$d\sigma_{ij}(\theta,E) = \frac{k_i}{k_f} |f_{ij}(\theta,E)|^2. \quad (3)$$

The total cross section is obtained by a direct integration of the differential cross section over the entire unit sphere, resulting in

$$\sigma_{ij}(E) = \frac{\pi}{k_i^2} \sum_{\ell} (2\ell + 1)|S_{ij,\ell} - \delta_{ij}|^2. \quad (4)$$

In the present work, we study scattering of systems with two nuclei A and B which are isotopes. We study collisions $A^+ + B^-$ where the nuclear masses, $m_A$ and $m_B$, may not necessarily be the same. The electronic part of the problem has inversion symmetry and the electronic states are labeled gerade $(g)$ or ungerade $(u)$, respectively. We can now distinguish a number of different cases caused by the colliding ions and the particular detection system of the experiment where the reaction products are measured:

1. If the nuclear masses of the colliding ions are different ($m_A \neq m_B$), we do not have inversion symmetry but the electronic states of the collision complex can be labeled as gerade and ungerade, respectively. If we assume that we can measure the masses of the different reaction products $M_A$ and $M_B$, we have one case (a), whereas if we cannot distinguish them we have another case, (b). We thus now need to formally study all cases.

2. When ions with identical nuclei collide (A = B ⇒ $m_A = m_B$), the overall symmetry of the total wave function of the collision complex (AB) must either be (a) antisymmetric or (b) symmetric, depending on the spin of the nuclei. When deriving the formulas of the differential cross sections for the system with total inversion symmetry, we follow the ideas of Masmou-Seeuws and Salin [37].

To formulate scattering amplitudes where the electrons are localized on one of the nuclei, the direct and exchange amplitudes are evaluated as complex-valued linear combinations of the scattering amplitudes of the gerade and ungerade states [37,38],

$$f_{ij}^{di}(\theta,E) = \frac{1}{4} \left[ f_{ij}^g(\theta,E) + f_{ij}^u(\theta,E) \right],$$

$$f_{ij}^{ex}(\theta,E) = \frac{1}{4} \left[ f_{ij}^g(\theta,E) - f_{ij}^u(\theta,E) \right]. \quad (5)$$

For collisions of ions with nonidentical nuclei ($m_A \neq m_B$ such as H$^+$+D$^-$), the electronic part of the Schrödinger equation still possesses the same inversion symmetry as when $m_A = m_B$. For a system with moving nuclei of different masses, the inversion symmetry is broken due to the shift between the center of mass and the center of charge [39,40]. This causes mixing between the gerade and ungerade states; however, this is neglected here.

Case I(a). Assuming the mass of the detected atom at an angle $\theta$ is not specified, the differential cross section at this angle is obtained by incoherently adding the contributions from the direct and exchange scattering at angles $\theta$ and $\pi - \theta$, respectively [39,40]. The differential cross section becomes

$$d\sigma_{ij}(\theta,E) = \frac{1}{4} \frac{k_i}{k_f} \left[ f_{ij}^g(\theta,E) + f_{ij}^u(\theta,E) \right]^2$$

$$+ \frac{1}{4} \frac{k_i}{k_f} \left[ f_{ij}^g(\pi - \theta,E) - f_{ij}^u(\pi - \theta,E) \right]^2. \quad (6)$$
The total cross section is then expressed as

$$\sigma_{ij}(E) = \frac{\pi}{2k_i^2} \sum_{\ell} (2\ell + 1)|S_{ij,\ell}^e - \delta_{ij}|^2 + \frac{\pi}{2k_i^2} \sum_{\ell} (2\ell + 1)|S_{ij,\ell}^o - \delta_{ij}|^2.$$  

(7)

Note that for collisions of ions with nonidentical nuclei, the differential cross section exhibits the gerade-ungerade effect [39].

Case 1(b). If the mass of the reaction products at an angle $\theta$ can be measured separately such that one can detect if it was an atom with mass $M_A$ or $M_B$ that was found, the differential cross section is given by one of the two terms of Eq. (6), depending on the experimental arrangement.

Case 2(a). For collisions of ions with identical spin-$1/2$ nuclei (e.g., $H^++H^-$ or $T^++T^-$), the overall wave function has to be antisymmetric and hence the symmetric spin function has to be combined with an antisymmetric scattering amplitude and vice versa. The symmetric and antisymmetric scattering amplitudes are calculated by linear combinations of the direct and exchange scattering amplitudes [37,39,40]. By combining the symmetrized spatial amplitudes with the corresponding spin factors, the differential cross section becomes

$$\frac{d\sigma_{ij}}{d\Omega}(\theta, E) = \frac{3k_i}{4k_j} |f_{ij,\text{odd}}(\theta, E) + f_{ij,\text{even}}(\theta, E)|^2 + \frac{1}{4k_j} |f_{ij,\text{even}}(\theta, E) + f_{ij,\text{odd}}(\theta, E)|^2.$$  

(8)

Here the superscript even or odd refers to a summation over even or odd angular momentum quantum numbers when the amplitudes are computed. The total cross section is again obtained by a direct integration

$$\sigma_{ij}(E) = \frac{3\pi}{4k_j^2} \sum_{\ell, \text{odd}} (2\ell + 1)|S_{ij,\ell}^e - \delta_{ij}|^2 + \frac{3\pi}{4k_j^2} \sum_{\ell, \text{even}} (2\ell + 1)|S_{ij,\ell}^o - \delta_{ij}|^2 + \frac{\pi}{4k_j^2} \sum_{\ell, \text{even}} (2\ell + 1)|S_{ij,\ell}^e - \delta_{ij}|^2 + \frac{\pi}{4k_j^2} \sum_{\ell, \text{odd}} (2\ell + 1)|S_{ij,\ell}^o - \delta_{ij}|^2.$$  

(9)

which is the same expression as given in Ref. [4].

Case 2(b). For collisions of ions that have spin 1 (D$^+$+D$^-$), the overall wave function has to be symmetric. The differential cross section becomes

$$\frac{d\sigma_{ij}}{d\Omega}(\theta, E) = \frac{k_i}{3k_j} |f_{ij,\text{odd}}(\theta, E) + f_{ij,\text{even}}(\theta, E)|^2 + \frac{2k_i}{3k_j} |f_{ij,\text{even}}(\theta, E) + f_{ij,\text{odd}}(\theta, E)|^2.$$  

(10)

and the total cross section is given by

$$\sigma_{ij}(E) = \frac{\pi}{3k_j^2} \sum_{\ell, \text{odd}} (2\ell + 1)|S_{ij,\ell}^e - \delta_{ij}|^2 + \frac{\pi}{3k_j^2} \sum_{\ell, \text{even}} (2\ell + 1)|S_{ij,\ell}^o - \delta_{ij}|^2 + \frac{2\pi}{3k_j^2} \sum_{\ell, \text{even}} (2\ell + 1)|S_{ij,\ell}^e - \delta_{ij}|^2 + \frac{2\pi}{3k_j^2} \sum_{\ell, \text{odd}} (2\ell + 1)|S_{ij,\ell}^o - \delta_{ij}|^2.$$  

(11)

III. EXPERIMENTAL METHOD

Using the ion-ion merged beam apparatus in operation at Université catholique de Louvain, the branching ratio among the principal quantum numbers populated by MN was determined between 11 and 185 eV. The apparatus has been described previously [41], and it is an evolution of the original setup of Szücs et al. [10]. The $\sim$7-keV H$^+$ and H$^−$ beams were extracted from an electron cyclotron resonance (ECR) and a duoplasmatron source, respectively, and merged in the ultrahigh-vacuum region of the apparatus. A 4.67-m-long drift tube and a pair of position- and time-sensitive particle detectors allow us to measure the time-of-flight (TOF) difference between hydrogen atoms resulting from MN reactions [42]. The long flight path compared to the short interaction length (7.5 cm) ensures that the small difference in exoergicity between hydrogen atoms resulting from MN reactions [42]. The long flight path compared to the short interaction length (7.5 cm) ensures that the small difference in exoergicity between hydrogen atoms resulting from MN reactions [42].

In order to measure the TOF difference between neutral atoms in coincidence mode, we operated with inclined beams intersecting under a shallow angle of $\sim$6 mrad. Each beam was pointed in such a way that all pairs of scattered atomic

![FIG. 1. Time-of-flight difference spectrum recorded at a collision energy of 58 eV (beam energies 6.1 and 7.9 keV, for H$^+$ and H$^-$, respectively) at the end of a 4.67-m-long drift tube. Numbers 1–4 on top indicate the expected time of flight for a reaction taking place in the center of the interaction region and producing H(1)+H(n) pairs.](https://example.com/fig1.png)
The angular scattering in the center-of-mass frame. Furthermore, from both the inclined beam geometry and the residual leading edge of the H\(^+\) peak, whose asymmetry results from both the inclined beam geometry and the residual angular scattering in the center-of-mass frame. Furthermore, no contribution of the ground-state products is observed, which would fall at the right-hand side of the spectrum depicted in Fig. 1. This finding is discussed below in Sec. IV C.

IV. RESULTS AND DISCUSSION

A. Computed differential cross sections

The scattering amplitudes are computed and total and differential cross sections are obtained by summing up over the angular momenta, \(\ell\), as described in the previous section. A similar convergence criterion as in Ref. [4] is introduced to terminate the summation. The calculation of the differential cross section is carried out at a number of fixed scattering energies, and the scattering angle is varied between 0° and 180°. The total differential cross section of mutual neutralization in collisions of H\(^+\) and H\(^-\) is presented in Fig. 2, for some selected energies. Here the contributions from all covalent states are added.

The differential cross section exhibits fast irregular oscillations as a function of the scattering angle reflecting contributions of high angular momenta. For all collision energies, the backward scattering dominates and there are even faster oscillations in the differential cross sections at large scattering angles. The arrows in Fig. 2 indicate the positions where the differential cross sections change their oscillatory behaviors. When the collision energy increases, the angle where the fast oscillations start becomes larger and the oscillations in the cross section become longer, with decreasing amplitudes, indicating a more classical motion of the particles. Additionally, as the energy increases, the cross section decreases, predominantly at \(\theta = 90°\), indicating that the forward and backward scattering become more pronounced, still with a dominance of the backward scattering.

The differential cross sections are computed for mutual neutralization in collisions of all possible isotopes of the hydrogen cations and anions. The results at a collision energy of 0.1 eV are shown in Fig. 3 and it is clear that the differential cross sections are very similar for all combinations of isotopes. For collisions of ions with nonidentical nuclei the figure shows the differential cross section where the mass of the detected atom is not distinguished [using Eq. (6)]. This corresponds to case 1(a), described in Sec. II. The overall magnitudes and shapes of the differential cross sections are very similar, although the exact form of the oscillations varies. The isotope effects are very small and for all cases the backward scattering dominates and the differential cross section shows fast oscillations at large scattering angles. This does not seem to be the case for mutual neutralization of heteronuclear ions, where the molecular system has no inversion symmetry. For example, quantum-mechanical ab initio studies of mutual neutralization in collisions of Li\(^+\) and H\(^-\) [43] as well as Li\(^+\) and F\(^-\) [44] produce differential cross sections peaked at the forward direction. At small scattering angles, there are fast oscillations, and at large angles, the oscillations are slow. Using a semiclassical analysis of interfering branches of the deflection function, Delvigne and Los [45] have discussed that the angle where there is a transition between fast and slow oscillations can be understood as the Coulomb scattering angle, where the transition takes place at the distance of the closest approach. When the collision energy increases, this angle decreases.
The present system has inversion symmetry and it is clear from Fig. 3 that the backward scattering dominates for collisions of all isotopes with the fast oscillations at large angles. The differential cross sections are computed using Eqs. (6), (8), or (10), depending on the spin of the nuclei. Since isotope effects are negligible, here we only present an analysis of the results for collisions of nonidentical nuclei, where Eq. (6) is applied. In Fig. 4, the contributions to the differential cross section from the direct and exchange scattering amplitudes are displayed for the D$^+$ and H$^-$ system at 0.1 eV collision energy. It is clear that exchange scattering dominates at large angles. At $\theta \approx 60^\circ$, the direct and exchange terms switch their dominance, with the direct term having a small dominance at smaller angles. Note that these cross sections correspond to case 1(b); i.e., the masses of the products $M_2$ and $M_8$ are possible to distinguish in an experimental measurement.

The direct and exchange amplitudes, given by Eq. (5), are obtained as the sum (direct) and the difference (exchange) of the complex-valued gerade and ungerade scattering amplitudes, $f_{fg}^j(\theta, E) \pm f_{fu}^j(\theta, E)$. We thus need to consider both the magnitudes and the phases of these terms when computing the likewise complex-valued direct and exchange scattering amplitudes. This construction is illustrated in Fig. 5, where the matrix elements for scattering to the lowest covalent state converging to the $n = 3$ limit are considered at a collision energy of 0.1 eV. For both $f_{fg}^j$ and $f_{fu}^j$, the largest magnitudes are obtained at small scattering angles. For $\theta = 0^\circ$ [see Fig. 5(a)], the $f_{fg}^j$ and $f_{fu}^j$ are of similar magnitudes, but almost out of phase. The magnitude of the direct term, $f_{fg}^j(\theta, E) + f_{fu}^j(\theta, E)$, is thus relatively small and has approximately the same phase as $f_{fg}^j$. The exchange term, $f_{fg}^j(\theta, E) - f_{fu}^j(\theta, E)$, will be considerably larger than the direct scattering term and this will give rise to the large differential cross section observed in the backward direction. For $\theta = 180^\circ$, the gerade and ungerade scattering amplitudes have different magnitudes, where $|f_{fg}^j|$ is larger than $|f_{fu}^j|$. The gerade amplitude is located in the third quadrant of the complex plane while the much smaller ungerade amplitude is found in the fourth quadrant. Figure 5(b) illustrates the consequence: the direct and exchange amplitudes have about the same magnitudes and are both found in the third quadrant of the complex plane. This kind of analysis, when carried out for all angles and all isotope combinations, explains how the differential cross section varies with the relative collision angle as shown in Fig. 4. The large differential cross section in the backward direction can hence be understood as an interference effect due to the out-of-phase gerade and ungerade scattering amplitudes at small angles. Since inversion symmetry is not present in heteronuclear systems [43,44], the dominance of the backward scattering in the differential cross section is not likely to be found there.

B. Isotope dependence of the computed total cross section

By integrating the differential cross section, we obtain the same total cross section for MN in H$^+$+H$^-$ collisions as Stenrup et al. [4] computed directly using the scattering matrix elements [using Eq. (9)]. The total MN cross sections are computed for collisions of all hydrogen isotopes, and the
results are presented in Fig. 6. We compare the calculated total cross section with two experimental measurements. One measurement is by Peart and Hayton [7], using a merged beam apparatus, for collisions of H\(^+\) and H\(^-\). The measured data cover the energy range 3–500 eV. At lower energies, the measured cross section is smaller than the cross section for H\(^+\) + H\(^-\) MN here computed, while at higher energies they are comparable. The other measurement is by Moseley et al. [6], who used a merged beam technique to measure the H\(^+\) + H\(^-\) MN total cross section for collision energies larger than 0.1 eV. This cross section is about a factor of 3 larger than our calculated cross section and, as pointed out previously [7–10], for the whole energy range it is larger than other results.

For collision energies approaching zero, the cross sections for all isotopes are exhibiting the E\(^-1\) characteristics of a Coulomb attraction [46]. The isotope dependence of the total cross section is not very large. At low energies the collision complex with larger reduced mass produces a slightly larger cross section. At 0.001 eV, the ratio of the total cross section for the heavier isotopes to that of H\(_2\) is HD, 1.10; HT, 1.15; D\(_2\), 1.30; DT, 1.38; and T\(_2\), 1.47. Between 10 and 100 eV, the cross sections have a minimum and then they start to increase again. The inset of Fig. 6 shows the high-energy region where the n = 2 channel starts to become important. The oscillations in the cross sections are possibly quantum interference effects (Stueckelberg oscillations [47]). The position of the minimum is shifted toward larger energies with increasing reduced mass of the molecular system. A very similar isotope dependence for the present mutual neutralization reaction is obtained by carrying out a semiclassical Landau-Zener [26,27] calculation.

In Fig. 7 the total mutual neutralization cross section is calculated using the multistate Landau-Zener model [5]. The electronic couplings between the ionic and covalent states are here obtained using the formula obtained by Janev [48] assuming a one-electron asymptotic method [49]. This model only considers the avoided crossings between the ionic and covalent n = 2 and n = 3 states occurring at large internuclear distances.

By comparing Figs. 6 and 7, it is clear that the relatively simple Landau-Zener model supports the isotope effects observed in the fully quantum study. At low collision energies, the system with heaviest reduced mass has the largest cross section, while it is the opposite as the energy becomes large. This isotope dependence was not observed by Croft et al. [43], where their ab initio quantum treatment of mutual neutralization in collisions of Li\(^+\) with H\(^-\) or D\(^-\) produced a larger cross section at low energies for the lighter isotope. As the energy increases, the isotope dependence became negligible.

C. Calculated and measured final state distributions

From the scattering calculations, we also obtain information about the final state distributions in the mutual neutralization process. The present model includes all covalent 1\(^2\Sigma^+\) and 3\(^2\Sigma^+\) molecular states associated with the H(1)H(n \(\leq\) 3) limits. For all energies, the contribution to the H(1)+H(1) channel is very small, with a ratio to the total cross section of the order of 10\(^{-6}\). Figure 8 presents the n = 2 and n = 3 branching ratios for mutual neutralization in collisions of different isotopes of hydrogen ions. At low collision energies the n = 3 channel dominates and the mutual neutralization reaction is completely driven by the avoided crossing between the ionic and covalent states at an internuclear distance of about 35\(\text{a}_0\). At larger energies, the avoided crossing at smaller distances can be reached and the n = 2 channel starts to become important. The minimum in the total neutralization cross section can be understood from the change of dominance from the n = 3 to the n = 2 dissociation channels. As can be seen, the switch over occurs at lower energies for the lighter isotopologs.

In Fig. 8, the measured branching ratios for H\(^+\) + H\(^-\) MN using the merged beam technique, described in Sec. III, are displayed. The measured final state distributions show a similar trend as the ones calculated, with a dominance of the n = 3 channel at low collision energies and the increasing significance of the n = 2 channel as the energy increases, and a complete absence of n = 1 contribution. At E > 50 eV the
measured $n = 2$ ratio is slightly larger than what is predicted by the theoretical calculation. At higher energies, effects not considered in the present theoretical model (such as higher electronic states, rotational couplings, or autoionization) could start to be important.

V. CONCLUSION

Mutual neutralization in low-energy $H^+$ and $H^-$ collisions was studied both theoretically using a fully quantum \textit{ab initio} model as well as experimentally using a merged beam setup. The theoretical model includes $\Sigma_{1/2}^-$ states associated with $H(1)+H(n \leq 3)$ channels and the reaction is studied for collisions of all possible hydrogen isotopes. The computed differential cross section exhibits fast and irregular oscillations as a function of the scattering angle. For all isotopes, there is a clear dominance of backward scattering which can be explained by the fact that the collisions cause large scattering amplitudes at small angles for the gerade and ungerade manifold of states, which are out of phase with each other.

The isotope effects are studied in terms of the differential and total neutralization cross sections as well as the final state distributions. The observed dependencies of the total cross sections upon the molecular reduced mass are compared with semiclassical calculations using a multistate Landau-Zener model. The total cross section is compared with two experimental results and at higher energies, it agrees well with the cross section by Peart and Hayton [7] while it is about a factor of 3 lower than the cross section by Moseley \textit{et al.} [6]. The measured final state distributions obtained with a merged beam apparatus show a similar form as the ones computed theoretically.

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Theoretical study of the mechanism of $\text{H}_2\text{O}^+$ dissociative recombination

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By combining electronic structure and scattering calculations, quasidiabatic potential energy surfaces of both bound Rydberg and electronic resonant states of the water molecule are calculated at the multireference configuration-interaction level. The scattering matrix calculated at low collision energy is used to obtain explicitly all couplings elements responsible for the electronic capture to bound Rydberg states. These are used to estimate the cross section arising from the indirect mechanism of dissociative recombination. Additionally, the role of the direct capture and dissociation through the resonant states is explored using wave-packet propagation along one-dimensional slices of the multidimensional potential energy surfaces.

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I. INTRODUCTION

There have been a number of experimental studies of the dissociative recombination (DR) of the water ion. However, there are significantly fewer theoretical studies of this reaction. There are several unanswered questions about the mechanism and the dynamics of the DR process in this system. Here we take a first step toward a theoretical study of the reaction, attempting to obtain a better understanding of the process.

The first measurement of the total cross section was carried out in 1983 by Mul et al. [1]. The absolute cross sections of DR have been measured for both the $\text{H}_2\text{O}^+$ [1–3] and $\text{HDO}^+$ ions [2]. At low energies (<2 eV), the cross section decreases significantly faster than the $E^{-1}$ behavior expected for the direct mechanism of DR [2]. Around 0.3–0.4 eV the cross section drops by a factor of 3, indicating the opening of a new autoionization channel. At higher collision energies, around 5 and 15 eV, there are pronounced peaks in the DR cross section that might reveal capture into higher-lying resonant states. The ratio of the $\text{HDO}^+/\text{H}_2\text{O}^+$ cross sections is about 0.6 and they display very similar energy dependences [2].

At zero collision energy, there are several dissociation channels open and the energetics of the DR process are shown below:

$$\text{H}_2\text{O}^+ + e^- \rightarrow \begin{cases} \text{O}(^3\text{P}) + \text{H}_2 & 7.6\text{ eV} \\ \text{OH} + \text{H}(^3\Sigma) & 7.5\text{ eV} \\ \text{O}(^3\Sigma) + \text{H}^2(5\Sigma) & 3.04\text{ eV} \\ \text{O}(^3\Pi) + \text{H}^2(5\Sigma) & 1.07\text{ eV} \\ \text{O}(^3\Pi) + \text{H}^2(5\Sigma) + \text{H} & \end{cases}$$

Here the energies are given for OH and H$_2$ in their electronic and vibrational ground states and with negligible rotational energy.

There are numerous measurements of the branching ratios. For DR of the water ion in the ground vibrational state, the three-body breakup dominates with measured ratios ranging from $0.57 \pm 0.07$ [2] to $0.73 \pm 0.06$ [3]. The propensity for three-body fragmentation is found in most experimental studies of DR on small molecular ions such as $\text{H}_2^+$ [4], $\text{NH}_2^+$ [5], and $\text{CH}_2^+$ [6]. No theoretical understanding of this observation is presently available. Interestingly, branching ratio measurements on the HDO$^+$ ion show that the OD-H channel is twice as probable as dissociation into OH+D [2].

Note that there are two three-body channels energetically open at zero collision energy, $\text{O}(^3\text{P})+\text{H}+\text{H}$ and $\text{O}(^3\text{D})+\text{H}+\text{H}$. Using an imaging technique, the $\text{O}(^3\text{P})/\text{O}(^3\text{D})$ ratios have been measured at the CRYRING ion storage ring and found to be $3.5 \pm 0.5$ [7,8]. The recoil kinetic energy of the hydrogen atoms have been detected and different H-O-H angular distributions are observed depending on the excited state of the oxygen atom [7]. For breakup into the ground-state fragments, it is found that the angle either significantly increases or decreases during the dissociation dynamics [8].

In order to study the DR reaction theoretically, the potential energy surfaces of bound and resonant electronic states of $\text{H}_2\text{O}^+$ must be computed. In this work, electron scattering calculations using the complex Kohn variational method [9] are combined with structure calculations using the multireference configuration-interaction method (see Sec. II A). From the electron scattering calculations, the autoionization widths of resonant states are computed. The resonant states are quasidiabatized as described below. As a first step toward understanding the mechanism of $\text{H}_2\text{O}^+$ DR, simplified models are applied to describe the direct and indirect processes. The direct capture and dissociation along the resonant states are modeled using one-dimensional wave-packet propagations, where either one or both bonds break while the H-O-H angle is frozen (see Sec. III A). No couplings between the electronic states are included and therefore we are not able to model the complicated dissociation dynamics and isotope dependence observed in the experiments. As outlined in Sec. III B, we perform electron-ion scattering calculations just above the ionization threshold and obtain all couplings elements directly from the scattering matrix calculated with the variational complex Kohn method. These are then used to compute the cross section for indirect DR.

Unless otherwise stated, atomic units are used throughout.

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II. COMPUTATIONAL DETAILS

A. Electronic-structure calculations

The $^1A_1$ ground state of H$_2$O has the dominant configuration $(1a_1)^2(2a_2)^2(1b_1)^2(3a_1)^2(1b_2)^2$ in $C_2v$ symmetry. The electron in the highest occupied molecular orbital is bound with 12.6 eV, which if removed leads to the formation of H$_2$O$^+$ in its $^2B_1$ ground state. There are two other low-lying ionic states corresponding to the removal of an electron in the $(3a_1)$ orbital leading to the $^2A_1$ and the $^2B_2$ formed by the removal of the $(1b_2)$ electron. The resonances seen in electron scattering from H$_2$O$^+$ are Rydberg states converging to these excited ionic states. They are crossed at large internuclear separations by states converging to even higher ionic excited states.

In this work, two sets of electronic structure calculations have been performed. The first of them was carried out to obtain Rydberg and resonant states involved in the direct DR process, therefore we were particularly interested in achieving a good description of the curve crossing between resonances and the ionic-core potential. The focus for the second set was on the indirect DR process and the calculations were optimized to describe as well as possible the ionic ground state and its Rydberg series at molecular geometries close to the equilibrium.

For the direct DR model, the potential energy surfaces of the ion as well as excited states of the neutral molecule are calculated using the multireference configuration-interaction (MRCI) method. This will provide us with the potential energy surfaces of the electronically bound states that are situated below the ground state of the ion. We also use the structure calculations to interpolate the potentials of the resonant states between resonances and the ionic-core potential. The focus for the second set was on the indirect DR process and the calculations were optimized to describe as well as possible the ionic ground state and its Rydberg series at molecular geometries close to the equilibrium.

In order to describe both the Rydberg series converging to the various excited ionic states, which are the electronic resonances, and the bound Rydberg states, we first carried out a self-consistent-field (SCF) calculation on the neutral with a basis set consisting of $(4s,1p)$ primitive functions contracted to $[3s,1p]$ for the hydrogen and $(9s,7p,1d)$ contracted to $[4s,4p,1d]$ for the oxygen atom. In the next step, these SCF orbitals were used in a MRCI calculation on the three lowest states of the ion, where the lowest orbital $(1a_1)$ in $C_2v$, or $(1a')$ in $C_s$, is frozen and the next four orbitals formed the active space. A full CI was done in the active space and single and double excitations from averaging the orbitals, over the lowest three ionic states. The reference configurations were generated by keeping the $(1a')$ core orbital occupied and by allowing all possible excitations among the following eight orbitals. The last difference in the bound-state calculations is the choice of expansion basis. The Rydberg energies were obtained by further expanding the natural orbitals by adding at the center of charge the diffuse universal Rydberg Gaussian basis set (8s,7p,6d) [11] to the initial Gaussian basis. Then the potential energy surfaces of the ion and the neutral system were generated using a MRCI calculation with an active space of eight orbitals (again keeping the core orbital frozen) and by allowing for single external excitations. By using this approach, we were able to obtain Rydberg states up to $n = 5$ and therefore guarantee the convergence of the quantum defects with respect to the principal quantum number.

B. Scattering calculations

The energy positions and autoionization widths of the electronic resonant states were determined using the complex Kohn variational method [9]. The trial wave function for the neutral $[\{N + 1\}-$electron] system is written as

$$\Psi_{rs} = \sum_{\Gamma} A[\Phi_T F_{rr_\Gamma}] + \sum_{\mu} d^0_\mu \Theta_\mu. \quad (2)$$

The first sum is defined as the $P$-space portion of the wave function and runs over the energetically open target states. Here the symbol index $\Gamma$ labels all quantum numbers representing a physical scattering state, i.e., internal state of the target and angular momentum quantum numbers of the scattered electron; $\Phi_T(r_1, \ldots, r_N)$ represents the target wave function for the ion; the function $F_{rr_\Gamma}(r_{N+1})$ is the one-electron wave function describing the scattered electron; and $A$ is an antisymmetrization operator for the electronic coordinates. As the target wave function we used the MRCI wave functions constructed with the direct and indirect DR picture in mind, respectively. The second term, defined as the $Q$-space portion of the wave function, contains the functions $\Theta_\mu(r_1, \ldots, r_{N+1})$, which are square-integrable $N + 1$ configuration state functions that are used to describe short-range correlations and the effects of closed channels. We used the same natural orbitals as those applied in the structure calculations as described in the previous section. The advantage of using natural orbitals is that the orbital space used to generate these states is kept manageable small. The one-electron scattering wave function $F_{rr_\Gamma}$ is in the case of electron-ion scattering further expanded.
as

$$F_{\text{Ry}}(r) = \sum_{j} c_{j}^{R} \phi_{j} + \sum_{l m} \left[ f_{jl}^{\Gamma} \delta_{l m} \delta_{\text{Ry}} + T_{\text{Ry}}^{\Gamma} g_{l m}^{j} \right] \times Y_{lm}(r)/r,$$

(3)

where $\phi_{j}(r)$ is a set of square-integrable functions and $f_{jl}^{\Gamma}(k_{F} r)$ and $g_{l m}^{j}(k_{F} r)$ are the incoming and outgoing Coulomb functions for a scattered electron with channel momenta $k_{F}$. In the calculation spherical harmonics $Y_{lm}$ with angular momenta $l \leq 6$ and $|m| \leq 4$ were included.

By inserting the trial wave function into the complex Kohn functional [9], the unknown coefficients in the trial wave function can be optimized. Also the $T$ matrix elements $T_{\text{Ry}}^{\Gamma}$, for elastic scattering is obtained and by fitting the eigenphase sum of the $T$ matrix to a Breit-Wigner form [12], the energy positions and autoionization widths of the resonant states were determined. These electron scattering calculations are carried out for a fixed geometry of the target ion.

Slightly bigger calculations were made to treat the indirect DR process. In order to be able to perform the scattering calculations, a different expansion basis was used to expand the molecular orbitals. The initial Gaussian basis set was augmented with a small set of diffuse orbitals (2$s, 3p, 2d$). As previously discussed [13], due to the relative large dipole moment of $H_{2}O^{+}$, the electron scattering calculations used for modeling the indirect mechanism were carried out with the center of charge of the molecular ion as the origin of the chosen reference frame. Thus, incoming and outgoing Coulomb functions and corresponding spherical harmonics were defined with respect to the center of charge instead of the usual center of mass. Since the effect of rotation of the molecular ion is not included, the cross section for vibrational capture is independent of the choice of the origin.

C. Quasiadiabatization

The water molecular ion has the equilibrium bond lengths $R_{OE} = 1.9086 a_{0}$ and a bond angle of $\theta = 108.5^\circ$. As mentioned above, the ionic ground state is dominated by the configuration $(1a_{1})^{2}(2a_{2})^{2}(1b_{1})^{2}(3a_{1})^{2}(1b_{2})$. In $C_{3v}$ this becomes $(1a_{1})^{2}(2a_{2})^{2}(3a_{1})^{2}(4a_{1})^{2}(1a_{1})^{2}$. When structure calculations are carried out, three types of states are obtained. These are the Rydberg states converging to the ground ionic cores, the states trying to describe the ionization continuum, and the resonant states. Both the Rydberg states and the states describing the ionization continuum have the same configuration as the ground state of the ion plus an outer electron in a diffuse orbital. The resonant states are more or less compact Rydberg states converging to excited ionic cores. These resonant states all have a vacancy in either the $(1b_{2})$ or $(3a_{1})$ or $(3a_{1})$ or $(4a_{1})$ in $C_{3v}$ orbitals. By identifying the states with this character, the resonant states can be diabatized relative to the Rydberg states and the ionization continuum. This is done in order to follow the resonant states when they cross the ionic ground state and interact with the Rydberg manifold situated below the ionic potential. This approach is also employed to obtain more data for the potential energy surfaces of the resonant states above the ion and interpolate and extrapolate between the energies of the resonant states calculated using the electron scattering formalism. It should be noted that this approach will provide us with the energy of the resonant state within the energy spread given by the autoionization width. The $H_{2}O$ system has resonant states that are very narrow and hence the use of structure data to obtain resonant states is relatively accurate.

We have only diabatized the resonant states relative to the Rydberg states by using the CI coefficients. We have not calculated any electronic couplings between the neutral states. In addition, we have not diabatized the resonant states among each other. As will be shown below, there are clear indications of avoided crossings among the resonant states.

III. THEORY

A. Direct process

In our theoretical model of the direct process, the water ion captures an electron and a doubly excited resonant state is formed. Here the dynamics were studied separately for the symmetric and asymmetric motions. In the symmetric mode both OH bond distances vary $R_{1} = R_{2}$, while the H-O-H angle $\theta = 108.5^\circ$ is frozen. When considering the asymmetric motion, $R_{1} = 1.9086 a_{0}$ and $\theta = 108.5^\circ$ are frozen, while $R_{2}$ varies. Using a time-dependent formalism, this can be described with the initial condition for a wave-packet propagation [14]

$$\Psi_{i}(R, t = 0) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{n_{i}}(R).$$

(4)

Here $R$ is a collective notation of the internuclear coordinates, $\Gamma_{i}$ is the autoionization width of resonant state $i$ obtained from the electron scattering calculations described above, and $\chi_{n_{i}}$ is the initial vibrational wave function of the water ion.

The dynamics then proceed quasiadiabatically along the resonant state

$$i \partial_{t} \Psi_{i}(R, t) = \left[ T + V_{i}(R) - i/2 \Gamma_{i}(R) \right] \Psi_{i}(R, t).$$

(5)

One-dimensional wave packets were propagated numerically using the Crank-Nicholson propagation algorithm [15]. Autoionization was here included within the boomerang model [16,17] as a local complex potential.

The wave packets were propagated in time and to prevent reflection toward the end of the grid, a complex absorbing potential was applied at large distances. The contributions to the direct DR cross section from resonant state $i$ was computed with

$$\sigma_{i}(E) = \frac{2\pi}{E} g_{i} \left| T_{i}(E) \right|^{2},$$

(6)

where $g_{i}$s the ratio of the multiplicity for the final and initial states and $E$ is the electron scattering energy. The transition matrix was obtained [18] using the half Fourier transform of the wave packet at an asymptotic internuclear distance $R_{c}$.

$$T_{i}(E) = \sqrt{\frac{2\pi}{1\mu}} \int_{0}^{\infty} \Psi_{i}(R_{c}, t) e^{iE \cdot t dt},$$

(7)

Here $K$ is the wave number associated with the dissociating fragments and $\mu$ is the reduced mass.

No couplings between the neutral states were included in the wave-packet propagation. At low collision energies, some of the resonant states are quasiadiabatically not open.
for dissociation. This explains some of the sharp thresholds observed in the calculated direct DR cross section (see Sec. IV C). Including electronic couplings between resonant states and also in the Rydberg manifold will allow for a redistribution of flux and open pathways for dissociation at energies below the threshold energy of the resonant state.

B. Indirect process

The approach employed in this work is similar to the one used to calculate the DR cross sections of highly symmetric ions [19,20] as well as of linear polyatomic ions in our recent works [13,21]. Thus, only a brief overview of the theory will be presented.

The starting point is the \textit{ab initio} calculation of the electronic ground state and its series of Rydberg state energies, as described in Sec. II A. As previously suggested in Refs. [22,23], the description of the vibrational dynamics in the simplified model of the indirect process developed by Jungen and Pratt [19,24] considered the electronic capture as the decisive step in the DR mechanism by neglecting autoionization, i.e., assuming that after the neutral molecule is formed all the flux is transferred into the dissociation channels. Hence, the calculated cross section for the indirect DR mechanism provides an upper bound limit because it does not reflect the competition between the dissociation and autoionization channels. Rotation of the molecular target was also neglected, therefore the model only accounts for the electronic and vibrational degrees of freedom. In addition, the cross section was averaged over the energy interval between consecutive resonances leading to a constant probability of electronic capture. Therefore, the cross section will be structureless without the usual rovibrational resonance features. The last simplification was the treatment of the nuclear motion as harmonic, which allows an analytical description of the vibrational states and results in an analytical expression for the final cross section [24].

The cross section can be obtained directly via the low-energy scattering matrix calculated through the variational complex Kohn method. In this approach, the scattering matrix is expressed in the spherical harmonic channel basis as \( S_{\ell_0}^{\ell_1} \), where \( Y_{\ell_0} (\theta, \phi) = \langle \ell_0 | \phi | \ell_1 \rangle \) are centered at a fixed origin in the molecular frame; \( \theta, \phi \) are polar angles. The indirect DR cross section is given by

\[
\begin{align*}
\langle \sigma \rangle = \frac{\pi}{2E} \sum_{\ell_0, \ell_1, \ell_2, \ell_3} S_{\ell_0}^{\ell_1} S_{\ell_2}^{\ell_3} | \langle \ell_0, \ell_1 | \ell_2, \ell_3 \rangle |^2 \delta (E_{\ell_0} - E).
\end{align*}
\]

In the above expression, the angular brackets on the left hand side indicate that the cross section is averaged over Rydberg resonances. Since at low energies only the first few vibrational states are important, we can approximate the vibrational wave functions \( \chi_n \) by harmonic oscillators in each of the three normal modes. Therefore, each individual \( S \)-matrix element was fitted to a quadratic form simplifying the matrix elements in Eq. (8). We took into consideration only the contribution of transitions from the ground vibrational state to the first and second vibrational states. The cross section is obtained by summing over the electronic symmetry of the scattering wave function \( \alpha \), the different vibrational transitions for the three modes \( \nu_n \), and all the elements of the scattering matrix. Here \( g_\alpha \) is the multiplicity ratio for the given electronic symmetry. The Heaviside step function guarantees that the contribution to the cross section becomes zero when the electronic energy is greater than the corresponding vibrational threshold \( E_{\nu_n} \).

IV. RESULTS

A. Resonant states for direct DR

We show slices of the calculated potential energy surfaces for two cases, the asymmetric and the symmetric modes. When considering the asymmetric motion, \( R_1 = 1.9086 \text{ \textit{a_0}} \) and \( \theta = 108.8^\circ \) are frozen, while \( R_2 \) varies. In the symmetric mode both OH bond distances vary \( R_1 = R_2 \), while the H-O-H angle \( \theta = 108.8^\circ \) is frozen.

By carrying out electron scattering calculations and combining these with the structure calculations, we can extract potential energy surfaces of the resonant states of H$_2$O. We calculated five resonant states in each of singlet and triplet \( ^1A' \) symmetries and two of each singlet and triplet \( ^1A'' \) symmetries. These are the resonant states with energies below the first excited state of the ion. As described above, the resonant states were diabatized relative to the Rydberg states converging to the ground ionic core. However, the resonant states were not diabatized relative to each other. In Fig. 1 we display the H$_2$O resonant states for the asymmetric mode. The energies of the resonant states calculated with the electron scattering calculation are displayed with solid (red) circles. As can be seen, these energies agree very well with energies obtained with structure calculations (shown with red solid curves). Especially at larger distances (roughly \( R > 3.0 \text{ \textit{a_0}} \)) one notes that resonances that are Rydberg states converging to excited ionic cores interact with lower resonant states leading to multiple avoided crossings.

In Fig. 2 the states are displayed for the symmetric mode. Here the potential energy surfaces of the lowest two electronic states of the ion are displayed (black thick solid lines) together with the resonant states in \( ^2C_\beta \) (solid colored lines) and \( ^2C_\gamma \) (dotted colored lines). We note that in \( ^2C_\beta \) symmetry potentials of resonant states belonging to different irreducible representations cross each other, while the corresponding potentials in \( ^2C_\gamma \) symmetry are not allowed to cross. (Note that in this figure, the potential energies of the electronic bound states are not shown.)

As a function of the angle, the potential energy surfaces of the resonant states show clear indications of conical intersections. Similar conical intersections are found among the potential energy surfaces of excited ionic states [25]. Since the resonant states are Rydberg states that converge to the excited ionic cores, the same behavior of the potentials is found for the resonant states. In Fig. 3 the resonant states of \( ^1A' \) symmetry are plotted as a function of the bending angle, when the bond lengths are frozen at the equilibrium distance. The energies of the resonant states decrease with increasing angle.

The electron scattering calculations provide us with not only the energy positions of the resonant states, but also the autoionization widths. The autoionization widths of the resonant states of H$_2$O are relatively small. As an example, in
Fig. 1. (Color online) Potentials of H$_2$O of (a) $1^A'$, (b) $1^A''$, (c) $1^A''$, and (d) $1^A''$ symmetries are displayed as functions of one OH coordinate, while the other OH distance $R_1 = 1.9086a_0$ and the angle $\theta = 108.5^\circ$ are frozen. The potential energy surfaces of the resonant states are shown with solid lines (red online), while the potential of the lowest two electronic states of the ion are displayed with thick solid black lines; the dash-dotted (blue) lines show the potentials of electronic bound states of H$_2$O.

Fig. 4 the autoionization widths of the resonant states of $1^A'$ symmetry are displayed for the case of asymmetric stretch. It can be noted that the magnitudes of the widths change as the resonant states change character at avoided crossings or conical intersections.

B. Quantum defects and eigenphases: Indirect DR

We have used two main criteria to check the accuracy of our bound-state calculations: the value of the permanent dipole moment and the value of the vibrational frequencies, which are presented in Table I and compared with different values available in the literature. We have also performed a separate coupled-electron-pair approximation (CEPA) calculation using the MOLPRO suite of codes [26] to have another basis for comparison. As can be seen in the table, our MRCI results, which are further used in both Rydberg bound states and continuum scattering calculations, agree well with other studies as well as with our CEPA calculations. Thus, it confirms that a good description of the core ion is achieved, indicating that the interaction potential and exchange with the Rydberg or continuum electron should be correctly represented.

As Sec. II B, we have chosen the center of charge as the origin of the reference frame in the electron scattering calculations. Our choice of origin leads to better convergence of the calculations and a simplification in the analysis of the results as it prevented the asymptotic coupling of partial waves through the long-range anisotropic dipole potential. Once the coupling due to the strong dipole potential is removed, what remain are the nonadiabatic couplings induced by geometry distortions and by the small dipole originating from the changes in geometry. We have extracted the quantum defects from the eigenphases of the scattering matrix given by the complex Kohn method using Seaton's theorem ($S = e^{i\varphi}$) [32]. The eigenphases are extracted at an energy just above the ionization threshold, approximately at 30 meV.

In the left panel of Fig. 5, we show the variation of the quantum defects of the singlet electronic states as functions of the asymmetric stretch normal mode coordinate. The eigenchannel quantum defects vary smoothly with changes in the nuclear mode coordinates. An angular momentum quantum number was assigned to each curve based on the dominant partial wave information extracted from the scattering matrix. Note that as a function of the asymmetric stretch coordinate, the $l = 0$ and 1 quantum defects in $1^A''$ symmetry are not parallel. This is due to the coupling between these states.

The geometry dependence of the quantum defects were obtained using the Rydberg formula

$$V_{n,a}(Q) = V^+(Q) = \frac{1}{2(n - \mu_a(Q))}.$$

(9)
FIG. 2. (Color online) Potential energy surfaces of the $\text{H}_2\text{O}$ resonant states of (a) $1^A'$, (b) $3^A'$, (c) $1^A''$, and (d) $3^A''$ symmetries are plotted as functions of the OH coordinate where both OH bond distances vary $R_1 = R_2$, while the H-O-H angle $\theta = 108.8^\circ$ is frozen. The solid lines show potential energy surfaces of resonant states in $C_{2v}$ symmetry, while the dotted lines are the potentials of the corresponding states in $C_s$ symmetry. The potentials of the lowest two ionic states are displayed with the black thick solid lines.

where $V^+(Q)$ is the ion energy and $V_{n,\alpha}(Q)$ represents the energy of the Rydberg state $|\alpha\rangle$ with corresponding principal quantum number $n$. In the right panel of Fig. 5 we show a comparison between these geometry-dependent quantum defects from the bound-state calculations and the eigenphase divided by $\pi$ from the scattering data. As discussed in Sec. III B, the variation of the quantum defect with the normal mode coordinate determines the indirect DR cross section. The

FIG. 3. (Color online) Potential energy surfaces of the resonant states of $\text{H}_2\text{O}$ of $1^A'$ symmetry as functions of the bending angle and for fixed radial coordinates ($R_{\text{OH}} = 1.986a_0$). Also, the potentials of the three lowest ionic states are shown with thick solid lines. Dotted (blue) lines show potential energy surfaces of electronically bound states.

FIG. 4. (Color online) Autoionization widths for the $1^A'$ resonant states of $\text{H}_2\text{O}$ plotted as functions of one OH coordinate, while the other OH distance $R_1 = 1.9086a_0$ and the angle $\theta = 108.8^\circ$ are frozen.
TABLE I. Vibrational frequencies of the symmetric stretch, bending, and asymmetric stretch normal modes and permanent dipole moments of H$_2$O$^+$ obtained in this study. For comparison, other theoretical and experimental results are also shown. Frequencies are given in cm$^{-1}$ and permanent dipole moments $\mu_e$ in debye.

<table>
<thead>
<tr>
<th>Symmetric Stretch</th>
<th>Bending</th>
<th>Asymmetric Stretch</th>
<th>$\mu_e$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3339.5</td>
<td>1522.7</td>
<td>3402.7</td>
<td>CEPA</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>3127.1</td>
<td>1538.9</td>
<td>3454.1</td>
<td>MRCI</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>3388</td>
<td>1518</td>
<td>3469</td>
<td>MCSCF CI</td>
<td>Ref. [27]</td>
<td></td>
</tr>
<tr>
<td>3380.6</td>
<td>1476.6</td>
<td>3436.3</td>
<td>2.370 MRCI CI</td>
<td>Ref. [28]</td>
<td></td>
</tr>
<tr>
<td>3182.7</td>
<td>1401.7</td>
<td>3219.5</td>
<td>Expt.</td>
<td>Ref. [30]</td>
<td></td>
</tr>
<tr>
<td>3212.9</td>
<td>3259</td>
<td>0.0</td>
<td>Expt.</td>
<td>Ref. [31]</td>
<td></td>
</tr>
</tbody>
</table>

agreement between the absolute values of the quantum defects is not exact. However, their variations along the normal mode coordinate agree. Therefore, cross sections obtained using quantum defects from bound Rydberg state calculations or obtained from the electron scattering calculations should be nearly identical. The indirect DR cross section was calculated using Eq. (8) [13] with the $S$ matrix obtained from the electron scattering calculations.

Extensive theoretical studies of the water Rydberg states have been carried out by Child and co-workers [33–36]. The quantum-defect functions were then generated by fitting a quantum-defect matrix to ab initio potential energy surfaces obtained using the configuration-interaction method. As an example, the eigenquantum defects for Rydberg states of $1B_1$ symmetry at approximately the equilibrium geometry of the water ion obtained by Theodorakopoulos et al. [34] are 1.44, 0.05, and 0.75. These should be compared with the numbers 1.49, 0.10, and 0.67 obtained here with the electron scattering calculation.

C. Cross sections: Direct and indirect DR

The cross section for direct DR is calculated for both the asymmetric and symmetric stretches where either one or both OH bonds break. For the asymmetric stretch, the electronic resonant states of H$_2$O are not open for dissociation at low collision energies. An energy larger than 2 eV is needed to break the bond if the states are followed quasidiabatically as described above. Figure 6 shows the cross section for direct DR when only one the OH bonds breaks. The resonant states produce cross sections with sharp peaks and oscillations. Some of the peaks can be explained by tunneling resonances (shape resonances) formed by barriers in the potential energy curves. As seen for other systems, the regular oscillations above 4 eV are due to energy dependence of the electron capture probability [37,38]. For collision energies below 3 eV electronic resonant states of $3A''$ symmetry dominate, while above this energy, $3A'$ states become important.
The calculation of the direct DR cross section for the symmetric stretch can be computed by following resonant states in either Cs or C2v symmetry. In Fig. 7 we compare the total cross section calculated with the two symmetries. For resonant states of Cs symmetry, we display the contributions from the different irreducible representations. When both bonds break some resonant states are open for dissociation at low collision energies. Most important are resonant states of 3A′ symmetry and it is the lowest resonant state of this symmetry driving the direct electron capture at low energies. When the states are diabatized conserving the C2v symmetry, the direct DR cross section does not significantly change compared to the Cs result. There are some differences in the cross sections at larger energies where the higher-lying resonant states contribute.

The indirect DR cross section has been calculated up to the energy that corresponds to ν = 2 of the asymmetric stretch threshold, as shown in Fig. 8. The sharp drop in the energy dependence of the indirect cross section results from the thresholds of the ν = 1 and 2 levels of the three normal modes of H2O+, as given by the expression (8). For comparison, we have also plotted the data reported from a single-pass merged beam measurement [1] and the results obtained in the ASTRID [2] and CRYRING [3] storage ring experiments. The cross section taken from the merged-beam measurement needed to be divided by 2 due to an error in their calibration procedure, as reported latter by Mitchell [39]. The ion-storage ring data shown in the figure are the measured rate coefficient divided by the velocity ⟨σ⟩/v. This will deviate from the cross section when the collision energy is comparable to the energy spread of the electrons [2]. At low collision energies where the indirect process dominates, computed and measured cross sections are in fairly good agreement. Above 1 meV, the calculated indirect cross section is larger than the experimental results. This is an expected behavior since in our theoretical model we neglect autoionization under the assumption that predissociation takes place on a much faster time scale.

At low energies the cross sections from the two ion-storage ring experiments have been fitted to stronger energy
dependences than the $E^{-1}$ dependence, as predicted by Wigners threshold law [40]. The CRYRING team reported a $E^{-1.24}$ behavior [3], while ASTRID found a cross section that goes like $E^{-1.35}$ [2]. This steeper slope has been attributed to the presence of an indirect mechanism driving the DR reaction [3]. We indeed find the indirect mechanism to be important at low energies. However, by definition, our cross section calculated with the simplified model has the form $(a_1 + a_2 + a_3)E^{-1}$, where the $a_i$ coefficients are related to the factors (capture probabilities) relevant to each normal mode $g_i$. Therefore, even though our cross section is the result of a pure indirect DR mechanism, it cannot reproduce the steep slopes found in the storage ring measurements. The theory predicts drops in the cross section at energies corresponding to the vibrational threshold energies. The storage ring experiments show no drop near the $v = 1$ threshold for the bend, but do for the $v = 1$ symmetric and asymmetric stretches and $v = 2$.

In Fig. 8 the total cross section for the direct DR along the symmetric and asymmetric stretches is included. Both calculations are performed following the resonant states in $C_2$ symmetry. The direct electron capture and dissociation along resonant states contribute to the low-energy DR cross section when both bonds simultaneously break. At low energies, the cross section from the direct mechanism is, however, almost two orders of magnitude smaller than the indirect one. The direct DR cross section calculated for the asymmetric stretch, where only one of the OH bonds breaks, contributes to the DR cross section for energies above 1 eV where the resonant states are open for dissociation. The calculated one-dimensional direct DR cross section is significantly smaller than the measured cross sections. In this case, we treated the direct and indirect mechanisms as independent processes. These should be treated together and couplings between the states involved should be considered. This will produce new pathways to dissociation resulting in a larger cross section and less-pronounced structures. In addition, including several dimensions will also soften these sharp peaks.

At higher scattering energies, the direct cross section due to the resonant states with energies below the first excited state of the ion drops. The direct cross section in this region ($E > 1.9$ eV) arises from capture into higher resonant states that lie above the first excited state of the ion. In order to estimate the contributions from these higher resonant states, it is necessary to include two target channels in the electron scattering calculations and also to compute not only the total autoionization width, but the partial width [41]. We carried out additional calculations to determine the energies and widths of several of these resonant states with vertical excitation energies less than 5 eV. We use this molecular data as input for wave-packet calculations. The contributions to the DR cross section from these states peak in the vicinity of the measured high-energy structure at 5 eV, as can be seen in Fig. 8. The experiments also observe a peak around 15 eV. This is due to higher-lying resonant states not considered in the present study.

V. CONCLUSION

Potential energy surfaces, autoionization widths, and elements of the scattering matrix were obtained by combining structure with electronic scattering calculations at the MRCI level of theory. Calculations on the direct and indirect mechanisms of dissociative recombination of $\text{H}_2^+$ were performed. One-dimensional wave-packet studies of direct dissociation along electronic resonant states were performed to estimate the cross section for direct DR. The contribution to the low-energy cross section from the direct mechanism was found when both bonds simultaneously break. At collision energies above 1 eV, also the two-body fragmentation seems to be important.

The indirect mechanism was modeled by performing a vibrational frame transformation of the scattering matrix elements obtained at low collision energies (where resonant states do not contribute). The model neglects the contribution from autoionization and only includes contributions from the $v = 1$ and 2 vibrational states. The calculation shows that the indirect mechanism is clearly important at electron collision energies less than 1 eV. At low collision energies the indirect DR cross section is slightly larger than measured ones and it drops at the opening of vibrationally excited states of the target ion.

Strong couplings are observed between the Rydberg states that mediate the indirect process and the dissociative resonant states. In order to obtain branching ratios and fragmentation patterns, multidimensional dynamics including the couplings must be done.

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