



Ultracold molecular gases

Thesis for the Degree of Doctor of Philosophy (PhD)

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UNIVERSITY OF DEBRECEN

Doctoral Council for Natural Sciences and Engineering

Doctoral School of Physics

Debrecen, 2026

Készült a

Debreceni Egyetem
Fizikai Tudományok Doktori Iskolában
és
HUN-REN Atommagkutató Intézetben
(HUN-REN ATOMKI)
és
Université Paris-Saclay
École doctorale Ondes et Matière (EDOM)
és
Laboratoire Aimé Cotton

Prepared at

The University of Debrecen
PhD School in Physics
and
HUN-REN Institute for Nuclear Research
(HUN-REN ATOMKI)
and
Université Paris-Saclay
École doctorale Ondes et Matière (EDOM)
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Ultracold molecular gases

Dissertation submitted in partial fulfilment of the requirements for the doctoral (PhD)
degree in physics

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Prepared in the framework of the Physics Doctoral School of the University of Debrecen
Atomic and molecular physics programme

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The date and venue of the dissertation defence: 20...

Acknowledgements

First of all, I would like to express my deepest gratitude to my supervisors, Dr. Andrea Orbán and Dr. Olivier Dulieu. Their guidance, support, and encouragement have meant a great deal to me from the very beginning, not only in my scientific work but also in my personal life. At times, when I needed it most, they went far beyond the role of supervisors and supported me almost like parents. When speaking about them with my family, I often referred to them affectionately as my “father and mother in science”. I am deeply grateful for everything they have done for me throughout these years.

I am especially grateful to my girlfriend, Dóra, who stood by me and encouraged me during the most difficult periods. It was never easy to say goodbye when I had to leave for France, and with every departure it seemed to become harder. Despite the distance and all the difficulties that came with it, she remained strong, patient, and supportive throughout these years. I am deeply thankful that we were able to go through all of this together.

I would also like to thank my family, especially my father, my mother, and my brother, for their constant support. They were always there for me whenever I needed them, and knowing that I could always rely on them meant more to me than I can express.

I would also like to express my sincere gratitude to Dr. Nadia Bouloufa-Maafa for her scientific support, encouragement, and the many helpful discussions we had throughout these years. Her support went far beyond scientific collaboration, and I am very grateful for all the help and encouragement she gave me.

I would also like to thank Dr. Romain Vexiau and Dr. Xiaodong Xing for the fruitful scientific collaboration and for their contributions to my research.

I would like to thank Charbel Karam and Zonghan Yu for all their help, friendship, and support during my stays in France. I have many fond memories of the time we spent together, especially our lunches, dinners at the Chinese restaurant, and the many interesting discussions we had. Those moments made my time in France much more enjoyable, and I miss them very much.

I gratefully acknowledge the financial support provided by the Hungarian and French governments through the scholarships that made this research possible.

I would also like to thank the HUN-REN Institute for Nuclear Research (Quantum physics research group) and Laboratoire Aimé Cotton (Théomol group) for their hospitality throughout these years and for supporting my travels between Hungary and France.

Finally, I would like to dedicate a few words to all young researchers who may sometimes doubt themselves. Do not give up. Even when the work is difficult and the goal seems far away, you can make it through. Believe in yourself. If you have reached this stage, you already have what it takes to successfully complete the journey. I heard these words many times throughout the years, and now I understand their meaning. If I could do it, you can do it too.

Bevezetés

A semleges atomok és atomi ionok ultrahideg, jóval 1 millikelvin alatti, hőmérsékletekre történő lézeres hűtésére és csapdázására irányuló kutatások olyan jelentős eredményekhez vezettek, mint például a kvantumdegenerált gázok előállítás vagy egyetlen csapdázott ion precíz manipulálása. Mintegy 25 évvel ezelőtt merült fel a két kísérleti technika egyesítésének gondolata, amely lehetővé tenné az atom-ion kölcsönhatások kvantummechanikai természetének vizsgálatát ezekben az úgynevezett hibrid csapdákban. Az ultrahideg semleges atomi gázokban nagy részecsketávolságoknál a dinamikát az R^{-6} szerint változó van der Waals-kölcsönhatás határozza meg. A hibrid csapdákban azonban az R^{-4} távolságfüggést mutató, töltés - indukált dipólus közötti kölcsönhatás dominál. A kvantummechanikai tartomány elérése ezért továbbra is jelentős kihívást jelent, mivel ehhez még alacsonyabb hőmérsékletekre van szükség. Az ilyen hibrid rendszerek többek között a töltéstranszport és a kvantumgázokban jelen lévő szennyeződések vizsgálatára is alkalmasak lehetnek, emellett ígéretes lehetőséget kínálnak a kvantum-szimulátorok területén.

A jelen doktori munka alkálifém atomok és alkáliföldfém ionok ultrahideg ütközéseinek kvantummechanikai leírásával foglalkozik, különös tekintettel azokra a rugalmatlan folyamatokra, amelyek a csapdázott részecskék számának csökkenéséhez vezethetnek. Doktori munkám során két, kísérleti szempontból releváns, ütközési rendszert vizsgáltam: Li-atomok Ba^+ ionokkal, valamint Rb-atomok Sr^+ -ionokkal történő ütközését, ahol az iont mindkét esetben metastabil gerjesztett állapotba preparálták. A disszertáció a kutatási terület áttekintésével kezdődik, a kísérletileg megvalósult atom-ion kombinációkra fókuszálva. Ezt követően bemutatom ezen rendszerek elméleti leírásához szükséges módszereket. A molekulaionok leírását a Born-Oppenheimer közelítés keretében tárgyalom, amely a csoportunkban fejlesztett kvantumkémiai programmal számított potenciális energia görbék meghatározásának alapját képezi. Ismertetem az impulzusmomentumok csatolásának alapjait a Hund-féle csatolási eseteken keresztül, valamint bevezetem a munkám szempontjából kulcsfontosságú spin-pálya kölcsönhatást. Ezt követően bemutatom a Langevin-modellt, amely az atom-ion ütközések hasznos klasszikus leírását adja. Munkám alapját a kvantummechanikai szóráselmélet képezi, amelynek főbb lépéseit, valamint az általam használt és továbbfejlesztett numerikus programot mutatom be. A módszer alkalmazása során két lépés játszott meghatározó szerepet. Egyrészt az atom-ion kölcsönhatást, amely a molekulaionhoz kötött koordináta-rendszerben egyszerűbben írható le, a dinamikai számolásokhoz a laboratóriumi vonatkoztatási

rendszerbe kell transzformálni, ami szükségessé tette a vonatkoztatási rendszerek közötti transzformációt. Másrészt az atom-ion kölcsönhatások összetettségét megfelelően kell modellezni, ami esetünkben kvázi-diabatikus eljárások alkalmazását jelentette. A disszertáció utolsó részében a Li/Ba^+ és Rb/Sr^+ rendszerekre vonatkozó eredményeimet mutatom be. A vizsgálatok több egymással versengő rugalmatlan folyamatot tártak fel, köztük a nem-radiatív töltéscserélődést, az elektronikus gerjesztési kicserélődést és a finomszerkezeti legerjesztődést. A számított hatáskeresztmetszetek és reakciósebességek jó egyezést mutatnak a rendelkezésre álló kísérleti adatokkal. Az eredmények rámutatnak a spin-pálya kölcsönhatás és a rotációs csatolás erős együttes hatására, amely az alapállapotú részecskék ultrahideg ütközéseire általában nem jellemző. A disszertációt a jövőbeli kutatási lehetőségek bemutatásával zárom, amelyek közé tartozik többek között a modellünkben a részecskék Zeeman-alszintjeinek figyelembevétele, valamint a módszer kiterjesztése más, kísérleti szempontból lényeges atom-ion rendszerre.

List of abbreviations

AE	alkaline-earth neutral atom
AE⁺	alkaline-earth ion
AI	associative ionization
AM	alkali-metal neutral atom
AM⁺	alkali-metal ion
BF	body-fixed (frame)
BO	Born–Oppenheimer
CIPSI	Configuration Interaction by Perturbation of a multiconfiguration wave function Selected Iteratively
CM	center-of-mass
CPP	core polarization potential
DL	dissociation limit
EC	elastic collision
ECP	effective core potential
EEE	electronic excitation exchange
FCI	full configuration interaction
FSQ	fine-structure quenching
LZ	Landau–Zener
MCQS	Multi-Channel Quantum Scattering
MFR	magnetic Feshbach resonance
MOT	magneto-optical trap
NACT	non-adiabatic coupling term
NRCE	non-radiative charge exchange
NRQ	non-radiative quenching
PDM	permanent dipole moment
PEC	potential energy curve
PES	potential energy surface
PP	pseudopotential
RCE	radiative charge exchange
SCF	self-consistent field
SF	space-fixed (frame)
SO	spin–orbit
SOC	spin–orbit coupling
TBR	three-body recombination
TDM	transition dipole moment

Shorthand notation for scattering channels and dissociation limits

D_{3/2}	shorthand notation for the $S + D_{3/2}$ dissociation limit
D_{5/2}	shorthand notation for the $S + D_{5/2}$ dissociation limit
Ion+S	AM ⁺ + AE(¹ <i>S</i>) dissociation limit
P+S	AM(² <i>P</i>) + AE ⁺ (² <i>S</i>) dissociation limit
S+D	AM(² <i>S</i>) + AE ⁺ (² <i>D</i>) dissociation limit
S+S	AM(² <i>S</i>) + AE ⁺ (² <i>S</i>) dissociation limit

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Chapter 1

Introduction

The ability to manipulate atomic systems at ultracold temperatures (*i.e.* when atoms have kinetic energies E equivalent to temperatures $T = E/k_B$ well below 1 millikelvin) has opened a unique window into the quantum world. In this regime, the wave-like nature of matter becomes dominant and observable, providing profound insights into the fundamental laws of quantum theory and the intricate coupling between matter and radiation. Beyond their fundamental importance, mastering these controllable quantum systems is a prerequisite for the advancement of next-generation quantum technologies. Trapped and laser-cooled atomic and ionic systems have been extensively used to explore the quantum world, achieving remarkable results in fields such as metrology and atomic clocks [1,2], quantum information [3–7], few- and many-body physics [8–12], cold chemistry [13], precision measurements [14], quantum simulation [15,16], and ultracold molecules [17–19].

During the past three decades, a new field has emerged that combines these platforms to investigate the quantum nature of atom-ion interactions, giving rise to the concept of hybrid traps. For trapping ions, the most commonly used trap is the radio-frequency quadrupole trap or Paul trap developed by Dehmelt and Paul [20], although the so-called Penning trap is used occasionally [21]. Hybrid traps combine the advantages of atomic and ionic platforms. They offer a high degree of control and individual addressing typical of ion-based systems, together with long coherence times and scalability of atomic systems. Experiments in hybrid traps span a wide range of research areas, including many-body and polaron physics [22–27] and charge mobility [28, 29]. Further applications include quantum simulation [30–32], quantum chemistry [33–39], and quantum information [40–43].

Experimental investigations began in 2003 when Makarov *et al.* proposed a setup including a trap for ultracold atoms combined with a trap for laser-cooled ions in the same confined space [44]. Two years later, Smith *et al.* successfully implemented this approach to investigate Na-Ca⁺ collisions [33]. A magneto-optical trap (MOT) is used for trapping and cooling neutral atoms. This type of trap usually includes counter-propagating laser beams in combination with two separated coils in anti-Helmholtz configuration. The first realization of a MOT was reported in 1987 by Raab *et al.* to trap and cool sodium atoms [45]. In the next Chapter, I

provide more information about experimental developments in relation with my thesis project.

The dynamics of ultracold gases is dominated by long-range interactions. Neutral atoms interactions are of van der Waals type, varying as $1/R^6$ where R denotes the interparticle separation. Hybrid traps offer the opportunity to study and control ion-atom interactions which vary as $1/R^4$, thus with a range significantly longer than in the van der Waals regime. Therefore, the quantum regime (*i.e.* when the interparticle dynamics is involving a single partial wave) is more difficult to observe, as it requires temperatures which are much lower than for neutral atoms. A limiting factor for reaching the quantum regime is the micromotion which is generated by the Paul trap since it uses radio-frequency field to trap the ion. When the ion shifts from the trap center, micromotion appears, leading to heating of the ion. Moreover, the electromagnetic fields must be precisely controlled, because the charged particles are sensitive to any stray fields. However, a new trapping technique was developed in 2020 [46], which uses an optical field to trap the ion, thus eliminating micromotion. However, reaching the quantum regime remains challenging, and the method has not yet been widely adopted. Heating effects still remain due to spontaneous scattering of photons from the high-intensity laser field.

The thesis focuses on a particular class of mixed systems that includes easily laser-coolable alkali-metal atoms (AM) and alkaline-earth ions (AE^+). For AM atoms, cooling is typically achieved via the closed optical cycling transition between ground state $^2S_{1/2}$ and the lowest excited state $^2P_{1/2,3/2}$. In AE^+ , the same cooling scheme is used with an important difference: the excited $^2P_{1/2,3/2}$ states can decay to metastable $^2D_{3/2,5/2}$ states located in between the $^2S_{1/2}$ and $^2P_{1/2,3/2}$ states. These states are dark for the cooling lasers, therefore repumper lasers are required to drive the $^2D_{3/2,5/2}$ states to the $^2P_{1/2,3/2}$ ones. The achievable temperatures for the atoms are in the nK range, while for the ions it can be in the μK range. The excited state in the cooling scheme may generate novel dynamics in the hybrid trap, as emphasized in [47]. Understanding and modeling dynamics leading to ion losses is crucial because it enables full control of the hybrid trap and reveals details of the ion-atom interactions, which can be very complex despite the apparent simplicity of the system, each with a single valence electron.

The thesis is structured as follows. Chapter 2 presents a selection of existing atom-ion hybrid trap experiments including combinations of AM- AE^+ and AM-AM $^+$ species. Chapter 3 summarizes the theoretical framework underlying my research. It describes the widely applied Born-Oppenheimer approximation in molecular physics, Hund's coupling cases for angular momenta, elements of computational approaches to determine the electronic structure of diatomic molecules, and asymptotic models of spin-orbit interactions. The chapter then shifts to the classical Langevin model for atom-ion collisions, followed by the foundations of quantum scattering theory. This part discusses the scattering amplitude, cross sections, and partial-wave expansion. It also outlines the methodology for solving coupled-channel equations. Finally, it introduces the scattering matrix which is used to derive transition probabilities and cross sections.

Electronic structure and spin-orbit couplings are conveniently defined in the body-fixed coordinate system, which rotates with the molecule. However, experimental observations are made in the space-fixed (laboratory) frame. A basis transformation is required to rigorously describe the dynamics, which is detailed in Chapter 4.

The Born-Oppenheimer approximation breaks down at certain internuclear distances where avoided crossings occur in the potential energy curves. This leads to mixing between electronic states. The treatment of these non-adiabatic effects that I achieved in this work relies upon an original quasi-diabatization approach developed in our group which is presented in Chapter 5. Such a quasi-diabatization procedure yields R -dependent spin-orbit couplings, and in a second step, allows for the treatment of perturbation of these couplings due to the above non-adiabatic effects.

The last two Chapters present the results that I obtained on the dynamics of a alkali-metal atom in the ground state ^2S and an alkaline-earth ion in a metastable state ^2D . The theoretical investigation of this system started in X. Xing's thesis [48]. Here I revisited this topic in detail in order to validate and generalize the multichannel quantum scattering code. I first apply the methodology to the Li-Ba^+ system (Chapter 6) which is of particular interest as it involves collisions between a light atom and a heavy ion. Due to the resulting relatively small reduced mass, the system is an ideal candidate for reaching the quantum regime through cooling. In this chapter, I analyze the elastic and inelastic processes observed experimentally and identify the main dynamical mechanisms responsible for fine-structure quenching, non-radiative charge exchange and non-radiative quenching.

Subsequently, in Chapter 7, I examine the system Rb-Sr^+ . In this case, the nearly equal masses of the colliding particles and the more complex excited electronic structure lead to dynamics that are similar to, yet distinct from, those of the Li-Ba^+ system. I investigated the experimentally observed inelastic processes, the fine-structure quenching and electronic excitation exchange, and I showed the complexity of the dynamics induced by non-adiabatic terms.

These two examples demonstrate that ultracold collisions involving metastable alkaline-earth ions cannot be described by a single inelastic process or simple semiclassical models. Instead, a complete multichannel quantum scattering treatment is required. In both cases, satisfactory agreement with the experiment has been found, allowing to infer the quality of the molecular data employed in this work.

Chapter 2

Hybrid atom-ion traps: a selection of experimental realizations

In this chapter I provide insights about the experimental context of my research. Thus, an experimentalist reader might rely the experimental developments to the processes expected in hybrid ion-atom traps. Conversely, a theorist might better appreciate the main experimental issues for such systems, for instance, why metastable levels are considered as responsible for the observed dynamics. I wrote this chapter without defining all experimental terms, assuming that as for usual scientific papers, the quoted references would help to understand these technical terms.

Several review articles have been devoted to the ongoing experiments with hybrid traps, involving neutral atoms and molecules, and atomic and molecular ions [13, 34, 49–51]. In this chapter, inspired by [49], I selected several cases of experimental studies to illustrate the main features of the dynamical processes occurring in hybrid traps. I focused on two distinct cases: combinations of neutral alkali-metal (AM) atoms and alkaline-earth ions (AE^+), and second, of atoms and parent ions allowing for resonant charge exchange.

2.1 Hybrid traps combining alkali-metal atoms and alkaline-earth and ytterbium ions

This case attracted a lot of attention for a good reason: both species AM and AE^+ have an electronic configuration with a single valence electron, so that very similar laser cooling setups could be used to prepare them. In general, a cloud of AM atoms is laser-cooled and trapped in one location, while AE^+ ions are first trapped and then laser-cooled. Both traps are merged to form the hybrid trap in which both species are trapped at the same location. Several combinations AM- AE^+ have been experimentally explored around the world, and a complete list is

displayed in Table 2.1.

AM	AE ⁺	DL	Location	Ref.
⁶ Li	⁴⁰ Ca ⁺	Li ⁺ (¹ S)+Ca(¹ S)	Osaka (JP)	[52-54]
	¹³⁸ Ba ⁺	Li(² S)+Ba ⁺ (² S)	Freiburg (D)	[39, 55, 56]
	^{171,174,176} Yb ⁺	Li ⁺ (¹ S)+Yb(¹ S)	Amsterdam (NL)	[57-61]
²³ Na	⁴⁰ Ca ⁺	Na ⁺ (¹ S)+Ca(¹ S)	Storrs (USA)	[33, 62]
³⁹ K	⁴⁰ Ca ⁺	K ⁺ (¹ S)+Ca(¹ S)	Duke (USA)	[38]
⁸⁷ Rb	⁴⁰ Ca ⁺	Rb ⁺ (¹ S)+Ca(¹ S)	Basel (CH)	[47, 63-65]
	⁸⁸ Sr ⁺	Rb ⁺ (¹ S)+Sr(¹ S)	Rehovot (IL)	[66-71]
	¹³⁸ Ba ⁺	Rb ⁺ (¹ S)+Ba(¹ S)	Basel (CH), Ulm (D)	[46, 72-75]
	^{171,174} Yb ⁺	Rb ⁺ (¹ S)+Yb(¹ S)	Oxford (UK)	[35, 76-78]

Table 2.1: List of the combinations AM-AE⁺ experimentally explored. The dissociation limit (DL) with the lowest energy for each pair is reported, being either AM(²S)+AE⁺(²S) or AM⁺(¹S)+AE(¹S) involving particles in their electronic ground state.

To cool an arbitrary alkaline-earth ion, the dipole-allowed transition between the ground state $^2S_{1/2}$ and the excited state $^2P_{1/2}$ is used similar to the cooling of alkali-metal atoms, where this transition is a closed cycling scheme. However, in the case of heavier alkaline-earth metal ions (Ca⁺, Sr⁺, Ba⁺), metastable states $^2D_{3/2,5/2}$ lie between the states $^2S_{1/2}$ and $^2P_{1/2}$. Thus, the excited electron can decay not only back to the ground state $^2S_{1/2}$ but also to the state $^2D_{3/2}$. To close the cooling cycle, a repumper laser is required to pump the electron back to the $^2P_{1/2}$ excited state. The cooling scheme illustrated in Fig. 2.1 for the three ions Ca⁺, Sr⁺, Ba⁺. We note that the species Be⁺ and Mg⁺ are not specified in Table 2.1. These two species are also amenable to laser cooling [79,80]. The laser cooling of these species is complicated due to their energy difference between $^2S_{1/2}$ and $^2P_{1/2}$ levels. The wavelength of the cooling lasers are in the UV-regime, 313 nm and 280 nm for Be⁺ and Mg⁺, respectively. Current experimental implementations are limited by the technical challenges associated with realizing stable, narrow-linewidth laser sources, particularly in the ultraviolet spectral region.

Due to the laser cooling scheme, the excited metastable states are populated, which opens collisional loss channels within the trap. Several experiments explored the dynamics of these losses, and this is the central topic of the present thesis. Nevertheless, these intermediate metastable states have several advantages. Since they are involved in the laser cooling scheme, they can be used for storing information (qubit) due to their long lifetime (compared to the excited state $^2P_{1/2}$) [3]. The stored information must be read, the shelving technique uses the metastable ^2D level to read the information [81]. A further possible application of the metastable ^2D level is precision spectroscopy. This state disposes long radiative lifetime, thus the natural linewidth of $^2S \rightarrow ^2D$ transition is extremely defined which makes it suitable for high-precision measurements. Such transitions are used in optical atomic clocks, testing fundamental constants and measuring

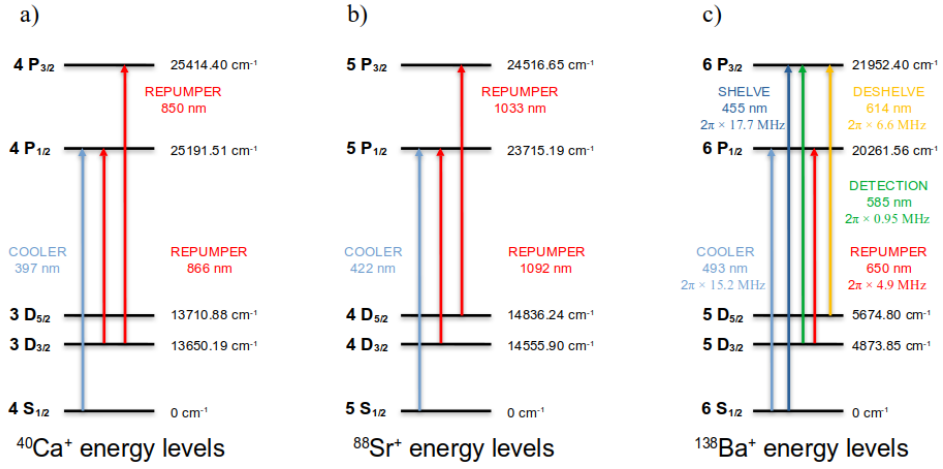


Figure 2.1: The energy levels that are included in the cooling scheme of Ca^+ , Sr^+ and Ba^+ .

relativistic effects [1, 82].

2.1.1 Li-Ba⁺

We see in Table 2.1 that one system stands out as qualitatively different from the others, namely $^6\text{Li}-^{138}\text{Ba}^+$, which differs from all other systems: its lowest asymptote involves Li and Ba^+ in their ground state in contrast to the other combinations AM-AE⁺ with the lowest asymptote involving a ground state AE atom and an AM⁺ ion with no valence electron. As a consequence, radiative charge exchange (RCE) [83]

$$\text{AM}(^2S_{1/2}) + \text{AE}^+(^2S_{1/2}) \rightarrow \text{AM}^+(^1S) + \text{AE}(^1S) \quad (2.1)$$

is energetically forbidden, offering the possibility of long interaction times. Another important aspect of the Li-Ba⁺ pair is the large mass imbalance between species. As shown in [84], a large mass ratio, ($m_{\text{atom}}/m_{\text{ion}}$), can mitigate the heating induced by excess micromotion in radio-frequency traps, thus facilitating access to the ultracold quantum regime. It increases the density of near-threshold bound states, which enhances the likelihood of observing Feshbach resonances [39, 56, 57], which is a further step to achieve full quantum control of the collision, to the formation of ultracold molecular ions [85] and for ultracold chemistry [86].

Experiments for this pair of species were conducted in the group of Prof. Tobias Schätz (Freiburg, Germany). In 2021, Weckesser *et al.* studied the interaction between ultracold ^6Li atoms and a single $^{138}\text{Ba}^+$ ion [39]. They adjusted the experimental parameters to study three-body reactions and their associated loss rates for the identification of resonances, as well as two-body reactions to examine sympathetic cooling of the ion within the ultracold atomic cloud. Indeed, they observed 11 magnetic Feshbach resonances (MFRs) in the 70 G-330 G magnetic field range with a step size of 400 mG. However, the multichannel quantum scatter-

ing calculations (MCQSC) predicted only five MFRs, which means that beyond the electronic interaction other ones might be important, such as second-order spin-orbit coupling. From the measured ion loss rate, they inferred that three-body recombination was the dominant process. Later in 2025, Thielemann *et al.* [56] investigated the collision energy dependence of MFRs when Li atoms were prepared in their hyperfine state and the Ba⁺ ion was prepared in its ground state or excited D_{3/2} state. Compared to the previous investigation, they identified 49 resonances in the 240 G-340 G with the step size of 200 mG. Then, they investigated the ion collision energy dependence of the MFR around 321.90 G, which corresponds to the *s*-wave. The survival probability of the ion was measured at different ion collision energies below the *s*-wave energy in the range of magnetic field 321.6 G-322.8 G and they found a strong collision energy dependence on MFRs. They also observed that even around the *s*-wave energy the dependence of higher partial waves are still not negligible.

As invoked above, the presence of AE⁺ ions prepared in the metastable states ²D_{3/2,5/2} induces loss channels in the hybrid trap, which we illustrate in Fig. 2.2 for the three pairs Li-Ca⁺, Li-Ba⁺, and Li-Yb⁺, for the sake of comparison. Losses from the trap can be generated by various processes:

- Non-radiative charge exchange (NRCE):

$$AM(^2S_{1/2}) + AE^+(^2D_j) \rightarrow AM^+(^1S) + AE^*$$
 where AE is left in an excited state;
- Non-radiative quenching (NRQ):

$$AM(^2S_{1/2}) + AE^+(^2D_j) \rightarrow AM(^2S_{1/2}) + AE^+(^2S_{1/2});$$
- Fine-structure quenching (FSQ):

$$AM(^2S_{1/2}) + AE^+(^2D_{5/2}) \rightarrow AM(^2S_{1/2}) + AE^+(^2D_{3/2});$$
- Electronic excitation exchange (EEE):

$$AM(^2S_{1/2}) + AE^+(^2D_j) \rightarrow AM^* + AE^+(^2S_{1/2})$$
 where AM is left in an excited state.

In my thesis I studied the processes that are indeed active in Li-Ba⁺(²D_j): NRCE, NRQ and FSQ. The results are presented in Chapter 6 and in a published paper [55].

2.1.2 Li-Yb⁺

The combination Li-Yb⁺ system also has a large mass imbalance and is a good candidate to reach the quantum regime at ultracold temperatures, despite the possibility for RCE to occur during the collision of ground state species. Experiments are performed in the group led by Prof. R. Gerritsma in Amsterdam (Netherlands). In 2017, the group first measured inelastic collision rates for ground and excited state collisions [58]. They found that RCE and radiative association producing molecular ions LiYb⁺ during ground state collisions have rates ≈ 1000 times smaller than the prediction of the semiclassical Langevin model, which is in agreement with other theoretical predictions [57, 83]. When the ion Yb⁺ is prepared in an excited

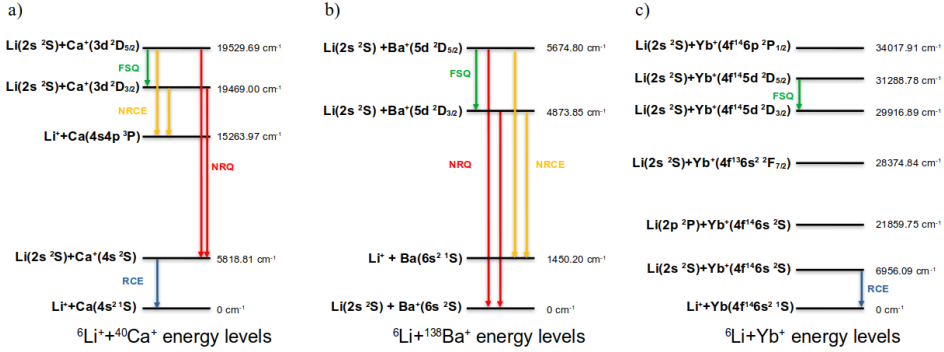


Figure 2.2: Energy thresholds and possible reaction pathways of AM-AE⁺ pairs involving Li and (a) Ca⁺, (b) Ba⁺, (c) Yb⁺. For simplicity, only selected energy thresholds are displayed for Li-Yb⁺, to illustrate the processes (the complete scheme is visible in [58]). The possible reaction paths are fine-structure quenching (FSQ) or spin-exchange, non-radiative charge-exchange (NRCE), radiative charge-exchange (RCE) or non-radiative quenching (NRQ).

state (see Fig. 2.2), they observed that NRCE is the primary inelastic mechanism and that its rate is independent of the chosen isotope of Yb⁺ and of the collision energy in the range 1–120 mK $\times$ k_B . In contrast, they found that the ion loss rate is one order of magnitude higher for Yb⁺(²F_{7/2}) than for Yb⁺(²D_{3/2}).

Later, the group investigated the spin dynamics of a single Yb⁺ ion embedded in a cold, spin-polarized cloud of ⁶Li atoms [59]. In their experiment, ¹⁷⁴Yb⁺ and ¹⁷¹Yb⁺ isotopes were used. They observed a strong spin exchange rate for both isotopes, the atom cloud leading to the polarization of the ion spin up to 93 %. Using *ab initio* electronic structure and quantum scattering calculations, the observed rates were theoretically explained.

In other papers, they tried to find ways to reach the quantum regime [60], and they assessed the importance of spin-orbit interaction in the shell transition $f \rightarrow d$ in order to determine precise spectra of LiYb⁺ [61].

2.1.3 Rb-Sr⁺

This combination is composed of two equally heavy particles with a quite high reduced mass, making the quantum regime hardly accessible. However, such a configuration has been used for sympathetic cooling of Sr⁺ by Rb atoms, which might allow to reach the requested temperature. These remarkable experimental efforts are undertaken in the group of Prof. R. Ozeri (Rehovot, IL).

In 2016, Meir *et al.* started their investigation with the collision of ultracold ⁸⁷Rb atoms with a ⁸⁸Sr⁺ ion [66]. The Rb atoms were prepared in the hyperfine level $F = 1$ of the ground state ²S_{1/2}, while the ion was prepared in the Zeeman sublevel $m = -1/2$ of the ground state ²S_{1/2}. The authors first measured the ion energy distribution and found that it is described by a Tsallis power-law instead of the usual Maxwell-Boltzmann distribution. Then, they proposed and

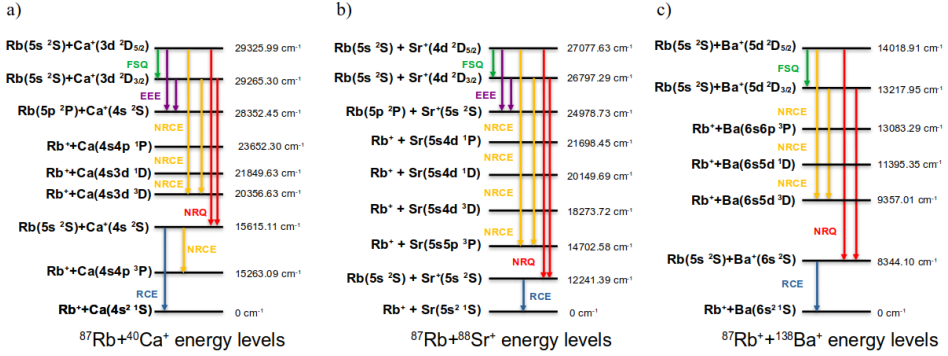


Figure 2.3: Energy thresholds and possible reaction pathways of AM-AE⁺ pairs involving Rb and (a) Ca⁺, (b) Sr⁺, (c) Ba⁺. The possible reaction paths are fine-structure quenching (FSQ) or spin-exchange, electronic excitation exchange (EEE), non-radiative charge-exchange (NRCE), radiative charge-exchange (RCE) or non-radiative quenching (NRQ).

implemented a method to measure the energy of a single-trapped ion in a single experimental realization [87]. With this new measurement, their ion energies were in agreement within 5 % with other thermometry methods that rely on averaging.

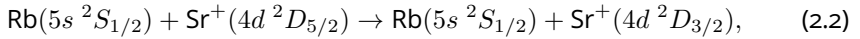
Sikorsky *et al.* demonstrated control of spin exchange and charge exchange dynamics by spin preparation [67]. The spin of the ion was mediated by the spin exchange process, which was governed by the hyperfine state of the atom. The Rb atoms were prepared in hyperfine levels $|F = 1, M_F = -1\rangle$ or $|F = 1, M_F = 0\rangle$, while the ion was prepared in spin states $|\uparrow\rangle_{\text{Sr}^+}$ or $|\downarrow\rangle_{\text{Sr}^+}$. The measured quantity was the probability $P(\downarrow)$ of finding the ion in the $|\downarrow\rangle_{\text{Sr}^+}$ state after a given interaction time. They found that approximately 90 % ion spin polarization was achieved for the $|\downarrow\rangle_{\text{Sr}^+}$ ion state, even the ion was originally prepared in the $|\uparrow\rangle_{\text{Sr}^+}$ or $|\downarrow\rangle_{\text{Sr}^+}$ state with the preparation of the atom in the $|F = 1, M_F = -1\rangle$ state. For the other atom preparation $|F = 1, M_F = 0\rangle$ this probability was around 50 %.

The charge exchange process between ground state Rb atoms and ground state Sr⁺ ion was further studied. Due to the low density and the fact that there is no crossing between PECs, the only way for charge exchange is radiative (see Table 2.1). RCE was observed only when the Rb atoms were prepared in the $F = 1$ hyperfine level. The Rb⁺ reaction product was identified by disappearance of ion fluorescence and resonant excitation mass spectroscopy, and they showed that RCE arises from two-body reaction. A simple theoretical model predicted the RCE rate to be a factor of 1.45 larger for Rb atoms prepared in $|F = 1, M_F = -1\rangle$, with the ion predominantly spin-pumped to $m = -1/2$, than for atoms prepared in $|F = 1, M_F = 0\rangle$ with a fully mixed ion spin state. The measured ratio of the RCE rates, 1.42 ± 0.20 , was consistent with this prediction. In 2018, Meir *et al.* used previously developed single-shot thermometry when a single Sr⁺ was immersed in an ultracold (μK) Rb bath to investigate sympathetic cooling of the ion. Sympathetic cooling was observed directly in two regimes [68]. One regime occurs

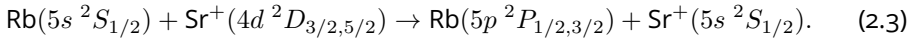
when energy transfer through collisions is efficient and leads to net cooling of the system. The other arises when collisions can induce both cooling and heating of the system as a consequence of non-equilibrium dynamics in the presence of the ion trap. Moreover, measurements of the scattering angles revealed predominantly forward-scattering events, a behavior that lies beyond the predictions of the Langevin model.

In 2023, Pinkas *et al.* observed loosely-bound molecular ions formed in binary collision [70]. Measurements of the electronic spin exchange rate were used to explore the dependence of the bound states on both the collision energy and the magnetic field. These measurements further enabled the extraction of the average molecular binding energy and the mean lifetime of the molecules. The results were in good agreement with the molecular dynamics simulations. The quantum control of the system at higher temperatures was investigated in a cooperative work between experiment and theory by Walewski *et al.* in 2025 [71]. They measured the probability of hyperfine relaxation of one neutral atom and a spin flip of a single ion for all possible spin projections of Rb atoms in the hyperfine state $F = 2$, used the resulting data to calibrate an extensive theoretical model. Once calibrated, the model showed that the spin flip dynamics in the $F = 1$ manifold of Rb atoms could be manipulated via tunable Feshbach resonances that extend well into the ultracold quantum regime. They predict that the control can be available at around 1 mK containing around 15 partial waves.

In 2020, Ben-shlomi *et al.* studied in a joint experimental and theoretical work collisions between Rb atoms and Sr^+ ions prepared in the $^2D_{3/2,5/2}$ states [69] (Fig. 2.3). They found that after few Langevin collisions, the $^2D_{3/2}$ and $^2D_{5/2}$ states of the ion quenched, and the ion gained kinetic energy. Using single-shot thermometry after the collision, two quenching pathways were identified: fine-structure quenching (FSQ)



and the electronic excitation exchange (EEE)



In general, charge exchange process in atom-ion collisions is present. However, here it was not observed. The observed inelastic processes were investigated with semi-classical Landau-Zener model, and possible pathways were found. They also found that the spin-orientation has no effect on the reactions, due to the strong Coriolis-spin mixing. In my thesis, I investigated these inelastic processes in Chapter 7.

2.1.4 Other atom - ion hybrid experiments

Li-Ca^+ : Another promising system to reach the quantum regime is the combination of ^6Li atoms and $^{40}\text{Ca}^+$ ions with a smaller atom-to-ion mass ratio than the systems described previously, hoping that the micromotion heating is less. For this purpose, Mukaiyama's group investigated the collision between Li atoms and Ca^+ ion [52]. They observed elastic collision in the 100 mK - 3 K temperature range. The

elastic cross section experimentally measured was in agreement with the semi-classical model [88]. Later, inelastic collisions in the mK regime were observed by Haze *et al.* in 2015 [53]. The reaction product was identified as Li^+ by mass spectrometry, indicating that the observed inelastic process was non-radiative charge exchange. The measured charge exchange cross sections were much smaller than those predicted by the Langevin model. Saito *et al.* further studied the charge exchange process in the system [54]. They investigated the energy and internal state dependence of the charge exchange collision cross section. The energy varied between $1 \text{ mK} \times k_B$ and $2 \text{ K} \times k_B$. In order to investigate the dependence upon the internal state, the ion was prepared in electronic states $^2S_{1/2}$, $^2P_{3/2}$, $^2D_{3/2}$, and $^2D_{5/2}$. The obtained cross sections were smaller than the Langevin cross section but followed its behavior. *Ab initio* potential energy curves were calculated by our group in Laboratoire Aimé Cotton and the route of charge exchange was identified.

Rb-Ca⁺: In 2011, Hall *et al.* experimentally studied ^{87}Rb - $^{40}\text{Ca}^+$ cold collisions in a hybrid atom-ion trap [47], in collaboration with our group in Laboratoire Aimé Cotton. The collisional energy was in the range $200 \text{ mK} \times k_B$ - $20 \text{ K} \times k_B$. As a result of collision Rb^+ product was observed showing charge exchange between Ca^+ and Rb that can be radiative charge exchange induced by photon emission or non-radiative charge exchange driven by non-adiabatic couplings between CaRb^+ molecular states. The molecular ion CaRb^+ was also formed by radiative association, and finally Rb_2^+ was observed in the presence of CaRb^+ . Molecular potential energy curves were calculated up to 22^{nd} dissociation limit, and possible pathways for the observed processes were identified. Further investigations were conducted for the processes mentioned above in 2013 by Hall *et al.* [63]. Quantum-chemical and quantum-scattering calculations were performed in order to compare them with experimental results. The average collision energy was larger than $20 \text{ mK} \times k_B$ while the calculations were performed from $10 \mu\text{K} \times k_B$ to $70 \text{ K} \times k_B$. They demonstrated that the reactive collision rates depend on the long-range charge-induced dipole interaction and follows the universal behavior predicted by the classical Langevin model. The magnitude of the rates are controlled by short-range non-adiabatic and radiative couplings, which lead to reaction channel specific chemical changes. Later, Eberle *et al.* improved the energy resolution of the hybrid trap, where the Rb atoms were pushed through Coulomb crystals using radiation pressure [64]. Thus the atom kinetic energy could be changed in the $30 \text{ mK} \times k_B$ - $350 \text{ mK} \times k_B$. In 2022, Xing *et al.* continued theoretical investigations on the system, and they showed that the formed CaRb^+ molecular ion by radiative association is protected against photodissociation by blackbody radiation and by the cooling laser [65]. They obtained that the non-radiative charge exchange is the dominant inelastic process in the collision, and their calculated reaction rates were in agreement with experimental observation and previous calculations.

Rb-Ba⁺: The group of Prof. Denschlag (Ulm, Germany) started their investigation with Rb-Ba^+ in addition to Rb-Rb^+ in 2010 [72]. The RbBa^+ experiment is different from the previous ones, because two heavy particles are in interaction. They observed both elastic and inelastic collisions. The elastic collisions were found important while the inelastic collisions were suppressed. The dominant inelastic channel was radiative charge exchange and was identified directly by mea-

suring the trap frequency. Later, RbBa^+ molecular ion formation was observed by Hall *et al.* (Basel, Switzerland) by false-color fluorescence imaging method. The molecular ion can be formed by radiative association [73]. Moreover, Rb^+ ion was observed which indicated the occurrence of radiative or non-radiative charge exchange process. Potential energy curves and reactive cross sections were calculated, and the theoretical rate coefficients were in agreement with experimental observations.

In 2016, Krückow *et al.* studied experimentally and theoretically three-body recombination (TBR) during the collision of two Rb atoms and a single Ba^+ ion in the mK regime [74]. They found that the TBR rate was proportional to $E_{\text{coll}}^{-3/4}$, where E_{coll} is the collisional energy. Classical trajectory calculations were performed to calculate TBR rate and their findings were in agreement with the experiment. Later, the same group showed that two-body reaction rate can be obtained from the TBR rate, and they found that the TBR rate dominates the two-body reaction, which is charge exchange. Following the earlier observation of RbBa^+ molecular ions, Mohammadi *et al.* investigated the evolution of weakly bound RbBa^+ molecular ions in 2021 [75], in collaboration with our group at Laboratoire Aimé Cotton. The RbBa^+ molecular ion underwent collisions with ultracold Rb atoms, involving elastic, inelastic, and reactive processes. Vibrational relaxation was found to be the dominant process, while radiative processes became increasingly important for more deeply bound molecular ions. As a result of these collisions, Ba^+ , Rb_2^+ and Rb^+ ions were observed as reaction products. Furthermore, the collision dynamics were shown to strongly depend on the electric state of the molecular ion.

Back in 2020, Schmidt *et al.* (Freiburg, Germany) demonstrated a new method to trap the atoms and a single ion simultaneously in an optical potential trap instead of the usual radio-frequency trap [46]. This method eliminates the disadvantage of radio-frequency trap that is the ion heating due to its micromotion in the trap. They showed that the Ba^+ could be cooled below the Doppler-temperature by sympathetic cooling via collision with ultracold Rb atoms. They state that, this method is general enough to leave the limitations of the radio-frequency trap which are the large atom-ion mass ratio, furthermore, it is not limited to Rydberg atoms, or homonuclear cases. Subsequently, the method may open the possibility to reach the quantum regime for atom-ion interaction.

2.2 Hybrid traps combining atoms and their parent ions

Owing to the symmetry of atom-ion collisions, in which the ionic and neutral species are identical, the number of possible reactive processes is reduced, therefore providing a clean environment for precise control of ultracold collisions. Such collisions are particularly suitable platform for investigating resonant charge exchange processes, charge transport and ion mobility in ultracold gases (see for instance [89]).

In typical experimental realizations, the neutral atoms are confined and cooled in a magneto-optical trap (MOT), which is spatially overlapped with a

radio-frequency trap used to confine the ions. Following the preparation of the ultracold atomic cloud, a controlled fraction of the atoms is photoionized by a laser pulse, and the resulting ions are subsequently trapped in the Paul trap. Due to the resonant charge transfer processes, *i.e.* charge transfer without energy release, losses in such hybrid traps are significantly reduced. Two kinds of experiments have been performed: either with AM-AM⁺ combinations, or with Yb-Yb⁺ combination. The latter offers the possibility to laser-cool both species, which has been indeed achieved.

2.2.1 Yb-Yb⁺

The first cold collision with trapped atoms and ions was performed in 2007 between Yb atom and Yb⁺ in the group of Vuletić [90], [91]. Neutral ytterbium, Yb(4*f*¹⁴ 6*s*²), has a closed-shell ground state, while its ion, Yb⁺(4*f*¹⁴6*s*), is alkali metal-like, having very similar electronic structure. As a result, resonant charge exchange in Yb + Yb⁺ collisions is highly efficient. Consequently, from an experimental point of view, trap losses are considerably reduced. Another favorable characteristic of the Yb/Yb⁺ system is that both species are laser-coolable. Moreover, ytterbium has stable bosonic and fermionic isotopes, which makes mass-dependent studies feasible. Due to the high atomic number *Z*, the spin-orbit interaction is relatively strong, leading to a well-separated excited state structure and consequently less complex dynamics.

In 2007, the group of Vuletić was the first to observe a cold collision with trapped atoms and ions in Yb-Yb⁺ collisions [91]. In their experiment, several stable isotopes, namely bosonic ¹⁷²Yb, ¹⁷⁴Yb and fermionic ¹⁷¹Yb, were used to investigate charge exchange collision. The reaction was studied between different isotopic combinations, $\alpha\text{Yb} + \beta\text{Yb}^+ \rightarrow \alpha\text{Yb}^+ + \beta\text{Yb}$, enabled by isotope-selective ion fluorescence detection. Measurements were done in the 35 mK and 40 K temperature range. Even at the lowest temperature, around 40 partial waves contributed to the collision, which is still in the semiclassical regime. The observed rate coefficients were in good agreement with theoretical predictions based on the semiclassical Langevin model.

2.2.2 Rb-Rb⁺

The collision between rubidium atoms and rubidium ions is one of the most studied systems in atom-ion hybrid traps, since rubidium atoms are easy to laser cool and the corresponding ions can be efficiently confined in Paul traps, allowing good control and spatial overlap between the two species. The system involves a single valence electron neutral Rb and a closed-shell ionic core with a noble-gas-like configuration, Rb⁺. The closed-shell structure of the ion implies that laser cooling is not possible with standard techniques. Cooling of alkali-metal ions is typically achieved via sympathetic cooling, *i.e.*, by co-trapping them with laser-cooled alkaline-earth metal ions, or via resonant charge transfer processes. [92]. The molecular states structure of the Rb-Rb⁺ system is less complex than that of the Yb-Yb⁺ system. In Rb-Rb⁺ collisions, charge exchange is also a resonant process

due to the identical atomic species, mainly governed by the non-adiabatic couplings, but in contrast to the Yb-Yb⁺ case is less efficient [91]: In the latter case, the presence of multiple closely spaced electronic states and e.g. stronger spin-orbit coupling leads to an increase of avoided crossings, which can enhance resonant charge transfer. In rubidium case due to nonzero nuclear spin hyperfine interactions can play an important role, opening up additional collisional channels while for bosonic ytterbium isotopes, where the nuclear spin is zero, thus hyperfine interactions play no role in the ultracold collisional dynamics.

The group of Prof. Denschlag investigated the interaction between an ion Rb⁺ with ⁸⁷Rb Bose-Einstein condensate in 2010 [72]. The experimental setup is described in detail in [93]. We note that using this same apparatus, it was possible to investigate the interaction between Rb atoms and a Ba⁺ ion. In Ref. [72], they demonstrated that a single ion can be used as a probe of the atomic density distribution. The number of remaining particles was measured as a function of the ion's position relative to the center of the atomic cloud. Their measurements were performed with three fractions of the condensate: a thermal cloud, a partially condensed atomic cloud, and an almost pure Bose-Einstein condensate. Based on their theoretical model, the temperature of the atomic sample T_{Rb} was obtained at 50, 35 and 25 nK for the three fractions.

In the same group, TBR was investigated in 2012 [94]. Two recombination processes were considered:

- $\text{Rb} + \text{Rb} + \text{Rb}^+ \rightarrow \text{Rb}_2 + \text{Rb}^+$. In this reaction, the ion acts as a catalyzer to produce Rb₂ molecules. Then the ion gains 2/3 of the released energy. Subsequently, the ion was sympathetically recooled via elastic two-body collisions with cold rubidium atoms.
- $\text{Rb} + \text{Rb} + \text{Rb}^+ \rightarrow \text{Rb}_2^+ + \text{Rb}$. In this second reaction, a molecular ion and a neutral atom may be produced, but Rb₂⁺ molecular ions were not observed in this experiment.

Furthermore, in the experiment, the dependence of the TBR probability on the kinetic energy of the ion (controlled by the micromotion of the ion) was investigated. They found that the probability can be increased by a factor of 5 with increasing micromotion.

The Rb atom Rb⁺ ion collision was studied from a different point of view by the team of Prof. Rangwala (Bangalore, India) to cool the ion by the atoms via resonant charge exchange [92,95]. As Rb⁺ cannot be laser-cooled, they suggest that resonant charge exchange could be an efficient cooling process. They showed that resonant charge exchange can cool the ion more efficiently than elastic collision, leading to a lower ion kinetic energy than considering only the elastic one. During the resonant charge exchange, the internal state of the interacting particles was unchanged, only the charge transferred from the atom to the ion. This produces cold ion and hot atoms that leave the trap. A similar demonstration of the beneficial affect of the resonant charge-exchange on the ion cooling in the Cs atom Cs⁺ collision was shown by the same group [96].

Chapter 3

Theoretical background

In this chapter, I will introduce the theoretical approaches and methods that are used during my research. In Section 3.1, I introduce the Born-Oppenheimer approximation for diatomic molecules, which is at the foundation of the so-called quantum chemistry, *i.e.* the resolution of the Schrödinger equation to determine the electronic states of the molecules. The angular momenta are very important for diatomic molecules. They can be coupled in various ways, leading to the formulation of the various Hund's coupling schemes based on the hierarchy of the interactions involved in the molecule. In Section 3.2, I give a brief presentation of Hund's cases (a), (c), and (e), which are relevant to the research of this thesis. Section 3.3 is devoted to the resolution of the time-independent Schrödinger equation given in Section 3.1 for the electronic dynamics. I present in Section 3.4 the spin-orbit interaction that plays a central role in my investigation. I recall in Section 3.5 the classical model for atom-ion collisions, the Langevin capture model, useful for the basic understanding of the processes studied. Finally, I describe in Section 3.6 the elements of scattering theory required for the investigated collisional processes.

3.1 Born-Oppenheimer approximation for a diatomic molecule

In this section, I explain the widely used approximation in molecular physics, the Born-Oppenheimer approximation [97]. It is based on the high ratio between the nucleus mass and the electron mass. The proton is 1836 times heavier than the electron.

Consider a diatomic molecule composed of atoms A and B with mass m_A and m_B and n electrons. The position vectors relative to the center of mass O_{CM} of the system are $\mathbf{R}_A$ and $\mathbf{R}_B$, while the electronic ones are $\mathbf{r}_i$, where $i = 1, 2, 3, \dots, n$, see Fig. 3.1. Using these notations, the relative distances between the particles are defined as follows: the internuclear distance is given by $R = |\mathbf{R}_B - \mathbf{R}_A|$, the distance between electrons i and j is $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and the nucleus-electron distance is $r_{iA/B} = |\mathbf{r}_i - \mathbf{R}_{A/B}|$.

The frame of reference with its origin in O_{CM} and one axis along the molecular axis is referred as the body-fixed (BF) frame, or the rotating frame. The BF frame provides a natural description of the molecular system, since it separates the rotation of the molecule from the internal degrees of freedom (vibration and electronic motion), thus simplifying the treatment of the electronic structure. The center-of-mass O_{CM} moves in the laboratory frame, also referred to as the space-fixed (SF) frame, with a position

$$\vec{R}_{CM} = \frac{m_A}{m_A + m_B} \vec{R}_A^{SF} + \frac{m_B}{m_A + m_B} \vec{R}_B^{SF}. \quad (3.1)$$

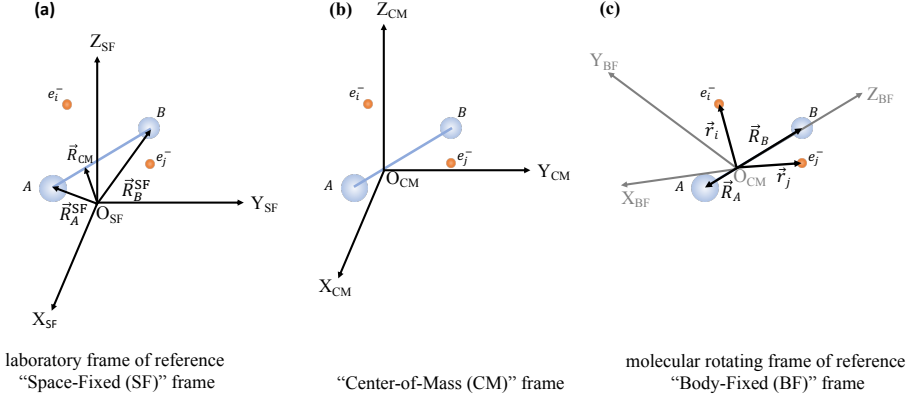


Figure 3.1: Different frames of reference: (a) The collision between the two colliding partners is described in the laboratory frame of reference, referred to as the space-fixed (SF) frame $\{X_{SF}, Y_{SF}, Z_{SF}\}$. (b) The center-of-mass frame which ignores the motion of center-of-mass O_{CM} in the SF frame. (c) The body-fixed (BF) frame $\{X_{BF}, Y_{BF}, Z_{BF}\}$ attached to the center-of-mass O_{CM} with Z_{BF} along the internuclear axis.

The time-independent Schrödinger equation for the molecule in the center of mass coordinate system can be written as

$$\hat{H}_{AB}(\mathbf{r}, \mathbf{R}) \Psi(\mathbf{r}, \mathbf{R}) = E \Psi(\mathbf{r}, \mathbf{R}), \quad (3.2)$$

The Hamiltonian of the molecule, $\hat{H}_{AB}$, in the non-relativistic case is the sum of the kinetic energy operator $\hat{T}$, and the potential energy term $\hat{V}$

$$\hat{H}_{AB}(\mathbf{r}, \mathbf{R}) = \hat{T}(\mathbf{r}, \mathbf{R}) + \hat{V}(\mathbf{r}, \mathbf{R}), \quad (3.3)$$

where $\mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_n\}$ represents all position vectors of the electrons. More explicitly, in the BF, the kinetic energy operator is written as the sum of the kinetic energy operator for the relative nuclear motion and the kinetic energy of the electrons,

$$\hat{T}(\mathbf{r}, \mathbf{R}) = \hat{T}_n(\mathbf{R}) + \hat{T}_e(\mathbf{r}) = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2, \quad (3.4)$$

where the reduced mass of the nuclei is noted $\mu = m_A m_B / (m_A + m_B)$ with the i index in the operator ∇_i^2 indicating that the derivatives are taken with respect to the $\mathbf{r}_i$. The potential energy operator is given by the sum of the Coulomb interactions between nuclei and electrons

$$\begin{aligned} \hat{V}(r, R) &= V_{n-n}(R) + V_{n-e}(r, R) + V_{e-e}(r) = \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{Z_A Z_B}{R} - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^n \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}, \end{aligned} \quad (3.5)$$

where Z_A and Z_B denote the atomic numbers of nuclei A and B . Throughout the thesis, atomic units will be used, which means $\frac{1}{4\pi\epsilon_0} = 1$, $\hbar = 1$ and $m_e = 1$. Due to their much larger mass, the nuclei move far more slowly than the electrons and can therefore be treated as fixed from the perspective of the electronic motion. Thus, we consider electrons moving in the Coulomb field of the nuclei for fixed $\mathbf{R}$ values, and the electronic Hamiltonian in atomic units is given by

$$\hat{H}_e(\mathbf{r}, R) = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \frac{Z_A Z_B}{R} - \sum_{i=1}^n \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}. \quad (3.6)$$

The molecular wave function is written as a product of an electronic wave function $\psi^m(\mathbf{r}, R)$ for every distance R and a nuclear wave function $\chi(\mathbf{R})$, also referred to as the BO ersatz,

$$\Psi^m(\mathbf{r}, \mathbf{R}) = \chi^m(\mathbf{R}) \psi^m(\mathbf{r}, R). \quad (3.7)$$

The wave function $\psi^m(\mathbf{r}, R)$ is the m^{th} solution at distance R of the Schrödinger equation with the electronic Hamiltonian

$$\hat{H}_e(\mathbf{r}, R) \psi^m(\mathbf{r}, R) = E_e^m(R) \psi^m(\mathbf{r}, R). \quad (3.8)$$

The wave function depends parametrically on R , as well as the corresponding electronic eigenenergies $E_e^m(R)$, resulting in the so-called adiabatic potential energy curve (PEC) of the m^{th} electronic state. The adiabatic approximation at this stage consists in solving the Schrödinger equation for nuclear motion and for a given electronic state m . Substituting Eqs 3.7 and 3.8 in Eq. 3.2 leads to

$$\left(\hat{T}_n(\mathbf{R}) + E_e^m(R) \right) \chi^m(\mathbf{R}) = E^m \chi^m(\mathbf{R}), \quad (3.9)$$

where E^m is the total energy of the molecule in the electronic state m . In the adiabatic approximation, the terms involving the derivatives of the electronic wave

function generated by the kinetic energy operator are neglected. These terms, usually referred to as "radial couplings", may become important in various situations, for example: (i) when two adiabatic PECs present an avoided crossing localized in internuclear distance reflecting an abrupt variation of the electronic wave function, and thus an important derivative with respect to R ; (ii) when we introduce additional terms in the electronic Hamiltonian, like spin-orbit interactions, which might couple different adiabatic states. A way to take into account such non-adiabatic effects consists in expressing the full molecular wave function as an expansion over the electronic adiabatic states $\psi^m(\mathbf{r}, R)$ solutions of Eq.3.8

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{m=1}^{\infty} \chi^m(\mathbf{R}) \psi^m(\mathbf{r}, R). \quad (3.10)$$

where the functions $\chi^m(\mathbf{R})$ are not anymore solutions of Eq. 3.9. Substituting Eq. 3.10 into the Schrödinger equation 3.2, the radial part of the nuclear kinetic energy operator $\hat{T}_n(\mathbf{R})$ acts on one term of this expansion as

$$-\frac{1}{2\mu} \frac{d^2}{dR^2} [\chi^m(R) \psi^m(\mathbf{r}, R)] = -\frac{1}{2\mu} \left[\psi^m \frac{d^2 \chi^m}{dR^2} + 2 \frac{\partial \psi^m}{\partial R} \frac{d\chi^m}{dR} + \chi^m \frac{\partial^2 \psi^m}{\partial R^2} \right]. \quad (3.11)$$

Projecting the resulting equation onto the electronic state ψ^q yields a set of coupled equations,

$$\left[\hat{T}_n + E_e^q(R) \right] \chi^q(R) + \sum_{m \neq q} \hat{W}^{qm}(R) \chi^m(R) = E \chi^q(R), \quad (3.12)$$

where $\hat{W}^{qm}$ are the non-adiabatic coupling terms

$$\hat{W}^{qm}(R) = -\frac{1}{2\mu} \left[2F^{qm}(R) \frac{d}{dR} + G^{qm}(R) \right], \quad (3.13)$$

with

$$F^{qm}(R) = \left\langle \psi^q \left| \frac{\partial}{\partial R} \right| \psi^m \right\rangle, \quad G^{qm}(R) = \left\langle \psi^q \left| \frac{\partial^2}{\partial R^2} \right| \psi^m \right\rangle. \quad (3.14)$$

To examine the effect of a small change in the internuclear distance, $R \rightarrow R + dR$, we differentiate the electronic Schrödinger equation (Eq. 3.8) with respect to R ,

$$\frac{\partial \hat{H}_e}{\partial R} \psi^m + \hat{H}_e \frac{\partial \psi^m}{\partial R} = \frac{\partial E_e^m}{\partial R} \psi^m + E_e^m \frac{\partial \psi^m}{\partial R}. \quad (3.15)$$

Projecting this equation onto another electronic eigenstate ψ^q , and using the orthogonality of the electronic states, $\langle \psi^m | \psi^q \rangle = 0$ for $m \neq q$, together with $\langle \psi^m | \hat{H}_e = E_e^m \langle \psi^m |$, yields

$$\left\langle \psi^q \left| \frac{\partial \hat{H}_e}{\partial R} \right| \psi^m \right\rangle = (E_e^m - E_e^q) \left\langle \psi^q \left| \frac{\partial}{\partial R} \right| \psi^m \right\rangle, \quad m \neq q. \quad (3.16)$$

Therefore, the first-order derivative coupling introduced above can be equivalently written as

$$F^{qm}(R) = \left\langle \psi^q \left| \frac{\partial}{\partial R} \right| \psi^m \right\rangle = \frac{\left\langle \psi^q \left| \frac{\partial \hat{H}_e}{\partial R} \right| \psi^m \right\rangle}{E_e^m(R) - E_e^q(R)}. \quad (3.17)$$

This expression shows that non-adiabatic coupling terms (NACTs) may become large when two adiabatic PECs approach each other in energy. Therefore, in the vicinity of an avoided crossing, where the energy gap becomes small and the electronic character of the states changes rapidly with R , the Born-Oppenheimer separation may break down and transitions between the coupled electronic states can occur. Away from avoided crossings, NACTs are generally small and can often be neglected. We will see in the next Sections how such coupling terms are handled in the context of our work.

The kinetic energy operator $\hat{T}_n(\mathbf{R})$ appearing in Eq. 3.12 can be expressed in polar coordinates (R, θ, ϕ) as

$$\begin{aligned} \hat{T}_n(\mathbf{R}) &= -\frac{1}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu} \frac{1}{R^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \\ &= -\frac{1}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu} \frac{\ell^2}{R^2}, \end{aligned} \quad (3.18)$$

where ℓ is the angular momentum associated with the mechanical rotation of the molecule. As $\hat{T}_n(\mathbf{R})$ has a well separated radial part and an angular one, the nuclear wave function $\chi^m(\mathbf{R})$ is written as the product of an R -dependent vibrational wave function $\chi_{\text{vib}}^m(R)$ and an angular-dependent part rotational wave function $\chi_{\text{rot}}^m(\theta, \phi)$

$$\chi^m(\mathbf{R}) = \chi_{\text{vib}}^m(R) \chi_{\text{rot}}^m(\theta, \phi). \quad (3.19)$$

Inserting Eq. 3.19 in Eq. 3.9 leads to the two equations for the radial and rotational wave functions

$$\left[-\frac{1}{2\mu} \frac{1}{R^2} \frac{\partial^2}{\partial R^2} + \frac{\ell(\ell+1)}{2\mu R^2} + E_e^m(R) \right] \chi_{\text{vib}}^m(R) = E \chi_{\text{vib}}^m(R) \quad (3.20)$$

$$\frac{1}{2\mu} \frac{\ell^2}{R^2} \chi_{\text{rot}}^m(\theta, \phi) = \frac{\ell(\ell+1)}{2\mu R^2} \chi_{\text{rot}}^m(\theta, \phi). \quad (3.21)$$

For diatomic molecules we use the conventional relation

$$\chi_{\text{rot}}^m(\theta, \phi) = \sqrt{\frac{2\ell+1}{4\pi}} D_{M_\ell, \Lambda_\ell}^{*\ell}(\theta, \phi, 0)$$

where D are the so-called Wigner functions that will be useful in the next Chapter. In the case, when the electronic wave functions are sensitive to the movement of

the nuclei, the motion of the nuclei and electrons will not be decoupled anymore, i. e., the coupling terms between nuclear and electronic motions in $\hat{T}_n(\mathbf{R})$ are not negligible, and the electronic states are mixed. Later in the thesis, we will show some examples, where the Born-Oppenheimer approximation is not valid, these are the so-called avoided crossings, which enable non-adiabatic transitions, thus inelastic processes. In Chapter 5, I will show examples for the treatment of the avoided crossings.

3.2 Couplings in diatomic molecules: Hund's cases

Being by essence a non-spherical object, the angular momenta play an important role in molecules. We defined in the previous Section the mechanical rotation of the molecule ℓ . The internal angular momenta of the molecule, namely the total electronic angular momentum $\mathbf{L}$ and the total electronic spin $\mathbf{S}$ must be considered too. The total nuclear spin $\mathbf{I}$ is neglected in our study, as the dynamics that will be modeled in the next chapters can be considered as independent from $\mathbf{I}$ at a first level of approximation. These angular momenta may be coupled to each other in various ways, depending on the relative strengths of the interactions that they characterize. Frederick Hund was the first to systematically categorize the various coupling schemes in a diatomic molecule. After his work, these groups are referred to as Hund's coupling cases [98]. Five main Hund's cases exist, labeled (a), (b), (c), (d), and (e). In this Section we present three Hund's cases (a), (c) and (e) which are relevant for our work. They are usefully illustrated by a classical vector model, and allow to determine a set of "good" quantum numbers as those who are conserved during the process, i.e. quantum numbers which appropriately characterize the quantum states (see Table 3.1).

Hund's case (a): In the Hund's case (a) coupling scheme (Fig. 3.2), the orbital angular momentum, $\mathbf{L}$, is strongly coupled to the internuclear axis, so that it precesses around the internuclear axis much faster than the electronic spin $\mathbf{S}$. The projections of $\mathbf{L}$ and $\mathbf{S}$ onto the molecular axis are well defined as $\pm\Lambda$ and $\pm\Sigma$, respectively, and their sum Ω , $\Omega = \Lambda + \Sigma$ is also well characterized. The electronic Hamiltonian (Eq.3.6) does not depend on the sign of these projections, thus neither do the resulting electronic energies. In the laboratory frame, and in the absence of external field, the mechanical rotation ℓ (which is perpendicular to the internuclear axis) can couple to their projections to form the total angular momentum $\mathbf{J}$ of the molecule which might depend on the sign of these projections, leading to a doublet of close energy levels, usually referred to as Λ -doubling or Ω -doubling. Note that the projection of $\mathbf{J}$ on the molecular axis is Ω , while it is denoted M along an arbitrary axis of the laboratory frame. The set of good quantum numbers in Hund's case (a) are then $|\Lambda|$, $|\Sigma|$, $|\Omega|$, J , M . Note that the parity of the total wave function of the molecule is also a good quantum number in the laboratory frame, as it will be discussed in Chapter 4.

Hund's case (c): in this case, both $\mathbf{L}$ and $\mathbf{S}$ rotate around the internuclear axis with similar velocity, so they add together to form the total electronic angular momentum $\mathbf{j} = \mathbf{L} + \mathbf{S}$ which in turn rotates around the axis with a fixed projection

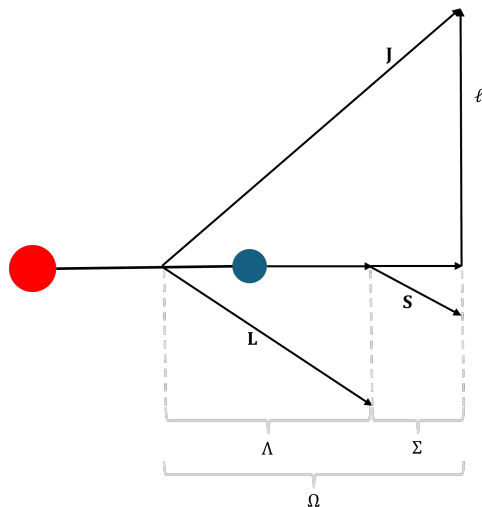


Figure 3.2: Vector coupling model for Hund's case (a) coupling case in diatomic molecules.

Ω . This is the case when the spin-orbit coupling is strong with respect to the electrostatic interaction of the electrons with the nuclei. The momentum ℓ then adds to Ω forming $\mathbf{J}$ (Fig. 3.3). The good quantum numbers that are now $|\Omega|, J, M$.

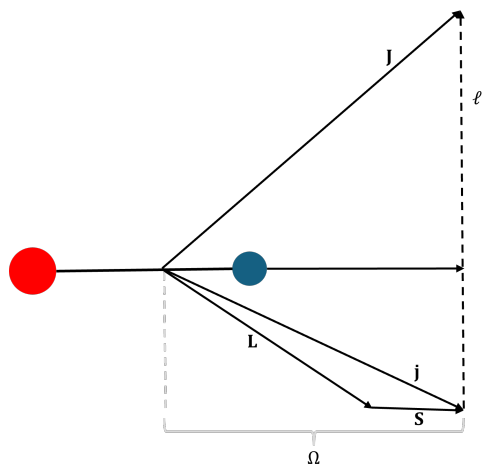


Figure 3.3: Vector coupling model for Hund's case (c) coupling case in diatomic molecules.

Hund's case (e): This case corresponds to a weak electrostatic interaction of the electrons with the nuclei, so that the total electronic momentum $\mathbf{j}$ and the rotation ℓ rotate with similar velocity around the total angular momentum around $\mathbf{J}$ (Fig. 3.4). This happens for instance at large internuclear distance where long-range

interaction between the two atoms takes place, without exchange energy, while the atomic spin-orbit interaction is dominant. The only good quantum numbers in this case are J and M . It is important to realize that in most cases, and in particular

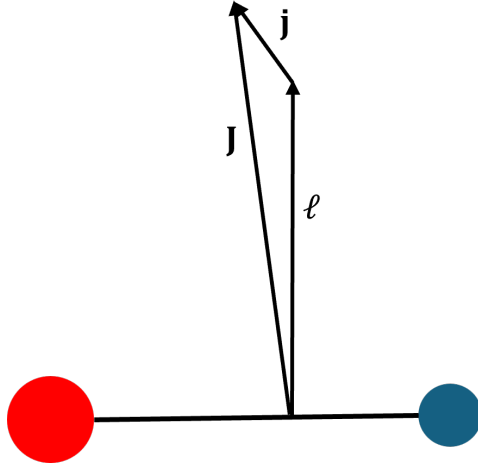


Figure 3.4: Vector coupling model for Hund's case (e) coupling case in diatomic molecules.

for describing a collision between two atoms, there is not a unique Hund's case under which the atom pair can be modeled at all distances. The electronic states are conveniently described in Hund's case (a) or (c) in the BF frame, while the collision starts under conditions of Hund's case (e) in the SF frame. Therefore it is important to set up appropriate transformations between these various frames. This will be the topic of Chapter 4.

Hund's Cases	Quantum numbers	Electronic	Spin-orbit	Rotation
(a)	$\Lambda, S, \Sigma, \Omega, J, M$	Strong	Medium	Weak
(c)	Ω, J, M	Medium	Strong	Weak
(e)	J, M	Weak	Medium	Strong

Table 3.1: Summary of the "good" quantum numbers characterizing Hund's case (a), (c) and (e), with the corresponding approximate interaction regime, including electronic interaction of electrons with nuclei, spin-orbit interaction, and rotational interaction.

3.3 Determination of the electronic structure of a diatomic molecule

In this section, I briefly describe the method used in our group for solving the electronic Schrödinger equation within the Born-Oppenheimer approximation (Section 3.1), in order to obtain Hund's case (a) PECs that are at the foundation of my work. More details about the methodology can be found in various articles from our group, e.g. [99–101]. I first recall Eq. 3.8 of the electronic Schrödinger equation for the electronic motion expressed at a fixed internuclear distance R ,

$$\hat{H}_e(\mathbf{r}, R)\psi^m(\mathbf{r}, R) = E_e^m(R)\psi^m(\mathbf{r}, R), \quad (3.22)$$

where

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{\alpha=1}^N \sum_{i=1}^n \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{i=1}^n \sum_{j>i}^n \frac{e^2}{r_{ij}} + \frac{Z_A Z_B}{R}. \quad (3.23)$$

Equations 3.22 and 3.23 describe a complex many-body system with two nuclei and n electrons (with n usually large), and their resolution is reputed to be one of the most complex to solve in quantum mechanics, a research field referred to as quantum chemistry. The first step consists of finding reasonable approximations that allow such a resolution with controlled numerical accuracy.

Our study focuses on diatomic molecules composed of an alkali-metal atom (Li, Rb) and an alkaline-earth ion (Ba^+ , Sr^+), both with a single valence electron moving in the field of singly-charged (Li^+ , Rb^+) or doubly-charged (Ba^{2+} , Sr^{2+}) closed-shell core. The system contains two valence electrons; therefore, it can be treated as an effective two-electron system. The closed-shell cores A^+ and B^{2+} are represented by the so-called pseudopotentials (PP) [102, 103]. More specifically, for each isolated atom, the mean field induced by inner-shell electrons on the valence electron is modeled by a parametric effective core potential (ECP) with spherical symmetry $V_{\text{ECP}}(r)$. For practical use in numerical calculations, a Gaussian form for the ECP is chosen

$$V_{\text{ECP}}(r) = -\frac{Z}{r} + \sum_{i=1}^{\infty} C_i r^{n_i} e^{-\alpha_i r^2}, \quad (3.24)$$

where Z is the charge of the core, and C_i , n_i and α_i are adjustable parameters that determine the amplitude and radial shape of the Gaussian terms. The parameters of the ECP are determined after performing an all-electron self-consistent field Hartree-Fock (SCF) calculation, and adjusting the obtained atomic energies to the experimental ones. In general the results are not fully satisfactory, as an important effect is neglected: the correlation between the valence electron and the core electrons. In the present context, it corresponds to the instantaneous deformation induced by the valence electron of the ionic core which is not a point charge, but rather a charge distribution characterized by a static dipole polarizability α^+ .

An additional term is added to V_{ECP} , namely, the core polarization potential

(CPP) $V_{\text{CPP}}(r)$ [104, 105]

$$V_{\text{CPP}}(r) = -\frac{1}{2}\alpha^+ \mathbf{f}^2, \quad (3.25)$$

$$\mathbf{f} = \frac{\mathbf{r}}{r^3} F_l(r, \rho_l). \quad (3.26)$$

The so-called cut-off functions $F_l(r, \rho)$

$$F_l(r, \rho_l) = \begin{cases} 0 & r < \rho_l \\ 1 & r > \rho_l. \end{cases} \quad (3.27)$$

involve cut-off radii ρ_l depending on the orbital angular momentum of the valence electron l , and are designed to limit its penetration within the ionic core. Practically, three cut-off radii ρ_s, ρ_p, ρ_d (for $l = 0, 1, 2$) are adjusted to reproduce the experimental energies of the lowest s, p and d levels of the considered atom [99, 105].

It is worth noticing that the behavior of the ECP at short internuclear distances is not rigorous as it involves only the coulombic repulsion between the two ionic closed-shell cores. But the repulsion between core electrons is even stronger due to Pauli exclusion principle. It has been shown [106, 107] that such an effect can be modeled by adding to the ECP a core-core repulsion term of the form $V_{cc}(R) = a_{cc}e^{-b_{cc}R}$. One efficient way to calculate the a_{cc} and b_{cc} parameters is to perform an Hartree-Fock calculation on the closed-shell molecule AB^{3+} at short R and fit the parameters to the results. However, under the typical conditions of the systems used here, such a term becomes significant only below 6 a.u. (this value is typical for alkali-metal ionic cores like Rb [107]), so that the repulsive branch of the PEC is noticeably affected when the minimum of a PEC lies close to that distance. In our work, the dynamics of the systems is controlled by patterns of the PECs typically beyond 10 a.u., so that we will not include V_{cc} in the used PECs.

The main outcome of the simplifications above is that standard techniques of quantum chemistry can be applied by performing a full configuration interaction calculation (FCI) in the chosen Hilbert space for the two valence electrons. This opens the way to obtain results for highly-excited electronic states, in contrast with method using incomplete configuration interaction. This Hilbert space is built by centering a large Gaussian basis set on each ionic core and setting up two-electron configurations. The molecular wave functions are obtained from Hartree-Fock single-electron calculations, followed by FCI, resulting in Hund's case (a) PECs for each molecular symmetry $^{2S+1}\Lambda$. Calculations are performed using the CIPSI package (Configuration Interaction by Perturbation of a multiconfiguration wave function Selected Iteratively) originally developed in Toulouse (France) [108], which was further adapted in our group to run via an automatic procedure. This method has been successfully applied to several systems in our group [83, 99–101, 109–111], to calculate Hund's case (a) PECs, permanent dipole moments (PDMs) and transition dipole moments (TDMs).

As a preliminary step to Chapters 6 and 7, Fig. 3.5 shows the calculated PECs for the LiBa^+ and RbSr^+ molecules of relevance for my thesis. While having both two valence electrons, their molecular structure is vastly different from each other. Indeed, their dissociation limits originate from the combination of the spectrum

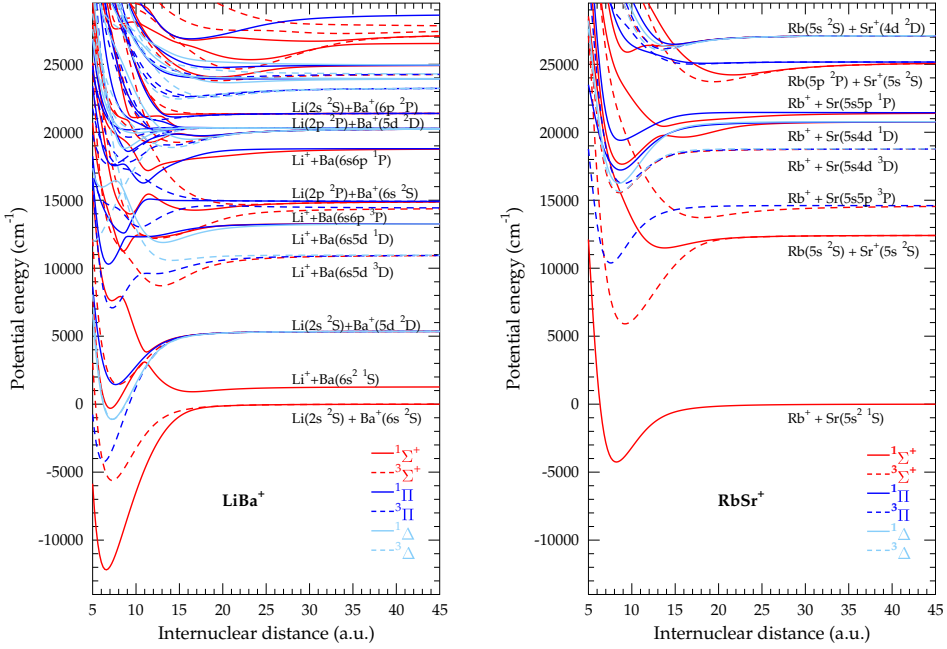


Figure 3.5: Hund's case (a) PECs of LiBa^+ (left panel) and RbSr^+ (right panel), presented with the same energy scale. The origin of energies is fixed at the dissociation limit of the electronic ground state. Singlet states are displayed with solid lines, and triplet states with dashed lines.

of several atomic species, namely A , A^+ , B and B^+ . Being a heavy species, Ba and Ba^+ exhibit more energy levels in the energy range considered than Li , Rb and Sr . However, within the energy range relevant to the present study, up to the metastable ionic entrance channel correspond to the third and eighth dissociation limits of LiBa^+ and RbSr^+ , respectively. Up to these limits, the LiBa^+ exhibits a simpler structure with fewer relevant dissociation limits than RbSr^+ . The $^2S \rightarrow ^2P$ in alkali-metal atom (*i.e.* the usual D line) have comparable energies in Li and Rb , so that each panel includes the dissociation limits $\text{Li}(2s) + \text{Ba}^+(6s)$ and $\text{Rb}(5s) + \text{Sr}^+(5s)$ within the same energy range.

In contrast, the lowest asymptote is different for the two systems. From a collisional point of view, the initial channel with neutral alkali-metal atom and alkaline-earth ion in their ground state has the lowest energy in LiBa^+ , and not in RbSr^+ : therefore there is no possibility of radiative charge exchange in the former system, in contrast to the latter one [83].

The metastable excited state of alkaline-earth ions, namely $\text{Ba}^+(5d)$ and $\text{Sr}^+(4d)$ in the present case, plays an important role in their laser-cooling cycle, as briefly addressed in Chapter 2. Therefore, collisions might occur between ground state alkali-metal atoms and metastable alkaline-earth ions, which is the main topic of my work. Surprisingly enough, despite the significantly lower number

of asymptotes in RbSr^+ by comparison with LiBa^+ , the Hund's case (a) PECs correlated to the $\text{Li}(2s^2S)+\text{Ba}^+(5d^2D)$ and to $\text{Rb}(5s^2S)+\text{Sr}^+(4d^2D)$ asymptotes mostly interact via real crossings or avoided crossings with PECs correlated to a single lower asymptote, *i.e.* $\text{Li}^++\text{Ba}(6s^2^1S)$ and $\text{Rb}(5p^2P)+\text{Sr}^+(5s^2S)$. We immediately notice that the resulting dynamics will be different, as charge exchange is expected in the former case, and not in the latter. We will come back to these issues in Chapters 6 and 7.

3.4 Spin-orbit interaction in a diatomic molecule: asymptotic model

In heavy atoms such as Rb, Ba and Sr considered in this work, the spin-orbit (SO) interaction is strong and generates SO doublets (see Table 3.2), so that within the molecule containing them, it might become stronger than the electrostatic interaction. As explained in Section 3.2, this situation refers to Hund's case (c) coupling case. The molecular SO coupling is expected to depend on the internuclear coordinate R in a non-trivial manner, starting from the atomic values for infinite atomic separation. This will be discussed in Chapter 5. In order to capture the essential features of the system, it is wise to design an asymptotic model to build the SO Hamiltonian. We will show later that the structure of the atomic and molecular SOC matrices are identical.

Atom/ion	Level	SO doublet	Energy splitting (cm^{-1})	A_{SO} (cm^{-1})
Rb	$5p$	$1/2, 3/2$	237.595	158.397
Sr^+	$5p$	$1/2, 3/2$	801.46	534.307
Sr^+	$4d$	$3/2, 5/2$	280.34	112.136
Ba^+	$6p$	$1/2, 3/2$	1690.843	1127.229
Ba^+	$5d$	$3/2, 5/2$	800.955	320.382
Li	$2p$	$1/2, 3/2$	0.34	0.227

Table 3.2: Spin-orbit splittings and corresponding spin-orbit constants A_{SO} of relevant energy levels in several atomic and ionic species studied in this work [112].

Thus, spin-orbit coupling can be handled in a two separated atom framework at large internuclear distances. More precisely, we consider a neutral alkali-atom and a singly-charge alkaline-earth ion, so that one valence electron is bound to each ionic core. We consider the effective spin-orbit Hamiltonian that can be added to the molecular Hamiltonian,

$$\hat{H}_{SO} = A_{SO}^A \hat{l}_A \cdot \hat{s}_A + A_{SO}^B \hat{l}_B \cdot \hat{s}_B, \quad (3.28)$$

where A_{SO}^A and A_{SO}^B are the atomic splitting constants for atoms A and B, respectively. The molecular wave function in Hund's case (a) $|\Lambda, S, \Sigma\rangle$ can then be written

as a linear combination of atomic orbitals, where each atom A and B is supposed to be in a well-defined atomic state with quantum numbers l_A, s_A and l_B, s_B

$$|\Lambda, S, \Sigma\rangle = \sum_{m_{s_A}=-s_A}^{s_A} \sum_{m_{s_B}=-s_B}^{s_B} C_{s_A, m_{s_A}; s_B, m_{s_B}}^{S, \Sigma} |s_A, m_{s_A}, s_B, m_{s_B}\rangle \times \\ \times \sum_{m_{l_A}=-l_A}^{l_A} \sum_{m_{l_B}=-l_B}^{l_B} C_{l_A, m_{l_A}; l_B, m_{l_B}}^{L, \Lambda} |l_A, m_{l_A}, l_B, m_{l_B}\rangle, \quad (3.29)$$

where C_{ijkl}^{pq} are Clebsch-Gordan coefficients [113]. It is easy to derive the matrix elements of $\hat{H}_{SO}$ for every possible value of $\Omega = \Lambda + \Sigma \equiv m_{l_A} + m_{l_B} + m_{s_A} + m_{s_B}$ using the usual ladder operators

$$\hat{l}^{\pm} |l, m_l, s, m_s\rangle = \sqrt{l(l+1) - m_l(m_l \pm 1)} |l, m_l \pm 1, s, m_s\rangle \quad (3.30)$$

$$\hat{s}^{\pm} |l, m_l, s, m_s\rangle = \sqrt{s(s+1) - m_s(m_s \pm 1)} |l, m_l, s, m_s \pm 1\rangle \quad (3.31)$$

$$\hat{l}^z |l, m_l, s, m_s\rangle = m_l |l, m_l, s, m_s\rangle \quad (3.32)$$

$$\hat{s}^z |l, m_l, s, m_s\rangle = m_s |l, m_l, s, m_s\rangle \quad (3.33)$$

$$\hat{H}_{SO} = A_{SO}^A \left(\hat{l}_A^{(z)} \hat{s}_A^{(z)} + \frac{1}{2} (\hat{l}_A^+ \hat{s}_A^- + \hat{l}_A^- \hat{s}_A^+) \right) + A_{SO}^B \left(\hat{l}_B^{(z)} \hat{s}_B^{(z)} + \frac{1}{2} (\hat{l}_B^+ \hat{s}_B^- + \hat{l}_B^- \hat{s}_B^+) \right). \quad (3.34)$$

We consider an atom or an ion with one valence electron and with spin-orbit in states ^2P or ^2D (see Table 3.2), characterized by the SO constants $A_P = 2\Delta E_P/3$ and $A_D = 2\Delta E_D/5$, while the other partner remains in a ^2S state. ΔE_P and ΔE_D are the atomic spin-orbit energy splitting of ^2P and ^2D states. This gives rise to asymptotic limits that we will denote $S + P$ and $S + D$ for simplicity. In each case we obtain Hamiltonian matrices containing the spin-orbit interaction on diagonal and off-diagonal matrix elements. These matrices are collected in Appendix A.

In this asymptotic framework, there is no SO coupling between states correlated to different asymptotic limits. However, considering R -dependent spin-orbit couplings, there may be couplings in the short-range that tend to zero at large internuclear distances. These are referred to as indirect spin-orbit couplings, whereas those involving the same asymptotic limit are known as direct spin-orbit couplings. This feature is investigated in Chapter 5, where I introduce the determination of R -dependent spin-orbit couplings, and their influence on the dynamics is illustrated on two specific examples in Chapter 6 and Chapter 7.

3.5 Langevin model: a useful classical model for ion-atom collisions

In 1905, Paul Langevin [114] proposed a classical model to describe possible trajectories for ion-atom collisions, in the context of ion mobility in neutral gases. In particular, he obtained orbiting trajectories of the ion around a neutral particle, thus corresponding to a capture (Fig. 3.6). This model was widely used afterward

to describe ion-neutral collisions in chemistry (see, for instance, [115–117]). In this approach, it is assumed that the ion-neutral collision rate is determined by the long-range part of the interaction potential, fixing the condition for the system to pass across the centrifugal barrier and then leading to capture or more generally to a reaction between the two particles.

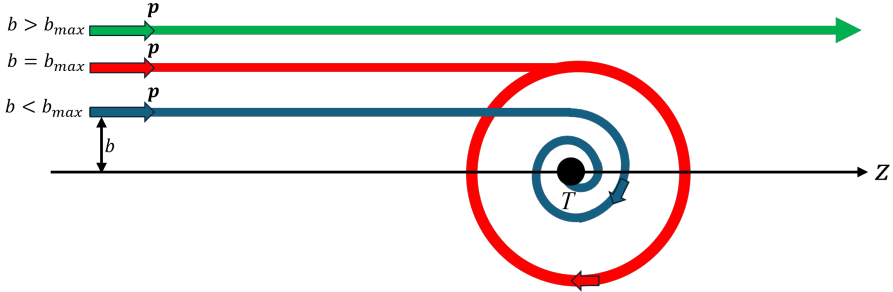


Figure 3.6: Possible trajectories of the Langevin model depending on the choice of the impact parameter b with respect to the critical impact parameter b_{max} . Blue curve: $b < b_{max}$ and the projectile is captured by the target in a spiral trajectory, and reaction occurs with unit probability. Red curve: $b = b_{max}$ corresponding to an orbiting trajectory around the target. Green curve: $b > b_{max}$ and the projectile is not significantly influenced by the target.

The long-range part of the interaction potential between an ion and a neutral particle (an atom in our case) is $V(R) = -C_4/R^4$ where C_4 is half of the static dipole polarizability α of the atom,

$$C_4 = \left(\frac{e}{4\pi\epsilon_0} \right)^2 \alpha/2. \quad (3.35)$$

This interaction competes with the rotational interaction between the particles (with reduced mass μ) quantified by partial waves ℓ , giving rise to the effective potential

$$V_{\text{eff}}(R) = -\frac{C_4}{R^4} + \frac{\ell(\ell+1)\hbar^2}{2\mu R^2}. \quad (3.36)$$

This potential exhibits a centrifugal barrier (Fig. 3.7) with a height depending on ℓ

$$V_{\text{eff}}(R^*) = \frac{\ell^2(\ell+1)^2\hbar^4}{16\mu^2 C_4}, \quad (3.37)$$

and located at the position

$$R^* = \sqrt{\frac{4\mu C_4}{\ell(\ell+1)\hbar^2}}. \quad (3.38)$$

Therefore, the collision energy must be larger than the height of the barrier for the capture to occur. In a classical approximation, the number of partial waves is

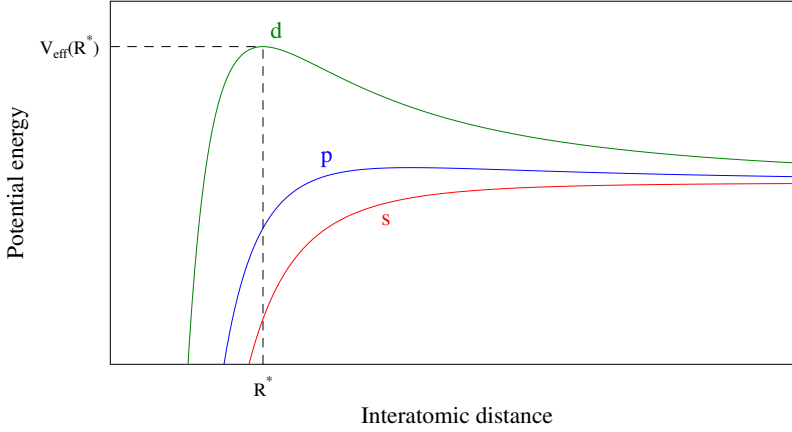


Figure 3.7: Effective potential energy of a hypothetical atom - positively charged ion system, including the centrifugal (rotational) term for $\ell = 0, 1, 2$. In the s -wave case ($\ell = 0$) there is no barrier, while for increasing values of ℓ , a centrifugal barrier emerges.

large, so that the magnitude of the angular momentum of the system is $L = \hbar\ell$, and its maximum value at a given collision energy $E_c = \hbar^2 k^2 / (2\mu)$ is

$$L_{max} = (16\mu^2 C_4 E_c)^{1/4}. \quad (3.39)$$

This corresponds to a maximum impact parameter for the classical collision $b_{max} = L/(\hbar k)$. The classical cross section $\sigma_{class}^{max} = \pi b_{max}^2$, usually denoted as the Langevin cross section, is

$$\sigma_L = 2\pi \sqrt{\frac{C_4}{E}}. \quad (3.40)$$

and the associated rate coefficient $K_L = \sqrt{\frac{2E}{\mu}} \sigma_L$

$$K_L = 2\pi \sqrt{\frac{2C_4}{\mu}}. \quad (3.41)$$

The Langevin rate is then constant with respect to the collision energy, which makes ion-atom collisions remarkable. Such a capture model does not take into account the possible quantum effects occurring at short ion-atom distances, so that the Langevin rate is an upper bound for the quantum reaction rate. This is the central goal of the present thesis: to determine the importance of these quantum effects and thus evaluate a realistic reaction rate to be compared to experimental measurements.

In [118] a generalized derivation of the capture cross section for $1/R^{-3}$ and $1/R^{-6}$ interactions is presented, and the Langevin cross section is discussed in detail.

3.6 Elements of quantum scattering theory

Assume a typical atomic collision as shown in Fig.3.8. A homogeneous, well-collimated, monoenergetic beam formed by A particles is aimed at a target B particle. After a collision between particles A and B, a detector placed outside of the path of the incident beam registers the particles emerging from the interaction. Several types of collisions are possible:

1. Elastic collisions, when particles A and B are in the same internal state before and after the collision:



2. Inelastic collisions, when the internal quantum state of particle A and/or B changes during the collision, for example, the B particle is left in an excited state after the collision:



3. Reactive collisions, when, after the collision, two different particles are created compared to the colliding ones



In the following, we present the main aspects of quantum scattering theory that are relevant to our study:

- definition of the scattering amplitude and the cross section for the scattering of particles and its relation to the underlying wave function of the system;
- scattering by a central potential allowing for the so-called partial wave expansion of the wave function to determine the scattering amplitude;
- extension to the scattering for a multichannel problem, leading to the resolution of coupled Schrödinger equations;
- choice of the log-derivative algorithm for solving the coupled equations;
- extraction of $\mathcal{S}$ matrix of scattering amplitudes.

3.6.1 Scattering amplitude and cross section

Let us consider the incident ionic beam A directed along the z -axis toward the target atom B , see Fig. 3.8.

The incident flux of atom A is denoted by F . The number of atoms scattered into a small solid angle $d\Omega$ in the direction θ, ϕ in unit time is denoted by dN . The number of scattered atoms is proportional to $d\Omega$ and F , the proportionality factor $\sigma(\theta, \phi)$ is the differential cross section and has the dimension of area.

$$dN = \sigma(\theta, \phi) F d\Omega. \quad (3.45)$$

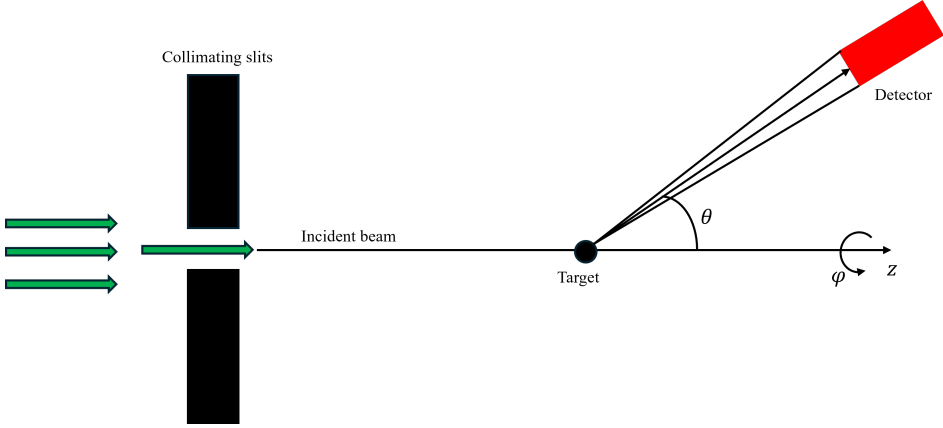


Figure 3.8: Schematic view of a scattering experiment in the lab, when a beam of particles A collides a target of particles B , and products detected at a certain angle θ with respect to the incident beam.

The total scattering cross section is obtained by integrating the differential cross section over the whole solid angle

$$\sigma = \int_0^{2\pi} d\phi \int_0^\pi \sigma(\theta, \phi) \sin \theta d\theta. \quad (3.46)$$

In quantum scattering, the cross section reflects the intrinsic properties of the full wave function of the interacting system, and thus the underlying interactions at work during the collision. We derive below this relationship.

The collision between two particles with masses m_A and m_B , interacting via a potential, $V(\mathbf{R})$ that depends only on their relative coordinate $\mathbf{R}$, can be separated into the free motion of the center of mass and the relative motion of the particles. The latter is equivalent to the motion of a single particle of reduced mass, $\mu = m_A m_B / (m_A + m_B)$, in the potential $V(\mathbf{R})$. Therefore, we consider the simplest collision problem: the non-relativistic scattering of a spinless particle by a potential $V(\mathbf{R})$. The Schrödinger equation for the relative motion is

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{R}) \right] \Psi(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t). \quad (3.47)$$

The potential $V(\mathbf{R})$ is taken to be real and time independent. Typically, it will be a single Born-Oppenheimer (BO) potential energy curve derived along the lines of the previous subsections. Thus, the stationary solution of Eq. 3.47 is

$$\Psi(\mathbf{R}, t) = \psi(\mathbf{R}) e^{-iEt/\hbar}. \quad (3.48)$$

The wave function $\psi(\mathbf{R})$ is the solution of the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{R}) \right] \psi(\mathbf{R}) = E\psi(\mathbf{R}), \quad (3.49)$$

with $E = (\hbar^2 k_i^2)/(2\mu)$ being the energy of relative motion and k_i is the magnitude of the incident wave vector $\mathbf{k}_i$. Equation 3.49 can be rewritten using the scaled potential $U(\mathbf{R}) = 2\mu V(\mathbf{R})/\hbar^2$ as

$$\left[\nabla^2 + k^2 - U(\mathbf{R}) \right] \psi(\mathbf{R}) = 0. \quad (3.50)$$

For potentials $U(\mathbf{R})$ vanishing faster than $1/R$ for large R values, the scattering wave function satisfies the Schrödinger equation for a free particle

$$\left[\nabla^2 + k^2 \right] \psi(\mathbf{R}) = 0. \quad (3.51)$$

In general, the wave function at large distances is expressed as the superposition of the incident wave function $\psi_{\text{in}}(\mathbf{R})$ and the scattered wave function $\psi_{\text{sc}}(\mathbf{R})$,

$$\psi(\mathbf{R}) \underset{R \rightarrow \infty}{\sim} \psi_{\text{in}}(\mathbf{R}) + \psi_{\text{sc}}(\mathbf{R}). \quad (3.52)$$

The function ψ_{in} is represented by a plane wave traveling along the internuclear axis Z with momentum $\mathbf{k}_i$,

$$\psi_{\text{in}}(\mathbf{R}) = e^{i\mathbf{k}_i \mathbf{R}} \equiv A e^{ik_i Z}, \quad (3.53)$$

where A is a normalization factor. The function ψ_{sc} is written as an outgoing spherical wave

$$\psi_{\text{sc}}(\mathbf{R}) = A f(k_i, \theta, \phi) \frac{e^{ik_i r}}{R}, \quad (3.54)$$

where $f(k_i, \theta, \phi)$ is the scattering amplitude depending on the energy and direction of $\mathbf{R}$. Thus, the scattering wave function must satisfy the asymptotic boundary condition

$$\psi(\mathbf{R}) \underset{R \rightarrow \infty}{\sim} A \left[e^{ikZ} + f(k, \theta, \phi) \frac{e^{ikR}}{R} \right]. \quad (3.55)$$

The current of probability density $\mathbf{j}$ is defined as

$$\mathbf{j} = \frac{\hbar}{2\mu i} \left[\psi^*(R) (\nabla \psi(R)) - (\nabla \psi^*(R)) \psi(R) \right]. \quad (3.56)$$

At large distances for the flux through a spherical surface, only the radial component of $\mathbf{j}$ contributes,

$$\mathbf{j} \cdot \hat{\mathbf{R}} \equiv j^R = \frac{\hbar}{2\mu i} \left[\psi^*(R) \left(\frac{\partial}{\partial R} \psi(R) \right) - \left(\frac{\partial}{\partial R} \psi^*(R) \right) \psi(R) \right], \quad (3.57)$$

where $\hat{\mathbf{R}} = \mathbf{R}/R$ is the radial unit vector. The scattered radial current reads as

$$\begin{aligned} j_{\text{sc}}^R &= \frac{i\hbar}{2\mu} \left[\psi_{\text{sc}}^*(R) \frac{\partial \psi_{\text{sc}}(R)}{\partial R} - \psi_{\text{sc}}(R) \frac{\partial \psi_{\text{sc}}^*(R)}{\partial R} \right] \\ &= \frac{\hbar k_i}{\mu} |A|^2 |f(k_i, \theta, \phi)|^2 \frac{1}{R^2}, \end{aligned} \quad (3.58)$$

and the incident current in the Z -direction

$$j_{\text{in}}^R = \frac{\hbar k}{\mu} |A|^2. \quad (3.59)$$

The incoming flux through the unit area is proportional to j_{in}^R , while the number of scattered particles in the $d\Omega$ solid angle in unit time is proportional to $j_{\text{sc}}^R d\Omega$. The differential cross section is the ratio of these two currents,

$$\sigma(\theta, \phi) = \frac{j_{\text{sc}}^R R^2 d\Omega}{j_{\text{in}}^R d\Omega} = |f(k_i, \theta, \phi)|^2. \quad (3.60)$$

This equation expresses the relationship between the cross section and the wave functions through the scattering amplitude.

3.6.2 Partial wave expansion

A very common situation is the scattering of a particle by a central (or spherically symmetric) potential $V(R)$, thus conserving the total angular momentum $\mathbf{L}$. In this case the Hamiltonian commutes with the operators $\hat{L}^2$ and $\hat{L}_z$, and the Schrödinger equation is separable in spherical coordinates. Since the incident direction of the particle coincides with the Z -axis, the wave function, the scattering amplitude, and the differential cross section are independent of the azimuthal angle ϕ . Therefore, the scattering wave function can be expanded in a series of Legendre polynomials

$$\psi(k_i, R, \theta) = \sum_{\ell=0}^{\infty} \mathcal{R}_{\ell}(k_i, R) P_{\ell}(\cos \theta). \quad (3.61)$$

where the index ℓ is the quantum number associated to $\mathbf{L}$. The radial wave functions, $\mathcal{R}_{\ell}(k_i, R)$, satisfies the Schrödinger equation

$$\left[\frac{d^2}{dR^2} + \frac{2}{R} \frac{d}{dR} - \frac{\ell(\ell+1)}{R^2} - U(R) + k_i^2 \right] \mathcal{R}_{\ell}(k_i, R) = 0, \quad (3.62)$$

where $U(R)$ is defined in Eq. 3.50. This equation can be simplified by introducing the function $u_{\ell}(k_i, R) = R \times \mathcal{R}_{\ell}(k_i, R)$,

$$\left[\frac{d^2}{dR^2} - \frac{\ell(\ell+1)}{R^2} - U(R) + k_i^2 \right] u_{\ell}(k_i, R) = 0. \quad (3.63)$$

The solutions can be written as a power series

$$u_{\ell}(k_i, R) = \sum_{n=0}^{\infty} a_n R^n. \quad (3.64)$$

Equation 3.63 admits two linearly independent solutions: one with a regular behavior at the origin

$$u_{\ell}(k_i, R) \underset{R \rightarrow 0}{\sim} R^{\ell+1}, \quad (3.65)$$

and the other which is irregular at the origin

$$u_\ell(k_i, R) \underset{R \rightarrow 0}{\sim} R^{-\ell}. \quad (3.66)$$

The physical solution of Eq. 3.62 must be regular for $R = 0$, so that $\mathcal{R}_\ell(k_i, R) \sim R^\ell$ when $R \rightarrow 0$.

The long-range behavior of $\mathcal{R}_\ell(k_i, R)$ is determined assuming that the rescaled potential $U(R)$ vanishes in a region $R > R_0$. Equation 3.62 reduces to a free particle equation which is conveniently rewritten using a new variable $\rho = k_i R$,

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2} \right) \right] \mathcal{R}_\ell(\rho) = 0, \quad (3.67)$$

known as the spherical Bessel differential equation. The general solution is a linear combination of the spherical Bessel function $j_\ell(\rho)$ and the spherical Neumann function $n_\ell(\rho)$

$$j_\ell(\rho) = \left(\frac{\pi}{2\rho} \right)^{1/2} \mathcal{J}_{\ell+1/2}(\rho) \quad (3.68)$$

$$n_\ell(\rho) = (-1)^{\ell+1} \left(\frac{\pi}{2\rho} \right)^{1/2} \mathcal{J}_{-\ell-1/2}(\rho), \quad (3.69)$$

where $\mathcal{J}_{\ell+1/2}(\rho)$ is the Bessel function of half-integer order.

The long-range behavior of $j_\ell(\rho)$ and $n_\ell(\rho)$ is

$$j_\ell(\rho) \underset{\rho \rightarrow \infty}{\sim} \frac{1}{\rho} \sin(\rho - \ell\pi/2), \quad (3.70)$$

$$n_\ell(\rho) \underset{\rho \rightarrow \infty}{\sim} -\frac{1}{\rho} \cos(\rho - \ell\pi/2). \quad (3.71)$$

At large distances $R > R_0$, $\mathcal{R}_\ell(\rho)$ is written as a linear combination of Bessel functions with coefficients B_ℓ and C_ℓ depending on k_i

$$\mathcal{R}_\ell(\rho) = \frac{u_\ell(\rho)}{R} = B_\ell(k_i)j_\ell(\rho) + C_\ell(k_i)n_\ell(\rho). \quad (3.72)$$

The asymptotic form of $\mathcal{R}_\ell(\rho)$ is

$$\mathcal{R}_\ell(\rho) \underset{\rho \rightarrow \infty}{\sim} B_\ell(k_i) \frac{\sin(\rho - \ell\pi/2)}{\rho} - C_\ell(k_i) \frac{\cos(\rho - \ell\pi/2)}{\rho}. \quad (3.73)$$

Since the $\sin$ and $\cos$ terms in Eq. 3.73 have the same argument, it is convenient to rewrite their linear combination as a single $\sin$ function with a phase shift

$$\mathcal{R}_\ell(\rho) \underset{\rho \rightarrow \infty}{\sim} \frac{A_\ell(k_i)}{\rho} \sin(\rho - \ell\pi/2 + \delta_\ell(k_i)). \quad (3.74)$$

Using the trigonometrical identity $\sin(\alpha + \beta) = \sin \alpha \cos \beta + \cos \alpha \sin \beta$ with the notation $\alpha = \rho - \ell\pi/2$ and $\beta = \delta_\ell$, the Eq. 3.74 becomes

$$\mathcal{R}_\ell(\rho) \underset{\rho \rightarrow \infty}{\sim} \frac{A_\ell(k_i)}{\rho} (\cos \delta_\ell \sin(\rho - \ell\pi/2) + \sin \delta_\ell \cos(\rho - \ell\pi/2)). \quad (3.75)$$

Comparing Eq.3.73 and Eq.3.75, one can identify $B_\ell(k_i) = A_\ell(k_i) \cos \delta_\ell(k_i)$ and $-C_\ell(k_i) = A_\ell(k_i) \sin \delta_\ell(k_i)$. Defining the phase shift $\delta_\ell(k_i)$ as

$$\tan \delta_\ell(k_i) = -C_\ell(k_i)/B_\ell(k_i) \quad (3.76)$$

and the normalization function as $A_\ell(k_i) = \sqrt{B_\ell^2(k_i) + C_\ell^2(k_i)}$ the desired form is achievable. We see that the presence of potential $U(R)$ induces a phase shift $\delta_\ell(k_i)$ on the wave function compared to the free wave function. The overall normalization $A_\ell(k_i)$ is arbitrary and does not affect the phase shift.

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{A_\ell(k_i)}{k_i R} \sin [k_i R - \ell\pi/2 + \delta_\ell(k_i)]. \quad (3.77)$$

Since $A_\ell(k_i)$ can be arbitrary, a convenient choice is $A_\ell(k_i) = -2ie^{i\delta_\ell(k_i)}$. In this manner, the radial wave function in the asymptotic region is

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{A_\ell(k_i)}{k_i R} \sin [k_i R - \ell\pi/2 + \delta_\ell(k_i)] \quad (3.78)$$

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{-2ie^{i\delta_\ell(k_i)} \left(e^{i(kR - \ell\pi/2 + \delta_\ell)} - e^{-i(kR - \ell\pi/2 + \delta_\ell)} \right)}{2ik_i R} \quad (3.79)$$

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{e^{-i(kR - \ell\pi/2)} - e^{i(kR - \ell\pi/2)}}{k_i R} e^{2i\delta_\ell} \quad (3.80)$$

We can define the $S_\ell(k_i) = e^{2i\delta_\ell(k_i)}$ as a single element of the scattering matrix or $\mathcal{S}$ matrix.

Another useful choice of $A_\ell(k_i)$ is possible in order to obtain the the scattering amplitude $f(k_i, \theta)$. Using Eq. 3.55, the plane wave can be expanded in terms of Legendre polynomials

$$Ae^{ik_i Z} = Ae^{ik_i R \cos \theta} = A \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) j_\ell(k_i R) P_\ell(\cos \theta). \quad (3.81)$$

thus Eq.3.55 becomes

$$\begin{aligned} \psi(\mathbf{r}) &\underset{r \rightarrow \infty}{\sim} A \left[\sum_{\ell=0}^{\infty} i^\ell (2\ell+1) \frac{\sin(k_i r - \ell\pi/2)}{k_i r} P_\ell(\cos \theta) + f(k_i, \theta) \frac{e^{ik_i r}}{r} \right] = \\ &= A \left\{ \frac{e^{ik_i r}}{r} \left[f(k_i, \theta) - \sum_{\ell=0}^{\infty} \left(\frac{i}{2k_i} \right) (2\ell+1) P_\ell(\cos \theta) \right] + \right. \\ &\quad \left. + \frac{e^{-ik_i r}}{r} \left[\sum_{\ell=0}^{\infty} (-1)^\ell \left(\frac{i}{2k_i} \right) (2\ell+1) P_\ell(\cos \theta) \right] \right\}, \end{aligned} \quad (3.82)$$

where we used the asymptotic form of $j_\ell(kr)$ and the identity

$$\sin(k_i r - \ell\pi/2) = \frac{i^{-\ell} e^{ik_i r} - i^\ell e^{-ik_i r}}{2i} \quad (3.83)$$

On the other hand, the asymptotic form of $\psi(\mathbf{r})$, based on Eq. 3.61 and 3.77, can be written as

$$\psi(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} \sum_{\ell=0}^{\infty} A_{\ell}(k) P_{\ell}(\cos \theta) \frac{e^{i(kr - \ell\pi/2 + \delta_{\ell}(k))} - e^{-i(kr - \ell\pi/2 + \delta_{\ell}(k))}}{2ikr}. \quad (3.84)$$

Combining the two equations (Eq. 3.82 and Eq. 3.84) we obtain the normalization coefficient for each partial wave

$$A_{\ell}(k_i) = A i^{\ell} (2\ell + 1) e^{i\delta_{\ell}(k_i)}, \quad (3.85)$$

and then the partial wave expansion of the scattering amplitude

$$f(k_i, \theta) = \frac{1}{2ik_i} \sum_{\ell=0}^{\infty} (2\ell + 1) (e^{2i\delta_{\ell}} - 1) P_{\ell}(\cos \theta), \quad (3.86)$$

or in a more natural form, using the definition of $\mathcal{S}$ matrix

$$f(k_i, \theta) = \frac{1}{2ik_i} \sum_{\ell=0}^{\infty} (2\ell + 1) (S_{\ell}(k_i) - 1) P_{\ell}(\cos \theta), \quad (3.87)$$

and finally the differential cross section

$$\begin{aligned} d\sigma(k, \theta) &= \frac{1}{k_i^2} \sum_{\ell=0}^{\infty} \sum_{\ell'=0}^{\infty} (2\ell + 1)(2\ell' + 1) e^{i[\delta_{\ell}(k_i) - \delta_{\ell'}(k_i)]} \times \\ &\times \sin(\delta_{\ell}(k_i)) \sin(\delta_{\ell'}(k_i)) P_{\ell}(\cos \theta) P_{\ell'}(\cos \theta). \end{aligned} \quad (3.88)$$

It is independent of the A normalization factor, since it cancels out during the matching of Eq. 3.82 and Eq. 3.84. The total cross section is obtained by integrating the differential cross section over the solid angle

$$\begin{aligned} \sigma(k_i) &= 2\pi \int_0^{\pi} d\sigma(k_i, \theta) \sin \theta d\theta \\ &= \frac{4\pi}{k_i^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_{\ell}(k_i) \\ &= \sum_{\ell=0}^{\infty} \sigma_{\ell}(k_i) \end{aligned} \quad (3.89)$$

The partial cross section $\sigma_{\ell}(k_i)$ reaches a maximum value of $4\pi(2\ell + 1)/k_i^2$. In the atom-ion experiment, the ongoing goal is to reach the s -wave regime ($\ell = 0$), where the maximal cross section is $4\pi/k_i^2$.

A third possible parametrization of $A_{\ell}(k_i)$ is when $A_{\ell}(k_i) = [\cos \delta_{\ell}(k_i)]^{-1}$. Us-

ing this definition the radial wave function in the asymptotic limit is

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{A_\ell(k_i)}{k_i R} \sin[k_i R - \ell\pi/2 + \delta_\ell(k_i)] \quad (3.90)$$

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{1}{k_i R \cos \delta_\ell(k_i)} \left[\sin(k_i R - \ell\pi/2) \cos \delta_\ell(k_i) + \right. \\ \left. + \cos(k_i R - \ell\pi/2) \sin \delta_\ell(k_i) \right] \quad (3.91)$$

$$\mathcal{R}_\ell(k_i, R) \underset{R \rightarrow \infty}{\sim} \frac{1}{k_i R} [\sin(k_i R - \ell\pi/2) + K_\ell(k_i) \cos(k_i R - \ell\pi/2)] \quad (3.92)$$

where we defined $K_\ell(k_i) = \tan \delta_\ell(k_i)$ and it is called reaction matrix. The relation between reaction and scattering matrix is

$$S_\ell(k_i) = \frac{1 + iK_\ell(k_i)}{1 - iK_\ell(k_i)} \quad (3.93)$$

3.6.3 Coupled-channel equations

Up to now, we have recalled the basics of scattering theory by considering only a single state, commonly referred to as a scattering channel, or channel, in short. In general, a collisional event induces transformations of the system via inelastic or reactive processes (see the introduction of this Section.) In other words, a collision involves several channels, as illustrated in Fig.3.9, which are coupled with each other via specific terms in the Hamiltonian of the system. A collisional channel is asymptotically well-defined by its momentum $\mathbf{k}$ and appropriate quantum numbers specific to the considered system. A channel is *open* (resp. *closed*) if its asymptotic energy is smaller (resp. larger) than the one of the incoming channel including the initial collision energy.

My work focuses on the description of ion-atom collisions. As discussed in Chapter 2, several processes might occur such as charge exchange or excitation exchange. It means that the entrance channel, described by a given adiabatic (or Born-Oppenheimer) state, is actually coupled to other BO states through non-adiabatic couplings, which are induced, for example, by radial or spin-orbit couplings (see Section 3.1). The Schrödinger equation of Eq.3.49, which was written for a single PEC, can be generalized to the so-called coupled-channel form for a collision energy E as

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{\hbar^2}{2\mu R^2} \hat{L}^2 + \hat{V}(R) \right] \Psi(R) = E \Psi(R) \quad (3.94)$$

where the wave function Ψ is expanded on a finite set of BO states $|\Phi_\alpha\rangle$ as

$$\Psi(R, r) = \sum_{\alpha=1}^N \frac{1}{R} F_\alpha(R) |\Phi_\alpha\rangle, \quad (3.95)$$

and the $\hat{V}$ operator is now expressed as a matrix with R -dependent diagonal elements

$$V_{\alpha\alpha} \equiv V_\alpha = \langle \Phi_\alpha | \hat{V} | \Phi_\alpha \rangle \quad (3.96)$$

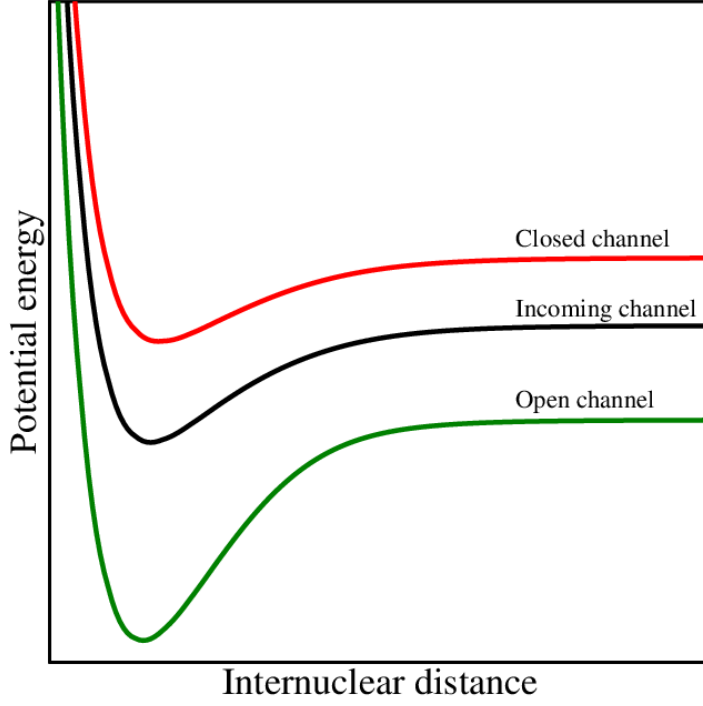


Figure 3.9: Schematic illustration of open and closed scattering channels with respect to an incoming channel. Each channel is represented by a single potential energy curve.

being the PECs of the BO states α , and R -dependent off-diagonal elements

$$V_{\beta\alpha} = \langle \Phi_\beta | \hat{V} | \Phi_\alpha \rangle \quad (3.97)$$

representing the non-adiabatic couplings between BO states α and β . Substituting 3.95 in 3.94 and projecting the equation on state $|\Phi_\beta\rangle$ we obtain a set of radial coupled equations of the generic form

$$\left[\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} - \frac{\ell(\ell+1)}{R^2} \right) + V_{\beta\beta}(R) + E \right] F_\beta(R) = \sum_{\alpha} V_{\beta\alpha}(R) F_\alpha(R). \quad (3.98)$$

As all interactions are assumed to vanish for $R \rightarrow \infty$, the PEC of each state $|\Phi_\alpha\rangle$ reaches its asymptotic value ϵ_α . If the entrance channel is a given BO state $|\Phi_i\rangle$,

its asymptotic energy ϵ_i can be considered as the origin of energy, to which the collision energy E is added. Therefore, a channel α is open if $\epsilon_\alpha < \epsilon_i + E$. In the next subsection, we present the numerical approach that we chose to solve this system of coupled Schrödinger equations.

3.6.4 Solving the coupled channel equations: the log-derivative algorithm

To solve the coupled Schrödinger equations, we use the robust approach proposed by Johnson [119], the log-derivative algorithm, that we implemented in a numerical code developed in our group in Orsay. This algorithm offers several advantages for coupled-channel scattering calculations compared to other ones. It is simple to include in a numerical code, treats the closed channels without special numerical difficulties, and allows the propagation step size to be modified easily. In addition, the method is self-starting, meaning that the propagation can be initiated directly from the inner boundary condition without constructing the wavefunction amplitudes at several initial grid points. It can also be started inside the classically forbidden region without introducing numerical instabilities. Moreover, Johnson showed that the method can be computationally more efficient than the matrix Numerov method for calculating the S -matrix [119,120].

We briefly recall below the main steps of the method. The system of coupled differential equations illustrated by Eq. 3.98 is first recast in compact matrix form (after global multiplication by $2\mu/\hbar^2$)

$$[D^2 + \mathcal{W}] \mathbf{F} = 0, \quad (3.99)$$

where D^2 is the diagonal matrix associated with the kinetic energy operator

$$D^2 = \frac{d^2}{dR^2} \mathbf{I}, \quad (3.100)$$

$\mathbf{I}$ being the identity matrix. The square matrix $\mathcal{W}$ includes the rescaled total energy, centrifugal, and interaction terms

$$\mathcal{W} = \left[-\frac{\ell(\ell+1)}{R^2} + k^2 \right] \mathbf{I} - \mathbf{U}, \quad (3.101)$$

where $\mathbf{U} = (2\mu/\hbar^2)\mathbf{V}$. Equation 3.99 admits N linearly-independent solutions represented by the square matrix $\mathbf{F}$. Each column of $\mathbf{F}$ represent one independent solution of the coupled-channel equations, expressed in the BO states (Eq. 3.95). To solve the system of coupled second-order linear differential equations (Eq. 3.99), we first transform it into a system of first-order nonlinear equations by inserting the logarithmic derivative (log-derivative in short) of the $F_\alpha(R)$ functions

$$Y_\alpha(R) = \frac{d}{dR} \ln F_\alpha(R), \quad (3.102)$$

leading to the log-derivative matrix $\mathbf{Y}$

$$\mathbf{Y} = \mathbf{F}' \mathbf{F}^{-1}. \quad (3.103)$$

This allows to rewrite Eq. 3.99 in the form of a matrix Riccati equation

$$\mathbf{Y}' + \mathbf{Y}^2 + \mathbf{W} = 0. \quad (3.104)$$

A direct numerical integration of this Riccati equation is problematic because the log-derivative matrix may diverge at nodes of the wave function. The Johnson algorithm avoids this difficulty.

The radial interval $[R_{\min}, R_{\max}]$ is discretized on a uniform grid,

$$R_n = R_{\min} + nh, \quad n = 0, \dots, N, \quad (3.105)$$

where h is the radial step size. The number of grid points is chosen to be odd, consistent with the Simpson-type quadrature used in the Johnson recurrence. In scattering problems, a usual boundary condition is $\mathbf{F}(R_{\min}) = 0$, while its derivative can be chosen arbitrarily, provided that the resulting solutions remain linearly independent. A convenient choice is $\mathbf{F}'(R_{\min}) = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix. Therefore, the log-derivative matrix formally diverges at this boundary. Following Johnson [119], this condition is implemented numerically by choosing a large diagonal initial value $\mathbf{Y}(R_{\min}) = 10^{20}\mathbf{I}$. Since the interaction matrix $\mathbf{W}$ is real and symmetric and the initial log-derivative matrix $\mathbf{Y}(R_{\min})$ is diagonal, the propagated $\mathbf{Y}(R)$ remains symmetric up to the numerical precision. The Riccati equation is then propagated outward using Johnson's fixed-step recurrence relation. The method uses Simpson-type quadrature weights on the radial grid. The system of Eq. 3.104 is solved using a recurrence algorithm to determine the value of $\mathbf{Y}_n \equiv \mathbf{Y}(R_n)$,

$$\mathbf{Y}_n = (\mathbf{I} + h\mathbf{Y}_{n-1})^{-1}\mathbf{Y}_{n-1} - (h/3)w_n\mathbf{u}_n, \quad (3.106)$$

where the matrices $\mathbf{u}_n$ are local effective interaction matrices entering the Johnson propagator. Their different forms at even and odd grid points arise from the Simpson-type discretization used in the recurrence relation.

$$\mathbf{u}_n = \begin{cases} \mathbf{W}(R_n) & n = 0, 2, 4, \dots, N \\ [\mathbf{I} + (h^2/6)\mathbf{W}(R_n)]^{-1}\mathbf{W}(R_n) & n = 1, 3, 5, \dots, N-1 \end{cases} \quad (3.107)$$

and w_n weights are the same as those appearing in the Simpson's integration rule assigned to every grid point

$$w_n = \begin{cases} 1 & n = 0, N \\ 4 & n = 1, 3, 5, \dots, N-1 \\ 2 & n = 2, 4, 6, \dots, N-2. \end{cases} \quad (3.108)$$

The truncation error of the method scales as h^4 , as discussed in Ref. [119]. As emphasized in [119], recurrence is designed to provide the log-derivative matrix at the final matching point $R_{\max}$. This is sufficient for scattering calculations, since the $\mathbf{K}$ and $\mathbf{S}$ matrices are extracted by matching the propagated solution to the asymptotic channel functions at $R_{\max}$.

3.6.5 Scattering matrix

Along the lines similar to Section 3.6.2, the matrix of solutions $\mathbf{F}$ can be written in the asymptotic region ($R \rightarrow \infty$) as

$$\mathbf{F} \underset{R \rightarrow \infty}{=} \mathbf{J} + \mathbf{N}\mathbf{K} \quad (3.109)$$

where now appears the reaction matrix $\mathbf{K}$ containing all the information about the scattering process, which has the block structure incorporating the open (index "o") and closed (index "c") channels

$$\mathbf{K} = \begin{pmatrix} \mathbf{K}_{oo} & \mathbf{K}_{oc} \\ \mathbf{K}_{co} & \mathbf{K}_{cc} \end{pmatrix}. \quad (3.110)$$

This expression illustrates how closed channels have an influence on open channels, through the off-diagonal blocks $\mathbf{K}_{oc}$ and $\mathbf{K}_{co}$. The diagonal matrices $\mathbf{J}$ and $\mathbf{N}$, with elements depending on the nature of channels:

- Open channels: the elements are Ricatti-Bessel functions

$$\mathbf{J}_{ij}(R) = \delta_{ij} k_j^{-1/2} j_{\ell_j}(k_j R), \quad (3.111)$$

$$\mathbf{N}_{ij}(R) = \delta_{ij} k_j^{-1/2} n_{\ell_j}(k_j R). \quad (3.112)$$

- Closed channels: the elements are modified spherical Bessel functions

$$\mathbf{J}_{ij}(R) = \delta_{ij} k_j^{1/2} I_{\ell_j+1/2}(k_j R) \quad (3.113)$$

$$\mathbf{N}_{ij}(R) = \delta_{ij} k_j^{1/2} K_{\ell_j+1/2}(k_j R) \quad (3.114)$$

The reaction matrix in the asymptotic region, based on Eq. 3.103 and 3.109, reads as

$$\mathbf{K} = [\mathbf{Y}(R)\mathbf{N}(R) - \mathbf{N}'(R)]^{-1} [\mathbf{Y}(R)\mathbf{J}(R) - \mathbf{J}'(R)] \quad (3.115)$$

The unitary scattering matrix $\mathbf{S}$ we defined as

$$\mathbf{S} = \frac{\mathbf{1} + i\mathbf{K}_{oo}}{\mathbf{1} - i\mathbf{K}_{oo}}, \quad (3.116)$$

considering only the open-open block of the reaction matrix, since the contribution of possible resonances are negligible. The quantity $|S_{\alpha,\beta}|^2$ is the probability for a system initially in channel α to scatter into channel β . In our investigations, we will model scattering processes in the space-fixed frame in the absence of external fields, where the total angular momentum J and parity p are good quantum numbers. Therefore, the partial cross section for the inelastic process from channel α to β , for a given total angular momentum J and parity p , and after averaging over all projections of J , is given by

$$\sigma(\beta \leftarrow \alpha, J, p, k_\alpha) = \frac{\pi}{k_\alpha^2} (2J+1) |S_{\alpha,\beta}^{J,p}|^2, \quad (3.117)$$

The total inelastic cross section for a given parity is obtained by summing partial cross sections for all values of J which energetically allowed in the entrance channel

$$\sigma(\beta \leftarrow \alpha, p, k_\alpha) = \sum_J \sigma(\beta \leftarrow \alpha, J, p, k_\alpha). \quad (3.118)$$

In the calculations, the two parity cases are treated separately, thus the unitarity of the associated $\mathcal{S}$ matrices is assured independently. Therefore, the total state-to-state inelastic cross section reads as

$$\sigma(\beta \leftarrow \alpha, k_\alpha) = \frac{\sigma(\beta \leftarrow \alpha, p = 1, k_\alpha) + \sigma(\beta \leftarrow \alpha, p = -1, k_\alpha)}{2}. \quad (3.119)$$

To compare our calculations to experimental observations, rate coefficients are determined,

$$K(\beta \leftarrow \alpha, k_\alpha) = \frac{\hbar k_\alpha}{\mu} \sigma(\beta \leftarrow \alpha, k_\alpha). \quad (3.120)$$

Assuming a Maxwell-Boltzmann distribution of collision energies, thermalized rate coefficients at an effective temperature T_{eff} are obtained by averaging the energy-dependent rate coefficient over the corresponding collision-energy distribution,

$$K(T_{\text{eff}}; f) = \frac{2}{\sqrt{\pi}(k_B T_{\text{eff}})^{3/2}} \times \int_0^\infty K(E; f) \sqrt{E} e^{-E/k_B T_{\text{eff}}} dE, \quad (3.121)$$

where the effective temperature in the center-of-mass frame [38] is given by

$$T_{\text{eff}} = \frac{m_A T_{B^+} + m_{B^+} T_A}{m_A + m_{B^+}}. \quad (3.122)$$

The presented quantum scattering model for the description of ion-atom collisions, considering all the relevant channels, will be referred to later in the thesis as the Multi-Channel Quantum Scattering calculation, MCQS.

Chapter 4

Frame transformation: from body-fixed to space-fixed frame

The developments presented in Chapter 3, while being general, assume that the diatomic molecule of interest is described in its own frame, referred to as the body-fixed (BF) frame. This choice is very convenient to describe the electronic states of the molecule through potential energy curves (PECs) depending of the internal coordinate R along the molecular axis. But the molecule rotates in the lab frame, referred to as the space-fixed (SF) frame, so that it is submitted to Coriolis effect. In other words, the angular momentum ℓ associated to the rotation of the molecule in the SF frame can be coupled to the electronic angular momentum and spin which are well-defined in the BF frame. In many ultracold atom-ion collisions involving ground state colliding partners, the electronic structure is relatively simple, and the ℓ can be used to characterize the relative motion of the colliding partners. In the systems considered in this thesis, however, the alkaline-earth ion is prepared in a metastable D state carrying a non-zero electronic angular momentum j . Consequently, the mechanical rotation ℓ and the electronic angular momentum j must be coupled to form the total angular momentum J . To properly account for this angular momentum coupling in the scattering calculations, the molecular states defined in the BF frame must be expressed in the SF frame. This is the purpose of the so-called "frame transformation" presented in this Chapter. We first define the total parity of the molecular state which is an additional "good" quantum number of the system, and then the mathematical formalism based on rotations allowing to transform quantum numbers valid in the BF frame into quantum numbers valid in the SF frame.

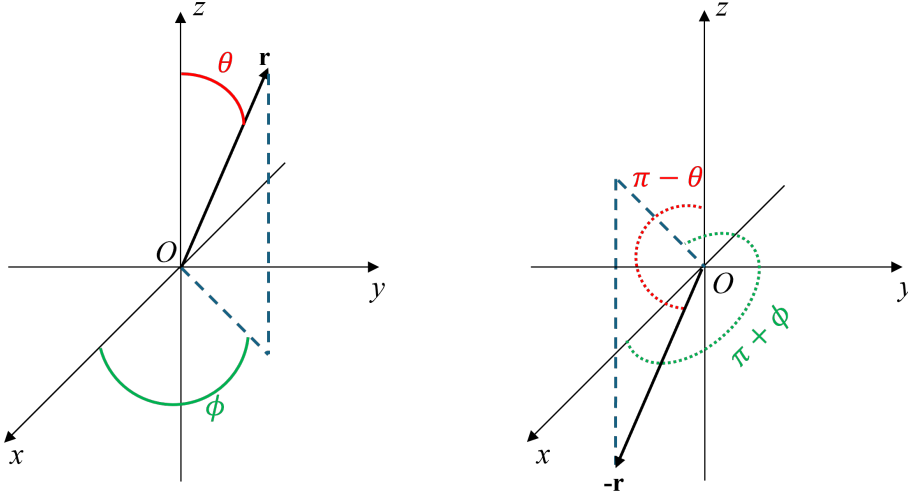


Figure 4.1: The action of the parity operator on the position vector of a single electron. In spherical coordinates (r, θ, ϕ) , it corresponds to the transformations $r \rightarrow r, \theta \rightarrow \pi - \theta$ and $\phi \rightarrow \pi + \phi$.

4.1 Parity

The parity is associated with spatial inversion. The parity operator $\hat{P}$ acts only on the spatial coordinates by inverting the sign $\mathbf{r} \rightarrow -\mathbf{r}$. For a single-particle wave function $\Psi(\mathbf{r})$, the action of the parity operator is defined as

$$\hat{P}\Psi(\mathbf{r}) = \Psi(-\mathbf{r}). \quad (4.1)$$

The parity operator is linear, unitary, Hermitian and satisfies the following relation

$$\hat{P}^2 = \hat{I}, \quad (4.2)$$

where $\hat{I}$ is the identity operator. This implies that the eigenvalues of the parity operator are $p = \pm 1$. If the particle wave function $\Psi(\mathbf{r})$ is an eigenfunction of the parity operator $\hat{P}$, then

$$\hat{P}\Psi(\mathbf{r}) = p\Psi(\mathbf{r}), \quad (4.3)$$

with $p = +1$ corresponding to even parity, and $p = -1$ to odd parity. Consequently,

$$\Psi(-\mathbf{r}) = \begin{cases} +\Psi(\mathbf{r}) & \text{even parity} \\ -\Psi(\mathbf{r}) & \text{odd parity.} \end{cases} \quad (4.4)$$

Assuming that the wave function of a single electron in an atom is characterized by quantum numbers (n, l, m_l) , the wave function can be written as

$$\Psi_{n,l,m_l}(\mathbf{r}, \theta, \phi) = R_{n,l}(r)P_{l,m_l}(\cos \theta)e^{im_l\phi}, \quad (4.5)$$

where n is the principal quantum number, l is the orbital angular momentum quantum number, m_l its projection, and $P_{l,m_l}(\cos \theta)$ is a Legendre polynomial. Due to the spatial inversion, $\theta \rightarrow \pi - \theta$ and $\phi \rightarrow \pi + \phi$, see Fig. 4.1 the angular dependent parts of the wave function becomes

$$\begin{aligned} P_{l,m_l}(-\cos \theta) &= (-1)^{l-m_l} P_{l,m_l}(\cos \theta) \\ e^{im_l(\pi+\phi)} &= (-1)^{m_l} e^{im_l\phi}. \end{aligned} \quad (4.6)$$

The effect of the parity operator $\hat{P}$ on the wave function is

$$\hat{P}\Psi_{n,l,m_l}(\mathbf{r}, \theta, \phi) = (-1)^l \Psi_{n,l,m_l}(\mathbf{r}, \theta, \phi). \quad (4.7)$$

Hence, the parity of the wave function of a single electron in an atom is

$$P = (-1)^l. \quad (4.8)$$

If the atom has many electrons, then the parity is

$$P = (-1)^{\sum_{i=1}^n l_i}, \quad (4.9)$$

where n is the number of electrons.

In this work, I focus on diatomic molecules rotating in the space-fixed frame with a rotational angular momentum ℓ with quantum number ℓ . The inversion operation will also act on the spatial coordinates of the nuclei, inducing a parity of $(-1)^\ell$, leading to a total parity of the rotating diatomic molecule of

$$P = (-1)^{l_A+l_B+\ell}. \quad (4.10)$$

4.2 Euler rotations and Wigner functions in diatomic molecule

To describe the rotational degree of freedom of a diatomic molecule, we introduce the BF coordinate system (X_{BF}, Y_{BF}, Z_{BF}) , where the Z_{BF} axis coincides with the internuclear axis. The orientation of the BF frame relative to the SF frame, (X_{SF}, Y_{SF}, Z_{SF}) , is specified by the Euler angles (α, β, γ) . The CM motion is eliminated by a simple translation leading to the CM frame (X_{CM}, Y_{CM}, Z_{CM}) , which can then be rotated to the BF frame (X_{BF}, Y_{BF}, Z_{BF}) , through the following steps:

- Rotate the Z_{CM} axis with an angle α until the Y_{CM} axis becomes perpendicular to the molecular axis, leading to the frame $(X'_{CM}, Y'_{CM}, Z'_{CM})$.
- Rotate the Y'_{CM} axis with an angle β until the Z'_{CM} axis aligns with the molecular axis, leading to the frame (X_{BF}, Y_{BF}, Z_{BF}) .

The first rotation on the Z_{CM} axis is described by the $\mathbf{R}_z(\alpha, \beta, \gamma)$ rotation matrix,

$$\mathbf{R}_z(\alpha, \beta, \gamma) = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (4.11)$$

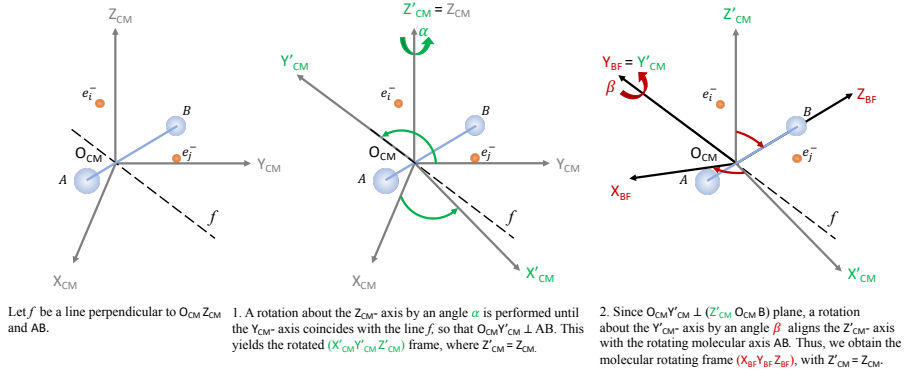


Figure 4.2: Illustration of the two-step rotation from the CM to the molecular rotating BF frame of reference, corresponding to transition from panel b) to panel c) of Fig. 3.1 (the change from panel a) to panel b) is obtained by a simply translation).

Then, the rotation on the Y'_{CM} is described by the rotation matrix $R_y(\alpha, \beta, \gamma)$

$$R_y(\alpha, \beta, \gamma) = \begin{pmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{pmatrix}. \quad (4.12)$$

In case of diatomic molecules, a third rotation is not necessary to fully determine the orientation of the molecule, *i.e.* $\gamma = 0$. Consequently, the full rotation matrix is

$$R(\alpha, \beta, 0) = R_z(\alpha, \beta, 0) R_y(\alpha, \beta, 0) = \begin{pmatrix} \cos \alpha \cos \beta & -\sin \alpha & \cos \alpha \sin \beta \\ \sin \alpha \cos \beta & \cos \alpha & \sin \alpha \sin \beta \\ -\sin \beta & 0 & \cos \beta \end{pmatrix}. \quad (4.13)$$

It is known that the angular momentum is a generator of rotation, thus a general rotation operator with angles (α, β, γ) angle in the frame (x, y, z) can be written as

$$\hat{R}(\alpha, \beta, \gamma) = e^{-i\alpha \hat{J}_z} e^{-i\beta \hat{J}_y} e^{-i\gamma \hat{J}_z}, \quad (4.14)$$

where $\hat{J}_z$, $\hat{J}_y$, and $\hat{J}_x$ are the components of the total angular momentum operator $\hat{J}$. The components satisfy the identity $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$.

The Wigner function D gives the matrix elements of the rotation operator in $|JM\rangle$ basis representation [121]. In this case, the Wigner function D with Euler angles (α, β, γ) is

$$\begin{aligned} D_{M'M}^J(\alpha, \beta, \gamma) &= \langle JM' | R(\alpha, \beta, \gamma) | JM \rangle \\ &= \langle JM' | e^{-i\alpha \hat{J}_z} e^{-i\beta \hat{J}_y} e^{-i\gamma \hat{J}_z} | JM \rangle, \end{aligned} \quad (4.15)$$

where M and M' are the projections of $\mathbf{J}$ on the molecular axis in BF frame of reference and on the Z-axis in SF frame of reference, and $M, M' = -J, \dots, +J$.

4.3 Transformation matrix

The state describing the collision between an atom and an ion is a continuum state of a diatomic molecular ion. For large interparticle separations, the wave function can be expanded, to a good approximation, in terms of the eigenstates of the separated atomic system, while for small separations, it is more conveniently expanded in the molecular Born–Oppenheimer electronic states. The aim is to determine the transformation between these two representations of the molecular states. The molecular basis $|\Lambda S \Sigma\rangle$ for Hund's case (a) states in the asymptotic region can be expanded on the basis of products of atomic states [122]

$$|\Lambda S \Sigma\rangle = \sum_{\Lambda_A, \Lambda_B} |l_A \Lambda_A\rangle |l_B \Lambda_B\rangle |S \Sigma\rangle \langle \Lambda_A \Lambda_B | \Lambda \rangle, \quad (4.16)$$

where $\Lambda = \Lambda_A + \Lambda_B$, and Λ_A, Λ_B are the quantum numbers for the projections on the molecular axis of $\mathbf{l}_A$ and $\mathbf{l}_B$, respectively. The coefficient $\langle \Lambda_A \Lambda_B | \Lambda \rangle$ combining the two atomic projections on the molecular one is 1, for cases where one of the angular momenta is zero. This will be the case in our study, since one of the colliding partners is in the ground state s , while the other partner is in the state s, p or d . In the coupled atomic basis, the molecular basis can be written as

$$\begin{aligned} |\Lambda S \Sigma\rangle &= \sum_{\Lambda_A, \Lambda_B} |l_A \Lambda_A\rangle |l_B \Lambda_B\rangle \sum_{\Sigma_A, \Sigma_B} C_{s_A \Sigma_A s_B \Sigma_B}^{S \Sigma} |s_A \Sigma_A\rangle |s_B \Sigma_B\rangle \\ &= \sum_{\substack{\Lambda_A, \Lambda_B \\ \Sigma_A, \Sigma_B}} C_{s_A \Sigma_A s_B \Sigma_B}^{S \Sigma} \sum_{j_A, \Omega_A} C_{l_A \Lambda_A s_A \Sigma_A}^{j_A \Omega_A} |(l_A s_A) j_A \Omega_A\rangle \times \\ &\times \sum_{j_B, \Omega_B} C_{l_B \Lambda_B s_B \Sigma_B}^{j_B \Omega_B} |(l_B s_B) j_B \Omega_B\rangle. \end{aligned} \quad (4.17)$$

The states $|j_A \Omega_A\rangle$ and $|j_B \Omega_B\rangle$ defined in the BF frame can be transformed to the SF frame by means of the Wigner function $D_{m_q \Omega_q}^q(\alpha \beta 0)$

$$|j_{A/B} \Omega_{A/B}\rangle = \sum_{m_j^{A/B}} |j_{A/B} m_j^{A/B}\rangle D_{m_j^{A/B} \Omega_{A/B}}^{j_{A/B}}(\alpha \beta 0), \quad (4.18)$$

where m_q and Ω_q are the quantum numbers related to the projection of the angular momentum $\mathbf{q}$ on a SF and on the molecular axis, respectively. The α, β angles are the Euler angles for the rotation between the SF and BF frames (Fig. 4.2). Using this transformation and expanding the product of two Wigner functions D with

the same arguments in a series of Wigner functions [113], Eq. 4.17 becomes

$$\begin{aligned}
|\Lambda S \Sigma\rangle &= \sum_{\substack{\Lambda_A, \Lambda_B \\ \Sigma_A, \Sigma_B}} \sum_{\substack{j_A, \Omega_A \\ j_B, \Omega_B}} \sum_{m_j^A, m_j^B} C_{s_A \Sigma_A s_B \Sigma_B}^{S \Sigma} C_{l_A \Lambda_A s_A \Sigma_A}^{j_A \Omega_A} C_{l_B \Lambda_B s_B \Sigma_B}^{j_B \Omega_B} \times \\
&\times D_{m_j^A \Omega_A}^{j_A} D_{m_j^B \Omega_B}^{j_B} |j_A m_j^A\rangle |j_B m_j^B\rangle \\
&= \sum_{\substack{\Lambda_A, \Lambda_B \\ \Sigma_A, \Sigma_B}} \sum_{\substack{j_A, \Omega_A \\ j_B, \Omega_B}} \sum_{m_j^A, m_j^B} C_{s_A \Sigma_A s_B \Sigma_B}^{S \Sigma} C_{l_A \Lambda_A s_A \Sigma_A}^{j_A \Omega_A} C_{l_B \Lambda_B s_B \Sigma_B}^{j_B \Omega_B} \times \\
&\times \sum_{\substack{j \\ m_j, \Omega}} C_{j_A m_j^A j_B m_j^B}^{j \Omega} D_{m_j \Omega}^j C_{j_A \Omega_A j_B \Omega_B}^{j \Omega} |(l_A s_A) j_A m_j^A\rangle |(l_B s_B) j_B m_j^B\rangle,
\end{aligned} \tag{4.19}$$

where, for simplicity, the argument of the Wigner functions is not written. For small internuclear distances, the symmetrized molecular basis can be given as

$$\begin{aligned}
|\Lambda S \Sigma \Omega J M p\rangle &= \frac{1}{\sqrt{2 - \delta_{\Lambda,0} \delta_{\Sigma,0}}} \sqrt{\frac{2J+1}{8\pi^2}} [D_{M\Omega}^{J*}(\alpha \beta 0) |\Lambda S \Sigma\rangle + \\
&+ (1 - \delta_{\Lambda,0} \delta_{\Sigma,0}) (-1)^{p+J-S+\sigma} D_{M-\Omega}^{J*}(\alpha \beta 0) |-\Lambda S -\Sigma\rangle],
\end{aligned} \tag{4.20}$$

where M is the quantum number of the projection of the total angular momenta $\mathbf{J}$ on a SF axis, $p = \pm 1$ is the parity eigenvalue, and $\sigma = 1$ for the electronic state Σ^- , and is zero for other symmetries. The term $D_{M\Omega}^{J*}(\alpha \beta 0) |\Lambda S \Sigma\rangle$ can be further expanded using Eq.4.19 and the properties of Wigner D -function regarding the product of two D functions and the relation with the spherical harmonics

$$\begin{aligned}
D_{M\Omega}^{J*}(\alpha \beta 0) |\Lambda S \Sigma\rangle &= \sum_{\substack{\Lambda_A, \Lambda_B \\ \Sigma_A, \Sigma_B}} \sum_{\substack{j_A, \Omega_A \\ j_B, \Omega_B}} \sum_{m_j^A, m_j^B} \sum_{\substack{j \\ m_j, \Omega}} \sum_{\ell, \mu} (-1)^{J-\ell-\Omega+\Sigma-S} \sqrt{\frac{2j_A+1}{2l_A+1}} \times \\
&\times \sqrt{\frac{2j_B+1}{2l_B+1}} C_{j_A m_j^A j_B m_j^B}^{j \Omega} C_{j m \ell -\mu}^{J M} C_{j -\Omega J l \Omega}^{\ell 0} \times \\
&\times C_{s_B \Sigma_B s_A \Sigma_A}^{S \Sigma} C_{j_A -\Omega_A s_A \Sigma_A}^{l_A \Lambda_A} C_{j_B -\Omega_B s_B \Sigma_B}^{l_B \Lambda_B} C_{j_B -\Omega_B j_A -\Omega_A}^{j -\Omega} \times \\
&\times |(l_A s_A) j_A m_j^A\rangle |(l_B s_B) j_B m_j^B\rangle Y_{\ell-\mu}(\beta, \alpha).
\end{aligned} \tag{4.21}$$

The products of four Clebsch–Gordan coefficients can be recast in terms of $9j$ symbols [113]

$$\begin{aligned}
\sum_{\beta \gamma \epsilon \varphi} C_{b \beta c \gamma}^{a \alpha} C_{e \epsilon f \varphi}^{d \delta} C_{e \epsilon b \beta}^{g \eta} C_{f \varphi c \gamma}^{j \mu} &= \sqrt{2a+1} \sqrt{2d+1} \sqrt{2g+1} \sqrt{2j+1} \times \\
&\times \sum_{k \kappa} C_{g \eta j \mu}^{k \kappa} C_{d \delta a \alpha}^{k \kappa} \begin{Bmatrix} c & b & a \\ f & e & d \\ j & g & k \end{Bmatrix}.
\end{aligned} \tag{4.22}$$

Thus the expression in Eq. 4.21 simplifies to

$$\begin{aligned}
D_{M\Omega}^{J*}(\alpha \beta 0) |\Lambda S \Sigma\rangle &= (-1)^{J-\Omega-S+\Sigma} \sum_{\Lambda_A, \Lambda_B} \sum_{j_A, j_B} \sum_{m_j^A, m_j^B} \sum_{j, \ell, \mu} (-1)^{-\ell} \times \\
&\times C_{j_A m_j^A j_B m_j^B}^{j m_j} C_{j m_j \ell - \mu}^{J M} C_{j - \Omega J \Omega}^{\ell 0} \sqrt{2j_A + 1} \sqrt{2j_B + 1} \times \\
&\times \sqrt{2j + 1} \sqrt{2S + 1} \sum_{L, M_L} C_{j - \Omega S \Sigma}^{L M_L} C_{l_B - \Lambda_B l_A - \Lambda_A}^{L M_L} \times \\
&\times \left\{ \begin{matrix} s_A & j_A & l_A \\ s_B & j_B & l_B \\ S & j & L \end{matrix} \right\} |(l_A s_A) j_A, m_j^A\rangle |(l_B s_B) j_B, m_j^B\rangle Y_{\ell - \mu}(\beta, \alpha)
\end{aligned} \tag{4.23}$$

Considering the coupled basis for the electronic total angular momentum $\mathbf{j}$ in the SF frame

$$|(j_A j_B) j m_j\rangle = \sum_{m_j^A, m_j^B} C_{j_A m_j^A j_B m_j^B}^{j m_j} |(l_A s_A) j_A, m_j^A\rangle |(l_B s_B) j_B, m_j^B\rangle, \tag{4.24}$$

and the symmetry properties of Clebsch-Gordan coefficients and $9j$ symbols, we obtain

$$\begin{aligned}
D_{M\Omega}^{J*}(\alpha \beta 0) |\Lambda S \Sigma\rangle &= (-1)^{J-\Omega} \sum_{j_A, j_B} \sum_{j, m_j} \sum_{\ell, -\mu} (-1)^{-\ell} \times \\
&\times C_{j m_j \ell - \mu}^{J M} C_{j - \Omega J \Omega}^{\ell 0} \sqrt{2j_A + 1} \times \\
&\times \sqrt{2j_B + 1} \sqrt{2S + 1} \sum_{L, \Lambda_A, \Lambda_B} \sqrt{2L + 1} \times \\
&\times C_{L \Lambda S \Sigma}^{j \Omega} C_{l_A \Lambda_A l_B \Lambda_B}^{L \Lambda} \left\{ \begin{matrix} l_A & s_A & j_A \\ l_B & s_B & j_B \\ L & S & j \end{matrix} \right\} |(j_A j_B) j, m_j\rangle Y_{\ell - \mu}(\beta, \alpha).
\end{aligned} \tag{4.25}$$

Considering the coupled basis for the total angular momentum $\mathbf{J}$ in the SF frame

$$|(j \ell) J M\rangle = \sum_{m_j, -\mu} C_{j m_j \ell - \mu}^{J M} |(j_A j_B) j m_j\rangle Y_{\ell - \mu}(\beta, \alpha), \tag{4.26}$$

for a given j_A, j_B, j, ℓ, J and M

$$\begin{aligned}
D_{M\Omega}^{J\star}(\alpha\beta 0) |\Lambda S \Sigma\rangle &= (-1)^{J-\Omega-\ell} \sqrt{2j_A+1} \sqrt{2j_B+1} \sqrt{2S+1} \times \\
&\times C_{j-\Omega J \Omega}^{\ell 0} \times \\
&\times \sum_{L, \Lambda_A, \Lambda_B} \sqrt{2L+1} C_{L \Lambda S \Sigma}^{j \Omega} C_{l_A \Lambda_A l_B \Lambda_B}^{L \Lambda} \times \\
&\times \left\{ \begin{matrix} l_A & s_A & j_A \\ l_B & s_B & j_B \\ L & S & j \end{matrix} \right\} |(j \ell) J M\rangle
\end{aligned} \tag{4.27}$$

Thus, the transformation matrix element from Hund's case (a) BF frame basis to the Hund's case (e) SF frame basis reads as

$$\begin{aligned}
\langle (j \ell) J M | D_{M\Omega}^{J\star}(\alpha\beta 0) |\Lambda S \Sigma\rangle &= (-1)^{J-\Omega-\ell} \sqrt{2j_A+1} \sqrt{2j_B+1} \sqrt{2S+1} \times \\
&\times C_{j-\Omega J \Omega}^{\ell 0} \sum_{L, \Lambda_A, \Lambda_B} \sqrt{2L+1} C_{L \Lambda S \Sigma}^{j \Omega} C_{l_A \Lambda_A l_B \Lambda_B}^{L \Lambda} \times \\
&\times \left\{ \begin{matrix} l_A & s_A & j_A \\ l_B & s_B & j_B \\ L & S & j \end{matrix} \right\}.
\end{aligned} \tag{4.28}$$

For the symmetrized state, Eq.4.20, the transformation matrix element for a given parity becomes

$$\begin{aligned}
\langle (j \ell) J M p | \Lambda S \Sigma \Omega J M p \rangle &= \frac{1 + p(-1)^{l_A+l_B+\ell}(1 - \delta_{\Lambda,0} \delta_{\Sigma,0})}{\sqrt{2[1 + \delta(\Sigma,0)\delta(\Lambda,0)]}} \times \\
&\times (-1)^{J-\Omega-\ell} \sqrt{2j_A+1} \sqrt{2j_B+1} \sqrt{2S+1} \times \\
&\times C_{j-\Omega J \Omega}^{\ell 0} \sum_{L, \Lambda_A, \Lambda_B} \sqrt{2L+1} C_{L \Lambda S \Sigma}^{j \Omega} C_{l_A \Lambda_A l_B \Lambda_B}^{L \Lambda} \times \\
&\times \left\{ \begin{matrix} l_A & s_A & j_A \\ l_B & s_B & j_B \\ L & S & j \end{matrix} \right\},
\end{aligned} \tag{4.29}$$

where the first factor ensures parity conservation and reflects the normalization of the symmetrized basis, including the $\Lambda = \Sigma = 0$ case, in which the $\Sigma^\pm$ states are built from only a single Ω term. As an example, Hund's case (a) and Hund's case (e) bases for $J = 0, 1, 2, 3$ are presented in Appendix B.

Chapter 5

Quasi-diabatization: a way to treat dynamical couplings

With knowledge of the molecular interactions described and elements of quantum molecular dynamics presented in Chapters 3 and 4, it is in principle possible to fully predict the reactions that can occur during the collision of a neutral atom and an atomic ion of the types that are exposed in Chapter 2. However, we adopted the adiabatic representation of the potential energy curves describing the electronic states of the relevant molecules, meaning that we neglected the so-called non-adiabatic couplings that can exist between adiabatic states. In general, such couplings are responsible for any transformation (change of internal state, chemical reaction, etc) of a quantum molecular system. We have seen in Chapter 2 examples of situations where such couplings might be strong in a diatomic system. In the vicinity of an avoided crossing between two PECs, the relevant electronic wave functions abruptly vary with the internuclear distance R , thus generating large derivative terms in the Schrödinger equation. Such terms are usually tedious to evaluate theoretically, as their accurate calculation may require an arbitrary small grid step in R . This issue is even worse for polyatomic systems, as such couplings are multidimensional quantities that could be singular at conical intersections of potential energy surfaces (PESs), making them impossible to fit easily.

To solve such a problem, scientists continuously search for a general solution, consisting of finding appropriate representations of the electronic states of the system other than the adiabatic one, in which they would be represented by PECs (or PESs) and couplings (usually referred to as non-adiabatic coupling terms, or NACT) which smoothly vary with the internal coordinates (*i.e.* the internuclear distance R for a diatomic system). The very first approach that has been formulated in this context is probably the famous Landau-Zener (LZ) model [123, 124], a semi-classical linearization approach which is remarkably intuitive and accurate given its simplicity. We present it in Section 5.1.

As numerical calculations on computers were developing, a wealth of proposals have been published in the scientific literature which are impossible to quote

here, being far beyond the purpose of this thesis. A well-known reference textbook has been written by M. Baer in 2006 [125], describing in mathematical terms the adiabatic-to-diabatic transformations allowing one to transform a diagonal (adiabatic) Hamiltonian matrix into a non-diagonal (diabatic) one, based on the seminal works of F. Smith [126] and W. Lichten [127]. A two-state analytical model is proposed, and examples mostly devoted to multidimensional systems (with at least three atoms) are provided. In principle, both representations must provide the same results when treating the dynamics of the system, provided that some mathematical conditions (presented in [125]) are fulfilled, which is practically not often the case. In practice, numerical approximate models are developed, so that it is usual to refer to quasi-diabatic approaches, which we will use in this chapter.

Our group was concerned for a long time with quasi-diabatic approaches. This started with modeling the process of associative ionization (AI) occurring between two excited sodium atoms [128, 129], producing a molecular ion and an electron. Schematically, the Hilbert space of the diatomic system is divided in two subspaces, one for (singly-excited) Rydberg states, and one for doubly-excited states. The AI process is then described as the interaction between these two blocks of states with a well defined character, so that dynamics occurs when coupling terms are strongly mixing these two characters. This approach is referred to as "diabatization by block diagonalization". An approach based on projection operators has been used in the context of long-range photoassociation of two excited sodium atoms [130]: the Hilbert space was projected on a subspace with covalent states (*i.e.* associated with two neutral atoms) and a subspace with ionic states (*i.e.* associated with a positive and negative ion pair). It happens that local avoided crossings (and thus NACTs) are present in the relevant PECs. With such a separation, it was then possible to introduce the spin-orbit (SO) interaction on the neutral sodium atoms and then determine the molecular SOCs via the projection backwards.

In the present work, I have a similar objective: introducing SO interaction in the theoretical description of cold atom-ion collisions. To that end, the group has explored another quasi-diabatic approach, based on a rotation of the Hilbert space onto a set of reference states representing the atomic states, thus allowing the introduction of atomic SO operators. In Section 5.2, we present the principle of this approach. Similarly as in the example above [130], NACTs are present between adiabatic states of our molecular systems. We present in Section 5.3 the second step of our quasi-diabatic method.

5.1 Landau-Zener model

In 1932 L. Landau and C. Zener independently published their seminal works entitled "Non-Adiabatic Crossing of Energy Levels" [124] and "On the Theory of Energy Transfer" [123]. The Landau-Zener model provides a simple semiclassical description of the transition probability between two electronic states in the vicinity of an avoided crossing. Although the model is based on a local linearization of the potential energy curves, it gives a useful physical picture of how non-adiabatic transitions may occur during a molecular collision. Let us consider a diatomic system, where R denotes the internuclear distance and $\mathbf{r}$ represents the electronic co-

ordinates. In the Born-Oppenheimer representation, the electronic Schrödinger equation is solved at fixed values of R , as discussed in Section 3.3,

$$\hat{H}_e(\mathbf{r}, R)\psi^m(\mathbf{r}, R) = E_e^m(R)\psi^m(\mathbf{r}, R), \quad (5.1)$$

provides the adiabatic potential energy curves (PECs). As two PECs related to states of the same symmetry cannot cross, they might undergo avoided crossings when they approach each other. In the vicinity of such a region, the electronic wave functions change rapidly with R , leading to significant non-adiabatic couplings. These couplings can induce transition between adiabatic states during the collision.

The scheme of Fig.5.1 illustrates this situation. The two PECs have different characters on the two sides of the avoided crossing. For example, a curve that has a character of mainly type 1 for $R < R_c$ may acquire a character of mainly type 2 for $R > R_c$. Thus, following the same adiabatic curve through the avoided crossing does not necessarily mean preserving the same diabatic character.

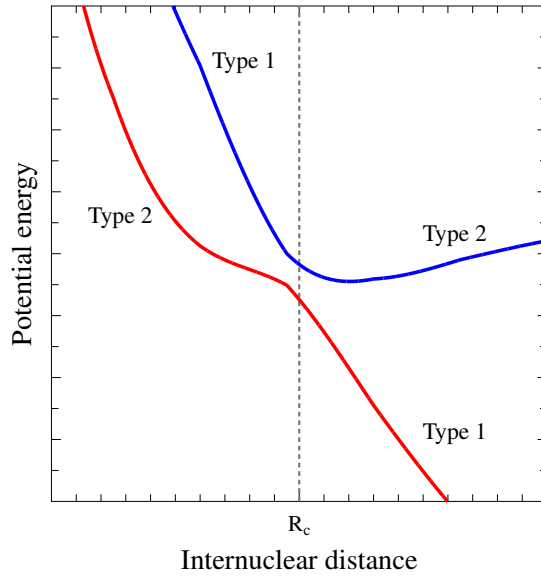


Figure 5.1: Schematic representation of two adiabatic potential energy curves forming an avoided crossing. The two curves have different electronic characters, denoted here as type 1 and type 2. Around the avoided crossing at R_c , the characters of the adiabatic curves are exchanged.

The essence of the Landau-Zener model can be understood from a simple two-state Hamiltonian. First, consider two uncoupled diabatic states $|1\rangle$ and $|2\rangle$

assuming their energy variation is linear with R described by

$$E_1(R) = \frac{\alpha R}{2}, \quad E_2(R) = -\frac{\alpha R}{2}, \quad (5.2)$$

where $\alpha > 0$ is constant, leading to the simple Hamiltonian

$$\mathbf{H} = \begin{pmatrix} \frac{\alpha R}{2} & 0 \\ 0 & -\frac{\alpha R}{2} \end{pmatrix}. \quad (5.3)$$

If there is no coupling between the two states, the PECs cross at $R = 0$ (Fig. 5.2). When an off-diagonal coupling W_c is introduced between the two states, the Hamiltonian becomes

$$H = \begin{pmatrix} \frac{\alpha R}{2} & W_c \\ W_c & -\frac{\alpha R}{2} \end{pmatrix}. \quad (5.4)$$

The eigenvalues of this Hamiltonian are

$$E_{\pm}(R) = \pm \sqrt{\left(\frac{\alpha R}{2}\right)^2 + W_c^2}. \quad (5.5)$$

The coupling produces an avoided crossing between the two PECs (Fig. 5.2). The energy gap is minimal at $R = 0$ with a value $2|W_c|$.

This example illustrates the difference between the "diabatic" and "adiabatic" descriptions. In the diabatic representation, the states preserve their character, and the coupling appears as an off-diagonal matrix element. In the adiabatic representation, the Hamiltonian is diagonal, but the character of the eigenstates changes rapidly around the avoided crossing. A non-adiabatic transition corresponds to a change between adiabatic curves during the nuclear motion through the crossing region. The Landau-Zener transition probability depends on the coupling strength at the crossing point, the relative velocity of the particles, and the difference between the slopes of the diabatic curves. In atomic units, the probability can be written as

$$P = \exp\left(\frac{-2\pi W_c^2}{v_c \Delta F_c}\right), \quad (5.6)$$

where W_c is the energy difference between the adiabatic curves, v_c is the relative radial velocity at R_c

$$v_c = \sqrt{\frac{2(E_i - U_c)}{\mu}}, \quad (5.7)$$

where μ is the reduced mass, E_i is the initial relative energy to the entrance channel, and U_c the potential energy at R_c . The difference between the slopes of the two diabatic curves at the crossing point is defined as

$$\Delta F_c = \left| \frac{dV_1}{dR} - \frac{dV_2}{dR} \right|_{R=R_c}. \quad (5.8)$$

At ultracold temperatures, E_i is small compared to the potential energy such that the relative velocity is characterized mainly by U_c .

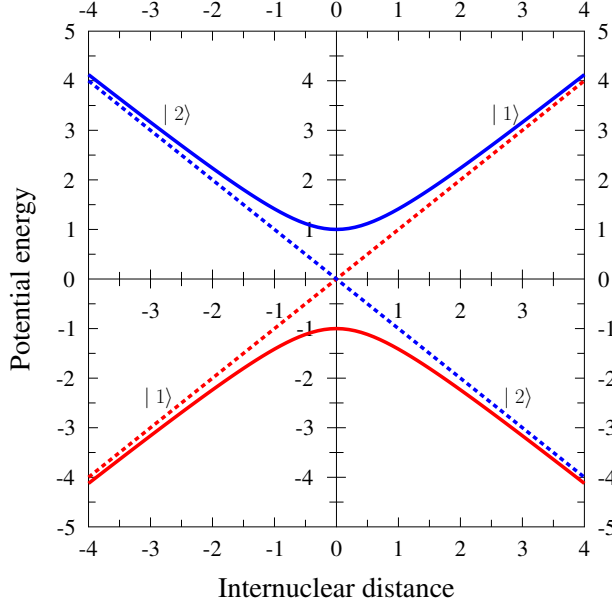


Figure 5.2: Avoided crossing produced by the off-diagonal coupling W_c . The dashed lines represent the uncoupled diabatic curves, while the solid lines are the adiabatic eigenvalues of the coupled two-state Hamiltonian. The minimum energy gap at the crossing point is $2|W_c|$.

The Landau-Zener model can also be used as a practical tool for constructing a quasi-diabatic representation from adiabatic PECs displaying an avoided crossing. In this approach, the adiabatic curves are locally replaced by two crossing diabatic curves, and a coupling function is introduced to reproduce the original avoided crossing. In the present work, the coupling between the two diabatic curves is modeled by a Gaussian function

$$G(R) = 2W_c \exp\left(-\left(\frac{R-R_c}{\delta}\right)^2\right) \quad (5.9)$$

where $2W_c$ is the energy gap between the two curves at the crossing point and δ characterizes the width of the coupling region. The parameters R_c , W_c and δ are chosen so that the resulting adiabatic curves reproduce the original avoided crossing as closely as possible. This quasi-diabatic representation makes it possible to include the effect of localized radial non-adiabatic couplings in scattering calculation without explicitly evaluating the derivative couplings between adiabatic electronic wave functions.

5.2 Quasi-diabatization of Hund's case (a) PECs: obtaining molecular spin-orbit couplings

From the presentation of various experiments in Section 2.1, it appears that spin-dependent processes take place, therefore, spin-orbit (SO) interaction plays an important role and must be included in our theoretical model. The asymptotic (R -independent) model of spin-orbit couplings (SOCs) presented in Section 3.4 provides an appropriate description at large interatomic distances. Since reactivity is expected to be significant in short range, it is necessary to determine SOCs varying with R . Of course, commercial quantum chemistry packages offer such a possibility, but as we are interested in highly-excited states, we relied on the calculations described in Section 3.3 performed with the code CIPSI available in the group. Note that a version of this code, called CIPSO, has been developed in the past to include SO interaction by determining an effective SO operator adapted to the employed ECPs and CPPs [131].

Instead, in our group, we determined R -dependent SOCs based on a so-called "quasi-adiabatic" method: The idea carried by this word is to express the adiabatic states of a given Hamiltonian (in our case, the Hund's case (a) states) in a representation in which the electronic states possess a well-defined character. As SO interaction is well known in atoms (being characterized by the fine-structure splitting of atomic energy levels resulting from the diagonalization of atomic SO matrices $\mathbf{w}_{\Omega}^{\text{so}}$ of Eqs. A.1-A.9) ¹, it is wise to express the adiabatic states in an atomic representation, so that atomic SO (Section 3.4) could be accurately introduced. The principle of the chosen approach was first published in 1985 [133] and applied to the van der Waals molecule NaCd in 1996 [134]. Since then, our group has applied to KCs [135], RbCa⁺ [65], LiBa⁺ [55], RbSr⁺ [132].

The quasi-diabatization is applied to the lowest N_a Hund's case (a) molecular states of symmetry $^{2S+1}\Lambda^p$ with electronic wave functions $\psi^i(^{2S+1}\Lambda^p; \mathbf{r}, R)$, $i = 1, \dots, N$, noted in short $|\psi_a^i\rangle = \psi_a^i(\mathbf{r}, R)$ in the following, where $\mathbf{r}$ holds for all electronic coordinates. In this work, we consider the symmetries $^{1,3}\Sigma^+$, $^{1,3}\Pi$, $^{1,3}\Delta$ (see Chapters 6 and 7). The corresponding Hund's case (a) PECs are assembled in a $N_a \times N_a$ diagonal matrix $\mathbf{W}_a(R)$.

For each molecular symmetry $^{2S+1}\Lambda^p$, at a sufficiently large internuclear distance R_{ref} , a set of N_a reference states is defined as the lowest N_a Hund's case (a) states $|\psi_{\text{ref}}^i\rangle = \psi_a^i(\mathbf{r}, R_{\text{ref}})$. The distance R_{ref} is chosen sufficiently large to ensure that these states are a good representation of the separated ion-atom pair. We will name the ensemble $\{|\psi_{\text{ref}}^i\rangle\}$ as the "atomic basis" or "atomic states", in short. Then, at each distance $R < R_{\text{ref}}$ the set of adiabatic states $\{|\psi_a^i\rangle\}$ is rotated to the atomic basis through the unitary transformation matrix $\mathcal{U}(R)$ applied to $\mathbf{W}_a(R)$,

$$\mathbf{W}_a^{\text{qd}}(R) = \mathcal{U}(R) \mathbf{W}_a(R) \mathcal{U}^T(R), \quad (5.10)$$

to form the quasi-diabatic matrix $\mathbf{W}_a^{\text{qd}}(R)$. This matrix contains on the diagonal the energies of quasi-diabatic states $|\psi_{\text{qd}}^k\rangle = \psi_{\text{qd}}^k(\mathbf{r}, R)$ expressed on the atomic

¹In the following, we adopt the notation of our paper [132] to present the quasi-diabatic approach.

basis, while off-diagonal terms are their couplings. The rotation matrix $\mathcal{U}$ is chosen so that the quasi-diabatic states resemble as much as possible the "atomic states", thus by maximizing the sum of overlaps at each R

$$\rho = \frac{1}{N_\rho} \sum_{i=1}^{N_\rho} |\langle \psi_a^i | \psi_{\text{ref}}^i \rangle|^2, \quad (5.11)$$

on the lowest $N_\rho < N_a$ atomic states of interest for the considered system. Thus, the closer ρ is to 1, the better the transformation. In the present case, we chose $N_a = 30$, and $N_\rho = 10$ for LiBa^+ up the asymptote $\text{Li}(2s)+\text{Ba}^+(6p)$, or $N_a = 40$, $N_\rho = 8$ for RbSr^+ up the asymptote $\text{Rb}(5s)+\text{Sr}^+(4d)$.

At this stage, the molecular states are expressed in the "atomic basis" for every symmetry $^{2S+1}\Lambda^p$, with the corresponding quasi-diabatic potential energy matrix $\mathbf{W}_a^{\text{qd}}$. Following Section 3.4, the matrices $\mathbf{W}_a^{\text{qd}}$ involved in every value of Ω can be collected into a larger block-matrix $\mathbf{W}_{a,\Omega}^{\text{qd}}$ at every R , in which we distribute the spin-orbit matrix elements reported in Eqs. A.1-A.9 (e.g. for $P + S$ and $S + D$ dissociation limits),

$$\mathbf{W}_{a,\Omega}^{\text{qd-so}}(R) = \mathbf{W}_{a,\Omega}^{\text{qd}}(R) + \mathbf{w}_\Omega^{\text{so}}. \quad (5.12)$$

Diagonalizing the matrix $\mathbf{W}_{a,\Omega}^{\text{qd-so}}(R)$ at every R yields the Hund's case (c) PECs for a given Ω symmetry (Fig. 5.3, panel a) for LiBa^+ and panel b) for RbSr^+): using this quasi-diabatic methodology, the PECs now include R -dependent SOCs between Hund's case (a) states. The avoided crossings present in Hund's case (a) PECs are highlighted with circles in the figure, now showing a complex structure which will be discussed in connection with the studied inelastic processes in Chapters 6 and 7.

The molecular SOCs can be extracted by performing the inverse rotation from the "atomic basis" back to the Hund's case (a) representation, applied on $\mathbf{W}_{a,\Omega}^{\text{qd-so}}$ as

$$\mathbf{W}_{a,\Omega}^{\text{so}}(R) = \mathcal{U}(R)^T \mathbf{W}_{a,\Omega}^{\text{qd-so}}(R) \mathcal{U}(R) \quad (5.13)$$

leading to the matrix $\mathbf{W}_{a,\Omega}^{\text{so}}$ containing Hund's case (a) PECs on its diagonal for all symmetries which are relevant for the chosen value Ω , and SOCs as off-diagonal elements. The resulting R -dependent SOCs are displayed in Fig. 5.4 for LiBa^+ , and in Fig. 5.5 for RbSr^+ . At large distances, direct SOCs (concerning states correlated to the same asymptote) reach their atomic value (see Section 3.4). The quasi-diabatization allows one to determine the indirect SOCs (also referred to as second-order SOCs [136, 137]) between states correlated to different asymptotes and that are obviously not accessible in the asymptotic model. These couplings vanish at large distances.

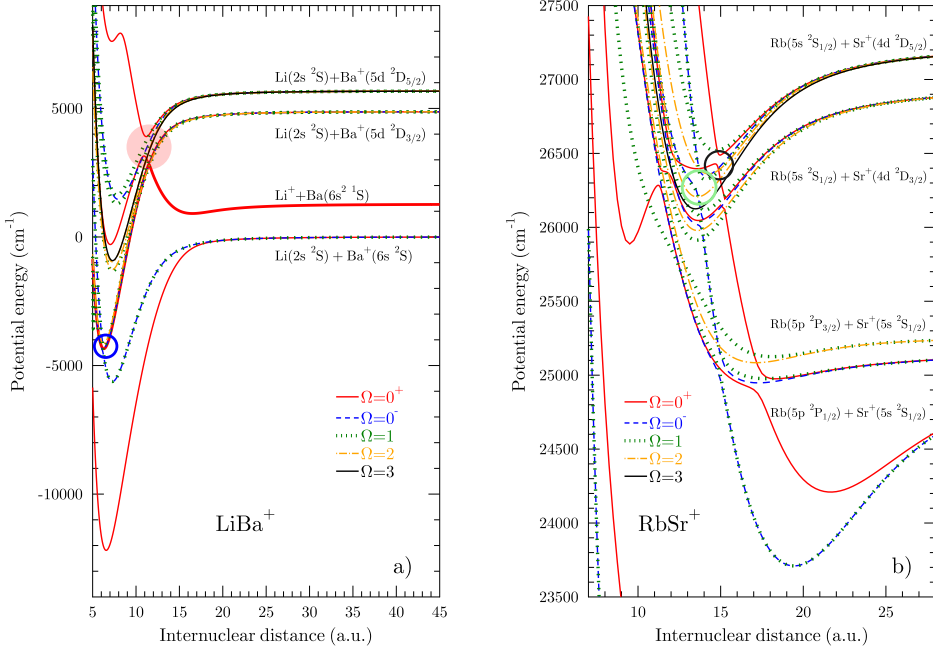


Figure 5.3: Hund's case (c) PECs for a) LiBa^+ , and b) RbSr^+ , panel b), tending to the dissociation limits relevant for the studied inelastic processes, after the diagonalisation of matrix $\mathbf{W}_{a,\Omega}^{\text{qd-so}}(R)$ or $\mathbf{W}_{a,\Omega}^{\text{so}}(R)$. The region of the avoided crossings between Hund's case (a) PECs is marked with red shaded area and blue, green, black circles.

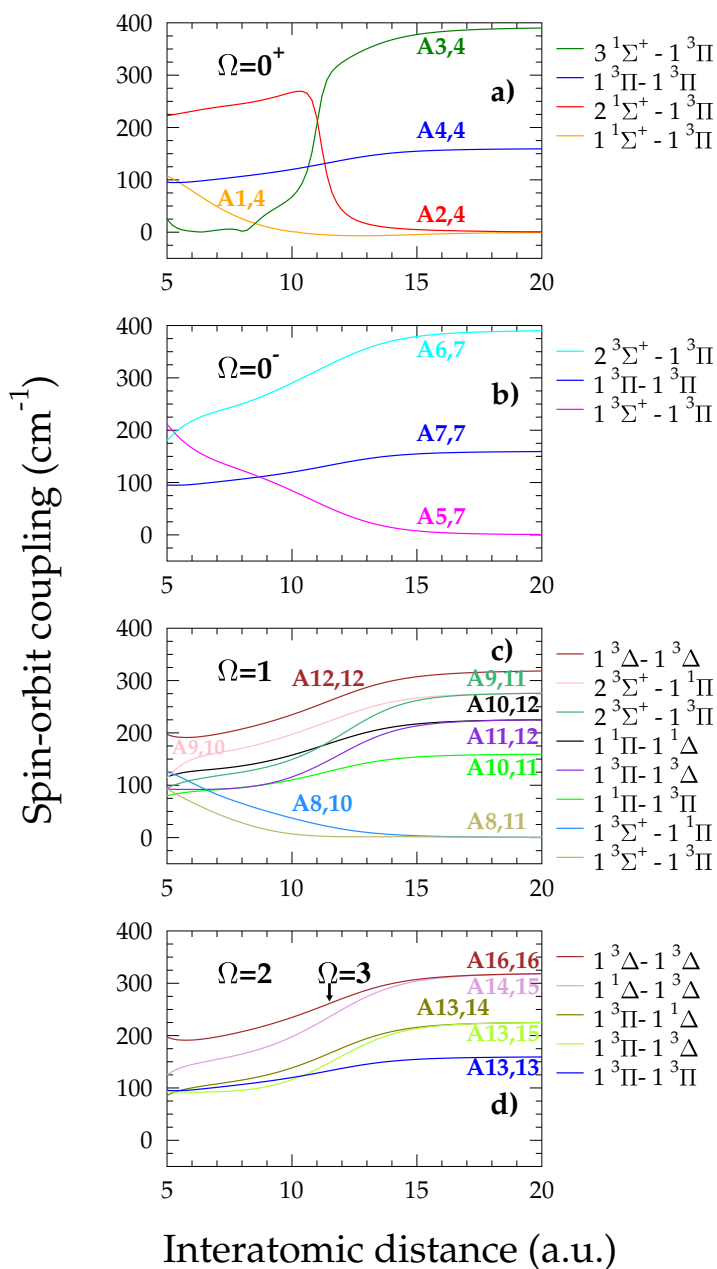


Figure 5.4: Calculated molecular SOCs $A_{p,q}$ (this notation anticipated the dynamical treatment of LiBa^+ in Chapter 6, see Table 6.3) as a function of internuclear distance for the asymptotes $S + P$ and $S + D$, and symmetries (a) $\Omega = 0^+$, (b) $\Omega = 0^-$, (c) $\Omega = 1$, (d) $\Omega = 2, 3$.

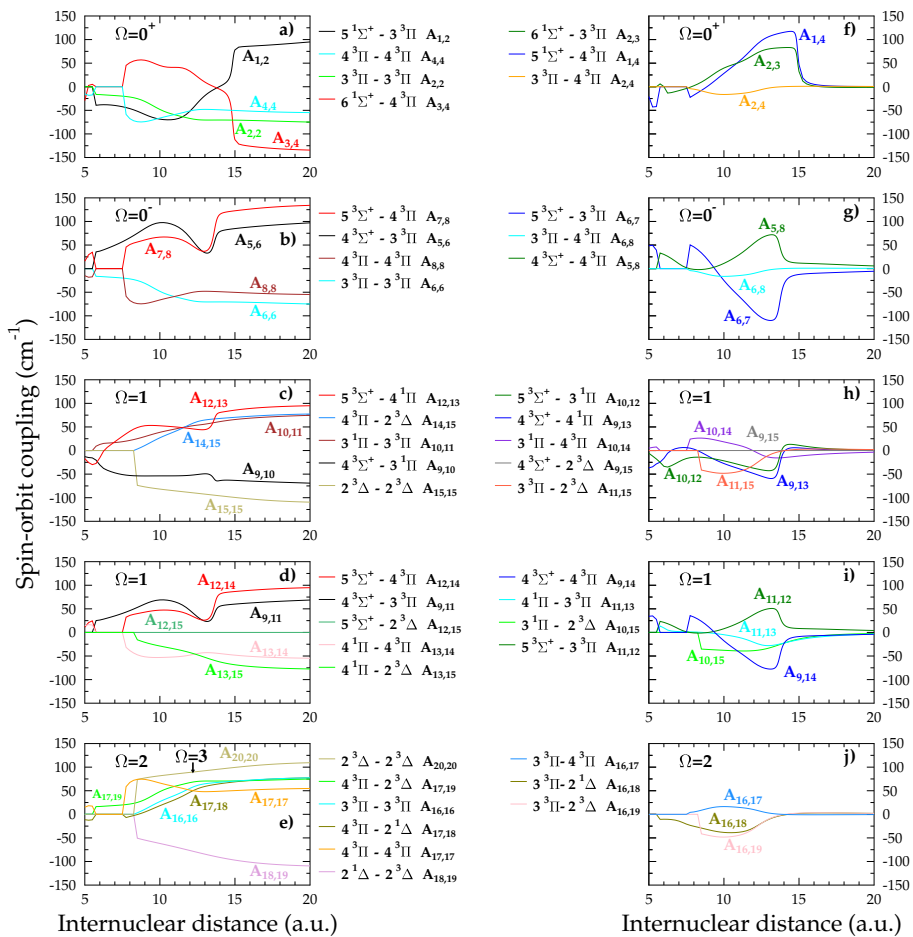


Figure 5.5: Calculated molecular SOCs A_p, q (this notation anticipated the dynamical treatment of RbSr^+ in Chapter 7, see Table 7.1) for the asymptotes $P + S$ and $S + D$. a), f): $\Omega = 0^+$; b), g): $\Omega = 0^-$; c), d), h), i): $\Omega = 1$; e), j): $\Omega = 2, 3$.

5.3 Quasi-diabatization of spin-orbit couplings

Hund's case (a) PECs generally exhibit avoided crossings between adiabatic states of same symmetry, as illustrated in Fig. 3.5 for LiBa^+ and RbSr^+ for $^1\Sigma^+$ and $^3\Sigma^+$ symmetries. They reflect abrupt changes in electronic wave functions, so that SOC's will reflect them too. Their existence induces complex patterns in Hund's case (c) PECs (Fig. 5.3). As these avoided crossings are localized and distinct in Fig. 3.5, they can easily be "diabatized" with the Landau-Zener approach (Section 5.1), as recalled in Fig. 5.6 for convenience: the local linearization of the PECs allows for determination of diabatic states with smooth energy variation with R , maintaining their smooth electronic character. We will use this simple model in the dynamical calculations for LiBa^+ (Chapter 6), in which the linearization of the avoided crossing between the PECs $2^1\Sigma^+$ and $3^1\Sigma^+$ is easily transferred to their SOC's with the $1^3\Pi$ state via a smooth ("manual") connection before and after the crossing (see Fig. 6.4). However, this linearization must be properly implemented in the quasi-diabatization of the previous section to derive accurate SOC's, for a more complex case like RbSr^+ . As illustrated by Figs. 5.5 and Fig. 5.4, SOC's exhibit a more complex behavior than in LiBa^+ . The two avoided crossings in the relevant RbSr^+ states generates more complex patterns in the SOC's (see panels for $\Omega = 0^+, 0^-, 1$) making tedious such a "manual" matching.

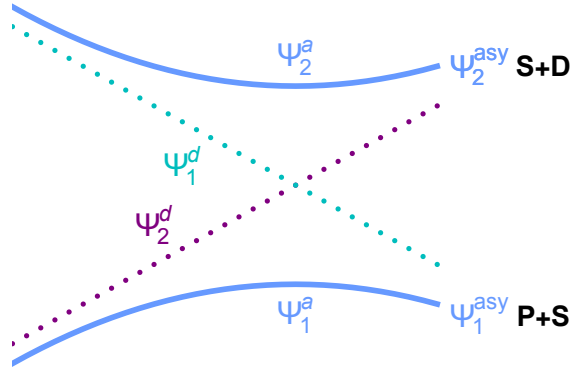


Figure 5.6: Landau-Zener model: local linearization of the potential energy of two adiabatic states Ψ_1^a and Ψ_2^a , yielding linear potential energies of two diabatic states Ψ_1^d and Ψ_2^d . Index 1 holds for the wave function that relate to the PECs tending to the lower dissociation limit, ($P + S$ here), and index 2 for those tending to the higher one ($S + D$ here)

The Hund's case (a) PECs and the corresponding electronic wave functions $|\psi_a^i\rangle$ are calculated independently at each internuclear distance R . Therefore, the global phase of a given electronic wave function is arbitrary and may change from one grid point to the next. Such phase changes are also transferred to the transformation matrix $\mathcal{U}$, which connects the set of N_a adiabatic states $\{|\psi_a^i\rangle\}$ to the N_a reference states $\{|\psi_{\text{ref}}^i\rangle\}$ used to construct the quasi-diabatic states $\{|\psi_{\text{qd}}^i\rangle\}$. When the adiabatic states are uncoupled or only weakly coupled through NACTs, their

character can be followed smoothly from large to short internuclear distances. A consistent phase convention can then be maintained by comparing the wave functions at neighboring grid points and, when necessary, inverting their global sign. In this way, the quasi-diabatic states can be correlated continuously with the reference states. When NACTs are locally strong (*i. e.* for a localized avoided crossing between two Hund's case (*a*) PECs), the atomic decomposition of ψ_{qd}^i might abruptly vary, making the phase tracking tedious or even wrong. Therefore the quasi-diabatic states before and after the avoided crossing could be improperly correlated, thus yielding erroneous SOCs in the procedure described in the previous section.

To ensure phase consistency in our work, we therefore check the evolution of the unitary matrix $\mathcal{U}(R)$ as a function of the internuclear distance. Arbitrary phase changes were detected and corrected by looking at the discontinuity in the derivative of the unitary transformation. The calculations were done on a fairly dense internuclear grid (0.01 a.u. near crossings) to discriminate between rapid changes of character and actual discontinuity. To make discontinuity easier to detect, it is recommended to have some arbitrary phase convention set in the quantum chemistry code used. In this way, phase changes occur at a few distances instead of being completely chaotic.

Through an avoided crossing between two PECs, the two corresponding adiabatic wavefunctions $|\psi_a^i\rangle$ undergo an abrupt change of character, as recalled in Fig. 5.6. This transformation can be viewed as a rotation $\mathcal{T}(\varphi(R))$ applied to the wavefunctions $|\psi_a^i\rangle$ characterized by a 2×2 matrix

$$\begin{pmatrix} |\psi_a^1(R)\rangle \\ |\psi_a^2(R)\rangle \end{pmatrix} = \begin{pmatrix} \cos \varphi(R) & \sin \varphi(R) \\ -\sin \varphi(R) & \cos \varphi(R) \end{pmatrix} \begin{pmatrix} |\psi_a^1(R)\rangle \\ |\psi_a^2(R)\rangle \end{pmatrix}, \quad (5.14)$$

yielding diabatic wavefunctions $|\psi_d^i\rangle$ which do not exhibit an abrupt change of character at the crossing point. We need to choose the angle of the inverse rotation $\varphi(R)$ correctly, otherwise the diabatic wavefunction will incorrectly acquire an extra phase compared to the asymptotic wavefunction. In general, in the full numerical calculation including all adiabatic states, it is difficult to extract a single effective rotation angle in order to ensure a proper determination of SOCs. We have indicated above that a straightforward approach can be applied in a case like LiBa^+ by manually smoothly connect the pre-crossing SOC curve to the post-crossing curve. However, to visualize and ensure that we are doing the connection correctly in a case like RbSr^+ , we developed a reduced 2×2 toy model for the example of the $5^1\Sigma^+$ and $6^1\Sigma^+$ states in RbSr^+ .

First, we looked, for each symmetry, at the off-diagonal element, $\sin \theta(R)$, of the unitary matrix $\mathcal{U}(R)$ that couples the two states we are focusing on. These R -dependent $\sin \theta(R)$ values correspond to the rotation from the atomic basis (*e.g.* $|\psi(5p\,5s)\rangle$, $|\psi(5s\,4d)\rangle$) to the adiabatic basis (*e.g.* $|\psi(5^1\Sigma^+)\rangle$, $|\psi(6^1\Sigma^+)\rangle$) (see Fig. 5.7 panel b)). The corresponding values of $\cos \theta(R)$ are then obtained, allowing the transformation matrix $\mathcal{U}(R)$ to be constructed. This leads to the equation in which we ignored the R -dependence of the rotation angle,

$$\begin{pmatrix} |\psi(5^1\Sigma^+)\rangle \\ |\psi(6^1\Sigma^+)\rangle \end{pmatrix} = \begin{pmatrix} \cos \theta_{1\Sigma^+} & -\sin \theta_{1\Sigma^+} \\ \sin \theta_{1\Sigma^+} & \cos \theta_{1\Sigma^+} \end{pmatrix} \begin{pmatrix} |\psi(5p\,5s)\rangle \\ |\psi(5s\,4d)\rangle \end{pmatrix}. \quad (5.15)$$

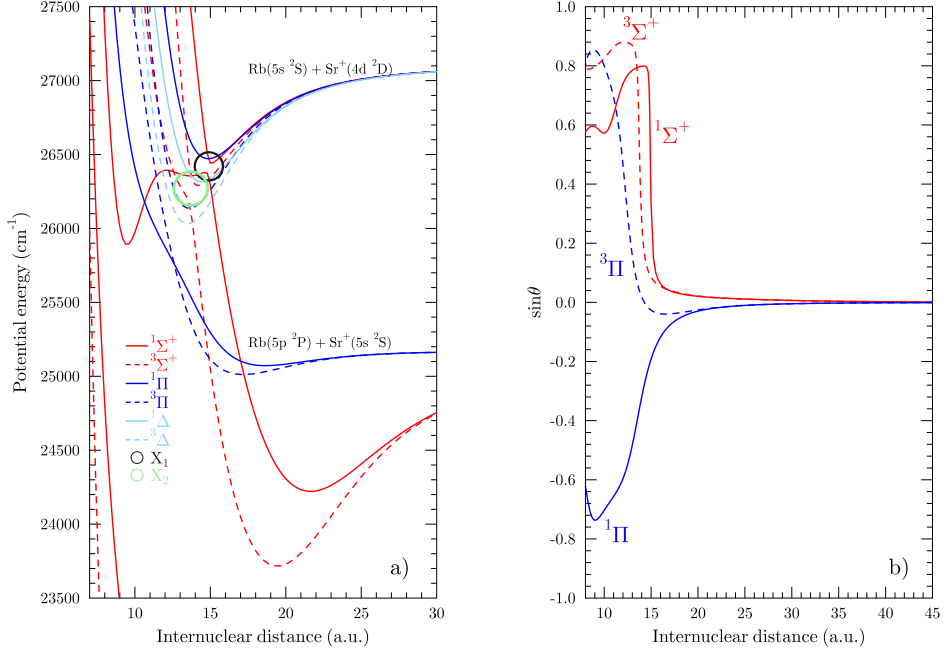


Figure 5.7: Panel a) shows the Hund's case (a) PECs of RbSr^+ tending to the $P + S$ and $S + D$ dissociation limits, with the two avoided crossings encircled. Panel b) shows the off-diagonal element of the rotational matrix, $\sin \theta_{1\Sigma^+}$, in red solid line, the $\sin \theta_{3\Sigma^+}$ in red dashed line, $\sin \theta_{1\Pi}$ in blue solid line and $\sin \theta_{3\Pi}$ in blue dashed line, associated with the avoided crossings marked by black and green circles, and the ones not highlighted on panel a) between the 1Π states and 3Π states, respectively.

We note here that we rescaled the rotation angle values so that $\theta(R) \in [-\pi/2; \pi/2]$. Equivalent equations for the wave functions as Eq. 5.15 can be written for the other relevant symmetry $^3\Sigma^+$ in RbSr^+ . The diabatic states can be expressed by the adiabatic ones, see Eq. 5.14, as

$$\begin{pmatrix} \psi_d^1 \\ \psi_d^2 \end{pmatrix} = \begin{pmatrix} \cos \varphi_{1\Sigma^+} & \sin \varphi_{1\Sigma^+} \\ -\sin \varphi_{1\Sigma^+} & \cos \varphi_{1\Sigma^+} \end{pmatrix} \begin{pmatrix} \psi(5^1\Sigma^+) \\ \psi(6^1\Sigma^+) \end{pmatrix}, \quad (5.16)$$

where ψ_d^1 (resp. ψ_d^2) is the diabaticized $^1\Sigma^+$ state converging to the lower asymptote $P + S$ (resp. the upper asymptote $S + D$). Based on Eqs. 5.15 and 5.16 the diabatic basis as a function of the atomic basis can be thus expressed as:

$$\begin{aligned} \Psi_1^d = & \cos \varphi_{1\Sigma^+} \cos \theta_{1\Sigma^+} \Psi(5p\ 5s) \\ & + \sin \varphi_{1\Sigma^+} \sin \theta_{1\Sigma^+} \Psi(5p\ 5s) \\ & - \cos \varphi_{1\Sigma^+} \sin \theta_{1\Sigma^+} \Psi(5s\ 4d) \\ & + \sin \varphi_{1\Sigma^+} \cos \theta_{1\Sigma^+} \Psi(5s\ 4d) \end{aligned} \quad (5.17)$$

and

$$\begin{aligned} \Psi_2^d = & \cos \varphi_{1\Sigma^+} \sin \theta_{1\Sigma^+} \Psi(5p\ 5s) \\ & - \sin \varphi_{1\Sigma^+} \cos \theta_{1\Sigma^+} \Psi(5p\ 5s) \\ & + \cos \varphi_{1\Sigma^+} \cos \theta_{1\Sigma^+} \Psi(5s\ 4d) \\ & + \sin \varphi_{1\Sigma^+} \sin \theta_{1\Sigma^+} \Psi(5s\ 4d). \end{aligned} \quad (5.18)$$

Let's analyze these diabatic states far away from the crossing, i.e., in long range and in short range. At long range, before we reach the avoided crossing, the diabatic state coincides with the atomic state, i.e. $\Psi_1^d = \Psi(5p\ 5s)$ and $\Psi_2^d = \Psi(5s\ 4d)$, see Fig. 5.6. Furthermore, considering Fig. 5.7 we can see that in long range $\theta_{1\Sigma^+} = 0$, which based on Eqs. 5.17 and 5.18, implies that $\varphi_{1\Sigma^+} = 0$. In short range, below the avoided crossing, the adiabatic element can have a complex behavior as the state can remain slightly mixed but the rotation tends toward $\theta = \pm\pi/2$, see Fig. 5.7. In particular for the $^1,3\Sigma^+$ states we have $\theta_{1,3\Sigma^+} = \pi/2$. The $P + S$ ($S + D$)-character of the diabatic state Ψ_1^d (Ψ_2^d) is preserved also in the short range, which implies that $\varphi_{1\Sigma^+} = \pi/2$ based on Eqs. 5.17 and 5.18. With the above definition of the rotation matrix $\mathcal{T}(R)$ and defining $\varphi \in [0; \pi/2]$ we ensured that there is no extra phase factor.

In the adiabatic basis we compute the adiabatic SOC's of the toy model, e.g. $\langle \Psi(5^1\Sigma^+) | \hat{H}_{SO} | \Psi(4^3\Pi) \rangle$, using the fact that $E_{P+S} = \langle \Psi(5s\ 5p) | \hat{H}_{SO} | \Psi(5s\ 5p) \rangle$, $E_{S+D} = \langle \Psi(4d\ 5s) | \hat{H}_{SO} | \Psi(4d\ 5s) \rangle$ are the known asymptotic SOC's (fine-structure splitting of $\text{Rb } 5p$ and $\text{Sr}^+ 4d$ level, respectively) and that the terms connecting two different asymptotes in the atomic basis vanish. We note that the obtained "toy" curves are recognizable compared to the full numerical results showing the weak influence on the system of far away electronic states. We have equivalent matrix for the $^3\Sigma^+$ symmetry (only Σ states were diabaticized in this work). We now analyze the effect of the diabaticization of the adiabatic states on the SOC's through

the example of the $\Omega = 0^+$ symmetry. Thus, we focus on the SOCs between the adiabatic states $5, 6^1\Sigma^+$ and $3, 4^3\Pi$ (the SOCs $A_{1,2}$, $A_{2,3}$, $A_{1,4}$, $A_{3,4}$, of Fig. 5.5). We introduce the following notations for the adiabatic SOCs presented in panel a) of Fig. 5.8:

$$\begin{aligned} V_{11}^a &= A_{1,2} = \langle \Psi(5^1\Sigma^+) | \hat{H}_{SO} | \Psi(3^3\Pi) \rangle \quad P + S \\ V_{21}^a &= A_{2,3} = \langle \Psi(6^1\Sigma^+) | \hat{H}_{SO} | \Psi(3^3\Pi) \rangle \quad (P + S) - (S + D) \\ V_{12}^a &= A_{1,4} = \langle \Psi(5^1\Sigma^+) | \hat{H}_{SO} | \Psi(4^3\Pi) \rangle \quad (S + D) - (P + S) \\ V_{22}^a &= A_{3,4} = \langle \Psi(6^1\Sigma^+) | \hat{H}_{SO} | \Psi(4^3\Pi) \rangle \quad S + D. \end{aligned} \quad (5.19)$$

On the right hand side in color are indicated the dissociation limits of the involved adiabatic states they are tending to in the long range. Black and red colors are for couplings between states tending to the same dissociation limit, namely $P + S$ and $S + D$. The adiabatic SOCs in green and blue are for couplings between states tending to different dissociation limits $(P + S) - (S + D)$ and $(S + D) - (P + S)$, respectively. The colors correspond to the colors of the adiabatic SOCs of panel a) of Fig. 5.8.

Considering the diabaticized states Ψ_1^d and Ψ_2^d related to the NACT between the adiabatic states $5^1\Sigma^+$ and $6^1\Sigma^+$ we introduce the following notations for the diabaticized SOCs:

$$\begin{aligned} V_{11}^d &= \langle \Psi_1^d | \hat{H}_{SO} | \Psi(3^3\Pi) \rangle \\ V_{21}^d &= \langle \Psi_2^d | \hat{H}_{SO} | \Psi(3^3\Pi) \rangle \\ V_{12}^d &= \langle \Psi_1^d | \hat{H}_{SO} | \Psi(4^3\Pi) \rangle \\ V_{22}^d &= \langle \Psi_2^d | \hat{H}_{SO} | \Psi(4^3\Pi) \rangle, \end{aligned} \quad (5.20)$$

where we neglected the weak non-adiabatic coupling between the adiabatic states $3^3\Pi$ and $4^3\Pi$. These compact notations also apply for the other relevant couplings ($3^3\Sigma^+ - 3^3\Pi$ and $3^3\Sigma^+ - 1^1\Pi$) related to the X_2 avoided crossing in Fig. 5.7. Note that, because we only diabaticized Σ states, the SOCs between two Π states, as well as those involving the Δ states, remain unchanged. Now, if we take the Eqs. 5.20 and expand the diabatic wavefunctions using Eq. 5.16 we obtain the diabaticized SOCs matrix elements:

$$\begin{aligned} V_{11}^d &= V_{11}^a \cos \varphi_{1\Sigma^+} + V_{21}^a \sin \varphi_{1\Sigma^+} \\ V_{21}^d &= V_{21}^a \cos \varphi_{1\Sigma^+} - V_{11}^a \sin \varphi_{1\Sigma^+} \\ V_{12}^d &= V_{12}^a \cos \varphi_{1\Sigma^+} + V_{22}^a \sin \varphi_{1\Sigma^+} \\ V_{22}^d &= V_{22}^a \cos \varphi_{1\Sigma^+} - V_{12}^a \sin \varphi_{1\Sigma^+}. \end{aligned} \quad (5.21)$$

The diabaticized couplings, Eqs. 5.21, at long range with $\varphi_{1\Sigma^+} = 0$, are equal to the asymptotic values

$$\begin{aligned}
V_{11}^d &= V_{11}^a = E_{P+S} \quad P + S \\
V_{21}^d &= V_{21}^a = 0 \quad (P + S) - (S + D) \\
V_{12}^d &= V_{12}^a = 0 \quad (S + D) - (P + S) \\
V_{22}^d &= V_{22}^a = E_{S+D} \quad S + D,
\end{aligned} \tag{5.22}$$

while as we reach short range with $\varphi_{1\Sigma^+} = \pi/2$, we have:

$$\begin{aligned}
V_{11}^d &= V_{21}^a \quad (P + S) - (S + D) \\
V_{21}^d &= -V_{11}^a \quad P + S \\
V_{12}^d &= V_{22}^a \quad S + D \\
V_{22}^d &= -V_{12}^a \quad (S + D) - (P + S).
\end{aligned} \tag{5.23}$$

The toy model above is useful to understand this issue of the phase tracking of the states through the avoided crossing. This procedure has been implemented in a more general way in our numerical code for the two avoided crossings relevant in RbSr^+ . Thus, the matrix $\mathbf{W}_{a,\Omega}^{\text{qd-so}}(R)$ (eq. 5.12) is transformed into a matrix $\mathbf{W}_{a,\Omega}^{\text{qd-so}2}(R)$ including the diabaticized SOC's after this second step.

In panel b) of Fig. 5.8, the long-range diabaticized SOC's are plotted on the right-hand side of the X_1 avoided crossing according to Eqs. 5.22, whereas the short-range diabaticized SOC's are plotted on the left-hand side according to Eqs. 5.23. In this later case, we can see that the black and blue curves change sign with respect to the short range part of panel a). The shaded area of panel b) around the X_1 avoided crossings hides the region where the adiabatic SOC's are strongly mixed, resulting in an abrupt behavior of certain diabaticized SOC's.

In panel c) of Fig. 5.8 the diabaticized SOC's are presented connecting "by hand" the long-range and short-range regions based on Eqs. 5.22 and 5.23. In panel c) we choose the color of the diabaticized SOC being identical with the one of the adiabatic one in long range, thus in short range the green of panel b) becomes black, the black becomes green, the red becomes blue and finally the blue becomes red. In Appendix C the diabaticization procedure of SOC's is presented for the $\Omega = 0^-$, Fig C.1, and for the $\Omega = 1$, Fig C.2 and Fig C.3, symmetries.

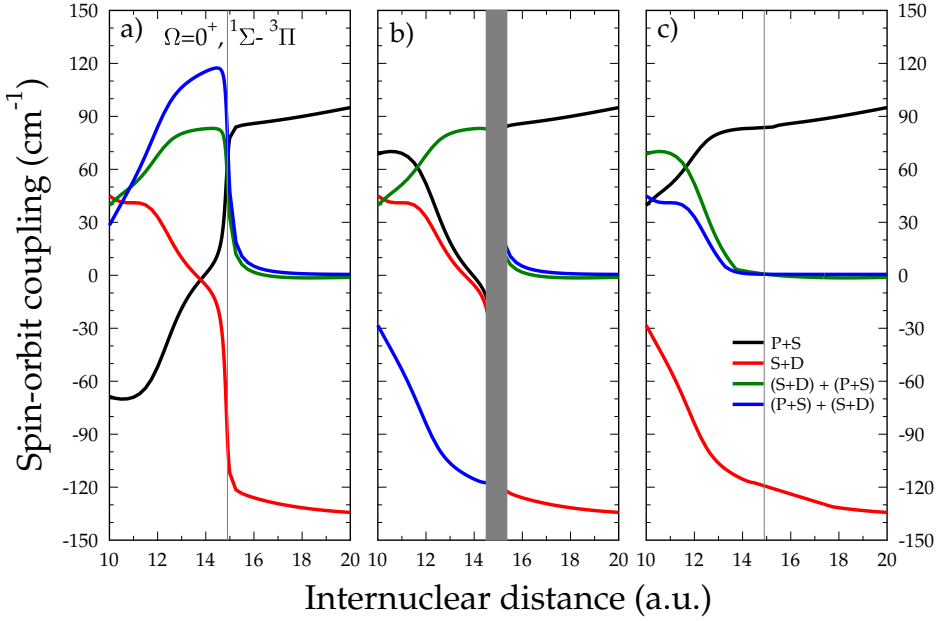


Figure 5.8: The relevant SOC in the $\Omega = 0^+$ symmetry. Panel a) shows the *adiabatic* spin-orbit couplings between $^1\Sigma - ^3\Pi$ states for all asymptotic limits we consider in our calculations. Black ($A_{1,2}$) and red ($A_{3,4}$) solid lines are the SOC between states belonging to the same asymptotic limit, i.e. P+S and S+D, respectively. Green ($A_{2,3}$) and blue ($A_{1,4}$) solid lines are the SOC between states belonging to different asymptotic limits, i.e. one of them belonging to the P+S and the other to S+D limit. In the later case the SOC are tending to 0 asymptotically. $A_{i,j}$ notation corresponds to the SOC notation of Fig. 5.5. Grey vertical line indicates the position of the X_1 avoided crossing. Panel b) shows the inverted black and blue curves before the crossing point according to the phase convention. Panel c) shows the *diabatized* curves used in the calculations. The black curve is the $A'_{1,2}$, the red curve is the $A'_{3,4}$, the blue curve is the $A'_{1,4}$ and the green curve is the $A'_{2,3}$ SOC of Fig. 7.2 and Hamiltonian matrix 7.1.

Chapter 6

Competing excitation quenching and charge exchange in ultracold Li-Ba⁺ collisions

The present chapter is based on the first paper that I co-authored during this thesis [55]. Our study was motivated by the experiment reported in [55,138], where ultracold collisions between a single $^{138}\text{Ba}^+$ ion and a cloud of ^6Li atoms were investigated in a hybrid atom-ion setup. The combination Li-Ba⁺ is particularly interesting because of its large mass imbalance with one light component, which is favorable for approaching the quantum regime of atom-ion collisions. As was mentioned in Chapter 2 the ground state collision of Li+Ba⁺ is related to the energetically lowest asymptotic limit of LiBa⁺. Radiative charge exchange, which is a typical process in ion-atom collisions, is thus suppressed. This makes the system an experimentally promising candidate for obtaining a stable ion-atom mixture for various applications.

6.1 Experiment and relevant observables

In the experiment, the Ba⁺ ion was prepared in one of the two metastable fine structure states, $5^2D_{3/2}$ or $5^2D_{5/2}$, and immersed in an ultracold gas of ground state ^6Li atoms. The relevant energy levels of Ba⁺ used for state preparation and detection are shown in Fig. 6.1. The detailed laser excitation sequence is not discussed here, since the present chapter focuses on the theoretical interpretation of the observed inelastic processes. The complete experimental sequence and detection protocol are described in detail in [55,138]. The radiative lifetimes of these metastable states are much longer than the interaction time, so that changes in the internal state of the ion can be attributed to collision induced processes.

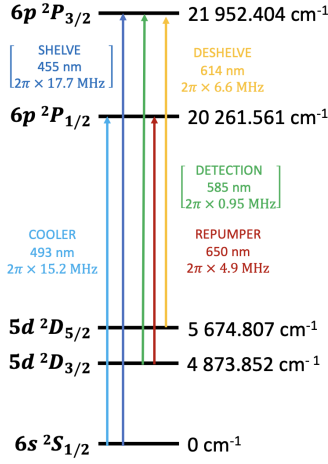


Figure 6.1: Relevant energy levels of $^{138}\text{Ba}^+$ involved in the laser cooling, preparation and detection of the metastable $5\ ^2D_{3/2}$ and $5\ ^2D_{5/2}$ states used in the experiment. The state preparation and the full experimental protocol is described in Ref. [55].

In Fig. 6.2 the scheme of relevant energy levels of Li-Ba $^+$ pair is presented together with the experimentally observed inelastic processes.

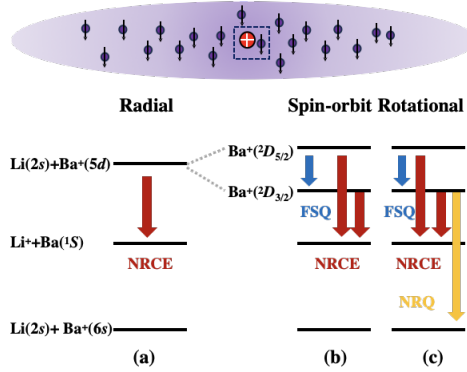
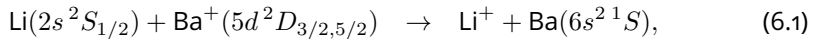
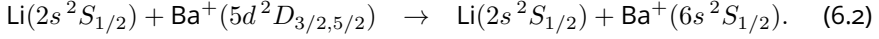


Figure 6.2: Schematic representation of the relevant energy levels of the Li-Ba $^+$ system and the observed inelastic processes, including non-radiative charge exchange (NRCE), non-radiative quenching (NRQ), and fine-structure quenching (FSQ). The panels illustrate the hierarchy of couplings governing the dynamics: (a) radial (non-adiabatic) coupling, (b) radial and spin-orbit couplings, and (c) radial, spin-orbit, and rotational couplings.

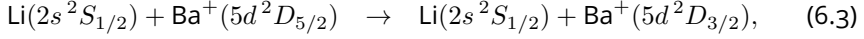
Several competing inelastic processes were identified. Non-radiative charge exchange (NRCE) corresponds to



while non-radiative quenching (NRQ) transfers the ion from the metastable $5d^2D$ state to the ground $6s^2S_{1/2}$,



For ions initially prepared in the $5^2D_{5/2}$ state, fine structure quenching (FSQ) can also occur,



as a result the ion's initial fine structure state is changed to $5^2D_{3/2}$.

The experimentally determined branching ratios, together with the rate coefficients normalized to the Langevin rate, prove the reference observables for the theoretical comparison. The experimental observations for the initial state $5^2D_{3/2}$ show that the inelastic processes are dominated by NRQ, while NRCE represents a weak contribution. For the initial state $5^2D_{5/2}$, both FSQ and NRCE were observed, and not NRQ. These experimental probabilities, together with the theoretical results obtained in the present work, are summarized in Table 6.4. The aforementioned asymptotic limits, namely $\text{Li}(2s^2S_{1/2}) + \text{Ba}^+(5d^2D_{3/2,5/2})$, $\text{Li}^+ + \text{Ba}(6s^2^1S)$ and $\text{Li}(2s^2S_{1/2}) + \text{Ba}^+(6s^2S_{1/2})$ are referred to further in the text as S+D, Ion+S and S+S respectively. Another shorthand notation is defined for the incoming channels $\text{Li}(2s^2S_{1/2}) + \text{Ba}^+(5d^2D_{3/2})$ and $\text{Li}(2s^2S_{1/2}) + \text{Ba}^+(5d^2D_{5/2})$ as $D_{3/2}$ and $D_{5/2}$.

6.2 Electronic structure of the LiBa^+ ion

An accurate treatment of inelastic processes relies on the precise characterization of the PECs of the LiBa^+ molecular system, including those associated with excited electronic configurations, as well as the couplings between them. The electronic structure methods used to obtain the LiBa^+ potential energy curves and spin-orbit couplings were introduced in Sections 3.3 and 5.2. In the present section, only the features relevant for the multichannel quantum scattering (MCQS) treatment are discussed: the Hund's case (a) PECs, the avoided crossings, the R -dependent SOCs, and the resulting interaction matrix used in the scattering calculations.

The theoretical investigation of the Li-Ba^+ collision dynamics was initially started in the framework of Xiaodong Xing's thesis [48]. In the present work, this system is revisited in detail with two main objectives: first, to validate the developments I have optimized a general MCQS Fortran code for describing collisions between an alkali-metal atom and an alkaline-earth ion used throughout this thesis, and second, to provide a deeper analysis of the dynamical mechanisms underlying the experimentally observed inelastic processes.

6.2.1 Hund's case (a) PECs

The Hund's case (a) PECs obtained from quantum-chemistry calculations (Section 3.3) are shown in Fig. 6.3, and their spectroscopic constants are displayed in Table 6.1. The calculated PECs include the molecular symmetries $^1,3\Sigma^+$, $^1,3\Pi$ and

$1,3\Delta$. These curves provide the electronic-structure basis for the subsequent scattering calculations. Here, we focus on the features that are directly relevant to the collision dynamics, namely the dissociation limits involved in the experiment, the crossings and avoided crossings between PECs that enter the MCQS model.

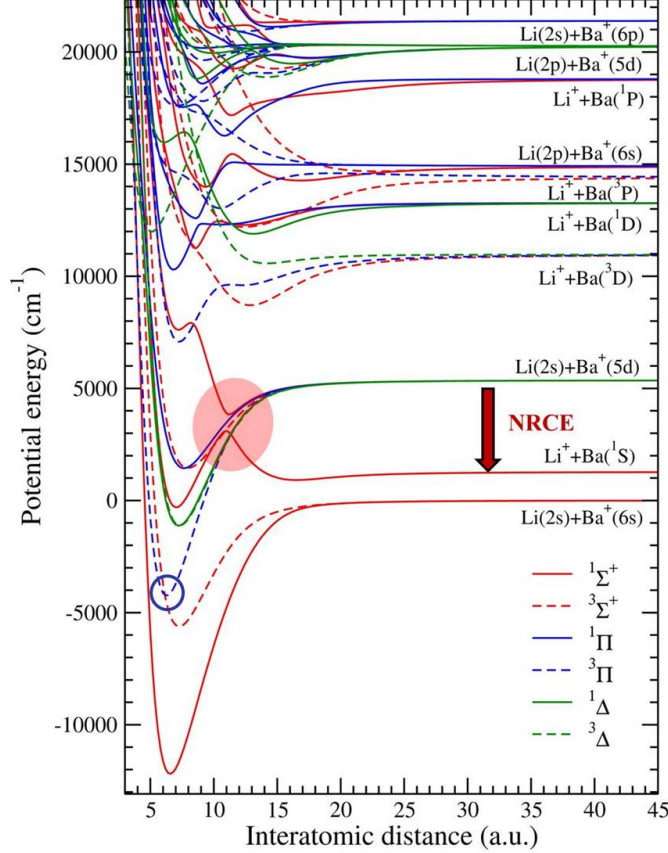


Figure 6.3: Potential energy curves of the LiBa^+ molecule in Hund's case (a), calculated in the body-fixed (BF) frame up to the $\text{Li}(2s)+\text{Ba}^+(6p)$ dissociation limit. The red shaded region highlights the X_1 avoided crossing occurring between the $2^1\Sigma^+$ and $3^1\Sigma^+$ PECs, which gives rise to NRCE. The blue circle marks the X_3 crossing between the $1^3\Sigma^+$ and $1^3\Pi$ states, responsible for NRQ. (Note that this figure is extracted from [55] so that the notations for atomic states is different –but consistent– with those used in this thesis.)

The three lowest dissociation limits relevant to the present study namely $\text{Li}(2s^2S)+\text{Ba}^+(6s^2S)$, $\text{Li}+(^1S)+\text{Ba}(6s^2^1S)$ and $\text{Li}(2s^2S)+\text{Ba}^+(5d^2D)$ are well separated from the higher ones. A notable feature of the PECs is the avoided crossing (hereafter denoted X_1) between the $3^1\Sigma^+$ state correlated with the $\text{Li}(2s)+\text{Ba}^+(5d)$ entrance channel and the $2^1\Sigma^+$ state around $R = 11$ a.u.. This avoided crossing reflects a strong localized non-adiabatic coupling that we do not extract from our electronic structure calculations. It plays an important role in the present study,

State	R_e (a.u.)	D_e (cm $^{-1}$)	C_6 (a.u.)
$1^1\Sigma^+$	6.60	12189	−14820.26
	6.70 [139]	11627 [139]	
	6.61 [140]	11846 [140]	
	6.75 [39]	11860 [39]	
	6.71 [141]	11674 [141]	
$1^3\Sigma^+$	7.28	5619	−14821.26
	7.56 [139]	4784 [139]	
	7.41 [140]	5401 [140]	
	7.46 [39]	5178 [39]	
$2^1\Sigma^+$	7.02	1580	−21744.76
	7.57 [139]	1206 [139]	
	7.05 [140]	2246 [140]	
$3^1\Sigma^+$	11.20	1524	−2327.73
	10.90 [139]	1833 [139]	
	11.41 [140]	1569 [140]	
$2^3\Sigma^+$	7.98	3905	−2327.73
	7.48 [139]	5961 [139]	
	8.11 [140]	3952 [140]	
$1^1\Pi$	7.60	3915	−3180.61
	7.75 [140]	4034 [140]	
$1^3\Pi$	6.28	9589	−3180.72
	6.42 [139]	8935 [139]	
	6.29 [140]	9390 [140]	
$1^1\Delta$	7.29	6473	−5686.68
	7.18 [139]	5729 [139]	
	7.35 [140]	6250 [140]	
$1^3\Delta$	7.20	6477	−5686.68
	7.42 [140]	6235 [140]	

Table 6.1: Equilibrium distances R_e and potential well depths D_e of the LiBa^+ potential energy curves. The last column lists the van der Waals coefficients C_6 employed for the long-range extrapolation of the PECs.

as being responsible for the occurrence of NRCE. The NACT is modeled by linearizing the two adiabatic PECs around the position R_{X1} of avoided crossing, where the adiabatic PECs are split with an energy $2W_{X1} = 0.00359$ a.u. (or 781.7 cm $^{-1}$). We suppose a Gaussian-type variation of the coupling with R

$$G_{X1} = 2W_{X1} \exp\left[-\frac{(R - R_{X1})^2}{\delta^2}\right], \quad (6.4)$$

where the width of the function is chosen with a value $\delta = 0.75$ a.u.. These fea-

tures define the minimal electronic-structure landscape required for dynamical calculations: the entrance channel, the charge exchanged asymptote, and the non-adiabatic connection between them through the avoided crossing X_1 .

Another remarkable feature is the crossing between the $1^3\Sigma^+$ and $1^3\Pi$ states near 6 a.u., hereafter labeled X_3 . This crossing contributes to the complexity of the spectrum of magnetic Feshbach resonances (MFRs) experimentally recorded in the ground-state manifold [39] and plays an important role in the occurrence of NRQ process. The position and energy of crossings X_1 and X_3 are listed in Table 6.2.

	Position (a.u.)	Energy (cm ⁻¹)
X_1	11.06	3450
	10.88 [139]	4171 [139]
	11.30 [140]	3465 [140]
X_3	6.15	-4205
	6.02 [139]	-2326 [139]
	6.14 [140]	-3973 [140]

Table 6.2: Positions and energies of the X_1 and X_3 crossings with respect to the lowest dissociation limit $\text{Li}^+(^1S) + \text{Ba}(6s^2^1S)$, compared with other theoretical determinations. The agreement between our result and [140] is excellent, while a larger discrepancy with Ref. [139] is observed most probably due to the different used method and basis.

6.2.2 Spin-orbit couplings

We have determined R -dependent SOC's based on the first step of quasi-diabatization described in Sections 5.2. The calculated SOC's for the three relevant asymptotic limits are shown in Fig. 6.4 for the $\Omega = 0^+, 0^-, 1, 2, 3$ symmetries.

At large internuclear separations, the SOC's between states correlated with the dissociation limit $\text{Li}(2s^2S) + \text{Ba}^+(5d^2D)$ match energies defined by the fine-structure splitting $\Delta E_D = 800.955 \text{ cm}^{-1}$ of $\text{Ba}^+(5d^2D)$. In contrast, SOC's between states correlated with different dissociation limits (hereafter referred to as indirect SOC's) vanish asymptotically.

A subtle point arises from the avoided crossing X_1 , where the two states involved $1^3\Sigma^+$ undergo an abrupt exchange of electronic character in this region. Since these two adiabatic states are diabaticized around R_{X_1} , the effect of the related NACTs on the related SOC's must also be considered for consistency. The consequence on SOC's is clearly visible in Fig. 6.4 panel a), with a clear character exchange between $A_{2,4}$ and $A_{3,4}$. As both terms $A_{2,4}$ and $A_{3,4}$ involve the same adiabatic state $1^3\Pi$, they follow the same behavior as the electronic wave functions of the two states $1^3\Sigma^+$. We used here a simple "diabatic" model in which the left- and right-hand branches of the couplings were smoothly connected along the black dashed curves. This procedure ensures that each coupling maintains a

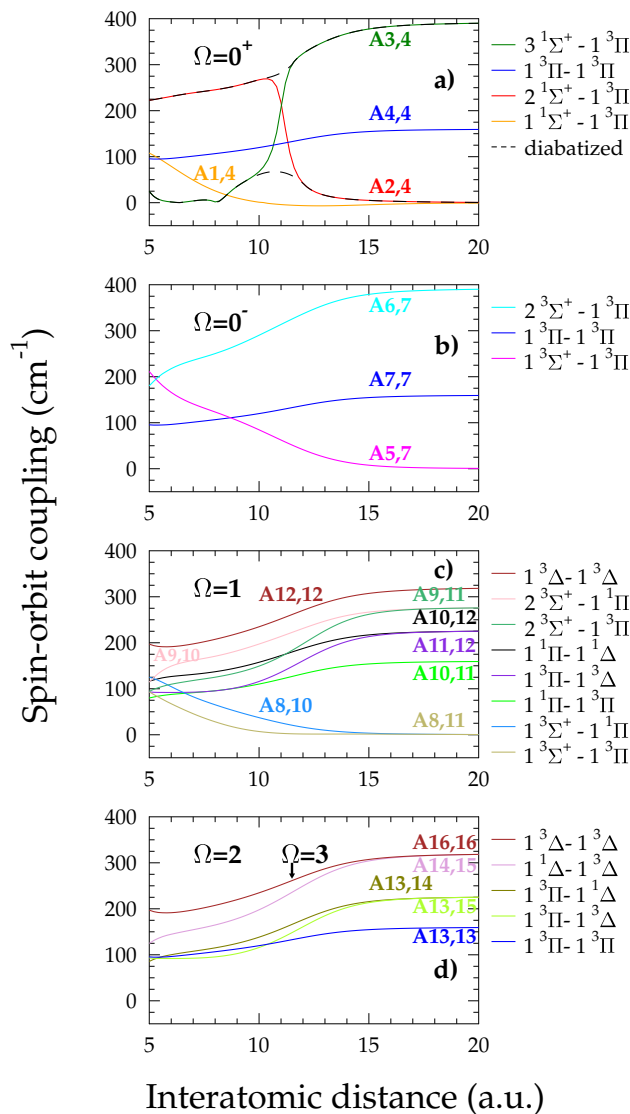


Figure 6.4: Molecular spin-orbit couplings (SOCs) labeled according to the notation A_{pq} introduced in Table 6.3, for pair of states correlated with the three lowest dissociation limits of LiBa^+ . a) $\Omega = 0^+$; b) $\Omega = 0^-$; c) $\Omega = 1$; d) $\Omega = 2, 3$. In panel a), the dashed black curves represent the diabatic SOC (Section 5.3) generated by the presence of the X_1 avoided crossing.

consistent physical character throughout the range of internuclear distances explored in the scattering calculation. This step, together with the diabaticization of the adiabatic PECs is important because in this way the different asymptotic char-

acter of the scattering state evolves into its short range in a consistent way.

6.2.3 The interaction matrix in BF frame

Using Hund's case (a) PECs, R -dependent SOCs, and Gaussian coupling associated with the avoided crossing X_1 , the interaction energy matrix can be constructed in the BF frame. The resulting matrix is a real symmetric 16×16 block-diagonal matrix, shown schematically in Table 6.3. It is organized according to the Ω quantum number and includes the electronic states that tend to the three relevant dissociation limits of LiBa^+ . The PECs appear on the diagonal elements, while the off-diagonal elements contain spin-orbit couplings and the non-adiabatic Gaussian coupling G_{X_1} . Colored entries denote direct SOCs between states correlated with the same dissociation limit, whereas blank entries correspond to indirect SOCs connecting different limits. Empty entries represent zero matrix elements.

$\Omega=0^+$				$\Omega=0^-$			$\Omega=1$				$\Omega=2$			$\Omega=3$
S+S	Ion+S	S+D		S+S	S+D		S+S	S+D			S+D			S+D
$1^1\Sigma^+$	$2^1\Sigma^+$	$3^1\Sigma^+$	$1^3\Pi$	$1^1\Sigma^+$	$2^1\Sigma^+$	$1^3\Pi$	$1^1\Sigma^+$	$2^1\Sigma^+$	$1^1\Pi$	$1^3\Pi$	$1^1\Delta$	$1^3\Pi$	$1^1\Delta$	$1^3\Delta$
$V(1^1\Sigma^+)$	0	0	$A_{1,4}$											
$2^1\Sigma^+$	0	$V(2^1\Sigma^+)$	$G_{2,3}$											
$3^1\Sigma^+$	0	$G_{3,2}$	$V(3^1\Sigma^+)$											
$1^3\Pi$	$A_{4,1}$	$A_{4,2}$	$A_{4,3}$	$V(1^3\Pi)$	$A_{4,4}$									
$1^3\Sigma^+$				$V(1^3\Sigma^+)$	0	$A_{5,7}$								
$2^3\Sigma^+$				0	$V(2^3\Sigma^+)$	$A_{6,7}$								
$1^3\Pi$				$A_{7,5}$	$A_{7,6}$	$V(1^3\Pi)$								
$1^3\Sigma^+$							$V(1^3\Sigma^+)$	0	$A_{8,10}$	$A_{8,11}$	0			
$2^3\Sigma^+$							0	$V(2^3\Sigma^+)$	$A_{9,10}$	$A_{9,11}$	0			
$1^1\Pi$							$A_{10,9}$	$A_{10,9}$	$V(1^1\Pi)$	$A_{10,11}$	$A_{10,12}$			
$1^1\Pi$							$A_{11,9}$	$A_{11,9}$	$A_{11,10}$	$V(1^1\Pi)$	$A_{11,12}$			
$1^1\Delta$							0	0	$A_{12,10}$	$A_{12,11}$	$V(1^1\Delta)$			
$1^3\Pi$												$V(1^3\Pi)$	$A_{13,14}$	$A_{13,15}$
$1^1\Delta$												$A_{14,13}$	$V(1^1\Delta)$	$A_{14,15}$
$1^3\Delta$												$A_{15,13}$	$A_{15,14}$	$V(1^3\Delta)$
$1^3\Delta$														$V(1^3\Delta)$

Table 6.3: Schematic representation of interaction energy matrix $\bar{\mathbf{W}}_a^{\text{so-qd}}(R)$ for LiBa^+ in the BF frame constructed from the Hund's case (a) PECs, the R -dependent SOCs, and the Gaussian coupling G_{X_1} associated with the X_1 avoided crossing. Empty cells denote zero matrix elements.

6.2.4 Long-range extrapolation of PECs and SOCs

Ab initio PECs and SOCs are calculated up to 45.0 a.u., whereas the atom-ion interaction extends over much larger internuclear distances due to its long-range charge-induced dipole character. Therefore, both the PECs and the SOCs must be extrapolated toward the asymptotic region before they are used in the scattering calculations.

The PECs are extrapolated using the usual multipolar expansion of atom-ion interaction $D_e - C_4/R^4 - C_6/R^6$, where D_e is the dissociation energy of the considered PEC (Table 6.1). The coefficient $C_4 = 82.2$ a.u. corresponds to half of the

static dipole polarizability of the Li atom, evaluated with the same electronic structure calculation as for PECs for consistency [142]. The values of the van der Waals coefficient C_6 were then evaluated at $R = 45$ a.u. using the above expression. The values obtained for C_6 are listed in Table 6.1.

We checked that the R -dependent SOCs have nearly reached their asymptotic value at $R = 45$ a.u.. Therefore, beyond this distance, the direct SOCs were set equal to the corresponding atomic fine-structure values, whereas the indirect SOCs were set to zero.

6.3 Results

Before introducing the full multichannel quantum-scattering model, it is useful to recall why such a treatment is required for the Li-Ba⁺ collision. Previously in our group, simplified descriptions provided valuable qualitative insight into the role of the most important crossings. A simple Landau-Zener model was first used to estimate the efficiency of the avoided crossing X_1 associated with NRCE. This approach was then extended to a four-channel Landau-Zener model based on the $\Omega = 0^+$ Hund's case (c) PECs. In addition, a reduced quantum-scattering calculation was performed within the same subspace of $\Omega = 0^+$ symmetry. Although these models, based on the same Hund's case (a) PECs as in the present calculations, capture part of the underlying mechanism, they do not reproduce the experimentally observed hierarchy of inelastic processes.

This limitation indicates that the collision dynamics cannot be described solely within a single molecular symmetry or by a purely local treatment of the avoided crossings. In particular, the competition between NRCE, NRQ, and FSQ requires the simultaneous inclusion of the relevant R -dependent spin-orbit and rotational couplings. Therefore, in the following, we use the complete MCQS model, based on the 16×16 interaction matrix introduced above. The complete 16×16 potential energy matrix is given in Table 6.3. The total angular momentum of the collision complex is defined as

$$\mathbf{J} = \mathbf{j}_{\text{Li}} + \mathbf{j}_{\text{Ba}^+} + \boldsymbol{\ell} \equiv \mathbf{j} + \boldsymbol{\ell}, \quad (6.5)$$

where $\mathbf{j}_{\text{Li}}$ and $\mathbf{j}_{\text{Ba}^+}$ denote the total electronic angular momentum of Li and Ba⁺, and $\boldsymbol{\ell}$ the rotational angular momentum of the colliding partners. The associated quantum numbers are J , j , and ℓ .

The Hamiltonian $\mathbf{H}_\ell$ that describes the system includes electronic interactions through potential energy curves and spin-orbit couplings, and is written as

$$\mathbf{H}_\ell(R) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \mathbf{I} + \frac{\hbar^2 \ell(\ell+1)}{2\mu R^2} \mathbf{I} + \bar{\mathbf{W}}_a^{\text{so}-qd}(R), \quad (6.6)$$

where $\mu = 10481.62$ a.u. is the reduced mass of LiBa⁺ and $\mathbf{I}$ denotes the identity matrix. The matrix $\bar{\mathbf{W}}_a^{\text{so}-qd}$ (the bar indicating that the matrix of Section 5.2 is restricted to the submatrix involving states correlated to $S + D$, $S + S$, and Ion+ S asymptotes) contains Hund's case (a) PECs on the diagonal (including the locally-linearized PECs $2^1\Sigma^+$ and $3^1\Sigma^+$), the Gaussian coupling functions, and the molecular spin-orbit couplings.

Coupled equations are solved using the log-derivative method described in Subsection 3.6.4, employing a constant propagation step size of 0.005 a.u. up to $R_{\max} = 10^4$ a.u., chosen sufficiently large to ensure that the interaction potential becomes negligible compared to collision energy

6.3.1 Hund's case (*e*) PECs

The transformation connecting Hund's case (*c*) and Hund's case (*e*) molecular representations is described in Chapter 4. The relevant quantum numbers associated with the $S+S$, $\text{Ion}+S$, and $S+D$ dissociation limits are summarized in Appendix ???. The Hund's case (*e*) PECs are obtained by diagonalizing the potential energy matrix expressed in the SF frame for a given value of the total angular momentum J and parity p . The Hund's case (*e*) PECs for $J = 0, 1, 2, 3$ are shown in Figure 6.5 for both parities.

Due to the available angular momenta (see Appendix ??), the number of coupled channels (listed in Table B.5) quickly saturates with up to 12 or 13 channels for $J \geq 3$ depending on the particular combination (J, p) . For example, the $(J = 0, p = +)$ case involves only the $\Omega = 0^+$ subspace together with $\ell = 2$ (Figure 6.5 panel a)). The variation of the maximum number of channels originates from the contribution of the single $\Omega = 0^+$ state correlated with the $\text{Ion}+S$ dissociation limit. This channel is present for $(J \text{ even}, p = +)$ and $(J \text{ odd}, p = -)$ symmetries, while it is absent for $(J \text{ odd}, p = +)$ and $(J \text{ even}, p = -)$.

At short internuclear distances, the Hund's case (*e*) PECs closely resemble those obtained in Hund's case (*c*) shown in Fig. 5.3 panel a). However, the inclusion of rotational (Coriolis) couplings leads to a more complex structure. In particular, the avoided crossing X_1 remains clearly visible, although its detailed pattern now depends on the value of J .

A notable modification is observed for the crossing X_3 located near $R \approx 6.2$ a.u., which becomes an avoided crossing in this representation (Figure 6.5 panels j) and k)). This behavior arises from the combined action of rotational coupling and indirect spin-orbit interaction and is associated with the matrix element $A_{8,11}$ in Table 6.3. As a consequence, the present model strongly suggests that the NRQ process might play a significant role in the dynamics. We recall that this crossing was previously considered in [39]. A related mechanism involving indirect spin-orbit coupling has also been proposed to account for anomalous hyperfine relaxation in cold Rb-Yb^+ collisions [143].

6.3.2 Cross sections and rate coefficients

The cross sections and rate coefficients are calculated according to the methodology exposed in Section 3.6.5. Calculations were performed for the two possible incoming channels $\text{Li}(2^2S_{1/2})+\text{Ba}^+(5^2D_{3/2})$ and $\text{Li}(2^2S_{1/2})+\text{Ba}^+(5^2D_{5/2})$, and extracted for each inelastic process (FSQ, NRCE, NRQ). Both parities can be treated separately as they characterize two independent Hilbert spaces of the system. Before comparing to experiment, it is worth investigating parity-dependent cross sections to decipher their dependency on total angular momentum quantum number J and thus identify the role of possible resonances.

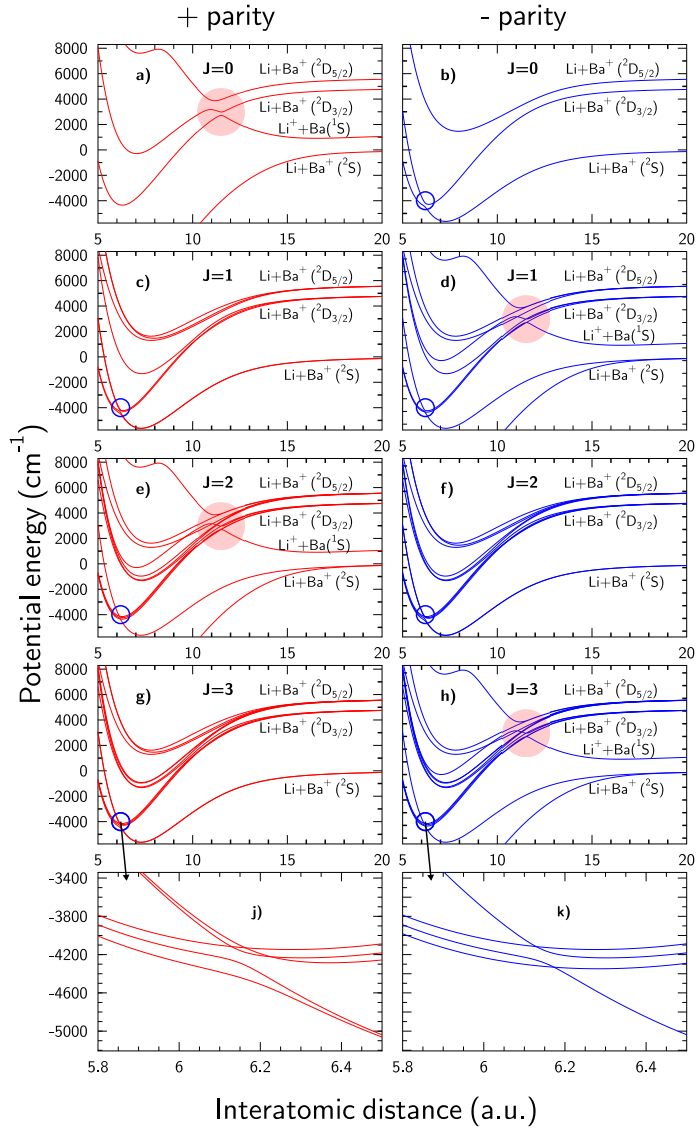


Figure 6.5: Hund's case (*e*) potential energy curves associated with the three dissociation limits $S + S$, $\text{Ion} + S$, and $S + D$, shown for both values of parity $+/-$ and for total angular momentum values $J = 0, 1, 2, 3$. The red shaded area highlights the avoided crossing X_1 . Panels j) and k) magnify the PECs in the vicinity of the X_3 avoided crossing highlighted by blue circles in panels g) and h).

The infinite sum over J , see Eq.3.118, was truncated. The maximal value, $J_{\max}$, was determined as follows: first we determined the partial wave ℓ' for which the potential barrier exceeds the collisional energy. In the case of the $S + D$ -limit $J_{\max} = \ell' + 3$. As an example, at $T = 3 \times 10^{-5}$ K, where the measurements were performed, $\ell' = 2$ thus $J_{\max} = 5$. The largest partial wave to be considered for the limit $S + D$ is $\ell_{\max} = 8$. A characteristic distance $R_{\max}$ can be associated with each partial wave, defined as the separation at which the kinetic energy begins to dominate the effective potential. For the previously discussed case with $\ell_{\max} = 8$, this distance is $R_{\max} \sim 6000$ a.u., as illustrated in Fig.6.6.

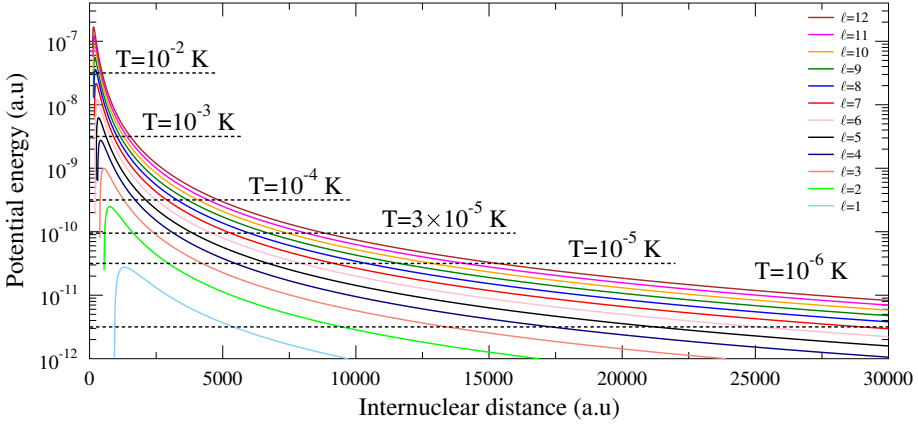


Figure 6.6: Long-range effective potential energy curves of LiBa^+ (in atomic units), represented by $-C_4/R^4 + \ell(\ell + 1)/(2\mu R^2)$, as the function of the internuclear distance R , are shown for different values of partial wave ℓ , in colored solid lines. The horizontal dashed black lines indicate the collisional energies expressed as temperature $T = E_{\text{col}}/k_B$.

Fixing $\ell = 8$, we can see that $R_{\max}$ increases as the temperature decreases. For example, at $T = 10^{-5}$ K the $R_{\max}$ is $\sim 10\,000$ a.u., while at $T = 10^{-4}$ K it falls below $\sim 5\,000$ a.u.. This example highlights that, at low energies, even though fewer partial waves need to be considered, the large value of $R_{\max}$ increases the computational cost. Although $R_{\max}$ decreases for higher temperatures, the number of partial waves increases considerably, which also increases the computational cost.

Inelastic partial cross sections for parity

The results of the quantum scattering calculation in the parity-dependent case are shown in Fig. 6.7, together with the predictions of the Langevin model varying as $E_{\text{col}}^{-1/2}$ with energy, presented in Section 3.5. In addition, we determined a so-called "scaled Langevin cross section" $\bar{\sigma}_L$ by adjusting the coefficient ξ of the function $\xi E_{\text{col}}^{-1/2}$ to match the cross section in the classical regime involving many

partial waves ($E_i \gtrsim k_B \times 1 \text{ mK}$). This confirms that the computed cross sections reflect the expected Langevin behavior controlled by long-range interactions varying as R^{-4} . This is better viewed on the same results drawn on a linear scale in energy, see Fig. 6.8.

Partial cross sections for inelastic and elastic collisions (EC) are presented in Appendix D and Appendix E, respectively. These results are useful to understand the underlying structures visible in the total cross sections.

The calculated cross sections reveal the same hierarchy between the inelastic processes for both parities. Comparing scaled quantities $\bar{\sigma}_L$, the FSQ process is dominant for the entrance channel $\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{5/2})$, with $\bar{\sigma}_L(\text{FSQ}) \approx 4\bar{\sigma}_L(\text{NRCE}) \approx 3000\bar{\sigma}_L(\text{NRQ})$ for parity "+", and $\bar{\sigma}_L(\text{FSQ}) \approx 8\bar{\sigma}_L(\text{NRCE}) \approx 2000\bar{\sigma}_L(\text{NRQ})$ for parity "-". The FSQ process does not obviously occur from the entrance channel $\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{3/2})$, and NRQ now dominates NRCE, with $\bar{\sigma}_L(\text{NRQ}) \approx 10\bar{\sigma}_L(\text{NRCE})$ for parity "+", and $\bar{\sigma}_L(\text{NRQ}) \approx 22\bar{\sigma}_L(\text{NRCE})$ for parity "-". This hierarchy is consistent with the Hund's case (c) PECs shown in Fig. 5.3:

- NRQ is induced by the crossing X_3 that involves a PEC correlated to $\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{3/2})$, which implies that this process is negligible if the collision starts from the other entrance channel.
- When the collision starts from $\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{3/2})$, our results demonstrate that the X_3 crossing at short distances is predicted to be more efficient than the X_1 crossing at intermediate distance, as NRQ dominates NRCE in this case.
- The outgoing channel of FSQ ($\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{3/2})$) is the closest in energy to the entrance channel ($\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{5/2})$) and thus easier to reach than the NRCE outgoing channel.

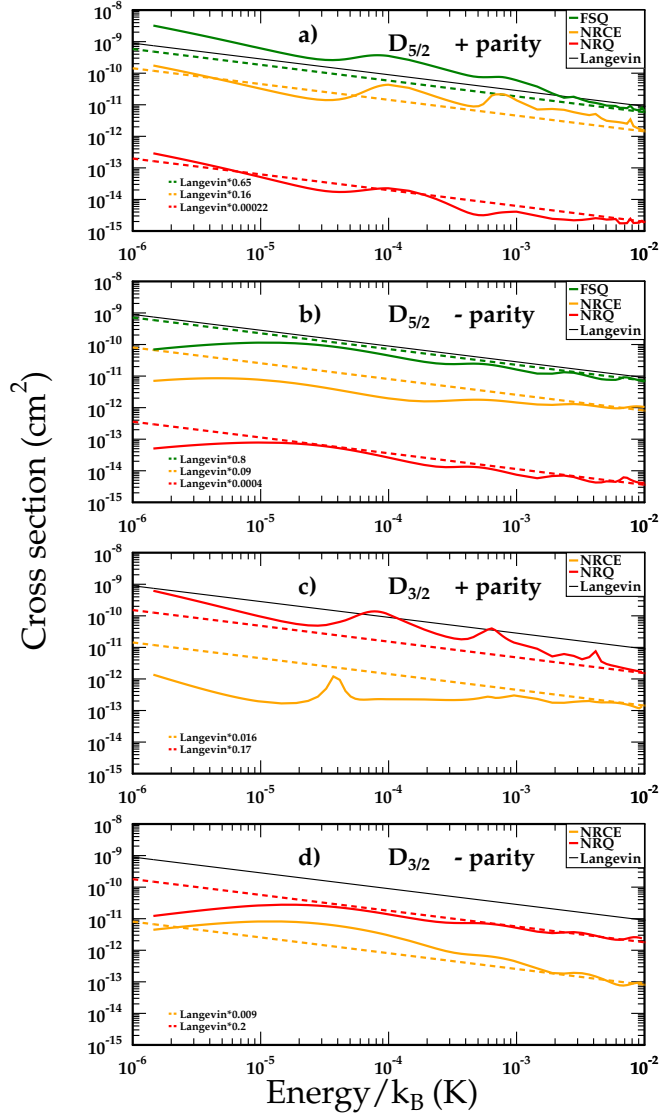


Figure 6.7: Parity-resolved total cross sections (Eq. 3.117) as a function of collision energy E_{col}/k_B expressed as a temperature for the inelastic processes FSQ (solid green line), NRCE (solid orange line) and NRQ (solid red line). The shortened notations $D_{5/2}$ and $D_{3/2}$ refer to the two entrance channels $\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{5/2})$ and $\text{Li}(2^2S_{1/2}) + \text{Ba}^+(5^2D_{3/2})$. Black line: Langevin cross section σ_L . Dashed colored lines: scaled Langevin cross sections $\bar{\sigma}_L$ (see text).

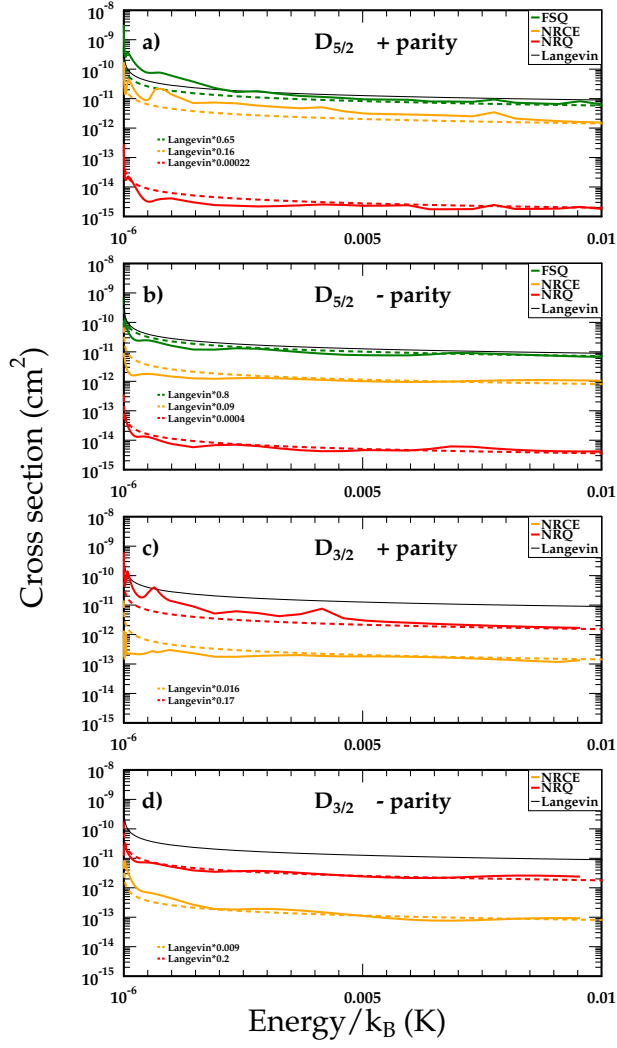


Figure 6.8: Same as Fig. 6.7 with a linear scale in E_{col}/k_B .

Total cross sections

The total state-to-state cross sections $\sigma(\beta \leftarrow \alpha, k_\alpha)$ (Eq. 3.119) and rate coefficients $K(\beta \leftarrow \alpha, k_\alpha)$ (Eq. 3.120) for each inelastic process are presented in Fig. 6.9 for both entrance channels $S + D_{5/2}$ and $S + D_{3/2}$, where resonant structures are still visible after the summation over J .

To compare our theoretical results with the experimental observations, we also calculated the thermalized rate coefficients $K(T_{\text{eff}}; f)$ (Eq. 3.121) assuming a Maxwell-Boltzmann distribution of collision energies. The resonant structures are significantly smoothed out (Fig. 6.9 panels c) and d)), thus they would likely remain unobserved in experiments.

The experimental rate coefficients were determined from the measurement of survival probabilities and branching ratios. The atomic density n was obtained from independent measurements, such as atom number, trapping frequencies, cloud size, and temperature. This calibration gives $n_{3/2} = 1.3(2) \times 10^{11} \text{ cm}^{-3}$ and $n_{5/2} = 1.6(4) \times 10^{11} \text{ cm}^{-3}$ for the ion initially prepared in the $5^2D_{3/2}$ and $5^2D_{5/2}$ state, respectively. The measured rate coefficient for the $S + D_{3/2}$ incoming channel was $\mathcal{R}_L = 610(100) \text{ s}^{-1}$, while for the $S + D_{5/2}$ channel $\mathcal{R}_L = 770(180) \text{ s}^{-1}$. The experimental Langevin rate coefficients are obtained as

$$K_L^{\text{exp}} = \frac{\mathcal{R}_L}{n}, \quad (6.7)$$

resulting in $K_L^{\text{exp}, 3/2} = 4.69 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for $S + D_{3/2}$ and $K_L^{\text{exp}, 5/2} = 4.81 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for $S + D_{5/2}$. The survival probability of the ion in the $5^2D_{3/2}$ state in the atomic cloud was experimentally found to be $P_{\text{sur}}^{3/2} = 0.30(4)_{\text{stat}}(6)_{\text{sys}}$, while in the $5^2D_{5/2}$ state $P_{\text{sur}}^{5/2} = 0.17(5)_{\text{stat}}(3)_{\text{sys}}$. The statistical and systematic errors are denoted by "stat" and "sys", respectively. A total of 510 and 116 events, including elastic and inelastic ones, see Table 6.4, were recorded for the ions initially prepared in the $5^2D_{3/2}$ and $5^2D_{5/2}$ states, respectively.

To obtain the reaction rate coefficient for each inelastic process, the survival probabilities and the measured branching ratios of the different processes were considered. For the incoming channel $S + D_{3/2}$, 90.6% of the observed inelastic events is NRQ, while 9.4% is NRCE, see Table 6.4. Therefore, the corresponding rate coefficients are

$$\begin{aligned} K_{\text{exp}}^{\text{NRQ}} &= 0.906 \times P_{\text{sur}}^{3/2} \times K_L^{\text{exp}, 3/2} \\ &= 7.22 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \end{aligned} \quad (6.8)$$

$$\begin{aligned} K_{\text{exp}}^{\text{NRCE}} &= 0.094 \times P_{\text{sur}}^{3/2} \times K_L^{\text{exp}, 3/2} \\ &= 7.49 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}. \end{aligned} \quad (6.9)$$

Similarly, for the incoming channel $S + D_{5/2}$, the branching ratios are 66% for FSQ and 34% for NRCE, see Table 6.4, yielding

$$\begin{aligned} K_{\text{exp}}^{\text{FSQ}} &= 0.66 \times P_{\text{sur}}^{5/2} \times K_L^{\text{exp}, 5/2} \\ &= 9.52 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}, \end{aligned} \quad (6.10)$$

$$\begin{aligned}
K_{\text{exp}}^{\text{NRCE}} &= 0.34 \times P_{\text{sur}}^{5/2} \times K_L^{\text{exp},5/2} \\
&= 4.90 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.
\end{aligned} \tag{6.11}$$

The experimental and theoretical results are collected in Table 6.4. The table lists the event statistics, the experimental branching ratios, the deduced experimental rate coefficients normalized to the Langevin rate, and the corresponding MCQS predictions. Theoretical values are reported for the experimental temperature $T_{\text{eff}} = 30 \mu\text{K}$.

Table 6.4: Experimental and theoretical reaction rate coefficients for the observed processes in the collision between Ba^+ ion, initially prepared in the $5^2D_{3/2}$ or $5^2D_{5/2}$ state, and Li atom in its $2^2S_{1/2}$ ground state. The total number of counts of the elastic (EC), inelastic (FSQ, NRQ) and reactive (NRCE) processes, their relative abundance (%) with respect to the total number of counts, excluding EC, are also listed. $K_{\text{exp}}^{\text{proc.}}/K_L^{\text{exp}}$, for each process are given, normalizing the experimental rate coefficients ($K_{\text{exp}}^{\text{proc.}}$) by the experimental Langevin rate coefficients (K_L^{exp}). The theoretical ones are obtained similarly: the non-thermalized rate coefficients (K_{MCQS}) obtained from the MCQS calculations are normalized with the theoretical Langevin rate coefficients (K_L^{th}). The ratio between the scaled Langevin rate coefficients, which is adjusted to the high energy tail of MCQS rate coefficients, and Langevin rate, is also presented in order to give a range of acceptable theoretical values in the last column of the table. The non-thermalized rates are calculated at collisional energy $T = 30 \mu\text{K}$, that is stated in Ref. [39].

Event	Process	Counts	Ratio(%)	$K_{\text{exp}}^{\text{proc.}}/K_L^{\text{exp}}$	$K_{\text{MCQS}}/K_L^{\text{th}}; K_{\text{MCQS-L}}/K_L^{\text{th}}$
$5^2D_{3/2}$: $K_L^{\text{exp}} = 4.69 \times 10^{-9} \text{ cm}^3/\text{s}$; $K_L^{\text{th}} = 4.81 \times 10^{-9} \text{ cm}^3/\text{s}$					
	EC	177	-	-	-
Hot	NRQ	302	90.6(16)	$0.154(45)_{\text{stat}}(27)_{\text{sys}}$	0.21;0.18
Loss	NRCE	31	9.4(16)	$0.016(5)_{\text{stat}}(3)_{\text{sys}}$	0.021;0.012
Total		510			
$5^2D_{5/2}$: $K_L^{\text{exp}} = 4.81 \times 10^{-9} \text{ cm}^3/\text{s}$; $K_L^{\text{th}} = 4.81 \times 10^{-9} \text{ cm}^3/\text{s}$					
	EC	41	-	-	-
Cold+Hot	FSQ	42 + 8	66(6)	$0.198(26)_{\text{stat}}(40)_{\text{sys}}$	1.06;0.725
Loss	NRCE	25	34(6)	$0.102(14)_{\text{stat}}(20)_{\text{sys}}$	0.052;0.16
Total		116			

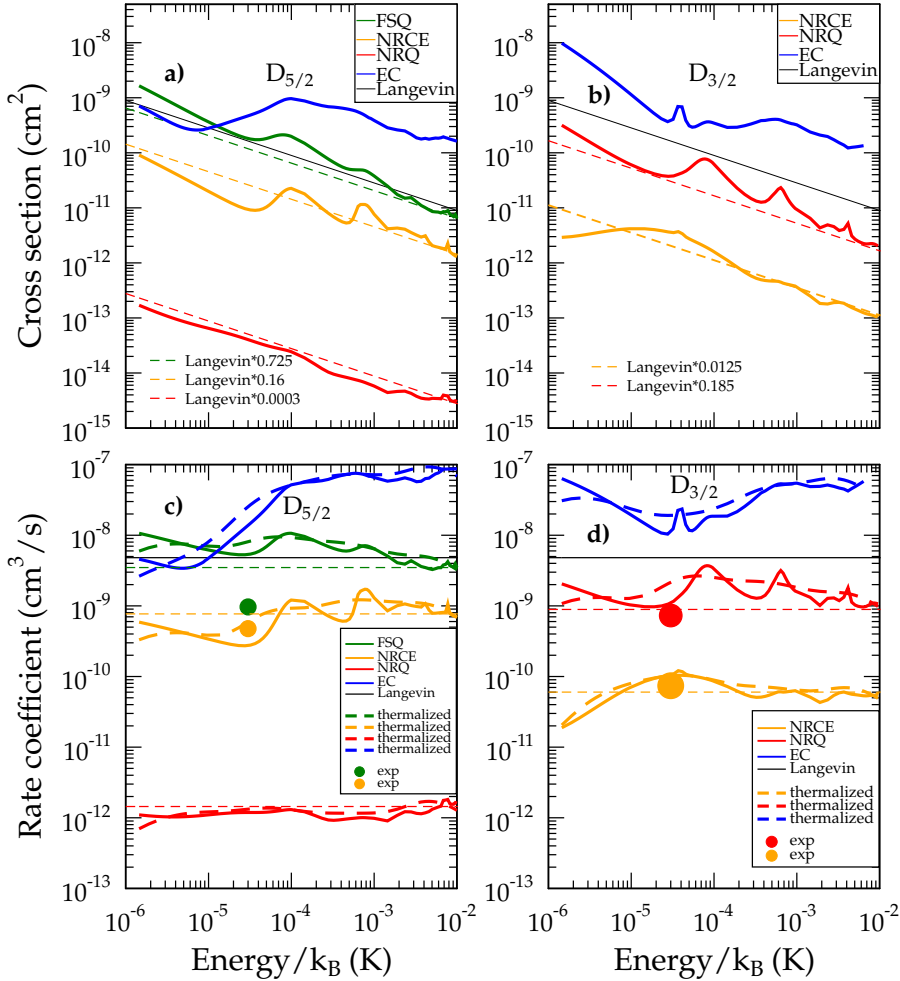


Figure 6.9: Total elastic (blue solid lines) and inelastic (colored solid lines) cross sections and rate coefficients for the entrance channels $S + D_{5/2}$ panels a) and c), $S + D_{3/2}$ panels b) and d). Black solid lines and colored dashed lines show the Langevin and scaled Langevin cross sections and rate coefficients. The thermalized rate coefficients are displayed in thick long-dashed lines. Experimental rate coefficients at $T_{\text{eff}} = 30 \mu\text{K}$, given in Eqs.6.8-6.11, are shown as filled circles, with size reflecting the combined statistical and systematical uncertainties.

In conclusion, we can say that the agreement between theory and experiment is very good, confirming the importance of the coupling between internal angular momenta and the relative rotation of the colliding partners, as already suggested in [69]. However, a notable discrepancy is observed for the FSQ process in the $\text{Li}(2^2S_{1/2})+\text{Ba}^+(5^2D_{5/2})$ channel, where the calculated rate exceeds the experimental value by approximately a factor of four. This deviation may originate from residual inaccuracies in the spin-orbit couplings obtained within the quasi-diabatic representation or the absence of hyperfine levels in the model, since the collisional partners are polarized in the experiment.

One limitation of the present model is that Li atoms are not explicitly treated as being polarized in the $|f = 1/2, m_f = -1/2\rangle$ hyperfine state. A more complete treatment would require an enlarged Hilbert space including additional SF frame angular momentum projections and hyperfine degrees of freedom. Such an extension could be important for describing collisions involving spin-polarized partners or different hyperfine preparations. Nevertheless, previous results on $\text{Rb}-\text{Sr}^+$ collisions suggest that strong Coriolis mixing involving higher partial waves can reduce the sensitivity to the relative spin orientation [69].

Chapter 7

Quantum study of electronic excitation exchange between ultracold metastable Sr^+ ion and Rb atoms

In this chapter, I present the results that I obtained on a second ion-atom system, namely RbSr^+ . The chapter is based on the paper that I co-authored and recently submitted [132]. It might contain several repetitions of arguments presented in the previous Chapter, as it follows a similar progression, but I decided to keep them for internal consistency.

The combination Rb-Sr^+ is interesting because the colliding partners have comparable masses, which might enable efficient energy transfer in elastic collisions and is therefore favorable for sympathetic cooling of the ion. When the ion Sr^+ is excited in a metastable state due to the presence of cooling and trapping lasers in the experiment, inelastic processes compete with elastic energy transfer and limit the efficiency of sympathetic cooling. In 2020, our group contributed to a joint experimental and theoretical study [69] in which the $^{88}\text{Sr}^+(4d\ ^2D_{5/2,3/2})$ ion collides with ground state $^{87}\text{Rb}(5s\ ^2S_{1/2})$ atoms. Two inelastic processes were identified as the dominant loss mechanisms in the experiment. Theoretical investigations [69] demonstrated the complexity of PECs that need to be considered for the proper description of the collision, and established a strong mixing of internal angular momenta with the rotational one. The semiclassical Landau-Zener model was applied on these PECs, and did not reproduce the experimental observations, which suggested the need for quantum scattering calculations. In this chapter I will present a full quantum scattering description of this collision in the ultracold domain.

7.1 Electronic structure of RbSr^+ molecular ion

7.1.1 Hund's case (a) PECs

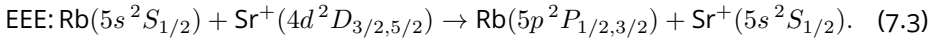
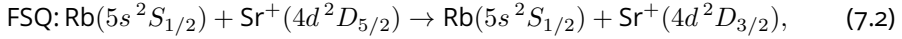
The adiabatic Hund's case (a) PECs of RbSr^+ , obtained using the quantum chemistry approach described in Section 3.3, are presented in Fig. 7.1. The calculated PECs are displayed up to the eighth dissociation limit $\text{Rb}(5s^2S) + \text{Sr}^+(4d^2D)$ including all possible molecular symmetries. A real crossing X_3 occurs around $R = 7$ a.u. the PECs ($1^3\Sigma^+$ and $1^3\Pi$), which is responsible for the complexity of the spectrum of magnetic Feshbach resonances in the ground-state entrance channel $\text{Rb}(5s^2S) + \text{Sr}^+(5s^2S)$ [71]. Two avoided crossings X_1 and X_2 are also highlighted between PECs of states $5^1\Sigma^+$ and $6^1\Sigma^+$, and of states $4^3\Sigma^+$ and $5^3\Sigma^+$. As in the previous chapter, the couplings around these avoided crossings are treated by local linearization of adiabatic PECs at the avoided crossing, and modeled by a gaussian function $G_{X_i}(R)$ in the interaction Hamiltonian matrix

$$G_{X_i}(R) = U_{X_i} \exp\left(-\left(\frac{R-R_{X_i}}{\delta_{X_i}}\right)^2\right), \quad (7.1)$$

The resulting parameters for the crossings are:

- X_1 : $R_{X_1} = 14.9$ a.u., $U_{X_1} = 2.51 \times 10^{-4}$ a.u., $\delta_{X_1} = 0.15$ a.u.
- X_2 : $R_{X_2} = 13.7$ a.u., $U_{X_2} = 5.74 \times 10^{-4}$ a.u., $\delta_{X_2} = 0.30$ a.u..

These avoided crossings induce two main inelastic processes, fine-structure quenching (FSQ) and electronic excitation exchange (EEE):



The entrance channels will be called $S + D$, or $S + D_{3/2,5/2}$, and the outgoing channel of EEE as $P + S$, or $P_{1/2,3/2} + S$. Based on the energy-level scheme of Fig. 2.3 panel b), non-radiative quenching (NRQ) and non-radiative charge exchange (NRCE) are also energetically allowed. However, the PECs in Fig. 7.1 do not show any obvious manifestation of NACTs for these processes.

7.1.2 Spin-orbit couplings

The R -dependent SOC's have been determined following the two steps of quasi-diabatization described in Sections 5.2 and 5.3. They are presented in Fig. 7.2. At long distances, direct SOC's (panels a-e) approach the atomic values related to the atomic SO splitting of $\text{Sr}^+(4d^2D)$ or $\text{Rb}(5p^2P)$, while indirect SOC's vanish. Due to the necessity of a second step for quasi-diabatization (Section 5.3), SOC's for $\Omega = 0^+, 0^-, 1$ are identified by primes and drawn with thick lines when they involve Hund's case (a) states of $^1\Sigma^+$ or $^3\Sigma^+$ symmetry. Other SOC's remain unaffected by the diabaticization procedure.

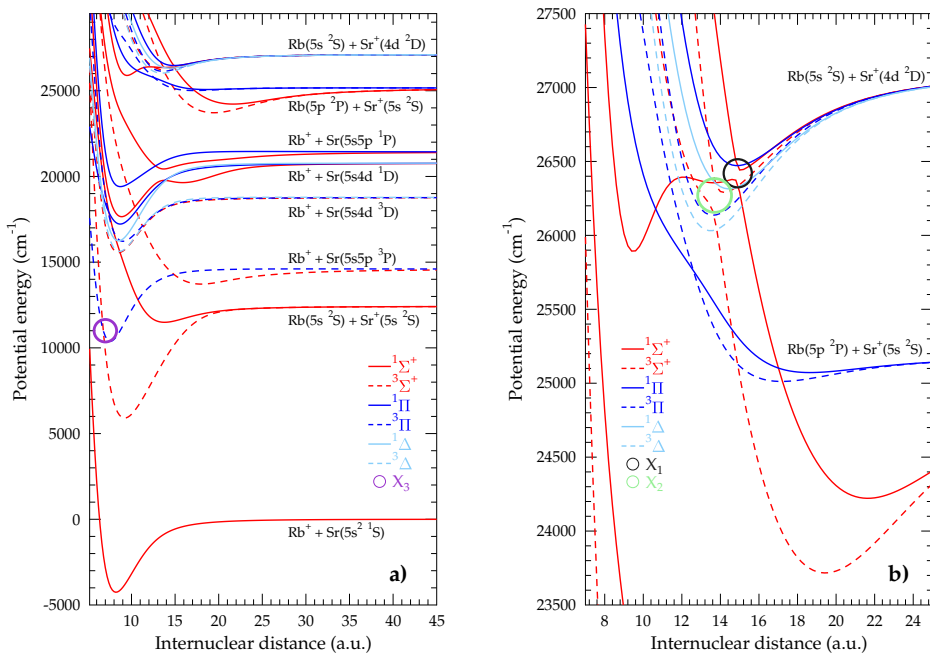


Figure 7.1: a) Hund's case (a) PECs of RbSr^+ up to the eighth dissociation limit. The X_3 crossing is highlighted by a circle. b) Blow-up of panel around the dissociation limits $\text{Rb}(5s^2S) + \text{Sr}^+(4d^2D)$ and $\text{Rb}(5p^2P) + \text{Sr}^+(5s^2S)$ relevant for the present calculations. The avoided crossings X_1 and X_2 are highlighted by a black and a green circle, respectively.

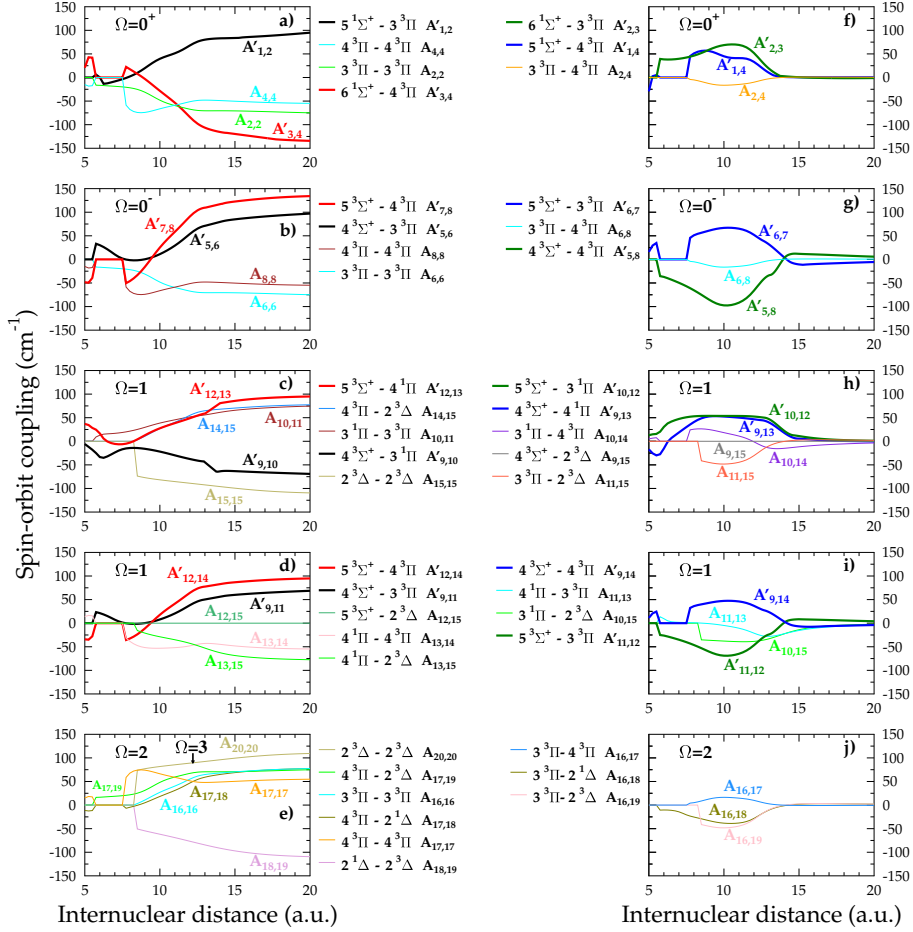


Figure 7.2: Direct (panels a-e) and indirect (panels f-j) molecular SOCs A_{pq} and A'_{pq} as a function of the internuclear distance between Hund's case (a) states correlated to the dissociation limits $S + D$ and $P + S$. $\Omega = 0^+$: panels a), f). $\Omega = 0^-$: panels b), g). $\Omega = 1$: panels c), d), h), i). $\Omega = 2, 3$: e), j). Thick lines and primes correspond to diabaticized SOCs (Section 5.3).

7.1.3 Interaction matrix in the BF frame

Using the Hund's case (a) PECs and the SOCs diabatized via the two steps described in Chapter 5, the interaction energy matrix is constructed in the BF frame. The first step of quasi-diabatization of the SOCs (Section 5.2) results in the matrix $\bar{\mathbf{W}}_{a,\Omega}^{\text{so-qd}}(R)$ matrix, and the second step of quasi-diabatization step of the SOCs (Section 5.3) leads to the matrix $\bar{\mathbf{W}}_{a,\Omega}^{\text{so-qd}2}(R)$ presented in Table 7.1. The matrix is a 20×20 symmetric block-diagonal matrix organized according to the $\Omega = \Lambda + \Sigma$ quantum number. Each Ω block is further divided according to the two considered asymptotic limits, $P + S$ and $S + D$. The notation of the matrix elements in the interaction matrix is consistent with that used in Fig. 7.2, and the labels A.1-A.9 refer to the matrices given in Section 3.4. Diagonalization of this matrix yields the Hund's case (c) PECs previously presented in Fig. 5.3 panel b) and recalled in Fig. 7.3 for convenience. The X_1 and X_2 avoided crossings are still recognizable, but a series of avoided crossings emerges due to the strong spin-orbit coupling between the electronic states. Therefore, simple models such as the Landau-Zener approach cannot accurately predict possible outcomes, as discussed in Ref. [69]. Consequently, a full quantum mechanical treatment is needed in order to explain the experimentally observed events.

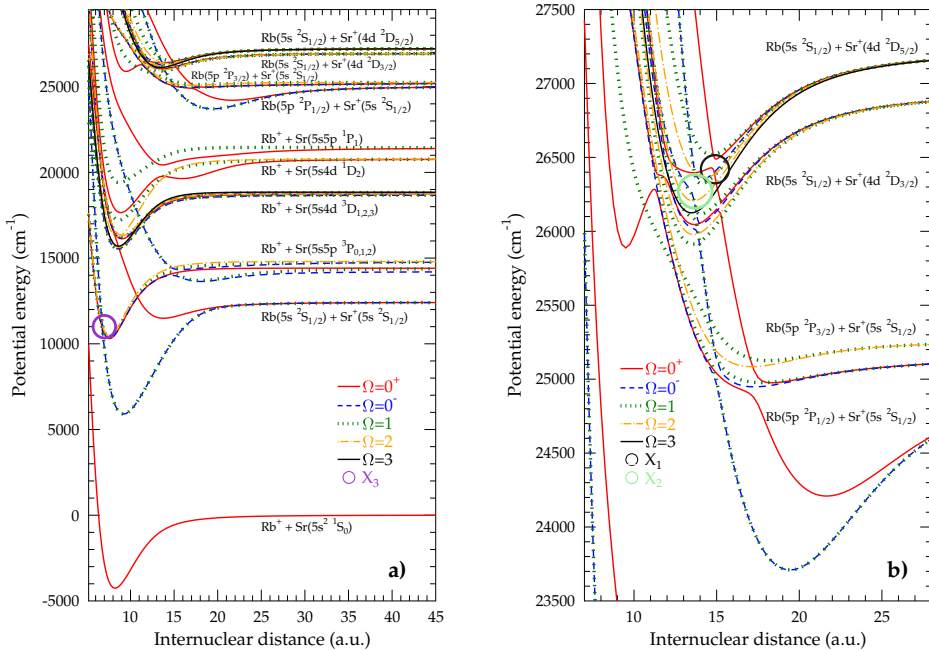


Figure 7.3: Hund's case (c) PECs of RbSr^+ in the BF frame up to the eighth dissociation limit, namely $\text{Rb}(5s \ ^2S) + \text{Sr}^+(4d \ ^2D)$, panel a), after the diagonalisation of matrix $\bar{\mathbf{W}}_{a,\Omega}^{\text{qd-so}}(R)$ or $\bar{\mathbf{W}}_{a,\Omega}^{\text{so}}(R)$. Panel b) is a zoom for the highest two dissociation limits, $S + D$ and $P + S$ relevant for the experimentally observed processes.

	$\Omega=0^+$				$\Omega=0^-$				$\Omega=1$				$\Omega=2$				$\Omega=3$		
	P+S		S+D		P+S		S+D		P+S		S+D		P+S		S+D		S+D		
	5 Σ^+	3 Π	6 Σ^+	4 Π	4 Σ^+	3 Π	5 Σ^+	4 Π	4 Σ^+	3 Π	3 Π	5 Σ^+	4 Π	4 Π	2 Δ	3 Π	4 Π	2 Δ	2 Δ
	$V(5 \Sigma^+)$		$A_{1,2}$	G_1	$A_{1,4}$														
	3 Π	$A_{2,1}$	$V(3 \Pi)$		$A_{2,3}$	$A_{2,4}$													
	6 Σ^+	G_1	$A_{3,2}$	$V(6 \Sigma^+)$		$A_{3,4}$													
	4 Π	$A_{4,1}$	$A_{4,2}$	$A_{4,3}$		$V(4 \Pi)$		$A_{4,4}$											
	4 Σ^+					$V(4 \Sigma^+)$		$A_{5,6}$	G_2	$A_{5,8}$									
	3 Π					$A_{6,5}$		$V(3 \Pi)$	$A_{6,7}$	$A_{6,8}$									
	5 Σ^+					G_2		$A_{7,6}$	$V(5 \Sigma^+)$		$A_{7,8}$								
	4 Π					$A_{8,5}$		$A_{8,6}$	$A_{8,7}$		$V(4 \Pi)$		$A_{8,9}$						
	4 Σ^+									$V(4 \Sigma^+)$		$A_{9,10}$	$A_{9,11}$	G_2	$A_{9,13}$	$A_{9,14}$	$A_{9,15}$		
	3 Π									$A_{10,9}$		$V(3 \Pi)$	$A_{10,11}$	$A_{10,12}$	$A_{10,14}$	$A_{10,15}$			
	5 Σ^+									$A_{11,9}$		$A_{11,10}$	$V(3 \Pi)$	$A_{11,12}$	$A_{11,13}$	$A_{11,14}$	$A_{11,15}$		
	4 Π									G_2		$A_{12,10}$	$A_{12,11}$	$V(5 \Sigma^+)$	$A_{12,13}$	$A_{12,14}$	$A_{12,15}$		
	2 Δ									$A_{13,9}$		$A_{13,10}$	$A_{13,11}$	$A_{13,12}$	$V(4 \Pi)$	$A_{13,14}$	$A_{13,15}$		
	3 Π									$A_{14,9}$		$A_{14,10}$	$A_{14,11}$	$A_{14,12}$	$A_{14,13}$	$V(4 \Pi)$	$A_{14,15}$		
	4 Π									$A_{15,9}$		$A_{15,10}$	$A_{15,11}$	$A_{15,12}$	$A_{15,13}$	$A_{15,14}$	$V(2 \Delta)$	$A_{16,15}$	
	2 Δ																	$V(3 \Pi)$	
	3 Π																	$A_{16,16}$	
	4 Π																	$A_{16,17}$	
	2 Δ																	$A_{16,18}$	
	2 Δ																	$A_{16,19}$	
	2 Δ																	$A_{17,16}$	
																		$V(4 \Pi)$	
																		$A_{17,17}$	
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																		$V(2 \Delta)$	
																		$A_{34,19}$	
																		$V(2 \Delta)$	

Table 7.1: Schematic representation of the 20×20 interaction energy matrix $\bar{\mathbf{W}}_a^{\text{so}-\text{qd}2}(R)$ in the BF frame. The PECs denoted by V appear on the diagonal, V' being the linearized PECs. Spin-orbit couplings terms are denoted as $\mathbf{A}_{p,q}$, with a prime ($\mathbf{A}'_{p,q}$) when they are corrected by the second step of quasi-diabatization. Cells with colored background correspond to states and couplings correlated to the same asymptotic limit, whereas cells with white background correspond to indirect SOCs. Blank elements denote zero matrix elements. The G_1 and G_2 terms denote the Gaussian couplings associated with the X_1 and X_2 avoided crossings, respectively.

7.1.4 Long-range extrapolation of PECs and SOCs

PECs

The PECs and SOCs were calculated up to a distance of 45.0 a.u., which is insufficient to accurately describe the long-range behavior of the atom-ion interaction. Therefore, the PECs are extrapolated up to 10^4 a.u. using the multipolar expansion valid at large distances

$$V(R) = D_0 + \frac{C_3}{R^3} - \frac{C_4}{R^4} - \frac{C_6}{R^6}, \quad (7.4)$$

where C_3 , C_4 , and C_6 are the coefficients associated with the charge–quadrupole, charge–induced dipole, and van der Waals interactions, respectively. Energies D_0 of the corresponding dissociation limits are determined from the sum of atomic energy levels displayed in Table 7.2, calculated within the framework of the CIPSI code as the Hund’s case (a) PECs to ensure consistency with the calculated PECs. By construction, the first four rows of the table below are exact, because the parameters of the ECPs and CPPs were optimized to reproduce the corresponding experimental values. The energies of neutral Sr atom result from FCI calculations, and thus cannot be exact. However, the calculated energy levels agree with the corresponding NIST energies within a few 100 cm^{-1} .

Level	Energy (a.u.)
Rb(5s)	−0.153507732592
Rb(5p)	−0.095471900952
Sr ⁺ (5s)	−0.405204475915
Sr ⁺ (4d)	−0.338269312485
Sr(5s ² ¹ S)	−0.615276171121
Sr(5s5p ³ P)	−0.548793716582
Sr(5s4d ³ D)	−0.529764040902
Sr(5s4d ¹ D)	−0.520635929285
Sr(5s5p ¹ P)	−0.517653559858

Table 7.2: Atomic energy levels calculated with the CIPSI code, in the case of the first four values the calculations were optimized to reproduce the corresponding experimental values.

In general, the coefficients C_3 , C_4 , and C_6 are obtained by fitting Hund’s case (a) PECs on 25 points in internuclear distance between 40 a.u. and 45 a.u.. When Rb in its ground state is involved, the coefficient $C_4 = \alpha_d^{(0)}/2$ related to the static dipole polarizability $\alpha_d^{(0)}$ is fixed to the value previously calculated in the group [142], namely, $C_4(S + S) = C_4(S + D) = 159.05 \text{ a.u.}$. These parameters are collected in Table 7.3.

The reliability of the long-range behavior of the calculated Hund’s case (a) PECs and the consistency of the fitting are demonstrated by an analysis of the

C_3 and C_4 coefficients. Regarding the ratio of the fitted C_3 coefficients for the Σ^+ and Π symmetries in the $P + S$ asymptote, we obtain -2.13 . This value is in reasonably good agreement with the analytical result given in the next paragraph.

Relation between the quadrupole moment of Rb(5p) and the C_3 coefficient

Considering the multipolar expansion of the electrostatic interaction $\hat{V}_{AB}(R)$ between an atom A and an ion B , R being the internuclear distance, the matrix element in the separated, uncoupled atomic basis $|n_A l_A m_A n_B l_B m_B\rangle$ can be written as [144]

$$\begin{aligned} & \langle n_A l_A m'_A n_B l_B m'_B | \hat{V}_{AB}(R) | n_A l_A m_A n_B l_B m_B \rangle = \\ & = \sum_{p_A, p_B=0}^{+\infty} \sum_{m=-p_<}^{+p_<} \frac{f_{p_A, p_B, m}}{R^{1+p_A+p_B}} \frac{C_{l_A, m_A, p_A, m}^{l_A, m'_A} C_{l_B, m_B, p_B, -m}^{l_B, m'_B}}{\sqrt{(2l_A+1)(2l_B+1)}} \times \\ & \times \langle n_A l_A || \hat{Q}_{p_A} || n_A l_A \rangle \langle n_B l_B || \hat{Q}_{p_B} || n_B l_B \rangle, \end{aligned} \quad (7.5)$$

where the quantum numbers l_A and l_B are the angular momenta of atom A and ion B , m_A , m_B are the corresponding magnetic quantum numbers, and all the remaining quantum numbers are given in the compact form $n_{A,B}$. The Clebsch-Gordan coefficients are denoted by C , $\hat{Q}$ denotes the multipole tensor operator, and $\langle || \rangle$ represents the reduced matrix elements. The $f_{p_A, p_B, m}$ factor is

$$f_{p_A, p_B, m} = \frac{(-1)^{p_B} (p_A + p_B)!}{\sqrt{(p_A + m)!(p_A - m)!(p_B + m)!(p_B - m)!}},$$

and $p_< = \min(p_A, p_B)$ is the smaller of p_A and p_B . Here, p_A and p_B are the ranks of the multipole tensor operators. In our specific case, the Rb atom is in a P state and the ion in an S state, thus $l_A = 1$ and $l_B = 0$. The quadrupole moment of the atom is associated with a tensor of rank 2, therefore $p_A = 2$, while the charge of the ion is associated with a tensor of rank 0, thus $p_B = 0$. For the P state m_A can be 0 or ± 1 , while for the S state $m_B = 0$. Substituting these values into the equation 7.5, we obtain $C_3^\Sigma = -\sqrt{\frac{2}{15}}$ for $m_A = 0$ and $C_3^\Pi = \frac{1}{\sqrt{30}}$ for $m_A = \pm 1$. The ratio between these two values is $C_3^\Sigma / C_3^\Pi = -2$, which is in good agreement with the fitted value of -2.13 .

The dipole polarizability of Rb(5p) and the C_4 coefficient

The quality of the calculated PECs is further strengthened by the fitted C_4 coefficients, which are in good agreement with previously reported theoretical values [145]

The anisotropic coefficient $C_4(P + S; \Lambda)$ for Rb(5p) can be written as

$$C_4(P + S; \Lambda) = 0.5 \times \left[\alpha_d^{(0)} + \alpha_d^{(2)} \frac{3\Lambda^2 - L(L+1)}{L(2L-1)} \right], \quad (7.6)$$

where $\alpha_d^{(0)}(5p)$ is the static dipole polarizability (isotropic), and $\alpha_d^{(2)}(5p)$ is the tensor dipole polarizability (anisotropic). The static dipole polarizabilities calculated in [145], $\alpha_d^{(0)}(5p^2P_{1/2})/2 = 407$ a.u. and $\alpha_d^{(0)}(5p^2P_{3/2})/2 = 437.5$ a.u., lead to the statistically averaged value of 427 a.u. for $\alpha_d^{(0)}(5p)/2$, where the statistical weights are 2 and 4 for $\alpha_d^{(0)}(5p^2P_{1/2})$ and $\alpha_d^{(0)}(5p^2P_{3/2})$ respectively. This value is in good agreement with the value obtained with our CIPSI code, after applying the same summation over atomic transitions with dipole moments as in [145], resulting $\alpha_d^{(0)}(5p)/2 = 430$ a.u.. The agreement for the tensor dipole polarizabilities is also satisfactory, the data reported in [145] being $\alpha_d^{(2)}(5p^2P_{3/2}) = -167$ a.u., while the one calculated by CIPSI is $\alpha_d^{(2)}(5p) = -162$ a.u.. Based on Eq. 7.6 we obtain $C_4(P+S; \Sigma) = 592.5$ a.u. and $C_4(P+S; \Pi) = 348.5$ a.u., which are in good agreement with the C_4 coefficients obtained from the fit, see Table 7.3.

Asymptote	State	C_3 (a.u.)	C_4 (a.u.)	C_6 (a.u.)
$(S+D)$	$6^1\Sigma$	0.00	159.05	10138.70
	$5^3\Sigma$	0.00	159.05	10138.70
	$4^1\Pi$	0.00	159.05	9336.57
	$4^3\Pi$	0.00	159.05	9336.57
	$2^1\Delta$	0.00	159.05	13121.60
	$2^3\Delta$	0.00	159.05	13121.60
$(P+S)$	$5^1\Sigma^+$	-25.43	477.59	194309.02
	$4^3\Sigma^+$	-25.43	477.59	194309.02
	$3^1\Pi$	11.94	345.59	-17451.10
	$3^3\Pi$	11.94	345.59	-17451.10
$(S+S)$	$2^1\Sigma^+$	0.00	159.05	11879.36
	$1^3\Sigma^+$	0.00	159.05	11879.36

Table 7.3: Long-range coefficients C_3 , C_4 , C_6 Hund's case (a) PECs determined in the present work.

SOCs

The long-range extrapolation of SOC's $A_{p,q}$ follows the approach proposed of [146] using the function

$$A(R) = \alpha + \frac{\beta_k}{R^k}, \quad (7.7)$$

where α is the asymptotic value of the coupling (Table 7.4) and β_k a fitting parameter. According to [146], the exponent is $k = 6$ for the direct SOC's and $k = 3$ for indirect SOC's. Thus, SOC's are fitted on 9 points in R between 43 a.u. and 45 a.u., and resulting fitted parameters are collected in Table 7.4.

Direct SOCs				Indirect SOCs		
Ω	$A_{i,j}$	α	β_6 (a.u)	$A_{i,j}$	α	β_3 (a.u)
$\Omega = 0^+$	$A'_{1,2}$	$A_P \frac{1}{\sqrt{2}}$	-12430.53	$A'_{1,4}$	0.0	0.04
	$A_{2,2}$	$-A_P \frac{1}{2}$	4809.16	$A'_{2,3}$	0.0	0.02
	$A'_{3,4}$	$-A_D \sqrt{\frac{3}{2}}$	2139.57	$A_{2,4}$	0.0	0.0083
	$A_{4,4}$	$-A_D \frac{1}{2}$	878.59			
$\Omega = 0^-$	$A'_{5,6}$	$A_P \frac{1}{\sqrt{2}}$	-12462.81	$A'_{5,8}$	0.0	-0.12
	$A_{6,6}$	$-A_P \frac{1}{2}$	4809.16	$A'_{6,7}$	0.0	0.11
	$A'_{7,8}$	$A_D \sqrt{\frac{3}{2}}$	-2151.52	$A_{6,8}$	0.0	0.0083
	$A_{8,8}$	$-A_D \frac{1}{2}$	878.59			
$\Omega = 1$	$A'_{9,10}$	$-A_P \frac{1}{2}$	8803.81	$A'_{9,13}$	0.0	-0.028
	$A'_{9,11}$	$A_P \frac{1}{2}$	-8812.54	$A'_{9,14}$	0.0	-0.084
	$A_{10,11}$	$A_P \frac{1}{2}$	-4812.24	$A_{9,15}$	0.0	0.0
	$A'_{12,13}$	$A_D \frac{\sqrt{3}}{2}$	-1513.28	$A'_{10,12}$	0.0	-0.012
	$A'_{12,14}$	$A_D \frac{\sqrt{3}}{2}$	-1521.35	$A_{10,14}$	0.0	-0.048
	$A_{12,15}$	0.0	0.0	$A_{10,15}$	0.0	-0.028
	$A_{13,14}$	$-A_D \frac{1}{2}$	882.45	$A'_{11,12}$	0.0	0.080
	$A_{13,15}$	$-A_D \frac{1}{\sqrt{2}}$	1254.05	$A_{11,13}$	0.0	-0.048
	$A_{14,15}$	$A_D \frac{1}{\sqrt{2}}$	-1254.80	$A_{11,15}$	0.0	0.028
	$A_{15,15}$	$-A_D$	1787.54			
$\Omega = 2$	$A_{16,16}$	$A_P \frac{1}{2}$	-4809.16	$A_{16,17}$	0.0	-0.0083
	$A_{17,17}$	$A_D \frac{1}{2}$	-878.59	$A_{16,18}$	0.0	0.021
	$A_{17,18}$	$A_D \frac{1}{\sqrt{2}}$	-1254.82	$A_{16,19}$	0.0	0.021
	$A_{17,19}$	$A_D \frac{1}{\sqrt{2}}$	-1254.80			
	$A_{18,19}$	$-A_D$	1787.57			
$\Omega = 3$	$A_{20,20}$	A_D	-1787.54			

Table 7.4: Parameters used for the long-range extrapolation of the direct and indirect SOCs. The factors $A_D = \frac{2}{5}\Delta E_D = 112.136 \text{ cm}^{-1}$ and $A_P = \frac{2}{3}\Delta E_P = 158.39 \text{ cm}^{-1}$ are related to the atomic fine-structure splittings of $\text{Sr}^+(4d)$ $\Delta E_D = 280.34 \text{ cm}^{-1}$ and of $\text{Rb}(5p)$ $\Delta E_P = 237.595 \text{ cm}^{-1}$.

7.2 Results

The input of our quantum scattering calculations are the PECs of the system in Hund's case (e) expressed in the SF frame, obtained by the procedure of Chapter 4. They are shown in Fig. 7.4 for parity "+" and "-", and for the lowest values of J between 0 and 3. For $J = 0, 1, 2$ the number of channels are 4, 11 and 15, respectively, reaching a maximum value of 16 for $J \geq 3$, smaller than the dimension of the interaction matrix (20×20). Indeed, the symmetry $\Omega = 0^+$ is allowed for even values of J for parity "+", and for odd values of J for "-" parity. The trace of the avoided crossings X_1 and X_2 in Hund's case (a) avoided crossings remains visible, with an increased complexity of consecutive avoided crossings resulting from the couplings between the internal angular momenta and the rotational one.

7.2.1 Cross section and rate coefficients

In Subsection 3.6.3, the general coupled-channel formalism was introduced. In the following, this approach is applied to the Rb-Sr⁺ system using the interaction Hamiltonian $\mathbf{H}_\ell$

$$\mathbf{H}_\ell(R) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \mathbf{I} + \frac{\hbar^2 \ell(\ell+1)}{2\mu R^2} \mathbf{I} + \bar{\mathbf{W}}_a^{so-qd2}(R), \quad (7.8)$$

where $\mu = 79\,664.38$ a.u. is the reduced mass of RbSr⁺ and $\mathbf{I}$ the identity matrix. The matrix $\bar{\mathbf{W}}_a^{so-qd2}$ contains the Hund's case (a) PECs together with the four linearized PECs and the two Gaussian coupling functions describing the avoided crossings X_1 and X_2 . The bar above $\mathbf{W}$ indicates that only the subspace related to the limits $P + S$ and $S + D$ are considered. All other notations are similar as in case of Eq. 6.6.

As an illustration, we give the long-range behavior of the PECs governed by the charge-induced dipole interaction and the centrifugal term up to 10^4 a.u. (Fig. 7.5). A similar figure 6.6 has been shown in Chapter 6 where detailed explanations can be found. Comparing Figs. 6.6 and 7.5, it can be seen that for the same temperature-range a significantly larger number of partial waves (30) is required to describe the collision Rb+Sr⁺ than for the collision Li+Ba⁺ (12). This difference comes from the substantially larger reduced mass of RbSr⁺, by a factor of 7.6.

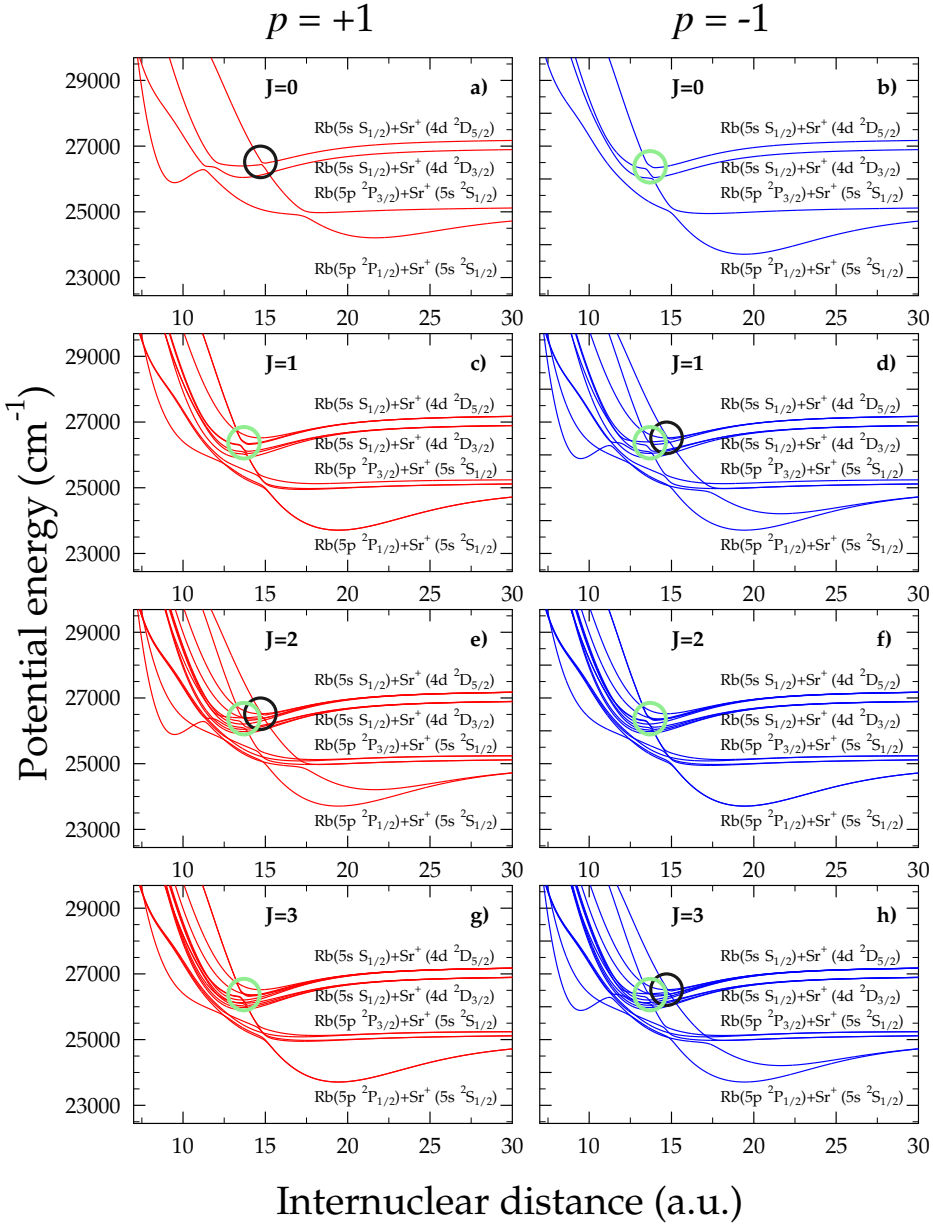


Figure 7.4: Hund's case (e) PECs related to the $P + S$ and $S + D$ dissociation limits for parities "+" and "-", and for total angular momentum $J = 0, 1, 2, 3$.

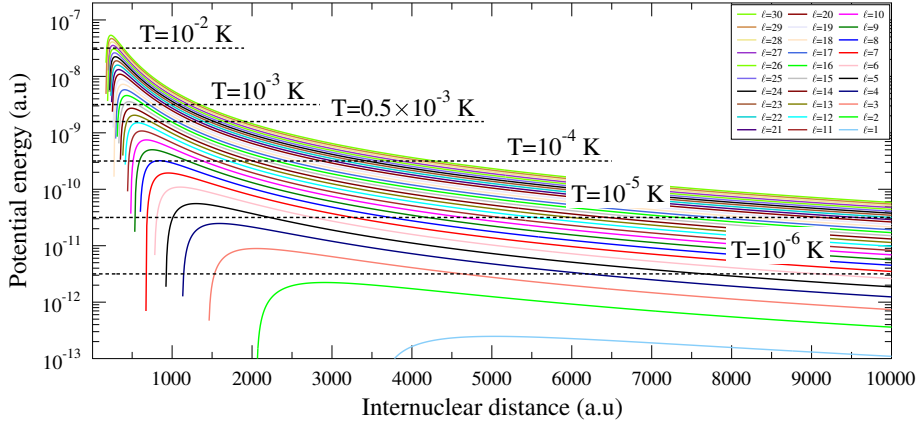


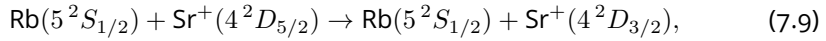
Figure 7.5: The long-range PECs of RbSr^+ , described by $-C_4/R^4 + \ell(\ell+1)/(2\mu R^2)$, as a function of the internuclear distance R , are plotted for the partial wave up to $\ell = 30$, represented by colored solid lines. The horizontal black dashed lines denote the collision energies, expressed as temperatures.

Inelastic partial cross sections for parity

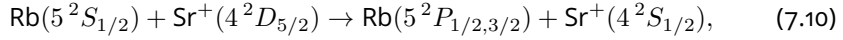
Calculations are performed for each parity value "+" and "-" for the incoming channels $\text{Rb}(5^2S_{1/2}) + \text{Sr}^+(4^2D_{5/2})$ and $\text{Rb}(5^2S_{1/2}) + \text{Sr}^+(4^2D_{3/2})$, referred to as $S + D_{5/2}$ and $S + D_{3/2}$ in the following.

Like in the preceding Chapter 6, partial cross sections for inelastic and elastic collisions (EC) are presented in Appendix F and Appendix G, respectively. These results are useful to understand the underlying structures visible in the total cross sections.

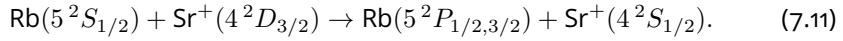
Two inelastic processes take place in Rb-Sr^+ when the ion is prepared in its metastable state. Starting first from the ion in the $4^2D_{5/2}$ state, fine-structure quenching (FSQ) was also present in Li-Ba^+ ,



the second process being electronic excitation exchange (EEE)



with two possible outgoing channels with Rb left in its $5^2P_{1/2}$ or $5^2P_{3/2}$ state. If the ion is prepared in $4^2D_{3/2}$, only EEE can occur,



The resulting cross sections for FSQ and EEE inelastic processes are shown in Fig. 7.6. The classical Langevin cross section $\sigma_L = 2\pi\sqrt{C_4/E_{\text{col}}}$ (Eq. 3.40) is shown together with the scaled Langevin cross sections $\bar{\sigma}_L = A 2\pi\sqrt{C_4/E_{\text{col}}}$, where A is the scaling factor. The scaling factor is obtained by fitting this expression to the cross section between 10 mK and 100 mK. The scaling factors for each case are listed in Table 7.5.

For the $S + D_{5/2}$ incoming channel, the FSQ process is the dominating inelastic process for both parities, similarly as in the case of the Li-Ba^+ collision (Fig. 6.7). The cross sections represent a significant fraction of the Langevin cross section which suggests that the system is very reactive.

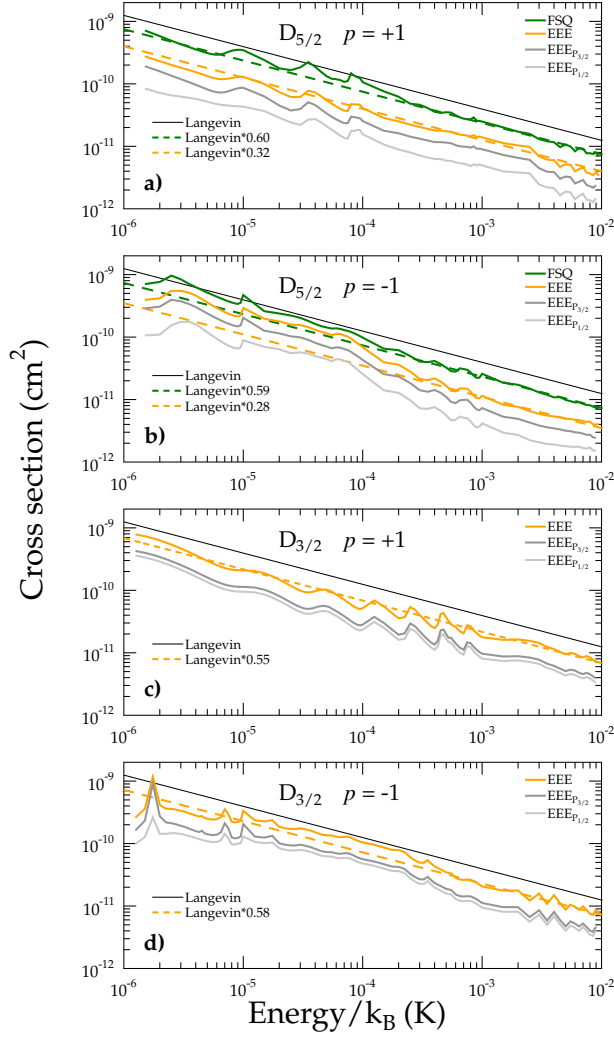


Figure 7.6: Parity-resolved total cross sections (Eq. 3.117) as a function of collision energy E_{col}/k_B expressed as a temperature for the inelastic processes FSQ (solid green line), EEE (solid orange line) in Rb-Sr^+ . The shortened notations $D_{5/2}$ and $D_{3/2}$ refer to the two entrance channels $S+D_{5/2}$ and $S+D_{3/2}$. Black line: Langevin cross section σ_L . Dashed colored lines: scaled Langevin cross sections $\bar{\sigma}_L$ (see text). Gray line: cross sections for EEE toward the final channel $P_{1/2} + S$ and $P_{3/2} + S$.

In. channel	Process	"A"
$p = +1$		
$D_{5/2}$	FSQ	0.60
	EEE	0.32
$D_{3/2}$	EEE	0.55
$p = -1$		
$D_{5/2}$	FSQ	0.59
	EEE	0.28
$D_{3/2}$	EEE	0.58

Table 7.5: Scaling factor "A" for the scaled Langevin cross section associated with the FSQ and EEE processes, evaluated for the two possible incoming channels for both parities in Fig.7.6.

Total cross sections

The parity-averaged elastic and inelastic cross sections and the rate coefficients of FSQ and EEE processes in the incoming channels $S + D_{5/2}$ and $S + D_{3/2}$ are shown in Fig. 7.7. Thermalized rate coefficients are also calculated assuming a Maxwell-Boltzmann energy distribution in the atomic cloud.

Elastic collisions are found to dominate the dynamics over the entire energy range explored here. This is expected in the classical regime valid here, far from the quantum regime occurring well below $1 \mu\text{K}$. The inelastic cross sections exhibit the characteristic dependence in $E_{\text{col}}^{-1/2}$ of the classical Langevin cross section over the entire energy range of our study, which is consistent with large number of involved partial waves previously noted. Weak structures superimposed to this variation at low energies, induced by the individual contribution of partial cross sections for given values of J .

In the experiment, the cloud of Rb atom was cooled down to $3 \mu\text{K}$, and the ion to $40 \mu\text{K}$ [69]. Due to the micromotion in the trap the ion gains extra energy, which was estimated in the experiment as 0.5 mK . We deduced experimental rate coefficients $\mathcal{K}_{\text{process}}^{\text{in.channel}}$ for each process from the measured and calculated probabilities

$$\mathcal{K}_{\text{process}}^{\text{in.channel}} = \mathcal{P}_{\text{process}}^{\text{in.channel}} \times \mathcal{K}_{\text{L}}, \quad (7.12)$$

where the compact notation $5/2(3/2)$ of "in. channel" is used for the incoming channels $S + D_{5/2}(D_{3/2})$, and $K_{\text{L}} = 2.43 \times 10^{-9} \text{ cm}^3/\text{s}$ is the Langevin rate coefficient defined in Eq. 3.41. In the experiment [69], these probabilities are meant to express the frequency of inelastic collisions with respect to the so-called "Langevin collisions" representing the upper limit for the inelastic rate. Therefore, a fraction of Langevin collisions are actually elastic. These probabilities are collected in Table 7.6.

Both Figure 7.7 and Table 7.6 illustrate that our MCQS calculations are in good agreement with experiment for EEE in both entrance channels, with the right hierarchy between the two channels: indeed we can expect that EEE is more probable from the entrance channel $S + D_{3/2}$ which is closer in energy to the outgoing channels $S + P_{1/2,3/2}$ than the $S + D_{5/2}$. This agreement strongly supports the quality of our representation of molecular interactions described in the previous chapters.

In contrast, MCQS calculations predict that the FSQ dominates inelastic collisions over EEE, and overestimate the experimental FSQ rate by a factor of $\approx 7 - 8$. We found a similar pattern in the previous Chapter on Li-Ba⁺. Here too, the explanation arises from the fact that the colliding partners in the experiment [69] were polarized: the $^{87}\text{Rb}(5s^2S_{1/2})$ atoms in the hyperfine Zeeman level $|f_{\text{Rb}} = 2, m_f = -2\rangle$ implying an electronic spin projection $m_s = -1/2$, and the $^{88}\text{Sr}^+(4d^2D_{5/2})$ ion in $m_j = \pm 5/2$ ($^{88}\text{Sr}^+$ having no nuclear spin). Such polarization effects are not yet included in our model and will be the topic of further studies. Despite this default, we found above that our calculations are in satisfactory agreement for EEE with the experiment involving spin-polarized $^{88}\text{Sr}(4d^2D_{5/2})$ and unpolarized $^{88}\text{Sr}(4d^2D_{3/2})$ ion. This observation implies that the EEE process depends less on the initial Zeeman sublevel than FSQ. This might be consistent with Hund's case (e) PECs (Fig. 7.4) showing that the entrance flux

has to travel through multiple crossings where the memory of initial Zeeman sub-levels would be lost. In contrast, FSQ dynamics relies on a very specific avoided crossing that we expect to strongly depend on initial Zeeman sublevels.

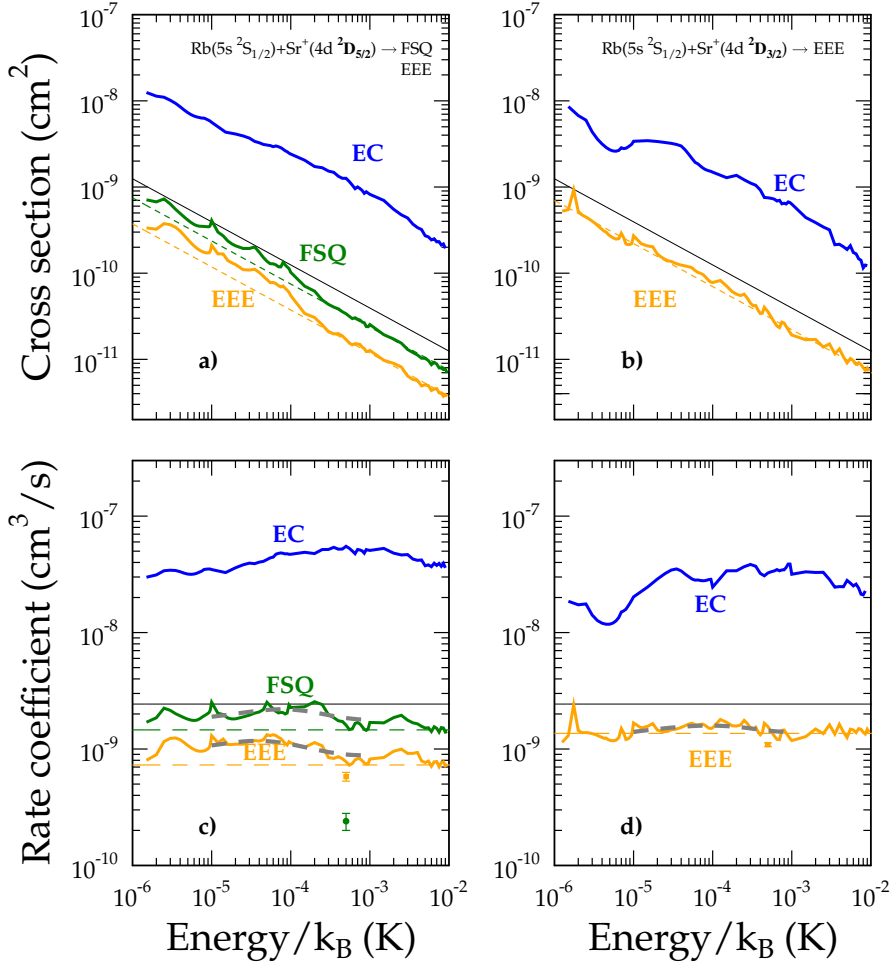


Figure 7.7: Computed total elastic (EC) and inelastic cross sections (panel a) and b)) and rate coefficients (panel c) and d)) for the incoming channel $S + D_{5/2}$ (panels a) and c)), and $S + D_{3/2}$ (panels b) and d)), respectively. The classical Langevin cross section is displayed with black solid line, as well as the scaled Langevin ones with dashed colored lines. The scaling factors are listed in Table 7.5. The panel c) and d) also show the thermalized rate coefficients, assuming Maxwell-Boltzmann distribution for the collisional energy, with thick long-dashed gray lines. The green dot and yellow square with error bars represent the rate coefficients deduced from experimental probabilities for the FSQ and EEE processes, respectively.

Probability	Experiment	This work
$\mathcal{P}_{\text{process}}^{\text{in.channel}}$		$K^{f \leftarrow i}(E_i)/K_L$
$\mathcal{P}_{EEE}^{3/2}$	0.45 ± 0.018	0.64
$\mathcal{P}_{EEE+FSQ}^{5/2}$	0.34 ± 0.017	0.96
$\mathcal{P}_{EEE}^{5/2}/P_{EEE}^{3/2}$	0.53 ± 0.043	0.50
$\mathcal{P}_{FSQ}^{5/2}/P_{EEE}^{5/2}$	0.39 ± 0.050	2.05
$\mathcal{P}_{FSQ}^{5/2}$	0.10 ± 0.01	0.66
$\mathcal{P}_{EEE}^{5/2}$	0.24 ± 0.02	0.32

Table 7.6: Experimental and calculated inelastic probabilities for FSQ and EEE processes in the two incoming channels $S + D_{5/2}$ and $S + D_{3/2}$ at the experimental temperature of 0.5 mK. The probabilities $\mathcal{P}$ are labelled with the angular momentum of Sr^+ (3/2 or 5/2), and by the process EEE and FSQ. The first four lines (in boldface) were reported in Ref. [6g], while the two last lines are deduced from the previous one for the present work.

Summary and outlook

In this thesis, I investigated the quantum dynamics of ultracold collisions between alkali-metal atoms and alkaline-earth ions in hybrid-trap experiments. Such systems combine several advantages of neutral-atom and trapped-ion platforms and provide a promising environment for studying controlled atom-ion interactions, cold chemistry, and quantum many-body phenomena. However, before these systems can be fully exploited for such applications, the quantum dynamics leading to trap losses must be understood. Inelastic collisions represent one of the possible loss mechanisms, especially when the ion is prepared in a metastable electronic excited state.

A particular motivation of this work is that metastable D -states of alkaline-earth ions are naturally involved in laser cooling schemes and can also be deliberately prepared as entrance channels of the collision. These excited entrance channels open additional energetically accessible reaction pathways compared to ground-state collisions. Their theoretical description requires molecular potential energy curves, R -dependent spin-orbit couplings, non-adiabatic couplings, quasidiabatic transformations, frame transformations, and coupled-channel quantum scattering calculations. The dynamical calculations therefore not only provide cross sections and rate coefficients, but also serve as a validation of the underlying electronic-structure data and coupling models.

The first system investigated in detail was LiBa^+ . In this case, three inelastic processes compete when Ba^+ is initially prepared in a metastable ($5d\ ^2D$) state: fine-structure quenching (FSQ), non-radiative charge exchange (NRCE) and non-radiative quenching (NRQ). For this system, parity dependent cross sections were calculated for both entrance channels. The partial wave contributions were then analyzed in order to identify the origin of the main structures in the cross sections. Finally, parity independent cross section, non-thermalized and thermalized rate coefficients were obtained and compared with the available experimental data.

The LiBa^+ calculations reproduce the main experimental trends and the observed hierarchy between the dominant inelastic channels. In particular, the NRCE and NRQ rates are found to be in good agreement with experiment for both investigated entrance channels. The analysis shows that NRCE is driven by a localized non-adiabatic coupling between the relevant $^1\Sigma^+$ states at a prominent avoided crossing between two potential energy curves, whereas NRQ results from a more complex mechanism involving electronic state crossings, indirect spin-orbit couplings at short internuclear distance, and rotational couplings. In contrast, the FSQ rate is overestimated by the present model. This discrepancy is most likely related

to the fact that the experiment involves spin-polarized collision partners, whereas the present calculations do not explicitly include the corresponding hyperfine and Zeeman structures.

The second system considered was RbSr^+ , where two inelastic processes were experimentally observed : fine-structure quenching (FSQ) and electronic excitation exchange (EEE). In contrast to many other atom-ion systems, no charge exchange process was observed in the experiment when the ion was prepared in one of the excited ^2D states. Compared with LiBa^+ , the RbSr^+ system involves a more complex excited electronic manifold, since the asymptotic limit $\text{Rb}(5p^2P)+\text{Sr}^+(5s^2S)$ lies close to the $\text{Rb}(5s^2S)+\text{Sr}^+(4d^2D)$ channels. As a consequence, several electronic states are involved and avoided crossings appear between the $^1,^3\Sigma^+$ states. To describe this structure, a two-step quasi-diabatization procedure was applied to obtain a consistent set of diabatic PECs and spin-orbit couplings.

The calculations show that EEE can be described in satisfactory agreement with experiment, confirming the quality of the molecular data and the quasi-diabatic treatment of the spin-orbit couplings. The analysis also shows that the dynamics is strongly affected by the interplay between non-adiabatic, spin-orbit, and rotational couplings. However, as in LiBa^+ , the calculated FSQ rate is larger than the experimental value. This suggests that FSQ is particularly sensitive to the initial spin preparation of the collision partners. Because one or both reactants are prepared in specific spin states in the experiments, a spin-resolved treatment including the relevant hyperfine and Zeeman degrees of freedom would likely be required for a fully quantitative description of this process.

Taken together, the LiBa^+ and RbSr^+ studies demonstrate that ultracold collisions involving metastable alkaline-earth ions cannot be understood in terms of a single inelastic process or by a single isolated coupling mechanism. Instead, the observed inelastic dynamics results from the combined action of non-adiabatic couplings, spin-orbit interactions, and molecular rotation. Simplified models, such as Landau-Zener-type approaches, provide useful qualitative insight, but a complete multichannel quantum scattering treatment is necessary to obtain the experimental observations. The results of this thesis therefore contribute to a more detailed understanding of loss mechanisms in hybrid atom-ion systems and provide a theoretical framework for interpreting future experiments involving electronically excited collision partners.

The limitations identified above naturally define several possible directions for future work. The most direct extension would be the inclusion of hyperfine and Zeeman degrees of freedom in the molecular basis [147]. This would make it possible to describe the experimentally prepared spin states explicitly, rather than treating only the fine-structure channels. Such an extension would provide a direct test of whether the overestimation of the FSQ rates in LiBa^+ and RbSr^+ is indeed related to the spin-polarized character of the entrance channels. More generally, a spin-resolved model would allow for a closer comparison with state-selective hybrid-trap experiments.

Another promising direction is the application of the present methodology to other experimentally relevant atom-ion systems. In particular, LiCa^+ represents an interesting candidate. Similarly to LiBa^+ , the large mass imbalance between

the light Li atom and the heavier Ca^+ ion is favorable for approaching the quantum regime. In addition, experimental data are available for several collision energies (1 mK–1 K), providing multiple reference points for comparison with the theory [54]. Since Landau–Zener-type studies have already been performed for this system [54], a complete multichannel quantum scattering treatment would make it possible to assess the validity of simplified models and to identify the quantum mechanisms responsible for the observed energy dependence of the inelastic processes.

A further perspective concerns the formation and control of molecular ions. The observation of Feshbach resonances in atom–ion systems, such as those reported in LiBa^+ and RbSr^+ experiments [39, 71], indicates the presence of near-threshold molecular states that could be exploited for creating weakly bound molecular ions. Such molecular ions may be formed through magnetoassociation across a Feshbach resonance [39, 71], radiative association [63, 65, 73, 83] or laser-assisted photoassociation [47, 148] schemes. Their stability and internal structure could also be probed through photodissociation, which provides complementary information on molecular binding energies and transition pathways.

Finally, the control of inelastic atom–ion collisions by external fields represents a particularly appealing long-term direction. In analogy to optical-shielding schemes proposed in other cold collision contexts [149–151], one could investigate whether one- or two-photon couplings can be used to modify the collision dynamics before the particles reach short internuclear distances. By coupling the entrance channel to a suitably chosen repulsive molecular potential, external laser fields may suppress unwanted inelastic losses by preventing the collision complex from accessing the short-range region or redirect the dynamics toward desired final channels. Such a possibility would connect the microscopic molecular description developed in this thesis with the broader goal of controlling atom–ion collisions in hybrid traps.

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Appendix A

Atomic spin-orbit coupling matrices

In this appendix we present the spin-orbit coupling matrices which were used related to LiBa^+ and RbSr^+ molecular ions.

- $P + S$ asymptotic limit:

$$\mathbf{H}_{\Omega=0+}^{so} = \begin{pmatrix} 5^1\Sigma^+ & 3^3\Pi \\ 0 & \frac{A_P}{\sqrt{2}} \\ \frac{A_P}{\sqrt{2}} & -\frac{A_P}{2} \end{pmatrix} \begin{matrix} 5^1\Sigma^+ \\ 3^3\Pi \end{matrix} \quad (\text{A.1})$$

$$\mathbf{H}_{\Omega=0-}^{so} = \begin{pmatrix} 4^3\Sigma^+ & 3^3\Pi \\ 0 & \frac{A_P}{\sqrt{2}} \\ \frac{A_P}{\sqrt{2}} & -\frac{A_P}{2} \end{pmatrix} \begin{matrix} 4^3\Sigma^+ \\ 3^3\Pi \end{matrix} \quad (\text{A.2})$$

$$\mathbf{H}_{\Omega=1}^{so} = \begin{pmatrix} 4^3\Sigma^+ & 3^1\Pi & 3^3\Pi \\ 0 & -\frac{A_P}{2} & \frac{A_P}{2} \\ -\frac{A_P}{2} & 0 & \frac{A_P}{2} \\ \frac{A_P}{2} & \frac{A_P}{2} & 0 \end{pmatrix} \begin{matrix} 4^3\Sigma^+ \\ 3^1\Pi \\ 3^3\Pi \end{matrix} \quad (\text{A.3})$$

$$\mathbf{H}_{\Omega=2}^{so} = \begin{pmatrix} 3^3\Pi \\ \frac{A_P}{2} \end{pmatrix} 3^3\Pi \quad (\text{A.4})$$

- $S + D$ asymptotic limit:

$$\mathbf{H}_{\Omega=0+}^{so} = \begin{array}{cc} & \begin{array}{cc} 6^1\Sigma^+ & 4^3\Pi \end{array} \\ \left(\begin{array}{cc} 0 & -A_D\sqrt{\frac{3}{2}} \\ -A_D\sqrt{\frac{3}{2}} & -\frac{A_D}{2} \end{array} \right) & \begin{array}{c} 6^1\Sigma^+ \\ 4^3\Pi \end{array} \end{array} \quad (\text{A.5})$$

$$\mathbf{H}_{\Omega=0-}^{so} = \begin{array}{cc} & \begin{array}{cc} 5^3\Sigma^+ & 4^3\Pi \end{array} \\ \left(\begin{array}{cc} 0 & A_D\sqrt{\frac{3}{2}} \\ A_D\sqrt{\frac{3}{2}} & -\frac{A_D}{2} \end{array} \right) & \begin{array}{c} 5^3\Sigma^+ \\ 4^3\Pi \end{array} \end{array} \quad (\text{A.6})$$

$$\mathbf{H}_{\Omega=1}^{so} = \begin{array}{cccc} & 5^3\Sigma^+ & 4^1\Pi & 4^3\Pi & 2^3\Delta \\ \left(\begin{array}{cccc} 0 & A_D\frac{\sqrt{3}}{2} & A_D\frac{\sqrt{3}}{2} & 0 \\ A_D\frac{\sqrt{3}}{2} & 0 & -\frac{A_D}{2} & -\frac{A_D}{\sqrt{2}} \\ A_D\frac{\sqrt{3}}{2} & -\frac{A_D}{2} & 0 & \frac{A_D}{\sqrt{2}} \\ 0 & -\frac{A_D}{\sqrt{2}} & \frac{A_D}{\sqrt{2}} & -A_D \end{array} \right) & \begin{array}{c} 5^3\Sigma^+ \\ 4^1\Pi \\ 4^3\Pi \\ 2^3\Delta \end{array} \end{array} \quad (\text{A.7})$$

$$\mathbf{H}_{\Omega=2}^{so} = \begin{array}{ccc} & 4^3\Pi & 2^1\Delta & 2^3\Delta \\ \left(\begin{array}{ccc} \frac{A_D}{2} & \frac{A_D}{\sqrt{2}} & \frac{A_D}{\sqrt{2}} \\ \frac{A_D}{\sqrt{2}} & 0 & -A_D \\ \frac{A_D}{\sqrt{2}} & -A_D & 0 \end{array} \right) & \begin{array}{c} 4^3\Pi \\ 2^1\Delta \\ 2^3\Delta \end{array} \end{array} \quad (\text{A.8})$$

$$\mathbf{H}_{\Omega=3}^{so} = \begin{array}{cc} & 2^3\Delta \\ \left(\begin{array}{c} A_D \end{array} \right) & 2^3\Delta \end{array} \quad (\text{A.9})$$

When both valence electrons are on the same atom (which might happen in our case when the initial alkaline-earth ion will be neutralized by charge exchange) the considered states are ^3P or ^3D . The definitions of the SO constants are $A'_P = \Delta E_{3P}/3$ and $A'_D = \Delta E_{3D}/5$, where ΔE_{3P} and ΔE_{3D} are the corresponding atomic spin-orbit energy splitting. The resulting atomic spin-orbit Hamiltonian matrix are:

- Rb⁺+Sr(5s5p ³P):

$$\begin{array}{c} {}^3\Pi \\ \mathbf{H}_{\Omega=0+}^{so} = \left(\begin{array}{c} -A'_P \end{array} \right) \quad {}^3\Pi \end{array} \quad (\text{A.10})$$

$$\begin{array}{c} {}^3\Sigma^+ \quad {}^3\Pi \\ \mathbf{H}_{\Omega=0-}^{so} = \left(\begin{array}{cc} 0 & A'_P\sqrt{2} \\ A'_P\sqrt{2} & -A'_P \end{array} \right) \quad \begin{array}{c} {}^3\Sigma^+ \\ {}^3\Pi \end{array} \end{array} \quad (\text{A.11})$$

$$\begin{array}{c} {}^3\Sigma^+ \quad {}^3\Pi \\ \mathbf{H}_{\Omega=1}^{so} = \left(\begin{array}{cc} 0 & A'_P \\ A'_P & 0 \end{array} \right) \quad \begin{array}{c} {}^3\Sigma^+ \\ {}^3\Pi \end{array} \end{array} \quad (\text{A.12})$$

$$\begin{array}{c} {}^3\Pi \\ \mathbf{H}_{\Omega=2}^{so} = \left(\begin{array}{c} A'_P \end{array} \right) \quad {}^3\Pi \end{array} \quad (\text{A.13})$$

- Rb⁺+Sr(5s4d ³D):

$$\begin{array}{c} {}^3\Pi \\ \mathbf{H}_{\Omega=0+}^{so} = \left(\begin{array}{c} -A'_D \end{array} \right) \quad {}^3\Pi \end{array} \quad (\text{A.14})$$

$$\begin{array}{c} {}^3\Sigma^+ \quad {}^3\Pi \\ \mathbf{H}_{\Omega=0-}^{so} = \left(\begin{array}{cc} 0 & A'_D\sqrt{6} \\ A'_D\sqrt{6} & -A'_D \end{array} \right) \quad \begin{array}{c} {}^3\Sigma^+ \\ {}^3\Pi \end{array} \end{array} \quad (\text{A.15})$$

$$\begin{array}{c} {}^3\Sigma^+ \quad {}^3\Pi \quad {}^3\Delta \\ \mathbf{H}_{\Omega=1}^{so} = \left(\begin{array}{ccc} 0 & A'_D\sqrt{3} & 0 \\ A'_D\sqrt{3} & 0 & A'_D\sqrt{2} \\ 0 & A'_D\sqrt{2} & -2'A_D \end{array} \right) \quad \begin{array}{c} {}^3\Sigma^+ \\ {}^3\Pi \\ {}^3\Delta \end{array} \end{array} \quad (\text{A.16})$$

$$\begin{array}{c} {}^3\Pi \quad {}^3\Delta \\ \mathbf{H}_{\Omega=2}^{so} = \left(\begin{array}{cc} A'_D & A'_D\sqrt{2} \\ A'_D\sqrt{2} & 0 \end{array} \right) \quad \begin{array}{c} {}^3\Pi \\ {}^3\Delta \end{array} \end{array} \quad (\text{A.17})$$

$$\mathbf{H}_{\Omega=3}^{so} = \begin{pmatrix} {}^3\Delta \\ 2A'_D \\ {}^3\Delta \end{pmatrix} \quad (\text{A.18})$$

Appendix B

Hund's case (a) and Hund's case (e) basis functions

The states in Hund's case (a) basis functions are defined with $|L, \Lambda, S, \Sigma\rangle$, where L and S are the orbital angular momentum and electronic spin of the molecule, respectively, Λ and Σ are their projection on the molecular axis. The angular momentum and spin can vary as $|l_A - l_B| \leq L \leq l_A + l_B$ and $|s_A - s_B| \leq S \leq s_A + s_B$. Their projections can vary as $-L \leq \Lambda \leq L$ and $-S \leq \Sigma \leq S$. The Hund's case (e) basis functions are defined with $|j, \ell, J, M, p\rangle$, where j is the electronic angular momentum and it is defined $j = j_A + j_B$, J is the total angular momentum, it is determined $J = j + \ell$. The electronic angular momentum for atom A is $j_A = l_A + s_A$ and for ion B , $j_B = l_B + s_B$. M is the projection of the total angular momentum on the molecular axis. The parity is defined $p = (-1)^{l_A + l_B + \ell}$. The l_A and l_B establish a clearly defined dissociation limit of the systems treated in this work, namely, associating alkali-metal (AM) and alkaline-earth (AE) species. The limits of interest are $\text{AM}(^2S) + \text{AE}^+(^2S)$, $\text{AM}(^2P) + \text{AE}^+(^2S)$, $\text{AM}(^2S) + \text{AE}^+(^2D)$, and $\text{AM}^+ + \text{AE}(^1S)$, where the states ^2S and ^1S are ground states, while ^2P and ^2D hold for the lowest level in the symmetry. They are hereafter labeled with the shortened notations $S + S$, $P + S$, $S + D$, and $\text{Ion} + S$. For the limit $\text{Ion} + S$, the two electrons lie on the same atom. As an illustration the basis functions (indicating the good quantum numbers) for the three considered Hund's cases at a given dissociation limit are collected in Tables B.1, B.2, B.3, B.4 for $J = 0, 1, 2, 3$.

In Table B.5 we present the number of states in different Hund's case representations for the LiBa^+ and RbSr^+ molecular ions.

$J = 0$					
$(a) ({}^{2S+1}\Lambda_{ \Omega })$		$(c) (\Omega)$		$(e) (j_A, j_B, j, \ell)$	
$p = +1$	$p = -1$	$p = +1$	$p = -1$	$p = +1$	$p = -1$
$S + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 0, 0)$	$(\frac{1}{2}, \frac{1}{2}, 1, 1)$
$\text{Ion} + S$					
$1\Sigma_0^+$	—	0^+	—	$(0, 0, 0, 0)$	—
$P + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 1, 1)$	$(\frac{1}{2}, \frac{1}{2}, 0, 0)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{3}{2}, \frac{1}{2}, 1, 1)$	$(\frac{3}{2}, \frac{1}{2}, 2, 2)$
$S + D$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{3}{2}, 2, 2)$	$(\frac{1}{2}, \frac{3}{2}, 1, 1)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{1}{2}, \frac{5}{2}, 2, 2)$	$(\frac{1}{2}, \frac{5}{2}, 3, 3)$

Table B.1: The good quantum numbers in Hund's case (a), (c) and (e) for given total angular momentum $J = 0$.

$J = 1$					
$(a) ({}^{2S+1}\Lambda_{ \Omega })$		$(c) (\Omega)$		$(e) (j_A, j_B, j, \ell)$	
$p = +1$	$p = -1$	$p = +1$	$p = -1$	$p = +1$	$p = -1$
$S + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 1, 0)$	$(\frac{1}{2}, \frac{1}{2}, 0, 1)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{1}{2}, 1, 2)$	$(\frac{1}{2}, \frac{1}{2}, 1, 1)$
$\text{Ion} + S$					
—	$1\Sigma_0^+$	—	0^+	—	$(0, 0, 0, 1)$
$P + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 0, 1)$	$(\frac{1}{2}, \frac{1}{2}, 1, 0)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{1}{2}, 1, 1)$	$(\frac{1}{2}, \frac{1}{2}, 1, 2)$
$1\Pi_1$	$1\Pi_1$	1	1	$(\frac{3}{2}, \frac{1}{2}, 1, 1)$	$(\frac{3}{2}, \frac{1}{2}, 1, 0)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{3}{2}, \frac{1}{2}, 2, 1)$	$(\frac{3}{2}, \frac{1}{2}, 1, 2)$
$3\Pi_1$	$3\Pi_1$	1	1	$(\frac{3}{2}, \frac{1}{2}, 2, 3)$	$(\frac{3}{2}, \frac{1}{2}, 2, 2)$
$S + D$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{3}{2}, 1, 0)$	$(\frac{1}{2}, \frac{3}{2}, 1, 1)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{3}{2}, 1, 2)$	$(\frac{1}{2}, \frac{3}{2}, 2, 1)$
$1\Pi_1$	$1\Pi_1$	1	1	$(\frac{1}{2}, \frac{3}{2}, 2, 2)$	$(\frac{1}{2}, \frac{3}{2}, 2, 3)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{1}{2}, \frac{5}{2}, 2, 2)$	$(\frac{1}{2}, \frac{5}{2}, 2, 1)$
$3\Pi_1$	$3\Pi_1$	1	1	$(\frac{1}{2}, \frac{5}{2}, 3, 2)$	$(\frac{1}{2}, \frac{5}{2}, 2, 3)$
$3\Delta_1$	$3\Delta_1$	1	1	$(\frac{1}{2}, \frac{5}{2}, 3, 4)$	$(\frac{1}{2}, \frac{5}{2}, 3, 3)$

Table B.2: The good quantum numbers in Hund's case (a), (c) and (e) for given total angular momentum $J = 1$.

$J = 2$					
$(a) ({}^{2S+1}\Lambda_{ \Omega })$		$(c) (\Omega)$		$(e) (j_A, j_B, j, \ell)$	
$p = +1$	$p = -1$	$p = +1$	$p = -1$	$p = +1$	$p = -1$
$S + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 0, 2)$	$(\frac{1}{2}, \frac{1}{2}, 1, 1)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{1}{2}, 1, 2)$	$(\frac{1}{2}, \frac{1}{2}, 1, 3)$
$\text{Ion} + S$					
$1\Sigma_0^+$	—	0^+	—	$(0, 0, 0, 2)$	—
$P + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 1, 1)$	$(\frac{1}{2}, \frac{1}{2}, 0, 2)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{1}{2}, 1, 3)$	$(\frac{1}{2}, \frac{1}{2}, 1, 2)$
$1\Pi_1$	$1\Pi_1$	1	1	$(\frac{3}{2}, \frac{1}{2}, 1, 1)$	$(\frac{3}{2}, \frac{1}{2}, 1, 2)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{3}{2}, \frac{1}{2}, 1, 3)$	$(\frac{3}{2}, \frac{1}{2}, 2, 0)$
$3\Pi_1$	$3\Pi_1$	1	1	$(\frac{3}{2}, \frac{1}{2}, 2, 1)$	$(\frac{3}{2}, \frac{1}{2}, 2, 2)$
$3\Pi_2$	$3\Pi_2$	2	2	$(\frac{3}{2}, \frac{1}{2}, 2, 3)$	$(\frac{3}{2}, \frac{1}{2}, 2, 4)$
$S + D$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{3}{2}, 1, 2)$	$(\frac{1}{2}, \frac{3}{2}, 1, 1)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{3}{2}, 2, 0)$	$(\frac{1}{2}, \frac{3}{2}, 1, 3)$
$1\Pi_1$	$1\Pi_1$	1	1	$(\frac{1}{2}, \frac{3}{2}, 2, 2)$	$(\frac{1}{2}, \frac{3}{2}, 2, 1)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{1}{2}, \frac{3}{2}, 2, 4)$	$(\frac{1}{2}, \frac{3}{2}, 2, 3)$
$3\Pi_1$	$3\Pi_1$	1	1	$(\frac{1}{2}, \frac{5}{2}, 2, 0)$	$(\frac{1}{2}, \frac{5}{2}, 2, 1)$
$3\Pi_2$	$3\Pi_2$	2	2	$(\frac{1}{2}, \frac{5}{2}, 2, 2)$	$(\frac{1}{2}, \frac{5}{2}, 2, 3)$
$1\Delta_2$	$1\Delta_2$	2	2	$(\frac{1}{2}, \frac{5}{2}, 2, 4)$	$(\frac{1}{2}, \frac{5}{2}, 3, 1)$
$3\Delta_1$	$3\Delta_1$	1	1	$(\frac{1}{2}, \frac{5}{2}, 3, 2)$	$(\frac{1}{2}, \frac{5}{2}, 3, 3)$
$3\Delta_2$	$3\Delta_2$	2	2	$(\frac{1}{2}, \frac{5}{2}, 3, 4)$	$(\frac{1}{2}, \frac{5}{2}, 3, 5)$

Table B.3: The good quantum numbers in Hund's case (a), (c) and (e) for given total angular momentum $J = 2$.

$J = 3$					
(a) ($^{2S+1}\Lambda_{ \Omega }$)		(c) ($ \Omega $)		(e) (j_A, j_B, j, ℓ)	
$p = +1$	$p = -1$	$p = +1$	$p = -1$	$p = +1$	$p = -1$
$S + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 1, 2)$	$(\frac{1}{2}, \frac{1}{2}, 0, 3)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{1}{2}, 1, 4)$	$(\frac{1}{2}, \frac{1}{2}, 1, 3)$
$\text{Ion} + S$					
—	$1\Sigma_0^+$	—	0^+	—	$(0, 0, 0, 3)$
$P + S$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{1}{2}, 0, 3)$	$(\frac{1}{2}, \frac{1}{2}, 1, 2)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{1}{2}, 1, 3)$	$(\frac{1}{2}, \frac{1}{2}, 1, 4)$
$1\Pi_1$	$1\Pi_1$	1	1	$(\frac{3}{2}, \frac{1}{2}, 1, 3)$	$(\frac{3}{2}, \frac{1}{2}, 1, 2)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{3}{2}, \frac{1}{2}, 2, 1)$	$(\frac{3}{2}, \frac{1}{2}, 1, 4)$
$3\Pi_1$	$3\Pi_1$	1	1	$(\frac{3}{2}, \frac{1}{2}, 2, 3)$	$(\frac{3}{2}, \frac{1}{2}, 2, 2)$
$3\Pi_2$	$3\Pi_2$	2	2	$(\frac{3}{2}, \frac{1}{2}, 2, 5)$	$(\frac{3}{2}, \frac{1}{2}, 2, 4)$
$S + D$					
$1\Sigma_0^+$	$3\Sigma_0^+$	0^+	0^-	$(\frac{1}{2}, \frac{3}{2}, 1, 2)$	$(\frac{1}{2}, \frac{3}{2}, 1, 3)$
$3\Sigma_1^+$	$3\Sigma_1^+$	1	1	$(\frac{1}{2}, \frac{3}{2}, 1, 4)$	$(\frac{1}{2}, \frac{3}{2}, 2, 1)$
$1\Pi_1$	$1\Pi_1$	1	1	$(\frac{1}{2}, \frac{3}{2}, 2, 2)$	$(\frac{1}{2}, \frac{3}{2}, 2, 3)$
$3\Pi_0$	$3\Pi_0$	0^+	0^-	$(\frac{1}{2}, \frac{3}{2}, 2, 4)$	$(\frac{1}{2}, \frac{3}{2}, 2, 5)$
$3\Pi_1$	$3\Pi_1$	1	1	$(\frac{1}{2}, \frac{5}{2}, 2, 2)$	$(\frac{1}{2}, \frac{5}{2}, 2, 1)$
$3\Pi_2$	$3\Pi_2$	2	2	$(\frac{1}{2}, \frac{5}{2}, 2, 4)$	$(\frac{1}{2}, \frac{5}{2}, 2, 3)$
$1\Delta_2$	$1\Delta_2$	2	2	$(\frac{1}{2}, \frac{5}{2}, 3, 0)$	$(\frac{1}{2}, \frac{5}{2}, 2, 5)$
$3\Delta_1$	$3\Delta_1$	1	1	$(\frac{1}{2}, \frac{5}{2}, 3, 2)$	$(\frac{1}{2}, \frac{5}{2}, 3, 1)$
$3\Delta_2$	$3\Delta_2$	2	2	$(\frac{1}{2}, \frac{5}{2}, 3, 4)$	$(\frac{1}{2}, \frac{5}{2}, 3, 3)$
$3\Delta_3$	$3\Delta_3$	3	3	$(\frac{1}{2}, \frac{5}{2}, 3, 6)$	$(\frac{1}{2}, \frac{5}{2}, 3, 5)$

Table B.4: The good quantum numbers in Hund's case (a), (c) and (e) for given total angular momentum $J = 3$.

Hund's case (<i>a</i>)			Hund's case (<i>c</i>)			Hund's case (<i>e</i>)				
$2S+1\Lambda$	LiBa ⁺	RbSr ⁺	Ω	LiBa ⁺	RbSr ⁺	J	LiBa ⁺		RbSr ⁺	
							<i>p</i> = +1	<i>p</i> = −1	<i>p</i> = +1	<i>p</i> = −1
$1\Sigma^+$	3	2	0^+	4	4	0	4	3	4	4
$3\Sigma^+$	2	2	0^-	3	4	1	8	9	11	11
1Π	1	2	1	5	7	2	12	11	15	15
3Π	1	2	2	3	4	$\geq \mathbf{3}$	12	13	16	16
1Δ	1	1	3	1	1					
3Δ	1	1	3	1	1					
number of states:	9	10		16	20		36	36	46	46

Table B.5: Number of molecular states in the Hund's case (a) (Section 3.3) corresponding to the restricted number of dissociation limits included in the dynamical calculations for LiBa⁺ and RbSr⁺ (Chapters 6 and 7). They generate the number of states in Hund's case (c) (Sections 3.4, 5.2), and Hund's case (e) (Section 4.3) representations. The total number of states related to the Rb-Sr⁺ collision is considerably larger because, in the experiment [69], population of the excited Rb(5*p*) atom was observed, introducing one additional unit of angular momentum in our calculations. For Li-Ba⁺ collision the Li atom was either ionized or remained in the Li(2*s*) ground state [55]. The number of states for Hund's case (e) representation corresponds to a quantum scattering calculations where the total angular momentum quantum number **J** is considered up to 3. The difference of 10 in the number of states between the two collisional systems holds for all cases in which the largest **J** considered is greater than 3.

Appendix C

Diabatized SOC for $\Omega = 0^-$ and $\Omega = 1$ symmetries

Figures C.1 shows the steps of the diabatization method for the $\Omega = 0^-$ symmetry, while figures C.2 and C.3 for the $\Omega = 1$ symmetry related to the SOC between the $^3\Sigma^+$ state and $^1\Pi$ and $^3\Pi$, respectively. These diabatizations of SOC are necessary due to the presence of the X_2 avoided crossing, see panel a) of Fig. 5.7.

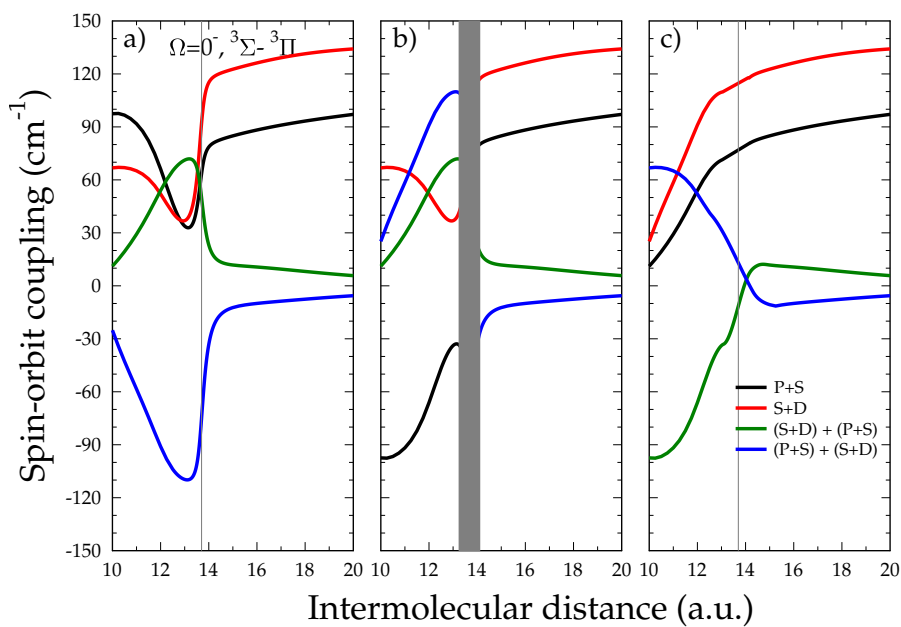


Figure C.1: The relevant spin-orbit couplings in the $\Omega = 0^-$ symmetry. Grey vertical line indicates the position of the X₂ avoided crossing. In panel a): black is $A_{5,6}$, red is $A_{7,8}$, green is $A_{6,7}$, and blue is $A_{5,8}$ adiabatic SOCs. Panel c): black is $A'_{5,6}$, red is $A'_{7,8}$, green is $A'_{6,7}$, and blue is $A'_{5,8}$ diabatic SOCs. For more explanation see the caption of Fig. 5.8.

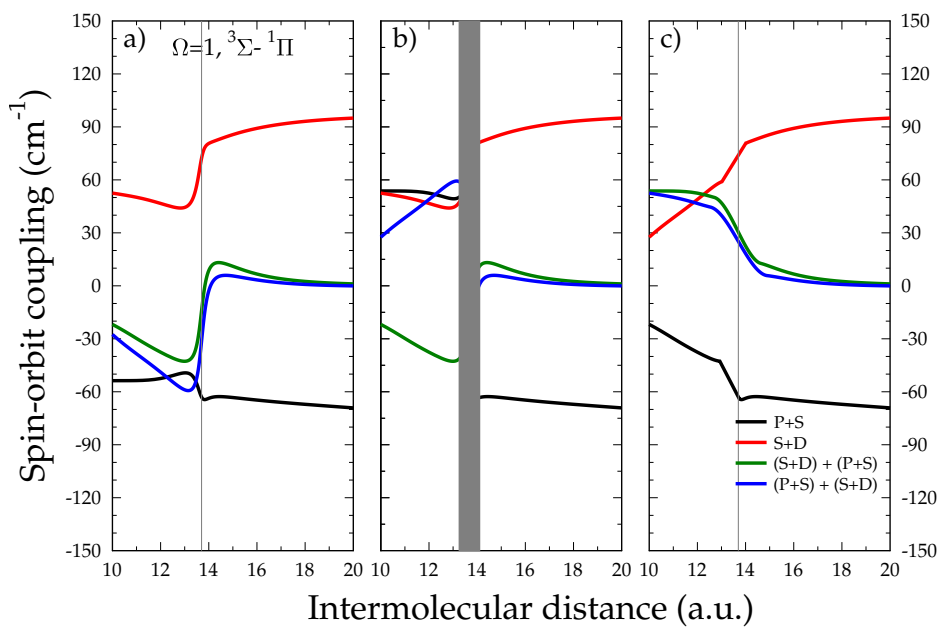


Figure C.2: The relevant SOCs in the $\Omega = 1$ symmetry between $^3\Sigma^- - ^1\Pi$ states. Grey vertical line indicates the position of the X_2 avoided crossing. Panel a): black is $A_{9,10}$, red is $A_{12,13}$, green is $A_{10,12}$, and blue is $A_{9,13}$ adiabatic SOCs. Panel c): black is $A'_{9,10}$, red is $A'_{12,13}$, green is $A'_{10,12}$, and blue is $A'_{9,13}$ diabatic SOCs. For more explanation see the caption of Fig. 5.8.

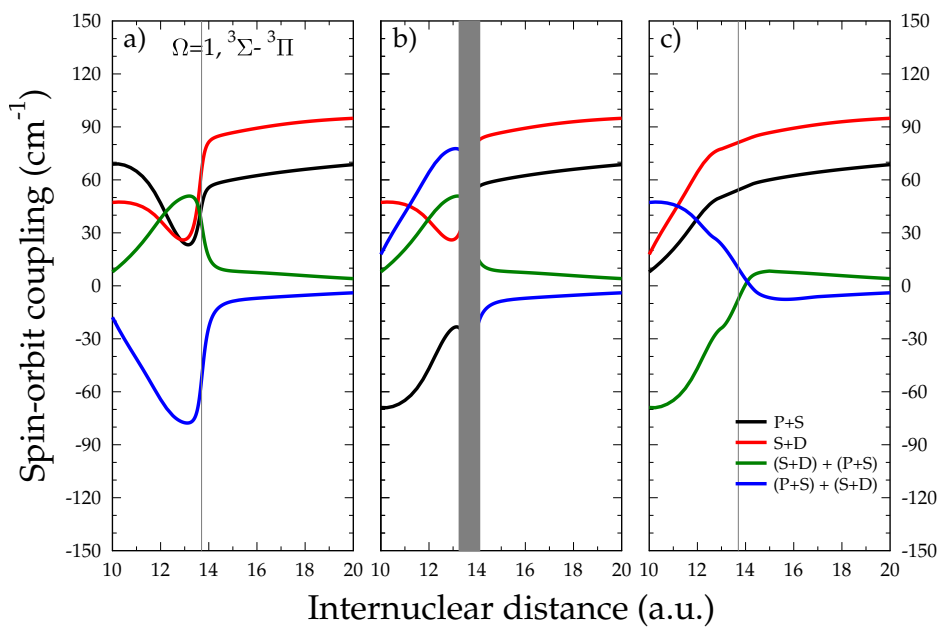


Figure C.3: The relevant SOCs in the $\Omega = 1$ symmetry between $^3\Sigma^- - ^3\Pi$ states. Grey vertical line indicates the position of the X_2 avoided crossing. Panel a): black is $A_{9,11}$, red is $A_{12,14}$, green is $A_{11,12}$, and blue is $A_{9,14}$ adiabatic SOCs. Panel c): black is $A'_{9,11}$, red is $A'_{12,14}$, green is $A'_{11,12}$, and blue is $A'_{9,14}$ diabatic SOCs. For more explanation see the caption of Fig. 5.8.

Appendix D

Inelastic partial cross sections for Li-Ba^+ collisions

We note that the partial cross sections for parity "−" decrease at low collision energy, in contrast to those for parity "+". This comes from the fact that the latter only involve even partial waves ℓ , and thus the s -wave at very low energy, allowing for barrier-less processes. This is illustrated by a series of graphs in the next pages (Figs. D.1, D.2, D.3, D.4, D.5) showing the partial inelastic cross sections for each process, depending on parity and J . The non-vanishing contributions to the inelastic cross section are those of $J = 2, 3$, which indeed involve $\ell = 0$ (s -wave) as $j_{\text{Li}} = 0$ and $j_{\text{Ba}^+} = 2$.

For low collisional energies the MCQS cross sections locally exceed the Langevin cross section due to the presence of quantum shape resonances associated with specific values of J that are clearly visible in the partial cross sections depending on J and on parity "+". In contrast, partial cross sections for "−" parity are much smoother without marked resonances. The positions in energy of these resonances are highly sensitive to molecular potentials and cannot be reliably predicted; however, the model clearly indicates that they contribute to the dynamics in the ultracold regime. As expected, when the collision energy increases, all J values tend to contribute equally to the total cross section, thus reproducing the semiclassical behavior of the Langevin cross section.

For example, in the entrance channel $S + D_{5/2}$ with parity "+", a pronounced shape resonance is observed in the FSQ process around 10^{-4} K, which is mainly the result of $J = 4$ and $J = 5$ (Fig. D.1). As a consequence, the FSQ cross section slightly exceeds the Langevin limit. The cross sections for NRCE and NRQ are weaker, but they are also structured by shape resonances in the case of parity "+". For NRCE, only even values of J contribute since the only molecular state correlated to the limit $\text{I}_{01} + S$ is $2^1\Sigma^+$, which appears for combinations with even J and parity "+", and odd J and parity "−". The states $J = 2$ and $J = 4$ generate the strongest resonances in this energy region. We observe similar patterns in the entrance channel $S + D_{3/2}$ with parity "+", with prominent resonances in the dominant NRQ process due to $J = 1$ and $J = 3$, and for the NRCE process due to the $J = 4$ around $E_{\text{col}}/k_B \approx 10^{-4}$ K.

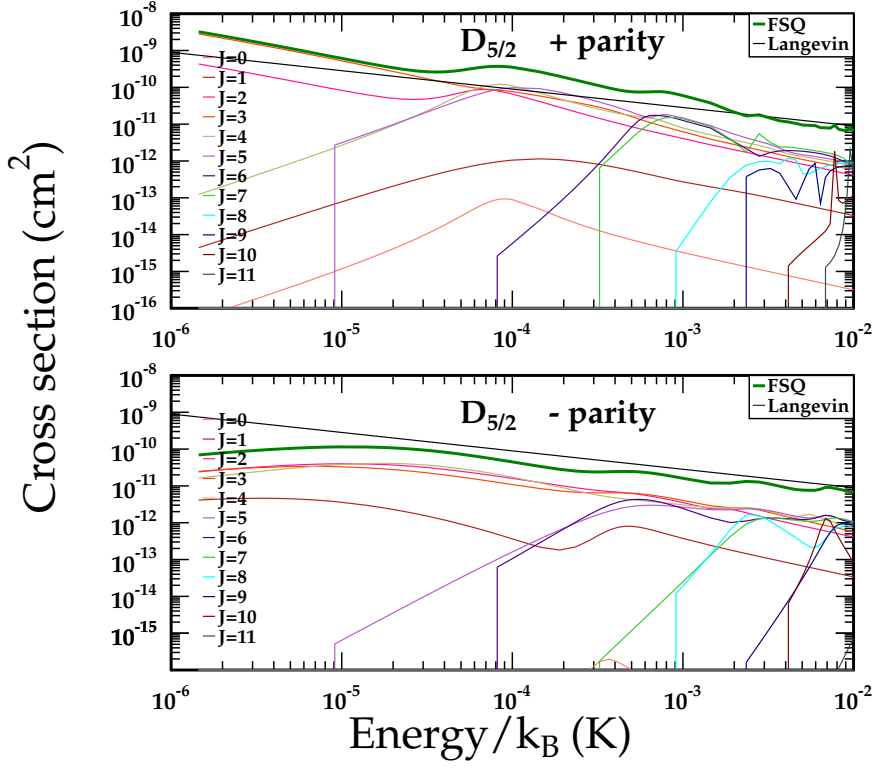


Figure D.1: Partial cross sections (Eq.3.117) up to $J = 11$ and for parity "+" and "-" for the FSQ process (starting from the $S + D_{5/2}$ entrance channel) as a function of temperature E_{col}/k_B (colored solid lines). Green solid line: total parity-dependent cross section for FSQ. Black solid line: Langevin cross section.

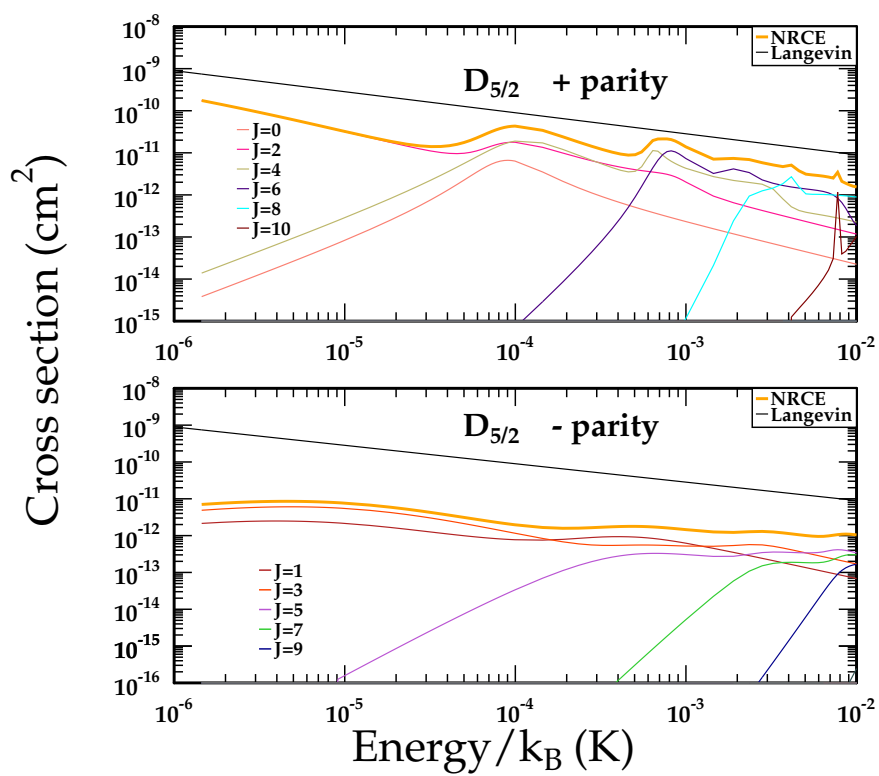


Figure D.2: Same as Figure D.1 for NRCE, with the total cross section drawn in orange solid line.

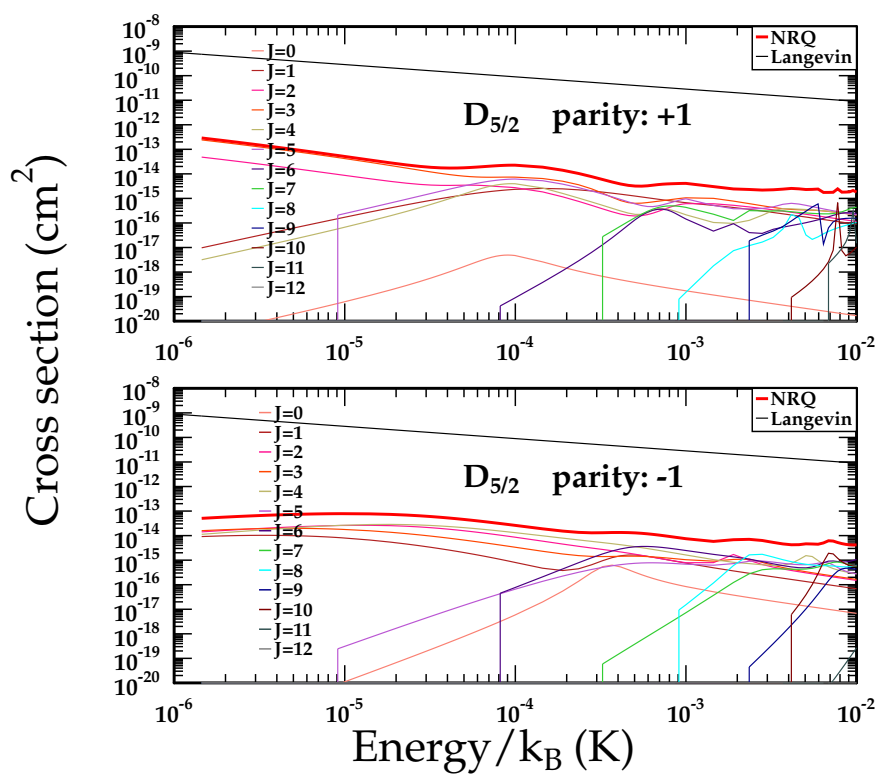


Figure D.3: Same as Figure D.1 for NRQ, with the total cross section drawn in red solid line.

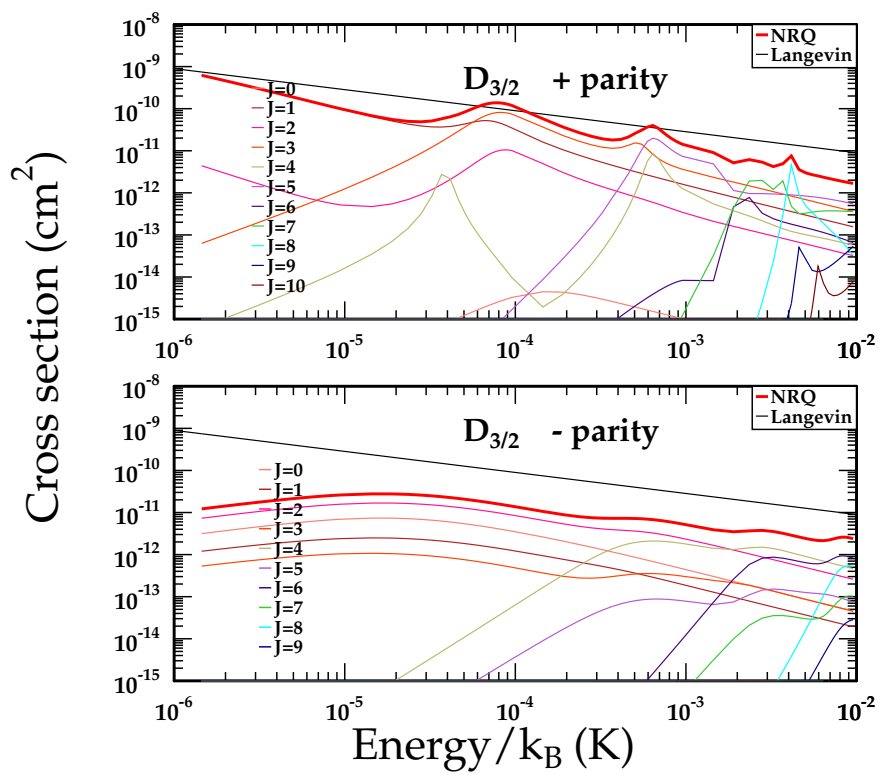


Figure D.4: Same as Figure D.3 for the entrance channel $S + D_{3/2}$.

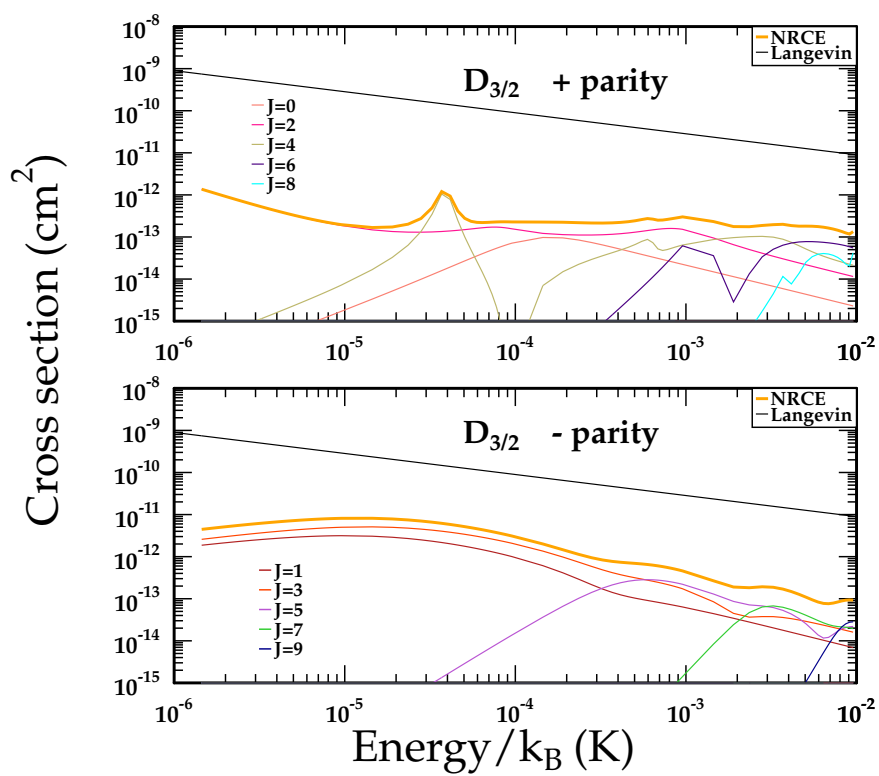


Figure D.5: Same as Figure D.4 for NRCE, with the total cross section drawn in orange solid line.

Appendix E

Elastic partial cross sections for Li-Ba⁺ collisions

The elastic channel deserves particular attention. The calculations predict that elastic collisions dominate the overall dynamics over most of the investigated temperature range, cross sections exceeding the Langevin estimate for inelastic cross sections, see Fig. 6.9 panel a) and b). This is expected as in the classical picture, only collisions with an impact parameter smaller than b_{max} might induce an inelastic process, while all other collisions are elastic (see Section 3.5).

Figures E.1 and E.2 show at low energies that $J = 2$ and $J = 3$ with parity "+" containing the s -wave (see above) are the only noticeable contributions, decreasing in $1/E$ with increasing energy, as expected. Extending calculations at even lower energy would show a saturation toward a constant cross section proportional to the squared scattering length characterizing the set of used PECs.

At low collision energy ($E_{col}/k_B < 10 \mu K$), the FSQ cross section exceeds the elastic one, due to the contribution of the s -wave. This might be the manifestation of a resonant feature at very low temperature, but the inelastic cross section is expected to vanish as the energy decreases, as predicted by scattering theory [152].

We note a prominent narrow feature in the $D_{3/2}$ entrance channel and parity "+" associated to the $J = 4$ cross section, probably induced by a Feshbach resonance in the entrance channel. This resonance was also visible in the NRCE cross section (Fig. D.5).

For the $D_{5/2}$ entrance channel and parity "+", the low-temperature elastic cross section below $5 \mu K$ is mainly governed by the $J = 2$ and $J = 3$ contributions.

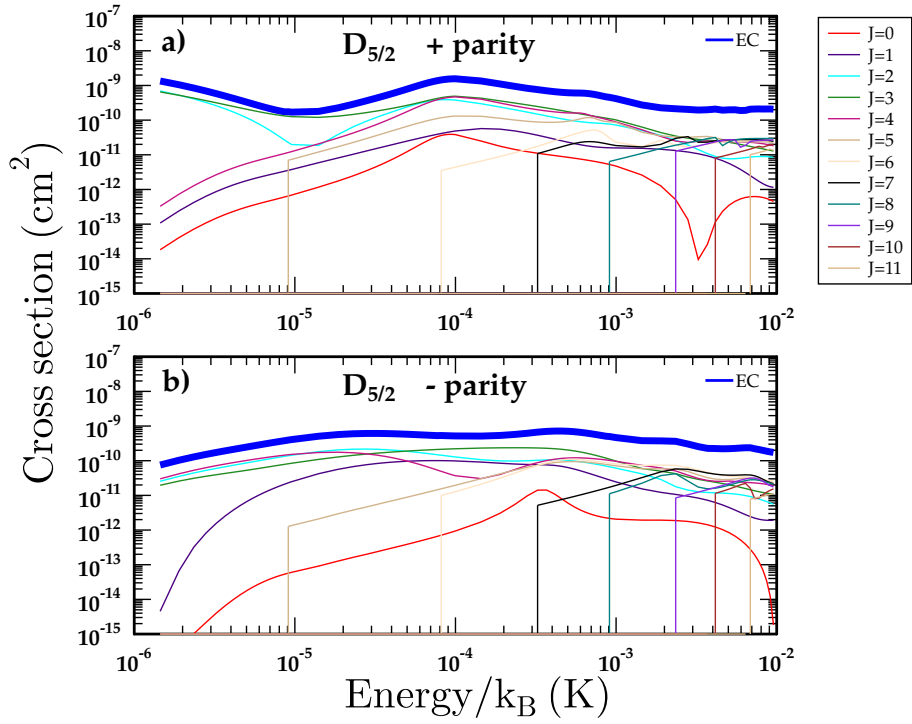


Figure E.1: The parity dependent elastic collision (blue thick line) and the first eleven J -dependent partial cross sections (thin colored lines) as a function of the temperature for $D_{5/2}$ incoming channel.

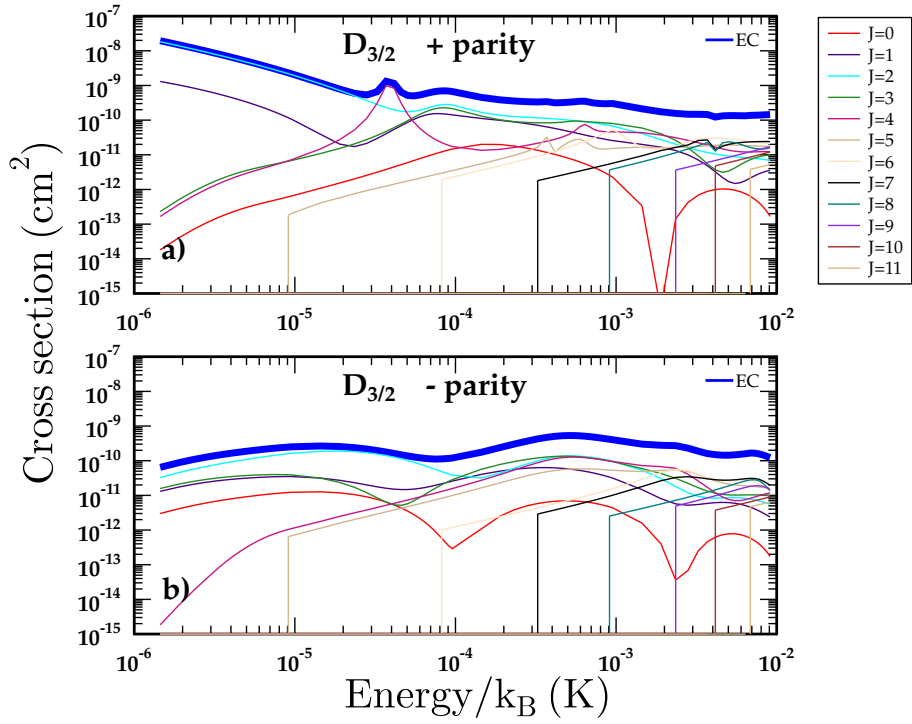


Figure E.2: The parity dependent elastic collision (blue thick line) and the first eight J -dependent partial cross sections (thin colored lines) as a function of the temperature for $D_{3/2}$ incoming channel.

Appendix F

Inelastic partial cross sections for Rb-Sr^+ collisions

These cross sections are displayed in the series of Figs. F.1, F.2, F.3. As more partial waves than in LiBa^+ participate to the processes, the cross-sections undergo small oscillations that are induced by their cumulative effect without any real prominent feature. In other words, the displayed energy regime already corresponds to the classical collisional regime. Most of the partial cross sections have a smooth variation in energy consistent with the influence of the top of the centrifugal barrier. Sharper structures are visible in the partial cross section for $J = 7, 8$ in the $S + D_{5/2}$ and $S + D_{3/2}$ entrance channels and for parity “-”, and for all processes, which are consistent with the presence of Feshbach resonances.

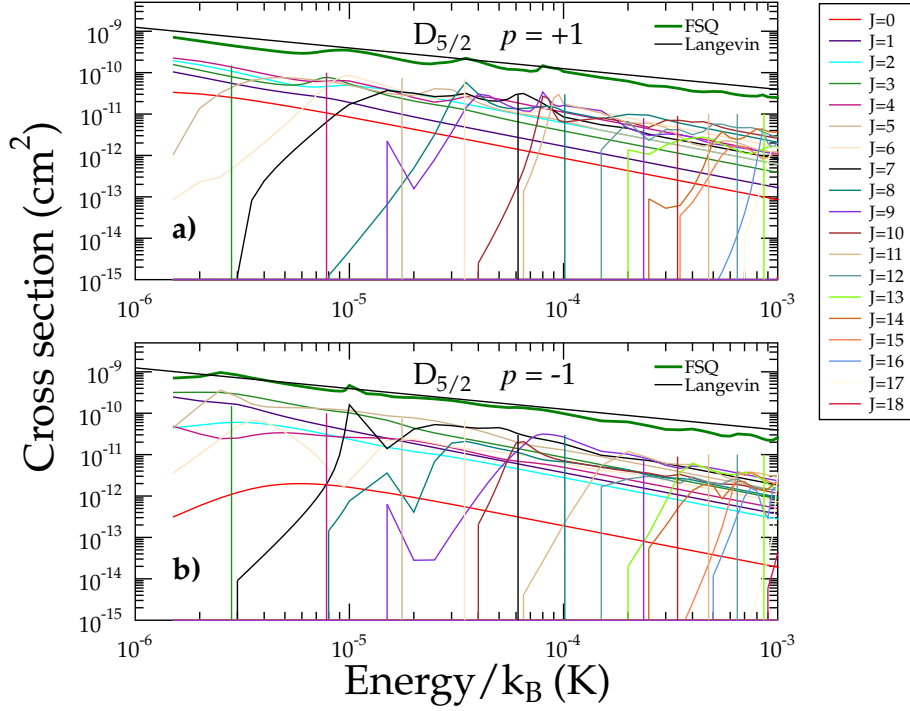


Figure F.1: Partial cross sections up to $J = 18$ and for parity "+" and "-" for the FSQ process starting from the entrance channel $S + D_{5/2}$ incoming channel as functions of temperature E_{col}/k_B (colored solid lines). Green solid line: total parity-dependent cross section for FSQ. Black line: Langevin cross section. Vertical colored lines indicate the centrifugal barrier heights corresponding to different ℓ values. The barriers for $\ell = 1, 2$ lie below 1 μK and are not visible in the figure.

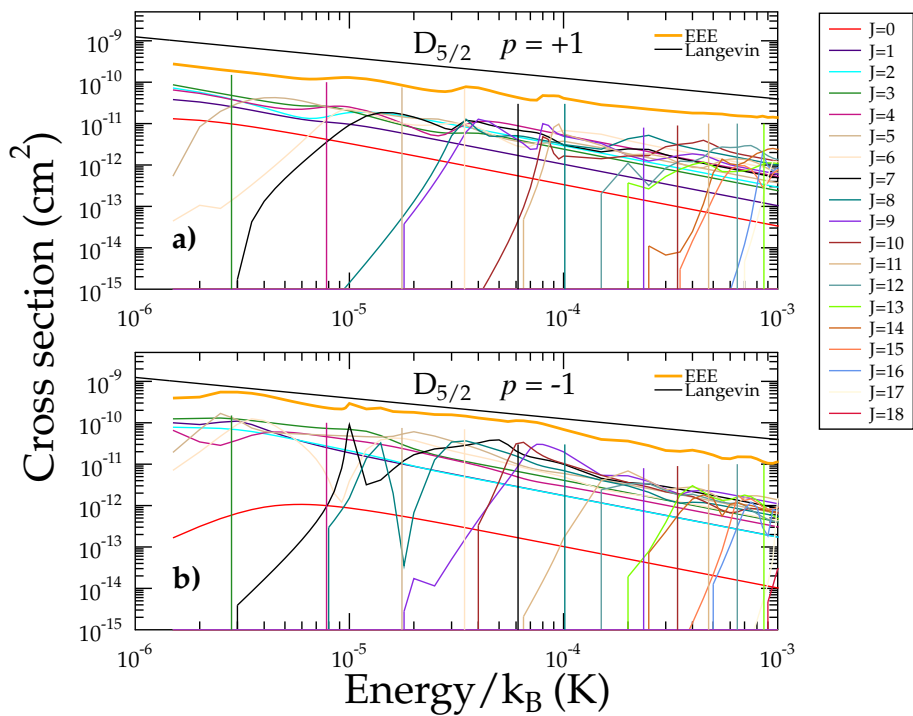


Figure F.2: Same as Figure F.1 for EEE, with the parity-resolved total cross section drawn in yellow solid line.

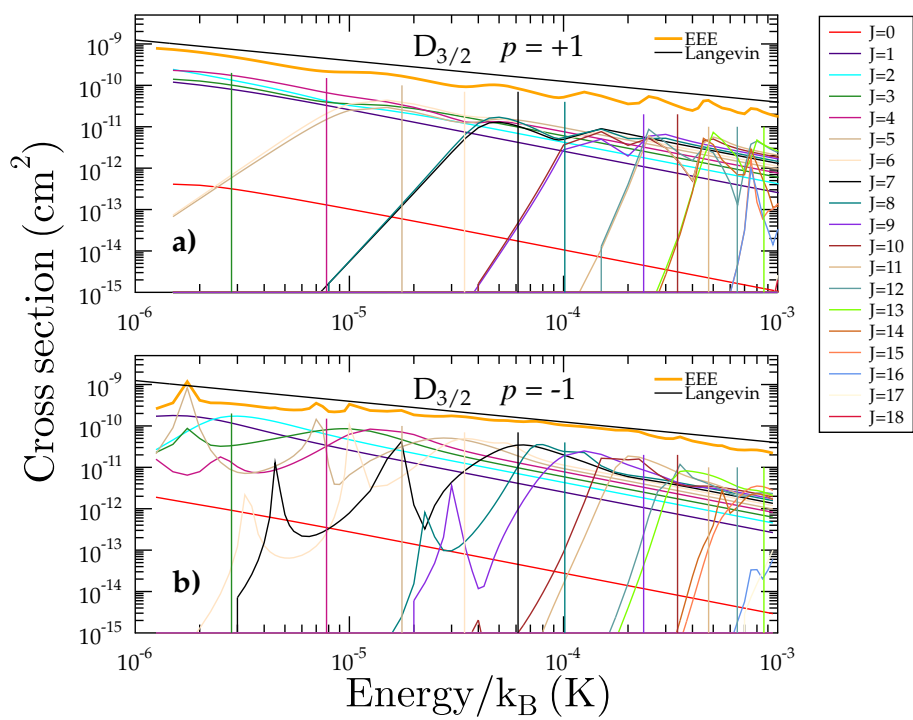


Figure F.3: Same as Figure F.2 for the entrance channel $S + D_{3/2}$.

Appendix G

Elastic partial cross sections for Rb-Sr^+ collisions

In addition to the inelastic partial cross sections, we also determined elastic partial cross sections, which are shown in Fig. G.1 and G.2 for the two incoming channels. Elastic collisions play an important role in the sympathetic cooling when a cold ion collides with ultracold atoms to reduce the kinetic energy of the ion. Since in the present case the collision partners have almost equal masses, the efficiency of sympathetic cooling could be high.

The overall behavior of the partial elastic cross sections is similar to that of the inelastic ones, building up a monotonous cross section with temperature. A structure consistent with a Feshbach resonance is visible in $J = 4$ and parity “-” of the entrance channel $S + D_{3/2}$, while being of low magnitude. We note the oscillating behavior of the $J = 0$ contribution in both entrance channels, for which we have not found a satisfactory explanation.

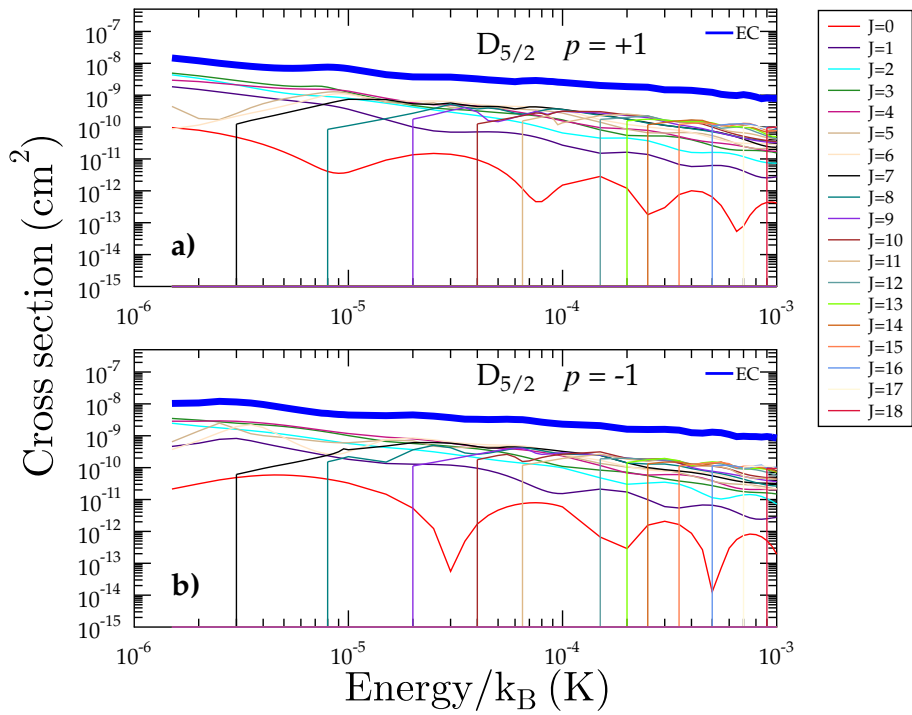


Figure G.1: Partial elastic cross sections up to $J = 18$ and for parity “+” and “-” in the entrance channel $S + D_{5/2}$ as functions of temperature E_{col}/k_B (colored solid lines). Solid blue line: parity-dependent cross section after summation on J .

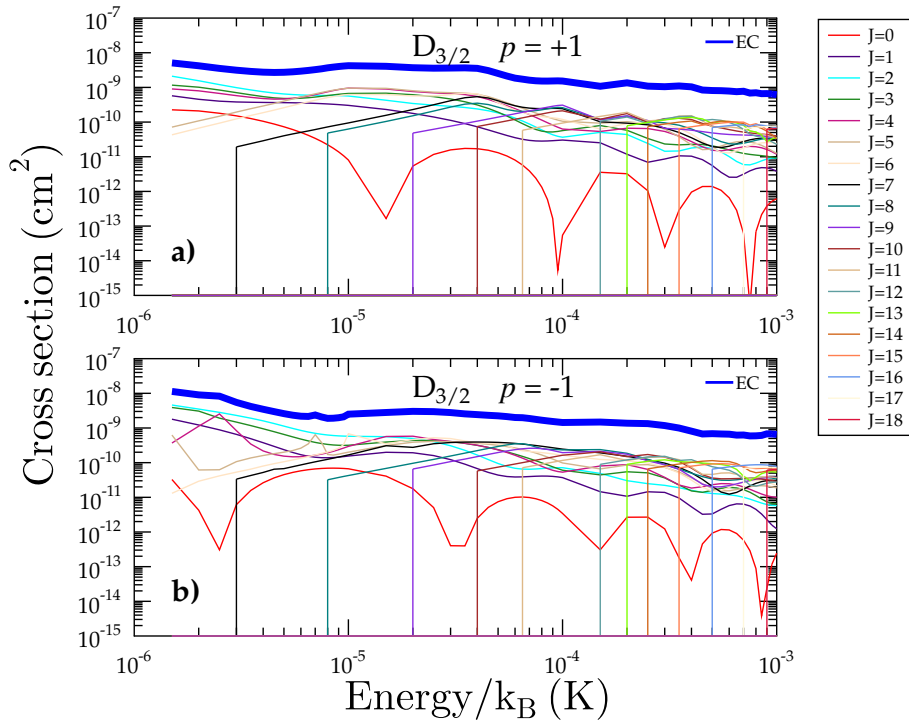


Figure G.2: The same as Fig. G.1 but for entrance channel $S + D_{3/2}$. Partial elastic cross sections up to $J = 18$ and for parity "+" and "-".

Összefoglalás és kitekintés

Doktori munkám során alkálifém atomok és alkáliföldfém ionok hibrid csapdákban lejátszódó ultrahideg ütközései során fellépő rugalmatlan folyamatok kvantummechanikai leírásával foglalkoztam. Ezen rendszerek egyesítik a semleges atomokkal és a csapdázott ionokkal végzett kísérletek számos előnyét, és ígéretes lehetőséget kínálnak többek között a kontrollált atom-ion ütközések, a hideg kémia, a töltéstranszport és a szennyeződések tartalmazó rendszerek vizsgálatára, valamint a kvantum-szimulátorok területén. Mielőtt azonban ezen rendszerek teljes mértékben alkalmazhatók lennének a fentebb említett célokra, elengedhetetlen a csapdaveszteséget okozó kvantummechanikai folyamatok megértése. Ebben a rugalmatlan folyamatok fontos szerepet játszanak, mivel a csapdázott részecskék számának csökkenését eredményezik, ami az alkalmazások szempontjából kedvezőtlen. A rugalmatlan folyamatok szerepe akkor nő meg különösen, amikor a kísérletben jelen levő hűtő és csapdázó lézerek hatására az ion metastabil állapotba kerül, és a gerjesztett bemeneti csatorna többletenergija miatt több, egymással versengő reakció nyílnak meg.

A munkám egyik fontos motivációját az adja, hogy az alkáliföldfém ionok lézeres hűtési sémáiban a metastabil D -állapot is szerepet játszik, ugyanakkor ezek az állapotok az ütközések kezdeti csatornáiként célzottan is preparálhatók. A gerjesztett kezdeti állapotok az alapállapotú ütközésekhez képest további, energetikailag megengedett reakciócsatornákat nyitnak meg. E megnyíló reakciócsatornák kvantitatív leírása képezi doktori munkám fő célját: a kísérletileg megfigyelt rugalmatlan folyamatok hatáskeresztmetszeteinek és reakciósebességeinek elméleti meghatározása, a folyamatokért felelős nem-adiabatikus csatolások azonosítása, valamint az elméleti eredmények összehasonlítása a rendelkezésre álló kísérleti adatokkal. Számításaim sok-csatornás kvantummechanikai szóráselméleti megközelítéssel alapulnak, amelynek során molekuláris potenciális energia görbéket, spin-pálya és nem-adiabatikus csatolásokat vettem figyelembe, bázis transzformációt, valamint csatolt-csatornás számításokat végeztem. A dinamikai számítások ezért nemcsak hatáskeresztmetszeteket és reakciósebességeket szolgáltatnak, hanem egyúttal lehetőséget adnak a felhasznált molekulaszervezeti adatok és csatolási modellek ellenőrzésére is.

Az első részletesen vizsgált rendszerben alapállapotban levő ${}^6\text{Li}$ -atom és metastabil ($5d^2D_{3/2}$ vagy $5d^2D_{5/2}$) állapotban levő ${}^{138}\text{Ba}^+$ -ion ultrahideg ütközését vizsgáltam. A kísérletileg megvalósítható két bemeneti csatorna esetén, amikor a Ba^+ ion kezdetben metastabil ($5d^2D$) állapotban van három rugalmatlan folyamat verseng egymással: a finomszerkezeti legerjesztődés (fine-

structure quenching, FSQ), a nemradiatív töltéscicserélődés (non-radiative charge exchange, NRCE) és a nemradiatív legerjesztődés (non-radiative quenching, NRQ). Mindkét bemeneti csatornára paritásfüggő hatáskeresztmetszeteket határoztam meg. Ezt követően elemeztem az egyes parciális hullámok járulékait annak érdekében, hogy azonosítsam a hatáskeresztmetszetekben megjelenő főbb struktúrák eredetét. Végül paritásfüggetlen hatáskeresztmetszeteket, valamint nem termalizált és termalizált reakciósebességeket számítottam, amelyeket összehasonlítottam a rendelkezésre álló kísérleti eredményekkel. A rugalmatlan folyamatok mellett a rugalmas ütközésre vonatkozó hatáskeresztmetszeteket és reakciósebességeket is meghatároztam, amelyek ugyanazon dinamikai számításokból egyidejűleg adódnak.

A Li-Ba⁺ rendszerre végzett számítások jól reprodukálják a kísérletben megfigyelt főbb tendenciákat, valamint a domináns rugalmatlan folyamatok egymáshoz viszonyított erősségét. Különösen az NRCE és NRQ folyamatokra kapott reakciósebességek mutatnak jó egyezést a kísérleti eredményekkel mindkét vizsgált bemeneti csatorna esetén. Az elemzés alapján az NRCE folyamatot elsősorban két $^1\Sigma^+$ állapot közötti lokalizált nem-adiabatikus csatolás idézi elő, amely a hozzájuk tartozó potenciális energia görbék úgynevezett "avoided crossing"-ja közelében válik jelentőssé. Ezzel szemben a nem-radiatív legerjesztődés, NRQ, egy összetettebb mechanizmus eredménye, ahol az egymást keresztező potenciális energia görbéknek van fontos szerepe, amit a kis magtávolságoknál fellépő indirekt spin-pálya csatolások és rotációs csatolások együttesen határoznak meg. A finomszerkezeti legerjesztődés, FSQ, reakciósebességét ugyanakkor a jelenlegi modell felülbecsüli. Ezen eltérés legvalószínűbb oka, hogy a kísérletben a Li-atomokat a metastabil ^2D állapot valamely Zeeman alállapotába gerjesztik, amelyet a modellünk nem vesz figyelembe.

A második vizsgált rendszer az alapállapotban levő ^{87}Rb -atom és a metastabil állapotban levő $^{88}\text{Sr}^+(4d^2D_{3/2,5/2})$ -ion ultrahideg ütközésének tanulmányozására irányult, ahol a kísérletben két rugalmatlan folyamatot figyeltek meg: a finomszerkezeti legerjesztődést, FSQ, és az elektronikus gerjesztési kicserélődést (electronic excitation exchange, EEE). Számos más atom-ion rendszerrel ellentétben ebben az esetben nem figyeltek meg töltéscicserélődést. A LiBa⁺ molekulaionhoz képest a RbSr⁺ jóval összetettebb gerjesztett elektronállapottal rendelkezik a bemenő ütközési csatornák közelében, Rb($5s^2S$)+Sr⁺($4d^2D$), a Rb($5p^2P$)+Sr⁺($5s^2S$) aszimptotikus limit közelsége miatt. Ennek következtében több elektronállapot vesz részt a dinamikában, valamint a megjelenő két "avoided crossing" két $^1\Sigma^+$, illetve két $^3\Sigma^+$ adiabatikus állapot között még összetettebbé teszi az ütközés leírását. A modellünkben a potenciális energia görbék diabatizálása az "avoided crossing"-ok jelenléte miatt szükségessé tette egy kétlépéses kvázi-diabatizációs eljárás alkalmazását a molekuláris spin-pálya csatolások meghatározásánál.

Az EEE folyamatra számolt reakciósebességek kielégítő egyezést mutatnak a kísérleti eredményekkel. Ez alátámasztja a felhasznált molekuláris adatok megbízhatóságát, valamint a spin-pálya csatolások kvázi-diabatikus kezelésének fontosságát. Vizsgálataink azt is megmutatták, hogy az ütközési dinamikát jelentősen befolyásolja a nem-adiabatikus-, a spin-pálya- és a rotációs csatolások együttes hatása. Ugyanakkor, a LiBa⁺ rendszerhez hasonlóan, a modellünk

ebben az esetben is felülbecsüli a FSQ folyamat reakciósebességét a kísérleti-
leg mért értékhez képest. Ez arra utal, hogy a finomszerkezeti legerjesztődés
különösen érzékeny lehet az ütköző részecskék kezdeti spinállapotára. Mivel a
kísérletekben az egyik vagy mindkét ütköző részecskét meghatározott spinállapot-
ban preparálják, a folyamat teljes kvantitatív leírásában figyelembe kell venni a
releváns hiperfinom- és Zeeman-alszinteket is.

A Li-Ba^+ és Rb-Sr^+ ütközési rendszerek összehasonlítása rávilágít arra,
hogy metastabil alkáliföldfém ionokkal való ultrahideg ütközések nem írhatók
le egyetlen rugalmatlan folyamattal, egyetlen izolált csatolási mechanizmussal,
vagy egyszerűsített modellekkel. A megfigyelt rugalmatlan dinamika ehelyett
a nem-adiabatikus csatolások, a spin-pálya kölcsönhatás és a molekuláris rotá-
ció együttes hatásának eredménye. Az egyszerűsített modellek, például a
Landau-Zener-típusú közelítések, hasznos kvalitatív képet adhatnak az egyes
folyamatokról, azonban a kísérleti megfigyelések kvantitatív leírásához teljes,
sok-csatornás kvantumszórási leírásra van szükség. A disszertációban bemu-
tatott eredmények így hozzájárulnak a hibrid atom-ion rendszerek veszteségi
mechanizmusainak részletesebb megértéséhez, és elméleti keretet biztosítanak
a gerjesztett elektronállapotú ütköző részecskékkel végzett jövőbeli kísérletek
értelmezéséhez.

A fent azonosított korlátok több lehetséges irányt is kijelölnek a modellünk
továbbfejlesztésére. Ilyen továbblépést jelent a hiperfinom- és Zeeman-alszintek
figyelembe vétele a molekuláris bázisban [147]. Ez lehetővé tenné a kísérleti-
leg preparált spinállapotok explicit leírását ahelyett, hogy kizárólag a finomszerkezeti
csatornákat vennénk figyelembe. Egy ilyen kiterjesztés közvetlenül vizsgálhatóvá
tenné, hogy a Li-Ba^+ és Rb-Sr^+ rendszerekben tapasztalt FSQ reakciósebességek
felülbecslése valóban a bemeneti csatornák spin-polarizált jellegével függ-e
össze. Általánosabban, egy a hiperfinom- és Zeeman-alszinteket explicit mó-
don figyelembe vevő modell pontosabb összehasonlítást tenne lehetővé az
állapotszelektív hibrid csapdás kísérletekkel.

Egy másik ígéretes kutatási irány a jelenlegi módszertan alkalmazása további,
kísérleti szempontból releváns atom-ion ütközésekre. Különösen érdekes jelölt
a Li-Ca^+ rendszer, mivel a Li-Ba^+ -hoz hasonlóan a könnyű Li-atom és a jóval ne-
hezebb Ca^+ ion közötti nagy tömegkülönbség kedvező a kvantumos tartomány
megközelítése szempontjából. Emellett több ütközési energián (1 mK–1 K) is ren-
delkezésre állnak kísérleti adatok, amelyek több referenciapontot biztosítanak az
elméleti eredményekkel való összehasonlításhoz [54]. Mivel erre a rendszerre már
végeztek Landau-Zener-típusú vizsgálatokat [54], egy teljes sok-csatornás kvan-
tumszórási számítás lehetőséget adna az egyszerűsített modellek érvényességi
tartományának felmérésére, valamint a rugalmatlan folyamatokat létrehozó kvan-
tummechanikai mechanizmusok azonosítására.

További perspektívát jelent a molekulaionok létrehozása és kontrollálása. Az
atom-ion rendszerekben megfigyelt Feshbach-rezonanciák, például a Li-Ba^+ és
 Rb-Sr^+ kísérletekben megfigyelt rezonanciák [39, 71], a disszociációs küszöbhez
közeli molekuláris kötött állapotok jelenlétére utalnak, amelyek felhasználhatók
gyengén kötött molekulaionok létrehozására. Ilyen molekulaionok előállíthatók
például egy Feshbach-rezonancián keresztül történő mágneses asszociációval [39,
71], radiatív asszociációval [63, 65, 73, 83], illetve lézeres fotóasszociációval [47,

148]. Stabilitásuk és belső szerkezetük fotódisszociáció segítségével is vizsgálható, amely további információt szolgáltat a molekuláris kötési energiákról és az átmeneti útvonalakról.

Végül, hosszabb távon különösen ígéretes lehet a rugalmatlan atom-ion ütközések külső terekkel történő szabályozása. Más hideg ütközési rendszerekre javasolt optikai árnyékolási eljárásokhoz hasonlóan [149–151] vizsgálható lenne, hogy egy- vagy kétfotonos csatolások segítségével módosítható-e az ütközési dinamika még azelőtt, hogy a részecskék elérnék a kis magtávolságok tartományát. A bemeneti csatornának egy megfelelően megválasztott taszító molekuláris potenciálhoz történő csatolásával a külső lézerterek a nem kívánt rugalmatlan veszteségeket csökkenthetik azáltal, hogy megakadályozzák, hogy az ütköző partnerek közel kerüljenek egymáshoz. Egy ilyen lehetőség közvetlen kapcsolatot teremtené a disszertációban kidolgozott mikroszkopikus molekuláris leírás és a hibrid csapdák atom-ion ütközéseinek kontrollja között.