THEORETICAL AND COMPUTATIONAL METHODS FOR THREE-BODY PROCESSES

by

JUAN DAVID BLANDON ZAPATA M.S. University of Central Florida, 2006 B.S. University of Florida, 2004

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics in the College of Sciences at the University of Central Florida Orlando, Florida

Summer Term 2009

Major Professor: Viatcheslav Kokoouline

© 2009 Juan David Blandon Zapata

ABSTRACT

This thesis discusses the development and application of theoretical and computational methods to study three-body processes. The main focus is on the calculation of three-body resonances and bound states. This broadly includes the study of Efimov states and resonances, three-body shape resonances, three-body Feshbach resonances, three-body pre-dissociated states in systems with a conical intersection, and the calculation of three-body recombination rate coefficients. The method was applied to a number of systems. A chapter of the thesis is dedicated to the related study of deriving correlation diagrams for three-body states before and after a three-body collision.

More specifically, the thesis discusses the calculation of the H+H+H three-body recombination rate coefficient using the developed method. Additionally, we discuss a conceptually simple and effective diabatization procedure for the calculation of pre-dissociated vibrational states for a system with a conical intersection. We apply the method to H_3 , where the quantum molecular dynamics are notoriously difficult and where non-adiabatic couplings are important, and a correct description of the geometric phase associated with the diabatic representation is crucial for an accurate representation of these couplings. With our approach, we were also able to calculate Efimov-type resonances.

The calculations of bound states and resonances were performed by formulating the problem in hyperspherical coordinates, and obtaining three-body eigenstates and eigen-energies by applying the hyperspherical adiabatic separation and the slow variable discretization. We employed the complex absorbing potential to calculate resonance energies and lifetimes, and introduce an uniquely defined diabatization procedure to treat X_3 molecules with a conical intersection. The proposed approach is general enough to be applied to problems in nuclear, atomic, molecular and astrophysics.

To my Mother, my Sister and my Homeland. To all the people who have helped me along the path of life. To the wellbeing and progress of mankind.

ACKNOWLEDGMENTS

This thesis is not the work of an individual, instead, it was possible thanks to the support and effort of many people. I would like to thank my advisor, Dr. Kokoouline for all the guidance and support throughout these past four and a half years. It has truly been the most difficult thing I have ever done in my life, with many ups and downs, and it was possible to complete it thanks to the patience, experience and wisdom of Dr. Kokoouline. I consider myself lucky to have had such a good advisor! Thank you to my thesis committee, Dr. Schelling, Prof. Saha, and Dr. Babikov, for reviewing my thesis, being supportive and helping me improve my research throughout my PhD years. Thank you to my collaborators, Prof. Masnou-Seeuws, Nicolas Douguet, Dr. Schelling, and Dr. Aubry for helping me develop as a physicist and researcher.

Thank you to my family, especially my mother and sister for all the support and strength they gave me. The physics staff has been great to me, and to them I would like to say thanks! I will miss all of you, special thanks to Mike Jimenez, Felix Ayala and Pat Korosec. To my fellow grad students, thank you for being there and for the helping hands here and there, which made the journey all that more tolerable. Thank you to my personal friends for all the advice that has helped me successfully navigate the PhD program. To the Florida Education Fund: the McKnight Doctoral Fellowship made a huge difference for me, as it made living through the PhD program more bearable. Also FEF, thank you Dr. Morehouse and Charles Jackson for the moral support, you have always been very supportive!

This research was supported by the donors of the American Chemical Society Petroleum

Research Fund, the National Science Foundation under Grant Number PHY-0427460 by an allocation of NCSA and NERSC supercomputer resources, and by the Florida Education Fund McKnight Doctoral Fellowship.

TABLE OF CONTENTS

LIST OF FIGURES			xi
LIST OF TABLES			xxii
LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS			xxiii
INTRO	DUCT	ION: IMPORTANCE OF THREE-BODY PROCESSES	1
1.1	Three-body bound states and resonances		
1.2	1.2 Experimental interest		4
	1.2.1	Three-body recombination	4
	1.2.2	Atomic and Molecular systems	7
	1.2.3	Universality: Efimov states	9
	1.2.4	Nuclear systems	12
1.3	Existi	ng theoretical approaches for three bodies	13
1.4	Obsta	cles in three-body calculations	16
OUR APPROACH			18
2.1	Hyperspherical coordinates in present method		18
2.2	Quantum formalism		24
	2.2.1	The adiabatic hyperspherical approximation	25
	2.2.2	'Slow' variable discretization	28
	2.2.3	Hyper-radial wave functions	30
	2.2.4	Hyperangular wave functions: symmetries of adiabatic Hamiltonian	
		and group theory for three bodies	32

	2.2.5	Normal coordinates and labelling of vibrational states	41
	2.2.6	Complex absorbing potential	47
	2.2.7	R-matrix with 'slow' variable discretization	52
2.3	Nume	rical Methods	55
	2.3.1	Mapped Fourier grid, mapped DVR basis set, and mapped grid in	
		hyperangles	55
	2.3.2	B-splines	60
	2.3.3	Parallel computers	61
2.4	Comp	arison with other methods	63
ONE T	HREE-	BODY POTENTIAL ENERGY SURFACE	64
3.1	SHAP	E RESONANCES IN MODEL NUCLEAR SYSTEM	64
	3.1.1	Our results	64
	3.1.2	Comparison to previous study	69
3.2	EFIM	OV RESONANCES IN MODEL BOSONIC SYSTEM	73
TWO THREE-BODY POTENTIAL ENERGY SURFACES			82
4.1	Feshba	ach resonances in coupled $1^2A'$ and $2^2A'$ potential energy surfaces of H ₃	82
	4.1.1	Geometric phase	85
	4.1.2	Diabatic basis for the coupled H_3 potentials $\hdots\hdddt\hdots\hdots\hdddt\hdots\hdddt\hdots\hdddt\hdots\hdddt\hdots\hdddt\hdots\hdddt\hdots\hdddt\hdd$	88
	4.1.3	Results	90
	4.1.4	A word on labelling system of vibrational states	98
	4.1.5	Estimation of three-body recombination rate coefficient	100
	4.1.6	Convergence tests	102

	4.1.7	Conclusion	106
4.2	Model	Van der Waals system: Preliminary results	107
CORRELATION DIAGRAMS IN COLLISIONS OF THREE IDENTICAL PARTICLES11			5112
5.1	Descri	ption of study	112
5.2	Applic	eation of our method to this study	116
CONCI	LUSION	τ	121
6.1	Summary and conclusions		121
6.2	Future Work		122
	6.2.1	Three-body recombination	122
	6.2.2	Systems with conical intersection	122
	6.2.3	Universality	123
	6.2.4	Improving computational efficiency of our approach $\ldots \ldots \ldots$	124
LIST OF REFERENCES			125

LIST OF FIGURES

1.1	Three possible outcomes in simple classical case of elastic (energy of 'particle'		
	conserved) scattering event. Figure taken from Ref. [Moi98]	2	
1.2	Illustration of Feshbach and shape resonances. $E = 0$ is the dissociation limit		
	for three free particles, while $E < 0$ dissociation limit represents one bound		
	two-body state plus a free particle	3	
1.3	Process of three-body recombination for three ultracold Cs atoms (figure taken		
	from Ref. [EG06]). In the recombination process, the binding energy of		
	the dimer is taken by the dimer and free atom as kinetic energy. R is the		
	dissociation coordinate	5	
1.4	Plot shows dependence of three-body energy on 2-body scattering length a		
	(figure taken from Ref. [KMW ⁺ 06]). Note energy of Efimov trimers is much		
	less than energy of non-Efimov trimers. Infinite family of Efimov states exists		
	only at $1/a = 0$ (see text)	11	
2.1	Three sets of mass-weighed Jacobi coordinates $(\vec{r}_0^{(k)}, \vec{R}_0^{(k)}), k = 1, 2, 3$, sketched		
	assuming $m_1 > m_2 > m_3$. For three identical particles, all sets are equivalent		
	due to particle indistinguishability.	21	

2.2	Physical arrangement of particles mapped into configuration space by hyper-	
	spherical coordinates ρ , θ and φ ; these coordinates define particle configura-	
	tion size (ρ) and shape (θ, φ) . Although it is difficult to tell from the figure, the	
	two-dimensional space of hyperangles displays C_{3v} symmetry (section 2.2.4)	
	for a system of identical particles. Particles are labeled by numbers 1, 2, and	
	3 for future reference	23
2.3	Example of hyper-radial wave functions $(\Psi_1(\rho) \text{ and } \Psi_2(\rho))$ of three-body sys-	
	tem with two adiabatic states $(U_1(\rho) \text{ and } U_2(\rho))$	31
2.4	Visual depiction of C_{3v} point symmetry group [LL03]. There is only one axis	
	of symmetry of the third order, with three intersecting vertical planes. $\ . \ .$	34
2.5	Table of characters of irreducible representations of C_{3v} [LL03]. The letters	
	x, y, and z label the representations by which the coordinates themselves are	
	transformed	37
2.6	Hyperangular wave functions for system with C_{3v} symmetry. Wave functions	
	are shown as contour plots, where each line represents an equipotential. All	
	irreducible representations of C_{3v} (A_1 , A_2 , and E) are displayed. Note the	
	symmetries that characterize each irreducible representation: A_1 and A_2 are	
	unchanged by $2\pi/3$ rotations of φ ; A_1 is symmetric through reflections across	
	$\varphi = 2\pi/3$ vertical planes while A_2 is anti-symmetric. E_a states are symmetric	
	through one vertical plane at $\varphi = \pi/2$, while E_b is anti-symmetric through	
	the same plane	39
2.7	Adiabatic channels for system of three identical particles	40

xii

2.8	Visual depiction of D_{3h} point symmetry group [LL03]. It is the same as C_{3v}	
	(Fig. 2.4), with the addition of three horizontal axes of symmetry of the	
	second order intersecting at $\pi/3$	41
2.9	Set of normal modes of vibration for X_3 system, where particle X has mass	
	m. Each particle is labeled by 1, 2 or 3. Superposition of degenerate normal	
	modes $(Q_x + iQ_y)$ produces nuclear motion on right. Each vibrational mode	
	can be characterized by a quantum number (v_1, v_x, v_y) . In the normal mode	
	approximation the symmetric mode is characterized by v_1 , while the asym-	
	metric stretch modes are characterized by v_2 and l_2 (see discussion in text).	
		45
2.10	Cartoon of CAP, where ρ is some dissociation coordinate (see text)	48
2.11	Example of table of optimization of CAP parameters, taken from Vibok <i>et al.</i>	
	[VBK92]	51
2.12	Non-uniform grid step along hyper-radius $\Delta\rho$ used in the calculation of Efimov	
	resonances.	58
2.13	Non-uniform grid step along hyperangle θ used in the calculation of Efimov	
	resonances. $\Delta \theta$ is grid step size such that $\theta_{i+1} = \theta_i + \Delta \theta_i$	59
2.14	Non-uniform grid step along hyperangle φ used in the calculation of Efimov	
	resonances. $\Delta \varphi$ is defined similarly to $\Delta \theta$ (caption of Fig. 2.13)	60

- 3.1 Hyperspherical adiabatic potentials of A_1 symmetry for the system with a potential barrier. Five A_1 adiabatic channels are displayed. There is only one bound state at -37.35 MeV. Resonant states are long-living states that tunnel through the potential barrier as shown in the inset. Note logarithmic scale in hyper-radius. The two arrows along hyper-radius point to the values of ρ where ground adiabatic curve has its minimum and to where CAP begins.

65

- 3.4 Resonance hyper-radial wave function for four-channel calculation. The wave function has a considerable amplitude in the region of the potential well (around 10^{-4} a.u.). Arrows along hyper-radius point to ground adiabatic curve minimum and to where CAP begins (see Fig. 3.1). CAP is placed around $\rho = 4 \times 10^{-3}$ a.u., the distance at which the outgoing dissociation flux starts to be absorbed. This can be compared with the continuum wave function shown in Fig. 3.3, for which the potential-well amplitude is very small. Comparing the amplitudes of the different components, it is clear that the principal contribution is due to the lowest adiabatic state.
- 3.5 Convergence of the position and width of the resonance with respect to the number of adiabatic states included in the calculation. The results for the resonance are circled; other data points represent the continuum states. Positions and widths of the continuum states depend on the CAP parameters. Notice that positions of the resonance and continuum states are at negative energies because the origin of energy is at the three-body dissociation, which is above the dissociation to the dimer + free particle configuration. 71

69

3.6 Comparison of our resonance linewidth calculations to linewidth calculation of Fedorov *et al.*, and to the WKB approximation. We show our halfwidths for one-channel and five-channel calculations. Our four-channel calculation is closer to WKB approximation than that of Fedorov *et al.* [FGJ03]. However, WKB estimation cannot be viewed as reliable for this particular situation. 73

 $\mathbf{X}\mathbf{V}$

- 3.11 First four adiabatic components $\psi_a(\rho)$ (a = 1 4) of the hyper-radial wave function of the first Efimov resonance. Real and complex parts of the components are shown in black and green lines. This resonance is considered non-Efimov. Wave function spans around three orders of magnitude in hyperradius, while the third resonance, which is considered of the Efimov type, spans four orders of magnitude in hyper-radius (Fig. 3.10). 80

79

3.12 Hyperangular vibrational wave functions for large hyper-radius ($\rho = 15 a_0$) for the Efimov system. Even at such modest hyper-radius the wave function for the ground adiabatic state a = 1 is already strongly localized around $X+X_2$ geometries. Wave functions of excited states are more diffuse in the hyperangular space, because they correspond to the X+X+X dissociation. 81

- 4.2 Illustration of 2π rotation in configuration space about equilateral three-body arrangement of adiabatic electronic wave functions ψ_1, ψ_2 (Eq. 4.2). Point of equilateral configuration corresponds to conical intersection (degeneracy) of $1^2A'$ and $2^2A'$ molecular states (see Fig. 4.1). Degeneracy is broken away from symmetric configuration. Rotation takes α from $\alpha \rightarrow \alpha + 2\pi$ (see Eq. 4.1). 86

4.9	Resonance hyper-radial probability densities for ground (no nodes, $v_1 = 0$),	
	first excited (one node, $v_1 = 1$), and third excited (three nodes, $v_1 = 3$)	
	vibrational states of H_3 . For a comparison, we also give the probability density	
	$ \Psi_c ^2$ of a continuum state (energy is -0.0091 Eh). Ψ_c is localized mostly in the	
	large- ρ dissociation region. The arrow points to the beginning of the complex	
	absorbing potential	98
4.10	Modulus squared hyper-radial wave function of fourth and fifth excited vibra-	
	tional states	99
4.11	Convergence of resonant states with respect to hyper-radial grid point density.	
	Uniform distribution of hyper-radial points is used here, with $\rho_{max} = 6 a_0$.	102
4.12	Convergence of resonant states with respect to CAP length. Here, $\rho_{max} = 6 a_0$.	103
4.13	Convergence of resonant states with respect to CAP strength ($\rho_{max} = 6 a_0$).	104
4.14	Convergence of resonant states with respect to number of adiabatic states	
	included ($\rho_{max} = 6 \ a_0$)	104
4.15	Convergence of resonant states with respect to ρ_{max}	105
4.16	Two-body Van der Waals potentials and coupling (Eqs. 4.15 and 4.16)	109
4.17	Adiabatic potentials of A_1 symmetry for Van der Waals Li-based system	110
4.18	Convergence of three-body resonant states (circled) with respect to CAP length.	.111
4.19	Convergence of three-body resonant states (circled) with respect to CAP	
	strength	111
5.1	Allowed rotational quantum numbers for short distances between particles. \boldsymbol{n}	
	is an integer. Table taken from Ref. [DBK08]	115

- 5.3 Correlation diagram for states of three interacting particle configuration (described by quantum numbers K, l_2), and states of dimer + free particle configuration (described by quantum numbers j_r, J_R) [DBK08]. Here $\vec{J} = \vec{j}_r + \vec{J}_R$. 117
- 5.5 Hyperangular vibrational wave functions of lowest adiabatic states of Hebased system (discussed in text) for $\rho = 9, 15, 30 \ a_0$ (left, center, and right columns, respectively). Color represents value of wave function $\phi(\theta, \varphi)$, which depends on two coordinates. Wave functions display A_1, A_2 and E symmetries of the C_{3v} group. E symmetry states are represented by components $E_a =$ Real (E_+) and $E_b = \text{Im}(E_+)$. Parity is defined (positive) but it is not specified here because it is controlled by Euler angle γ , which cannot be shown [DBK08].120

LIST OF TABLES

3.1	Stability of calculated resonance with respect to CAP parameters for system of	
	identical bosons interacting through a two-body potential with a barrier. The	
	de Broglie wavelength of the dissociating products is approximately 0.0006	
	a.u. The most deviant calculation, last row, is due to the short length of the	
	CAP for that calculation.	70
3.2	Stability of the calculated resonance with respect to type of CAP used	70
3.3	Comparison of complex energies (in atomic units) obtained in this work using	
	different number of included adiabatic states with the results of Nielsen $et al$.	
	[NSE02]. The imaginary part of the energies is the halfwidth of the resonances.	
	The overall agreement is good except for the position of the 4^{th} resonance,	
	which is probably not represented accurately in this study: the grid is not	
	long enough in the present calculation. In Ref. [NSE02], six adiabatic states	
	have been used	78
4.1	Positions, E_r (in units 10^{-2} Eh) and lifetimes, τ (in fs) of pre-dissociated	
	$2^2 A'$ vibrational levels. Energies are relative to the H(1s) + H(1s) + H(1s)	
	dissociation.	96

LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

a	two-body scattering length
ρ	hyper-radius
(heta,arphi)	hyperangles
ϕ_a	hyperangular wave function of a^{th} adiabatic state
α	normal asymmetric stretch mode phase
АРН	adjusting principal axes hyperspherical coordinates
BEC	Bose-Einstein Condensate
DFG	Degenerate Fermi Gas
CAP	Complex Absorbing Potential
DVR	discrete variable representation
ET	Efimov trimer
BOA	Born-Oppenheimer adiabatic
HSA	hyperspherical adiabatic
NCSA	National Center for Supercomputer Applications
NERSC	National Energy Research Scientific Computing Center

INTRODUCTION: IMPORTANCE OF THREE-BODY PROCESSES

This chapter gives context to our work. It offers an overview of the relevance of threebody processes in modern-day physics. These include three-body recombination, three-body Feshbach resonances, and three-body collisions. We also mention some prominent and widely used three-body methods.

1.1 Three-body bound states and resonances

In this thesis, we consider inelastic (also called 'reactive') scattering processes, where the 'particle' and 'target' can undergo a rearrangement that can make them different species at the beginning and at the end of the collision [Tay72] (e.g. three-body recombination). In a three-body scattering process (also called 'multichannel scattering' [Tay72]), there are several types of three-body resonances. Multichannel refers to the possible outcomes ('channels') available before and after a collision, e.g. for a collision of atoms a, b and c there are four possible channels: 1) a + b + c, 2) a + bc, 3) ac + b and 4) $a + (bc)^*$, where * denotes excitation of the bc dimer [Tay72]. Resonances fall into two broad categories: Shape resonances and Feshbach-type resonances [Bla06]. We introduce here some definitions, and to this end begin by using the simple case of classical single-channel elastic scattering where the 'target' is fixed.

In a scattering process, a resonant state is defined as 'a long-lived state of a system, which has sufficient energy to break-up into two or more sub-systems' [Moi98]. In the classic elastic



Figure 1.1: Three possible outcomes in simple classical case of elastic (energy of 'particle' conserved) scattering event. Figure taken from Ref. [Moi98].

scattering process, three possibilities arise: 1) an event where the incoming 'particle' gets trapped by the 'target' potential in a bounded orbit, which requires the presence of a third particle to take away the excess energy of the incoming particle (analog of quantum bound state, 'a' in Fig. 1.1), 2) a direct scattering event (analog of quantum continuum state, 'b' in Fig. 1.1), or 3) a scattering event where the 'particle' is temporarily trapped by the 'target' such that the lifetime of the target-particle sub-system is larger than the collision time in direct scattering (analog of quantum resonant state, 'c' in Fig. 1.1) [Tay72].

A shape resonance is broadly defined as a state that is temporarily trapped by a potential barrier, e.g. centrifugal potential barrier, through which it has a non-negligible probability of tunneling, thereby allowing the 'particle' to escape and the target-particle sub-system to dissociate (Fig. 1.2). A Feshbach-type resonance [Fes58] refers to a general situation where there are at least two potential energy surfaces (PESs) with two dissociation limits and with some kind of coupling between them; the excited PES has a potential well that can hold bound or quasi-bound states, which, due to the coupling between the two PESs can 'jump' from the top surface to the lower one (Fig. 1.2). Since the lower surface has a lower dissociation limit, the (quasi-) bound state will then have enough energy to dissociate in this channel; whereas it did not have enough energy to dissociate in the upper PES.



Feshbach Resonance

Figure 1.2: Illustration of Feshbach and shape resonances. E = 0 is the dissociation limit for three free particles, while E < 0 dissociation limit represents one bound two-body state plus a free particle.

In order to correctly calculate Feshbach resonances, it is important to have an accurate representation of the couplings involved between the multiple channels or PESs (see, for example, section 4.1). In this thesis, we present calculations of vibrational states using one (chapter 3) or two (chapter 4) potential energy surfaces of the three-body system.

1.2 Experimental interest

Currently, there is strong experimental interest in three-body processes (in nuclear, atomic and molecular systems). For example, experimentalists are interested in accurately knowing the energies (positions) and lifetimes (widths) of three-body resonances for several reasons. We discuss them in this section.

1.2.1 Three-body recombination

Three-body recombination (Fig. 1.3) occurs when three free atoms collide to form a predissociated 'temporary' three-body state, which goes on to decay into a dimer and a free atom: $X + Y + Z \rightarrow XYZ$ (finite lifetime, τ) $\rightarrow XY + Z + E_{kinetic}$, for some atoms X, Y and Z. Therefore, three-body resonances play an important role in the process of three-body recombination. Three-body recombination is important in the primordial medium of star formation [FH07], and in Bose-Einstein condensates (BECs) [EG06]. In BECs, it causes the ultracold quantum gas to heat up by releasing extra kinetic energy, placing a fundamental limit on BEC lifetime [EG06]. Figure 1.3 illustrates this collisional process [EG06].

There are several mechanisms by which three-body recombination at ultracold temperatures occurs depending on the sign of the s-wave two-body scattering length a. In atomic BECs, *a* characterizes the net effect attributable to complex, short-range atomic interactions: a < 0 means an attractive collective interaction (e.g. unstable BEC), and a > 0 means a repulsive collective interaction (e.g. stable BEC) [BJL⁺02]. In the elastic scattering of slow particles, *a* is defined as

$$a \approx \frac{\delta_0}{k},$$
 (1.1)

where δ_0 and k are the s-wave scattering phase shift and wave vector, respectively [LL03]. The scattering length is an important quantity, as it determines the scattering cross section [Dav76].



Figure 1.3: Process of three-body recombination for three ultracold Cs atoms (figure taken from Ref. [EG06]). In the recombination process, the binding energy of the dimer is taken by the dimer and free atom as kinetic energy. R is the dissociation coordinate.

Figure 1.3 shows three-body adiabatic potentials as a function of molecule dissociation coordinate (say, hyper-radius R) of the three-body system, which is a measure of the size of the triangular configuration of a three-body system: a larger hyper-radius means a larger triangle (of whatever shape). Hence, as one moves along the hyper-radial coordinate, the triangular shape dissociates into either three free atoms or a free atom plus a dimer (section 2.1).

The red potentials in Fig. 1.3 are those of the three-body system before recombination takes place, while the black potentials are for the system after recombination. The blue line gives the energy of the three incident atoms. If a > 0, right frame of Fig. 1.3, we see the transition from the red potential to the black one at some hyper-radius $R \sim a$. There are two mechanisms for this transition. In the first mechanism, the system jumps from the red to the black potential when still decreasing in size to $R \sim a$ (blue pathway). The hyperradius decreases as the free atom rebounds off the dimer at which point R increases (still in the recombined state), eventually leading to dissociation. Note that the size of the triangle decreases before the system dissociates. In the second mechanism (yellow path), the three atoms initially rebound elastically (in the red potential) to then recombine (and enter the black potential) when they cross around $R \sim a$. The green arrow represents the outgoing channel where quantum-mechanical interference between these two paths may occur [EG06].

For a < 0 there is just one mechanism for the transition, which occurs at $R \ll |a|$. To recombine, the system must first quantum-mechanically tunnel into the small-R region of the red potential. The existence of resonances (as indicated by the red line) in this small-Rpotential well enhances the tunneling probability. The resonance positions change with the scattering length (red arrow). This tunes the system in and out of resonance, yielding a series of peaks in the recombination length, for instance [EG06]. The behavior of the recombination length as a function of a has been calculated [EG06], and also observed by Kraemer *et al.* in their experiments on Cesium recombination; see Ref. [KMW+06] for details.

In the recombination process, the binding energy of the dimer is approximately taken by

the dimer and free atom as kinetic energy (Fig. 5 of Ref. [Bla06]). This dimer and/or free atom may then cause additional collisions, escape of atoms from the trap, and heating of the trap. This process places a fundamental restriction on the lifetime of atomic BECs (see Ref. [SZM04] and references therein).

The three-body recombination of hydrogen $H + H + H \leftrightarrow H_2 + H$ is also an important problem. It is of great interest to the astrophysics community to have an accurate value for the three-body recombination rate coefficient of H+H+H, which cannot be measured experimentally. This reaction is believed to be a significant source of H_2 from free H atoms in the primordial medium of stars [FH07]. The abundance of H_2 in this medium is important, since, the rovibrational modes of H_2 (and also HD) are believed to provide the only significant means for cooling of the medium, which heats up due to gravitational contraction in the process of star formation [FH07]. With our approach, we were able to make an estimation of this rate coefficient (section 4.1.5). In principle, a more accurate calculation is possible by the inclusion of the R-matrix method into our approach (see chapter 6)

1.2.2 Atomic and Molecular systems

Molecular three-body systems of experimental interest include Li₃ [LPB⁺08], Rb₃ [SGC⁺07], Cs₃ [KMW⁺06], H₃ [FH07], and He₃ [ELG96]. Cs₃ provided the first experimental observation of Efimov states [KMW⁺06]. Any atomic species that can currently be used to create atomic BECs, or can be trapped in optical lattices, is of interest as three-body processes are of considerable importance in these systems [SZM04].

An interesting example, is the control of the two-body interaction of atoms in optical

lattices using an external electro-magnetic field. Isolated three-body states can form within each lattice site. These experiments contribute into the progress of the field of quantum computing. Understanding the relevant three-body processes contributes to this field.

Three-body methods can also be used to study chemical reactions (at thermal, cold and ultracold temperatures), as a chemical reaction is simply a collision of atoms and molecules. In fact, any chemical reaction in the gas phase can usually be viewed as a 'three-body problem.' As an example, we mention the following chemical reactions: $O + OH \rightarrow H + O_2$ at cold temperatures, $O + H_2 \rightarrow OH + H$, and $N + H_2 \rightarrow NH + H$ (all three of which play an important role in combustion and atmospheric chemistry, see Refs. [LG08], [QBK08], [ZXLG08] and references therein), and F + HCl at ultracold temperatures ([QB08]. Some of these chemical processes are also related to current efforts into the production of H_2 for alternative fuel technology. Other atmospheric three-body processes of interest, such as $O_2 + O$ scattering [BKW⁺03a], are important in the formation of the ozone [BKW⁺03b], $[BKW^+03c]$. The H_3^- system is also of interest as an intermediate species in the following reactions: $H_2(v) + H^- \rightarrow H_2(v') + H^-$ [MZL96], $D_2 + H^- \rightarrow HD + D^-$ [HSG97], [ZL92] and $H_2 + D^- \rightarrow HD + H^-$ [HSG97], [ZL92], which have implications to low temperature hydrogen plasmas [MZL96], and constitute prototype systems for detailed dynamical studies [HSG97], [ZL95], [PS04], [GS06], [MJ05], [YJCH06].

Three-body atomic systems, such as the ground state of the He atom, were amongst the first three-body quantum systems considered [BS57], [Gro37]. There are several interesting three-body atomic systems: H⁻ scattering [Lin95], e^--H^- [Ho83], e^--Be scattering, e^+-He^+ scattering [Ho97], e^+-H scattering, as well as several other systems involving positrons [Ho97].

1.2.3 Universality: Efimov states

Universality refers to properties, in systems with short range interactions, that do not depend on the details of the structure of particles or their interactions at short distances [BH06]. Universality has recently become a more prominent topic, especially due to interest in Efimov states. Efimov bound states and resonances represent an example of universality, where, at low energies and large two-body scattering length, there is universal behavior in the scaling of the energies and linewidths of Efimov states (see, for example, Eqs. 1.3, 1.6).

Efimov states were originally theorized to exist in three-body nuclear systems in the early 1970s by Vitali Efimov [Efi79], [Efi71]. In his 1971 paper [Efi71], Efimov theorized the existence of an infinite family of loosely-bound (large spatial extent) trimer states which formed even though the two-body attraction cannot hold a bound pair. This counterintuitive state is called an Efimov bound state. Experimentally proving the existence of Efimov states has been facilitated by the ability to tune the two-body interaction in ultracold quantum gases through Feshbach resonances, as was the case in 2006 when Kraemer and coworkers observed Efimov states in an ultracold gas of Cs atoms [KMW⁺06]. These experimental results confirm key predictions, and open up few-body quantum systems to further experiment [EG06].

Efimov states appear when the two-body scattering length a is much larger than the radius of the forces r_0 , or equivalently, if there exists a very shallow two-body bound or virtual state [Efi71]. Efimov studied a system of three particles that interact only within a vanishingly small range and derived a three-body potential-energy curve in terms of the three-body dissociation coordinate (hyper-radius ρ , section 2.1) [EG06], [Efi71]. The effective ρ -dependence of the interaction potential in this case turns out to be of the form s_i^2/ρ^2 . The constants s_i are roots of a transcendental equation and may be real and imaginary. There is one imaginary root, $|s_0| \sim 1$, such that the three-body potential has a universal, negative coefficient of proportionality and Efimov states appear [Efi71]. The properties of this potential are well-known since it resembles the potential of a charged particle in the field of a dipole:

$$\left(-\frac{d^2}{d\rho^2} - \frac{1}{\rho}\frac{d}{d\rho} + \frac{s_i^2}{\rho^2}\right)F_{s_i}(\rho) = EF_{s_i}(\rho)$$
(1.2)

Solving the time-independent Schroedinger equation for this system yields that the energy levels condense to zero exponentially,

$$E_n = E_{n-1} e^{-2\pi/|s_0|} \approx 1.94 \times 10^{-3} E_{n-1}, \qquad (1.3)$$

where $|s_0| = 1.006$ is related to the strength of the so-called effective dipole moment [NSE02], [EG06]. The most favorable conditions for the formation of Efimov states are for identical, spinless, neutral bosons with zero relative angular momentum l [Efi71].

Figure 1.4, taken from [KMW⁺06], shows the energy scaling of consecutive Efimov trimers, and their dependence on a. In this figure, we are looking at a plot of inverse scattering length a^{-1} versus the three-body energy for a region where $r_0 \ll a$. For a < 0 the gray region corresponds to the dissociation of the system to three free atoms, while for a > 0the gray area corresponds to the dimer + free atom dissociation. Considering a system with a virtual 2-body bound state just above the dissociation limit (e.g. a is large and negative),



Figure 1.4: Plot shows dependence of three-body energy on 2-body scattering length a (figure taken from Ref. [KMW⁺06]). Note energy of Efimov trimers is much less than energy of non-Efimov trimers. Infinite family of Efimov states exists only at 1/a = 0 (see text).

Fig. 1.4 predicts the first Efimov state to appear at $a_1 \sim -22r_0$ [Efi71]. As we increase |a|, we find the second Efimov state at $a_2 \sim 22a_1$, the third Efimov state at $a_3 \sim 22a_2$, and so on... The n + 1 state appears at [Efi71]

$$a_{n+1} \approx 22a_n. \tag{1.4}$$

For a given a > 0 there is a finite number of Efimov trimer levels N(a) given by [Efi71] (with logarithmic accuracy)

$$N(a) = \frac{|s_0|}{2\pi} \ln\left(\frac{a}{r_0}\right). \tag{1.5}$$

As $a \to \infty$, i.e. as the energy of the two-body bound or virtual state approaches zero, there is a "condensation" of three-body bound states and an infinite number of bound states, Efimov trimers (ETs), appear.

The ability to manipulate the interactions between atoms, i.e. to tune a, in ultracold quantum gases using Feshbach resonances has facilitated the possibility of observing Efimov physics.

The experimental evidence for the existence of Efimov bound states from Kraemer *et al.* [KMW⁺06], makes a study of Efimov resonances specially relevant. An Efimov resonance occurs when a pre-dissociated ET dissociates into a dimer and a free atom (e.g. at $a = a'_1$ in Fig. 1.4), or into three free atoms ($a = a_1$ in Fig. 1.4). This can occur when the three free atoms threshold or the dimer + free atom threshold meets the Efimov trimer, i.e. near those values of the scattering length given by Eq. 1.4, where ETs meet continuum states. In principle, at these respective junctures one may observe a dissociation of an ET into three free atoms or a dimer + free atom. In this case, the linewidths Γ of the Efimov resonances scale similar to the energies [NSE02]

$$\Gamma_n = \Gamma_{n-1} \mathrm{e}^{-2\pi/|s_0|}.\tag{1.6}$$

In this thesis, we calculate Efimov-type resonances for a model system (section 3.2).

1.2.4 Nuclear systems

While the emphasis of this thesis has been on three-body problems in atomic and molecular systems, our approach can, in principle, be applied to interesting three-body nuclear problems. Section 3.1 discusses our study of a model nuclear system.

Current three-body phenomena of interest in nuclear systems include three-body halo nuclei [NFJG01], [ZDF⁺93], and Efimov states (section 1.2.3). Efimov states were originally formulated as a phenomenon in nuclear systems [Efi71], and they still constitute an interesting problem in nuclear systems, e.g. ¹²C and ¹¹Li [GFJ06], [JFARG07].

Halo nuclei are a new type of nuclear structure found in extremely neutron rich light nuclei, e.g. ¹¹Li and ⁶He [VDE07], [ZDF⁺93]. Of special interest are the Borromean nuclei, where the nuclear structure, when considered as a three-body system, does not have any bound states in the two-body sub-systems, but has three-body bound states (similarly to Efimov states) [ZDF⁺93]. In principle, it is possible to adapt our approach to study such systems.

1.3 Existing theoretical approaches for three bodies

There are several methods available for calculating three-body bound states and resonances, some of which are discussed in this chapter, so why are we working in this area? Simply, each method has its advantages and limitations, and in this thesis we believe we show some of the advantages of our approach in studying interesting three-body processes. Additionally, in principle, our proposed approach is general enough to be applicable to the study of several important three-body processes (chapter 6).

While there are many different three-body methods currently used, there are several prominent methods (time-dependent and -independent) worth briefly mentioning. These include the Faddeev equations, the hyperspherical adiabatic approximation (section 2.2.1), the 'slow' variable discretization (section 2.2.2), Jacobi coordinates (section 2.1), hyperspherical coordinates (section 2.1), complex scaling, complex absorbing potential (section 2.2.6), the R-matrix [AGLK96], and time-dependent wave packets [KK86]. Each method has its pros
and cons. The purpose of this section is to briefly introduce some of those important methods not discussed later in the thesis. It will provide a frame against which we can compare our theoretical approach.

We begin with the Faddeev equations method. The Faddeev equations are a set of integro-differential equations used to solve the three-body Schroedinger equation [Fad61], which were originally intended to be solved in momentum space, but have been generalized to coordinate space as well as to *n*-body systems [NFJG01]. If the Schroedinger equation can be written as

$$H(\mathcal{Q})\Psi = [H_0(\mathcal{Q}) + V_{n-body}(\mathcal{Q})]\Psi = z\Psi$$
(1.7)

where H_0 gives the kinetic energy of the system for some convenient set of coordinates Q, and the potential energy can be written as a sum of pairwise pieces

$$V_{n-body} = V_1 + V_2 + V_3 + \dots + V_n, \ n \in [2, \infty),$$
(1.8)

and if z is not an eigenvalue of H_0 , then $H_0 - z$ is invertible and the eigenstate Ψ can be written as a sum

$$\Psi = \sum_{i=1}^{n} \psi_i,\tag{1.9}$$

where ψ_i are

$$\psi_i = \frac{-1}{H_0 - z} V_i \sum_{j=1}^n \psi_j.$$
(1.10)

It is then possible to derive the differential Faddeev equations,

$$(H_0 + V_i - z)\psi_i = -V_i \sum_{j \neq i}^n \psi_j.$$
 (1.11)

Inverting Eq. 1.11 (e.g. z not eigenvalue of $H_0 + V_i$), produces the Faddeev integral equations [Mot08],

$$\psi_i = \frac{-1}{H_0 + V_i - z} V_i \sum_{j \neq i}^n \psi_j.$$
(1.12)

In order to calculate resonance positions and widths, the complex scaling method is often employed [Ho83]. The complex scaling method is based on the mathematical work of Aguilar and Balslev in the early 1970s [AC71], [BC71]. This method consists of rotating the dissociation coordinate R (e.g. hyper-radius: see section 2.1) into the complex plane $R \rightarrow$ $Re^{i\beta}$ [FGJ03], or equivalently, rotating the interparticle distances into the complex plane [Ho83]. This transforms the spectrum of the three-body Hamiltonian such that resonant states have eigenvalues of the form

$$E = E_{res} - i\frac{\Gamma}{2},\tag{1.13}$$

where E_{res} gives the resonance position while $\Gamma/2$ is the halfwidth of the resonance.

Another widely-used method is the time-dependent propagation of wave packets. The idea is to solve the time-dependent Schroedinger equation, and obtain the time evolution of the wave packet in space and time to extract the required observables from the timedependent wave packet.

Another method worth mentioning is the adiabatically adjusting principal axes hyperspherical coordinates (APH) approach [PP87]. This method allows accurate representation of wave functions which are strongly localized in classically allowed regions of configuration space. This is done by expanding the wave function in potential-adapted basis functions (instead of hyperspherical harmonics) that have large amplitudes only in the energetically allowed regions. This, in turn, greatly reduces the number of coupled differential equations that must be solved [Wil05].

Finally, there is the hyperpherical diabatic-by-sector method, where the scattering matrix and state-to-state differential cross sections are obtained by solving the time-dependent three-body vibrational Schroedinger equation [Wil05], [LL89], [LL91]. After solving the hyperangular part of the Hamiltonian and obtaining adiabatic eigen-energies and eigen-states, the hyper-radial axis is divided into sectors and the total wave function is expanded in the potential-adapted angular basis for each sector (similar to APH). This produces a set of coupled differential equations in hyper-radius, which are used to propagate a logarithmic derivative matrix along hyper-radius. Reactance matrix (and, therefore, scattering matrix and cross sections) is obtained when the logarithmic derivative matrix is analyzed in terms of asymptotic solutions on the hyper-sphere where the propagation is stopped [Wil05].

1.4 Obstacles in three-body calculations

The quantum three-body problem has been considered as 'difficult' ever since it was first studied nearly 80 years ago [BS57], and is still considered as 'unsolved' [NFJG01]. Even the classical three-body problem of the Earth-Moon-Sun system, as of relatively recently, has unanswered questions [Gut98], [HM96], [LR95]. One of the main obstacles in three-body calculations is that there is no exact way of solving the three-body Schroedinger equation. This is complicated by the fact that sometimes the three-body term in the potential may not be known or may not be exact (analytically or numerically), and must therefore be approximated. When calculating three-body resonances, it is crucial to have an accurate representation of the relevant potential energy surfaces and couplings. An additional complication arises if one considers loosely bound three-body states, which extend to large distances and require very large grids to calculate. Here, we propose a way to treat such states (chapter 2).

Even though powerful computational methods have been developed, and powerful supercomputers are available to solve the three-body Schroedinger equation, the computational load can still be overwhelming. For example, to study Li₃ it is necessary to include hundreds of adiabatic states that are closely coupled (similar to Fig. 4.5), which available supercomputers cannot handle in a reasonable amount of time. This is just considering the vibrational dynamics for zero total three-body angular momentum; if one were to include all other relevant degrees of freedom the computation time necessary could be several times longer. The computational problems become greater as one considers systems with heavier atoms, like Cs or Rb for instance, which are of great interest to experimentalists. Such systems are more complicated and the calculations have to be more involved in order to obtain accurate results.

When solving a given three-body scattering problem, it seems that it is inevitable to come up against some approximations, such as the Born-Oppenheimer adiabatic approximation, which causes the method to only be applicable under limited conditions.

OUR APPROACH

This chapter lays out our overall approach to calculate three-body bound states and resonances. The challenge is to solve the full three-body Hamiltonian. The backbone of our approach is a combination of hyperspherical coordinates, the 'slow' variable discretization method, and the complex absorbing potential. This chapter also introduces necessary background information.

2.1 Hyperspherical coordinates in present method

The use of hyperspherical coordinates to treat few-body problems has become widespread. They were first introduced into atomic physics in 1937 [Gro37]. One important aspect of hyperspherical coordinates is that they can be applied to any three-body system irrespective of the masses of the particles [Lin95]. So, they have been applied to study such diverse three-body systems as, for example, two-electron atoms, atom-diatom scattering, trinucleon bound states, and nonrelativistic model of baryons [Lin95].

Six hyperspherical coordinates are required to describe the physical configuration of a three-body system. Five of these coordinates are 'angular' (i.e. they have a finite range): two of these 'internal' coordinates give the shape of the triangle formed by the three bodies ('hyperangles' θ , φ), while the other three are Euler angles (α , β , γ) that specify the spatial orientation of the plane formed by the three bodies ('external' coordinates). Ranges for

Euler angles are

$$0 \le \alpha \le 2\pi,$$
$$0 \le \beta \le \pi,$$
$$0 \le \gamma \le 2\pi.$$

It is the angular motion of this plane with respect to the laboratory frame of reference that gives the three-body system angular momentum. For simplicity, we only consider systems with zero total three-body angular momentum and, therefore, we will not need to specify Euler angles. In principle, we could include nonzero three-body angular momentum into our calculations without any major difficulties, as will be discussed later in the thesis.

The sixth coordinate, called the hyper-radius, is a measure of the size of the triangle, making it the dissociation coordinate for the three-body system: the three-body system dissociates as the hyper-radius becomes very large.

There are several ways to define hyperspherical coordinates (see for example, [BG00], [ELG96], [LL89], [Joh80]). In this work, we used the modified version of the Smith-Whitten coordinates defined in Ref. [Joh80]. Smith-Whitten hyperspherical coordinates begin with mass-weighed Jacobi coordinates, which are constructed as follows. Let $\vec{x}^{(i)}$ be the position of the i^{th} atom, M and μ be the total and reduced mass,

$$M = m_1 + m_2 + m_3,$$
$$\mu = \sqrt{\frac{m_1 m_2 m_3}{M}},$$

and let us define a mass-weighed factor

$$d_i = \sqrt{\frac{m_i}{\mu} \left(1 - \frac{m_i}{M}\right)};\tag{2.1}$$

then we can define two sets of vectors ($\vec{r}^{(k)}$ and $\vec{R}^{(k)}$ in Fig. 2.1), each of which specifies the configuration of the three-body system,

$$\vec{r}^{(k)} = \frac{1}{d_k} (\vec{x}^{(j)} - \vec{x}^{(i)}), \qquad (2.2)$$

$$\vec{R}^{(k)} = d_k \left[\vec{x}^{(k)} - \frac{m_j \vec{x}^{(j)} + m_i \vec{x}^{(i)}}{m_j + m_i} \right], \qquad (2.3)$$

where i, j and k are different. As seen in Fig. 2.1, for a given three-body configuration, anyone of these sets of $(\vec{r}^{(k)}, \vec{R}^{(k)})$ vectors can be used. However, for some configurations one set of vectors may be more convenient to use than the others. These vectors define the hyper-radius ρ of the system,

$$\rho^2 = \left| \vec{r}^{(k)} \right|^2 + \left| \vec{R}^{(k)} \right|^2, \tag{2.4}$$

such that ρ increases as the particles get further and further apart (i.e. as $\vec{r}^{(k)}$ or $\vec{R}^{(k)}$ increases). Thus, as ρ increases the three-body system dissociates. ρ^2 is proportional to the larger of the three principal moments of inertia of the system. Notice that ρ is not proportional to the area of the triangle formed by the three-body configuration, as ρ must be nonzero for collinear configurations, where the area of the triangle is zero. Finally, ρ is always positive and invariant under rotations of the system, and also independent of index k [Joh83].

Smith-Whitten hyperspherical coordinates define the 'shape of the triangle' by two hyperangles ($\tilde{\theta}$ and $\tilde{\varphi}^k$) in the following way. If we break $\vec{r}^{(k)}$ and $\vec{R}^{(k)}$ into x and y Cartesian components of the principal axes of inertia coordinate system, then we can define the hy-



Figure 2.1: Three sets of mass-weighed Jacobi coordinates $(\vec{r}_0^{(k)}, \vec{R}_0^{(k)}), k = 1, 2, 3$, sketched assuming $m_1 > m_2 > m_3$. For three identical particles, all sets are equivalent due to particle indistinguishability.

perangles in terms of these components

$$\vec{r}_x^{(k)} = \rho \cos \tilde{\theta} \cos \tilde{\varphi}^k,$$

$$\vec{r}_y^{(k)} = -\rho \sin \tilde{\theta} \sin \tilde{\varphi}^k,$$

$$\vec{R}_x^{(k)} = \rho \cos \tilde{\theta} \sin \tilde{\varphi}^k,$$

$$\vec{R}_y^{(k)} = \rho \sin \tilde{\theta} \cos \tilde{\varphi}^k.$$
(2.5)

The range of $\tilde{\varphi}^k$ is defined by Eq. 2.5 as

$$0 \le \tilde{\phi}^k \le 2\pi$$

The range of $\tilde{\theta}$ is determined by equations

$$\sin 2\tilde{\theta} = \frac{4A}{\rho}$$
$$\cos 2\tilde{\theta} = \frac{Q}{\rho^2},$$
(2.6)

where A is the area of the triangle formed by the three-body configuration, and Q is related to the moments of inertia along the principal axes coordinate system (see Refs. [Joh80] and [Smi62] for a detailed description):

$$Q = (\vec{r}_x^{(k)})^2 + (\vec{R}_x^{(k)})^2 - (\vec{r}_y^{(k)})^2 - (\vec{R}_y^{(k)})^2 \ge 0.$$
(2.7)

The range of $\tilde{\theta}$ is then restricted to

$$0 \le \theta \le \pi/4.$$

In order to overcome serious disadvantages mapping potential energy surfaces into threedimensional configuration space [Kup75], these Smith-Whitten hyperspherical coordinates are modified. Ref. [Joh80] makes the substitutions

$$\theta = \pi/2 - 2\hat{\theta},$$

$$\varphi^k = 2\pi - 2\tilde{\phi}^k,$$
(2.8)

such that,

$$0 \le \theta \le \pi/2,$$

$$0 \le \varphi^k < 4\pi.$$
 (2.9)

For convenience the ranges of the branches are defined as $0 \leq \varphi_a^k \leq 2\pi$ and $2\pi \leq \varphi_b^k < 4\pi$, with $\varphi_b^k = \varphi_a^k + 2\pi$. Each physical arrangement of the particles corresponds to two hyperspherical points, $(\rho, \theta, \varphi_a^k)$ and $(\rho, \theta, \varphi_b^k)$, that map to the same point in configuration space [Joh80]. To specify a given physical arrangement, we only need one point in configuration space (ρ, θ, φ) , dropping the k label as it is arbitrarily chosen without loss of generality and with $0 \leq \varphi \leq 2\pi$



Figure 2.2: Physical arrangement of particles mapped into configuration space by hyperspherical coordinates ρ , θ and φ ; these coordinates define particle configuration size (ρ) and shape (θ , φ). Although it is difficult to tell from the figure, the two-dimensional space of hyperangles displays C_{3v} symmetry (section 2.2.4) for a system of identical particles. Particles are labeled by numbers 1, 2, and 3 for future reference.

We can now write the distance between particles:

$$|\bar{r}^{(1)}| = \frac{d_1\rho}{\sqrt{2}}\sqrt{1 + \sin\theta\sin\varphi},$$

$$|\bar{r}^{(2)}| = \frac{d_2\rho}{\sqrt{2}}\sqrt{1 + \sin\theta\sin(\varphi - \epsilon_2)},$$

$$|\bar{r}^{(3)}| = \frac{d_3\rho}{\sqrt{2}}\sqrt{1 + \sin\theta\sin(\varphi + \epsilon_3)},$$

(2.10)

where

$$\epsilon_2 = 2 \arctan\left(\frac{m_3}{\mu}\right),$$

$$\epsilon_3 = 2 \arctan\left(\frac{m_2}{\mu}\right)$$
(2.11)

with $0 \leq \epsilon_i \leq \pi$.

Our particle configurations can now be mapped to configuration space, as shown in Fig. 2.2, where the ranges of ρ , θ and φ are

$$0 \le \rho < \infty,$$

$$0 \le \theta \le \pi/2,$$

$$0 \le \varphi \le 2\pi.$$
(2.12)

2.2 Quantum formalism

In this section, we discuss the quantum mechanics in our theoretical approach. It consists of the Born-Oppenheimer-like hyperspherical adiabatic separation of hyper-radius and hyperangles, the 'slow-variable discretization,' and the complex absorbing potential (CAP). Combined with Smith-Whitten hyperspherical coordinates, this forms the backbone of our theoretical method. In order to study three-body recombination, we remove the CAP from our calculations and instead use the R-matrix. The R-matrix is also discussed at the end of the section.

2.2.1 The adiabatic hyperspherical approximation

The hyperspherical adiabatic approach treats the hyperradius as the adiabatic parameter. It consists of (1) formulating the three-body problem in hyperspherical coordinates as defined in the previous section and (2) obtaining the vibrational eigenenergies and eigenfunctions in a two-step procedure. It is analogous to the Born-Oppenheimer approximation in diatomic molecules. It involves solving the three-body Schroedinger equation

$$(K(\rho,\theta,\varphi) + V(\rho,\theta,\varphi))\Phi_n(\rho,\theta,\varphi) = E_n^{vib}\Phi_n(\rho,\theta,\varphi)$$
(2.13)

by fixing hyper-radius at ρ_i and diagonalizing the adiabatic Hamiltonian in a two-dimensional space of hyperangles

$$H^{ad}_{\rho_i}\phi_a(\rho_i,\theta,\varphi) = U_a(\rho_i)\phi_a(\rho_i,\theta,\varphi), \qquad (2.14)$$

where a labels eigenenergies and eigenfunctions of H^{ad} at fixed ρ_i . Each adiabatic eigenenergy U_a and eigenstate ϕ_a will obey certain symmetry transformations according to the symmetries of the three-body system, as will be explained in section 2.2.4. Eigenstates ϕ_a are plotted in the two-dimensional hyperangular space and depend parametrically on hyper-radius, and we refer to them as 'hyperangular adiabatic wave functions.' For a fixed hyper-radius ρ_i , the hyperangular wave functions are orthonormal,

$$\langle \phi_a(\rho_i; \theta, \varphi) | \phi_{a'}(\rho_i; \theta, \varphi) \rangle = \delta_{a,a'} \tag{2.15}$$

However, hyperangular wave functions are not orthonormal for different hyper-radii (see section 2.2.2, Eq. 2.28)

$$\langle \phi_a(\rho_i; \theta, \varphi) | \phi_a(\rho_j; \theta, \varphi) \rangle \neq \delta_{i,j}.$$
 (2.16)

The adiabatic Hamiltonian in the above equation is

$$H_{\rho_i}^{ad} = \frac{\Lambda_0^2 + \frac{15}{4}}{2\mu {\rho_i}^2} + V_{3body}(\rho_i; \theta, \varphi), \qquad (2.17)$$

where

$$\Lambda_0^2 = -4 \left[\frac{1}{\sin(2\theta)} \frac{\partial}{\partial \theta} \sin(2\theta) \frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2} \right], \qquad (2.18)$$

is the square of the grand angular momentum operator associated with the hyperspherical coordinates. Here and everywhere below, we assume that the total angular momentum of the system is 0.

This procedure is repeated for many hyper-radii defining a set of adiabatic channels that depend on ρ : $U_a(\rho)$. We obtain the hyper-radial wave functions and the vibrational eigenenergies by solving a set of multi-channel hyper-radial coupled Schroedinger equations with the adiabatic energies taking the place of one-dimensional three-body potentials,

$$[K(\rho) + U_a(\rho)]\psi_{a,n}(\rho) + \sum_{a'} [W_{a,a'}\psi_{a',n}(\rho)] = E_n^{vib}\psi_{a,n}(\rho), \qquad (2.19)$$

where $K = \frac{-1}{2\mu} \frac{d^2}{d\rho^2}$ is the kinetic energy operator, *n* labels the three-body vibrational level of the trimer, $\psi_{a,n}(\rho)$ is the *a*th component of the hyper-radial wave function $\Psi_n(\rho)$, and

$$W_{a,a'} = \frac{-1}{2\mu} \langle \phi_a(\rho,\theta,\varphi) | \frac{d^2}{d\rho^2} | \phi_{a'}(\rho,\theta,\varphi) \rangle + \frac{1}{\mu} \langle \phi_a(\rho,\theta,\varphi) | \frac{d}{d\rho} | \phi_{a'}(\rho,\theta,\varphi) \rangle \frac{d}{d\rho}, \qquad (2.20)$$

represents the non-adiabatic coupling elements. Solving Eq. 2.19 numerically would yield a numerically exact solution for the original Schroedinger equation, Eq. 2.13, assuming all *a*-channels are taken into account. However, if the non-adiabatic couplings have a spiky dependence on ρ then a numerical solution becomes very difficult. Therefore, in many applications these coupling terms are ignored. This is called the adiabatic approximation. The procedure relies on separating the total wave function into a product of hyperangular and a hyper-radial components for each channel a, and it makes the following approximation for the total three-body vibrational wave functions and eigenenergies:

$$\Phi_n(\rho,\theta,\varphi) \approx \Phi_{a,v}(\rho,\theta,\varphi) = \psi_{a,v}(\rho)\phi_a(\rho,\theta,\varphi)$$
(2.21)

i.e. only the main component of $\Psi_n(\rho)$ is considered as a hyper-radial part of the eigenfunction in the adiabatic approximation, and

$$E_n^{vib} \approx \epsilon_{a,v}.\tag{2.22}$$

where $\epsilon_{a,v}$ is the vibrational energy obtained if we ignore the coupling elements in Eq. 2.19, i.e when we solve Eq. 2.24. For numerical calculations, we expand $\psi_{a,v}$ in a basis set $\pi_j(\rho)$:

$$\psi_{a,v}(\rho) = \sum_{j=1}^{N} c_{j,a,v} \pi_j(\rho).$$
(2.23)

The computer code which calculates the three-body resonances uses B-spline basis [PBP02], [Esr97] and the discrete variable representation (DVR) basis set [Wil92], [WZ96], [KDKMS99], [MBK89]. These are commonly used basis functions, for example, like sines or Legendre polynomials. The numerical method through which the DVR basis is applied, mapped DVR basis, is discussed later in this chapter in section 2.3.1. Since this method does not account for non-adiabatic couplings between the different channels, say, a and a', then we are essentially solving the following eigenvalue problem:

$$[K(\rho) + U_a(\rho)]\psi_{a,v}(\rho) = \epsilon_{a,v}\psi_{a,v}(\rho).$$
(2.24)

In order to account for non-adiabatic couplings between different channels, we use the slow variable discretization method of Tolstikhin *et al.* [TWM96], which is described in the next section.

2.2.2 'Slow' variable discretization

This section gives an overview of the 'slow' variable discretization (SVD) method developed by Tolstikhin, Watanabe, and Matsuzawa in 1996 (Ref. [TWM96]). Therefore, this section will, in most part, be a review of Ref. [TWM96]. The method is an integral part of our approach.

In this section we will abbreviate slow variable discretization by SVD (not to be confused with 'single value decomposition', an unrelated mathematical procedure). Solving Eq. 2.19 would solve the three-body problem exactly. SVD offers an opportunity to keep the hyper-radius as the dissociation coordinate and to obtain essentially exact vibrational eigenfunctions, $\Phi_n(\rho, \theta, \varphi)$ [KMS06]. The SVD method bases the adiabatic separation of hyper-radius and hyperangles on the *smoothness* (as opposed to *slowness*) of $H^{ad}_{\rho_i}$ with respect to ρ [TWM96]. The SVD method applied here is slightly modified from Ref. [TWM96] in order to be able to apply the DVR basis.

We begin, just like in the adiabatic approach, by solving for the adiabatic eigenenergies $U_a(\rho)$ and eigenfunctions at $\phi_a(\rho_i, \theta, \varphi)$ a fixed hyper-radius ρ_i . However, instead of approximating the vibrational eigenfunction $\Phi_n(\rho, \theta, \varphi)$ by Eq. 2.21, we now expand in the basis with hyper-radial eigenfunctions as the expansion coefficients

$$\Phi_n(\rho_i, \theta, \phi) = \sum_{a,i} \psi_{a,n}(\rho_i) \phi_a(\rho_i; \theta, \varphi), \qquad (2.25)$$

The sum is over the adiabatic channels. Next, the hyper-radial eigenfunctions are expanded in a localized basis (e.g. DVR, B-splines, Legendre polynomials...) as in Eq. 2.23

$$\psi_a(\rho) = \sum_j c_{j,a} \pi_j(\rho), \qquad (2.26)$$

where index n is now implicit and omitted for simplicity. Using Eqs. 2.25 and 2.26, the following one-channel hyper-radial Schroedinger equation is obtained [TWM96]

$$\sum_{i',a'} \left[\langle \pi_i | K(\rho) | \pi_{i'} \rangle \mathcal{O}_{ia,i'a'} + \langle \pi_i | U_a(\rho) | \pi_{i'} \rangle \delta_{aa'} \right] c_{i'a'} = E \sum_{i',a'} \langle \pi_i | \pi_{i'} \rangle \mathcal{O}_{ia,i'a'} c_{i'a'} , \qquad (2.27)$$

where

$$\mathcal{O}_{ia,i'a'} = \langle \phi_a(\rho_i;\theta,\varphi) | \phi_{a'}(\rho_{i'};\theta,\varphi) \rangle, \qquad (2.28)$$

represent overlapping matrix elements between hyperangular adiabatic states at different hyper-radii. When we use the DVR basis representation, Eq. 2.27 becomes

$$\sum_{i',a'} [\langle \pi_{i'} | K(\rho) | \pi_i \rangle \mathcal{O}_{i'a',ia} + U_a(\rho_i) \delta_{i',i} \delta_{a',a}] c_{i',a'} = E \sum_{a'} \mathcal{O}_{i'a',ia} c_{i,a'}$$
(2.29)

Usually, the $\langle \pi_{i'}|K(\rho)|\pi_i\rangle$ term can be evaluated analytically [KMS06]. Equation 2.29 has the form of a generalized eigenvalue problem, which can be solved through commonly known methods. If we take M to be the number of adiabatic channels taken into account, and Nto be the number of basis functions (Eq. 2.26) then H and \mathcal{O} are $NM \ge NM$ matrices. In the SVD method, then, the non-adiabatic coupling terms $W_{a,a'}$ in Eq. 2.19 are replaced by the overlapping matrix elements $\mathcal{O}_{i'a',ia}$. Therefore, there is no need to calculate first and second derivatives of $\phi_a(\rho_i; \theta, \varphi)$ (see Eq. 2.20), nor is it necessary, if one wanted to use a minimal number hyper-radial grid points, to have a priori knowledge of the location of avoided crossings (where non-adiabatic couplings are especially strong). Consequently, it becomes easier to implement a computer solution to the Schroedinger equation [KMS06].

2.2.3 Hyper-radial wave functions

In the SVD approach, the hyper-radius is the dissociation coordinate. In this sense, hyperradial 'motion' means the separation of the particles at large ρ . The hyper-radial wave functions for a given vibrational state contain information about the dynamics of that state at the dissociation limit, and at short and intermediate inter-particle distances.

As explained in section 2.2.1, hyper-radial and hyperangular wavefunctions arise from the separation of the hyper-radial (ρ) and hyperangular 'motions' (θ, φ) in solving the threebody Hamiltonian. In SVD, the hyperangular wave functions form the basis set for the total vibrational wave function with hyper-radial wave functions as expansion coefficients (see Eq. 2.25). Thus, for a given vibrational state n the sum of the probabilities should equal unity,

$$\sum_{a} \int |\psi_{a,n}(\rho)|^2 d\rho = 1.$$
 (2.30)

Hyper-radial wave functions $\psi_{a,n}$ are obtained in the second step of the SVD, by solving a set of coupled Schroedinger equations (see Eq. 2.27). The couplings mean that the threebody system can jump from one adiabatic state to another. Each adiabatic state component $\psi_{a,n}$ has a real and imaginary part due to the addition of a CAP to the adiabatic potentials (see section 2.2.6). Figure 2.3 shows an example of channel by channel component hyperradial wave functions for a calculation employing two adiabatic channels. The contribution of a given adiabatic channel to the total three-body vibrational wave function is determined by the modulus squared of the real and imaginary parts. The most probable dissociation channel, i.e. the $X_2(v, j_r) + X(nl)$ channel or X(nl) + X(nl) + X(nl) channel, where n and l are atomic principal and angular momentum quantum numbers, respectively, and v and



Figure 2.3: Example of hyper-radial wave functions $(\Psi_1(\rho) \text{ and } \Psi_2(\rho))$ of three-body system with two adiabatic states $(U_1(\rho) \text{ and } U_2(\rho))$.

 j_r are two-body vibrational and rotational quantum numbers, respectively, is determined by the modulus squared of the wave function components $|\psi_{a,n}|^2$ and by the hyper-radial velocity. Knowing the relevant dissociation channels for a given vibrational state is also important in determining the optimal CAP strength (see section 2.2.6) and, therefore, in obtaining a more accurate energy and width for that vibrational state. Knowing the extent of the hyper-radial wave functions also helps determine the placement of CAP.

As will be shown, hyper-radial wave functions also help distinguish bound, quasi-bound, and continuum states. This is because the wave functions show at which hyper-radial distance(s) the three-body state is most likely to be: Short distances imply bound states, long distances imply continuum states, and a combination of both implies quasi-bound states.

In the calculation of Efimov states (states with very large spatial extent, see section 1.2.3), the hyper-radial wave functions are especially important in helping determine the size of the hyper-radial grid and distinguishing Efimov resonances from normal ones.

Finally, hyper-radial wave functions can also be important in confirming the convergence of the energies and widths of three-body states. For example, for a fixed grid size, the hyperradial wave function of a converged resonant state should not change very much with changes in, say, the number of adiabatic states included in the calculation, or in the placement of CAP. When the grid size is increased the hyper-radial wave function is renormalized, however, this is a computational problem and does not reflect on the physics of the system.

2.2.4 Hyperangular wave functions: symmetries of adiabatic Hamiltonian and group theory for three bodies

The hyperangular wave functions complement information about the dynamics of the threebody vibrational state given by the hyper-radial wave function: they give information about the vibrational modes of the three-body system. They are obtained by solving Eq. 2.17. For a fixed hyper-radius, they are plotted in the two-dimensional configuration space of the three-body physical arrangement (see Fig. 2.2).

Hyperangular wave functions are especially important in determining the convergence of the adiabatic energies. A smooth wave function with the correct symmetries is a good sign of convergence of adiabatic energies. This is crucial since the energies and widths of three-body vibrational states depend directly on the accuracy of the adiabatic energies. In this section, we will discuss hyperangular wave functions in more detail. We begin with the symmetries of the adiabatic states.

The quantum mechanical applications of group theory are based on the fact that the Schroedinger equation for the physical system is invariant with respect to symmetry transformations of the system [LL03]. In this thesis, we focus on systems of three identical particles with zero total three-body angular momentum J = 0. Relative motion of three identical structureless particles is characterized by the C_{3v} point group, which includes $2\pi/3$ rotations and vertical plane reflections. Since hyper-radius doesn't affect the shape of the three-body configuration, then in the space of hyperangles certain symmetries exist [KG03]. In the SVD approach, the adiabatic Schroedinger equation (2.14) contains these C_{3v} symmetries. Consequently, hyperangular wave functions will also posses C_{3v} symmetries. Considering these symmetries greatly simplifies the study of three-body systems.

Each eigenstate of the adiabatic Hamiltonian (Eq. 2.17) transforms according to one of the irreducible representations of the C_{3v} or D_{3h} symmetry groups. Thus, hyperangular wave functions are characterized by one of the irreducible representations of the corresponding symmetry group (C_{3v} or D_{3h}). C_{3v} has three irreducible representations labelled as E, A_1 , and A_2 , where E is doubly degenerate. We use E_a and E_b states as a basis in the E space. A_1 and A_2 are one-dimensional representations [LL03]. Each irreducible representation obeys certain symmetry properties. We expound on this below, by reviewing some group theory for three identical bodies.

Systems of three identical particles are described by the S_3 group of permutations, which leaves the Schroedinger equation invariant. S_3 is isomorphous to the C_{3v} group, which means



Figure 2.4: Visual depiction of C_{3v} point symmetry group [LL03]. There is only one axis of symmetry of the third order, with three intersecting vertical planes.

there is a one-to-one correspondence between the elements of each group [Gal02]. Isomorphic groups have identical properties in the abstract sense, so instead of studying a complicated group directly, it may be more convenient to consider a simpler isomorphic group to it.

 C_{3v} is a point group, meaning that at least one point of the system must remain fixed when any transformations are applied. This means all axes and planes of symmetry must have at least one common point, as shown in Fig. 2.4 [LL03]. The C_{3v} group has a single axis of symmetry (see Fig. 2.4).

 $2\pi/3$ rotations about this axis leaves the system unchanged. There are three planes of symmetry which pass through this axis, intersecting along the axis at angles of $\pi/3$ [LL03]. The system then remains unchanged after reflections σ_v through the vertical planes. In total, C_{3v} has 6 elements (i.e. its order g = 6), including the identity element.

Let us now discuss the irreducible representations of C_{3v} . Consider the function Υ_1 which

is a single-valued function of the coordinates in the configuration space of the physical system [LL03]. In our approach, for example, this configuration space would be the two-dimensional space of hyperangles. Then, upon an operation of one of the elements of the symmetry group \hat{G} , the function Υ_1 is transformed into some other function. This is true for each element of the group, so that from Υ_1 we obtain g different functions, and f of these will be linearly independent ($f \leq g$). Thus, each element \hat{G} of a symmetry group can be considered to be a matrix which acts like an operator on a set of linearly independent functions Υ_k like

$$\hat{G}\Upsilon_k = \sum_{i=1}^f G_{ik}\Upsilon_i, \qquad (2.31)$$

where Υ_k can always be chosen as to be orthonormal, and k = 1, 2, 3, ... f. A representation of a group is the set of matrices of all elements \hat{G} in a group and Υ_k are called the basis of that representation [LL03]. Integer f is called the *dimension* of the representation. Expansion coefficients G_{ik} are elements of the matrix operator \hat{G}

$$G_{ik} = \int \Upsilon_i^* \hat{G} \Upsilon_k dQ,$$

where integrand dQ is over configuration space.

If we make some linear transformation \hat{S} of the base functions

$$\Upsilon'_k = \hat{S}\Upsilon_k,\tag{2.32}$$

producing a new set of orthonormal functions Υ'_k , then the matrix of the operator \hat{G} in the new primed representation is the matrix of the operator

$$\hat{G}' = \hat{S}^{-1} \hat{G} \hat{S}$$

in the old unprimed representation [LL03].

If \hat{S} in Eq. 2.32 is a suitable transformation such that the base functions divide into sets of $f_1, f_2, ...(f_1 + f_2 + ... = f)$ functions so that, when any element of the group acts on them, the functions in each set are transformed only into combinations of themselves, then the representation in question is called *reducible* [LL03].

A representation is called *irreducible* if the number of base functions that are transformed only into combinations of themselves cannot be reduced by any linear transformation of them. Irreducible representations play an important role in quantum mechanical applications of group theory [LL03].

Any reducible representation can be decomposed into irreducible ones. There are three irreducible representations of the C_{3v} group: E, A_1 and A_2 . They are determined in the following way. Firstly, there are several ways to check that the representation you have is in fact irreducible. For example, if the number of irreducible representations is equal to the number of classes in a group [Gal02]. A class is defined by a group element that is conjugate to all other elements in the group. Figure 2.5 shows the classes of C_{3v} : all reflections σ_v belong to one class, cyclic rotations make up a second class, while the identity operation makes up the third and final class - hence three irreducible representations for C_{3v} . The *character* (or trace) of a group element \hat{G} also enables us to determine whether a representation is reducible or not. This is because the sum of the moduli squared of the characters ($\chi_{irrep}(G)$) of an irreducible representation equals the order of the representation,

$$\sum_{G} |\chi_{irrep}(G)|^2 = g; \qquad (2.33)$$

This sum is greater than g if the representation is reducible. The character of the identity element also equals the dimension of the representation [LL03]. Additionally, the dimensions

of the irreducible representations of a group divide its order [LL03]. Characters for the C_{3v} symmetry group are shown in Fig. 2.5.

C_{3v}		$2C_3$	3σ _v
$A_{l};z$	1	1	1
A_2	1	1	-1
<i>E; x, y</i>	2	-1	0

Figure 2.5: Table of characters of irreducible representations of C_{3v} [LL03]. The letters x, y, and z label the representations by which the coordinates themselves are transformed.

Now then, fixing the irreducible representation determines the behavior of the given state with respect to the various symmetry transformations. The trivial irreducible representation of any group is the one given by a single base function that satisfies all symmetry operations of the group, in the case of C_{3v} it is the A_1 representation. When one makes a reflection about one of the vertical planes (σ_v operation), or apply any number of $2\pi/3$ rotations about the principal axis, z in Fig. 2.4, the A_1 irreducible representation leaves the system unaltered. Next, we consider another base function that is also invariant with respect to rotations, but is antisymmetric with respect to σ_v reflections. This is the A_2 representation. The Arepresentations are one-dimensional, i.e. f = 1, since they are also base functions of the cyclic C_3 group, which is Abelian and therefore only has one-dimensional representations.

Finally, we consider functions multiplied by $e^{2\pi i/3}$ and $e^{4\pi i/3}$ which change into each other upon reflection. These are the *E* symmetry base functions. The *E* representation is twodimensional, i.e. f = 2, and is separated into E_a and E_b states. These states are chosen to be symmetric (E_a) and antisymmetric (E_b) with respect to exchange of two particles, say (12). According to Eq. 2.33 and Table 2.5, we have all the irreducible representations of C_{3v} since the square of the characters add to the group order: $1^2 + 1^2 + 2^2 = 6$.

When carrying out numerical calculations, the E hyperangular functions turn out to be mixed like $E_{1,2} = E_a \cos \alpha \pm E_b \sin \alpha$. Pure E_a and E_b functions are extracted by constructing a matrix of (12) permutations in the basis of the $E_{1,2}$ states and diagonalizing it [KG03]. Figure 2.6 shows examples of hyperangular wave functions for a C_{3v} system, and the symmetry properties of each irreducible representation, e.g. A_1 remains unchanged after $2\pi/3$ rotations, etc...

For a Schroedinger equation that is invariant under symmetry transformations, applying a symmetry operation to an eigenfunction (Υ , say) of a stationary state of the system belonging to a given adiabatic energy level must yield another eigenfunction which also gives the same eigenenergy. By applying all other symmetry transformations to Υ , we produce a set of eigenfunctions (Υ_k) that transform into linear combinations of one another (exactly like functions Υ_k of Eq. 2.31). Thus, this set gives a representation of the group, which is in fact irreducible. This is because functions that transform into linear combinations of themselves under a symmetry operation must invariably belong to the same energy. It would be an improbable coincidence to have a set of equal eigenergies corresponding to different groups of functions ($h_1, h_2, ...$), into which the basis of a reducible representation can be divided, which are not transformed into linear combinations of one another [LL03]. Hence, to each energy level of the system there corresponds some irreducible representation of its symmetry



Figure 2.6: Hyperangular wave functions for system with C_{3v} symmetry. Wave functions are shown as contour plots, where each line represents an equipotential. All irreducible representations of C_{3v} (A_1 , A_2 , and E) are displayed. Note the symmetries that characterize each irreducible representation: A_1 and A_2 are unchanged by $2\pi/3$ rotations of φ ; A_1 is symmetric through reflections across $\varphi = 2\pi/3$ vertical planes while A_2 is anti-symmetric. E_a states are symmetric through one vertical plane at $\varphi = \pi/2$, while E_b is anti-symmetric through the same plane.

group. So, for a system of three identical particles, hyperangular wave functions ϕ_a are not only eigenfunctions of the adiabatic Hamiltonian, but are also automatically identified as belonging to one of the C_{3v} irreducible representations: A_1 , A_2 , or E. The dimension of the representation equals the degeneracy of the level. Therefore, in a system of three identical particles, degenerate adiabatic energies are readily identified as E_a and E_b symmetry states.



Figure 2.7: Adiabatic channels for system of three identical particles.

Additionally, note the implication that adiabatic channels of one-dimensional representations (i.e. A_1 and A_2 symmetry) cannot self-cross, but instead form *avoided crossings* at points where they would cross. For example, an A_1 symmetry channel cannot cross another A_1 symmetry channel. However, channels of different symmetries may cross with each other (see Fig. 2.7).

When rotation of the space-fixed coordinate system has to be accounted for, i.e. total three-body angular momentum $J \neq 0$, then the symmetry of the system is represented by the D_{3h} group. If we add inversion I to the group of permutations S_3 , then we obtain a group isomorphous to point group $D_{3h} = C_{3v} \otimes \sigma_h$, where σ_h is now a reflection through the 'horizontal' plane formed by the three-body system (see Fig. 2.8). This gives D_{3h} twice as many elements as C_{3v} : all the previous C_{3v} elements plus these elements multiplied by σ_h . D_{3h} has six irreducible representations: $A'_1, A''_1, A'_2, A''_2, E', E''$, where E' and E'' are



Figure 2.8: Visual depiction of D_{3h} point symmetry group [LL03]. It is the same as C_{3v} (Fig. 2.4), with the addition of three horizontal axes of symmetry of the second order intersecting at $\pi/3$.

two-dimensional and the rest are one-dimensional. D_{3h} will be applied to the study of good quantum numbers in three-body collisions in chapter 5.

2.2.5 Normal coordinates and labelling of vibrational states

Vibrational and rotational motions of a three-body molecular system can be treated separately due to the so-called *Sayvetz conditions* [Cal73]. Vibrations are conveniently described by normal coordinates, which are adapted to the geometry of the system. These normal coordinates arise out of a classical ball-and-spring model that is made of the atoms and their two-body interactions. The atoms are assumed to be point masses, and the springs holding them together are assumed to be massless and to obey Hooke's Law. The validity of this approximation is judged *a posteriori* by comparing how well its physical properties fit experimental data [Cal73]. We present a brief review of normal coordinates, but the reader is referred to Refs. [Cal73], [WDC55] or [Rei02] for thorough discussions normal coordinates.

A molecule of N atoms has 3N degrees of freedom, but 3N + 6 coordinates associated with it: three Euler angles describing rotation, three Cartesian coordinates for the center of mass of the molecule, and 3N coordinates connecting the atoms to the rotating frame [WDC55]. Therefore, all the coordinates cannot be independent and six conditions must exist connecting them. Three conditions locate the center of mass at the origin of the rotating system, ensuring the rotating frame moves with the molecule. The other three conditions tie the coordinate system to the molecule so that they rotate together. These conditions are used to separate vibrations from rotations or translations [WDC55].

To treat small vibrations, we define interatomic distances r_1, r_2 , and r_3 for a system of three identical particles (upper left of Fig. 2.9), and displacements from equilibrium distances r_e as $\Delta r_i = r_i - r_e$. Here, it is assumed that while one atom moves, the others remain in place. Also, due to the symmetry of the molecule (Fig. 2.9), only bond lengths, and not angles, are considered [Rei02]. We use this to define mass-weighed Cartesian coordinates

$$q_i = \sqrt{m_i} \Delta r_i, \tag{2.34}$$

and express the kinetic energy as a function of the time derivative of q_i $\left(\frac{dq_i}{dt} = \dot{q}_i\right)$

$$2T = \sum_{i=1} \dot{q}_i^2, \tag{2.35}$$

where $m_i = m$ is the same for all three atoms. For simplicity of writing the equations, it is assumed in this section that sums over each q_i must cover x, y, and z components. It is then assumed that the potential energy V is some function of the displacements and can thus be expanded about $q_i = 0$,

$$2V = 2V_0 + 2\sum_i \left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \frac{1}{3}\sum_{i,j,k} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_0 q_i q_j q_k + \dots \quad (2.36)$$

where subscript 0 indicates $q_i = 0$ [Cal73]. We can shift the zero of the potential energy $(V_0 = 0 \text{ since we are only interested in the } q_i \text{ dependence})$, and apply the the condition that V has a minimum at r_e

$$F_i = \left(\frac{dV}{dq_i}\right)_0 = 0, \qquad (2.37)$$

so that to the first approximation V becomes

$$2V = \sum_{i,j} F_{ij} q_i q_j. \tag{2.38}$$

The F_{ij} are *force constants* that represent the proportionality between displacement and restoring force [Cal73]. Combining the equations of motion of the Langrangian with Eqs. 2.38 and 2.35

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) + \left(\frac{\partial V}{\partial q_i}\right) = 0, \qquad (2.39)$$

we obtain

$$\ddot{q}_i + \sum_j F_{i,j} q_j = 0.$$
(2.40)

The solutions are of the form

$$q_i = A_i \cos(\omega t + \eta), \qquad (2.41)$$

where ω is the frequency of vibration, and the maximum amplitude is A_i . Equation 2.40 can be rewritten as

$$\sum_{j} (F_{ij} - \lambda \delta_{ij}) A_j = 0, \qquad (2.42)$$

where $\lambda_k = \omega_k^2$, and δ_{ij} is the Kroenecker delta [Cal73].

In order to obtain the normal coordinates, we first write Eqs. 2.35 and 2.38 as matrix products

$$2T = \dot{\mathbf{q}}^t \dot{\mathbf{q}},$$
$$2V = \mathbf{q}^t \mathbf{F} \mathbf{q} \tag{2.43}$$

where \mathbf{q} is a column vector containing all q_i displacements, \mathbf{F} is a $3N \ge 3N$ symmetric matrix whose components are the F_{ij} force constants, and t denotes transpose [Cal73]. In principle, it is possible to find a new set of coordinates \mathbf{Q} , which are obtained via a linear transformation \mathcal{L}^{-1} of \mathbf{q}

$$\mathbf{Q} = \mathcal{L}^{-1} \mathbf{q},\tag{2.44}$$

or equivalently,

$$Q_k = \sum_i l'_{ki} q_i, \qquad (2.45)$$

such that T and V will become diagonal. The l'_{ki} are the matrix elements of \mathcal{L}^{-1} . This choice of coordinates, which simplifies the problem greatly, are called the *normal coordinates*. Normal coordinates allow for the solution of the Schroedinger equation, since these coordinates make it possible to write T and V as a sum of separate terms, each of which is a function of a single coordinate [Cal73]. Q_i must also satisfy the *Sayvetz conditions* [Cal73].

V and T can now be written as

$$2V = \mathbf{Q}^t \mathbf{\Lambda} \mathbf{Q}$$
$$2T = \dot{\mathbf{Q}}^t \dot{\mathbf{Q}}$$
(2.46)

where Λ is diagonal, with normal frequency parameters λ_k for matrix elements [Cal73].



Figure 2.9: Set of normal modes of vibration for X₃ system, where particle X has mass m. Each particle is labeled by 1, 2 or 3. Superposition of degenerate normal modes $(Q_x + iQ_y)$ produces nuclear motion on right. Each vibrational mode can be characterized by a quantum number $(v_1, v_x, v_y...)$. In the normal mode approximation the symmetric mode is characterized by v_1 , while the asymmetric stretch modes are characterized by v_2 and l_2 (see discussion in text).

Combining Eqs. 2.35, 2.38, 2.44 and 2.46 imposes the conditions (see Ref. [Cal73])

$$\mathcal{L}^{t}\mathcal{L} = \mathbf{I},$$

$$\mathbf{F} - \mathbf{I}\lambda_{k}|\mathcal{L}_{k} = 0.$$
 (2.47)

Equations 2.44 and 2.47 tell us that for each normal coordinate Q_i , the corresponding row of \mathcal{L} , i.e. λ_i , determines which x, y and z displacements take part in that normal coordinate, the frequency of vibration ω_k of all the atoms, and the amplitudes A_{ik} of each atom. A mode like this, where all the atoms vibrate with the same frequency, but different amplitudes is called a normal mode of vibration (see Fig. 2.9).

If we chose for our coordinates \mathbf{q} the Eliashevich vectors \mathbf{S} (see Ref. [Rei02]), then it is possible to obtain normal coordinates

$$Q_1 = \left(\frac{m}{3}\right)^{1/2} \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$
$$Q_x = \left(\frac{m}{3}\right)^{1/2} \frac{1}{\sqrt{3}} (2\Delta r_1 - \Delta r_2 - \Delta r_3)$$
$$Q_y = \left(\frac{m}{3}\right)^{1/2} (\Delta r_3 - \Delta r_2).$$

 Q_x can be Q_y alternatively written as

$$Q_x = Q_r \cos \alpha$$
$$Q_y = Q_r \sin \alpha \tag{2.48}$$

Coordinate Q_1 describes the symmetric stretch of the molecule (breathing mode), whereas (Q_x, Q_y) , or equivalently (Q_r, α) , describe bends and the asymmetric stretch. Q_r and α describe the $Q_x + iQ_y$ radial and angular motion, respectively (see Fig. 2.9).

When one or more λ_k coincide, say $\lambda_k = \lambda_l$, this means the normal vibration is degenerate and it reflects some symmetry of the system [Cal73]. In this case, Eq. 2.42 can have solutions of the form $aA_{jk} + bA_{jl}$ for any a and b. For example, the X₃ system of Fig. 2.9 has 3 x 3 - 6 = 3 normal modes of vibration two of which, the Q_x and Q_y modes, are degenerate. These can be combined to produce the motion of $Q_x + iQ_y$, which is still a normal mode as it moves with the same frequency ω_k [Cal73].

The symmetry of the hyperangular wave function is connected to the vibrational modes of the three-body system. The number of nodes in the θ and φ directions vary according to the excitation of the vibrational state. If we consider the normal mode approximation, one can assign to each vibrational state three quantum numbers v_1 , v_2 and l_2 , which describe the three-dimensional harmonic oscillator of the C_{3v} symmetry. Quantum number v_1 describes the symmetric stretch mode, while v_2 describes the asymmetric stretch mode radial vibrational quanta. Finally, l_2 describes the quanta of the vibrational angular momentum mode and is restricted to $-v_2$, $-v_2 + 2$, ..., $v_2 - 2$, v_2 [DBK08]. Figure 2.9 shows normal vibrational coordinates for a three-body system of identical particles with the corresponding quantum numbers.

Hyper-radius is the variable associated with symmetric stretch modes since it does not affect the symmetry of the three-body configuration. Therefore, in the normal mode approximation v_1 is the quantum of excitation in hyper-radius. The quantum of excitation in hyperangles can similarly be recast as v_2 and l_2 .

The $(v_1, v_2^{l_2})$ triad of quantum numbers are only approximations to realistic systems, which do not behave exactly according to the normal mode approximation. In fact, as it will be shown in later chapters, it is not always clear how to label three-body vibrational states, as non-adiabatic couplings do not allow for the normal mode approximation labels, and there are different labelling conventions used. Also, it is not always clear how to label molecular terms.

2.2.6 Complex absorbing potential

Complex absorbing potentials (CAPs), first introduced in the field of time-dependent wave packet propagation by Kosloff and Kosloff (1986) [KK86], are used to absorb wave packets near the edges of grids in quantum dynamical calculations [VBK92]. They are useful in scattering problems. In the absence of a CAP, the outgoing flux would be bounced back from the right side of the grid. Such a behavior is unphysical. The presence of a CAP simulates the infinite grid: the outgoing flux is never coming back. This means a minimization of both reflection (R) (from the CAP) and transmission (T) (through the CAP) of the outgoing wavepacket at the edge of the grid, i.e. a gradual attenuation of the asymptotic part of the outgoing wavepacket. Figure 2.10 shows a cartoon sketch of a CAP.



Figure 2.10: Cartoon of CAP, where ρ is some dissociation coordinate (see text).

CAP effectiveness is related to CAP form:

$$V(\bar{\rho}) = -iA_1 [\bar{\rho}]$$

$$V(\bar{\rho}) = -iA_2 \left[\frac{3}{2}\bar{\rho}^2\right]$$

$$V(\bar{\rho}) = -iA_3 \left[2\bar{\rho}^3\right]$$

$$V(\bar{\rho}) = -iA_4 \left[\frac{5}{2}\bar{\rho}^4\right]$$

$$V(\bar{\rho}) = -iA_5 \left[N \exp\left(\frac{-2}{\bar{\rho}}\right)\right]$$
(2.49)

where

$$\bar{\rho} = \frac{\rho_{max} - \rho}{L}$$

and where ρ can be the hyper-radius or some other inter-atomic distance, and L is the damping length of the potential. Therefore, $0 \leq \bar{\rho} \leq 1$. For numerical calculations, since CAP is placed at the end of the grid, then $\bar{\rho}$ is replaced by

$$\rho' = \frac{\rho - (\rho_{max} - L)}{L}$$

In our approach, we place the CAP in the adiabatic potentials to absorb the outgoing flux of hyper-radial wave functions (i.e. $U_a(\rho) \rightarrow U_a(\rho) + iV(\rho')$ in Eq. 2.27). The best form of CAP to use is determined by the amount of space available for CAP. For example, where only small CAP lengths are possible, exponential CAPs attenuate the wavepacket less efficiently than linear CAPs.

The extent to which the different potentials transmit or reflect the wave packet can be quantified. Optimal CAP parameters (strength A_i , and length L) to minimize R + T for each type of potential are derived for use with any chosen mass or kinetic energy in Ref.
[VBK92]. In order to determine L and A_i for some value of R + T, we must first know the deBroglie wavelength λ_{dB} of the dissociating flux in the asymptotic region, i.e. the deBroglie wavelength of the dissociating particles. Obtaining kinetic energy from $E_{kin} =$ $|E_{dissociation}| - |E_{resonance}|$, we then determine

$$\lambda_{dB} = \frac{2\pi}{\sqrt{2\mu E_{kin}}},$$

where μ is the reduced mass of the dissociating products. We then use λ_{dB} to determine CAP damping length L. The longer the L the better the attenuation, but obviously one would always like to devote a minimal region to the CAP so as to not interfere with the small distance physics and to minimally affect the physics of the system [VBK92]. Usually, CAP length that is two to four deBroglie wavelengths is good enough. For a given L/λ_{dB} ratio, one obtains the optimal CAP strength A_i for preselected (and very small) R+T values from a table in Ref. [VBK92] (see Fig. 2.11).

The CAP method can also be used to determine resonance lifetimes and energies [RM93]. The addition of the CAP is like a perturbation of the Hamiltonian that makes it non-Hermitian,

$$H \to H^{(c)} = H + iV,$$

and changes the energy spectrum dramatically [RM93]. The CAP-modified Hamiltonian has a purely discrete spectrum (for proof see Ref. [RM93]). In fact, CAPs provide a means for distinguishing continuum states from resonant states: If CAP damping length L is such that it is far from the small-distance region of the potential then it shall not affect bound and resonant eigenvalues (Eq. 2.50) as much as it affects continuum eigenvalues. Therefore,

						_
L/λ	A_2/E	R + T	L/λ	A_2/E	R + T	
1.00	2.750	1.29E-03	8.50	1.040	5.31E-11	
1.50	2.640	7.14E-05	9.00	0.986	3.91E-11	
2.00	2.510	6.14E-06	9.50	0.949	2.91E-11	
2.50	2.380	7.74E-07	10.00	0.903	2.18E-11	
3.00	2.230	1.36E-07	10.50	0.870	1.64E-11	
3.50	2.090	3.16E-08	11.00	0.840	1.25E-11	
4.00	1.940	9.38E-09	11.50	0.813	9.49E-12	
4.50	1.800	3.40E-09	12.00	0.788	7.29E-12	
5.00	1.670	1.46E09	12.50	0.764	5.66E-12	
5.50	1.550	7.20E-10	13.00	0.741	4.48E-12	
6.00	1.440	3.97E-10	13.50	0.718	3.62E-12	
6.50	1.340	2.39E-10	1 4.00	0.697	3.00E-12	
7.00	1.250	1.54E-10	14.50	0.678	2.58E-12	
7.50	1.170	1.04E-10	15.00	0.663	2.32E-12	
8.00	1.100	7.35E-11				

TABLE III: Optimized Parameters for Quadratic Complex Absorbing Potential (Eq 9)^a

^a The first column, L/λ , lists the values of the reduced damping length. The second column, A_2/E , presents the optimized values of the potential premultiplier (eq 9) in reduced form. The last column, R + T, gives the value of the reflection plus transmission obtained with these potential parameters. The parameters are determined by minimizing the values of the reflection plus transmission given in the final column.

Figure 2.11: Example of table of optimization of CAP parameters, taken from Vibok *et al.* [VBK92].

continuum eigenvalues will show more dramatic changes in E_{res} and Γ to small changes in CAP length or strength than resonant states.

There are some instances where the non-Hermitian Hamiltonian can be solved analytically; see for instance, Ref. [RM93]. In the CAP method, resonance states are given by eigenvalues E_n^{vib} of the complex Hamiltonian that are exposed as poles in the complex plane with the form

$$E_n^{vib} = E_{res} - i\frac{\Gamma}{2}.$$
(2.50)

This is similar to the method of complex-coordinate rotation where the imaginary part $\Gamma/2$ of the eigenenergy is the resonance halfwidth, and the real part E_{res} gives the position of the resonance. Numerically solving the eigenvalue Eq. 2.27 in the presence of CAP yields three-body vibrational state energies and lifetimes, and complex hyper-radial wave functions $\psi_{a,n}(\rho)$ (section 2.2.3).

For completion of discussion, we mention another way of obtaining (E_{res}, Γ) using the CAP, but that is not used in our approach: Defining a complex inner product for eigenfunctions of $H^{(c)}$ as

$$(\psi_m|\psi_n) := \int_0^\infty \psi_m(\rho)\psi_n(\rho)d\rho,$$

and defining the matrix elements of a complex operator as

$$H_{mn}^{(c)} := (\psi_m | H^{(c)} | \psi_n) := (\psi_m | H^{(c)} \psi_n),$$

one can obtain a matrix representation of $H^{(c)}$ that is complex but symmetric with respect to the defined complex product. Additionally, its eigenvectors form a complex orthogonal system. Knowing complex eigenfunctions $\psi(\rho)$ of $H^{(c)}$ it is possible to obtain resonance energies (E_{res}) and widths (Γ) from the eigenvalue equation $H^{(c)}\psi = (E_{res} - i\frac{\Gamma}{2})\psi$ as [RM93]

$$E_{res} = Re \frac{\langle \psi | H^{(c)} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\Gamma = -2Im \frac{\langle \psi | H^{(c)} | \psi \rangle}{\langle \psi | \psi \rangle}.$$
(2.51)

2.2.7 R-matrix with 'slow' variable discretization

We present an adaptation of the R-matrix method to the SVD approach. Although no calculations using the R-matrix method are presented in this thesis, we present the method, as it will be used in future work (see chapter 6). The eigenchannel R-matrix approach consists

of solving the three-body vibrational Schroedinger equation at a chosen energy E subject to scattering conditions, and then calculating a set of linearly independent eigenstates Ψ of the R-matrix at the specified energy [AGLK96]. These solutions are used to obtain the R-matrix. From the R-matrix, it is then possible to obtain the K-matrix and S-matrix. In some instances, it is possible to have an analytical expression of the R-matrix [AGLK96].

The R-matrix method is a variational approach, so a preselected eigen-energy to the three-body Hamiltonian, say E, is used to obtain eigenstates Ψ_{β} of the R-matrix within a preselected hyperspherical reaction volume dV (hyper-sphere)

$$E = \frac{\int \Psi_{\beta}^* (-\frac{1}{2\mu} \nabla^2 + U) \Psi_{\beta} \, dV}{\int \Psi_{\beta}^* \Psi_{\beta} \, dV},\tag{2.52}$$

where ∇^2 and U are hyper-radial kinetic and potential energy operators, μ the three-body reduced mass. This implies that Ψ_β should have a normal logarithmic derivative

$$b_{\beta} = -\frac{\partial \Psi_{\beta}(\rho, \theta, \varphi)}{\partial \rho} \tag{2.53}$$

that is independent of hyperangles (θ, φ) [AGLK96]. Combining Eqs. 2.53 and 2.52 using Greene's theorem for the kinetic energy operator integral, and the Bloch operator $\frac{1}{2\rho}\delta(\rho - \rho_0)\frac{d}{d\rho}\rho$ (where ρ_0 is the hyper-radius of the hyper-sphere) yields,

$$\frac{1}{2\mu} \int \Psi_{\beta}^* b_{\beta} \delta(\rho - \rho_0) \Psi_{\beta} \, dV = \int \Psi_{\beta}^* E \Psi_{\beta} \, dV - \int (\frac{1}{2\mu} |\nabla \Psi_{\beta}|^2 + \Psi_{\beta}^* V \Psi_{\beta}) dV. \tag{2.54}$$

Seeking solutions of the form $\Psi_{\beta} = \sum_{k} C_{k} y_{k}(\rho, \theta, \varphi)$, where y_{k} is expanded in terms of hyper-radial and hyperangular wave functions, $y_{k}(\rho, \theta, \varphi) = \pi_{j}(\rho)\phi_{a,j}(\rho_{j}, \theta, \varphi)$, and using the

desired boundary conditions of the hyper-sphere,

$$\frac{\delta b_{\beta}}{\delta \Psi_{\beta}} = 0$$
$$=> \frac{\partial b_{\beta}}{\partial C_{k}} = 0$$

for all k, it is possible to obtain C_k , or equivalently, Ψ_β . It is done by solving the generalized eigenvalue problem

$$\Gamma \vec{C} = b_{\beta} \Lambda \vec{C} \tag{2.55}$$

where

$$\Gamma_{kl} = 2\mu \int \left(\frac{1}{2\mu} \frac{\partial y_k^*}{\partial \rho} \frac{\partial y_l}{\partial \rho} + y_k (E - U) y_l\right) dV$$
$$= \langle \pi_{j'} | \pi_j \rangle \mathcal{O}_{ja,j'a'} + \langle \pi_{j'} | E - U | \pi_j \rangle \mathcal{O}_{ja,j'a'}$$

and $\Lambda_{kl} = \int y_k^* y_l d\Sigma$, where integrand $d\Sigma$ is over the surface of the hypersphere. It is now possible to obtain the R-matrix

$$R_{ij} = -\sum_{\alpha} Z_{i\alpha} \frac{1}{b_{\alpha}} (Z_{j,\alpha}^{-1})$$

$$(2.56)$$

where

$$Z_{i\alpha} = \langle \phi_i | \Psi_{\alpha} \rangle |_{\rho = \rho_0}. \tag{2.57}$$

Once the R-matrix is known, it is straightforward to obtain the K-matrix and S-matrix, which, in turn, will allow the calculation of the three-body recombination coefficient k_3 [EGB99], along with other quantities of interest.

2.3 Numerical Methods

This section lays out details on the numerical methods used in our calculations. Section 2.3.1 discusses a mapping procedure used to make our calculations of higly excited, loosely bound vibrational states more efficient.

2.3.1 Mapped Fourier grid, mapped DVR basis set, and mapped grid in hyperangles

This method aims to avoid the implementation of very large grids. One of the purposes of using a mapping procedure is to reduce the calculation time while improving the accuracy of the calculations [FBK96]. For instance, when considering a system like the loosely bound helium trimer one must take into account large distances between the particles (large ρ). This necessitates the use of a large number N of basis functions $\pi_j(\rho)$ in the expansion of the hyper-radial wave function (Eq. 2.23), and thus leads to the diagonalization of a large $N \ge N$ Hamiltonian matrix [KMS06]. However, computation time can be reduced by using a mapping procedure that defines a new set of basis functions by performing a change of variable in hyper-radius: $\rho \to x(\rho)$. The mapping is made such that a relatively small number of basis functions $\pi_j(x)$ are needed to represent the required eigenfunctions of the Hamiltonian. In our method, we used the DVR basis in this mapping.

By doing this we can accurately represent wave functions for which the deBroglie wavelength varies by more than one order of magnitude from small to large inter-nuclear distances, for instance. When the deBroglie wavelength is small, a smaller grid step is required than when the deBroglie wavelength is large. This means that in the momentum representation the wave function is not localized. To represent the wave function using a constant grid step, therefore, makes the DVR basis unnecessarily large [KMS06]. The solution is to make the change in variable such that in the new variable x the wave function $\psi_{a,v}$ has a local deBroglie wavelength that is approximately constant. In practice, this mapping of $\rho(x)$ can be done by estimating the local deBroglie wavelength [KMS06]. Since the eigenfunction in the conjugated momentum space is much more localized, then a smaller number of $\pi_j(x)$ basis functions is needed for accurate representation. Hence, in the ρ representation this procedure produces a non-uniform DVR grid along ρ . For example, for wave functions of weakly bound two-body states, which may oscillate much more at short internuclear distances than at larger ones, the grid would be more dense at small internuclear distances where the wave function oscillates more.

We apply this mapping procedure to the hyper-radius. This is the first time a mapped DVR basis is applied in hyper-radius [KMS06]. The grid steps $\Delta \rho$ and Δx are related by

$$\Delta \rho = J(x)\Delta x \tag{2.58}$$

where

$$J(x) = \frac{d\rho}{dx}.$$
(2.59)

We can write Eq. 2.24 as

$$[K(\rho(x)) + U_a(\rho(x))]\theta_{a,v}(x) = \epsilon_{a,v}\theta_{a,v}(x), \qquad (2.60)$$

where $\theta_{a,v}(x)$ is given by

$$\theta_{a,v}(x) = \sqrt{J(x)}\psi_{a,v}(x), \qquad (2.61)$$

such that it is normalized to 1,

$$\int |\theta_{a,v}(x)|^2 dx = \int J(x) |\psi_{a,v}(x)|^2 \frac{d\rho}{J(x)} = \int |\psi_{a,v}(x)|^2 d\rho = 1.$$
(2.62)

In the x coordinate we can rewrite the kinetic energy operator as

$$K(x) = K(\rho(x)) = \frac{-1}{2\mu} \frac{d^2}{d\rho(x)^2} = \frac{1}{4\mu} \left[\frac{-1}{J^2} \frac{d^2}{dx^2} - \frac{d^2}{dx^2} \frac{1}{J^2} + \frac{7}{2} \frac{(J')^2}{J^4} - \frac{J''}{J^3} \right],$$
 (2.63)

where J is a function of x. The primes represent derivatives with respect to x. Equation 2.60 is solved to determine all levels up to a maximum energy ϵ_{max} . This mapping procedure can also be used when solving Eq. 2.27.

In practice, J(x), $\rho(x)$, and the step sizes $\Delta \rho$ and Δx are determined in the following way. We know that Δx is constant, and can be chosen to equal 1 for simplicity. $\Delta \rho$ is variable and chosen according to the desirable density in a given region of hyper-radius. So we have $J(x) = \Delta \rho(x)$ and determining $\Delta \rho$ is sufficient to determine J(x) and $\rho(x)$. We begin with the smallest value of ρ , ρ_1 , and determine the step size $\Delta \rho_1$ according to the required accuracy. The next point in the grid is given by $\rho_2 = \rho_1 + \Delta \rho_1$. We determine $\Delta \rho_2$ according to the required accuracy, and the next point will be given by $\rho_3 = \rho_2 + \Delta \rho_2$, and so on. This is repeated until we reach the end of the grid. The corresponding values of xfor ρ_i are $x_i = i$ [KMS06]. Figure 2.12 gives an example of the mapping procedure in hyperradius that was used to calculate Efimov-type resonances in a model system (see section 3.2). The reason to use this linear grid mapping is that Efimov states have large spatial extension (several orders of magnitude, see Figs. 3.10 and 3.11), but their short distance (short wavelength) behavior must be accurately described to obtain the correct phase of the wave function. Therefore, in order to make efficient calculations, a small step size is required at short distance, while a large step size can be used at large distances.



Figure 2.12: Non-uniform grid step along hyper-radius $\Delta \rho$ used in the calculation of Efimov resonances.

To determine $\Delta \rho_i$ at a given ρ_i we must consider how dense the grid must be at that particular region. For instance, if $\psi_{a,v}(\rho(x))$ in the neighborhood of ρ_i can be effectively represented by just a few $\pi_j(x)$ basis functions, then the step size $\Delta \rho_i = J(x)$ can be relatively large. Kokoouline *et al.* showed in Ref. [KDKMS99] that wave functions of excited levels, which have many oscillations, are well represented using the mapped DVR basis with the grid step given by

$$\Delta \rho_i = \beta \frac{\pi}{\sqrt{2\mu E_{kin}(\rho_i)}}.$$
(2.64)

The kinetic energy in the above equation is calculated using the semi-classical approximation that at a given point ρ_i , it is the difference, $E_{kin}(\rho_i) = E_{max} - U_a(\rho_i)$, between the maximum energy considered in the calculation (E_{max} , constant for all ρ_i) and the value of the threebody potential $U_a(\rho)$ at ρ_i . The constant $\beta < 1$ is introduced to uniformly control the accuracy of the calculations by uniformly reducing the step size, which would produce more accurate eigenenergies and wave functions. When several channels a are involved, the same grid can be used for all channels, in view of calculations involving non-adiabatic couplings. In that case, E_{kin} becomes $E_{kin}(\rho_i) = E_{max} - \min[U_a(\rho_i)]$, where $\min[U_a(\rho_i)]$ is the lowest potential curve at ρ_i .

The approach for determining $\Delta \rho$ using $E_{kin}(\rho_i)$ is only efficient for excited states having many nodes. If only the ground state and/or a few weakly excited states are considered then the step size should be adapted to the local variation of the states [KMS06].



Figure 2.13: Non-uniform grid step along hyperangle θ used in the calculation of Efimov resonances. $\Delta \theta$ is grid step size such that $\theta_{i+1} = \theta_i + \Delta \theta_i$.

When plotting hyperangular wave functions, it is also convenient to use a non-uniform grid. This is specially true when, at large values of hyper-radius, the hyperangular wave functions become very localized [FBK96]. Figure 3.12 shows a good example of this. In such a case, one can produce a grid on the qualitative features of the wave functions, such as the nonuniform grid steps ($\Delta\theta$ and $\Delta\varphi$) in θ and φ shown in Figs. 2.13 and 2.14, respectively. The idea is to have more grid points in regions where the wave function is mostly concentrated. Unlike step sizes in hyper-radius (Eq. 2.64), this hyperangular mapping procedure is not based on the local deBroglie wavelength λ_{dB} . These procedures help optimize the computer power at our disposal (section 2.3.3).



Figure 2.14: Non-uniform grid step along hyperangle φ used in the calculation of Efimov resonances. $\Delta \varphi$ is defined similarly to $\Delta \theta$ (caption of Fig. 2.13).

2.3.2 B-splines

Basis splines, or B-splines, are a commonly used basis set in numerical calculations. In our case, we are able to accurately represent wave functions with a small number of basis functions, and thus minimal calculation effort. B-splines are defined in the following way.

Given m + 1 values $t_i \in [0, 1]$, called knots, with $t_0 \leq t_1 \leq \cdots \leq t_m$, a spline of degree n

is a parametric curve S(t) composed of basis B-splines $b_{i,n}(t)$ of degree n [PBP02], [Wik]

$$S(t) = \sum_{i=0}^{m-n-1} P_i b_{i,n}(t) , t \in [t_n, t_{m-n}].$$
(2.65)

The P_i are called control points or de Boor points. There are m < n control points. In our case, we use cubic, e.g. t^3 , B-splines. An excellent description of B-splines and its application to numerical calculations can be found in Appendix C of Ref. [Esr97], and in [PBP02].

2.3.3 Parallel computers

The way the three-body dissociation problem is formulated allows us to take advantage of parallel computations on supercomputers. For each hyper-radial point a separate and independent calculation is made. Therefore, for a grid which contains N hyper-radial points we can simultaneously employ N processors. The computers we used allowed us to submit jobs to be carried out in "nodes". A node consists of a fixed number of processors and therefore the number of hyper-radial points in our grid had to be a multiple of this number. The more nodes we used the faster a given job will be done for the same total computational cost.

We changed the parameters of the problem through the use of input files, which allowed changing of variables such as number of states, number of basis functions, interaction strength, or CAP parameters without compiling the program each time.

We used National Center for Supercomputer Applications (NCSA) and National Energy Research Scientific Computer Center (NERSC) supercomputer resources which were allocated through different grants. We submitted interactive and regular jobs through the use of an SSH (Secure Shell) console. This was done through executable and batch files. For parallel calculations we use MPI (Message Passing Interface) software. The program itself is written in Fortran.

Let us label the number of hyperangular basis functions in the φ direction by n_{φ} , and the number in the θ direction by n_{θ} . In a typical run for the three identical bosons with nucleon mass model, for instance, for 256 hyper-radial points we observed convergence for $n_{\varphi} \approx 170$ and $n_{\theta} \approx 40$. Calculation times generally increase more with n_{θ} than with n_{φ} . The number of hyper-radial points we used was 256, the maximum. Typical runs may last around two hours (for these we used 16 or 32 processors using NCSA resources, where a node = 16 processors), but for the Efimov resonance problem some runs lasted up to 6 to 7 hours due to the large number of hyperangular basis functions required (see section 3.2) and we used up to 64 processors. It was more than double the number required for the first model. However, due to long queues, especially at NCSA, it may be a day or more before your program runs. We were also able to change the number of requested adiabatic states. There was no restriction on the number of requested states (channels), but sometimes if the number was 4 or less we did not observe convergence. So far all that has been discussed applies to the first part of the program, the second part took at most 30 minutes and most of the time we ran this part interactively. The second part relies on the results of the first part (adiabatic curves). In the second part of the program we specified the CAP parameters and obtained the vibrational eigenfunctions and eigenenergies.

2.4 Comparison with other methods

Compared to the Faddeev equations, our approach has the advantage of accounting for threebody terms of the potential, Eq. 2.14. As discussed in section 1.3, the Faddeev approach assumes a separability of the three-body potential into a pairwise sum, Eq. 1.8.

Comparing the CAP with the complex scaling method, there is no strong advantage to us to use one method over the other. In complex scaling, the complex variable plays the role of the absorber. This means necessary hyper-radial grid sizes to observe convergence would probably be very similar, as the CAP length and length of complex variable would be similar.

ONE THREE-BODY POTENTIAL ENERGY SURFACE

This chapter is dedicated to the early work in the thesis [BKMS], where we developed the method for calculating three-body resonances using only one three-body channel. With this method, we were able to calculate Efimov-type resonances, as well as three-body shape resonances in a model nuclear system.

3.1 SHAPE RESONANCES IN MODEL NUCLEAR SYSTEM

In this section, we discuss the very first application of our theoretical approach. The threebody system used is a model nuclear system previously studied - using the Faddeev equations approach - by Fedorov *et al* (Ref. [FGJ03]). We discuss our results, and compare them to the results of Ref. [FGJ03]. There were discrepancies between our results, which we analyze in section 3.1.2

3.1.1 Our results

We applied our method to a model three-body system of three identical bosons with nucleon mass [BKMS]. Pairwise potentials (in MeV) with a centrifugal barrier are given by [FGJ03]

$$V_2(r) = -55e^{-0.2r^2} + 1.5e^{-0.01(r-5)^2}.$$
(3.1)

 $V_2(r)$ holds only one bound state at $E_{2body} = -6.76$ MeV [FGJ03]. Three-body potentials are constructed as a simple sum of pairwise potentials: $V_{3body}(r_{12}, r_{23}, r_{31}) = V_2(r_{12}) + V_2(r_{23}) + V_2(r_{31})$. Solving the adiabatic Hamiltonian (Eq. 2.17) produces adiabatic potentials, the lowest of which has a potential barrier, see Fig. 3.1. This centrifugal barrier in the ground hyperspherical adiabatic curve arises from the barrier that exists between any given pair of particles. It allows for three-body shape resonances: three-body quasi-bound states that can tunnel across the potential barrier and thereby dissociate into a free particle and a two-body bound state (dimer). Given the size of the barrier, these quasi-bound states should be roughly in the range of -7 MeV to -5 MeV.



Figure 3.1: Hyperspherical adiabatic potentials of A_1 symmetry for the system with a potential barrier. Five A_1 adiabatic channels are displayed. There is only one bound state at -37.35 MeV. Resonant states are long-living states that tunnel through the potential barrier as shown in the inset. Note logarithmic scale in hyper-radius. The two arrows along hyperradius point to the values of ρ where ground adiabatic curve has its minimum and to where CAP begins.

This is because the dissociation energy of the ground adiabatic potential is negative and, therefore, corresponds to a free particle plus a dimer. The difference between the three-body bound state energy and the dissociation energy is transferred into the dissociating products (kinetic energy and two-body binding energy). A dissociation energy of 0 corresponds to three free particles. All excited adiabatic potentials have a three-free-bodies dissociation limit of 0 MeV.

For this system, we calculated one three-body vibrational bound state at $E_0 = -37.35$ MeV, and one three-body resonant state at $E_1 = -5.31$ MeV with half-width $\frac{\Gamma}{2} = 0.12$ MeV. The bound state is in good agreement with a previous study by Fedorov *et al.*, which calculated one three-body bound state at $E_0 = -37.22$ MeV [FGJ03]. With our method, we are capable of plotting the multi-channel hyper-radial wave function for this state (see Fig. 3.2).

Figure 3.2 shows that most of the wave function is constrained to the first adiabatic channel, in the small- ρ region near the potential well. Notice that the contribution of excited adiabatic channels to the hyper-radial wave function is orders of magnitude less than that of the ground channel. In contrast to bound states, continuum state wave functions are nonzero for large hyper-radius: in the dissociation region (see Fig. 3.3). Since this continuum state is located at E = -6.4 MeV, the ground state adiabatic channel again contributes the most to the total hyper-radial wave function.

The hyper-radial wave functions of resonant states are a mixture of continuum and bound state wave functions. They have nonzero probabilities in both inner and outer regions of adiabatic potentials (see Fig. 3.4). In our case, this feature is due to the tunneling of



Figure 3.2: Ground state hyper-radial wave function, $\psi(\rho)$, broken down into components for five-channel calculation. Upper-left frame shows modulus squared of normalized wave function. Other three frames show channel by channel components, a = 1 is ground channel, a = 2 is first excited state channel, and so on. Note logarithmic scale in hyper-radius for all hyper-radial wave functions.

the quasi-bound state between the bound and continuum regions in the ground adiabatic potential.

We tested the stability of this resonance with respect to CAP length and strength. Unlike continuum states (which exist mostly in the dissociation region), the three-body resonance is expected to be stable with respect to these parameters so long as the CAP is smooth enough. We also tested resonance stability with respect to type of CAP. Tables 3.1 and 3.2 show our results. As expected, the resonance position and width depend only weakly on the CAP.



Figure 3.3: Channel by channel components of a continuum state wave function for fourchannel calculation (E = -6.4 MeV.). Compared to the resonant wave function, Fig. 3.4, the amplitude of this wave function inside the potential-well region is negligible. Arrows along hyper-radius point to ground adiabatic curve minimum and to where CAP begins (see Fig. 3.1).

It is worth mentioning the role of non-adiabatic couplings in our calculations. Their importance can be seen when we carry out calculations with one channel only, i.e. only using the adiabatic approximation and not including the SVD couplings between channels. Figure 3.5 shows that before we begin to see a convergence in resonance energy and width, we must include at least four adiabatic channels and the corresponding SVD non-adiabatic couplings in our calculations.



Figure 3.4: Resonance hyper-radial wave function for four-channel calculation. The wave function has a considerable amplitude in the region of the potential well (around 10^{-4} a.u.). Arrows along hyper-radius point to ground adiabatic curve minimum and to where CAP begins (see Fig. 3.1). CAP is placed around $\rho = 4 \times 10^{-3}$ a.u., the distance at which the outgoing dissociation flux starts to be absorbed. This can be compared with the continuum wave function shown in Fig. 3.3, for which the potential-well amplitude is very small. Comparing the amplitudes of the different components, it is clear that the principal contribution is due to the lowest adiabatic state.

3.1.2 Comparison to previous study

We compared our results to calculations by Fedorov *et al.* (Ref. [FGJ03]) using the Faddeev equations. Fedorov and coworkers calculated a three-body resonant state for this system at $E_1 = -5.96$ MeV with half-width $\frac{\Gamma}{2} = 0.40$ Mev. This is not in good agreement with our calculations of $E_1 = -5.31$, $\frac{\Gamma}{2} = 0.12$ MeV, especially for the half width. The reason Table 3.1: Stability of calculated resonance with respect to CAP parameters for system of identical bosons interacting through a two-body potential with a barrier. The de Broglie wavelength of the dissociating products is approximately 0.0006 a.u. The most deviant calculation, last row, is due to the short length of the CAP for that calculation.

CAP strength (a.u.)	CAP length (a.u.)	CAP initial position (a.u.)	$E' - i\frac{\Gamma}{2}$ (MeV)
80,000	0.0028	0.0060	-5.307 - i0.116
104,000	0.0028	0.0060	-5.305 - i0.114
56,000	0.0028	0.0060	-5.310 - i0.117
80,000	0.0036	0.0052	-5.318 - i0.115
80,000	0.0020	0.0068	-5.344 - i0.107

Table 3.2: Stability of the calculated resonance with respect to type of CAP used.

CAP type	Energy (MeV)	Halfwidth (MeV)
quadratic	-5.319	0.1115
exponential	-5.318	0.1183

for the disagreement is not clear. To try to understand the discrepancy, we made several considerations.

Firstly, we are confident about the adiabatic states obtained because we obtained the same bound state as Fedorov and coworkers. We are also confident about the one-channel calculation (Fig. 3.5), which does not use SVD at all, giving a value of the complex energy that is close to the converged value. Secondly, we compared our results and those of Fedorov and coworkers with a calculation done using the WKB approximation. WKB works only for excited states and we are only talking about the first excited state in this case. Therefore, WKB can hardly be applied to this case. However, we provide the details of the calculation



Figure 3.5: Convergence of the position and width of the resonance with respect to the number of adiabatic states included in the calculation. The results for the resonance are circled; other data points represent the continuum states. Positions and widths of the continuum states depend on the CAP parameters. Notice that positions of the resonance and continuum states are at negative energies because the origin of energy is at the three-body dissociation, which is above the dissociation to the dimer + free particle configuration.

for completeness of the discussion. In the WKB approximation, the linewidth is given by

$$\Gamma = \frac{P_T}{T}.$$
(3.2)

The transmission probability P_T , and period T of oscillations are given by [Tie88]

$$P_T = \ln\left[1 + \exp\left(-\frac{2}{\hbar}\int_b^c \sqrt{2\mu\{U(\rho) - E_{trimer}\}}d\rho\right)\right],\tag{3.3}$$

$$T = \int_{a}^{b} \sqrt{\frac{2\mu}{E_{trimer} - U(\rho)}} d\rho, \qquad (3.4)$$

where μ is the three-body reduced mass and E_{trimer} is the energy of the resonance. For T, the limits of integration a and b are the classical turning points in the potential well. The limits of integration b and c for P_T are the 'entrance' and 'exit' points through which the three-body dissociating flux is tunneling. In Fig. 3.6, we compare our resonance linewidth to results previously obtained by Fedorov *et al.* [FGJ03] and WKB estimation. Our results are somewhat closer to the WKB approximation than those from Ref. [FGJ03], although as pointed out above WKB estimation does not provide a reliable result for this situation.

One reason for the discrepancy with Ref. [FGJ03] could be that in our calculation we used a longer grid (extending until $\rho_{max} \approx 0.01$ a.u.) than the grid in Ref. [FGJ03], where $\rho_{max} \approx$ 0.002 a.u. We found that to obtain converged results within our approach, ρ_{max} should be at least ≈ 0.005 a.u. or larger: CAP should be long enough to absorb the dissociation flux smoothly (see Figs. 3.2, 3.4, and 3.3). In Ref. [FGJ03], the situation could be different because no CAP was used. Instead, a complex scaling variable was employed. However, the complex scaling variable plays a role of an absorber. If the length of the complex scaling variable is too short, the outgoing dissociation flux is not absorbed completely and, thus, is reflected back from the end of the grid. This should give a wrong value for the resonance width.

To provide an insight into the hyperangular part of the total wave function, in Figs. 3.7 and 3.8 we give A_1 symmetry hyperangular wave functions calculated for two different values of hyper-radius, $\rho = 0.001$ and 0.01 a.u., correspondingly. For the small hyper-radius, the adiabatic states are delocalized. For the large hyper-radius, the lowest state is strongly localized: the amplitude is not zero only in the region where $\varphi \sim \pi/6$ and



Figure 3.6: Comparison of our resonance linewidth calculations to linewidth calculation of Fedorov *et al.*, and to the WKB approximation. We show our halfwidths for one-channel and five-channel calculations. Our four-channel calculation is closer to WKB approximation than that of Fedorov *et al.* [FGJ03]. However, WKB estimation cannot be viewed as reliable for this particular situation.

 $\theta \sim \pi/2$, corresponding to a dimer + free particle dissociation. Other adiabatic states at the large hyper-radius correspond to the three-body break-up: the corresponding wave functions are more delocalized, that means different possible rearrangements of the final dissociation products.

3.2 EFIMOV RESONANCES IN MODEL BOSONIC SYSTEM

For a description of Efimov resonances and bound states, see section 1.2.3. Using our approach, we were able to calculate Efimov resonances for a model system of identical bosons



Figure 3.7: Contour plots of hyperangular wave functions at $\rho = 0.0001$ a.u. for the system with potential given by Eq. 3.1. Values of contour lines are given by the legends. Upper left frame shows hyperangular axes: hyperangle θ runs in the radial direction from 0 to $\pi/2$, while φ runs in the polar angular direction from 0 to 2π . For this calculation we restrict φ to $\pi/6 \leq \varphi \leq \pi/2$, since we only consider A_1 adiabatic states. This value of ρ corresponds to the bound state region. All wave functions are delocalized: there is no preferred three-body arrangement.

with mass m = 1 a.u. [BKMS]. This system was previously studied by Nielsen and coworkers in Ref. [NSE02]. The pairwise interaction is governed by the short-range potential (in a.u.),

$$V_2(r) = -17.796 \exp(-r^2). \tag{3.5}$$



Figure 3.8: Contour plots of hyperangular wave functions at $\rho = 0.001$ a.u. for system with potential given by Eq. 3.1. Wave functions are represented in the same way as in Fig. 3.7. This value of ρ corresponds to the dissociation region. Note that the wave function of the lowest adiabatic state (left upper panel) is nonzero only in the small region of hyperangular space that represents the dimer plus free atom configuration for large hyper-radius.

This two-body potential produces ideal conditions for Efimov physics. It has a deeply bound state with energy $E_1^{(2)} = -7.153$ a.u. and a weakly bound state with energy $E_2^{(2)} =$ -1.827×10^{-9} a.u. [NSE02]. The *s*-wave scattering length is 23,394.87 a.u. for the shallow state [NSE02]. The large scattering length and the relatively small radius of the forces $r_0 \sim 1$ a.u. produces conditions for the formation of Efimov states [Efi71]. Because for this particular potential there is the deeply bound two-body state, then weakly bound three-body states can decay into a dimer and a free particle. Therefore, the three-body states are indeed resonant states with finite lifetimes (and widths).



Figure 3.9: Adiabatic potentials for Efimov-type system. The lowest dissociation limit ($E \sim$ 7 a.u.) belongs to the X₂+X breakup of the three-body state, while the E = 0 a.u. limit corresponds to breakup into three free particles.

Nielsen *et al.* [NSE02] determined positions and widths of these states using an R-matrix type approach and the hyper-radial coordinates. Instead of solving the eigenvalue problem along the hyper-radius, in Ref. [NSE02] the three-body scattering problem was considered. Namely, the energy-dependent scattering matrix S(E) was obtained for energies above the lowest dissociation limit (deeply bound dimer + a free particle). For the present situation when there is only one open channel, S(E) is a scalar function of E: $S = e^{2i\delta(E)}$. The positions and widths of the resonances were obtained considering the phase-shift $\delta(E)$. We use the results by Nielsen *et al.* [NSE02] to test the present method. Since the Efimov states are very weakly bound, their wave functions extend to very large distances. For example, Fig. 3.9 shows that the minimum of the lowest adiabatic state is around 1 a.u., but the exponentially decaying tail in the closed channel a = 2 of the E_4 state reaches the distance of 10^5 a.u. (see Fig. 1 of Ref. [NSE02]). At the same time, the component of the wave function corresponding to the open channel oscillates with the wavelength of $\lambda = 2.5$ a.u. when hyper-radius is large. Therefore, in order to represent the complete wave function, one has to have a grid with a large number of points. Nielsen *et al.* [NSE02] used about 3 million grid points in the interval $0.1 < \rho < 10^6$ a.u.

Our method allows us to use a much smaller grid. The exponentially decaying tail can be represented with a modest number of grid points (DVR points in our method). This can be made with a variable grid step, which grows logarithmically with hyper-radius. However, to be able to use the logarithmically-growing step, one has to absorb the outgoing dissociative flux at a small distance where the grid step is still small and the oscillating component of the wave function is still represented properly. Therefore, we place the CAP at the lowest adiabatic potential only at a small distance.

In a typical calculation, the variable grid in ρ has only 340 points and extends from 0.002 to 20,000 a.u. The grid step is constant from $\rho = 0.002$ to 0.1 a.u. This region corresponds to the minimum of the two lowest adiabatic states (Fig. 3.9). From $\rho = 1$ a.u. the grid step changes linearly with ρ : $\Delta \rho = 0.04\rho$. We use a quadratic absorbing potential placed at the lowest adiabatic state. CAP starts at $\rho = 12$ a.u; its length is L = 10 a.u., and the strength $A_2 = 11$ a.u. The parameters L and A_2 are chosen according to Ref. [VBK92] in order to minimize reflection and transmission coefficients for the outgoing dissociation flux. In the

Table 3.3: Comparison of complex energies (in atomic units) obtained in this work using different number of included adiabatic states with the results of Nielsen *et al.* [NSE02]. The imaginary part of the energies is the halfwidth of the resonances. The overall agreement is good except for the position of the 4^{th} resonance, which is probably not represented accurately in this study: the grid is not long enough in the present calculation. In Ref. [NSE02], six adiabatic states have been used.

	E_1 , units of 10^{-2}	E_2 , units of 10^{-4}	E_3 , units of 10^{-7}	E_4 , units of 10^{-9}
Ref. [NSE02]	-94.14 - i2.4705	-28.38 - i3.001	-58.42 - i5.79	-19.92 - i1.771
4 ad. states	-96.0 - i2.38	-28.8 - i2.91	-56.7 - i5.59	-22.6 - i1.67
5 ad. states	-96.0 - i2.39	-29.1 - i2.98	-57.2 - i5.72	-22.5 - i1.76
6 ad. states	-96.0 - i2.39	-29.2 - i3.00	-56.3 - i5.75	-22.6 - i1.77

calculation we used only 4 adiabatic states. The calculation of the four adiabatic states and the corresponding wave functions at 340 grid points of ρ is made in parallel on 96 processors and took about an hour. The size of the matrix for the hyper-radial eigenvalue problem is $(340 * 4) \times (340 * 4)$. The construction and diagonalization of the matrix is made on a single processor and takes also about one hour. With the modest calculation effort, we obtained all four Efimov resonances with a reasonable accuracy. Table 3.3 compares calculated energies and widths of the Efimov resonances with the results from Ref. [NSE02]. To give an idea about the wave function of an Efimov resonance, Fig. 3.10 shows the four components of the third resonance. The wave function 'lives' mainly in the first excited adiabatic state: the probability to find the system in the first excited state is the largest. Regular oscillations are present mainly in the lowest adiabatic state, which corresponds to the open dissociation path. Beyond 20 a.u., the oscillations decay because of the complex absorbing potential. Smaller oscillations visible in other adiabatic states are due to the coupling to the lowest state. Oscillations along the states decay with the distance ρ because the coupling becomes



smaller and the system can dissociate only through the lowest state.

Figure 3.10: First four adiabatic components $\psi_a(\rho)$ (a = 1 - 4) of the hyper-radial wave function of the third Efimov resonance. Real and complex parts of the components are shown in black and red lines. The main contribution to the wave function is from the second adiabatic ψ_a state having a minimum around 2 a.u. The only adiabatic state open for dissociation is the ground state, a = 1. However, the components with a = 2 - 4 have small oscillating tails (may not be visible), which are due to the coupling of the corresponding adiabatic states to $\phi_1(\rho; \theta, \phi)$. This is a generic property of the hyperspherical adiabatic approach: the couplings between adiabatic states decays slowly with ρ . Beyond $\rho = 20$ a.u., the oscillations on the lowest adiabatic state are damped due to the presence of the absorbing potential.

For a system of identical particles with infinite s-wave scattering length, the scaling parameter is predicted to be $\exp(\frac{-2\pi}{s_0}) \sim 1.94 \times 10^{-3}$ (Eqs. 1.3, section 1.2.3). Our calculated

energies and widths for the second, third and fourth states scale in a way similar to Eqs. 1.3 and 1.6, however the scaling parameter varies in the $2 - 4 \times 10^{-3}$ interval. The ratio Γ_2/Γ_1 is very different from the others due to the fact that the lowest resonance is strongly influenced by the short range physics and cannot be considered as a pure Efimov resonance. This is evidenced in the hyper-radial wave function components of the first resonance (Fig. 3.11) compared to the third resonance (Fig. 3.10).



Figure 3.11: First four adiabatic components $\psi_a(\rho)$ (a = 1 - 4) of the hyper-radial wave function of the first Efimov resonance. Real and complex parts of the components are shown in black and green lines. This resonance is considered non-Efimov. Wave function spans around three orders of magnitude in hyper-radius, while the third resonance, which is considered of the Efimov type, spans four orders of magnitude in hyper-radius (Fig. 3.10).

Figure 3.12 gives insight into the hyperangular vibrational wave functions calculated at a modestly large value of hyper-radius, $\rho = 15 a_0$. For this value hyper-radius, the lowest state

is already strongly localized: the amplitude is not zero only in the region where $\varphi \sim \pi/6$ and $\theta \sim \pi/2$, corresponding to a dimer + free particle dissociation. This localization of the wave functions becomes more pronounced as hyper-radius increases (in these calculations ρ extends to $\sim 10^4 a_0$), making it essential to have a mapping procedure (section 2.3.1) that can accurately depict the wave functions using a minimal number of hyperangular grid points. Other adiabatic states at the large hyper-radius are not as localized and correspond to the three-body break-up: That means different possible rearrangements of the final dissociation products.



Figure 3.12: Hyperangular vibrational wave functions for large hyper-radius ($\rho = 15 a_0$) for the Efimov system. Even at such modest hyper-radius the wave function for the ground adiabatic state a = 1 is already strongly localized around X+X₂ geometries. Wave functions of excited states are more diffuse in the hyperangular space, because they correspond to the X+X+X dissociation.

TWO THREE-BODY POTENTIAL ENERGY SURFACES

We extended our method of calculating predissociated states to include two coupled threebody potential energy surfaces (PESs). Including more than one PES is important for a more accurate description of predissociated states, such as Feshbach resonances. With this approach, we calculated three-body predissociated states in a model bosonic system interacting through Van der Waals forces. We also calculated predissociated states near a conical intersection in H_3 [BK09], where nonadiabatic couplings are important. Additionally, there is a geometric phase (Berry phase) near the conical intersection, which is important for an accurate description of these couplings (section 4.1.1).

The first part of this chapter discusses the H_3 system, and the last section presents preliminary results for a model Van der Waals system that is based on Li_3 .

4.1 Feshbach resonances in coupled $1^2A'$ and $2^2A'$ potential energy surfaces of H₃

Non-Born-Oppenheimer interaction near a conical intersection between two potential energy surfaces (PES) of polyatomic molecules plays an important role in dynamics of the molecules (see, for example, review [Yar96]). At the exact point of intersection, the interaction becomes infinite and the Born-Oppenheimer adiabatic (BOA) approximation breaks down. Therefore, the description of the nuclear motion of the molecule with energies around or above the energy of a conical intersection should explicitly take into account the two intersecting PESs coupled by the non-adiabatic interaction.

One of the simplest processes involving the interaction near a conical intersection is the $H+H_2(v',j') \rightarrow H+H_2(v,j)$ scattering process (and its isotopic variants) that has been extensively studied in theory and experiment [KRZ90, NJK⁺92]. The related processes are the collisional dissociation of H_2 and its inverse, the three-body recombination of hydrogen: $H+H+H \rightarrow H_2(v,j)+H$, which is responsible, for example, for the formation of the first generation of stars [FH07], as mentioned in section 1.2.1. The processes are governed by the two lowest molecular potential surfaces $1^2A'$ and $2^2A'$ of H₃ (see Fig. 4.1). The lowest $1^2A'$ potential is repulsive and leads to the H_2+H dissociation. The dissociation limit of the $2^2A'$ potential correlates with the H+H+H breakup and has a number of quasi-bound vibrational levels, which are predissociated towards to the H_2+H dissociation due to the coupling near the conical intersection. The predissociation of $2^2 A'$ vibrational states has been studied by Kupperman and collaborators [LAK07] using a time-independent scattering framework, the time-delay analysis, and a combination of Jacobi and hyperspherical coordinates. The calculation has been done with the two-channel diabatic potential of H_3 with non-diagonal diabatic couplings obtained directly from first derivatives of *ab initio* BOA electronic wave functions of the two interacting states. In another study by Mahapatra and Köppel [MK98], the time-dependent approach was employed by propagating a wave packet that is initially placed on the $2^2 A'$ PES; the lifetimes are then derived from the autocorrelation function. In Ref. [MK98], the authors also used a diabatic representation of the coupled H₃ potential, but the diabatization is done differently than in Ref. [LAK07] and does not require explicit calculation of first derivatives of the BOA electronic wave functions. The lifetimes obtained in the two studies are significantly different.



Figure 4.1: The two lowest *ab-initio* potential energy surfaces of H₃ shown as functions of hyperangles $0 \le \theta \le \pi/4$ and $0 \le \phi \le 2\pi$ for a fixed hyper-radius $\rho = 2.5 a_0$. The projection at bottom of the figure corresponds to $1^2 A'$ PES.

In this study, we suggest a general theoretical method to describe the nuclear dynamics involving two molecular potentials coupled by a non-adiabatic interaction near the conical intersection. As an example, we calculate lifetimes of several $2^2A'$ predissociated vibrational levels of H₃. The method can be used for other small polyatomic molecules where the conical intersection plays an important role. There are two main ingredients in the proposed method: (1) The diabatization procedure is made in a way that accounts for the Jahn-Teller coupling between the $1^2A'$ and $2^2A'$ molecular states and the D_{3h} symmetry of the total vibronic wave function. (2) Nuclear dynamics is described by Smith-Whitten hyperspherical coordinates [Joh83], adiabatic separations of hyperangles and hyper-radius along with the slow-variable discretization (SVD) [KMS06, BKMS], and a complex absorbing potential (CAP) to obtain resonance lifetimes.

Before further discussion, we present some brief background about the geometric phase, which plays an important role in the calculations.

4.1.1 Geometric phase

As mentioned above, conical intersections, such as the one shown in Fig. 4.1, are singularities of the Born-Oppenheimer approximation [BMK⁺03]. This conical intersection induces a geometric phase effect on the adiabatic basis that has been shown to significantly change the positions, linewidths, and wave functions of vibrational three-body states in the $2^2A'$ PES. For example, this effect can be seen in Ref. [LPK90], although their diabatization procedure is different from ours and we obtain different results. This effect (sometimes referred to as the molecular Aharonov-Bohm effect) is the result of a sign change in the electronic wave function as one moves the system in a closed path around the conical intersection in configuration space (Fig. 4.2)

Recall from section 2.2.5, Eq. 2.48, that one can describe the bends and the asymmetric stretch mode of the molecule with polar coordinates Q_r and α ,

$$Q_x = Q_r \cos \alpha$$
$$Q_y = Q_r \sin \alpha$$

where Q_x and Q_y also describe the bends and asymmetric stretch mode of the triatomic molecule, and form the Cartesian basis for the polar coordinate system. Rotating around the
three-body equilateral arrangement (i.e. moving hyperangle φ from $0 \rightarrow 2\pi$), as illustrated in Fig. 4.2, or equivalently varying α between 0 and 2π , introduces a geometrical phase of π in the electronic wave function (Eq. 4.2), thus multiplying it by -1. In general, α is proportional to a countour integral around the conical intersection [Rei02].



Figure 4.2: Illustration of 2π rotation in configuration space about equilateral three-body arrangement of adiabatic electronic wave functions ψ_1, ψ_2 (Eq. 4.2). Point of equilateral configuration corresponds to conical intersection (degeneracy) of $1^2A'$ and $2^2A'$ molecular states (see Fig. 4.1). Degeneracy is broken away from symmetric configuration. Rotation takes α from $\alpha \rightarrow \alpha + 2\pi$ (see Eq. 4.1).

The phase originates in the following way. Since the two electronic states are strongly coupled, the off-diagonal elements in the Hamiltonian cannot be neglected (Eq. 4.1). Additionally for X_3 molecules, which have degenerate vibrational modes induced by symmetry

(bottom right mode in Fig. 2.9, for example), there is a strong coupling of vibrational and electronic motions that must have a common treatment [Rei02]. Near the symmetric configuration, in the *diabatic* representation, the electronic Hamiltonian becomes [LH61]

$$\hat{H}_{el}(Q_r, \alpha) = \begin{pmatrix} W_0 + \frac{1}{2}EQ_r^2 & CQ_r e^{i\alpha} + DQ_r^2 e^{2i\alpha} \\ CQ_r e^{-i\alpha} + DQ_r^2 e^{-2i\alpha} & W_0 + \frac{1}{2}EQ_r^2 \end{pmatrix},$$
(4.1)

where C, D, E, W_0 are functions of hyperspherical coordinates [JP09]. Small values of Q_r yield wave functions

$$\psi_{e} = \frac{1}{\sqrt{2}} (\psi_{-} e^{i\alpha/2} + \psi_{+} e^{-i\alpha/2}),$$

$$\psi_{e'} = i \frac{1}{\sqrt{2}} (\psi_{-} e^{i\alpha/2} - \psi_{+} e^{-i\alpha/2}),$$

(4.2)

where ψ_{\pm} form the *diabatic* representation, and $\psi_{e,e'}$ form the *adiabatic* representation [Rei02] of the lower (unprimed) and upper (primed) potential energy surfaces. Equation 4.2 reveals the well-known effect of the geometric phase in the adiabatic representation: When $\alpha \rightarrow \alpha + 2\pi$: $\psi_e \rightarrow -\psi_e$; and when $\alpha \rightarrow \alpha + \pi$: (1) ψ_e changes continuously into $\psi_{e'}$, and (2) $\psi_{e'}$ into $-\psi_e$ (Fig. 4.3) [LH61]. Both the vibrational and electronic wave functions acquire a sign change when $\alpha \rightarrow \alpha + 2\pi$, in such a way that the effect is cancelled in their product (e.g. total vibronic wave function, Eq. 4.6) [LH61].

The *diabatic* representation is related to the *adiabatic* representation via the inverse unitary matrix transformation [Rei02],

$$\begin{pmatrix} \psi_{+} \\ \psi_{-} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\alpha/2} & ie^{i\alpha/2} \\ e^{-i\alpha/2} & -ie^{-i\alpha/2} \end{pmatrix} \begin{pmatrix} \psi_{e} \\ \psi_{e'} \end{pmatrix}.$$
(4.3)

Excellent discussions of the geometric phase effect in a system with a conical intersection



Figure 4.3: Illustration of geometric phase effect in adiabatic electronic wave functions (ψ_e and $\psi_{e'}$) as asymmetric mode phase α is varied from 0 to π . Figure taken from Ref. [LH61].

can be found in Refs. [LH61] and [Rei02]. The next section will discuss our treatment of the $H_3 \ 1^2 A'$ and $2^2 A'$ PESs.

4.1.2 Diabatic basis for the coupled H₃ potentials

We use the adiabatic *ab initio* $1^2A'$ and $2^2A'$ PESs from Ref. [VBM+87], which will be referred to as V_1 and V_2 . The dependence of the potentials on the two hyperangles is shown in Fig. 4.1. In our approach, we also use a diabatic representation of the interaction potential. However, we derive the non-diagonal diabatic coupling elements from the *ab initio* PESs without calculating them explicitly as derivatives of Born-Oppenheimer electronic states. This way of representing the non-adiabatic couplings has been very successful in diatomic molecules: If the two *ab initio* PESs have an isolated avoided crossing, the vibrational dynamics is well represented by a 2×2 diabatic potential with the geometry-independent non-diagonal matrix element equal to the half of the splitting between the *ab initio* PESs at the avoided crossing. The diabatic non-diagonal coupling in our model is derived in the following way.

The two $1^2A'$ and $2^2A'$ electronic states become degenerate at the equilateral configuration and should be referred to as two components of the E' irreducible representation of the D_{3h} symmetry group. It is convenient to use the basis functions $|E_+\rangle$ and $|E_-\rangle$ in the two-dimensional E' space [DBK08, LH61]. Although the electronic states $1^2A'$ and $2^2A'$ for clumped nuclei are classified according to the C_s symmetry group, the vibronic states of H_3 should be classified according to the D_{3h} group. The most general form of the diabatic potential in the basis of $|E_{\pm}\rangle$ for an arbitrary geometry is

$$\hat{V} = \begin{pmatrix} A & Ce^{i\alpha} \\ \\ Ce^{-i\alpha} & A \end{pmatrix}, \qquad (4.4)$$

where A, C, and f are real-valued functions of the three hyperspherical coordinates [KG03]. The diagonal elements A are the same because of the degeneracy of E_{\pm} states. The functions A and C transform in the D_{3h} symmetry group according to the A_1 representation, and α has the following property under the C_3 symmetry operator: $C_3\alpha = \alpha + 2\pi/3$. The A and C functions are uniquely determined from the $1^2A'$ and $2^2A'$ PESs: $A = (V_1 + V_2)/2$ and $C = (V_2 - V_1)/2$. The actual form of function α can be derived near the conical intersection: It is equal to the phase of the asymmetric normal mode distortion [LH61, KG03]. Although this form of α is derived near the conical intersection, we will use it everywhere. This is justified because (1) the transition between adiabatic states occur only near the conical intersection, (2) far from the conical intersection the phase factor $e^{\pm i\alpha}$ does not play a role as long as the symmetry property mentionned above is satisfied.

The vibrational wave functions ψ obtained from Eqs. 2.14 and 2.27 have two components ψ_{\pm} corresponding to the two diabatic E'_{\pm} basis functions. In the adiabatic basis, corresponding to the $1^2A'$ and $2^2A'$ electronic states, the two components $\psi_{1,2}$ of the ψ function have the form

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_- e^{i\alpha/2} + \psi_+ e^{-i\alpha/2}),$$

$$\psi_2 = i \frac{1}{\sqrt{2}} (\psi_- e^{i\alpha/2} - \psi_+ e^{-i\alpha/2}).$$
(4.5)

After applying the C_3 symmetry operator three times, the molecule returns back to its original position, however the components $\psi_{1,2}$ change sign $\psi_{1,2} \rightarrow -\psi_{1,2}$ because $\alpha \rightarrow \alpha + 2\pi$. It is a well-known property of adiabatic states in the presence of conical intersection, which is often referred as geometrical or Berry phase effect. Because the adiabatic electronic wave functions ψ_{e1} and ψ_{e2} also change sign, the total vibronic wave function

$$\Psi = \psi_1 \psi_{e1} + \psi_2 \psi_{e2} = \psi_+ |E'_+\rangle + \psi_- |E'_-\rangle \tag{4.6}$$

is unchanged after the identity operator C_3^3 is applied.

4.1.3 Results

After solving the hyperangular part of the three-body Hamiltonian, Eq. 2.14, for each BOA PES separately, we obtain two uncoupled 'families' of adiabatic potentials $U_a(\rho)$, which are shown in Fig. 4.4. The curves belonging to the different families can cross. When the coupling is turned on between the two electronic states, the crossings turn into avoided

crossings, which is demonstrated in Figs. 4.5 and 4.7. Figure 4.5 shows the hyperspherical adiabatic (HSA) curves obtained by solving Eq. 2.14 with the diabatic electronic potential of Eq. 4.4. Far from the (avoided) crossings the calculations with coupled and uncoupled electronic states produce almost the same HSA states. The coupling changes the HSA states at (avoided) crossings only. It is also worth to mention, that if the phase factors $e^{\pm i\alpha}$ in Eq. 4.4 are neglected, the dynamics described by such diabatic potential is *exactly* the same as the dynamics with the uncoupled BOA PESs. It is because the transformation diagonalizing the operator \hat{V} is independent of the nuclear coordinates if $\alpha \equiv 0$. Fig. 4.8 shows the vibrational HSA functions $\varphi_{a,j}$ for several adiabatic states calculated with the coupled potential \hat{V} of Eq. 4.4.

The E < 0 dissociation limits represent $H_2(v, j_r)$ plus H(1s) breakup, where v and j_r represent the two-body vibrational and rotational quantum numbers, respectively. H_2 has many vibrational and rotational states. The low energy two-body bound states approximately scale like the harmonic oscillator energies for dimer rotational states

$$\Delta E(j_r \to j_r + 1) = 2B_{\nu}(j_r + 1), \tag{4.7}$$

and dimer vibrational states

$$\Delta E(v \to v+1) = \hbar \omega_{\nu}, \tag{4.8}$$

where B_{ν} is the rotational constant and ω_{ν} is the frequency of the nuclear vibrations [LL03]. However, this is not true for higher energy dimer states since the hydrogen two-body potential is highly anharmonic.

As Figs. 4.4 and 4.7 show, the ground and first excited HSA potentials of the $2^2 A'$ family



Figure 4.4: Hyperspherical adiabatic potential curves, obtained from uncoupled $1^2A'$ (black curves) and $2^2A'$ (green curves) PESs of H₃. Different dissociation limits for the $1^2A'$ family correspond to different v and j. Here, we only show the curves of the A_1 irreducible representation. The lowest dissociation limit is for $(v = 0, j_r = 0)$ two-body state, and the next dissociation limit corresponds to $(v = 0, j_r = 2)$, etc...until the first vibrational state $(v = 1, j_r = 0)$ is reached, at which point the $(v = 1, j_r = 2)$ dimer state follows, and so on (see Fig. 4.6). For lower states, the scaling from one two-body rotational level to the next can be approximated by harmonic oscillator, $2B_{\nu}(j_r + 1)$. Close-up frame corresponds to Fig. 4.7, as discussed in text.

have minima and can have vibrational levels that are pre-dissociated due to the coupling with the $1^2A'$ state. Although each vibrational level has components from all the HSA curves shown in Fig. 4.4 (or Fig. 4.7), only one component is usually dominant. Thus, the vibrational levels can be characterized by (1) the dominant component a and by (2) the number v_1 of quanta along the hyper-radius. In addition, each HSA curve in the $2^2A'$



Figure 4.5: Hyperspherical adiabatic potential curves, obtained from the H₃ coupled twochannel potential of Eq. 4.4. Different dissociation limits for the $1^2A'$ family correspond to different vibrational v and rotational j_r quanta of the H₂ dimer (see Fig. 4.6). Here, we only show the curves of the A_1 irreducible representation. Close-up frame corresponds to Fig. 4.6

family can be characterized by the number v_2 of quanta in the hyper-angular space and the number l_2 of those v_2 quanta along the cyclic hyperangular coordinate φ . Therefore, each predissociated level can be numbered with the triad $\{v_1, v_2^{l_2}\}$ similar to the normal mode notations for C_{3v} molecules.

Below the H+H+H dissociation limit there are only two $\{v_10^0\}$ and $\{v_12^0\}$ series of A_1 predissociated levels. Their positions and lifetimes are given in Table 4.1. Lifetimes for the two series are very different. The reason for the difference is that the avoided crossings are significantly wider for the 0^0 curve than for the 2^0 curve (see Fig. 4.7). In Fig. 4.7 we see



Figure 4.6: Close-up look at boxed area in Fig. 4.5 shows $H(1s) + H_2(n, j_r)$ dissociation limits of H₃ adiabatic potentials. According to selection rules derived in chapter 5, for A_1 symmetry states with total angular momentum J = 0, only even j_r values are allowed. Lower vibrational and rotational states of H₂ approximately follow energy steps of harmonic oscillator.

that (1) the avoided crossings are larger for the ground potential, and (2) there are more dissociation channels crossing the ground potential because its potential well is wider than that of the first excited potential. For the second observation: probability of dissociation is enhanced by the larger number of lower family adiabats available for dissociation. With regard to the first observation: larger avoided crossings are equivalent to larger couplings, which enhance the probability of dissociation from the ground adiabat of the upper family into the lower family of adiabats. One reason why the avoided crossings in the ground potential are larger could be due to a smaller number of nodes in the hyperangular wave



Figure 4.7: Close up look at avoided crossings in hyperspherical adiabatic curves shown in Fig. 4.4. The horizontal dashed lines show the positions of predissociated $2^2A'$ levels. The non-adiabatic (non-Born-Oppenheimer and non-hyperspherically-adiabatic) transitions due to "fine structure" of the avoided crossings are accurately represented by a modest grid step $\Delta \rho = 0.05 a_0$ in the developed method.

functions (see Eq. 2.27). This is consistent with the fact that the hyper-radial wave function for $E_1^{(2)}$ has no nodes, and therefore it is expected that the hyperangular wave functions have more nodes to make up the difference. These two factors, we believe, are the primary reasons for the shorter lifetimes for the first series of Feshbach resonances.

Table 4.1 also compares the obtained results with two other studies [LAK07, MK98] of the $2^2A'$ predissociated levels. In Ref. [LAK07] the non-diagonal couplings in the diabatic basis are obtained from the accurate *ab initio* non-Born-Oppenheimer couplings between the $1^2A'$ and $2^2A'$ states, but not from PESs as in this study. The agreement with our study for

$\{v_1, v_2^{l_2}\}$	E_r, τ ; this work	$E_r, \tau;$ Ref. [LAK07]	$E_r, \tau;$ Ref. [MK98]
$\{0, 0^0\}$	-3.85, 13.	n.a.	$-3.74, \sim 3$
$\{1, 0^0\}$	-3.11, 13.	n.a.	$-3.01, \sim 3$
$\{2, 0^0\}$	-2.4, 14.	n.a.	-2.32, n.a.
$\{3, 0^0\}$	-1.8, 14.	n.a.	-1.70, n.a.
$\{4, 0^0\}$	-1.2, 16.	$-1.19, \sim 15.$	-1.14, n.a.
$\{5, 0^0\}$	-0.7, 18.	$-0.42, \sim 17.$	-0.65, n.a.
$\{0, 2^0\}$	-0.2, 130.	n.a.	$-0.22, \sim 4.5$

Table 4.1: Positions, E_r (in units 10^{-2} Eh) and lifetimes, τ (in fs) of pre-dissociated $2^2A'$ vibrational levels. Energies are relative to the H(1s) + H(1s) + H(1s) dissociation.

the lifetime and energy of the $\{40^0\}$ resonance is very good as well as for the lifetime of the $\{50^0\}$ level. The agreement for the energy of the $\{50^0\}$ level is not as good probably due to the somewhat special character of the $\{50^0\}$ level: its hyper-radial wave function extends to relatively large values ~ $7a_0$ of hyper-radius (and internuclear distances ~ $5a_0$), Fig. 4.10. In Ref. [MK98], the diabatization procedure was based on PESs similarly as it is made in the present study, but with one important difference: the diabatic electronic states in [MK98] are non-equivalent. It means that the D_{3h} character of the vibronic wave functions in Ref. [MK98] is broken. The lifetimes obtained in Ref. [MK98] are significantly different from the present values and values of Ref. [LAK07]. The disagreement is attributed to the choice of the diabatization procedure in [MK98] that does not respect the degeneracy of the diabatic electronic wave functions.

Figures 4.9 and 4.10 show the difference in the hyper-radial wave functions of Feshbach resonances and continuum states (Ψ_c). In contrast to continuum states, which have most of propability at large hyper-radial distances and negligible probability at shorter hyper-radial



Figure 4.8: Wave functions of HSA states $\varphi_{a,j}$ of the A_1 irreducible representation as functions of the hyperangles θ and φ for $\rho_j = 2.5 a_0$ and several different a. Each wave function has two components, φ_+ and φ_- corresponding to the two BOA electronic channels of the potential \hat{V} .

distances, wave functions of resonances have non-negligible probabilities at both small and large hyper-radial distances. These wave functions reinforce the conclusion that the reported states are indeed resonances.



Figure 4.9: Resonance hyper-radial probability densities for ground (no nodes, $v_1 = 0$), first excited (one node, $v_1 = 1$), and third excited (three nodes, $v_1 = 3$) vibrational states of H₃. For a comparison, we also give the probability density $|\Psi_c|^2$ of a continuum state (energy is -0.0091 Eh). Ψ_c is localized mostly in the large- ρ dissociation region. The arrow points to the beginning of the complex absorbing potential.

4.1.4 A word on labelling system of vibrational states

We would like to say a few words about the half-integer and integer conventions for the asymmetric mode quantum number v_2 , and the viabrational angular momentum $l_2 = -v_2, -v_2 + 2, ..., v_2 - 2, v_2$. In our work, we used the integer convention. However, both conventions are used in the literature, although the one that we used seems to be used more in experimental papers devoted to the spectroscopy of H₃ and H₃⁺ (for instance, see excellent papers by H. Helm and M. Jungen, Refs. [BLH91], [MRM⁺00], [MRHM01], and [GBM⁺05]).



Figure 4.10: Modulus squared hyper-radial wave function of fourth and fifth excited vibrational states.

Strictly speaking, the half-integer labels of v_2 and l_2 are defined for the (ro)vibrational part in the *adiabatic* Born-Oppenheimer representation of the total (ro)vibronic wave functions that is obtained when the two electronic potential are taken into account and coupled to each other (see Ref. [LH61], which is one of the original papers to derive the half-integer quantum numbers and to discuss their physical meaning). The total (ro)vibronic states are labeled with integers because the electronic states in the *adiabatic* representation should also be labeled with half-integers if one use this convention. The fact that the total wave function is labeled with an integer quantum number means that the corresponding observable (projection on the axis of symmetry) is single-valued (electronic and nuclear spin wave function parts are excluded from this discussion). There is no physically observable quantity that corresponds to half-integer v_2 and l_2 . Nevertheless, the two conventions (including or excluding the electronic half-unity into the labels) are appropriate as long as it is clear which one is meant. In fact, for our case there is an additional reason to use integer labels. Namely, in the *diabatic* representation that we used in this paper, both electronic and vibrational parts are labeled with integers. Each part of the total wave function in the *diabatic* representation is single-valued (in contrast to adiabatic representation).

4.1.5 Estimation of three-body recombination rate coefficient

As a tangent, we now discuss how with the above calculations, we were able to roughly estimate coefficient k_3 for the three-body recombination H+H+H \rightarrow H₂+H. For the estimation, we use the transition probability

$$P \sim \frac{1}{\tau\omega} \tag{4.9}$$

from the $2^2 A'$ molecular state to the $1^2 A'$ state. The quantity $\omega = \Delta E/\hbar$ is the frequency of oscillation in the $2^2 A'$ potential, ΔE is the splitting between the vibrational levels belonging to the same series $v_2^{l_2}$, i.e $\Delta E = E(\{v_1 + 1, v_2^{l_2}\}) - E(\{v_1, v_2^{l_2}\})$, and τ is the lifetime. Although ω and τ depend on the quantum number v_1 , their product is approximately energy-independent. Averaged over the series of predissociated resonances, the generalized recombination cross-section is given by the formula [EGB99, MKL⁺06]

$$\sigma_o \sim \frac{1152\pi^2}{k^5} P,$$
 (4.10)

where $k = \sqrt{2\mu E}/\hbar$ is the hyper-radial wave vector for the three-body system, and μ is the three-body reduced mass. We then account for contributions from rotational states with

non-zero angular momentum (J > 0),

$$\sigma_{tot} \sim \sigma_o \sum_{J=0}^{J_{max}} (2J+1)^2.$$
 (4.11)

The sum includes angular momenta J up to J_{max} , which is such that the lowest $2^2A'$ vibrational level moves above the H+H+H dissociation limit: No more vibrational levels are possible for $J > J_{max}$. Very roughly, J_{max} is estimated from the energy difference $\Delta \epsilon$ between the ground state $\{0, v_2^{l_2}\}$ of the $\{v_2^{l_2}\}$ series and the H+H+H dissociative limit (E = 0). Thus, J_{max} is obtained by considering that

$$J_{max}(J_{max}+1)B_v \sim \Delta\epsilon, \tag{4.12}$$

where

$$B_v = \left\langle \frac{\hbar^2}{2\mu\rho^2} \right\rangle \sim \frac{\hbar^2}{2\mu\rho_e^2} \tag{4.13}$$

is the three-body rotational constant for the rotation in plane of the H₃ molecule, and $\rho_e \sim 2.75 \ a_0$ is the value of hyper-radius at the potential minimum of the ground $2^2 A'$ adiabatic potential. Finally, we estimate rate coefficient k_3 by

$$k_3 = v\sigma_{tot} \,, \tag{4.14}$$

where $v = k\hbar/\mu$ is the hyper-radial velocity of the three-body system. This estimation is done for each irreducible representation of the system $(A_1, A_2, \text{ and } E)$. Summing the contributions from each irreducible representation gives $k_3 \sim 1 \ge 10^{-29} \text{ cm}^6/\text{s}$ at 300 K. With an error of about 50%, this is in good agreement with the estimation by Flower and coworkers [FH07] that yielded $k_3 = 2.2 \ge 10^{-30} \text{ cm}^6/\text{s}$ at 300 K. In Ref. [FH07] the rate coefficient was obtained from the inverse process $H_2+H\rightarrow H+H+H$, which is a simpler problem since H_2+H is a two-body problem, using the detailed balance principle.

4.1.6 Convergence tests

To conclude this section, we show that the states listed in Table 4.1 showed reasonable convergence with respect to several tests, and discuss some computational advantages of our present method. These include tests with respect to: (1) the number of adiabatic states included in the calculation, (2) hyper-radial point density, (3) CAP length and strength, and (4) total length of hyper-radial grid. These tests are shown in the following figures. For example, in Figures 4.11 and 4.12 we show the convergence with respect to CAP length and the hyper-radial point density, respectively. Convergence with respect to CAP length and strength is also important since the position and width of resonant states should not depend on CAP parameters.



Figure 4.11: Convergence of resonant states with respect to hyper-radial grid point density. Uniform distribution of hyper-radial points is used here, with $\rho_{max} = 6 a_0$.

It is worthwhile to note the relatively small number $N_{\rho} = 96$ of hyper-radial points ρ_j required to obtain converged lifetimes and positions of resonances considering the large number of sharp avoided crossings (see Fig. 4.7). It is an advantage of using the SVD procedure rather than the familiar $\langle \varphi_a | \partial^2 / \partial \rho^2 | \varphi_{a'} \rangle$ and $\langle \varphi_a | \partial / \partial \rho | \varphi_{a'} \rangle$ non-adiabatic couplings between the HSA states: It is not necessary to calculate the derivatives on a fine grid of hyper-radius near avoided crossings to describe the couplings locally. Instead, in the SVD approach, the overlap matrix elements $\mathcal{O}_{ia,i'a'}$ between the adiabatic states in Eq. 2.27 account globally for the non-adiabatic hyperspherical couplings. It allows us to reduce significantly the computational task.



Figure 4.12: Convergence of resonant states with respect to CAP length. Here, $\rho_{max} = 6 a_0$.

Note that the energies and lifetimes of states like $\{5, 0^0\}$ and $\{1, 2^0\}$ did not display good convergence under the parameters of the current calculation. One reason could be that the size of the hyper-radial grid is not long enough. We can already see small deviances in



Figure 4.13: Convergence of resonant states with respect to CAP strength ($\rho_{max} = 6 a_0$).



Figure 4.14: Convergence of resonant states with respect to number of adiabatic states included ($\rho_{max} = 6 a_0$).



Figure 4.15: Convergence of resonant states with respect to ρ_{max} .

convergence with respect to CAP length in states $\{4, 0^0\}$ and $\{5, 0^0\}$ (see Fig. 4.12). Figure 4.12 shows a drop in halfwidth for states $\{4, 0^0\}$ and $\{5, 0^0\}$ when CAP length is decreased from 1.63 a_0 to 1.14 a_0 . Figure 4.9 shows the modulus squared of the hyper-radial wave functions of quasi-bound and continuum states. We can see that wave functions for states $\{0, 0^0\}$ and $\{1, 0^0\}$ (Ψ_0, Ψ_1 , respectively) decay well before the beginning of CAP (arrow in Fig. 4.9). Thus, these states are not at all affected by changes in CAP length. This is in contrast to higher energy resonances, whose hyper-radial wave functions extend more into CAP region (like Ψ_4, Ψ_5 in Fig. 4.10). This is why $\{4, 0^0\}$ and $\{5, 0^0\}$ do not converge as well as the other states when we increase CAP length to $2.12a_o$, (see Fig. 4.12). We expect a similar situation in state $\{1, 2^0\}$.

When we increase the hyper-radial grid to $7a_0$, however, we obtain a better converged value for states $\{4, 0^0\}$ and $\{5, 0^0\}$ (see Fig. 4.15). Figure 4.15 shows a significant drop

in halfwidth of states $\{4, 0^0\}$ and $\{5, 0^0\}$, when ρ_{max} is extended to $7a_0$. These widths and positions are closer to previous calculations (see Table 4.1) than those obtained with $\rho_{max} = 6a_0$.

With bigger calculations, in principle, it is possible to obtain all other resonant states in both series. In general, higher energy states will have a larger extent in hyper-radius, more contributions to the total hyper-radial wave function from higher adiabatic states, and more nodes in the hyper-radial wave function. So, in principle, these states could be more accurately calculated if we increased one or several of the following parameters: hyperradial grid length, the number of included adiabatic states, and hyper-radial point density. However, the aim of this work is to show that we are able to calculate these Feshbach resonances, and so we did not, for now, try to calculate all the possible pre-dissociated vibrational states of the $1^2A'$ and $2^2A'$ orbitals of H₃.

4.1.7 Conclusion

The obtained results in the H₃ system allows the prediction of the three-body recombination rate coefficient of H+H+H, a quantity that cannot be directly measured in experiment, but is of great importance in the astrophysical community. In the treatment of the conical intersection in the H₃ system, we suggest an efficient and uniquely defined diabatization method to represent vibrational dynamics of the two coupled potential surfaces corresponding to the E electronic states (in symmetric configuration, E' and E''). The method is efficient because only the *ab initio* Born-Oppenheimer potentials are needed to derive the interaction Hamiltonian. The description of the quantum molecular dynamics near the conical intersection has long been considered as very complicated and counter-intuitive (in particular, because of the non-integer vibrational quantum numbers used in the adiabatic representation). The dynamics near conical intersection is even called 'diabolic' by some authors. The suggested method is simple conceptually and numerically and, in our opinion, can be used in many problems where two E electronic states are involved in the molecular dynamics near a conical intersection. It is not discussed in the article, but the presented treatment is easily generalized to system with E electronic states for $C_{\infty v}$ molecules (linear triatomic systems with Renner-Teller coupling). The simple concept of the diabatization may later be used to develop a simple theoretical (not numerical) method to estimate lifetimes of predissociated states in a situation similar to the one considered using just one of two parameters obtained from the *ab initio* calculation or even from experiment. There are several lines of research that can be pursued using the proposed diabatization procedure.

4.2 Model Van der Waals system: Preliminary results

We first tested our method with two coupled PESs on a model system of particles that interact via pairwise Van der Waals potentials. Each particle has 1/200 the mass of the ⁷Li atom. The reason for the small mass is that it requires use of smaller number of adiabatic channels (about 15) in our calculations, compared to using the mass of Li, which requires the inclusion of hundreds of closely coupled adiabatic channels. As mentioned in the introduction, there is great interest in three-body processes involving Li, as well as systems with heavier alkali atoms, all of which have conical intersections in their PESs.

The coupled three-body PESs are constructed in the following way. Ground and excited

two-body Van der Waals potentials,

$$V_{2body-gd}(r_{ij}) = \frac{C_{12}}{r_{ij}^{12}} - \frac{C_6}{r_{ij}^6}$$
$$V_{2body-exc}(r_{ij}) = V_{2gd}(r_{ij}) + 0.01 \text{ a.u.},$$
(4.15)

are coupled at every interparticle distance \boldsymbol{r}_{ij} by

$$C_{2body}(r_{ij}) = A \exp\left[-\left(\frac{r_{ij} - r_0}{w}\right)^2\right],\tag{4.16}$$

where r_0 lies at the two-body potential energy minimum, A and w give the corresponding strength and extension of the coupling (see Fig. 4.16). The coupling is chosen to be relatively weak and restricted to a small region near r_0 , as seen in Fig. 4.16. Stronger two-body couplings lead to stronger hyperspherical non-adiabatic couplings. We also wanted the twobody interaction to closely resemble that of Li₂. Therefore, we chose the following values for our interactions and couplings: $C_{12} = 1.1 \times 10^7$ a.u., $C_6 = 1.4 \times 10^3$ a.u., $A = 1.0 \times 10^{-3}$ a.u., $w = 2.5 \times 10^{-1} a_0$ and $r_0 = 5.0 a_0$. C_6 and C_{12} were chosen based on Ref. [BA85]

Ground and excited three-body PESs are constructed as sums of two-body potentials,

$$V_{3body-gd}(r_{12}, r_{23}, r_{13}) = V_{2body-gd}(r_{12}) + V_{2body-gd}(r_{23}) + V_{2body-gd}(r_{13}),$$
(4.17)

and

$$V_{3body-exc}(r_{12}, r_{23}, r_{13}) = \frac{1}{3} (V_{2body-gd}(r_{12}) + V_{2body-exc}(r_{23}) + V_{2body-exc}(r_{13}) + \dots \text{ symmetrization})$$

$$(4.18)$$

These PESs are then coupled by

$$C_{3body}(r_{12}, r_{23}, r_{13}) = \frac{2}{3} [C_{2body}(r_{13}) + C_{2body}(r_{23}) + C_{2body}(r_{12})].$$
(4.19)



Figure 4.16: Two-body Van der Waals potentials and coupling (Eqs. 4.15 and 4.16).

Therefore, in the diabatic representation V_{3body} takes the form

$$V_{3body} = \begin{pmatrix} V_{3body-gd} & C_{3body} \\ \\ C^*_{3body} & V_{3body-exc} \end{pmatrix}, \qquad (4.20)$$

We present some preliminary results for the aforementioned Li-based system. As of the time this thesis was written, there were still some bugs to work out in our calculations, but we believe these results are presentable and expect to obtain more accurate results to be published in a longer paper to also include more H_3 calculations (section 4.1).

Figure 4.17 shows 15 adiabatic channels included in our calculations. This is the smallest number of adiabatic channels before convergence of resonant states is observed. The system extends to about 70 a_0 . Note that these adiabatic potentials are essentially a superposition of two identical families of adiabatic potentials, with one family shifted up by about 0.02 a.u. This comes from the fact that the two-body potentials are identical but shifted. Since



Figure 4.17: Adiabatic potentials of A_1 symmetry for Van der Waals Li-based system.

all adiabatic potentials are A_1 symmetry, however, they form avoided crossings wherever the two families cross. In the one-dimensional case, the energy gap at the avoided crossings is $\sim 2A$ (Eq. 4.16).

Figures 4.18 and 4.19 show convergence tests of the three-body resonances with respect to CAP parameters. Other convergence tests included tests against total number of included adiabatic channels, against total hyper-radial grid length, and against the number of hyperangular basis functions used.



Figure 4.18: Convergence of three-body resonant states (circled) with respect to CAP length.



Figure 4.19: Convergence of three-body resonant states (circled) with respect to CAP strength.

CORRELATION DIAGRAMS IN COLLISIONS OF THREE IDENTICAL PARTICLES

This chapter discusses the work done by Nicolas Douguet on which I collaborated [DBK08]. The work consisted of searching for the 'good' quantum numbers before and after a threeparticle collision. The work was motivated by the increased relevance of three-body collisions in ultracold quantum systems (see chapter 1), and recent experiments involving few-atom interactions in optical lattices

Since the main part of the work was done by Nicolas Douguet, this thesis will only briefly summarize the study and will highlight the use of our theoretical approach to facilitate the study.

5.1 Description of study

If one considers a system of three colliding identical particles, there are only three possible configurations before, during, and after the collision: 1) three free particles, 2) two particles close to each other and one particle far away such that the only interaction is between the two close particles (dimer + free particle), and 3) three particles close enough that all three interact with each other (quasi-bound three-body state). For each configuration, one can assign a set of quantum numbers. It is possible, by studying the symmetry of the total wave function of the system, to find the relationship between these sets of quantum numbers before and after the collision. For example, some of the quantum numbers are conserved throughout the collision. This study provides a systematic description of the correlations between the quantum numbers for all possible configurations, deriving selections rules governing the change in quantum numbers. The study focuses on the coordinate part of the total wave function and proposes a similar approach to include the electronic and nuclear spin statistics.

The symmetry properties of a system of three colliding identical particles with nonzero total angular momentum are described by the D_{3h} group (section 2.2.4). Using the notation of Ref. [BJ98], the 12 elements of this group are written as **E**, (12), (13), (23),(123), (132), without inversion **E**^{*} and the same six plus inversion (in this notation, (12) denotes the permutation of particles 1 and 2). For convenience, two orthogonal basis states E'_{+} , E'_{-} with properties

$$(123)E'_{\pm} = e^{\pm i\omega}E'_{\pm}$$

 $(12)E'_{\pm} = E'_{\pm}$

are used to span the space of E' states ($\omega = 2\pi/3$). Basis states E''_+, E''_- are defined in the same way for the E'' representation. With this, it is now possible to project an arbitrary state of the system ψ onto any of the basis functions Γ spanning the irreducible representations by using the projector

$$\mathbf{P}_{\Gamma}(\psi) = \sum_{\mathbf{g}} \chi_g^{\Gamma} \mathbf{g} \psi \tag{5.1}$$

where **g** are any of the group elements of D_{3h} , and χ_g^{Γ} are the characters of the onedimensional irreducible representations (characters are discussed in section 2.2.4) [Gal02].

Although the quantum numbers of an arbitrary initial state ψ are not, in general, conserved during a collision, a given irreducible representation is, and can be viewed as a good quantum number, allowing the characterization of the possible final states. Therefore, decomposing ψ into irreducible representation components gives the selections rules for states before and after a collision. For example, if $\mathbf{P}_{\Gamma}(\psi)$ gives zero, then final states transforming according to Γ are not accessible.

Considering only the spatial part of the total wave function, it is then possible to derive the relations between the appropriate quantum numbers of different configurations and the irreducible representations that the quantum numbers correspond to. As an example, we briefly discuss how this is done for short distance configurations. This will be followed by a discussion of the derivation of the selection rules.

Short distances imply all particles are close enough to significantly interact with each other, e.g. that the pairwise interaction is much larger than the energy of relative rotational motion. It is defined in such a way, so as to allow the separation of vibrational and rotational motions and, hence, the assignment of vibrational and rotational quantum numbers. The spatial wave function is thus defined as the product of rotational and vibrational parts,

$$\psi = \mathcal{R}(\alpha, \beta, \gamma)\phi(\rho, \theta, \varphi) \tag{5.2}$$

where (α, β, γ) are Euler angles and (ρ, θ, φ) are the hyperspherical coordinates (section 2.1). The rotational part can be described by the symmetric top eigenstates

$$\mathcal{R}(\alpha,\beta,\gamma) = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} [D^J_{M,K}(\alpha,\beta,\gamma)]^*.$$
(5.3)

where J is the total angular momentum, and M and K are its projections on the space-fixed and molecular axes, respectively [LL03]. J, M, K are constants of motion and are sufficient to completely define the rotational state of the system. The relation between these numbers and the irreducible representations of the system are obtained by considering the symmetry

properties of the Wigner functions $D_{M,K}^J(\alpha,\beta,\gamma)$ and the characters χ_g^{Γ} in the D_{3h} group [BJ98], [VM88]. These relations are summarized in Fig. 5.1 (Table 2 of Ref. [DBK08]).

Г	K	J
$\overline{A_1'}$	0	even
A_2^i	0	odd
$A_1^{\tilde{i}} \bigoplus A_2'$	$K = 6n; n \neq 0$	
$A_1^{\tilde{\prime}} \bigoplus A_2^{\tilde{\prime}}$	K = 6n + 3	
E'_{\pm}	K is even and $\neq 3n$	
$E_{\pm}^{\overline{\prime\prime}}$	<i>K</i> is odd and $\neq 3n$	

Figure 5.1: Allowed rotational quantum numbers for short distances between particles. n is an integer. Table taken from Ref. [DBK08].

In a similar way, the allowed quantum numbers of the vibrational part $\phi(\rho, \theta, \varphi)$ can be related to the irreducible representations of the system. In the case of the rigid rotor approximation, the system obeys the symmetry properties of the C_{3v} group (as discussed in section 2.2.4). If one applies the normal-mode approximation, three quantum numbers v_1, v_2, l_2 describing the three-dimensional harmonic oscillator of C_{3v} symmetry can be assigned to each vibrational state (sections 2.2.5). It is well-known that the transformation properties of $\phi(\rho, \theta, \varphi)$ depend only on l_2 [BJ98], [SJBC85],[KG03] (see Fig. 5.2).

Similar relations can be found in the case of large distances, where the interaction of at least one particle with the others can be neglected (scenarios 1 and 2). It is then possible to derive the correlations between states (and their quantum numbers) belonging to different configurations. This is done by considering the conservation of the symmetry of the corresponding irreducible representations. For example, correlations between states of

Г	l_2
$ \begin{array}{c} A_1 \\ A_1 \bigoplus A_2 \\ E \end{array} $	$0l_2 = 3n; n \neq 0l_2 \neq 3n$

Figure 5.2: In normal mode approximation, relation between irreducible representations of the C_{3v} vibrational wave functions and vibrational angular momentum quantum number l_2 , which is the only relevant quantum number in this case [DBK08]. n is integer.

three interacting particles configuration and states of dimer + free particle configuration are shown for values of total angular momentum J = 0, 1 in Fig. 5.3. Since the symmetry for the short distance configuration only depends on quantum numbers K and l_2 , and the symmetry for the dimer + free particle configuration only depends on the values of j_r and J_R (where $\vec{J} = \vec{j}_r + \vec{J}_R$), then only these values are shown in Fig. 5.3.

5.2 Application of our method to this study

Using our approach to calculate vibrational states, we carried out calculations for a system of three identical He atoms that interact via pairwise potentials multiplied by a prefactor λ : $V_{2body}(r) = \lambda V_{He-He}(r)$. Varying λ effectively tunes the two-body *s*-wave scattering length, and can also make the calculations simpler by separating adiabatic states. For these calculations we used $\lambda = 5$, which produces several bound states of the He₂ dimer for $j_r = 0, 1, 2, 3$ ($\lambda = 1$ gives only one bound He₂ state). A thorough discussion can be found in section 2.1.7-2 of Ref. [Bla06].

The calculation of the adiabatic three-body potentials (Fig. 5.4) and the vibrational



Figure 5.3: Correlation diagram for states of three interacting particle configuration (described by quantum numbers K, l_2), and states of dimer + free particle configuration (described by quantum numbers j_r, J_R) [DBK08]. Here $\vec{J} = \vec{j}_r + \vec{J}_R$.

hyperangular wave functions $\phi(\rho, \theta, \varphi)$ (Fig. 5.5) of the He₃-based system allows the demonstration of how the rules derived in section 5.1 can be applied. These calculations were done for J = 0, restricting the symmetry of the rotational part of the wave function to A'_1 .

In Fig. 5.4, the dissociation energy of three free particles is E = 0. Negative adiabatic energies (E < 0) correspond to the dimer + free particle configuration, where the difference in energy from E = 0 goes into the kinetic energy of the dissociating products and the dimer binding energy (see section 2.1.1 of Ref. [Bla06]). The most negative dissociation limit corresponds to the ground rovibrational state of the dimer $(j_r = 0)$. Therefore, for large values of hyper-radius (e.g. large distances) the system will go into one of the two aforementioned configurations. Small values of hyper-radius (e.g. small distances) correspond to the three interacting particles configuration, and there is the possibility of three-body bound states.

In this system, the selection rules could be applied to the collision of three free particles, or to the decay of a quasi-bound three-body vibrational state into a dimer + free particle. For example, consider a quasi-bound state with E > 0 and J = 0. Because E > 0, this state could decay into three free particles or into a dimer + free particle. Since the initial state has A'_1 symmetry, then the selection rules in Fig. 5.3 indicate that if the initial state were to decay into a dimer + free particle, then this final state must have j_r even. This is confirmed in our calculations, as Fig. 5.4 clearly indicates that A'_1 states only have j_r even dissociation limits. Initial arrangement of three colliding identical particles can be controlled experimentally in, for example, ultra-cold quantum gas of fully polarized ⁴⁰K atoms.

Figure 5.5 shows the dependence of the vibrational wave functions on hyperangles (θ and φ , see section 2.1), which along with Euler angle γ , determine the irreducible representation of the coordinate wave function. Since J = 0, the γ dependence is trivial. The hyperangular dependence is shown for three values of hyper-radius: small, where system behaves as rigid rotor, intermediate, and large, where the system can be approximated by three non-interacting particles or a dimer + free particle. For each value, a wave function belonging to each of the C_{3v} irreducible representations $(A_1, A_2, \text{ and } E)$ is plotted. Note that the

symmetry of the wave functions depends only on φ . For example, cyclic permutations (123) and (132) are equivalent to a change in φ of $\pm 2\pi/3$.

To conclude, the derivation of these selection rules and their application to numerical calculations such as for the He₃ or H₃ systems, can facilitate, for example, the study of three-body processes in ultracold degenerate gases such as three-body recombination, and the formation and decay of three-body Feshbach resonances. Our numerical calculations, are in agreement with the derived selection rules and provide a means for visualizing some of the symmetries of the system, thereby facilitating the application of the selection rules.



Figure 5.4: Three-body adiabatic curves for model He-based system of three identical bosons, as discussed in text. Total three-body angular momentum is zero J = 0. j_r denotes dimer rotational quantum. As discussed in section 2.2.4, each adiabatic curve corresponds to an irreducible representation of the C_{3v} (or in this case D_{3h}) group. Hyperangular dependence of the lowest adiabatic states for three values of hyper-radius is shown in Fig. 5.5.



Figure 5.5: Hyperangular vibrational wave functions of lowest adiabatic states of He-based system (discussed in text) for $\rho = 9, 15, 30 a_0$ (left, center, and right columns, respectively). Color represents value of wave function $\phi(\theta, \varphi)$, which depends on two coordinates. Wave functions display A_1, A_2 and E symmetries of the C_{3v} group. E symmetry states are represented by components $E_a = \text{Real}(E_+)$ and $E_b = \text{Im}(E_+)$. Parity is defined (positive) but it is not specified here because it is controlled by Euler angle γ , which cannot be shown [DBK08].

CONCLUSION

6.1 Summary and conclusions

We developed a method to calculate three-body pre-dissociated states with one or two potential energy surfaces, including surfaces with a conical intersection. The method is formulated in the hyperspherical formalism, along with the 'slow' variable discretization. Additionally, a complex absorbing potential is used. The method was successfully applied to model systems of identical bosons, and the realistic system of H_3 , for which predissociated levels of the $2^2A'$ molecular electronic state were calculated. To treat the X₃ molecular system with a conical intersection, a conceptually simple and effective diabatization procedure is used. In model systems, Efimov resonances where considered, as well as a model nuclear system with a centrifugal barrier. The approach is general enough that it can be used to study other interesting three-body processes (discussed below), which may include fermions and mixtures of fermions and bosons. For example, a system of three identical fermions, which must obey the Pauli exclusion principle, is characterized by anti-symmetric A_2 wave functions (as opposed to symmetric A_1 wave functions for bosons), assuming the spin part of the total wave function is symmetric and the total three-body angular momentum is zero. A_2 states can be included in our approach by simply applying anti-symmetric boundary conditions at hyperangle $\varphi = \pi/6$. This work is part of a larger effort to develop methods to study other interesting three-body phenomena such as trimer formation in atomic ultracold quantum gases through optical or Feshbach resonances, the problem of weakly bound states
of resonantly interacting particles, and the quantum dynamics near a conical intersection.

6.2 Future Work

6.2.1 Three-body recombination

In section 4.1.5, we demonstrated how we can estimate the three-body recombination rate coefficient k_3 of H+H+H with our method. For future work, we would like to accurately calculate this value. To do this, we plan to remove the CAP and apply the R-matrix method [AGLK96] along with the SVD approach (discussed in section 2.2.7). Besides the application to H₃ at cold temperatures, we are interested in calculating k_3 for ultracold atomic systems of Li₃ and Cs₃ (e.g. in ultracold quantum gases, BECs, DFGs). We would also like to apply the approach to scattering of H₂ + D⁻ and isotopomers (discussed in section 1.2.2).

6.2.2 Systems with conical intersection

The derivation of α in sections 4.1.1 and 4.1.2 assume that, for points in configuration space corresponding to large distortions (far from the conical intersection), the detailed behavior of α is unimportant and it is everywhere equal to the phase of the asymmetric mode distortion. So the logical questions arise: How good is this approximation? What is the next best level of approximation to α ?

As mentioned in section 4.1.2, the choice of the diagonal and absolute values of the non-diagonal elements of the coupled potential in the diabatic representation (Eq. 4.4) is unique if we require both electronic channels in this representation to form the E irreducible representations of the D_{3h} group. We assume that we have *ab initio* Born-Oppenheimer

potentials, but no non-Born-Oppenheimer couplings are available. The phase of the nondiabatic coupling is exact near conical intersection in the harmonic oscillator approximation (see, for example, Ref. [LH61]). We argue that the diagonal elements, and modulus of the non-diagonal elements, are 'exact' even if the harmonic oscillator approximation is not valid, i.e. far from conical intersection. We don't have a formal proof, but it seems that similarly to the gauge transformation formalism, the actual form of the phase dependence is not important. What is important is that the phase changes by 2π if one goes around conical intersection and that the phase dependence respects the C_{3v} symmetry of the vibrational wave functions. If a different function is chosen for the phase of the electronic states, this choice will be compensated by the corresponding change in phase of the vibrational functions. These question will be addressed in some more detail in a forthcoming longer paper.

Additionally, we would like to use our approach to treat three-body systems of heavier alkali atoms, such as Li_3 , all of which involve conical intersections. Successful completion of calculations in the model Van der Waals system will open this possibility. Of course, there is still the obstacle of the heavy computational workload for these larger systems, but this may be overcome by other means.

6.2.3 Universality

One interesting topic that may be possible to explore with our method is the departure from universality. For example: How does a system depart from universality? At which point does universal behavior begin? These questions are interesting in light of the ability to tune the diatom interaction in ultracold quantum gases.

6.2.4 Improving computational efficiency of our approach

One of the main obstacles in treating realistic atomic systems with heavier elements than H, such as Li_3 , is that the computational workload is too large for available supercomputers. However, there is room to introduce more efficient numerical procedures to our approach.

In order to make the diagonalization of the SVD generalized eigenvalue problem (Eq. 2.27) more efficient, we will in the future switch to using B-splines to span the wave functions, as opposed to the DVR basis set currently employed.

LIST OF REFERENCES

- [AC71] J. Aguilar and J. M. Combes. Class of analytic perturbations for one-body Schrodinger Hamiltonians. *Commun. Math. Phys.*, 22:269, 1971.
- [AGLK96] M. Aymar, C. H. Greene, and E. Luc-Koenig. Multichannel Rydberg spectroscopy of complex atoms. *Rev. Mod. Phys.*, 68:1015, 1996.
- [BA85] B. Bussery and M. Aubertfrecon. Multipolar long-range electrostatic, dispersion, and induction energy terms for the interactions between 2 identical alkali atoms Li, Na, K, Rb, and Cs in various electronic states. J. Chem. Phys., 82:3224, 1985.
- [BC71] E. Balslev and J. M. Combes. Spectral properties of many-body Schrodinger operators with dilatation-analytic interactions. *Commun. Math. Phys.*, 22:280, 1971.
- [BG00] D. Blume and C. H. Greene. Vibrationally excited states and fragmentation geometries of Ne-N and Ar-N clusters, N=3-6, using hyperspherical coordinates. J. Phys. Chem., 113:4242, 2000.
- [BH06] E. Braaten and H. W. Hammer. Universality in few-body systems with large scattering length. *Phys. Rep.*, 428:259, 2006.
- [BJ98] P. Bunker and P. Jensen. Molecular Symmetry and Specstroscopy. Ottawa: NRC Research Press, 1998.

- [BJL⁺02] K. Burnett, P. S. Julienne, P. D. Lett, E. Tiesinga, and C. J. Williams. Quantum encounters of the cold kind. *Nature*, 416:225, 2002.
- [BK09] J. Blandon and V. Kokoouline. Geometrical phase driven predissociation: Lifetimes of $2^2A'$ levels of H₃. *Phys. Rev. Lett.*, 102:143002, 2009.
- [BKMS] J. Blandon, V. Kokoouline, and F. Masnou-Seeuws. Calculation of three-body resonances using slow-variable discretization coupled with a complex absorbing potential. *Phys. Rev. A*, 75.
- [BKW⁺03a] D. Babikov, B. K. Kendrick, R. B. Walker, R. T. Pack, P. Fleurat-Lesard, and R. Schinke. Formation of ozone: Metastable states and anomalous isotope effect. J. Chem. Phys., 119:2577, 2003.
- [BKW⁺03b] D. Babikov, B. K. Kendrick, R. B. Walker, R. T. Pack, P. Fleurat-Lesard, and R. Schinke. Metastable states of ozone calculated on an accurate potential energy surface. J. Chem. Phys., 118:6298, 2003.
- [BKW⁺03c] D. Babikov, B. K. Kendrick, R. B. Walker, R. Schinke, and R. T. Pack. Quantum origin of an anomalous isotope effect in ozone formation. *Chem. Phys. Lett.*, 372:686, 2003.
- [Bla06] J. Blandon. Development of theoretical and computational methods for fewbody processes in ultracold quantum gases. M.S. Thesis, University of Central Florida, Orlando, FL, U.S.A., 2006.

- [BLH91] M. C. Bordas, L. J. Lembo, and H. Helm. Spectroscopy and multichannel quantum-defect theory analysis of the np Rydberg series of H₃. *Phys. Rev. A*, 44:1817, 1991.
- [BMK⁺03] A. Bohm, A. Mostafazadeh, H. Koizumi, Q. Niu., and J. Zwanziger. The Geometric Phase in Quantum Systems: Foundations, Mathematical Concepts, and Applications in Molecular and Condensed Matter Physics. New York, NY: Springer, 2003.
- [BS57] H. A. Bethe and E. E. Salpeter. Quantum mechanics of one- and two-electron atoms. New York, NY: Springer Verlag, 1957.
- [Cal73] S. Califano. Vibrational States. New York, NY: John Wiley & Sons, 1973.
- [Dav76] A. S. Davydov. *Quantum Mechanics*. New York: Pergamon Press, 1976.
- [DBK08] N. Douguet, J. Blandon, and V. Kokoouline. Correlation diagrams in collisions of three identical particles. J. Phys. B: At. Opt. Mol. Phys., 41:045202, 2008.
- [Efi71] V. N. Efimov. Weakly-bound states of three resonantly-interacting particles. Sov. J. Nucl. Phys., 12:589, 1971.
- [Efi79] V. N. Efimov. Low-energy properties of three resonantly interacting particles. Sov. J. Nucl. Phys., 4:546, 1979.
- [EG06] B. D. Esry and C. H. Greene. Quantum physics a menage a trois laid bare. Nature, 440:289, 2006.

- [EGB99] B. D. Esry, C. H. Greene, and J. P. Burke. Recombination of three atoms in the ultracold limit. *Phys. Rev. Lett.*, 83:1751, 1999.
- [ELG96] B. D. Esry, C. D. Lin, and C. H. Greene. Adiabatic hyperspherical study of the helium trimer. *Phys. Rev. A*, 54:394, 1996.
- [Esr97] B. D. Esry. Many-body effects in Bose-Einstein condensates of dilute atomic gases. Ph.D. Thesis, University of Colorado, Boulder, CO, U.S.A., 1997.
- [Fad61] L. D. Faddeev. Scattering theory for three-particle system. Sov. Phys. JETP, 12:1014, 1961.
- [FBK96] E. Fattal, R. Baer, and R. Kosloff. Phase space approach for optimizing grid representations: The mapped Fourier method. *Phys. Rev. E*, 53, 1996.
- [Fes58] H. Feshbach. Unified theory of nuclear reactions. Ann. Phys., 5:357, 1958.
- [FGJ03] D. V. Fedorov, E. Garrido, and A. S. Jensen. Complex scaling of the hyperspheric coordinates and Faddeev equations. *Few-body Systems*, 33:153, 2003.
- [FH07] D. R. Flower and G. J. Harris. Three-body recombination of hydrogen during primordial star formation. Mon. Not. R. Astron. Soc., 377:705, 2007.
- [Gal02] J. A. Gallian. Contemporary Abstract Algebra. Boston, MA: Houghton Mifflin Company, 2002.

- [GBM⁺05] U. Galster, F. Baumgartner, U. Muller, H. Helm, and M. Jungen. Experimental and quantum-chemical studies on the three-particle fragmentation of neutral triatomic hydrogen. *Phys. Rev. A*, 72:062506, 2005.
- [GFJ06] E. Garrido, D.V. Fedorov, and A.S. Jensen. Efimov effect in nuclear three-body resonance decays. *Phys. Rev. Lett.*, 96, 2006.
- [Gro37] T. H. Gronwall. The helium wave equation. *Phys. Rev.*, 51:655, 1937.
- [GS06] K. Giri and N. Sathyamurthy. Influence of reagent rotation on (H⁻, D₂) and (D⁻, H₂) collisions: A quantum mechanical study. J. Phys. Chem. A, 110:13843, 2006.
- [Gut98] M. C. Gutzwiller. Moon-Earth-Sun: The oldest three-body problem. Rev. Mod. Phys., 70:589, 1998.
- [HM96] M. J. Holman and N. W. Murray. Chaos in high-order mean motion resonances in the outer asteroid belt. Astron. J., 112:1278, 1996.
- [Ho83] Y. K. Ho. The method of complex coordinate rotation and its applications to atomic processes. *Phys. Rep.*, 99:1, 1983.
- [Ho97] Y. K. Ho. Resonances in three-body atomic systems involving positrons. *Chin. J. Phys.*, 35:97, 1997.
- [HSG97] E. Haufler, S. Schlemmer, and D. Gerlich. Absolute integral and differential cross sections for the reactive scattering of H⁻+D₂ and D⁻+H₂. J. Phys. Chem. A, 101:6441, 1997.

- [JFARG07] A. S. Jensen, D. V. Fedorov, R. Alvarez-Rodriguez, and E. Garrido. Efimov effect and three-body decay. *Nuc. Phys. A*, 787:553C, 2007.
- [Joh80] B. R. Johnson. On hyperspherical coordinates and mapping the internal configurations of a 3-body system. J. Chem. Phys., 73:5051, 1980.
- [Joh83] B. R. Johnson. The quantum dynamics of three particles in hyperspherical coordinates. J. Chem. Phys., 79:1916, 1983.
- [JP09] Ch. Jungen and S. T. Pratt. Jahn-Teller interactions in the dissociative recombination of H_3^+ . *Phys. Rev. Lett*, 102:023201, 2009.
- [KDKMS99] V. Kokoouline, O. Dulieu, R. Kosloff, and F. Masnou-Seeuws. Mapped Fourier methods for long range molecules: Application to perturbations in the Rb₂(0⁺_u) spectrum. J. Chem. Phys., 110:9865, 1999.
- [KG03] V. Kokoouline and C. H. Greene. Unified theoretical treatment of dissociative recombination of D_{3h} triatomic ions: Application to H_3^+ and D_3^+ . *Phys. Rev.* A, 68:012703, 2003.
- [KK86] R. Kosloff and D. Kosloff. Absorbing boundaries for wave-propagation problems. J. Comput. Phys., 63:363, 1986.
- [KMS06] V. Kokoouline and F. Masnou-Seeuws. Calculation of loosely bound levels for three-body quantum systems using hyperspherical coordinates with a mapping procedure. *Phys. Rev. A*, 73:012702, 2006.

- [KMW⁺06] T. Kraemer, M. Mark, P. Waldburger, J. G. Danzl, C. Chin, B. Engeser, A. D. Lange, K. Pilch, A. Jaakkola, H.-C. Nägerl, and R. Grimm. Evidence for Efimov quantum states in an ultracold gas of caesium atoms. *Nature*, 448:315, 2006.
- [KRZ90] D. A. V. Kliner, K. D. Rinnen, and R. N. Zare. The D+H₂ reaction comparison of experiment with quantum-mechanical and quasi-classical calculations. *Chem. Phys. Lett.*, 166:107, 1990.
- [Kup75] A. Kuppermann. Useful mapping of triatomic potential-energy surfaces. Chem. Phys. Lett., 32:374, 1975.
- [LAK07] B. Lepetit, R. Abrol, and A. Kuppermann. Geometric phase effects in H₃ predissociation. *Phys. Rev. A*, 76:040702, 2007.
- [LG08] S. Y. Lin and H. Guo. Energy dependence of differential and integral cross sections for $O(^1D)+H_2(\nu(i)=0, j(i)=0) \rightarrow OH(\nu(f), j(f))+H$ reaction. J. Chem. Phys., 129:124311, 2008.
- [LH61] H. C. Longuet-Higgins. *Advances in Spectroscopy*, volume II. Interscience, 1961.
- [Lin95] C. D. Lin. Hyperspherical coordinate approach to atomic and other Coulombic
 3-body systems. *Phys. Rep.*, 257:2, 1995.
- [LL89] J. M. Launay and M. Ledourneuf. Hyperspherical close-coupling calculation of integral cross-sections for the reaction $H+H_2 \rightarrow H_2+H$. Chem. Phys. Lett., 163:178, 1989.

- [LL91] B. Lepetit and J. M. Launay. Quantum-mechanical study of the reaction He+H₂⁺ \rightarrow HeH⁺+H with hyperspherical coordinates. J. Chem. Phys., 95:5159, 1991.
- [LL03] L. D. Landau and E. M. Lifshitz. *Quantum Mechanics: Non-relativistic Theory*.Burlington MA: Butterworth Heinemann, 2003.
- [LPB⁺08] X. Li, G. A. Parker, P. Brumer, I. Thanopulos, and M. Shapiro. Laser-catalyzed production of ultracold molecules: The ${}^{6}\text{Li}+{}^{6}\text{Li}{}^{7}\text{Li} \xrightarrow{\hbar\omega} {}^{6}\text{Li}{}^{6}\text{Li} + {}^{7}\text{Li}$ reaction. *Phys. Rev. Lett.*, 101:043003, 2008.
- [LPK90] B. Lepetit, Z. Peng, and A. Kuppermann. Calculation of bound rovibrational states on the 1st electronically excited-state of the H₃ system. *Chem. Phys. Lett.*, 166:572, 1990.
- [LR95] J. Laskar and P. Robutel. Stability of the planetary three-body problem. Celestial Mechanics and Dynamical Astronomy, 62:193, 1995.
- [MBK89] C. C. Marston and G. Balint-Kurti. The Fourier grid Hamiltonian method for bound state eigenvalues and eigenfunctions. J. Chem. Phys., 91:3571, 1989.
- [MJ05] C. Morari and R. Jaquet. Time-dependent reactive scattering for the system $H^-+D_2 \leftrightarrow HD+D^-$ and comparison with $H^-+H_2 \leftrightarrow H_2+H^-$. J. Phys. Chem. A, 109:3396, 2005.

- [MK98] S. Mahapatra and H. Koppel. Spectra and time-dependent dynamics of H₃ near the conical intersection in the (2p)1E' ground electronic manifold. J. Chem. Phys., 109:1721, 1998.
- [MKL⁺06] I. A. Mikhailov, V. Kokoouline, A. Larson, S. Tonzani, and C. H. Greene. Renner-Teller effects in HCO⁺ dissociative recombination. *Phys. Rev. A*, 74:032707, 2006.
- [Moi98] N. Moiseyev. Quantum theory of resonances: calculating energies, widths and cross-sections by complex scaling. *Phys. Rep.*, 302:211, 1998.
- [Mot08] A. K. Motovilov. Progress in methods to solve the Faddeev and Yakubovsky differential equations. *Few-body Sys.*, 43:121, 2008.
- [MRHM01] I. Mistrik, R. Reichle, H. Helm, and U. Muller. Predissociation of H₃ Rydberg states. *Phys. Rev. A*, 63:042711, 2001.
- [MRM⁺00] I. Mistrik, R. Reichle, U. Muller, H. Helm, M. Jungen, and J. A. Stephens. Ab initio analysis of autoionization of H₃ molecules using multichannel quantumdefect theory and new quantum-defect surfaces. *Phys. Rev. A*, 61:033410, 2000.
- [MZL96] H. Muller, M. Zimmer, and F. Linder. State-resolved measurements of rotational excitation in H⁻+H₂ collisions at low energies. J. Phys. B: At. Mol. Opt. Phys., 29:4165, 1996.
- [NFJG01] E. Nielsen, D. V. Fedorov, A. S. Jensen, and E. Garrido. The three-body problem with short-range interactions. *Phys. Rep.*, 347:373, 2001.

- [NJK⁺92] D. Neuhauser, R. S. Judson, D. J. Kouri, D. E. Adelman, N. E. Shafer, D. A. V. Kliner, and R. N. Zare. State-to-state rates for the $D+H_2(V = 1, J = 1) \rightarrow$ HD(V',J')+H reaction - predictions and measurements. *Science*, 257:519, 1992.
- [NSE02] E. Nielsen, H. Suno, and B. D. Esry. Efimov resonances in atom-diatom scattering. *Phys. Rev. A*, 66:012705, 2002.
- [PBP02] H. Prautzsch, W. Boehm, and M. Paluszny. Bezier and B-spline techniques. New York, NY: Springer, 2002.
- [PP87] R. T. Pack and G. A. Parker. Quantum reactive scattering in 3 dimensions using hyperspherical (APH) coordinates - theory. J. Chem. Phys., 87:3888, 1987.
- [PS04] A. N. Panda and N. Sathyamurthy. Dynamics of (H⁻,H₂) collisions: A timedependent quantum mechanical investigation on a new ab initio potential energy surface. J. Chem. Phys., 121:9343, 2004.
- [QB08] G. Quemener and N. Balakrishnan. Cold and ultracold chemical reactions of F+HCl and F+DCl. J. Chem. Phys., 128:224304, 2008.
- [QBK08] G. Quemener, N. Balakrishnan, and B. K. Kendrick. Quantum dynamics of the O plus $OH \rightarrow H+O_2$ reaction at low temperatures. J. Chem. Phys., 129:224309, 2008.

- [Rei02] R. Reichle. Exotic Species of Hydrogen: Experimental and Theoretical Studies of the Negative Ion and the Triatomic Molecule of Hydrogen. Ph.D. Thesis, Albert-Ludwigs-Universität, Freiburg, Germany, 2002.
- [RM93] U. V. Riss and H. D. Meyer. Calculation of resonance energies and widths using the complex absorbing potential method. J. Phys. B: At. Mol. Opt. Phys., 26:4503, 1993.
- [SGC⁺07] G. Smirne, R. M. Godun, D. Cassettari, V. Boyer, C. J. Foot, T. Volz, N. Syassen, S. Duerr, G. Rempe, M. D. Lee, K. Goral, and T. Koehler. Collisional relaxation of Feshbach molecules and three-body recombination in ⁸⁷Rb Bose-Einstein condensates. *Phys. Rev. A*, 75:020702(R), 2007.
- [SJBC85] V. Spirko, P. Jensen, P. R. Bunker, and A. Cejchan. The development of a new Morse-oscillator based rotation vibration Hamiltonian for H⁺₃. J. Mol. Spectrosc., 112:183, 1985.
- [Smi62] F. T. Smith. A symmetric representation for three-body problems. J. Math. Phys., 3:735, 1962.
- [SZM04] P. Search, W. Zhang, and P. Myestre. Inhibiting three-body recombination in atomic Bose-Einstein condensates. *Phys. Rev. Lett.*, 92:140401, 2004.
- [Tay72] J. R. Taylor. Scattering theory: the quantum theory on nonrelativistic collisions. New York, NY: Wiley, 1972.

- [Tie88] E. Tiemann. On the spectroscopic determination of potential functions with a barrier for diatomic-molecules. *Molec. Phys.*, 65:359, 1988.
- [TWM96] O. I. Tolstikhin, S. Watanabe, and M. Matsuzawa. 'Slow' variable discretization: A novel approach for Hamiltonians allowing adiabatic separation of variables. J. Phys. B: At. Mol. Opt. Phys., 29:L389, 1996.
- [VBK92] A. Vibók and G. G. Balint-Kurti. Parametrization of complex absorbing potentials for time-dependent quantum dynamics. J. Phys. Chem., 96:8712, 1992.
- [VBM⁺87] A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais. A double many-body expansion of the 2 lowest-energy potential surfaces and nonadiabatic coupling for H₃. J. Chem. Phys., 86:6258, 1987.
- [VDE07] J. S. Vaagen, B. V. Danilin, and S. N. Ershov. Continuum spectroscopy of halo nuclei. Int. J. Mod. Phys. E-Nuc. Phys., 16:1033, 2007.
- [VM88] D. A. Varshalovich and A. N. Moskalev. Quantum Theory of Angular Momentum. Singapore: World Scientific, 1988.
- [WDC55] E. Wilson, J. E. Decius, and P. C. Cross. Molecular Vibrations. New York, NY: McGraw-Hill Book Company, 1955.
- [Wik] Wikipedia. http://en.wikipedia.org/wiki/b-spline.
- [Wil92] S. Wilson. Methods in Computational Chemistry: Molecular Vibrations, volume 4. New York NY: Plenum Press, 1992.

- [Wil05] K. Willner. Theoretical study of weakly bound vibrational states of the sodium trimer : numerical methods; prospects for the formation of Na₃ in an ultracold gas. Thèse de doctorat (Ph.D Thesis) and Doktor der Naturwissenschaften Dr. rer. nat., Université Paris-Sud XI and Universität Hannover, Orsay (France) and Hannover (Germany), 2005.
- [WZ96] R. E. Wyatt and J. Z. H. Zhang. Dynamics of Molecules and Chemical Reactions. New York NY: Marcel Deker, 1996.
- [Yar96] D. R. Yarkony. Diabolical conical intersections. *Rev. Mod. Phys.*, 68:985, 1996.
- [YJCH06] L. Yao, L. Ju, T. Chu, and L. Han. Time-dependent wave-packet quantum scattering study of the reactions $D^-+H_2 \rightarrow H^-+HD$ and $H^-+D_2 \rightarrow D^-+HD$. *Phys. Rev. A*, 74:062715, 2006.
- [ZDF⁺93] M. V. Zhukov, B. V. Danilin, D. V. Fedorov, J. M. Bang, I. J. Thompson, and J. S. Vaagen. Bound-state properties of Borromean halo nuclei - He-6 and Li-11. *Phys. Rep.*, 231:151, 1993.
- [ZL92] M. Zimmer and F. Linder. State-resolved energy and angular differential measurements of the product distribution in the rearrangement reaction $H^- + D_2$ $\rightarrow HD(v') + D^-$. Chem. Phys. Lett., 195:153, 1992.
- [ZL95] M. Zimmer and F. Linder. Crossed-beam study of the $H^-+D_2 \rightarrow HD(v')+D^$ rearrangement reaction in the collision energy-range 0.3-3 eV. J. Phys. B: At. Mol. Opt. Phys., 28:2671, 1995.

[ZXLG08] S. Zhou, D. Xie, S. Y. Lin, and H. Guo. A new ab initio potential-energy surface for $NH_2(X^2A'')$ and quantum studies of NH_2 vibrational spectrum and rate constant for the $N(^2D)+H_2 \rightarrow NH+H$ reaction. J. Chem. Phys., 128:224316, 2008.