A Theoretical Study of AtomicTrimers in the Critical Stability Region

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A Theoretical Study of Atomic Trimers in the Critical Stability Region
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Abstract

When studying the structure formation and fragmentation of complex atomic and nuclear systems it is preferable to start with simple systems where all details can be explored. Some of the knowledge gained from studies of atomic dimers can be generalised to more complex systems. Adding a third atom to an atomic dimer gives a first chance to study how the binding between two atoms is affected by a third. Few-body physics is an intermediate area which helps us to understand some but not all phenomena in many-body physics.

Very weakly bound, spatially very extended quantum systems with a wave function reaching far beyond the classical forbidden region and with low angular momentum are characterized as halo systems. These unusual quantum systems, first discovered in nuclear physics may also exist in systems of neutral atoms.

Since the first clear theoretical prediction in 1977, of a halo system possessing an Efimov state, manifested in the excited state of the bosonic van der Waals helium trimer $^2\text{He}_3$, small helium and different spin-polarised halo hydrogen clusters and their corresponding isotopologues have been intensively studied the last three decades.

In the work presented here, the existence of the spin-polarized tritium trimer ground state, $^3\text{H}_3$, is demonstrated, verifying earlier predictions, and the system’s properties elucidated. Detailed analysis has found no found evidence for other bound states and shape resonances in this system.

The properties of the halo helium trimers, $^2\text{He}_3$ and $^4\text{He}_2\text{-}^3\text{He}$ have been investigated. Earlier predictions concerning the ground state energies and structural properties of these systems are validated using our three-dimensional finite element method.

In the last part of this work we present results on the bound states and structural properties of the van der Waals bosonic atomic trimers Ne$_3$ and Ar$_3$. We believe to be the first to find evidence of a possible shape resonance just above the three-body dissociation limit of the neon trimer.
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Publications and Author’s contribution

[1] **Search for bound and quasibound states in the spin-polarized atomic tritium trimer.**

In this paper, I did all calculations in close collaboration with my supervisors. I wrote the paper.

[2] **Finite element investigation of the ground states of the helium trimers \( ^4\)He\(_3\) and \( ^4\)He\(_2\)^2He.**

In this paper, I did all calculations with several important suggestions from Evgeny Yarevsky and my supervisors. I wrote the paper.

[3] **Predissociation and rovibrational calculations of the bosonic van der Waals neon trimer.**

In this paper, I did all calculations with a few discussions with Evgeny Yarevsky and my supervisors. I wrote the paper.

[4] **Calculation of the vibrational bound states and structural properties of the weakly bound bosonic atomic argon trimer Ar\(_3\).**

I did everything.
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Chapter 1

Introduction

Quantum mechanics is a microscopic theory which is used when studying atomic phenomena, that is physical systems in the atomic scale, composed of particles of very small mass, e.g. electrons, protons, neutrons, atomic nuclei, systems of atoms, and chemical and biological systems, such as proteins, enzymes and DNA.

Since 80 years of its birth, quantum mechanics is still the only acceptable theory in the study of microscopic systems.

In this thesis we apply quantum mechanics to study three-body problems. The formal and numerical approaches, used in this work, are in principle applicable to any three-body system. Examples of such systems are, in atomic physics, e.g. the helium atom He \([3, 4, 5]\), the antiprotonic helium system \([-pHe^+e^- \ [6, 7], \) and \(H^- \ [8, 9]\); in nuclear physics, \({}^3\)He, \({}^6\)He, and \({}^{11}\)Li \([10, 11, 12]\), and in molecular physics, the van der Waals (vdW) halo atomic helium trimers \(\ell He_3\), and \(\ell^2He_2\) \([13, 14, 15, 16, 17, 18, 19]\), the spin-polarized halo atomic tritium trimer \(\ell^2H_3\) \((T^\uparrow_3\) \([20, 21]\), and the NeICl molecule \([22, 23, 24]\).

In atomic physics, e.g. the helium atom, being composed of two electrons and an alpha particle, the total (non-relativistic) potential of the system is known exactly; it is a sum of three pairwise long-range Coulomb potentials. In molecular or nuclear (three-body) systems, we do not know the potential exactly. Here the three particles are complex, i.e. composed of other particles. This means that the total potential of the (three-body) system can no longer be written as a sum of atom-atom or nucleon-nucleon interactions, since the total effective potential is

---

1There are however so called semi-classical methods \([1, 2]\), i.e. methods in which classical and quantum mechanics are combined to study e.g. molecular dynamic processes \([1, 2]\). The reason of this combination of two different disciplines of physics is mainly due to computational efficiency as the equations in quantum mechanics are in general more complicated to solve than the classical equations of motion. Note that the physical system in question must fulfill certain conditions in order for such methods to be legitimate for application.

2In general in atomic physics, the atomic nucleus is considered as a structureless particle of charge \(Ze\), where \(Z\) and \(e\) are here the atomic number and charge of the electron respectively. Therefore to an extremely good accuracy the potential is of Coulombic nature.

3In molecular physics, as in atomic physics, all interactions are governed by the Coulomb potential. However, within the Born-Oppenheimer approximation or the adiabatic approximation (see Chapter 2), the potential is not known exactly. In nuclear physics, as the interactions there are still not fully understood, the effective potential must often rely on experimental data.
dependent on the correlation of all particles in the system. Three-body corrections to the potential of the three-body system may thus in general be important.

This argument serves as a motivation for the importance of the study of small clusters of complex particles, in any area of quantum mechanics. Important information on inter-particle interactions and higher-body corrections may be revealed which in turn may be of fundamental importance in the study of larger more complex systems, such as superfluidity of finite-sized clusters of atoms \([25, 26, 27, 28]\). Besides this, the study of small clusters may give ready information of fundamental quantum mechanical effects occurring in few-body physics. In particular, the helium trimer \(\text{He}_3\) is predicted to possess a so called Efimov state \(^5\) manifested in its excited state \([29, 30, 13, 11, 15]\).

These loosely bound systems are interesting as such since they may be observed using laser cooling, magnetic tuning and other methods \([31, 32, 33, 34]\). Few-body systems in which the interaction takes place through very weak forces have recently become important since they may be active in forming stable structures at low temperatures \([35]\). These systems are also important when understanding ultracold atomic collisions and Bose-Einstein condensates in various aggregates \([36, 20]\).

The major part of this work is the study of vdW atomic trimers. vdW clusters are in general characterized as weakly bound complexes of closed shell atoms or molecules with relatively small dissociation energies of typically a few cm\(^{-1}\) to about 1000 cm\(^{-1}\), and with large bond lengths about 3-4 Å \([1, 37]\). Due to this, vdW clusters are only stable at very low temperatures, many of which may dissociate by a single infrared photon by the breaking of a vdW bond. The interaction potentials of these complexes along the vdW bonds are dominated by long-range attractive dispersion forces of dipole-dipole nature, the interaction potential behaving as \(r^{-6}\), where \(r\) is the vdW bond distance \(^6\). Due to the relatively weak coupling between the vdW modes a weak restoring force is present along the vdW bond distance, making the complex diffuse and unstructured in space.

In this work we studied the properties of the vdW atomic helium trimers \(\text{He}_3\), \(\text{He}_2\text{-}^3\text{He}\), and the neon \(\text{Ne}_3\) and argon \(\text{Ar}_3\) trimers, (see more in Papers 2-4). The above mentioned helium trimers together with the Borromean \(^7\) spin-polarized tritium trimer \(^3\text{H}_3\) (see Paper 1), are classified as atomic halo trimers \(^8\). Halo systems exhibit some unusual quantum characteristics, such as very weakly binding energies, with an abnormally large spatial extent of the nuclear wave function, reaching far outside the classical forbidden region. Since halos are so weakly bound, these clusters are only stable at very low temperatures, and for low total angular momentum \(^9\).

Accurate calculations of small halo clusters including vdW clusters in general, are, however, challenging, mainly due to their strongly anharmonic potential surfaces implying diffuse and delocalized probability distributions of the wave

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\(^4\)See more in Chapter 2.

\(^5\)For a qualitative discussion on Efimov states see Chapter 3.

\(^6\)See more details in Chapter 2.

\(^7\)See the definition of a Borromean system in Chapter 3.

\(^8\)Halos were first discovered in the nuclear domain, see more in Chapter 3.

\(^9\)In fact the above mentioned atomic halo trimers dissociate by a single rotational quanta, i.e. they only exist as bound states for total zero angular momentum.
function in configuration space. vdW clusters such as the helium trimer may impose numerical problems due to the hard-core structure of the potential, if not properly treated. Calculating resonance states of halos and vdW clusters is even a harder task than bound state calculations. From a computational perspective such threshold states are difficult to obtain, since they lead to representations having very small and very large eigenvalues. As such, calculations of atomic halos and vdW trimers provide a challenge for any formal/numerical method [13, 15, 14, 17, 16, 18, 19, 24, 38, 39, 40, 41].
Chapter 2

Theory

From a computational point of view, the three-body problem is much more difficult to solve than the two-body problem. The two-body problem in atomic and molecular physics which includes several modes of motion (electronic states) can be solved “numerically exact” to an accuracy beyond what is possible in most experiments. However, general three-body problems can only be solved “numerically exact” for a single mode of the electronic motion. To describe several modes of electronic motion in an atomic trimer, formal approximations need to be made to be able to obtain a numerical solution. This is one of the reasons of the very popular use of the Born-Oppenheimer approximation and the adiabatic approximation, both described below.

Depending on the three-body problem studied, the appropriate choice of coordinate system, the representation of the total rovibrational wave function and the exploitation of symmetry may be crucial for the efficiency of the numerical treatment.

Three-body cluster problems which energetically lie just above the fragmentational limits are in general difficult problems to solve. Different methods to treat such resonance problems are described below, including the very popular and successful complex scaling method to calculate resonance positions, widths and cross sections.

2.1 Adiabatic Representation

The non-relativistic Hamiltonian operator $\hat{H}$ for a closed-field, free, many-atomic system may be written as

$$\hat{H} = [H_{el}] + [H_{nu}] = \left[ -\frac{1}{2} \sum_i \Delta_i + \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_{i,\alpha} \frac{Z_\alpha}{r_{i\alpha}} \right]$$

$$+ \left[ -\frac{1}{2} \sum_\alpha \frac{1}{m_\alpha} \Delta_\alpha + \sum_{\alpha,\beta>\alpha} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \right]. \quad (2.1.1)$$
Here $\Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ denotes the Laplace operator of electron $i$ and similarly $\Delta_\alpha$ of nuclei $\alpha$. Furthermore, $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and $r_{\alpha\beta} = |\vec{r}_\alpha - \vec{r}_\beta|$ are the distance between the electrons $i$ and $j$ and the nuclei $\alpha$ and $\beta$, respectively. Here $Z_\alpha$ and $m_\alpha$ denotes the charge and mass of nuclei $\alpha$, respectively. Atomic units are used throughout ($e = m_e = \hbar = 1$) unless stated otherwise.

The first parenthesis in eq. (2.1.1) corresponds to the electronic Hamiltonian operator, $\hat{H}_{el}$, which contains the operators for the electronic kinetic energy, the electron-electron repulsion potential, and the electron-nucleus attraction potential. The second parenthesis corresponds to the nuclear Hamiltonian operator, $\hat{H}_{nu}$, which contains the nuclear kinetic energy operators and the nucleus-nucleus repulsion potentials.

Let $|\{\xi\}\rangle$ denote the quantum state of the whole closed system. Here, $\{\xi\}$ is the complete set of all simultaneously measurable physical observables which characterise the quantum state, e.g. the energy, total angular momentum, spin, and parity. The Schrödinger (S.E.) equation for this state with total energy, $E$, is given by

$$\hat{H}|\{\xi\}\rangle = E|\{\xi\}\rangle. \tag{2.1.2}$$

Here a suitable complete position basis set, $|\vec{r}_i, \vec{r}_\alpha\rangle$, of the spatial coordinates of all nuclei and electrons is used to correctly, and simply, represent the wave function of this state. Therefore, the state, $|\{\xi\}\rangle$, is expanded in the complete position basis set, $|\vec{r}_i, \vec{r}_\alpha\rangle$, as

$$|\{\xi\}\rangle = \int d\vec{r}_i d\vec{r}_\alpha |\vec{r}_i, \vec{r}_\alpha\rangle \langle \vec{r}_i, \vec{r}_\alpha|\{\xi\}\rangle \tag{2.1.3}$$

where

$$\Psi_{\{\xi\}}(\vec{r}_i, \vec{r}_\alpha) = \langle \vec{r}_i, \vec{r}_\alpha|\{\xi\}\rangle = \Psi_{tot}(\vec{r}_i, \vec{r}_\alpha) \tag{2.1.4}$$

denotes the wave function of the state, $|\{\xi\}\rangle$, in the basis, $|\vec{r}_i, \vec{r}_\alpha\rangle$. Note that the completeness relation has been used, i.e.

$$\int d\vec{r}_i d\vec{r}_\alpha |\vec{r}_i, \vec{r}_\alpha\rangle \langle \vec{r}_i, \vec{r}_\alpha| = 1. \tag{2.1.5}$$

The S.E. for the wave function, $\Psi_{tot}(\vec{r}_i, \vec{r}_\alpha)$, of the state, $|\{\xi\}\rangle$, is then written as

$$\hat{H}\Psi_{tot}(\vec{r}_i, \vec{r}_\alpha) = E\Psi_{tot}(\vec{r}_i, \vec{r}_\alpha). \tag{2.1.6}$$

Since the mass of the electrons, $m_{el}$, is much smaller than that of the nuclei, $m_{nu}$, i.e. $m_{el} << m_{nu}$, the electrons move much faster than the nuclei. If, for the present discussion, all nuclei are treated as particles with fixed coordinates when considering the motion of the electrons, the S.E. reduces to

$$\left[\hat{H}_{el}(\vec{r}_i, \vec{r}_\alpha) + V_{nu,nu}(\vec{r}_\alpha)\right] \psi_{el,n}(\vec{r}_i; \vec{r}_\alpha) = U_n(\vec{r}_\alpha) \psi_{el,n}(\vec{r}_i; \vec{r}_\alpha), \tag{2.1.7}$$

where $V_{nu,nu}$ is the nuclear-nuclear interaction term defined in eq. (2.1.1). The solutions of eq. (2.1.7), i.e. the eigenfunctions, $\psi_{el,n}(\vec{r}_i; \vec{r}_\alpha)$, and eigenvalues, $U_n(\vec{r}_\alpha)$,
are called the adiabatic eigenfunctions and adiabatic eigenvalues, respectively [2, 37, 1], corresponding to the quantum electronic state, \( n \). The eigenfunctions, \( \psi_{el,n} \), form a complete orthonormal set and parametrically depend on the nuclear configurations, \( \vec{r}_\alpha \). The set of all eigenvalues, \( \{ U_n \} \), represents the electronic energy including the inter-nuclear potentials. These eigenvalues are equal to the total energy of the system for the fixed configuration of the nuclei.

The total wave function, \( \Psi_{tot}(\vec{r}_i, \vec{r}_\alpha) \), may be expanded in the complete orthonormal set of adiabatic functions, \( \psi_{el,n}(\vec{r}_i; \vec{r}_\alpha) \), as

\[
\Psi_{tot}(\vec{r}_i, \vec{r}_\alpha) = \sum_n \phi_{nu,n}(\vec{r}_\alpha) \psi_{el,n}(\vec{r}_i; \vec{r}_\alpha). 
\] (2.1.8)

The expansion coefficients, \( \phi_{nu,n}(\vec{r}_\alpha) \), in eq. (2.1.8) are defined as the nuclear wave functions in the adiabatic representation [2, 37, 1]. Inserting eq. (2.1.8) into eq. (2.1.6), and multiplying by \( \psi_{el,m}^\ast \) on the left and then integrating over the electronic coordinates, a set of coupled partial differential equations can be derived

\[
\left[ T_{nu}(\vec{r}_\alpha) + U_m(\vec{r}_\alpha) \right] \phi_{nu,m}(\vec{r}_\alpha) + \sum_n S_{mn}(\vec{r}_\alpha) \phi_{nu,n}(\vec{r}_\alpha) = E \phi_{nu,m}(\vec{r}_\alpha). 
\] (2.1.9)

Here the diagonal terms, \( U_m \), are called adiabatic potentials [2, 37, 1], and can be thought of as the effective potentials in which the nuclei move. The influence of the nuclear Laplace operator, in eq. (2.1.1), on the different adiabatic eigenfunctions, \( \psi_{el,n} \), characterises \( S_{mn} \), which is the non-adiabatic coupling matrix element operator given by

\[
S_{mn}(\vec{r}_\alpha) = \sum_\alpha \frac{1}{m_\alpha} \left( G^{\alpha}_{mn} \frac{\partial}{\partial \vec{r}_\alpha} + \frac{1}{2} K^{\alpha}_{mn} \right). 
\] (2.1.10)

Here the non-diagonal matrices, \( G^{\alpha} \) and \( K^{\alpha} \), are defined as

\[
G^{\alpha}_{mn} = \langle \psi_{el,m} \mid \frac{\partial}{\partial \vec{r}_\alpha} \mid \psi_{el,n} \rangle, 
\] (2.1.11)

\[
K^{\alpha}_{mn} = \langle \psi_{el,m} \mid \frac{\partial^2}{\partial \vec{r}_\alpha^2} \mid \psi_{el,n} \rangle, 
\]

respectively. It is concluded from eq. (2.1.9) that in the adiabatic representation the potential energy is diagonal while the kinetic energy is not given by

\[
T_{mn}(\vec{r}_\alpha) = T(\vec{r}_\alpha) \delta_{mn} + S_{mn}(\vec{r}_\alpha). 
\] (2.1.12)

It is noted that no approximations have been made whatsoever so far, and eq. (2.1.9) is exact. However, to solve the coupled channel problem (2.1.9) in practice is very difficult due to the non-adiabatic coupling matrix in eq. (2.1.10). In general, however, the off-diagonal kinetic energy terms are very small and it is often a good approximation to neglect them. This approximation can be justified due to the huge difference in the mass of the nuclei and the electrons, implying much bigger electronic kinetic energies than the nuclear kinetic energies. As such, the electrons adapt almost perfectly to the nuclear motion. Thus, if the nuclear kinetic energy
is much smaller than the energy gap between the different adiabatic electronic states, the non-adiabatic couplings terms will be very small and the probability of mixing between different electronic states is also very small; only distortions of the electronic states will occur. In this framework the nuclei will move on a single potential energy surface. This approximation is called the adiabatic approximation \[2, 37, 1\]. Eq. (2.1.9) can then be decoupled with the corresponding Hamiltonian reducing to

\[
\hat{H}^{ad} = \hat{T}_{nu} + U_n + S_{nn}.
\]

The wave function of the whole system may then be written as a single product

\[
\Psi_{\text{tot}}(\vec{r}_i, \vec{r}_\alpha) = \psi_{\text{el}}(\vec{r}_i; \vec{r}_\alpha) \phi_{\text{nu}}(\vec{r}_\alpha).
\]

Another approximation that usually proves to be useful is to neglect the diagonal final term, \(S_{nn}\), in eq. (2.1.10). This is justified due to the generally very weak dependence of the electronic wave function on the nuclear coordinates. This term is thus often neglected in comparison to the adiabatic potential, \(U_n\). This results in the Born-Oppenheimer approximation \[2, 37, 1\]. The S.E. now reduces to

\[
\left[\hat{T}_{nu}(\vec{r}_\alpha) + U_n(\vec{r}_\alpha)\right] \phi_{nu,n}(\vec{r}_\alpha) = E\phi_{nu,n}(\vec{r}_\alpha).
\]

Throughout this thesis the Born-Oppenheimer approximation is used and which implies that the Schrödinger equation is solved using a single potential energy surface. As such, solutions are obtained neglecting those terms which are in general very small in the exact Hamiltonian, and which represent the interaction between the nuclear and electron motions that give rise to couplings between different electronic states \[1\], e.g. Feshbach type resonances \[42\]. Feshbach resonances may occur when there is interaction between a vibrational coordinate of one electronic state and bound levels of another electronic state. Fragmentation processes which are related to the shape of a single potential energy surface are an integral part of the theoretical framework in the present study.

From a general, physical perspective, both classically and quantum mechanically, an adiabatic process is characterised as a process in which a system’s physical environment changes very slowly relative to the internal motion of the system. If this slow motion of the environment does not change the internal motion of the physical system, then this characterises an adiabatic process. In our case, treating atomic trimers, the nuclei are considered as representing the environment and the electrons the internal physical system. The adiabatic condition may be formulated as a theorem as follows: A quantum system that is characterised by some initial quantum numbers will preserve its quantum numbers in an adiabatic process. For a proof see Ref. \[43\]. More concretely, if the system is described by a Hamiltonian

---

1In general the probability of an electronic transition increases with the dimensionality of the system, i.e. the number of atoms in the cluster. Simply, when the number of atoms increase so does the number of electrons. The greater the number of electrons, the more ways are there to distribute them among the different energy levels in the cluster of atomic nuclei (each distribution corresponding to a unique potential energy surface). This implies more potential surfaces and thus higher probability of surface crossings. However, it turns out that surface crossings are more important for light clusters of atoms. This may be simply understood by the expression of the non-diagonal coupling matrix in eq. (2.1.10).
that changes slowly along some coordinate, from some initial Hamiltonian, $H^i$, to some final form, $H^f$, the particle in the $n$th state of $H^i$ will still stay in the $n$th state of $H^f$, i.e. no transitions will occur. Note that the theorem just stated has one criterion: the environment must also change very slowly relative to the motion of the internal system. In contrast to the framework of perturbation theory where one considers small changes, often over short periods of time, the current framework involves changes that may be large but which must take place during an, in principle, infinite long time but, in practice, a finite time.

2.2 Modeling of Quantum Three-Body Systems

2.2.1 Coordinate Systems and Three-Body zero Angular Momentum Hamiltonian

Any system with $N$ particles has $3N$ degrees of freedom. If the particles are not positioned on a straight line, the degrees of freedom may be reduced to $3N-3$ [44]. Three degrees of freedom correspond to the rotational motion of the system as a whole and the rest describe the vibrational motion of the system $^2$. It is noted that the three variables describing the translational motion, i.e. centre of mass motion c.m., have been neglected. It is also noted that the reduction of the variables of any system corresponding to c.m. is possible only if the potential of the system $V$ in the Schrödinger equation is invariant to translation of the c.m., i.e. $V$ is only a function of the relative coordinates of the particles.

In the particular case of three particles and excluding only the c.m. motion, the rotating system possess six degrees of freedom; three correspond to the internal motion in the plane spanned by the three particles and three correspond to the rotational motion of the plane as a whole with respect to the space-fixed (SF) coordinate system.

Several different coordinate systems are available when treating three-body systems. A few of these are the Jacobi [1, 2, 7], hyperspherical [2, 15, 45], normal [1, 40], inter-atomic [46, 47] and Pekeris coordinates [48, 38]. In general, all of these are well suited when considering bound state calculations of the nuclear S.E. However, depending on the physical system studied, the appropriate choice of coordinate system may be crucial for the efficiency of the numerical treatment. The use of inter-atomic coordinates, for example, may impose inaccuracies at collinear configurations if not properly treated. This is discussed further in Paper 3. Normal coordinates, on the other hand, are well known to be impractical for highly vibrational states and are completely useless when treating fragmentation processes. Hyper-spherical coordinates, for $J = 0$, consist of a hyper-radius, providing the size of the cluster, and two hyper-angles, describing the radial and angular correlation of the three-body system, respectively. This coordinate system is particularly interesting since the three-dimensional problem now reduces to a one-dimensional hyper-radial problem, with a set of effective potentials obtained by solving a two-dimensional equation [15, 45]. Pekeris coordinates are especially convenient when

$^2$For a linear system, i.e. when all particles lie in a straight line, there are $3N-2$ degrees of freedom.
describing the wave function and the relative importance of different configurations of the system.

In describing most scattering processes, Jacobi coordinates are known to be a suitable choice and, in general, work equally well in bound state calculations for any three-body system, e.g. the extremely delocalised helium trimer systems (see Paper 2). As such, Jacobi-coordinates, \( \vec{R} = (x, y, z) \), have been used here to describe the internal motion of the three-body system, see Figure 2.1.

Here, \( x \) is the distance between particle 2 and 3, \( y \) is the distance between particle 1 and c.m. of the pair \( (2, 3) \), and \( \theta \) the angle between the vectors \( \vec{x} \), and \( \vec{y} \) and \( z = \cos \theta \). The inter-particle distances, \( r_{ij} \), are related to the Jacobi coordinates as

\[
\begin{align*}
r_{23} &= x, \\
r_{12} &= \left( y^2 + \frac{2m_2}{m_2 + m_3} xy \cos \theta + \left( \frac{m_2}{m_2 + m_3} - x \right)^2 \right)^{1/2}, \\\nr_{13} &= \left( y^2 - \frac{2m_3}{m_2 + m_3} xy \cos \theta + \left( \frac{m_3}{m_2 + m_3} - x \right)^2 \right)^{1/2}.
\end{align*}
\]

An advantage of Jacobi coordinates is their orthogonality, i.e. the kinetic energy operator is diagonal, meaning that there is no mixing of the different derivatives. The Hamiltonian operator, \( \hat{H} \), for any three-body system with zero total orbital angular momentum, \( J = 0 \), is expressed in Jacobi coordinates by [1]

\[
\begin{align*}
\hat{H} &= -\frac{1}{2\mu_{23}} \Delta_x - \frac{1}{2\mu_{1,23}} \Delta_y + V(x, y, \theta) = \left(- \frac{1}{2\mu_{1,23}} \frac{\partial^2}{\partial y^2} y + \frac{1}{2\mu_{23}} \frac{\partial^2}{\partial x^2} x \right) \\
&+ \frac{1}{2} \left( \frac{1}{\mu_{1,23} y^2} + \frac{1}{\mu_{23} x^2} \right) \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right) + V(x, y, \theta). \quad (2.2.1)
\end{align*}
\]
where $V(x, y, \theta)$ is the interaction potential, and the reduced masses, $\mu$, have been defined in terms of the particle masses, $m_i, i = 1, 2, 3$, as $\mu_{23} = m_2m_3/(m_2 + m_3)$, $\mu_{1,23} = m_1(m_2 + m_3)/[m_1 + (m_2 + m_3)]$, respectively.

2.3 Total Angular Momentum Representation of Quantum Three-Body Systems and the non-zero Angular Momentum Hamiltonian

Consider an isolated three-body system described by the quantum state, $|J, m, \rho\rangle$, where $J$ is the total orbital angular momentum, $m$ the projection of $J$ along the SF $z$-axis, and $\rho$ the spatial parity of the system. This state can then be rotated by an arbitrary unitary rotation operator, $\hat{D}^\dagger(\vec{\Omega}) = \hat{D}^{-1}(\vec{\Omega})$, i.e. $\hat{D}(\vec{\Omega})|J, m, \rho\rangle$, where $\vec{\Omega}$ specifies the Euler angles $\alpha, \beta, \gamma$ [44, 49]. It is noted that the Euler angles in quantum mechanics, just as in a classical description of rigid bodies, provide the most general rotation of any physical system in three dimensions, see Figure 2.2.

In general, when rotating the coordinate system, states differing from the original state will be obtained, i.e. states with different projections in the SF frame, while $J$ and $\rho$ remain conserved. The state will only be unchanged when rotating the coordinate system around the SF $z$-axis, apart from an unimportant phase factor. Any other rotation of the system of particles, i.e. around any other specified axis in the SF frame will result in a non-definite $m$-value.
Formally

\[ \hat{D}(\vec{\Omega})|J, m, \rho\rangle = \sum_{m'} |J, m', \rho\rangle \langle J, m', \rho| \hat{D}(\vec{\Omega})|J, m, \rho\rangle \] (2.3.1)

\[ = \sum_{m'} D^{(J)}_{m'm'}(\vec{\Omega}) |J, m', \rho\rangle, \] (2.3.2)

where

\[ D^{(J)}_{m'm}(\vec{\Omega}) = \langle J, m', \rho| \exp \left( -\frac{i \vec{J} \cdot \hat{n} \phi}{\hbar} \right) |J, m, \rho\rangle \] (2.3.3)

\[ = \langle J, m', \rho| \exp \left( -\frac{i J_z \alpha}{\hbar} \right) \exp \left( -\frac{i J_y \beta}{\hbar} \right) \exp \left( -\frac{i J_z \gamma}{\hbar} \right) |J, m, \rho\rangle \]

\[ = \exp \left( -i (m' \alpha - m \gamma) \right) d_{m'm}(\beta) \]

is the Wigner D-function (coefficient) \([44, 49]\) and is the amplitude that the rotated state is in the state \(|J, m', \rho\rangle\). The explicit expression of the unitary rotation operator, \(\hat{D}(\vec{\Omega}) = \exp \left( -\frac{i \vec{J} \cdot \hat{n} \phi}{\hbar} \right)\), with \(\vec{J}\) and \(\hat{n}\) denoting the total angular momentum vector and the unit vector determining the direction of rotation, respectively, has been used. Here, the angle \(\phi\) is the finite angle of rotation. A more detailed discussion on the non-diagonal matrix, \(d^J(\beta)\), and the rotation matrix orthogonality and its various symmetry properties can be found in \([50, 44]\). The Wigner coefficients, \(D^{(J)}_{m'm}(\vec{\Omega})\), are the elements of a rotation matrix of dimension \((2J + 1)\) corresponding to a total angular momentum \(J\). Each \(J\)-matrix is, from group theory, called the irreducible representation of the operator \(\hat{D}(\vec{\Omega})\) \([50, 44, 49]\). Thus, in general, when considering any rotation around an axis in a laboratory fixed frame, and in a field free environment, i.e. in an isotropic space, the full rotation matrix will be decomposed into several blocks of irreducible representations, each specified by its corresponding quantum number \(J\). This means that there is a \((2J + 1)\)-fold degeneracy of the system, as a whole, with respect to directions of the total angular momentum relative to a fixed coordinate system.

The degeneracy in the direction of \(J\) along a so called body-fixed (BF) \([51, 1, 2]\) axis in a body fixed coordinate system, a coordinate system rigidly fixed to the (three-body) physical system is not generally present. As such, when considering \(J\) distributed along the body-fixed axis, the rotational energy levels will generally be non-degenerate. In the particular case of asymmetric tops, i.e. systems with three different moments of inertia, there is no degeneracy of the rotational levels with respect to projections along the body-fixed axis \([44]\).

In the current approach the wave function of the quantum state, \(|J, m, \rho\rangle\), may be expanded in terms of an orthogonal set of symmetrical Wigner D-functions \([50, 52]\), in a so called parity adapted expansion \([51]\)

\[ \Psi^{Jm\rho} = \sum_{s=0,1} \frac{1}{\sqrt{2 + 2s_0}} \left[ D^{(J)}_{m's}(\vec{\Omega}) + \rho(-1)^s D^{(J)}_{m'-s}(\vec{\Omega}) \right] \psi^{(J\rho\rho)}(\vec{R}), \] (2.3.4)

11
where $\alpha, \beta,$ and $\gamma$ are the set of Euler angles that specify the rotation of the body-frame with respect to the laboratory fixed frame. The three dimensional body-fixed coordinate, $\mathbf{R}$, describes the dynamics of the three-particle system, and has been chosen to be Jacobi coordinates. The index $s$, the helicity quantum number, is the projection of $J$ on the body-fixed quantisation axis. $s$ varies as $s = 0, \ldots, J$ for positive parity $\rho = +1$, and as $s = 1, \ldots, J$ for negative parity $\rho = -1$. States with both parities may be considered within the present formalism. In the following discussion the sign specifying the parity of the wave function has been omitted.

Substituting eq. (2.3.4) into the Schrödinger equation and using an orthogonality relation for $D$-functions [50, 44] the following system of equations is derived [52]

\[-i\sqrt{1 + \delta_{s1}} \frac{\lambda_-(J, s)}{2\mu_{1,23}y^2} \left( \frac{\partial}{\partial \theta} + (1 - s) \cot \theta \right) \psi^{(Js-1)} + \left[ -\Delta_x^{(s)} - \Delta_y^{(s)} + V(x, y, \theta) - E \right] \psi^{(Js)} - i\sqrt{1 + \delta_{s0}} \frac{\lambda_+(J, s)}{2\mu_{1,23}y^2} \left( \frac{\partial}{\partial \theta} + (1 + s) \cot \theta \right) \psi^{(Js+1)} = 0. \tag{2.3.5}\]

The diagonal components, $\Delta_x^{(s)}$, of the kinetic energy operator are defined as follows

\[-\Delta_x^{(s)} = -\frac{1}{2\mu_{23}} \frac{1}{x^2} \left( x \frac{\partial^2}{\partial x^2} x + \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - \frac{s^2}{\sin^2 \theta} \right) \right), \tag{2.3.6}\]

\[-\Delta_y^{(s)} = -\frac{1}{2\mu_{1,23}} \frac{1}{y^2} \left( y \frac{\partial^2}{\partial y^2} y - (J(J + 1) - 2s^2) - \frac{\partial^2}{\partial \theta^2} - \cot \theta \frac{\partial}{\partial \theta} - \frac{s^2}{\sin^2 \theta} \right). \tag{2.3.7}\]

Here, both $\lambda_{\pm}(J, s) = [J(J + 1) - s(s \pm 1)]^{1/2}$ and $\psi^{(Js-1)} \equiv 0$. The components, $\psi^{(Js)}$, must satisfy the boundary conditions with respect to the angle, $\theta$, such that

\[\psi^{(Js)}(x, y, \theta) = \sin^s \theta \left( \tilde{\psi}^{(Js)}(x, y, \theta) \right), \tag{2.3.8}\]

where $\tilde{\psi}^{(Js)}(x, y, \theta)$ is a bounded function of its arguments.

From the coupled equations, (2.3.5), it is concluded that in the representation of the wave function in eq. (2.3.4), the potential matrix is diagonal with respect to different helicity quantum numbers, $s$. It is noted that this is valid only when considering potentials that are angular independent. The full Hamiltonian matrix for each $J$ will be decomposed into two independent blocks corresponding to the two different parities $\rho = \pm 1$. A very important property of the Hamiltonian matrix is its tridiagonality with respect to the helicity quantum numbers, i.e. only the components $\psi^{(Js-1)}$, $\psi^{(Js)}$ and $\psi^{(Js+1)}$ are coupled to each other. This reduces the computational cost in the solution of the eigenvalue problem significantly.
2.4 Symmetry

An important theorem in mathematical group theory, called the vanishing integral rule \[ 53, 44\], states that the integral of any physical observables operator, with respect to some basis, is zero whenever the integrand of the integral does not belong to the totally symmetric species \( \Gamma^{(s)} \). Here \( \Gamma^{(s)} \) refers to a species that is in general symmetric with respect to all kind of symmetry transformations of the physical system, e.g. reflections in planes, rotations about different axes, inversions and permutation of particles.

More formally, consider the integral
\[
\langle \beta | \hat{S} | \alpha \rangle = \int \psi^{(\beta)}(\hat{S}) \psi^{(\alpha)} dV, \tag{2.4.1}
\]
taken over all configuration space, where \( \hat{S} \) represents the operator of the physical observable which may correspond to e.g. the energy, a multipole moment, or some scalar quantity. Here \( \psi^{(\beta)} \) and \( \psi^{(\alpha)} \) represent the wave functions of the two different quantum states, \( |\beta\rangle \) and \( |\alpha\rangle \), respectively. If the symmetry of \( \psi^{(\beta)} \), \( \psi^{(\alpha)} \) and \( \hat{S} \) are denoted by \( \Gamma^{(\beta)} \), \( \Gamma^{(\alpha)} \) and \( \Gamma^{(\hat{S})} \), respectively, then the theorem states that the integral vanishes whenever
\[
\Gamma^{(\beta)} \otimes \Gamma^{(\hat{S})} \otimes \Gamma^{(\alpha)} \not\subset \Gamma^{(s)}. \tag{2.4.2}
\]
Here \( \otimes \) denotes the tensor product. In the current calculations, only non-relativistic interactions in field free environments are included. The Hamiltonian operator is then considered to be totally symmetric with respect to all symmetry species. This implies that the integral will be zero whenever
\[
\Gamma^{(\beta)} \otimes \Gamma^{(\alpha)} \not\subset \Gamma^{(s)} \tag{2.4.3}
\]
or
\[
\Gamma^{(\beta)} \neq \Gamma^{(\alpha)}, \tag{2.4.4}
\]
i.e., the integral will always be zero whenever \( \psi^{(\beta)} \) and \( \psi^{(\alpha)} \) are of different symmetry. Note that the theorem only states that the integral must vanish whenever the integrand does not belong to \( \Gamma^{(s)} \). However, the integral may also vanish if the integrand does belong to \( \Gamma^{(s)} \). If it is known from experimental observations that the integral vanishes and that the integrand belongs to \( \Gamma^{(s)} \), then this may be an indication that the symmetry of the problem has not been fully exploited.

2.4.1 Identical Particles

In quantum mechanics, when studying a closed system consisting of identical particles interacting with each other, a certain special condition has to be fulfilled by the wave function of the whole system. This condition is only dependent on the nature of the particles. Due to the uncertainty principle the identical particles are no longer distinguishable from each other, as they are in classical mechanics. This results in the so called principle of indistinguishability of identical particles \[ 44, 49\].
Consider a system composed of \( N \) identical particles and with a wave function
\[
\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_i, \vec{x}_j, ..., \vec{x}_N),
\]
where \( \vec{x}_i = (\vec{r}_i, m_i) \) denotes the position vector \( \vec{r}_i \) and spin component \( m_i \) of particle \( i \). If particles \( i \) and \( j \) are permuted with respect to all their dynamical physical properties, the state of the system must be physically unchanged due to the identity of the particles (only a phase factor \( e^{i\alpha} \) may be present), i.e.,
\[
\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_i, \vec{x}_j, ..., \vec{x}_N) = e^{i\alpha} \Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_j, \vec{x}_i, ..., \vec{x}_N).
\]
(2.4.6)

Repeating the exchange of the particles will result in a phase factor with either of the two values \( \pm 1 \), i.e., the wave function is either symmetric or antisymmetric with respect to the exchange of any two identical particles in the system. Specifically, if the particles are fermions, i.e. half-integer spins, the wave function of the whole system must change sign due to the permutations, i.e. it must be antisymmetric. If the particles are bosons, that is with integer spin, the wave function must not change sign, and it must be symmetrical with respect to any exchange of identical particles. Bosons are said to obey Bose-Einstein statistics and fermions Fermi-Dirac statistics [44, 49]. When considering systems composed of identical complex particles, e.g. atoms, the statistics, i.e. the behaviour of the wave function with respect to permutation of identical particles, depends on the parity of the number of fermions in the system. For an even number of fermions, the full system is then bosonic, otherwise it is fermionic. For example, in a system of three \(^4\)He atoms, the full three-body system is bosonic since each atom is a boson.

### 2.4.2 Permutational Symmetry in Three-Body Systems

This thesis mainly treats three-body systems composed of identical particles. Exploring the permutational symmetry of systems which are composed of identical particles is very important from a computational point of view as certain integrals may be identically zero. Consider for example the identical \(^4\)He trimer system. Due to the bosonic property of the trimer, the total rovibronic wave function must be symmetric with respect to any permutation of the atoms. However, since Jacobi coordinates are used in the present formalism, it is only possible to permute atoms 2 and 3, both lying along the \( x \)-coordinate. After permutation, the angle \( \theta \) transforms to \( \pi - \theta \). For the case of \( J = 0 \), by group selection rules [44, 53] the Hamiltonian matrix elements are zero when functions of different symmetries are considered, or in the current case, of different parity in the \( z \)-direction, i.e. functions of the angle \( \theta \) (see definition of Jacobi coordinates above in section 2.2.1). Thus only those matrix elements of the Hamiltonian with respect to functions in the \( z \)-direction that correspond to either a purely even or purely odd basis set may give non-zero matrix elements. The consequence of this is that the Hamiltonian matrix splits up into two blocks, one symmetric and one antisymmetric with respect to the permutation of atoms 2 and 3. The symmetric block contains the totally symmetric, \( A_1 \), states including the first component of the two-fold degenerate, \( E \), states, and the anti-symmetric block contains the antisymmetric, \( A_2 \), states accompanied with the second component of the two-fold degenerate,
\( E \) states \([39, 38]\). Here, \( A_1 \) refers to the symmetry species of the system that is totally symmetric with respect to all possible permutations of particles and inversion of the coordinate system. The symmetry species \( A_2 \) refers to those states that are symmetric with respect to permutations but antisymmetric with respect to inversion of the coordinate system.

When considering \( J \neq 0 \) the above classification of the energy terms is not trivial due to mixing of the components in the expansion of the total rovibrational wave function in eq. (2.3.4). As such symmetrical considerations are ignored, and we only treat the full basis set in the z-direction, i.e. mixing of even and odd polynomial degrees when calculating rovibrational states.

### 2.5 Quantum Scattering and Resonances

#### 2.5.1 Theory of Resonances

To find the energies of bound states in quantum systems requires solving the Schrödinger eigenvalue problem

\[
\hat{H} \psi = E \psi.
\]

The Hamiltonian operator, \( \hat{H} \), is self-adjoint implying a real eigenvalue spectrum. Bound states which have infinite lifetime, i.e. no uncertainty in the energy, have their wave functions embedded in the \( L_2 \) Hilbert space which contain all square integrable functions, i.e. those obeying

\[
\int_{\mathbb{R}^3} |\psi|^2 d\vec{r} < \infty.
\]

Intermediate or resonant states are an important class of systems which have a finite lifetime, i.e. with an uncertainty in the energy. In order to understand and describe their behaviour, classification of the various phenomena occurring in a scattering situation is necessary. In the current work, possible formation paths for three-body systems that may pass through intermediate quasi-bound states have been investigated, see Paper 1 and Paper 3.

To illustrate resonance phenomena, consider a general scattering experiment in which a particle \(^3\)A collides with a target \( B \) yielding products \( C \) and \( D \). There are several possible outcomes which can be used to categorise the interaction:

- If the states of \( C \) and \( D \) are identical to the states of \( A \) and \( B \), i.e. the quantum states (energies) of all particles are conserved, the process is described as "elastic scattering."

- If the states of \( C \) and \( D \) are different from the states of \( A \) and \( B \), i.e. the quantum numbers have changed, and all particles in each complex particle stay localised in its respective particle system, the collision is called "inelastic scattering."

\(^3\)A particle may in this framework be considered as complex, e.g. a nuclei or an atom.
• If particles \( C \) and \( D \) are different from \( A \) and \( B \) the collision is said to be “reactive scattering”.

These three distinct scattering modes are in some sense mutually exclusive.

• If \( C \) and \( D \) are formed instantaneously in a time scale relative to the motions of \( A, B, C \) and \( D \), the interaction is termed “direct scattering.”

• If a combined system, a so called collision complex \( AB \), is formed which has a non-negligible lifetime relative to the motions of \( A, B, C \) and \( D \) an intermediate short-lived state can be identified, also called a resonance state.

The latter statement may be considered as a description of a resonant system, \( AB \).

One characteristic of a resonance state, which may also serve as a definition, especially to experimentalists, is the violent behaviour of the measured (calculated) cross section at certain (resonance) energies, \( E_R \), resulting in sharp peaks in the cross section. This behaviour of the cross section is related to the fact that a particle with a certain energy has been trapped in the target system, resulting in a relatively long lived collision complex. Note that not all peaks in a cross section are related to resonances.

For practical purposes in the current discussion a resonance is defined as a quasi-stationary state in which the scattered particle remains in the (target) system for some time, \( \tau \), but which has sufficient energy to overcome the potential barrier, i.e. to breakup from the target. Physical systems that are not stable will eventually disintegrate, i.e. one or more particles in the system will escape to infinity and thus the motion of the whole system is infinite. Such systems have a quasi-discrete energy spectrum consisting of a series of broadened levels whose widths, \( \Gamma \), are related to the lifetime of the levels as \( \Gamma \sim 1/\tau \) [44].

Thus, in scattering problems, the wave functions of pure scattering states and resonance states have a distribution over all configuration space, i.e. they are continuum states. However, there is a very important difference between these two states. The wave function of a resonance state has a large amplitude in the interaction region, whereas the wave function of a purely scattering state has only a very small amplitude in the interaction region. In this sense, the longer the lifetime of the resonance complex, the more of a bound state property it possesses, i.e. the amplitude of the wave function in the interaction region gets larger.

In the limit where the mean lifetime of a resonance becomes shorter and shorter, however, this does not lead to a proper mathematical definition of a resonance. This has led to the mathematical criterion of a resonance as a complex pole of the resolvent, \((\hat{H} - E)^{-1}\), or similarly a complex pole of the \(S\)-matrix [54].

Physicists have developed a variety of approaches to treat scattering states to extract cross sections and resonance energies and widths, see Refs. [55, 56, 42, 57]. The use of analytical scattering theory is the most rigorous and conceptual treatment of resonances, e.g. by examining the dependence of the scattering matrix, or the resolvent, with respect to the energy, poles that may correspond to resonance states can be identified. However, in order to solve the stationary (few-body) Schrödinger equation for a scattering problem, the asymptotic form of the wave function must
in general be known. This is generally a very difficult problem, even for simple systems. In the example of the scattering of three charged particles, the complications are due to the presence of the long range Coulomb interaction [58, 57].

The boundary conditions for resonant problems representing outgoing spherical waves at infinity, corresponding to the particles finally leaving the system, are complex. This means that complex eigenvalues may be obtained when solving the Schrödinger equation, i.e.

\[ E = E_r - i\Gamma/2. \]

The time evolution of a quasi-stationary state is described with a time independent potential as

\[ e^{-iEt/\hbar} = e^{-iE_r t} e^{-(\Gamma/\hbar)t/2}. \]

The physical significance of this is that the probability of finding the system in a certain quantum state decays with time as \( e^{-\Gamma/\hbar}t \). The eigenfunctions, \( \psi_{res}(\vec{r}) \), corresponding to resonances grow at large distances, \( |\vec{r}| \), and thus do not belong to the Hermitian domain of \( \hat{H} \). In order to solve these kind of a problems the asymptotic behaviour of the resonances needs to be known.

### 2.5.2 Methods of Calculating Resonance states

A class of methods called \( L_2 \) methods [59] provides a possible approach for extracting resonance information without scattering calculations, i.e. without the need to consider the asymptotical boundary conditions of the wave function. One such method is the stabilization method [55, 2], which is a real \( L_2 \) method in the sense that it deals with real matrices and real basis sets, and which directly exploits the locality of the resonance in the interaction region. From a computational point of view, the physical size of the system is mapped over a large enough numerical grid. The dimension of the grid is then varied and the general behaviour of the energies, obtained by diagonalization of the Hamiltonian matrix, is obtained for each fixed grid size. If one or several of these eigenvalues stabilises beyond a certain grid size, i.e. if they become independent of the size, then they are classified as resonance energies, and are localised. If the energies decrease for all grid sizes, these states are classified as continuum states, and do not possess any bound states characteristics.

Complex \( L_2 \) methods [60, 22, 23, 59, 61] mathematically transform the Schrödinger equation itself to avoid the asymptotical boundary problems for resonances. The consequence of this transformation is that the eigenfunctions corresponding to the resonance states tend to zero at large distances, i.e. they become mapped into the \( L_2 \) Hilbert space. The price paid by this approach is that the problem looses its Hermitian property, i.e. the Hamiltonian matrix becomes complex. The so called complex absorbing potential method [59, 42], deals with complex matrices by adding a complex potential term to the real Hamiltonian making it non-Hermitian. The resulting wave functions become square integrable and complex energies of the complex matrix may correspond to the resonance energies. This method is relatively easy to implement. However, despite of the success of this approach in locating resonance energies and widths, the method is not mathematically proven to provide the resonance energies that exactly correspond to the poles of the S-matrix [42].
In the work reported here, a more sophisticated complex $L_2$ method, called the complex scaling method [63, 64, 65, 42], has been employed to search for possible resonant states in three-body systems. This method, briefly described here, is mathematically proven to provide complex energies that formally correspond to the S-matrix poles.

2.5.3 Complex Scaling

The complex scaling (CS) method [63, 64, 42] is one of few methods for studying resonant properties in few-body quantum systems.

Within the uniform CS method [42, 4] we construct the rotated Hamiltonian by considering the transformation of the real one dimensional coordinate $r$ as

$$ r \rightarrow \hat{U}(\theta) r = e^{\theta} r. \quad (2.5.1) $$

Since $\theta \in \mathbb{C}$, $\hat{U}(\theta)$ is non-unitary. The wave function $\psi(r)$ transform under the operator $\hat{U}(\theta)$ by definition as

$$ \psi(r) \rightarrow e^{\theta/2} \psi(e^\theta r). \quad (2.5.2) $$

If we define the scaled Hamiltonian $\hat{H}(\theta)$ as

$$ \hat{H}(\theta) = \hat{U}(\theta) \hat{H} \hat{U}^{-1}(\theta), \quad (2.5.3) $$

i.e. as a similarity transformation, then the real Hamiltonian given by

$$ \hat{H} = -\frac{1}{2} \Delta + V(r) \quad (2.5.4) $$

gets transformed to

$$ \hat{H}(\theta) = -\frac{1}{2} e^{-2\theta} \Delta + V(e^\theta r). \quad (2.5.5) $$

Due to the complex transformation, $\hat{H}(\theta)$ is a non-self adjoint complex operator that may have complex eigenvalues corresponding to the resonance states of the system.

Thus, through a similarity transformation of the Hamiltonian operator the S.E. transforms to [42]

$$ \left( \hat{U}(\theta) \hat{H} \hat{U}^{-1}(\theta) \right) \left( \hat{U}(\theta) \psi_{res} \right) = \left( E_r - i\Gamma/2 \right) \left( \hat{U}(\theta) \psi_{res} \right). $$

Here $\psi_{res}$ denotes the diverging resonance spherical outgoing eigenfunction corresponding to the complex resonance eigenvalues. The non-unitary transformation implies that

$$ \phi(r) \equiv \hat{U}(\theta) \psi_{res}(r) \rightarrow 0 \quad \text{as} \quad r \rightarrow \infty. $$

The new eigenfunction $\phi(r)$ of the Hamiltonian is now square integrable and thus embedded in the $L_2$ Hilbert-space. This implies that the resonant scattering problem may now be treated as a bound state problem.
The following spectral properties of $\hat{H}(\theta)$ are valid.

1) The bound states of the non-scaled real operator $\hat{H}(\theta = 0)$ are present also in $\hat{H}(\theta)$ for all $\theta$ fulfilling $|\arg \theta| \leq \alpha_{\text{crit}}$, i.e. whenever $\theta$ does not go beyond a certain critical angle $\alpha_{\text{crit}}$.

2) The continuous spectrum at each scattering threshold $E_i$ is rotated into the lower complex plane by an angle $2\Im \theta$ ($\Im \theta > 0$).

3) $\hat{H}(\theta)$ may have isolated complex eigenvalues corresponding to the resonance energies with corresponding $L_2$ square integrable complex eigenfunctions.

4) The resonance energies are independent on $\theta$, as long as the first criterion is fulfilled.

Note that, in order to be able to analytically continue the real Hamiltonian operator $\hat{H}$ to the complex one $\hat{H}(\theta)$, i.e. in order for the transformation to be legitimate the potential of the system must be given in an analytical form. This is certainly not the case for many physical systems. In general, solving complex quantum systems the potential in question can only be given numerically while it may be represented analytically asymptotically. This is very frequently the case for molecular systems, where the interior part of the potential, i.e. the part of the potential in the interaction region is only given numerically or by some complicated set of functions, whereas it may be fitted to some analytical form asymptotically. This problem was solved by introducing the exterior complex scaling (ECS) method [66] which also is known as the sharp ECS. This only requires the potential to have an analytical form asymptotically. The implication of this is that the coordinates are only scaled outside a hypersphere of radius $|\vec{r}| = R_0$, i.e. exclusion of the reaction region and the problems above.

The sharp ECS suffers from the fact that the derivative of the transformation is discontinuous [67]. The numerical grid and the set of basis functions always have to be optimized.

Therefore we apply the so called smooth ECS transformation [4], which is continuous at the onset of the complex scaling radius $R_0$. We replace the real valued three-dimensional coordinate vector $\vec{R}$ by its complex analogue. Only the magnitudes $R_i$ have to be scaled [66]. We define our smooth exterior complex scaling transformation of $x$ (and analogously for $y$) as

$$x \rightarrow \xi(x) = x + \lambda g(x),$$

where

$$g(x) = \begin{cases} 0, & x \leq R_0 \\ \left(1 - \exp\left[-\sigma(x - R_0)^2\right]\right), & x > R_0. \end{cases}$$

Here, $\lambda = \exp(i\theta) - 1$, $\theta$ is a rotation angle, $R_0$ is the external radius and $\sigma$ is the curvature parameter. Following [68, 69, 70] we see that this transformation approaches the sharp exterior scaling ray of [66] in the limit $\sigma \rightarrow \infty$. The function $g$ is non-decreasing and has bounded derivatives. Note that both the function and
its derivative are continuous at $R_0$. The angular Jacobi coordinate variable $\phi$ is obviously not changed by the transformation. The representation of the Hamiltonian in these complex coordinates and its properties can be found in Refs. [42, 4].

### 2.6 The Variational Principle

The variational principle [44, 49] in quantum mechanics is a way to minimise the energy of a bound quantum physical system, e.g. the ground-state of an atom. More precisely, it is to minimise the energy expressed as the expectation values of the Hamiltonian in the coordinate representation divided by $\langle \psi | \psi \rangle$, where $\psi = \psi(q)$ and $q$ stands for all the space coordinates and spin coordinates in the configuration space, i.e.

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \psi^* \hat{H} \psi dq}{\int \psi^* \psi dq}.$$  \hspace{1cm} (2.6.1)

By varying $\psi$ with respect to some parameters, the energy can be minimised. $E[\psi]$, which is the energy as a functional of $\psi$, is called the variational integral and the wave function, $\psi$, is the trial function. In this respect we say that for any $\psi$, it must be fulfilled that $E[\psi] \geq E_0$, where $E_0$ is the ground state of the system.

The proof is quite simple. Let the trial function $\psi$ be expanded in the “known” energy eigenfunctions $\phi_k$, satisfying $\hat{H}\phi_k = E_k \phi_k$, i.e.

$$\psi = \sum_{k=0}^{\infty} c_k \phi_k.$$ \hspace{1cm} (2.6.2)

Let $E_k = E_k - E_0 + E_0$, it then follows immediately that

$$E[\psi] = \frac{\sum_{k=0}^{\infty} |c_k|^2 E_k}{\sum_{k=0}^{\infty} |c_k|^2} \hspace{1cm} (2.6.3)$$

$$= \frac{\sum_{k=1}^{\infty} |c_k|^2 (E_k - E_0)}{\sum_{k=0}^{\infty} |c_k|^2} + E_0 \geq E_0 \hspace{1cm} (2.6.4)$$

The inequality above follows since for all $k \neq 0$, $E_k > E_0$, and the proof is finished.

An interesting aspect of the variational principle is that a not so well approximated trial function of the true ground state eigenfunction gives a relatively good approximation of the ground state energy. In other words if we have that

$$\psi \sim O(\epsilon)$$ \hspace{1cm} (2.6.5)

then

$$E[\psi] - E_0 \sim O(\epsilon^2)$$ \hspace{1cm} (2.6.6)

An equivalent statement of the variational principle is that we seek those trial functions $\psi$ which gives as a first variation of $E[\psi]$ zero. In other words if we were to vary $\psi$ by an arbitrarily small amount $\delta \psi$ by changing its parameters, that is

$$\psi \longrightarrow \psi + \delta \psi$$ \hspace{1cm} (2.6.7)
then we wish that $E[\psi]$ would be stationary, i.e.

$$\delta E = 0$$

(2.6.8)
in first order. In this respect the error we get in estimating the ground state is of second order with respect to the variation of the trial function, i.e. $(\delta \psi)^2$.

An extension of the variational principle from hermitian to non-hermitian operators, exists and is called the complex variational principle [71]. Simply it says that the following quotient for the complex scaled Hamiltonian $\hat{H}(\theta)$ in the complete basis $\Phi = U(\theta)\psi_{res} \in L^2$

$$E^{\theta}[\phi] = \frac{\langle \Phi|\hat{H}(\theta)|\Phi \rangle}{\langle \Phi|\Phi \rangle}$$

(2.6.9)
is stationary for arbitrary variations of $\Phi$ about the exact eigenfunction $\xi_{ex}$ corresponding to the exact resonance energy $E_{ex}^{\theta}$. In other words if

$$\Phi = \xi_{ex} + \delta \Phi \rightarrow E^{\theta} = E_{ex}^{\theta} + (\delta \Phi)^2.$$  \hspace{1cm} (2.6.10)

From a strict theoretical point of view [63], the complex energies of $\hat{H}(\theta)$ must be independent on the complex scaling angle if they are to be associated with true resonances; that is, positions $E$ and widths $\Gamma$ of resonances must be independent on the rotation angle $\theta$. However when numerical approximations are used, resonances become $\theta$ dependent. In this case, their positions and widths are obtained by the condition

$$\frac{dE}{d\theta} \bigg|_{\theta_r} = 0, \quad \frac{d\Gamma}{d\theta} \bigg|_{\theta_i} = 0.$$  \hspace{1cm} (2.6.11)

The two angles $\theta_r$ and $\theta_i$ converge to one angle as the accuracy of the calculation increases. This approach is dependent on the assumption that for resonances an eigenvalue, $E$, will converge to a limited value when varying the parameters in eq. (2.6.9) and extending the basis such that eq. (2.6.11) also is fulfilled.

In Figure 2.3 and Figure 2.4, below, is displayed the dependence of the position and width of a possible shape resonance on the complex scaling angle $\theta$, in the study of the bosonic van der Waals neon trimer system, see Paper 3 for more details. Since the physical resonances must be independent on the scaling angle, and we find both parameters, the position and the width of the resonance very stable beyond $\theta = 25$, we believe to converge on the complex resonance energy $-15.977-i1.863 \times 10^{-3}$, in atomic units.

### 2.7 Interaction Potentials

The total potential energy in few- or many-body systems of compound clusters is often approximated as the sum of all the two-body potentials. The applicability of this approximation depends entirely on the physical system. In some cases three-body correction terms are important. This is the case when treating not so spatially extended systems, i.e. when the classical inter-particle distances are not very big and when considering many-body clusters. So called relativistic retardation effects may affect the two-body potentials significantly when considering spatially very extended systems.
Figure 2.3: Resonance position with respect to the rotation angle $\theta$.

Figure 2.4: Resonance width with respect to the rotation angle $\theta$. 
2.7.1 Pairwise Interaction Potentials

Pairwise interaction potentials are generally calculated by *ab-initio* methods, empirically based methods and most often theoretical and experimental data are combined to obtain highly accurate pair potentials.

The interaction potential between two neutral atoms at a distance, \( r \), from each other which is large with respect to their atomic size may be derived from perturbation theory [44]. Considering the interaction between the atoms as a perturbation operator, \( \hat{V} \), the potential may be expanded in terms of \( r^{-1} \), resulting in dipole-dipole, \( (\sim r^{-3}) \), dipole-quadrupole, \( (\sim r^{-4}) \), quadrupole-quadrupole and dipole-octupole, \( (\sim r^{-5}) \), terms as

\[
\hat{V} = Cr^{-3} + Dr^{-4} + Er^{-5} + ... \quad (2.7.1)
\]

Here, \( C, D \) and \( E \) are quantities characterising the different multipole moments. These short range interactions which appear at large interatomic distances are a consequence of the instantaneous fluctuations in the multiple charge distributions of the atoms. All the terms in the expansion (2.7.1) will not contribute to the energy in a first order perturbation approximation for \( S \)-states [44]. This is due to the fact that the average of all multipole moments for any atom in field free space is always zero when it is in an \( S \)-state. However, in a second-order perturbation approximation, the expansion (2.7.1) may be non-zero for all terms resulting in the attractive terms

\[
-er^{-6} - dr^{-8} - er^{-10} - \ldots \quad (2.7.2)
\]

where \( c, d \) and \( e \) are constants describing the different terms. The attractive forces between atoms separated by large distances are called *van der Waals forces* [44, 1, 37].

2.7.2 Examples

In the particular case of the rare gas helium dimer system, \(^4\text{He}_2\), Tang *et al.* [72] used perturbation theory to derive a simple analytical form of the entire potential energy curve, i.e. both the inner repulsive and the asymptotic part of the potential. It may be written as

\[
V(r) = V_{\text{rep}}(r) + V_{\text{disp}}(r), \quad (2.7.3)
\]

where \( r \) is the inter-atomic distance in atomic units. The repulsive term is given by

\[
V_{\text{rep}}(r) = Dr^{7/2\beta-1} \exp \left[-2\beta r\right], \quad (2.7.4)
\]

The function \( V_{\text{disp}}(r) \), which characterises the attractive dispersion terms, is given by the sum

\[
V_{\text{disp}}(r) = -\sum_{n=3}^{N} C_{2n} f_{2n} r^{-2n}, \quad (2.7.5)
\]

where the coefficients, \( C_{2n} \), are obtained from the recursive formula

\[
C_{2n} = \left( C_{2n-2}/C_{2n-4} \right)^3 C_{2n-6}, \quad (2.7.6)
\]
while the functions, $f_{2n}(r)$, are given by

$$f_{2n}(r) = 1 - \exp\left(-b(r)\right) \sum_{k=0}^{2n} \frac{(br)^k}{k!}. \quad (2.7.7)$$

Here, $b(r)$ is given by

$$b(r) = 2\beta - \left[\frac{7}{2\beta} - 1\right] \frac{1}{r}. \quad (2.7.8)$$

Table I lists the parameters of the TTY potential, and the dimer potential is plotted in Figure 2.5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TTY [72]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$0.3157662067 \times 10^6$ K</td>
</tr>
<tr>
<td>$C_6$</td>
<td>1.461</td>
</tr>
<tr>
<td>$C_8$</td>
<td>14.11</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>183.5</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.3443 a.u.</td>
</tr>
<tr>
<td>$D$</td>
<td>7.449</td>
</tr>
<tr>
<td>$N$</td>
<td>12</td>
</tr>
<tr>
<td>$D$</td>
<td>1.4088</td>
</tr>
</tbody>
</table>

Aziz et al. combined theoretical and gas-phase data to obtain an analytical form of the HFD-B [73] and LM2M2 [74] potentials

$$V(r) = \epsilon \left[ A \exp(-\alpha x - \beta x^2) - F(x) \sum_{i=0}^{2} C_{2i+6} x^{2i+6} \right], \quad (2.7.9)$$

where

$$F(x) = \begin{cases} \exp\left[-\left(\frac{D}{x} - 1\right)^2\right], & x < D, \\ 1, & x \geq D \end{cases}$$

Both potential functions are identical in analytic form, except for an extra term, $BU(x)$, which is added to the LM2M2 potential and which is given by

$$BU(x) = \begin{cases} B \left[ \sin\left(\frac{2\pi(x-x_0)}{x_1-x_0} - \frac{\pi}{2}\right) + 1 \right], & x_1 \leq x \leq x_2, \\ 0, & x < x_1 \text{ or } x > x_2 \end{cases}$$

Here, $r$ is the interatomic distance,

$$x = \frac{r}{r_{\text{min}}}. \quad (2.7.10)$$

The parameters of the LM2M2 and the HFD-B potentials, are given in Table II, and the potentials are plotted in Figure 2.5.
Figure 2.5: The LM2M2, HFD-B, TTY, Spin_Trit_Pot, Neon_Morse and Argon_Morse dimer potentials are plotted using atomic units. Note that LM2M2, HFD-B, and TTY overlap in this figure.

Table II. Parameters for the LM2M2 and the HFD-B potentials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LM2M2 [74]</th>
<th>HFD-B [73]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>-10.97 K</td>
<td>-10.948 K</td>
</tr>
<tr>
<td>$A$</td>
<td>$1.896 \times 10^5$ K</td>
<td>$1.844 \times 10^5$ K</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>-10.70203539</td>
<td>-10.43329537</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.90740649 a.u.</td>
<td>2.27965105 a.u.</td>
</tr>
<tr>
<td>$c_6$</td>
<td>1.34687065</td>
<td>1.36745214</td>
</tr>
<tr>
<td>$c_8$</td>
<td>0.41308398</td>
<td>0.42123807</td>
</tr>
<tr>
<td>$c_{10}$</td>
<td>0.17060159</td>
<td>0.17473318</td>
</tr>
<tr>
<td>$D$</td>
<td>1.4088</td>
<td>1.4826</td>
</tr>
<tr>
<td>$r_{min}$</td>
<td>5.6115 a.u.</td>
<td>5.5992 a.u.</td>
</tr>
<tr>
<td>$B$</td>
<td>0.0026</td>
<td>-</td>
</tr>
<tr>
<td>$x_0$</td>
<td>1.003535949</td>
<td>-</td>
</tr>
<tr>
<td>$x_1$</td>
<td>1.454790369</td>
<td>-</td>
</tr>
</tbody>
</table>

Several different systems have been investigated as part of the research, and the potential functions for these systems are briefly discussed here.
In Paper 1 the tritium trimer, \((\text{T}^\uparrow)_3\), was investigated. The \(\text{T}^\uparrow\) atomic mass is 5496.91800 a.u. The \(\text{T}^\uparrow_2\) potential, here abbreviated by Spin_Trit_Pot, is plotted in Figure 2.5, does not support any bound states. However, the corresponding spin-polarised tritium trimer, \((\text{T}^\uparrow)_3\), does support one bound state. Therefore, \((\text{T}^\uparrow)_3\) is a so called Borromean system. These systems are discussed in detail in a later chapter on halo systems. Since the \((\text{T}^\uparrow)_2\) potential can only be given numerically we refer to Ref. [20] and references therein for information on the dimer potential. For more details on the \((\text{T}^\uparrow)_3\) system see Paper 1 or Chapter 5.

In Paper 2, the symmetric and the un-symmetric helium trimers, \(4\text{He}_3\) and \(2\text{He}_2-3\), respectively, were studied. Three different realistic He-He interactions were used: LM2M2 [74], HFD-B [73], and the TTY [72] potential, as described above. Though there is little obvious difference between the functions, at least on the scale used in Figure 2.5, there are some differences. It is known that the LM2M2 and TTY potentials give very similar results despite their different derivations and origins. Though the HFD-B and LM2M2 potentials are both based on \textit{ab-initio} results, the earlier HFD-B potential slightly overbounds the helium trimer. The mass of the \(4\text{He}\) and \(3\text{He}\) atoms are 7296.299402 a.u. and 5497.836156 a.u., respectively. The dissociation threshold and the equilibrium inter-atomic distance for all three potentials are all more or less the same, being \(D_e = -7.6 \text{ cm}^{-1}\) and \(r_e = 5.6 \text{ a.u.}\) respectively.

Paper 3 reports results on the rare-gas bosonic neon trimer Ne\(_3\) system. The interaction potential of the trimer is approximated as a sum of pairwise interaction potentials of the Morse type [38]

\[
V = \sum_{i<j} D \left[ \exp\left(-\alpha(r_{ij} - r_e)\right) - 1 \right]^2. \tag{2.7.11}
\]

This potential is fitted to the accurate potential of Aziz \textit{et al.} [75]. The relevant potential parameters are \(D = 29.36 \text{ cm}^{-1}\), \(\alpha = 2.088 \text{ Å}^{-1}\), and \(r_e = 3.091 \text{ Å}\). The neon atomic mass used for the above Morse potential is 36485.02795 a.u. The Morse-potential for the neon dimer Ne\(_2\) is plotted in Figure 2.5, abbreviated by Neon_Morse.

In Paper 4, we report results on studies on the bosonic vDW argon trimer. Here we consider the same Morse potential as in eq. (2.7.11). This potential is fitted to the accurate potential of Aziz \textit{et al.} [76]. The relevant potential parameters are \(D = 99 \text{ cm}^{-1}\), \(\alpha = 1.717 \text{ Å}^{-1}\), and \(r_e = 3.757 \text{ Å}\). The argon atomic mass used is 72820.80860 a.u.

### 2.7.3 Relativistic Retardation Effects

In 1948, in a classic paper, Casimir and Polder [77], for the first time showed theoretical evidence of a modification of the very form of the van der Waals \(r^{-6}\) dipole-dipole dependence between two neutral atoms, whenever the distance \(r\) between the atoms is much bigger than the bohr radii. This so called \textit{Casimir}
effect or more commonly retardation effect \(^5\), which is a long range relativistic effect has its origin in the fact that the speed of light \(c\) is finite \([78, 79]\).

For most systems it is a very good approximation to neglect this effect on the potential. However, when considering the spatial extent of large systems, a proper description of the interaction between the atoms should take the electromagnetic field into account. To illustrate this, consider two neutral atoms, \(A\) and \(B\), at a mean distance, \(r\). The expectation values of the multipole moments of any atom in its \(S\)-state is zero. However, at any given instant, atom \(A\) may have a non-zero multipole moment that may induce a multipole moment in atom \(B\) through the emission of a photon. If the time it takes for the photon to travel from \(A\) to \(B\) and back again, \(2r/c\), is much shorter than than the fluctuation time, \(\Delta E/\hbar\) (where \(\Delta E\) is the uncertainty in the energy of the atom), of atom \(A\) or \(B\), there will exist a perfect correlation between the atoms. Thus the term describing, e.g. the dipole-dipole interaction, \(\sim r^{-6}\), will be a good approximation. However, if \(2r/c\) is longer or much longer than \(\Delta E/\hbar\), then atom \(A\)'s multipole moments may change significantly before the photon returns back to \(A\). In this case the correlation between the atoms is no longer perfect but destroyed, and retardation effects \([77, 80, 78]\) may occur. In this case, the leading term, \(r^{-6}\), changes to a more rapidly decaying interaction, \(\sim r^{-7}\), thus weakening the energy of the dimer system.

Probably the best known example of a system of two neutral atoms where retardation effects are significant is in the \(^4\)He dimer (see Paper 2). This is known to be the most weakly bound dimer system and supports only one bound state, \(\sim -9.1 \times 10^{-4} \text{ cm}^{-1}\), with a mean separation of about 100 a.u. and a wave function that has a significant contribution up to 1000 a.u. Luo et al. \([80]\) evaluated the retardation effect on the LM2M2 \([74]\) potential, including not only the \(r^{-6}\) term, but also the other attractive terms, \(r^{-8}\) and \(r^{-10}\). They calculated a 10 percent decrease in the binding energy of the dimer due to the retardation effect on the \(r^{-6}\) term, and about 0.99 percent and 0.2 percent in the \(r^{-8}\) and \(r^{-10}\) terms, respectively. The effective 11 percent decrease in the binding energy resulted in an approximately 6 percent increase in the mean separation of the dimer.

### 2.8 Three-Body Interactions

The interaction between two particles is affected by the presence of a third, or more, particle. This gives rise to three-body, and higher-body, corrections to the total physical potential \([81, 40]\). Three-body effects are often very small or are within the inaccuracy of the available dimer potentials. However, as systems become more tightly bound, such effects become more important. For any general three-body system, the exact total potential may be written as

\[
V_{\text{trimer}}(r_{12}, r_{23}, r_{13}) = \sum_{i<j} V_{\text{dimer}}(r_{ij}) + V_3(r_{12}, r_{23}, r_{13}).
\]

\(^5\)Other systems studied, where the Casimir effect have a pronounced effect is in e.g., an electron and an atom or ion, in Rydberg helium like ions (with one electron in a \(1s\) state and the other electron in an \(nl\) state, with \(l \gg 1\)), atom and a wall, among others \([78]\).
The first term is related to the dimer interactions within the system while the second term is a general three-body correction which may be written out as a sum of different three-body interaction terms. One example of such a three-body correction is the Axilrod-Teller term [82], a triple-dipole interaction which is a very short range correction

\[ V_3(r_{12}, r_{23}, r_{13}) = \frac{3 c_{123} \cos \theta_1 \cos \theta_2 \cos \theta_3}{r_{12} r_{13} r_{23}}. \]  

(2.8.2)

Here, \( c_{123} \) is a constant characterised by the nature of the three atoms, \( \theta_i, i = 1, 2, 3 \) are the internal angles of the triangle spanned by the three atoms, and \( r_{ij} \) denote the distances between atoms \( i \) and \( j \). If \( R \) is defined as the size of the physical system, e.g. the hyper-radius, the Axilrod-Teller term is proportional to \( R^{-9} \).

Other examples of three-body corrections are the double-dipole-quadrupole, \( \sim R^{-11} \), dipole-quadrupole-quadrupole, \( \sim R^{-13} \), and the triple-quadrupole, \( \sim R^{-15} \) [40]. In most three-body applications, the Axilrod Teller term is the most important, while the other terms are usually neglected [81, 40].

Inclusion of the Axilrod-Teller correction weakens the binding of a trimer system with an equilateral geometry and decreases the total energy of a trimer with a collinear geometry [81]. These effects are both related to that fact that an equilateral configuration reduces the correlation in electron motions whereas a collinear configuration enhances the correlation. In the study of the spin-polarised tritium trimer, as described in Paper 1, inclusion of a damped Axilrod-Teller term weakened the energy by about 1.6 percent, since the only bound state of the system has an equilateral configuration. Inclusion of the same term into the description of the ground state of the halo helium trimer system changed the energy by less than one percent.

In studies into larger clusters of atoms, three-body effects have a more pronounced influence. For example, Blume et al. [20] calculated the ground state of the \( N=40 \) atomic cluster of spin-polarized tritium atoms and reported that the energy increased by about 6 percent when including the damped Axilrod-Teller term. In studies of rare gas solids, e.g. clusters of argon atoms, calculations showed that the inclusion of three-body corrections accounted for more than 10 percent of the total energy [40, 81]. However, despite the fact that these corrections become very important in the study of larger clusters, they are often not included. This is entirely due to the increased computational effort required to calculate the non-additive terms. For example, in a cluster made up of \( N \) atoms, the number of pair-wise interactions is given by \( N(N-1)/2 \), whereas the number of three-body corrections is \( N(N-1)(N-2)/6 \). This problem means it is sometimes impossible to include any three-body corrections when treating large clusters of atoms. The systems studied in the present work are spatially large, i.e. the classical inter-particle distances are relatively large. As such, the three-body corrections are very small.
Chapter 3

Halos and Efimov states in Three-Body Systems

3.1 Nuclear Halos

It is not so long ago that physicists thought about atomic nuclei in general as tightly bound shell structures. In the mid 1980s a series of experiments revealed that some neutron rich nuclei, such as $^6$He, $^7$Li and $^{14}$Be, have very large reaction cross sections (see [11, 12] and references therein). These exotic nuclear systems consist of a tightly bound core surrounded by one or several valence nucleons very weakly bound to the core, relative to the nucleons bound together in the core itself. In the particular example of the $^6$He nucleus, consisting of a core, alpha particle ($^4$He) and two neutrons, the approximate two neutron separation energy is 1 MeV, which may be compared to the much more tightly bound core with a binding energy of about 28 MeV. The wave function of such systems have an abnormally large spatial distribution, which extends way beyond the spatial extent of the nuclear core itself, i.e. significantly outside of the classical forbidden region.

Other characteristics that distinguish these unusual quantum systems from other previously encountered nuclear systems, is that they have low angular momentum, and that inter-particle interactions fall off faster than $r^{-2}$, where $r$ is the inter-particle distance. Nuclear systems possessing these properties are called nuclear halos and are said to either possess a halo structure or be a halo state. Some of these exotic nuclei have been modeled as three-body systems with an inert core and two loosely bound halo particles [11, 12, 83, 45].

Three-body halo nuclei may appear as one of two types of special state; Borromean and Efimov states [29, 30, 11, 12, 45]. Although both types of state share the properties of halo systems, there is one important difference between them. This difference manifests itself in the corresponding two-body spectrum. Borromean systems do not support any bound states of any binary subsystem, i.e. removing any particle from the system will result in an unstable system. One example of a Borromean system is $^6$He, since $^5$He is unstable. Because of this,
Borromean systems always have negative two-body scattering lengths $^1$.

Efimov states on the other hand have a zero or near zero two-body energy spectrum, corresponding to an infinite or very large magnitude two-body scattering length. Note that Efimov systems implies the halo property but not necessarily the Borromean property. However the halo property does not in general necessarily imply either the Borromean nor the Efimov property. No clear example of a physical system in the nuclear domain possessing the Efimov property exists in the literature, neither experimentally observed or theoretically predicted. This leaves the very existence of these exotic states in nuclear physics as an open question.

The Borromean property is simply explained in Figure 3.1, as Borromean wires, attached to each other in such a way that removing any wire from the system of the three bound wires will result in an unstable system.

### 3.2 Efimov States

To illustrate Efimov states in a qualitative fashion $^{15, 45}$, it is assumed that the potential, $V$, of the three-body quantum-mechanical system can be modeled by a

$$f_l(p) \rightarrow -a_l p^{2l}, \quad \text{as} \quad p \rightarrow 0$$

where $p$ is the momentum, $a_l$ the scattering length and $l$ the orbital angular momentum. In the low energy limit, i.e. when $p \rightarrow 0$, only the s-wave partial wave amplitude is appreciable, since the larger $l$ the more rapid the decrease in magnitude of $f_l(p)$. Thus, at extremely low energies, $f_s(p)$ approaches $-a_0$, i.e. the scattering length becomes isotropic. The scattering length provides useful information on the nature of the potential $^{84}$. In particular, a large positive (negative) scattering length characterises a very weakly attractive two-body potential (not) supporting a very weakly bound two-body bound state. In the limit where $|a| \rightarrow \infty$, the two-body spectrum support a zero-energy bound state.
sum of pair-wise interaction potentials \( U(r_{ij}) \) as
\[
V = \lambda \left[ U(r_{12}) + U(r_{23}) + U(r_{13}) \right],
\]
(3.2.1)

where, \( r_{ij} = |\vec{r}_i - \vec{r}_j| \) denotes the distance between particles \( i \) and \( j \). The scaling factor, \( \lambda \), is a measure of the interaction strength. The physical value of the system corresponds to \( \lambda = 1 \). When \( \lambda < \lambda_{Efimov} \), the total three-body energy, \( E = 0 \), corresponds to three free subsystems while for \( \lambda > \lambda_{Efimov} \), \( E = 0 \) corresponds to one free atom and a dimer bound-state. Here, \( \lambda_{Efimov} \) is the so called *Efimov limit* and corresponds to that value of the two-body potential strength that exactly supports a zero-energy two-body energy bound state.

When \( \lambda = 0 \), there are no interactions whatsoever, implying no bound states of the system or its subsystems. On increasing \( \lambda \) to \( \lambda_{Borromean} \), bound states start to appear, and the system is in the Borromean region, in the sense that the formation of a bound state of the three-body system is possible when no binary subsystem can support a bound state. Increasing \( \lambda \) even more to approach, and eventually equal, \( \lambda_{Efimov} \), the number of three-body bound states becomes extremely many or infinite, respectively, since one or several two-body subsystems supports a close-to-zero or zero-energy bound state, respectively. In such a state the system is extremely extended and diffuse in configuration space. Formally it is a property of the emergence of an effective attractive long-range potential energy of the three-particle system, asymptotically behaving as \( R^{-2} \), with radius, \( |a| \) [29, 30].

In this case, \( a \) is the two-body scattering length and \( R \) is the hyper-radius of the three-particle system, and which is proportional to the root-mean-square distance of the three-body system from its centre of mass, i.e.
\[
R^2 = \frac{1}{3} \left( r_{12}^2 + r_{23}^2 + r_{31}^2 \right).
\]
(3.2.2)

It is known that systems interacting with long range potentials can have infinitely many bound states. For example, this is the case of two particles interacting within the long range potential \( \sim r^{-2} \) [44].

The huge number of bound states which appear when approaching \( \lambda_{Efimov} \) disappear, as quickly as they appeared, into the continuum when increasing the interaction strength beyond the Efimov limit. This may be understood in the sense that the configuration space gets less diffuse, i.e. more localised when increasing \( \lambda \) beyond \( \lambda_{Efimov} \), and that this implies that the Efimov states no longer fit within the three-body potential well. In other words, by increasing \( \lambda \) beyond \( \lambda_{Efimov} \) the two-body energy decreases faster than the three-body energy as a function of \( \lambda \). Thus, any high lying Efimov energies will eventually move into the continuum when \( \lambda \) increases. Those bound states that disappear when increasing the interaction strength beyond the Efimov limit are defined as Efimov states. The existence of normal bound states is not due to the extremely large spatial extent of the system and, therefore, they remain and decrease in energy with increasing \( \lambda \).

In his original paper [29], Efimov derived an expression relating the scattering length, \( a \), of the two-body system, and the effective range, \( r_0 \), of the two-body potential to the number of possible Efimov states, \( N \), as
\[
N \approx \frac{1}{\pi} \ln \left( \frac{|a|}{r_0} \right).
\]
(3.2.3)
In the work discussed here, the systems are only extremely weakly bound, and it is assumed that \(|a| >> r_0\), i.e. a very big two-body scattering length relative to the effective two-body potential radius. When the two-body sub-system supports a close-to-zero- or zero-energy bound state, \(|a|\) becomes extremely large or infinite, respectively, which, in turn, results in a huge or infinite number of three-body Efimov states. Thus, when looking for possible candidates in three-body systems in the nuclear domain, or in other fields of quantum mechanics possessing the Efimov property, the system should obey \(|a| >> r_0\).

### 3.3 Halos in Atomic Trimers

Since halo and Efimov states in general only exist in systems with particles interacting with potentials falling off faster than \(r^{-2}\), a promising first place to look for these exotic states outside the domain of nuclear physics is in systems having this property. Systems of neutral atoms which have short range inter-atomic interactions may possess the halo or Efimov property. This argument rules out the possibility of halos in single atoms or systems of ions because of the presence of the long range Coulomb interaction.

Very weakly attracted bound small clusters of \(^4\)He atoms, especially dimers and trimers, have been studied quite intensively over the past few decades [13, 14, 16, 17, 18, 15, 19]. They reveal some unusual quantum properties that resemble the properties of halos in nuclear physics.

It is known that atomic helium, with two electrons, has a \(1s^2\) configuration in its ground state forming a closed shell. Atom-atom interaction is therefore extremely weak and is dominated by dispersion forces (proportional to \(r^{-6}\)).

For a long time it was thought that the helium dimer \(^4\)He\(^2\) did not support any bound states. However, in the mid 1980s it was predicted that the dimer would support one very weakly bound state, \((\sim -7 \times 10^{-4} \text{ cm}^{-1})\) [85, 14, 86]. This was observed experimentally in 1993 by Luo et al. [80], and independently later by Schöllkopf and Toennies [87], who also reported the observation of the helium trimer. Though Schöllkopf and Toennies [87] did not observe the excited state of the trimer, this was observed by Hegerfeldt and Köhler in 2000 [88].

The helium dimer \(^4\)He\(^2\) represents the largest dimer system ever encountered before it can support a bound state, having a huge positive scattering length about 190 a.u. As illustrated in Figure 3 the dimer system has a mean separation of about 5.6 a.u. These unusual properties of helium make it a good candidate in the search for possible halo and Efimov properties. Making use of eq. (3.2.3) with the potential data of the helium dimer, a numerical value for the number of Efimov states of \(\approx 1.12\) is obtained, clearly predicting a possible single Efimov state of the helium trimer system.

Several theoretical approaches on small clusters of atoms, e.g. the helium trimers, \(^4\)He\(^3\) and \(^4\)He\(^2\)-\(^3\)He, and the spin-polarized tritium trimer, \((T \uparrow)^3\), has revealed the fact that they do show halo character, with the excited state of \(^4\)He\(^3\) predicted to be an Efimov state. However, no experimental verification that the excited state of \(^4\)He\(^3\) is an Efimov state has been reported so far in the literature. Very recently, \(^2\) Retardation forces are neglected as discussed in Chapter 2.
however, in 2006, Kraemer et al. [34], reported for the first time experimental evidence for one Efimov state in a cluster of three ultracold Caesium atoms, a state which had earlier been theoretically predicted by Esry et al. [89] and by Braaten et al. [90]. Kraemer et al. experimentally manipulated the Caesium-Caesium scattering length by magnetic tuning in order to reach a value that was as close as possible to giving a two-body (resonance) zero energy bound state. They observed one such resonance at huge scattering length of -850 a.u. This clearly revolutionary experiment ignites a new era in the remarkable quantum phenomena that occur in the physics of few-body systems.
4.1 Finite Element Method

The formal theory presented here has been numerically realised using the finite element method (FEM) [91]. The accuracy of the present method has been tested in earlier studies of the helium atom, the anti-protonic helium system, the NeICl molecule and, recently, the weakly bound halo atomic trimer systems such as the spin-polarized atomic tritium trimer \( (T \uparrow)_3 \), and the helium trimers, \(^3\text{He}_3\) and \(^2\text{He}_2\cdot^2\text{He} \) [7, 92, 4, 24, 21, 19]. Detailed descriptions of the FEM technique are available in the literature [93, 61, 94] and so only a general discussion is given here.

The FEM has its origin in mechanical strength engineering where it is used in computation and design of airplanes, cars, bridges, etc. This method differs from other basis set method of solving (partial) differential equations in the sense that the wave function is expanded in terms of fully local (not global, i.e. defined in entire configuration space) linearly independent basis functions. Compared to any finite difference method (FDM), the (partial) differential equation is not approximated, but the corresponding differential equations functional in the form of an integral is analysed. The FEM generalises traditional variational methods in that it uses many elements or boxes whereas a traditional method uses only one box.

In the current treatment of the FEM, which is combined with a smooth ECS method, the following approach is used to solve the problem under study. The localised complex scaled resonance or real bound state wave function is denoted by \( \Psi \) and is expanded in terms of local independent real valued basis functions. The three-dimensional configuration space is divided into some number of rectangular boxes, see Figure 4.1.

In each of these boxes a set of linearly independent local basis functions is chosen to span the wave function. Though only a one dimensional approach is used here to simplify matters, it is important to note that the discussion is independent of spatial dimension.

Here \( \Psi \) is approximated by a finite series of basis functions \( f_{im} \) according to

\[
\Psi(r) = \sum_{i,m} c_{im} f_{im}(r), \quad i = 1, \ldots, N, \quad m = 1, \ldots, n, \quad (4.1.1)
\]
where \(c_{im}\) are the variational expansion coefficients, the indexes \(i\) and \(m\) enumerate the elements and the local basis functions in each element, respectively.

In the finite element algorithm the basis functions fulfill the condition

\[
f_{im}(r) \equiv 0, \quad r \notin [r_i, r_{i+1}], \quad i = 1, \ldots, N.
\]

The wave function may thus be discontinuous at the element boundaries, \(r_i\). To be able to define the matrix elements properly at least continuity of the wave function is required. This condition is a simple constraint on the expansion coefficients, \(c_{im}\). To see how this is achieved, the basis is first transformed by a simple linear transformation (see later) to fulfill the following boundary values at each element node

\[
\begin{align*}
\Psi_i(r_i) &= 1 \\
\Psi_i(r_{i+1}) &= 1 \\
f_{im}(r_i) &= f_{im}(r_{i+1}) = 0, \quad \text{otherwise}.
\end{align*}
\]

These boundary conditions on the basis functions imply that the continuity condition at node \(r_i\), i.e. \(\Psi(r_i - 0) = \Psi(r_i + 0)\), becomes a simple constraint on the expansion parameters, \(c_{im}\), and yields

\[
c_{i,2} = c_{i+1,1}.
\]

The construction of a set of finite element basis functions, \(f_{im}\), fulfilling the above conditions is achieved by the following scheme [61]: Consider a set of differentiable "fundamental functions" \(h_m(r), r \in [0,1], \quad m = 1, \ldots, p + 1\). A function \(B\) is then defined as the \(2 \times (p + 1)\) matrix of the boundary values of the \(h_m\)

\[
\begin{align*}
(B)_{1,m} &= h_m(0), \\
(B)_{2,m} &= h_m(1).
\end{align*}
\]
Decompose $B$ in the form

$$ B = (P, Q), $$

where $P$ contains the two first columns of $B$. The analogous matrix of the boundary values of the $f_{im}$ has the form $(1, 0)$, where $1$ stands for the $2 \times 2$ unit matrix. A $(p + 1) \times (p + 1)$ matrix, $W$, has be be found to map $h_m$ into $f_{im}$ such that the following expression is fulfilled

$$ (1, 0) = (P, Q) \cdot W. \tag{4.1.2} $$

One non-unique solution of eq. (4.1.2) is given by

$$ W = \begin{pmatrix} P^{-1} & -P^{-1} \cdot Q \\ 0 & 1 \end{pmatrix}. $$

From this expression, the basis functions

$$ f_{im}(r) = \sum_{m'} W_{m'm} h_{m'}(r) $$

have the required boundary values. When considering three dimensional problems, the basis functions $f_{im}(x, y, z)$ are expressed as products of one-dimensional basis functions

$$ f_{im}(x, y, z) = f_{im_1}(x)f_{im_2}(y)f_{im_3}(z). $$

This simplifies the evaluation of three-dimensional integrals.

The variational coefficients, $c_{im}$ from eq. (4.1.1), and the energy, $E$, are obtained by optimising the functional, $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$. Inserting the expansion of the wave function into this functional the following generalised eigenvalue problem is obtained:

$$ \tilde{H}c = E\tilde{S}c, \tag{4.1.3} $$

where

$$(\tilde{H})_{im,jk} = \langle f_{im} | H | f_{jk} \rangle \quad \text{and} \quad (\tilde{S})_{im,jk} = \langle f_{im} | f_{jk} \rangle. $$

The non-overlapping of the finite-element basis functions from different intervals implies that the only non-zero matrix elements are between $f_{im}$ from the same interval $[r_i, r_{i+1}]$. The consequence of this is that the Hamiltonian, $\tilde{H}$, and the overlap matrix, $\tilde{S}$, are sparse and have the symmetry of block diagonality [61].

In the general description of the FEM, a specific choice of elementary fundamental basis functions, $h_{m}(r)$, has not been mentioned. In the work discussed here a set of Legendre polynomials were used. In the next section it is demonstrated that in using a special basis set connected to a certain Gaussian integration method, the transformation of the fundamental basis set to one with the proper boundaries is totally unnecessary since the chosen basis intrinsically have this property $^2$.

$^1$Note that this procedure only works when searching for the ground state of the physical system. To find excited states, we make a spectral transformation, see more in the section of Computational Methods. In the case of resonances the (resonant) eigenvalues of the complex scaled Hamiltonian operator must fulfill the complex variational principle, as described above.

$^2$This does not mean that FEM, in the usual sense is a drawback, when compared to the combination FEM-DVR (see below). In fact FEM is particularly flexible in that it freely exploits fundamental sets with the proper boundary conditions. In this sense, usual FEM is an advantage, as one may use any basis set, specific to the problem at hand.
Exploitation of this property, which is characterised as the discrete variable representation (DVR) [95, 2], local potential operators are represented as diagonal matrices and the matrix elements of the kinetic energy are given by simple analytical formulas. Combining DVR with the FEM gives a very powerful numerical tool to solve boundary value problems [57].

4.2 FEM combined with DVR

Consider the elements $i = 1, ..., N$ constructed in FEM. Each one of these elements is subdivided with a set of Gauss quadrature points $\{x_m^i\}$, $m = 1, ..., n$. Since a typical Gaussian integration method is open, i.e. the endpoints of integration are not included to the integration domain, in the current approach a quadrature (defined as Gauss-Lobatto quadrature) that is closed has been chosen, i.e. the endpoints of each interval of integration are included as integration points. Note that this is important in solving boundary value problems and especially in FEM since the solution at all element nodes is known. The consequence of this is that for each element with $2n$ parameters ($n$ nodes and $n$ weights), only $2n - 2$ parameters in each element need to be considered to maximise the degree of the Gaussian integration rule.

It is desired in any Gaussian integration method to approximate integrals as

$$\int_{-1}^{1} g(x)dx \approx \sum_{m=1}^{n} g(x_m)w_m.$$

Here, $x_m$ and $w_m$ are the abscissas and weights, respectively, chosen to make the integral exact with a polynomial $g(x)$ of degree $2n + 1$. A generalisation of the quadrature rule over arbitrary intervals is accomplished by proper scaling of points and weights. Consider the integral over the interval $[r_i, r_{i+1}]$

$$\int_{r_i}^{r_{i+1}} g(x)dx \approx \sum_{m=1}^{n} g(x_m^i)w_m^i,$$

where the scaled points and weights are given by

$$x_m^i = \frac{1}{2} \left[ (r_{i+1} - r_i)x_m + (r_{i+1} + r_i) \right],$$

$$w_m^i = \frac{(r_{i+1} - r_i)}{2} w_m.$$

As mentioned earlier, in Gauss-Lobatto quadrature there are two constraints at the endpoints of each element, $x_1^i = r_i$ and $x_n^i = r_{i+1}$. This means that only $n - 2$ points are considered to approximate the integral, i.e.

$$\int_{r_i}^{r_{i+1}} g(x)dx \approx g(r_i)w_1^i + \sum_{m=2}^{n-1} g(x_m^i)w_m^i + g(r_{i+1})w_n^i.$$
The elementary basis functions are chosen to be Lobatto shape functions defined by

\[ f_{im}(x) = \prod_{j \neq m} \frac{(x - x_j)}{(x_m - x_j)}, \quad x \in [r_i, r_{i+1}] \]

\[ = 0, \quad \text{otherwise.} \]

Note that these functions are just the well-known Lagrange interpolating polynomials. The Lobatto shape functions have the property

\[ f_{im}(x_i') = \prod_{j \neq m} \frac{(x_i' - x_j)}{(x_m - x_j)} \]

\[ = \delta_{ii'} \prod_{j \neq m} \frac{(x_i' - x_j)}{(x_m - x_j)} = \delta_{ii'} \delta_{mm}. \]

This means that the following boundary conditions are fulfilled

\[ f_{i1}(r_i) = 1 \]
\[ f_{in}(r_{i+1}) = 1 \]
\[ f_{im}(r_i) = f_{im}(r_{i+1}) = 0, \quad \text{otherwise.} \]

Thus, by using the Lobatto shape functions as elementary basis functions in FEM, it is not necessary to make any linear transformation from the elementary basis functions, \( h_m \), to the finite element basis functions, \( f_{im} \), as discussed in section 4.1.

If the Gauss-Lobatto quadrature rule is used to approximate all integrals, the Lobatto functions are orthogonal, i.e.

\[ \int_0^\infty f_{im}(x)f_{im'}(x)dx = \delta_{ii'} \int_{r_i}^{r_{i+1}} f_{im}(x)f_{im'}(x)dx \]

\[ \cong \delta_{ii'} \sum_{j=1}^n f_{im}(x_j)f_{im'}(x_j)w_j^i \]

\[ = \delta_{ii'} \delta_{mm} w_m^i. \]

Note that it can be similarly shown that any local operator, \( V(x) \), is diagonal, i.e.

\[ \int_0^\infty f_{im}(x)V(x)f_{im'}(x)dx = \delta_{ii'} \int_{r_i}^{r_{i+1}} f_{im}(x)V(x)f_{im'}(x)dx \]

\[ \cong \delta_{ii'} \sum_{j=1}^n f_{im}(x_j)V(x_j)f_{im'}(x_j)w_j^i \]

\[ = \delta_{ii'} \delta_{mm} V(x_m^i)w_m^i. \]

Thus only one term contributes. To illustrate the power of DVR when combined with FEM in three dimensions, consider the integration of a three-dimensional
potential. In analogy with the one dimensional case, the following is obtained

\[ \int_0^\infty \int_0^\infty \int_0^\infty f_{i,m_1m_2m_3}(x,y,z)V(x,y,z)f_{i',m_1'm_2'm_3'}(x,y,z)dx dy dz = \delta_{ii'} \delta_{m_1m_1'} \delta_{m_2m_2'} \delta_{m_3m_3'} V(x_{m_1'}, y_{m_2'}, z_{m_3'}) w_{i,m_1}^i w_{i',m_2}^{i'} w_{i',m_3}^{i'}. \] (4.2.1)

If particular, if \( n \) quadrature points in each direction are chosen, then the number of evaluations of the potential, i.e. the number of terms in the Gaussian integration sum, will be \( n^3 \) if the technique of DVR is not used. However, from eq. (4.2.1), in using DVR this sum is reduced to only one term.

In the current formalism, an orthonormal basis set can be obtained if the following set is defined

\[ \chi_{im} \equiv f_{im}(x)/\sqrt{w_{im}}, \quad m = 2, ..., n - 1, \]
\[ \chi_{i1}(x) \equiv \left[ f_{in}(x) + f_{i+1,1}(x) \right]/\sqrt{w_{in} + w_{i+1}}. \]

The kinetic-energy matrix elements, \( T_{ii'}^{mm'} \), may be derived by ([57])

\[ T_{ii'}^{mm'} \equiv \frac{1}{2} (\delta_{ii'} + \delta_{i,i'+1}) \int_0^\infty dx \frac{d}{dx} \chi_{im}(x) \frac{d}{dx} \chi_{i'm'}(x). \]

Note that the matrix of the kinetic-energy operator has the structure of block-diagonality.

The first derivative of the basis functions may be derived to fulfill \([?, ?] \)

\[ f_{im}^i(x_{m'}) = \frac{1}{x_{m'} - x_{m'}} \prod_{k \neq m,m'} \frac{(x_{m'}^i - x_k^i)}{(x_k^i - x_{m'}^i)}, \quad m \neq m' \]
\[ = \frac{1}{2^m} \delta_{mn} - \frac{\delta_{m1}}{2w_{m}}. \quad m = m'. \]

To summarise this section, the combination of FEM with DVR leads to the fact that the potential operator matrix is diagonal. The only non-diagonal non-zero Hamiltonian matrix elements appear due to the kinetic-energy operator. Note that this property of matrix elements was certainly not present in traditional FEM, where Gauss-Legendre quadrature is used. The FEM-DVR scheme is currently implemented in the one-dimensional FEM code used here: FINE [61].

### 4.3 Finding Eigenvalues and Eigenfunctions

Several different algorithms exists to solve large eigenvalue problems such as eq. (4.1.3). Let the current eigenvalue problem be represented by

\[ Ax = \lambda x, \] (4.3.1)
where $A$ is an $n \times n$-matrix, $x$ is the eigenvector of length $n$, and $\lambda$ the eigenvalue.

In this thesis we solve the eigenvalue problem using the iterative Arnoldi method, see below. In general for iterative methods, an approximate solution is used until convergence has been reached.

### 4.3.1 The Power Method

The simplest of iterative methods is the power method [96], which is designed to find the largest eigenvalue in magnitude, and its corresponding eigenfunction. This method extracts the desired information by repeatedly multiplying an arbitrary starting vector, $x_0$, by the matrix, $A$, until convergence has been reached. To explain how this method works, suppose that the spectrum of the matrix $A$ is ordered as

$$|\lambda_1| > |\lambda_2| > \cdots > |\lambda_k|,$$

(4.3.2)

with the biggest eigenvalue in magnitude, $\lambda_1$, with corresponding eigenfunction, $v_1$. The starting vector, $x_0$, is expressed as a linear combination of the eigenvectors, $v_j$, of $A$ by

$$x_0 = \sum_{j=1}^{n} \alpha_j v_j.$$

(4.3.3)

After applying the matrix, $A$, on the vector, $x_0$, many times until convergence, the following expression is obtained:

$$x_k = Ax_{k-1} = A^2x_{k-2} = \cdots = A^kx_0 = A^k \sum_{j=1}^{n} \alpha_j v_j = \sum_{j=1}^{n} \lambda_j^k \alpha_j v_j = \lambda_1^k \left( \alpha_1 v_1 + \sum_{j=2}^{n} \left( \frac{\lambda_j}{\lambda_1} \right)^k \alpha_j v_j \right).$$

(4.3.4)

Only the term corresponding to the eigenfunction, $v_1$, with eigenvalue, $\lambda_1$, remains, since for all $j > 1$, $|\lambda_j/\lambda_1| < 1$, $(\lambda_j/\lambda_1)^k \to 0$.

### 4.3.2 The Inverse Iteration Method

If the eigenvalue of smallest magnitude is required, the so called inverse iteration method can be used [96]. This is exactly the same approach as the power method but here the solution is obtained by iterating with the inverse of the matrix $A^{-1}$, i.e. the following equation is solved for

$$A^{-1}x = \lambda^{-1}x.$$  

(4.3.5)

Here it is assumed that the matrix $A^{-1}$ exists. Since the eigenvalues of $A^{-1}$ are the reciprocals of those of $A$, i.e. $\lambda^{-1}$, the biggest eigenvalue of $A^{-1}$ is the smallest of $A$. Note that no inversion of the matrix $A$ is required as this might be very computationally expensive and with the loss of symmetry. Instead $A$ is LU-factorised [97, 96] only once before the iteration and the linear systems of equations are solved by forward and back substitution at each iterate.

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3In fact, in this thesis, we always solve the generalized eigenvalue problem: $Ax = zBx$. 40
To calculate eigenvalues and eigenvectors not lying on the periphery of the spectrum but in the interior, a *spectral transformation* of \( A^{-1} \) is a possible solution. The procedure for doing this is the so-called invert and shift method. More precisely, if an eigenvalue close to some number \( \sigma \) is required, the following eigenvalue problem is considered
\[
(A - \sigma)^{-1} x = (\lambda - \sigma)^{-1} x,
\]
(4.3.6)
Applying power iteration to eq. (4.3.6) will produce the greatest eigenvalue \( (\lambda - \sigma)^{-1} \). This means that the iteration has converged to the \( \lambda \) that lies closest to the shift \( \sigma \). Note that the eigenfunctions \( x \) are invariant to the shift of the spectrum.

### 4.3.3 The Arnoldi Method

If several eigenvalues need to be found at the same time, the methods mentioned above are not the optimum. More sophisticated methods such as the *Lanczos method* and the *Arnoldi method* are more frequently employed [98, 97, 96].

The Arnoldi method, which is a non-Hermitian generalisation of the Lanczos method, is an iterative method that is designed to compute simultaneously the largest, in magnitude, eigenvalues with their corresponding eigenvectors of a large sparse matrix. This method then differs from the single-vector power method which only spans a one-dimensional subspace and thus converges only to a single eigenvalue and eigenvector. The Arnoldi method uses the sequence of vectors generated by the power method, i.e. it constructs a \( k \)-dimensional subspace
\[
K_k(A, v_0) = \text{span}\left\{v_0, Av_0, A^2v_0, \ldots, A^{k-1}v_0\right\},
\]
(4.3.7)
which may contain information along eigenvector directions corresponding to extremal eigenvalues of matrix \( A \). Here, \( K_k(A, v_0) \) denotes the \( k \)-dimensional space of all linear combinations of the power methods first \( k \) iterates. The matrix, \( A \), is represented by an orthonormal basis, \( \{v_i, i = 0, \ldots, k\} \), stored as columns of the matrix, \( V_k \). The \( n \times n \) dimensional matrix, \( A \), thus reduces to a \( k \times k \) matrix in this representation, whose eigenvalues are approximations to those of matrix \( A \).

For a complex matrix, \( A \in \mathbb{C}^{n \times n} \), the Arnoldi method factorises the matrix, \( A \), as
\[
AV_k = V_k H_k + f_k e_k^T.
\]
(4.3.8)
Here, \( V_k \in \mathbb{C}^{n \times k} \) has orthonormal columns that span the space, \( K_k(A, v_0) \), and \( H_k \in \mathbb{C}^{k \times k} \) is an upper *Hessenberg matrix* [97, 96]. The eigenvalues of matrix, \( H_k \), will be approximations to that of \( A \) due to the in general non-zero residual vector, \( f_k \), which, however, becomes smaller with increasing \( k \). Here, \( e_k \) is the \( k \)th unit vector of length, \( n \).

The Arnoldi method, which reduces to the Lanczos method when treating real symmetric matrices, quickly converges to the eigenvalues lying on the periphery of the spectrum of the matrix, \( A \). As mentioned earlier, if eigenvalues in the middle of the spectrum need to be calculated, a spectral transformation accompanied with an inversion of the matrix, i.e. using the Arnoldi algorithm instead on \( (A - \sigma)^{-1} \), should find the eigenvalues in the desired region.


Chapter 5

Review of Papers

5.1 The Spin Polarised Atomic Tritium Trimer

\((T \uparrow)_3\)

Blume et al. [20], using a pair potential predicted the existence of a very weakly bound level, with \(J = 0\), of a bosonic system formed from three spin-polarised tritium atoms, \(((T \uparrow)_3)\), in a quartet quantum state. They solved the Schrödinger equation in the hyper-spherical formalism. Using 25 coupled adiabatic channels, the solution converged to the only allowed bound state of \((T \uparrow)_3\) with an energy of \(-3.19 \times 10^{-3} \pm 10^{-5}\) cm\(^{-1}\). The mass used for T\(\uparrow\) is 5496.9 a.u. Inclusion of a damped three-body Axilrod-Teller correction term [99], raises the ground state energy by about 1.6 percent.

The spin-polarised tritium dimer \((T \uparrow)_2\) has a very weakly attractive potential energy curve, with a well depth \(D_e = -4.6\) cm\(^{-1}\) and with a minimum inter-particle distance \(r_e = -7.8\) a.u. (see Figure 1). However, the potential is not deep enough to support a bound state \(^1\), thus \((T \uparrow)_3\) is Borromean. The \((T \uparrow)_2\) scattering length was calculated to be \(-82.1\) a.u.

Blume et al. investigated the possibility of this state being an Efimov state gave a negative result, since the energy decreased when scaling the potential by a factor beyond \(\lambda = 1\). Using the result reported in Ref. [100] that no bound states exist for any helium trimer for non-zero angular momentum, Blume et al. argued that since the potential energy surfaces of the helium trimer isotopomers are deeper than that of the tritium trimer system, the latter should not have any bound states for \(J > 0\) [20]. This was confirmed by our calculations as well (see Paper 1).

In the current study, using a three-dimensional finite element method, and using an extrapolation technique, based on the known asymptotics with respect to the finite element size and polynomial degree in FEM, we confirm the prediction

\(^1\)Compare this with the well depth of the \(\frac{4}{2}\)He\(_{2}\) potential energy curve \(D_e = -7.6\) cm\(^{-1}\) and with \(r_e = 5.6\) a.u. (see in Figure 2.5). The mass of \(\frac{4}{2}\)He is 7296.3 a.u. Thus it is not so surprising that \((T \uparrow)_2\) does not support a bound state since the bound state of \(\frac{4}{2}\)He\(_{2}\) is extremely loosely bound.
of a very weakly bound state of (T $\uparrow$)$_3$ which converges to $-3.20 \times 10^{-3} \pm 10^{-6}$ cm$^{-1}$. This is clearly in very good agreement with Blume et al.

The main aim of this work, however, was to find possible shape resonances for zero and non-zero total angular momentum. Using a smooth exterior complex scaling finite element method, no convergent solutions for any shape resonances were observed.

5.2 The Atomic helium trimers $^4$He$_3$ and $^4$He$^2$-$^3$He

In low temperature physics, vDW clusters of helium atoms, both $^4$He and $^3$He, are very interesting since they are building blocks in forming larger systems such as superfluid helium and Bose-Einstein condensates [25, 26]. In order to study these systems, information on the inter-particle interactions is essential. The study of small clusters of helium atoms, especially dimers and trimers, is therefore important. Furthermore, the helium trimer is very interesting by itself since it has been proposed that the excited state of $^4$He$_3$ has Efimov character [29, 30, 13, 15]. The halos are also of interest from a fundamental quantum mechanical point of view, since most of their probability distribution is in the classically forbidden region.

Computationally, the helium trimer is a very challenging problem. This is mainly due to the complicated hard-core structure of the two-body potential at small inter-particle distances, and the relatively big diffuseness of the wave function in configuration space. The hard-core problem is a consequence of the closed shell structure of helium. This may introduce large numerical errors, if not properly treated.

Esry et al. [15] studied helium trimers consisting of a mixture of helium isotopes, using the highly accurate helium dimer potential energy curve reported by Aziz and Slaman [74], having zero total angular momentum, $J = 0$. They solved the Schrödinger equation using the hyper-spherical formalism with a single channel, i.e. the adiabatic hyper-spherical approximation. Considering only pairwise interaction potentials they found two bound-states of the symmetric helium trimer, $^4$He$_3$, $E_0 = -7.374 \times 10^{-2}$ cm$^{-1}$ for the ground state and $E_1 = -1.472 \times 10^{-3}$ cm$^{-1}$ for the excited state, respectively. For the isotope $^4$He$_2$ -$^3$He, they predicted only one bound state at $-7.103 \times 10^{-3}$ cm$^{-1}$. Furthermore, they calculated the helium dimer energy to be $-9.1 \times 10^{-4}$ cm$^{-1}$. They argued that the excited state of $^4$He$_3$ is an Efimov state since it disappears into the continuum when increasing the interaction strength beyond the Efimov level. In a subsequent paper, using seven adiabatic couplings, they converged to the energies $E_0 = -8.70 \times 10^{-2}$ cm$^{-1}$ for the ground state and $E_1 = -1.57 \times 10^{-3}$ cm$^{-1}$ for the excited state of the symmetric helium trimer.

During the last three decades several groups using different formal and numerical approaches have also reported results on the helium trimer. Though Esry et al. used a similar, though not identical, interaction potential for the helium dimer, their reported results are consistent both with earlier and subsequent investigations. In 1977 Lim et al. [13] predicted the ground state and first excited state energies for the trimer of $E_0 = -5.977 \times 10^{-2}$ cm$^{-1}$ and $E_1 = -2.782 \times 10^{-3}$
cm⁻¹, respectively, and furthermore claimed that the excited state has the Efimov character. Cornelius and Glöckle [14] obtained $E_0 = -7.6 \times 10^{-2}$ cm⁻¹ and $E_1 = -1.11 \times 10^{-3}$ cm⁻¹. Kolganova et al. [17] found $E_0 = -9.105 \times 10^{-2}$ cm⁻¹ and $E_1 = -1.946 \times 10^{-3}$ cm⁻¹ while Nielsen et al. [16] found $E_0 = -8.702 \times 10^{-2}$ cm⁻¹ and $E_0 = -1.577 \times 10^{-3}$ cm⁻¹. Furthermore, Roudnev and Yakovlev [18], using the LM2M2 potential, converged on the energies $E_0 = -8.785 \times 10^{-2}$ cm⁻¹ and $E_0 = -1.578 \times 10^{-3}$ cm⁻¹. For more information regarding $J = 0$ results using different pairwise interaction potentials, see Paper 2.

The question of whether the helium trimer may possess further bound states for $J > 0$ was investigated by Lee et al. [100] though no such state was found. This was also confirmed by our calculations.

In Paper 2 the symmetric and asymmetric trimers, $^4$He$_3$ and $^4$He$_2$-$^3$He, respectively, were investigated using the Schrödinger equation for $J = 0$, realised through the three-dimensional finite element formalism [7]. The full hard-core potential was used in all calculations, i.e. no special boundary conditions were imposed on the wave function. Three different realistic He-He interactions were used: LM2M2 [74], HFD-B [73], and the TTY potential [72]. The helium dimer energies are calculated to be $-1.3083$ mK, $-1.6902$ mK, $-1.3186$ mK for the LM2M2, HFD-B and TTY potential, respectively. The helium dimer wave function for all three potentials has a significant contribution up to 1000 a.u.

Exploiting group theoretical selection rules [44, 53] of the bosonic helium trimer, earlier results have successfully been reproduced with competitive accuracy. It is especially noted that the solutions converged on the energies $E_0 = -8.73 \times 10^{-2}$ cm⁻¹ for the ground state of $^4$He$_3$ and $E_0 = -9.07 \times 10^{-3}$ cm⁻¹ for the only ground state of $^4$He$_2$-$^3$He.

In Figure 5.1 and 5.2, below, the wave functions of the ground state of both helium trimer isotopes, in Jacobi coordinates, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, using atomic units, are displayed. As seen in both figures, a significant distribution of the wave function in the collinear configuration is present, i.e. when the Jacobi coordinate distance $y$ is zero or close to zero. This together with the abnormal spatial distribution of the wave functions, indicates the diffuseness of the halo atomic helium trimers in configuration space. Comparing Figure 5.1 and 5.2 one can see that the wave function of $^4$He$_3$ is more localized in space than that of $^4$He$_2$-$^3$He.

Structural properties for the ground states of the two helium trimer isotopes for the different potentials are calculated. More specifically the average root mean square quantity $\sqrt{\langle r_{i,c.m.}^2 \rangle}$, where $r_{i,c.m.}$ denotes the distance between helium atom $i$ and center of mass c.m. of the whole three-body cluster. A perfect agreement of earlier results is obtained. Two extrapolation techniques supported by the FEM-method was employed. Our results are consistent with earlier results. For more details see Paper 2.
Figure 5.1: The absolute value of the wave function of the symmetric $^4$He$_3$ helium trimer ground state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function corresponds to our converged energy $-8.73 \times 10^{-2}$ cm$^{-1}$. Atomic units are used.

Figure 5.2: The absolute value of the wave function of the asymmetric $^{\Delta_2}$He$_2$-$^{3}_2$He helium trimer ground state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function correspond to our converged energy $-9.07 \times 10^{-3}$ cm$^{-1}$. Atomic units are used.
5.3 The Atomic neon Trimer Ne$_3$ and the argon Trimer Ar$_3$

Cutting edge experiments with vdW clusters can now be conducted with very high resolution, providing detailed information on the potential energy surfaces [101, 102]. Such data may give useful information on, for examples, the non-additivity of interatomic and intermolecular forces, as well as the influence of non-zero total angular momentum on the spectra.

Theoretical studies of zero and non-zero total angular momentum vdW clusters are, in general, a challenging problem. This is mainly due to their strong anharmonic potential energy surfaces, implying floppy, large amplitude and strongly delocalised motions of the physical system [15, 17, 18, 38, 103, 39, 46]. Studies into pre-dissociation phenomena in vdW complexes, e.g. calculation of positions, widths and cross sections of quantum resonances, have resulted in a dramatic increase in the knowledge of these complicated structures [60, 62, 24]. Studies on these complexes have mainly concentrated on systems in which a rare gas atom is weakly bound to a dimer system, e.g. HeICl [56], NeICl [24] and HeCl$_2$ [56]. These systems are relatively easy to study, since only the rare gas atom, along the vdW bond, may dissociate, e.g. due to flow of vibration energy from the excited dimer system. Similar studies of identical three-body vdW systems, such as He$_3$, Ne$_3$ and Ar$_3$ are much more complicated, due to the need to consider the increase in possible dissociation directions of the complex.

In Paper 3 the Schrödinger equation for the bosonic neon van der Waals trimer is solved using an exact Hamiltonian in a full angular momentum representation combined with a smooth exterior complex scaling method. The bound state results for $J = 0$, using a Morse-type potential are compared with previous calculations [38, 46, 47].

The Morse neon dimer potential supports only two bound states, and these are calculated to be -16.5186 cm$^{-1}$ and -1.83195 cm$^{-1}$. The same grid was used for both states. Beyond 25 a.u. the energies of the dimer did not change within the present accuracy.

Exploiting group theoretical selection rules of the bosonic neon trimer, it is demonstrated that the eigenvalues for $J = 0$ obtained with the current technique in a variational sense are the most accurately calculated to date. Structural properties for the $J = 0$ bound states are calculated. More specifically the average root mean square quantity $\sqrt{\langle r^2 \rangle_v}$, defined by

$$\sqrt{\langle r^2 \rangle_v} = \sqrt{\frac{r_{12}^2 + r_{23}^2 + r_{13}^2}{3}} = \sqrt{\frac{2}{3} y^2 + \frac{1}{2} x^2},$$

(5.3.1)

where the index $v$ characterizes the different vibrational quantum states. We have a perfect agreement with previous results. For details see Paper 3.

In Figure 5.3, 5.4 and 5.5 we present the wave functions of the neon trimers first three totally symmetric $A_1$ vibrational states, i.e. -50.10, -34.22 and -32.57 cm$^{-1}$. It is clear from Figure 5.4 that already the first excited state has a significant distribution in the collinear configuration ($y \approx 0$); the second excited state,
displayed in Figure 5.5, has an even bigger distribution at $y \approx 0$. Note that the higher the energy the more vibrational nodes are present and the more delocalized the wave function of the trimer becomes. For a detailed discussion, see Paper 3.

To our knowledge no rovibrational or any predissociation calculations are previously reported in the literature for this specific trimer. Rovibrational states up to $J = 3$ are calculated, and are presented together with their projections in the body-fixed frame and different parities.

More importantly, these results represent the first successful investigation to find evidence for a possible shape resonance for $J = 0$ of the neon trimer, and which lies just above the neon dimer ground state threshold -16.51 cm$^{-1}$. We believe to have converged to the energy -15.977-i1.863 $\times 10^{-3}$ in atomic units.

In Paper 4 we solve the Schrödinger equation for the bosonic argon van der Waals trimer, for total $J = 0$ using a Morse-type potential.

The Morse argon dimer potential in eq. (2.7.11) supports six bound states. These were calculated to be -83.92936, -57.52014, -36.08537, -19.62505, -8.139170, and -1.62741 cm$^{-1}$. The same grid was used for all states. Beyond 25 a.u. the energies of the dimer did not change within the present accuracy.

Exploiting the permutational symmetry of the bosonic argon trimer, the first few vibrational energy levels with all symmetries are calculated. The results, employing a Morse-type potential, are compared to previous ones [46, 47, 38]. Structural properties are calculated and discussed. In Figure 5.6, 5.7 and 5.8 we present the wave functions of the argon trimer Ar$_3$ first three totally symmetric $A_1$ vibrational states, i.e. -252.44, -220.94 and -208.24 cm$^{-1}$.
Figure 5.4: The absolute value of the wave function of the neon trimer Ne$_3$ first excited vibrational $A_1$ state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function correspond to our converged energy $-34.22$ cm$^{-1}$. Atomic units are used.

Figure 5.5: The absolute value of the wave function of the neon trimer Ne$_3$ second excited vibrational $A_1$ state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function correspond to our converged energy $-32.57$ cm$^{-1}$. Atomic units are used.
Figure 5.6: The absolute value of the wave function of the argon trimer $\text{Ar}_3$ ground vibrational $A_1$ state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function correspond to our converged energy $-252.44 \text{ cm}^{-1}$. Atomic units are used.

Figure 5.7: The absolute value of the wave function of the argon trimer $\text{Ar}_3$ first excited vibrational $A_1$ state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function correspond to our converged energy $-220.94 \text{ cm}^{-1}$. Atomic units are used.
Figure 5.8: The absolute value of the wave function of the argon Ar\textsubscript{3} trimer second excited vibrational $A_1$ state plotted against the Jacobi coordinate distances $x$ and $y$, with angle $\theta = \arccos(\hat{x}, \hat{y})$ fixed to 90 degrees, i.e. an equilateral configuration of the atoms. This wave function correspond to our converged energy $-208.24$ cm\(^{-1}\). Atomic units are used.

Comparing the wave functions of the first three vibrational states of the argon trimer to that of the neon trimer, displayed above, one can see that neither the first nor the second excited state of the argon trimer have a significant distribution in the collinear configuration. In fact it was predicted by Roy [38], that the argon trimer shows importance in the collinear configuration starting from the eighth totally symmetric excite state. The explanation of this is clear, the argon trimer is more tightly bound than the neon trimer and thus have a more localized wave function for the same vibrational quanta, see Paper 4.
Chapter 6

Conclusions

One of the aims of this thesis was to test our method, a three-dimensional finite element method combined with a smooth exterior complex scaling technique on extreme cases of three-body systems. In this case van der Waals (vdW) and halo atomic trimers. It is known from previous literature that these systems are relatively difficult to treat, concerning bound state and in particular shape resonance calculations.

vdW clusters in general, may impose numerical errors due to the intrinsic hard-core structure of the pairwise interaction potential if not properly treated. This is particularly the case for the helium trimer $^4$He$_3$. Another characteristic problem of vdW and halos clusters are their strongly anharmonic potential energy surfaces, implying relatively weak binding energies with corresponding wave functions sampling large proportions of configuration space, making the structures diffuse in space and difficult to numerically span.

However despite of these, apparently serious problems, we have demonstrated in Papers 1-4 for the bosonic halos: the spin polarized tritium trimer $(T \uparrow)_3$, and the vdW helium trimers $^4$He$_3$ and $^4$He$_2$-$^3$He, and the bosonic neon and argon trimers, Ne$_3$ and Ar$_3$ respectively, that our formal/numerical tool, works perfectly in the study of three-body very weakly bounded spatially extended quantum systems with hard-core potentials. The bound states and structural properties are in excellent agreement with previous results using different formal and numerical approaches. Furthermore we believe to be the first to find evidence for a possible shape resonance for $J = 0$ of the neon trimer, which lies just above the neon dimer ground state threshold.

Our finite element method has several advantages, one is that it is fully three-dimensional, in the sense that we use three degrees of freedom to optimize the grid. However, we have in this study only made use of a trial and error selection of the FEM grid. Thus in the present version, relatively large matrix dimensions with large bandwidths are produced. The FEM method as such has a built in mathematically well defined convergence criteria, such as the adaptive grid methods [91].

\footnote{Kolganova \textit{et al.} [17], however, were able to completely circumvent the hard-core problem using the so called boundary condition model combined with the Faddeev equations in configuration space representation, see more in Paper 2.}
Using these features, one should be able to obtain somewhat better results with a smaller but more appropriate, converged grid. It is our intention to continue this study by making use of these methods.

It is also planned in the near future to calculate the excited state of $^4\text{He}_3$ and investigate its possible Efimov character. Possible resonance states for both helium trimer isotopes and the neon and argon trimers, using our three-dimensional smooth exterior complex scaling method, are planned to be investigated.
Bibliography