



Rotation-Vibration States of Triatomic Molecules at Dissociation

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I, Bruno César Silva, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

For Sylvia

Abstract

Nuclear motion resonant states of triatomic molecules are calculated using an $\mathcal{L}^2$ method known as Complex Absorbing Potential (CAP). This method is implemented in a new program named RES3D which includes a new automatic procedure to obtain the resonant states' energies and lifetimes, allowing for the first time the quantification of the results' accuracy through a consistency test across different CAP functional forms. Its implementation is described in detail. Validation tests consisting of a comparison of HOCl resonances calculated with RES3D with those available in the literature, are presented.

The largest calculations to date of the vibrational states of H_3^+ and D_2H^+ of all bound state eigenvectors and up to about 2000 cm^{-1} above dissociation are also presented. The results of these calculations are analysed through studies of the convergence of bound states, the calculation of relevant observables, and the visual analysis of wavefunctions.

Based on eigenvectors obtained from these calculations, vibrational resonances for H_3^+ and D_2H^+ , as well as H_3^+ at $J = 3$ are calculated with RES3D. D_2H^+ is used to study the resonances in multi-channel systems by investigating two energy regions: the one where $\text{D}_2 + \text{H}^+$ is the only dissociation product and the one where $\text{HD} + \text{D}^+$ can also be formed. Branching ratios are obtained in the latter case by using different CAPs. It is shown that H_3^+ and D_2H^+ support narrow Feshbach-type resonances.

The findings from the study of resonant states made using RES3D and possible technical improvements to the program are discussed. A brief description of the work currently being done to use RES3D in an attempt to fully characterise the spectrum of H_2O is also presented.

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Chapter 1

Introduction

The H_3^+ molecule and its isotopologues, D_3^+ , D_2H^+ and H_2D^+ , represent benchmark systems for chemical physics [1]. It is the (electronically) simplest bound polyatomic molecule, having only two electrons and three nuclei. The three nuclei typically form an equilateral triangle at equilibrium, shaped by the two electrons that form a cloud around them. It was first discovered by Thomson in 1911 as an object with an atomic mass of three but a single positive charge [2; 3], long before a good understanding of quantum mechanics arose. Due to its simplicity, H_3^+ was the subject of many early theoretical studies [4], which predicted properties such as its equilibrium geometry [5]. This equilateral triangle geometry was confirmed by experiment in 1978 by a Coulomb explosion experiment [6]. However, it was not until after the development of useful lasers that the fundamental, infra-red, spectrum of H_3^+ could be recorded by Oka in 1980 [7]. Not long after in 1982, Carrington, Buttenshaw and Kennedy recorded a very interesting spectrum of H_3^+ and its isotopologues near dissociation [8].

As will be described later in this chapter, a full understanding of this spectrum can only be obtained by studying the so called *resonant states*. These are states that lie above the dissociation threshold and thought to have a fundamental role in understanding this so-called Carrington-Kennedy pre-dissociation spectrum.

1.1 Motivation and Aims

The study of chemically bound polyatomic molecular systems close to their dissociation limit presents considerable computational challenges. This is due to the number of bound states which are supported by normal molecular interaction and the fact that the characteristics of highly excited states must be very different from the those of the lower states. In fact one might expect states which approach dissociation to exhibit features suggestive of dissociation, such as very long-range extension. For example, for nuclear kinetic energies which lie in the range between the classical and the quantum dissociation limit, there is virtually no limit on the extent of the molecule, other than the zero point energy constraints in the dissociation products. This leads to great technical difficulties related with performing accurate calculations that do not impose artificial barriers to the extent of the wavefunction [9].

The situation described above is very similar to that of resonant states. In the case of the so-called Feshbach-type resonances, there is neither a zero-point energy constraint to the wavefunction extent nor any potential barrier through which tunnelling could occur. These are states completely embedded in the energy continuum.

The inherent computational difficulties associated with theoretical studies on such states, and particularly so for nuclear motion resonances, means that there are relatively few studies which investigate vibrational-rotational levels near dissociation for chemically bound species.

This thesis is focused on an attempt to create a program that alleviates some of these difficulties. Tentatively named RES3D, it performs the calculation of these resonant states by using parallel computing techniques and algorithms that allow an almost completely automatic identification of resonant states. It is also designed to extend the functionality of the DVR3D suite of programs for computation of triatomic molecular spectra [10].

Besides its scientific importance, a calculation of the resonant states involved in the Carrington-Kennedy experiment provides an opportunity to explore the limitations of both the theory and the program's algorithms. Although H_3^+ and its isotopologues are extremely simple to describe, their exact behaviour is an enormous challenge to theory. They support a very large range of dynamics even at fairly low energies: for instance, at energies above linearity the classical behaviour is mostly chaotic [11], the quantum scars of this behaviour are therefore also very complicated. Due to H_3^+ 's floppiness, the harmonic approximation fails particularly quickly in this case. Additionally, strong Coriolis coupling between motions makes rotational calculations difficult. The heavier isotopologues constitute an even more

challenging problem since they support many more bound states than H_3^+ .

It should be noted that the Ar_3 Van der Waals trimer also exhibits this type of “floppy” behaviour: it has also an equilateral triangle geometry at equilibrium with a low barrier to linearity. Although it has a shallower potential, its higher nuclear masses give Ar_3 a comparably high density of states [12; 13], and also exhibits a progression of highly localised states above the barrier to linearity, as what is observed in H_3^+ [12].

Due to the generalised nature of the DVR3D suite of programs, RES3D is tentatively designed to perform calculations of resonances for all triatomic molecules within the operational limits of DVR3D. One of the validation tests performed for HOCl is presented here. These results will then be compared to calculations previously done by this group with an independent program and “manual” visual inspection techniques, which have been published, showing good agreement with experiment [14].

1.2 Properties of the H_3^+ molecular ion.

At its ground-state, equilibrium geometry, the protons of H_3^+ form an equilateral triangle with sides of $1.65 a_0$. It has three vibrational modes, as described in Fig. 1.1. In the first mode, all the internuclear distances grow and shrink simultaneously. It is called the symmetric breathing mode. The second two are the degenerate bending modes, v_{2x} and v_{2y} . Because of the Pauli exclusion principle, the breathing modes for $J = 0$, i.e., A_1 ro-vibrational modes, are not physical. However, A_1 vibrational states are still considered in this work as they form band origins to $J > 0$ states that do not have A_1 symmetry and therefore can be populated. A consequence of the equilateral triangle configuration is that there is no permanent dipole moment at equilibrium and therefore there is no pure rotational spectrum for H_3^+ . However, it has been predicted that there should be an observable “forbidden” rotational spectrum [15; 16].

The ground electronic state of H_3^+ is a completely symmetric singlet state ($^1A_1$) which has a dissociation limit of $\text{H}^+ + \text{H}_2(^1\Sigma_g^+)$. The next singlet state dissociates to $\text{H}(1s) + \text{H}_2(^2\Sigma_g^+)$ instead. As in the preceding work [17] both states are considered. This is because there is an avoided crossing between them and at some long range configurations of the molecule: the surface from the 2^1A_1 state actually has a lower energy than the surface for the 1^1A_1 state. Therefore a correct long range electronic potential must consider the effect of this avoided crossing in order to treat the near dissociation states correctly.

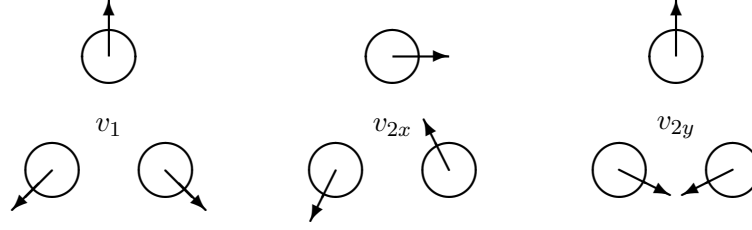


Figure 1.1: Vibrational modes of H_3^+ . From left to right, the v_1 breathing mode and the degenerate v_{2x} and v_{2y} bending modes.

Table 1.1: Allowed symmetries and spin statistical weights for H_3^+ .

Γ_{rve}	Γ_{ns}	Γ_{tot}	g_{ns}
A'_1	—	—	0
A''_1	—	—	0
A'_2	A'_1	A'_2	4
A''_2	A''_1	A''_2	4
E'	E'	A'_2	2
E''	E'	A''_2	2

It is also often important to consider the symmetry effects of the protons. Formed from three fermions (spin-half protons) H_3^+ must obey Fermi-Dirac statistics. Under odd permutations of the protons the total wavefunction must change sign and under even permutations of the protons the total wavefunction must be invariant. In the molecular symmetry group of H_3^+ (D_{3h}^{MS}) the total wavefunctions must therefore have either A'_2 or A''_2 symmetry. This implies that ro-vibrational electronic wavefunctions with A'_1 or A''_1 symmetry cannot exist as there is no way of forming total wavefunctions with A'_2 or A''_2 symmetry. The allowed symmetries for the ro-vibrational electronic wavefunctions (Γ_{rve}), the nuclear-spin wavefunctions (Γ_{ns}) and the total wavefunctions (Γ_{tot}) are shown in table 1.1, along with the spin statistical weights g_{ns} [18].

1.3 The infra-red pre-dissociation spectrum of H_3^+

An extremely complex spectrum of H_3^+ near dissociation was recorded by Carrington *et al* and has remained to date without a complete explanation of its underlying mechanisms. Carrington, Buttenshaw and Kennedy reported in 1982 a very unusual photo-dissociation spectrum of H_3^+ [8]. It is important to understand the exper-

imental apparatus due to its implications in the interpretation of its outcome. A diagrammatic representation of the experiment is shown in Fig. 1.2.

The incident photons were produced by a tunable infra-red CO_2 laser, while H_3^+ was produced by the electron impact ionisation of H_2 . The positive potential of the electron impact ionisation source accelerated the hot H_3^+ toward a bending magnet, which then selected the ions by their mass-charge ratio, thereby only bringing the H_3^+ molecular beam in line with the laser.

The H_3^+ molecular beam then entered the drift tube where it could interact with the laser collinearly. The frequency of interaction between the infra-red photons and the H_3^+ was controlled by altering the ion-accelerating potential and thereby altering the ion velocity, causing the relative frequency of the laser through Doppler shift.

Protons ejected from the drift tube were then measured using an electrostatic analyser (ESA) and a electron multiplier. Protons of different energies could then be selected by varying the ESA voltages. The off-axis electron multiplier allowed the measurement of the proton current at those energies. An additional electric potential was introduced in the drift tube. This allowed Carrington and co-workers to monitor the protons resulting from interactions within it as they had a different energy.

In 1984, Carrington and Kennedy published their completed work on near-dissociation H_3^+ which included the recording of over 27,000 transitions and similar spectra for D_3^+ , H_2D^+ , and H_2D^+ [19]. The high-resolution spectrum appeared to have very little structure with no hope of any assignment. The only structure found was that of four peaks formed from many lines when the spectrum is looked at a low resolution [20]. These four collections of peaks occur at 876, 928, 978 and 1,034 cm^{-1} .

Early on the conclusion was reached that resonances must play a role in this spectrum: many of the states recorded had more energy than the photons from the CO_2 laser, suggesting that some of the initial states are also above dissociation. As it was only the H_3^+ -photon interactions that happened within the drift tube that were recorded, any resonant states of either H_3^+ or its isotopologues had to survive long enough to enter the drift tube for it to be part of the recorded spectrum. The time taken to transport the ions into the drift tube gave a lower limit to the lifetimes of the initial states involved in the pre-dissociation. With a beam potential of 5kV the initial state lifetimes must have been greater than $3\mu\text{s}$. The final states of H_3^+ then had to be short lived enough that dissociation could occur within the drift tube, otherwise the ejected protons would not have been recorded. At the same beam potential of 5kV the final state lifetime must have been less than $0.7\mu\text{s}$.

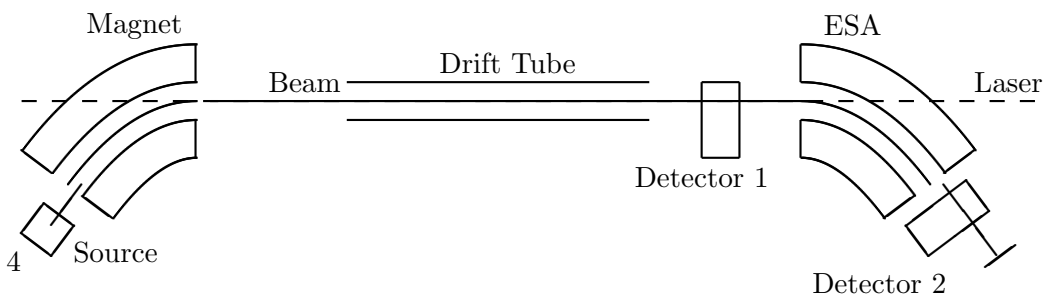


Figure 1.2: A holistic representation of the Carrington-Kennedy experiment. The molecular ions travel through the apparatus from left to right.

Ions which fragmented quicker than about 7ns resulted in lines that were too broad to discern against the background noise of the spectrum. The final state lifetimes range were directly measured as line-widths in the spectrum ($\tau = \hbar/\Gamma$).

This remarkable spectrum created a large interest in the theoretical community. Studies on the kinetic energy release of H^+ and D^+ from the isotopologue D_2H^+ [21; 22] prompted further research. After significant improvements to their experimental apparatus, Carrington, McNab and West repeated some of the earlier experiments at higher accuracy and extended them to include the recording of lines from products that had a much higher kinetic energy [23]. The ESA used to record the spectrum was tuned to only allow H^+ fragments with a particular kinetic-energy to charge ratio into the detector. This window was varied over a range of kinetic energies from 0 cm^{-1} to 3000 cm^{-1} . When centred at 0 cm^{-1} , many lines with a range of widths and intensities were detected. When centred at 500 cm^{-1} , a large number of weak lines were detected (*ca.* 60 per cm^{-1}). Finally at 3000 cm^{-1} a relatively clean spectrum was detected with few number of strong transitions. But even with these ideal conditions, no pattern was observed. This later study demonstrated effectively that the results were truly reproducible as it was previously thought that details of the recorded spectra were sensitive to the exact experimental conditions.

There is an important experimental limitation in this apparatus, preventing the observation of a clean H_2D^+ spectrum, which has consequences to the work presented here. The magnetic analyser cannot separate H_2D^+ from D_2^+ – it exhibits a very strong IR photo-dissociation because of the excitation to an electronic repulsive state, and the fragment D^+ ions arising from this diatomic ion cannot be distinguished from those arising from H_2D^+ [19].

This experimental limitation and theoretical reasons cause the isotopologue calculations presented in this work to be confined only to D_2H^+ . Firstly, the fact that

D_3^+ is heavier than D_2H^+ makes the computation of the states of this isotopologue expensive due to the higher density of states, and consequent requirement of prohibitively large basis sets. It also has reportedly similar characteristics to that of H_3^+ making the potential cost even less appealing. Finally, the study of D_2H^+ opens also the interesting possibility of analysing the dissociation either through the $HD + D^+$ or the D_2+H^+ channels, both studied in this work.

1.3.1 Explanations for the spectrum

Early analysis suggested that long-range $H_2 - H^+$ type complexes near dissociation [24] with significant rotational excitation could explain the near-dissociation spectrum [25]. This proposal has not been invalidated, but it now appears that a wider range of states, including close-coupling of all three nuclei, qualitatively fit the experimental data [26]. These *Horseshoe* states [11; 27] have been found to support strong dipole transitions [28] and with rotational excitation can form resonances with long lifetimes [26], trapped by the centrifugal potential barrier in the effective rotational potential energy surface. It should also be noted that these Horseshoe-like states will exist at higher rotational excitations than long range $H_2 - H^+$ type complexes because the effective centrifugal potential reduces the range of states involved. Figure 9 in the work of Berblinger *et al* [11] effectively portrays this for J greater than about 30.

However, recent work by Munro *et al.* [29] predicts the existence of the so-called Asymptotic Vibrational States (AVS). These states arise in the energy region between the real (quantum) dissociation limit and the classical dissociation limit. This suggests that the interpretation of H_2-H^+ cannot be entirely discarded due to the atom-diatom-like configuration of these states. The work presented here and reported elsewhere also suggests that Feshbach-type resonances may also play an important role in this spectrum.

1.4 Previous near-dissociation calculations

So far, the only aspect of the recorded spectrum which is fully understood is its behaviour with respect to isotopic substitution, whose explanation rests on semi-classical rather than fully quantum mechanical analysis [21; 30; 31]. Nevertheless, it is accepted that this spectrum involves transitions between bound and quasi-bound states near dissociation and with life-times ranging from about 10^{-9} to 10^{-6} s. Despite attempts to understand the nature of these states [32], there has been no successful simulation of the spectrum as yet.

There have been a number previous attempts at a full quantum mechanical calculation on H_3^+ up to dissociation. With the aim of studying the high angular momentum limit variationally, Miller and Tennyson [33] calculated many states of H_3^+ and H_2D^+ at high J using a small basis set.

Carter and Meyer [34] calculated the vibrational states up to about $25,000\text{ cm}^{-1}$ above the ground state, the energy at which the potential [35] is still valid, some $10,000\text{ cm}^{-1}$ below the dissociation energy. Henderson and Tennyson [36] made the first attempt at calculating *all* the vibrational bound states using the same potential. A second attempt was made by Henderson *et al* [37] achieving a better convergence of $\approx 2\text{ cm}^{-1}$.

Next, Bramley *et al* [38] used a novel approach based upon an efficient iterative diagonalisation of a sparse Hamiltonian to calculate all the bound states to a much higher accuracy of about 0.01 cm^{-1} . Their approach allowed for a very efficient calculation of the vibrational energies but not the wave functions which could only be produced at a considerable cost. However, the use of a potential that is not strictly valid at dissociation [35] make these results somewhat qualitative in nature.

Later, Mandelshtam and Taylor [39] calculated all the bound states using a filter diagonalisation technique. They also calculated a number of vibrational resonances (Feshbach-type, which will be explained later) using a Complex Absorbing Potential method very similar to the method employed in RES3D. Again, as the behaviour of the potential of Meyer *et al* [35] used in this calculation is not correct at dissociation these results are only qualitatively useful.

Kostin *et al* [40] used a new surface [41] to calculate near-dissociation states. This new surface made calculations much more difficult. The dissociation channels close to dissociation allowed for very long states and therefore required much larger basis sets. With this surface they did manage to calculate a large number of states up to dissociation, but with fairly poor convergence.

Calculations of rotational states are somewhat more difficult. The number of states for a particular J scales at roughly $(2J + 1)$ and the basis set size required scales at a similar and perhaps worse rate. There have only been three attempts at calculating ro-vibrational states all the way up to dissociation. Henderson and Tennyson for $J = 1, 2$ [42], Kostin *et al* for $J = 2, 8$ [40] and those performed by Munro [17] for $J = 3$.

The work presented here builds upon the previous steps by Munro [9; 17; 29] to simulate the Carrington-Kennedy spectrum. Using his parallelised version of the DVR3D [10] program suite – PDVR3D – for the simulation of molecular spectra of triatomics, the author performed $J = 0$, bound-state calculations of D_2H^+ , and

improved the convergence of previous $J = 0$ H_3^+ calculations. Using RES3D, resonances were then calculated using as a basis the eigenvectors obtained from these bound-state calculations and those obtained in previous $J = 3$ H_3^+ work [17], culminating in the first rotational resonances of H_3^+ ever published.

Theoretical Background

The theory of diatomics is very well understood up to energies close to dissociation [43] and for geometries with large inter-nuclear distances [44]. For molecules of higher nuclear count, the underlying theory is equally well understood, but similarly to what happens in classical mechanics, the increased number of interacting bodies creates difficult analytical and computational challenges.

In the case of tri-atomic molecules, the Born-Oppenheimer approximation helps to alleviate the analytical problem in part by conceptually separating the electronic motion from the nuclear motion. Effectively, this approximation splits what originally was a four or more body dynamics problem into an electron motion equation with three nuclear positions defined parametrically, and a three-body nuclear motion problem in an effective potential generated by electronic structure. This potential is the interpolation of energy values parametrically dependent on the nuclear positions through a real continuous function of the nuclear coordinates, referred to as Potential Energy Surface (PES). This formalism allows the calculation of the so-called bound states of the molecule, where all particles have their motion constrained by the interaction potential.

Understanding what occurs in the system at energies above the dissociation energy limit requires an understanding of collisions within the context of quantum mechanics. This theoretical framework is known as scattering theory. Within it, the nature of states known as resonances is defined: metastable states above the theoretical dissociation energy. These resonances account for the famous H_3^+ spectrum observed by Carrington and Kennedy [8; 19].

In this chapter the theoretical framework required for the description of nuclear motion resonant states is presented in the context of the work previously done by Jonathan Tennyson's group for the calculation of bound molecular states. It is the

foundation of the new results presented in this dissertation.

2.1 The Schrödinger Equation

Quantum Mechanics is at the heart of the description of molecular systems. Central to its formalism is the Schrödinger Equation (SE), which traditionally is viewed as having its most general form in its time-dependent (TD) formulation given by:

$$-i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi , \quad (2.1)$$

where Ψ is the system's wavefunction containing all the information that can be known about the system for all time t , $\hat{H}$ is the Hamiltonian operator and $\hbar$ is Plank's constant h divided by 2π .

For the study of the interaction between photons and molecules, particularly in spectroscopic studies, it is sufficient to calculate the energy states of these molecules to know the absorption/emission line positions, and use the resulting wavefunctions to calculate dipole transition moments to obtain line intensities. Time-dependent details of how molecular state transition occur are not necessary to determine how much energy involved. Therefore one seeks to simply calculate start and end stationary states in the transition. Starting from Eq.(2.1) these states must be such that the wavefunction assumes the separate form:

$$\Psi(\mathbf{q}, t) = \psi(\mathbf{q})\phi(t) , \quad (2.2)$$

where $\mathbf{q}$ is a set of generalised coordinates, ψ the stationary wavefunction, and the TD part of the wavefunction is given by $\phi(t) = \exp\{-iEt/\hbar\}$. Replacing the trial solution given by Eq.(2.2) in Eq.(2.1) gives the time-independent (TI) SE:

$$\hat{H}\psi = E\psi. \quad (2.3)$$

The fact that the use of TI SE allows the calculation of wavefunctions using real arithmetic is also advantageous.

Some authors claim that this is the most fundamental form of the SE, from which its TD form can be derived: beginning with an entangled state of a TI quantum system coupled to its TI quantum environment, Briggs *et al.* [45] have shown that the TD SE of any quantum system is derived from the TI expression in the limit where one of the environment variables becomes a classical variable.

2.1.1 Variational Method

The Rayleigh-Ritz variational method is the most commonly used to calculate energy levels and wavefunctions of bound systems, effectively relying on an algebraic technique that lends itself very well to current computational tools, such as multi-core CPUs. The idea is to exploit the fact that, for any normalised trial wavefunction ζ :

$$\langle \zeta | \hat{H} | \zeta \rangle \geq E_0 , \quad (2.4)$$

where E_0 is the ground state energy of the bound system defined by the TI SE:

$$\hat{H} \xi_i = E_i \xi_i . \quad (2.5)$$

This statement can be proved if one expands the trial function ζ into an orthonormal complete set of basis functions, such that:

$$\zeta = \sum_{i=1}^{\infty} c_i \xi_i . \quad (2.6)$$

Consequently, by application of Eq.(2.6) to Eq.(2.4):

$$\begin{aligned} \langle \zeta | \hat{H} | \zeta \rangle &= \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} c_i c_j \langle \xi_i | \hat{H} | \xi_j \rangle \\ &= \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} c_i^* c_j E_j \delta_{ij} \\ &= \sum_{i=1}^{\infty} |c_i|^2 E_i , \end{aligned} \quad (2.7)$$

which, if ζ is normalised, always obeys the inequality:

$$\sum_{i=1}^{\infty} |c_i|^2 E_i \geq E_0 . \quad (2.8)$$

This statement has also been shown to be true for excited states as well, under the requirement that their trial wavefunctions be orthogonal to each other [46], meaning:

$$E_0 \leq W^0; E_1 \leq W^1; \dots; E_n \leq W^n , \quad (2.9)$$

where n is the last index in the truncated expansion. This provides the means to obtain an approximation to the true solution for all energy levels of a system through

a parametrised test wave-function, ζ , by successive application of the formula:

$$W = \frac{\langle \zeta | \hat{H} | \zeta \rangle}{\langle \zeta | \zeta \rangle} . \quad (2.10)$$

The trial wavefunction that provides the lowest energy eigenvalues is the closest to the true solution of the TI SE (2.4). If the trial function is defined as a truncated basis set expansion where the basis functions ξ and the coefficients c are real, then Eq.(2.10) can be written as:

$$W = \frac{\sum_{ij}^N c_i c_j \langle \xi_i | \hat{H} | \xi_j \rangle}{\sum_{ij}^N c_i c_j \langle \xi_i | \xi_j \rangle} . \quad (2.11)$$

If one defines:

$$H_{ij} \equiv \langle \xi_i | \hat{H} | \xi_j \rangle \quad (2.12)$$

and

$$S_{ij} \equiv \langle \xi_i | \xi_j \rangle , \quad (2.13)$$

where the S_{ij} term is often called the overlap integral. It is possible to rearrange Eq.(2.11) into:

$$\sum_{ij}^N c_i c_j (H_{ij} - W S_{ij}) = 0 . \quad (2.14)$$

Exploiting the inequality in Eq.(2.8) means that minimising this estimate relatively to coefficients will give the optimal value of W possible for that particular basis set. This minimisation will have to be done for each coefficient, so that:

$$\frac{\partial W}{\partial c_k} = 0 , \quad k = 1, 2, \dots, N . \quad (2.15)$$

After some manipulation, Eq.(2.15) leads to:

$$W \frac{\partial}{\partial c_k} \sum_{ij}^N c_i c_j S_{ij} = \frac{\partial}{\partial c_k} \sum_{ij}^N c_i c_j H_{ij} . \quad (2.16)$$

which then becomes:

$$W \sum_i^N c_i S_{ij} \delta_{jk} = \sum_i^N c_i H_{ij} \delta_{jk} , \quad (2.17)$$

or:

$$W \sum_{kj}^N c_j S_{kj} = \sum_{kj}^N c_j H_{kj} .$$

Since the basis functions are orthonormal, $S_{ij} = \delta_{ij}$, hence:

$$Wc_k = \sum_{kj}^N c_j H_{kj} . \quad (2.18)$$

Simultaneous minimisation of all the coefficients is equivalent to solving a system of N homogeneous equations given by Eq.(2.18). This corresponds to the eigenvalue problem:

$$W\mathbf{c} = H\mathbf{c} , \quad (2.19)$$

where $\mathbf{c}$ is the eigenvector that is associated with the energy estimate eigenvalue, W , and H is the square matrix of size N and elements given by $\langle \xi_i | \hat{H} | \xi_j \rangle$. The implication is that N such eigenvector-eigenvalue pairs exist, and the full problem can be written as:

$$C\mathbf{W} = H\mathbf{C} , \quad (2.20)$$

where C is the matrix whose columns are the $\mathbf{c}_n$ eigenvectors and $\mathbf{W}$ is a diagonal matrix whose elements are the W_n eigenvalues. This problem can be readily treated computationally using eigensolver libraries.

2.2 The Molecular Hamiltonian Operator

So far only a general approximation approach to solving a generic, bound state, quantum mechanical problem has been described. It is now necessary to look at the molecular Hamiltonian in detail.

The complete molecular Hamiltonian operator describes all the interactions between the electrons and nuclei that constitute the molecule, which in the case of the work presented here are seen as structureless particles. Table 2.1 lists all the terms in the molecular Hamiltonian [17], according to the formalism due to Bunker and Jensen [47].

In practise, many of these interactions may be neglected in order to make this problem computationally treatable. The molecular Hamiltonian may be treated as follows:

$\hat{T}_{\mathbf{cm}}$ Calculations are performed in the molecule's frame of reference, in internal coordinates. $\hat{T}_{\mathbf{cm}}$ is therefore separate and can be discarded.

$\hat{T}^0$ All terms are included in the calculation.

$\hat{T}'$ Some of the cross terms are zero by construction. The nuclear cross terms are zero if one uses orthogonal internal coordinates. The cross term between the

Table 2.1: Terms in the complete molecular Hamiltonian $\hat{H}$. Formalism due to Bunker and Jensen.

Term	Description
$\hat{T}_{\text{cm}}$	Kinetic energy of the centre of mass
$\hat{T}^0$	Intra-molecular kinetic energy ($\hat{T}_n + \hat{T}_e$)
$\hat{T}'$	Cross terms in intra-molecular kinetic energy
$\hat{V}$	Electrostatic potential energy ($V_{ee} + V_{nn} + V_{ne}$)
$\hat{H}_{\text{es}}$	Interaction energy of the electron spin magnetic moments ($\hat{H}_{\text{so}} + \hat{H}_{\text{sr}} + \hat{H}_{\text{ss}}$)
$\hat{H}_{\text{so}}$	Electron spin–electron orbit interaction
$\hat{H}_{\text{sr}}$	Electron spin–nuclear motion interaction
$\hat{H}_{\text{ss}}$	Electron spin–electron spin interaction
$\hat{H}_{\text{hfs}}$	Interaction energy of the nuclear magnetic and electric moments ($\hat{H}_{\text{ns}} + \hat{H}_{\text{quad}}$)
$\hat{H}_{\text{ns}}$	Interaction energy of the nuclear spin magnetic moments ($\hat{H}_{\text{nso}} + \hat{H}_{\text{nsr}} + \hat{H}_{\text{nss}} + \hat{H}_{\text{nses}}$)
$\hat{H}_{\text{nso}}$	Nuclear spin–electron orbit interaction
$\hat{H}_{\text{nsr}}$	Nuclear spin–nuclear motion interaction
$\hat{H}_{\text{nss}}$	Nuclear spin–nuclear spin interaction
$\hat{H}_{\text{nses}}$	Nuclear spin–electron spin interaction
$\hat{H}_{\text{quad}}$	Interaction energy of the nuclear electric quadrupole moments with the electric field gradients

two electrons is included in the electronic potential. The small nuclei–electron cross terms are not included within the Born–Oppenheimer approximation.

V The electrostatic potential energy is included, even including the electron – electron potential in the solution to the electron problem.

$\hat{\mathbf{H}}_{\text{es}}$ Not included, apart from symmetry considerations.

$\hat{\mathbf{H}}_{\text{hfs}}$ Not included, apart from symmetry considerations.

Note that the terms $\hat{\mathbf{T}}_{\text{cm}}$, $\hat{\mathbf{T}}^0$, and $\hat{\mathbf{T}}'$ are the components of the full kinetic energy operator. The problem therefore reduces to what is called the spin-free rovibronic Hamiltonian ($\hat{T}^0 + \hat{T}' + V$). The molecular Hamiltonian may then be defined to a good approximation by considering electrostatic interactions only (electrostatic approximation), so that:

$$\hat{H} = \hat{T}_n + \hat{T}_e + V_{ee} + V_{nn} + V_{ne} , \quad (2.21)$$

The terms on the right-hand side of Eq.(2.21) are from left to right respectively the nuclear kinetic energy, the electronic kinetic energy, and the electrostatic potentials between electrons, nuclei and nuclei-electrons. In general, these terms are given by:

$$\hat{T}_n = -\frac{\hbar^2}{2} \sum_{n=1}^N \frac{\nabla_{\mathbf{x}_n}^2}{m_n} \quad (2.22)$$

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_{\chi_i}^2 \quad (2.23)$$

$$V_{ee} = +\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N_e-1} \sum_{j=i+1}^{N_e} \frac{1}{|\chi_i - \chi_j|} \quad (2.24)$$

$$V_{nn} = +\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{n_i n_j}{|\mathbf{x}_i - \mathbf{x}_j|} \quad (2.25)$$

$$V_{ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{N_e} \sum_j^N \frac{n_j}{|\chi_i - \mathbf{x}_j|} . \quad (2.26)$$

Here m_n is the mass of the n^{th} nucleus and $\nabla_{\mathbf{x}_j}^2$ is the usual Laplacian for proton $\mathbf{j}$ at position $\mathbf{x}_j$ in some coordinate system which may include a spin coordinate. N is the number of nuclei in the molecule, N_e is the number of electrons, and n_i is the charge number for the i^{th} nucleus, while χ_i is the position of i^{th} electron. In the case of triatomic molecules, $N = 3$.

Except for considering the effects of relativistic quantum mechanics (the small spin interaction terms), QED, and nuclear size effects, this provides a sufficiently complete description of triatomic molecules. By constructing this Hamiltonian with additional approximations in the calculation stage, such as quadrature approximations and finite basis sets, it is possible to calculate all the bound state energies and wave functions. The problem of calculating states above dissociation, also known as resonances, will be discussed in section 2.3.

2.2.1 The Born–Oppenheimer approximation

The Schrödinger Equation for the molecular Hamiltonian, as defined above, is still too difficult to treat exactly. Some simple bound systems may have a simple analytical solution to the SE without the need to perform any approximations. But in most cases it is impossible to determine the wavefunction without resorting to approximations and numerical techniques. This is the case for nearly all molecular systems, where the number of particles makes an analytical solution impossible and a direct numerical solution prohibitively costly.

Born and Oppenheimer devised an approximation that allows the separation of the molecular Hamiltonian into a nuclear and an electronic Hamiltonian, the former having a potential energy function with parametric dependence on the nuclear coordinates [48]. This is known as the Born-Oppenheimer Approximation (BOA). Historically, the reasoning behind this effective independence of events is the assumption that the velocity of the electrons is much greater than that of the nuclei due to the very low electron mass to nucleus mass ratio. Essén showed in 1977 [49] that this approximation arises naturally by a coordinate transformation within the molecular frame to that of charge-neutral subsystems and particles. This is done without any assumptions regarding velocity or mass ratios. Expanding the Hamiltonian around the equilibrium geometries at low energies, the separation is achieved. It is interesting to note that even very recent text books still propagate the mass ratio idea, which Essén attributes to a misinterpretation of the BOA seminal paper.

The BOA assumes that an expansion of the molecular wavefunction can be made such that:

$$\psi(\mathbf{x}_j, \chi_i) = \psi_e(\chi_i; \mathbf{x}_j) \psi_n(\mathbf{x}_j) , \quad (2.27)$$

where $\psi_e(\chi_i; \mathbf{x}_j)$ is the solution to the so called *clamped nuclei* electronic SE:

$$H_e(\chi_i; \mathbf{x}_j) \psi_e(\chi_i; \mathbf{x}_j) = E_e^{\mathbf{x}_j} \psi_e(\chi_i; \mathbf{x}_j) , \quad (2.28)$$

and the Hamiltonian H_e is defined by keeping the terms parametric with respect to

the nuclear positions $\mathbf{x}_j$, so that:

$$H_e = \hat{T}_e + V_{ee} + V_{ne} + V_{nn} . \quad (2.29)$$

Eq.(2.28) results in a set of electronic states ψ_e and energies E_e which depend parametrically upon $\mathbf{x}_j$. With this separation, it is possible to study the nuclear motion states independently, within a particular electronic energy state, as long as there are no near-intersections between the different states of equation Eq.(2.28) for easily accessible nuclear geometries. This is because, close to those crossings, the electronic state is highly dependent on the nuclear motion, meaning that the separation of electronic and nuclear motion is no longer valid. The parametric dependence of E_e on the nuclear coordinates $\mathbf{x}_j$ is equivalent to that of an interaction potential. The only technical difficulty that prevents E_e from being an effective interaction potential is the discreteness of the geometries chosen as calculation parameters. The interpolation of E_e between a set of discrete nuclear geometries produces the so-called Potential Energy Surface (PES) or Born-Oppenheimer potential.

The so called *ro-vibronic* Hamiltonian that describes the nuclear motion states can now be stated as $H_{rv} = T_n + V_e$, where $V_e = V_e(\mathbf{x}_j)$ is the PES. Its eigenstates and eigenvalues are determined by:

$$H_{rv}\psi_n = E_{rv}\psi_n . \quad (2.30)$$

2.2.2 Potential Energy Surface

The calculation of Born-Oppenheimer potentials is a difficult problem in itself. It is expensive for floppy molecules, such as H_3^+ , and more so when energies up to dissociation are required. This involves solving the electron problem (H_e) for a wide range of nuclear configurations $\mathbf{x}_i$, and finding a three-dimensional functional form that correctly fits and interpolates those data without introducing unphysical artifacts. For H_3^+ there have been several calculations of electronic surfaces [50; 51; 52; 35; 53; 54; 41; 55; 56], five of which have been constructed to work at high energy [51; 54; 41; 55; 56]. However, only the surface of Polyansky *et al* (PPKT) [41], the surface of Aguado *et al* [55], and that recently published by Viegas *et al* [56] have the correct long range terms and can be considered to describe the dissociative properties of the molecule accurately. A corrected version of the PPKT potential [29] is used in this work.

2.3 Theory of Resonances

In the context of Molecular Physics, resonances can be viewed as metastable states of a system which has enough energy to break up into two or more subsystems. There are two main types of resonances: *shape resonances* and *Feshbach-type resonances*. Fig. 2.1 illustrates the energy regimes and potential in which these types of resonances may occur. Shape resonances are purely quantum mechanical phenomena

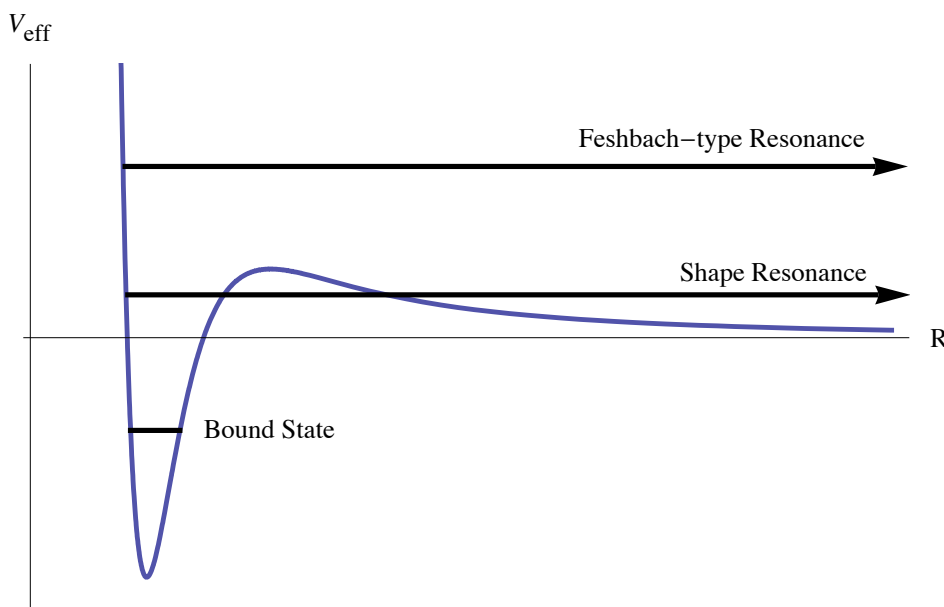


Figure 2.1: Illustration of the three main energy regimes, indicated by the horizontal lines. From top to bottom: Feshbach-type resonances that arise from energy trapped in degrees of freedom other than those of the dissociation coordinate; shape-type resonances that arise from tunnelling through the centrifugal barrier; and finally a bound state.

that arise by tunnelling through a potential barrier. These are expected to occur in rotationally excited states that give rise to a centrifugal energy term, proportional to $1/r^2$, which creates an effective potential barrier, as depicted in Fig. 2.1. Feshbach type resonances on the other hand do have a classical counterpart. Their origin is a trapping of energy in degrees of freedom other than that of the open channel through which the particle may escape. These may occur even in the presence of rotational excitation, having energies typically above the centrifugal barrier maximum.

To understand how to treat resonances, it is also necessary to understand how its mathematical concept arises. It has its roots in scattering theory, particularly the concept of *phase shift* – a quantity that contains all the information about the asymptotic form of the free particle wave-function. A brief introduction to this concept will now be made so to introduce the mathematical definition of a resonance.

These derivations follow closely those of reference [57].

2.3.1 Scattering Phase Shift

By choosing the wave vector $\mathbf{k}$ to lie along the direction of motion, the wavefunction of an elastic scattering system in its asymptotic form can be written as:

$$\psi(r, \theta) \simeq e^{ikr \cos \theta} + f_k(\theta) \frac{e^{ikr}}{r} , \quad (2.31)$$

where $f_k(\theta)$ is a measure of the anisotropy of the scattering event known as *scattering amplitude*, which in the case of elastic scattering is given by an expansion in terms of Legendre polynomials $P_l(\cos \theta)$ weighed by a constant f_l :

$$f_k(\theta) = \sum_l f_l P_l(\cos \theta) . \quad (2.32)$$

Eq.(2.31) may be expressed as superpositions of the so called *partial waves* proportional to Legendre polynomials and labelled by the “orbital” angular momentum number l . This approach is called *partial wave analysis*. Applying this type of solution to the SE leads to an equation of the form:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u_l}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} u_l + V u_l = E u_l . \quad (2.33)$$

where μ is the reduced mass of the system, r is the radial coordinate, and $u_l = r R_l$, with R_l being the radial component of the partial wavefunction for angular momentum number l . The solution to Eq.(2.33) has the form:

$$\psi_l(r, \theta) = \frac{1}{r} u_l(r) P_l(\cos \theta) . \quad (2.34)$$

Taking the limit where $r \rightarrow \infty$ and the interaction potential $V(r) \rightarrow 0$ faster than $1/r$, one obtains the free particle equation:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u_l^0}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} u_l^0 = E u_l^0 . \quad (2.35)$$

Here, u_l^0 is the free particle radial wavefunction. Eq.(2.35) can be rearranged into:

$$\frac{d^2 u_l^0}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} \right] u_l^0 = 0 , \quad (2.36)$$

which yields solutions in the form:

$$u_l^0 \simeq A_l \hat{j}_l(kr) + B_l \hat{n}_l(kr) , \quad (2.37)$$

where A_l and B_l are constants, $\hat{j}_l(kr)$ is the Riccati-Bessel function, and $\hat{n}_l(kr)$ is the Riccati-Neumann function. Taking the asymptotic behaviour of these functions and their relationship with spherical Bessel functions and Neumann functions, it can be shown that:

$$u_l^0 \simeq A_l \sin(kr - \frac{1}{2}l\pi) + B_l \cos(kr - \frac{1}{2}l\pi) . \quad (2.38)$$

Substituting $A_l = C_l \cos \delta_l$ and $B_l = C_l \sin \delta_l$:

$$u_l^0 \simeq C_l \sin(kr - \frac{1}{2}l\pi + \delta_l) , \quad (2.39)$$

which contains the phase term δ_l which is known as the *scattering phase shift*. It contains all the information about the asymptotic form of the scattering wavefunction, and therefore can be used to determine scattering cross-sections.

The partial-wave scattering state in Eq.(2.34) can be re-written using Eq.(2.39) to give:

$$\psi(r, \theta) \simeq \sum_l \frac{C_l}{r} P_l(\cos \theta) \sin(kr - \frac{1}{2}l\pi + \delta_l) \quad (2.40)$$

It can be shown that the asymptotic form of the (complete) scattering state can be written as:

$$\psi(r, \theta) \simeq \sum_l \left[i^l (2l+1) \frac{\sin(kr - \frac{1}{2}l\pi)}{kr} + f_l \frac{e^{ikr}}{r} \right] P_l(\cos \theta) , \quad (2.41)$$

where the term f_l is the constant associated with the scattering amplitude $f_k(\theta)$ in Eq.(2.32). Comparing Eq.(2.40) with Eq.(2.41) and after some algebraic manipulation, it is possible to establish the equalities:

$$C_l = \frac{i^l (2l+1)}{k} e^{il\pi/2} , \quad f_l = \frac{(2l+1)}{k} e^{i\delta_l} \sin \delta_l \quad (2.42)$$

therefore, the scattering amplitude is related to the phase shift by:

$$f_k(\cos \theta) = \frac{1}{k} \sum_l (2l+1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta) . \quad (2.43)$$

The differential scattering cross-section, σ , is simply given by:

$$\sigma = |f_k(\theta)|^2 . \quad (2.44)$$

Therefore:

$$\sigma = \frac{1}{k^2} \sum_{l,l'} (2l+1)(2l'+1) e^{\delta_l - \delta_{l'}} \sin \delta_l \sin \delta_{l'} P_l(\cos \theta) P_{l'}(\cos \theta) \quad (2.45)$$

Through the orthogonality property of Legendre polynomials:

$$\int_0^\pi P_l(\cos \theta) P_{l'}(\cos \theta) \sin \theta d\theta = \frac{2}{2l+1} \delta_{ll'} , \quad (2.46)$$

where, in this case $\delta_{ll'}$ is the Kronecker delta, the integral scattering cross-section is:

$$\sigma_{int} = \sum_l \sigma_l , \quad (2.47)$$

with:

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2 \delta_l . \quad (2.48)$$

which establishes the sought after relationship between the scattering cross-section and the phase shift.

2.3.1.1 Scattering off a square well potential

To define the concept of resonances and simplify the analysis, it is useful to consider scattering off a square well potential defined by:

$$V(x) = \begin{cases} -V_0 & \text{if } r \leq a \\ 0 & \text{if } r > a \end{cases} \quad (2.49)$$

Considering regions above dissociation, which if potential zero is set at the asymptotic limit of the potential means that $E > 0$, Eq.(2.33) can be written as:

$$\frac{d^2 u_l}{dr^2} + \left[K^2 + \frac{l(l+1)}{2\mu r^2} \right] u_l = 0 , \quad (2.50)$$

where:

$$K^2 = \frac{2\mu(E + V_0)}{\hbar^2} . \quad (2.51)$$

Using a similar approach to the solution of Eq.(2.35), the constants can be chosen so that u_l outside the well, i.e. $r > a$, has the form:

$$u_l = A_l \cos \delta_l \hat{j}_l(kr) + A_l \sin \delta_l \hat{n}_l(kr) . \quad (2.52)$$

Inside the well, i.e. $r \leq a$, because u_l must vanish at the origin, it must have the form:

$$u_l = B_l \hat{j}_l(Kr) . \quad (2.53)$$

Because u_l and its derivative must be continuous at $r = a$:

$$B_l \hat{j}_l(Kr) = A_l \cos \delta_l \hat{j}_l(kr) + A_l \sin \delta_l \hat{n}_l(kr) , \quad (2.54)$$

$$K B_l \frac{d\hat{j}_l(Kr)}{dr} = k A_l \cos \delta_l \frac{d\hat{j}_l(kr)}{dr} + k A_l \sin \delta_l \frac{d\hat{n}_l(kr)}{dr} . \quad (2.55)$$

These two equations can be combined by division of the second by the first to give an expression for the phase shift for a given energy in terms of K and k . If S-wave scattering only is considered, i.e. $l = 0$, it can be shown that the S-wave phase shift is given by [57]:

$$\delta_0 = -ka + \arctan \left(\frac{k}{K} \tan Ka \right) . \quad (2.56)$$

To understand resonances, Eq.(2.56) must be studied in some detail.

2.3.2 Resonant phase shift

Eq.(2.56) has two distinct parts. Defining:

$$\delta_{\text{bg}}(E) = -ka , \quad \delta_{\text{res}}(E) = \arctan \left(\frac{k}{K} \tan Ka \right) , \quad (2.57)$$

then the partial-wave cross-section can be expressed as:

$$\sigma_0(E) = \frac{4\pi}{k^2} \sin^2(\delta_{\text{bg}} + \delta_{\text{res}}) . \quad (2.58)$$

It can be shown that $\delta_{\text{bg}}(E)$ is the scattering phase shift for the S-wave scattering by a hard sphere of radius a [57]. Therefore, the partial-wave cross-section of a square well differs from that of a sphere by a term proportional to δ_{res} . For energies in the range $0 \leq E \ll V_0$, then $k/K \ll 1$, which implies that $\delta_{\text{res}} \approx 0$ for most of the energy range. This means that in this energy range, $\sigma_0(E)$ is dominated by the contribution of δ_{bg} , i.e. the hard sphere behaviour is dominant. However, there are particular energies at which δ_0 varies rapidly. The energies at which these rapid

variations occur can be denoted as $E = E_{\text{res}}$ which correspond to:

$$K_{\text{res}} = \frac{(2n+1)\pi}{2a}, \quad n = 0, 1, 2, \dots \quad (2.59)$$

and the *resonance phase shift* is:

$$\delta_{\text{res}}(E_{\text{res}}) = \frac{1}{2}\pi + n\pi, \quad n = 0, 1, 2, \dots \quad (2.60)$$

The term $n\pi$ comes from the modulo- π ambiguity in the phase definition.

The interpretation of this result is that at energies close to E_{res} the incident particle will have a considerable intensity in the region $r \leq a$, which is the type of behaviour associated with resonant phenomena [58].

It can also be shown that for an S-wave scattering of a spherical square well:

$$\sin^2 \delta_{\text{res}} = \frac{k^2}{k^2 + K^2 \cot^2 Ka}. \quad (2.61)$$

This result will be useful to relate the resonance phase shift and the resonant energy, as well as introduce the concept of *resonance width*, Γ .

2.3.3 Breit-Wigner resonances

For energies close to E_{res} such that $|E - E_{\text{res}}| \ll E_{\text{res}} + V_0$, the expression for $\delta_{\text{res}}(E)$ in Eq.(2.57) can be simplified by approximation to:

$$\tan \delta_{\text{res}}(E) = \frac{\Gamma/2}{E_{\text{res}} - E}, \quad (2.62)$$

where:

$$\Gamma/2 = \frac{\hbar k_{\text{res}}}{\mu a}, \quad k_{\text{res}}^2 = \frac{E_{\text{res}} 2\mu}{\hbar^2}. \quad (2.63)$$

By comparing the left and the right sides of Eq.(2.62) and by construction of a right triangle whose legs are $\Gamma/2$ and $|E_{\text{res}} - E|$ and hypotenuse equal to $[(\Gamma/2)^2 + (E_{\text{res}} - E)^2]^{1/2}$, Eq.(2.62) can be rewritten to obtain what is known as the Breit-Wigner formula:

$$\sin^2 \delta_{\text{res}} = \frac{(\Gamma/2)^2}{(\Gamma/2)^2 + (E_{\text{res}} - E)^2}. \quad (2.64)$$

As mentioned earlier, Γ is referred to as the resonance width. The Breit-Wigner expresses the behaviour of the resonant phase shift for energies near E_{res} . It expresses the fact that δ_{res} peaks for energies in the vicinity of E_{res} , and is zero for energies where $|E_{\text{res}} - E| \gg \Gamma$.

2.3.4 Poles in the S matrix

So far, nothing has been said about the physical significance of the scattering phase shift δ_l and consequently δ_{res} . Eq.(2.40) and the expression for C_l in Eq.(2.42) imply that:

$$\psi(r, \theta) \simeq \sum_l \frac{i^{l-1}(2l+1)}{2kr} P_l(\cos \theta) \left(-e^{-i(kr-l\pi/2)} + e^{i(kr-l\pi/2)} e^{2i\delta_l} \right) . \quad (2.65)$$

This means that δ_l is simply the phase by which the outgoing wave component is shifted relative to the incoming wave with equal l , hence the name “scattering phase shift”. Let this phase shift be written as:

$$S_l = e^{2i\delta_l} . \quad (2.66)$$

This quantity is a particular case of a *scattering matrix element*. By replacing Eq.(2.57) into Eq.(2.56), and considering a particular number for the angular momentum, l , the scattering matrix element may be written as:

$$S_l = e^{2i\delta_{l,\text{bg}}} e^{2i\delta_{l,\text{res}}} . \quad (2.67)$$

Utilising the same technique employed to derive the final step to the Breit-Wigner formula, S_l becomes:

$$S_l = e^{2i\delta_{l,\text{bg}}} \left[\frac{(E - E_{\text{res}})^2 - (\Gamma/2)^2 + 2i(E - E_{\text{res}})(\Gamma/2)}{(E - E_{\text{res}})^2 + (\Gamma/2)^2} \right] , \quad (2.68)$$

which can be rearranged to give:

$$S_l = e^{2i\delta_{l,\text{bg}}} \left[\frac{E - E_{\text{res}} - i\Gamma/2}{E - E_{\text{res}} + i\Gamma/2} \right] . \quad (2.69)$$

It is then said that a resonance is defined as a pole in the scattering matrix if energy is considered a complex number. This extension of the energy concept brings forth the definition of *resonance energy* given by:

$$E_R = E_{\text{res}} - i\Gamma/2 . \quad (2.70)$$

The presence of an imaginary energy term implies a decay in the state. This can be easily understood by examining the consequence of a complex energy, namely the

imaginary term, in the time-dependent wavefunction. Simply put:

$$e^{-iE_R t/\hbar} = e^{-iE_{\text{res}} t/\hbar} e^{-\Gamma t/(2\hbar)} , \quad (2.71)$$

which decays in time as $e^{-\Gamma/(2\hbar)}$. Defining the time that takes the wavefunction to decay by $1/e$ as τ , then:

$$\tau = \frac{\hbar}{\Gamma} . \quad (2.72)$$

The time τ is the life-time of the resonance. This result could alternatively be obtained from the uncertainty principle for time and energy.

So far, the analysis of resonances has been made from the stand point of scattering of an incident particle. This process can also be considered in reverse, as a state that is generated immediately before the dissociation of a bound system, or pre-dissociation state. τ will then correspond to the life-time of this state with energy E_{res} above the dissociation threshold. It should also be noted that so far there was no specification of scattered particle being considered. This analysis is general enough to encompass ro-vibrational states of nuclear motion, where the bound/scattered particle is a nucleus or molecular fragment.

2.3.5 $\mathcal{L}^2$ methods

Although the analysis above gives a good qualitative understanding of what resonant states are from the point of view of scattering theory, the actual calculations of the resonance energies and their wavefunctions is technically very difficult if one wants to apply basis set methods. This is mainly due to the asymptotic form of the wavefunction which is not $\mathcal{L}^2$, meaning in effect that the norm integral does not converge. In order to resolve this difficulty, some $\mathcal{L}^2$ basis set methods have been developed that allow a variational treatment of this problem.

2.3.5.1 Stabilisation method

The stabilisation method consists of defining an $\mathcal{L}^2$ basis set as the solution to the scattering problem. The idea is to identify which states in the continuum energy regions will be stable. It has in deed been show that by changing the basis set size, a number of continuum eigenvectors remain stable, and that these states are associated with resonances.

The reasoning behind this method lies in the assumption that the properties of resonant states are determined by components of their wavefunction that closely resemble those of bound states. Although these states are in theory not bound by

the potential, some of their characteristics will be associated with the potential that describes the system under analysis.

This method was first described qualitatively in a paper by Taylor *et al.* [59] as the general case for many so-called quasi-stationary methods involving the usage of exponentially decaying wave-functions. These wavefunctions would be chosen to approximate the “bound” characteristics of resonances for specific potentials, excluding the asymptotic behaviour. These wave-functions were originally selected on the basis of experimental results and physical intuition. This allowed the *ab initio* calculation of resonance energies. The approach is similar to that of the variational method, where by “improving” the selected basis, one obtains stability of the eigenvalues. Once a wavefunction in a suitable basis from an initial guess is calculated, small corrections should be added to produce stability of the eigenvalue. On the other hand, if small corrections are added without achieving a stable eigenvalue, it is likely that the initial guess for the wavefunction was not that of a resonance. In other words, the choice of basis functions is poor. Also, there are issues related with the existence of very close resonances. Determining a consistent and systematic approach to do this wavefunction construction is then an important problem.

This approach was later developed by Hazi and Taylor [60] into a fully $\mathcal{L}^2$ method where the stability of the eigenvalues was probed by a systematic change in the basis set parameters.

For simplicity, considering a 1D potential $V(x)$, one computes the matrix $\mathbf{H}^N$ of the exact Hamiltonian $H(x)$ using the first N functions of some well suited orthonormal basis set $|\phi_n(x)\rangle$, i. e., $\langle\phi_m(x)|\phi_n(x)\rangle = \delta_{nm}$, where δ_{ij} is the Kronecker delta. The resulting matrix elements H_{mn} from this finite basis are then given by:

$$H_{mn} = \langle\phi_n(x)|H(x)|\phi_m(x)\rangle . \quad (2.73)$$

The resulting matrix $\mathbf{H}^N$ is then diagonalised to yield a set of N eigen-energies ϵ_j^N and corresponding eigenvectors $\psi_j^N(x)$, such that:

$$\epsilon_j^N \delta_{ij} = \langle\psi_i^N(x)|H(x)|\psi_j^N(x)\rangle . \quad (2.74)$$

Consequently, the eigenfunctions are linear combinations of the first N basis functions:

$$\psi_i^N(x) = \sum_{n=1}^N C_{in} \phi_n(x) . \quad (2.75)$$

These eigenvectors are square integrable functions and can also be normalised to give $\langle\psi_i(x)|\psi_j(x)\rangle = \delta_{ij}$.

The diagonalisation procedure described above is repeated for increasing values of N in small increments and monitoring the behaviour of the energy eigenvalues ϵ_j^N and also the eigenvectors $\psi_i^N(x)$ as a function of N .

Energy positions and widths can be approximately calculated by fitting the expression for the phase shift in Eq.(2.56) to that obtained from the $\psi(x)_j$.

The phase shifts, δ_j , can be extracted from the eigenvectors $\psi(x)_j$ through the following expression:

$$\tan \delta_j = - \frac{\int_0^\infty \psi_j^*(x) [\epsilon_j - H(x)] S(x) dx}{\int_0^\infty \psi_j^*(x) [\epsilon_j - H(x)] C(x) dx} , \quad (2.76)$$

where $S(x)$ and $C(x)$ are zero at the origin and behave like $\sin kx$ and $\cos kx$ respectively as $x \rightarrow \infty$.

As will be shown later, the Complex Absorbing Potential method incorporates some ideas associated with the stabilisation method, namely the concept of stability of eigenvalues to identify resonant energies and widths.

2.3.5.2 Complex Scaling

In the theory of resonances described in section 2.3.4, the concept of “complex energy” has emerged as a necessity to interpret the results so to lead to the concept of resonances. The implication of this idea is that if one were to build a Hamiltonian yielding complex eigenvalues, such a Hamiltonian would be non-Hermitian. In his review of quantum theory of resonances Moiseyev [58] formally details this fact by analysing the S matrix for those cases where resonances arise, i. e., when the returning wave component is zero. These constitute poles in the complex plane where the scattering Hamiltonian yields complex eigenvalues, $(\epsilon_n - i\Gamma_n/2)$, and its wavefunctions (or eigenvectors), ψ_n^{res} are not $\mathcal{L}^2$. Therefore, there is the need to extend the variational principle and other theorems of quantum mechanics to this class of operator. The idea behind complex scaling is to make similarity transformations $\hat{S}$ such that the wavefunctions created with non-Hermitian operators become $\mathcal{L}^2$:

$$\hat{S} \hat{H} \hat{S}^{-1} \hat{S} \psi_n^{\text{res}} = (\epsilon_n - i\Gamma_n/2) \hat{S} \psi_n^{\text{res}} , \quad (2.77)$$

such that:

$$\hat{S} \psi_n^{\text{res}} \rightarrow 0, \text{ as } r \rightarrow \infty , \quad (2.78)$$

and $\hat{S} \psi_n^{\text{res}}$ are in the Hilbert space, even though ψ_n^{res} are not. This complex scaling operator can be defined in many ways [61]. Following closely the derivation in

reference [58], the form chosen for $\hat{S}$ is:

$$\hat{S} = e^{i\theta r \partial / \partial r} , \quad (2.79)$$

such that, for any analytical function $f(r)$:

$$\hat{S}f(r) = f(e^{i\theta}) . \quad (2.80)$$

It can be shown that the Feshbach-type resonant wavefunctions associated with poles of the complex matrix have the asymptotic form:

$$\psi_n^{\text{res}}(r \rightarrow \infty) = B(k_n)e^{i|k_n|e^{-i\varphi_n}r} = B(k_n)e^{ia_nr}e^{b_nr} , \quad (2.81)$$

where:

$$\begin{aligned} a_n &= (2\mu)^{1/2}(\epsilon_n^2 + (\Gamma_n/2)^2)^{1/4} \cos \varphi_n / \hbar , \\ b_n &= a_n \tan \epsilon_n > 0 , \\ \varphi_n &= \arctan(\Gamma_n/2\epsilon_n) . \end{aligned}$$

Applying this expression and the operator defined in Eq.(2.80) to the $\mathcal{L}^2$ condition in equation Eq.(2.78), one obtains the scaled form of the wavefunction:

$$\hat{S}\psi_n^{\text{res}}(r \rightarrow \infty) = B(k_n)e^{i|k_n|\exp(i(\theta-\varphi_n))r} = B(k_n)e^{i\alpha_nr}e^{-\beta_nr} , \quad (2.82)$$

where

$$\begin{aligned} k_n &= |k_n|e^{-i\varphi_n} , \\ \alpha_n &= a_n(\cos \theta - \tan \varphi_n \sin \theta) , \\ \beta_n &= a_n(\sin \theta - \tan \varphi_n \cos \theta) , \\ \varphi_n &= \arctan(\Gamma_n/2\epsilon_n) . \end{aligned}$$

It can immediately be seen from Eq.(2.82) that the exponential factor β_n becomes positive for sufficiently large values of θ . This means that for values of θ above a critical angle θ_c , the wavefunction becomes $\mathcal{L}^2$. It can be shown that this critical angle is given by:

$$\theta_c = \varphi_n \equiv \arctan \frac{\Gamma_n}{2(\epsilon_n - E_t)} , \quad (2.83)$$

where ϵ_n and Γ_n are the real part and the imaginary part of the complex energy and E_t is the threshold or dissociation energy of the system, which is normally chosen

to be zero.

One of the interesting aspects of this procedure is the fact that the resonant state becomes associated with a single $\mathcal{L}^2$ wavefunction.

This method can be viewed as a form of compressing the information about the evolution of a resonant state at infinity in a finite region of space. It is also possible to show that the resonant complex eigenvalues are independent of theta, i. e., they are stable relatively to that angle. However, there is a maximum limit for θ .

2.3.5.3 Smooth Exterior Complex Scaling

The Moiseyev-Hirschfelder [62] generalisation of complex scaling provides the association between the poles in the S-matrix at energies $E = E_r + iE_i$ with the θ -independent complex eigenvalues of the 1D Hamiltonian $\hat{H}$ given by:

$$\hat{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial z^2} + V(z) , \quad (2.84)$$

where $z = F(x)$ is a path in the complex plane such that:

$$z = F(x) \rightarrow xe^{i\theta} \text{ as } x \rightarrow \infty . \quad (2.85)$$

This presents a disadvantage in that it is necessary to perform an analytical continuation of the potential through this complex coordinate transformation which is often difficult to obtain.

The so called ‘‘Smooth Exterior’’ complex scaling was originally developed as a way to work around the need for the analytical continuation of the potential. It is based on the introduction of a specific integration path $F(x)$ that leads to a Hamiltonian of the form:

$$\hat{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V[F(x)] + \hat{V}_{\text{CAP}} , \quad (2.86)$$

where the operator $\hat{V}_{\text{CAP}}$ is given by:

$$\hat{V}_{\text{CAP}} = V_0(x) + V_1(x) \frac{\partial}{\partial x} + V_2(x) \frac{\partial^2}{\partial x^2} . \quad (2.87)$$

The most important aspect of this method for the purposes of the work presented here is that it is possible to find an integration path $F(x)$ such that $V[F(x)] = V(x)$. The implication of this is that it is possible to add to the *unscaled* Hamiltonian matrix a universal $\hat{V}_{\text{CAP}}$ potential, in the same basis as the unscaled Hamiltonian, to produce the resonant energies and widths [58].

2.3.5.4 Complex Absorbing Potential Method

If only the zeroth order term in Eq.(2.87) is kept and rotated by $e^{-i\pi/2}$, the smooth exterior scaling method reduces to the *Complex Absorbing Potential method*, as employed in this work. The CAP method is usually seen as an augmentation the dissociating system's PES with a complex functional form that absorbs the continuum part of the wavefunction. Ideally, this non-Hermitian Hamiltonian will produce $\mathcal{L}^2$ wavefunctions above the dissociation threshold that represent the resonant states in question. Riss and Meyer[63] have studied this method in some depth, providing a basic understanding of the way the CAP affects the spectra of several families of one-dimensional Hamiltonians.

Formally, an imaginary negative potential that acts on the dissociation coordinate, R , is added to the system's Hamiltonian, $\hat{H}$:

$$\hat{H}' = \hat{H} - i\lambda W(R) \quad , \quad (2.88)$$

where λ is a parameter used to control the CAP's intensity. The resulting non-Hermitian Hamiltonian, $\hat{H}'$, defines the energy of the n^{th} resonance, E_n , its width, Γ_n , and the corresponding $\mathcal{L}^2$ wavefunction, Ψ_n , through the relationship:

$$\hat{H}'(\lambda)\Psi_n(\lambda) = \left(E_n(\lambda) - i\frac{\Gamma_n(\lambda)}{2} \right) \Psi_n(\lambda) \quad . \quad (2.89)$$

To solve Eq.(2.89), $\hat{H}'$ can be projected on a suitable basis and diagonalised. In the infinite basis set limit, the eigenvalues corresponding to the resonant states will be found in the limit where $\lambda \rightarrow 0$. Fortunately the use of a finite basis set is both necessary and beneficial: the error introduced by the CAP and the finite basis set have opposite phase. This implies that these errors will cancel each other out at some optimal value, λ_{op} , thus yielding the complex "observable" associated with the resonant state.

The search for λ_{op} is done by studying the behaviour of the complex eigenvalues of Eq.(2.89) with values of λ ranging from zero to a large arbitrary value. This results in N trajectories in the complex plane, each associated with an eigenvalue $E_n - i\Gamma_n/2$. Through graphical analysis of these trajectories it is possible to identify the point in the complex plane that corresponds to the optimal value λ_{op} , and hence estimate the value for the position, E_n , and with, Γ_n , of the resonant state. This graphical method consist of locating cusps, loops and stability points in the eigenvalue trajectory, which are known to occur in positions around the true eigenvalue for the resonances on the complex plane.[64]

One of the greatest advantages of this methods is that it allows one to first diagonalise $\hat{H}$ of the system under study and store the basis elements ϕ_i , and eigenvalues ε_i lying near the dissociation limit. As one can expand the functions Ψ_n of Eq.(2.89) onto the basis set obtained from the bound state calculation:

$$|\Psi_n(\lambda)\rangle = \sum_i c_n^i(\lambda) |\phi_i\rangle . \quad (2.90)$$

The coefficients $c_n^i(\lambda)$, the resonance energies $E_n(\lambda)$ and the resonance widths $\Gamma_n(\lambda)/2$ can then be obtained by diagonalising the Hamiltonian:

$$H'_{ji} = \langle \phi_j | \hat{H}' | \phi_i \rangle = \varepsilon_i \delta_{ji} - \imath \lambda \langle \phi_j | W(R) | \phi_i \rangle , \quad (2.91)$$

where ε_i is the i^{th} eigenvalue and ϕ_i is the i^{th} eigenvector obtained from the diagonalisation of $\hat{H}$.

Calculations of resonant energies and widths relying solely on the use of minima and maxima in the eigenvalue trajectories were performed by Skokov *et al.* [65] and later on by Mussa and Tennyson [14] to identify resonant states of HOCl, which showed good agreement with experiment [66].

Unlike the complex scaling method where a single wavefunction is associated with a resonant state, this method resembles the stabilisation method, where the wavefunction is expanded in the basis of the $\mathcal{L}^2$ eigenvectors from the original unperturbed Hamiltonian. It also borrows from the stabilisation method the idea that the eigenvalue trajectories will exhibit stability relatively to a basis set parameter. Therefore, the CAP method may seen as a compromise between the stabilisation and complex scaling methods: the resonant states will be found from stability in the eigenvalues relative to the introduction of a “complex exterior scaling” function. The obvious benefit of this method is that one can search for stability of eigenvalues without performing costly full Hamiltonian calculations to test varying basis set sizes. This would constitute a serious difficulty for highly demanding problems such that of H_3^+ and D_2H^+ studied in this work.

2.3.5.5 Complex Absorbing Potentials

There are a number of complex absorbing potentials available [67; 68; 69; 70], as well as techniques to produce potentials with optimal properties.[71; 72] For this reason two functional forms of CAP were chosen for study, one for its simplicity and the other for its optimal properties.

The simplest and most commonly employed CAP is the n^{th} order monomial

potential given by:

$$W_n(R) = \left(\frac{R - r_{min}}{r_{max} - r_{min}} \right)^n, \quad r_{min} \leq R < r_{max}. \quad (2.92)$$

More formally motivated is the potential due to Manolopoulos[69]. This potential was more recently refined by Gonzalez-Lezana *et al.* [70] (GLM) to:

$$W_{GLM}(R) = \frac{\hbar^2}{2\mu} \left(\frac{2\pi}{r_{max} - r_{min}} \right)^2 y(x), \quad r_{min} \leq R < r_{max}, \quad (2.93)$$

with $y(x)$ approximately given by:

$$y(x) = \frac{4}{(c-x)^2} + \frac{4}{(c+x)^2} - \frac{8}{c^2}, \quad (2.94)$$

where

$$c = \sqrt{2}K(1/\sqrt{2}), \quad (2.95)$$

and

$$x = c \frac{R - r_1}{r_2 - r_1}, \quad (2.96)$$

where $K(1/\sqrt{2})$ is a standard elliptic integral. In both these CAPs, r_{max} is placed at the end and r_{min} at the start of the CAP in the dissociation coordinate R .

The two most interesting features of the GLM CAP are its minimum reflection properties and the scale factor in Eq.(2.93) that couples the CAP amplitude to its length, $\Delta r = r_{max} - r_{min}$, as a single parameter for locating the stability points λ_{op} . Unfortunately, the CAP technique used to make computational savings clashes with the coupling of this CAP's amplitude: to scan all the necessary energies (amplitudes) one would have to build a new CAP matrix for each amplitude. This would significantly increase computational cost due to the number of energy points required for a detailed search of such a dense spectrum. For this reason the scale factor in Eq.(2.93) has been replaced with the usual amplitude parameter, λ , while keeping the optimal form of Eq.(2.94).

2.4 Nuclear Hamiltonian DVR solutions

As discussed in section 2.3.5.4, to obtain complex energies associated with resonant states though the CAP method it is necessary to obtain a basis of $\mathcal{L}^2$ eigenvectors of the system under analysis. These states must have energy above the dissociation threshold. Since the focus of this thesis is on the participation of resonances in

ro-vibrational spectra, the wavefunctions will be those of nuclear motion states.

Light and co-workers [73; 74] created a procedure to calculate the nuclear motion states of molecules known as the Discrete Variable Representation (DVR). It has a number of advantages over other basis set methods in both the development of compact representations for multi-dimensional Hamiltonians and the simplicity of most of the matrix elements. A drawback of DVR is the fact that it is not strictly variational.

Tennyson and co-workers published a triatomic ro-vibrational spectral package based on the use of a discrete variable representation for all three internal coordinates, called DVR3D [10]. It allows the calculation of rotation-vibration spectra of molecules tri-atomic molecules in either Radau or Jacobi (scattering) internal coordinates. At the intermediate stages of these calculations, DVR eigenvectors corresponding to the states involved in the desired spectrum are produced. These may then be used as the basis for resonance calculations. An overview of the DVR3D code suite will now be given.

2.4.1 Discrete Variable Representation

To understand the DVR, it is first necessary to look at what may be considered the usual method for representing a basis set, and therefore, the Hamiltonian matrix elements. This is called Finite Basis Representation (FBR), and as its name suggests, it is a truncation of an infinite basis set. FBR wavefunctions are therefore a superposition of basis functions, much in the same sense of the basic formalism presented in Eq.(2.6). The basis functions are usually chosen to be a set of orthogonal polynomials that may be integrated using a suitable Gaussian quadrature scheme.

The DVR takes advantage of the fact that the integration scheme may be built into the definition of the basis elements through a unitary transformation. With abscissa η and weights w_η , this method transforms an FBR basis given by orthonormal polynomials into a DVR basis through the transformation:

$$T_\eta^t = \sqrt{w_\eta} |t(\eta)\rangle \quad (2.97)$$

where $|t\rangle$ is the polynomial basis function [75]. In a three-dimensional case, the required composite transformation is written as a product of one-dimensional transformations:

$$T_{m,n,j}^{\alpha,\beta,\gamma} = T_m^\alpha T_n^\beta T_j^\gamma, \quad (2.98)$$

where m, n, j index the three FBR basis functions and α, β, γ index the DVR points, as demonstrated by Light *et al* in 1985 [75]. With this transform, it is found that

terms in the Hamiltonian are partially or wholly diagonalised. For instance, the potential is diagonalised because of the quadrature approximation [76]:

$$\sum_{mnj} \sum_{m'n'j'} T_m^\alpha T_n^\beta T_j^\gamma V_{m'n'j'}^{mnj} T_{\alpha'}^{m'} T_{\beta'}^{n'} T_{\gamma'}^{j'} \simeq V_{\alpha\beta\gamma} \delta_{\alpha\alpha'} \delta_{\beta\beta'} \delta_{\gamma\gamma'}. \quad (2.99)$$

This is probably the most attractive feature of DVR-based methods: no integration at all is required over the potential; it is diagonal in every coordinate.

It is important to note that DVR still relies on an approximation to the true Gaussian quadrature scheme and may cause the true energy of the system to be overshoot. This is due to the link between the accuracy of integration and the number of DVR basis points used [77]. Nevertheless, it still preserves convergence to an energy value as the basis set is improved.

The DVR approach presented here is just one of many possible approaches [74].

2.4.2 Coordinate Systems

One of the most fundamental aspects of describing a molecular system is the choice of coordinates to describe it. If adequately chosen, the coordinate system may simplify calculations by exploiting symmetry where it may exist. The two coordinate systems used in this work are the scattering (or Jacobi) coordinates and the Radau coordinates, both specially fitting for the description of systems with C_{2v} symmetry.

2.4.2.1 Jacobi coordinates

The scattering coordinates (r, R, θ) were originally created to describe in a physically intuitive way the collisions of particles with diatoms [78]. Fig. 2.2 illustrates this coordinate system. This coordinate system is now also used in the calculation of energy levels of molecules with large amplitude of motion. Since it is ideally suited for the calculation of atom collisions, it will be used as the system of choice for the calculation of specific dissociation channels. For example, A_3 may be set as H^+ in the dissociation of D_2H^+ into $D_2 + H^+$. Due to the formalism presented in this section, the r and R coordinates will be indexed as r_1 and r_2 respectively.

2.4.2.2 Radau coordinates

Radau coordinates (r_1, r_2, θ) were originally introduced over a century ago to study astronomical systems [79]. They have more recently become important to the study of light-heavy-light atom systems. Fig. 2.3 shows how the system is set up. Like

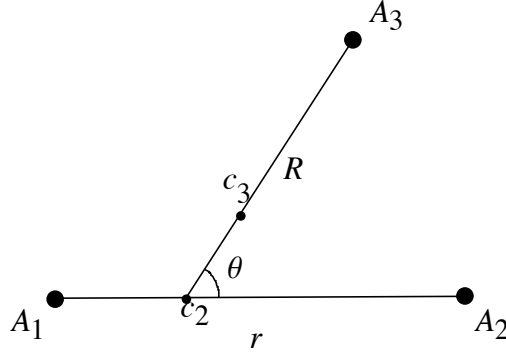


Figure 2.2: Illustration of the Jacobi coordinate system. r is the diatomic distance between atoms A_1 and A_2 . R is the distance from the diatomic centre of mass, c_2 , to the dissociating or colliding atom A_3 . c_3 is the triatomic centre of mass. θ is the angle between r and R .

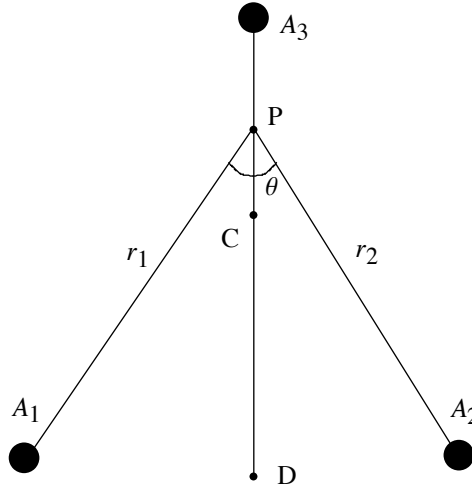


Figure 2.3: Illustration of the Radau coordinate system. r_1 is the distance between atom A_1 and the point P . r_2 is the distance A_2 and P . C is the triatomic centre of mass whereas D is the $A_1 - A_2$ diatomic centre of mass. The point P is a canonical point satisfying the condition $\overline{PD}^2 = \overline{A_3D} \cdot \overline{CD}$. θ is the angle between r_1 and r_2 .

the Jacobi coordinates, Radau coordinates are orthogonal and suitable for the description of molecules with large amplitude of motion. In the limit where the atom A_3 is much heavier than the remaining two, i. e., P is near atom A_3 , this coordinate system approximates the so called bond-length-bond angle coordinate system [80]. These coordinates are particularly suitable for systems with C_{2v} symmetry.

2.4.2.3 Generalised Coordinates

In an effort to create an easily interchangeable system of internal coordinates Brian Sutcliffe and Jonathan Tennyson [81] created the so-called generalised internal coordinates, where through a change in parameters the system can be converted to bond-length-bond-angle, Jacobi, or a variation of the Radau coordinates with similar properties. The system is depicted in Fig. 2.4.

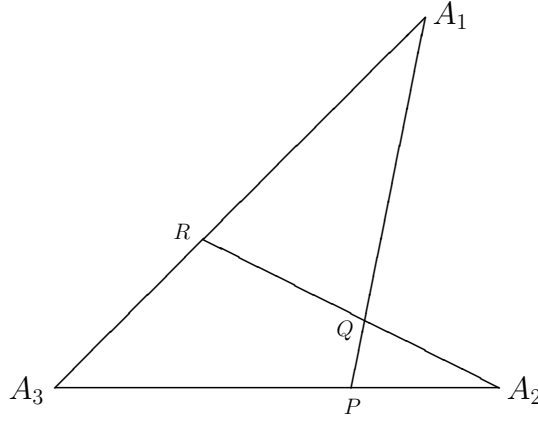


Figure 2.4: Internal coordinate system of Sutcliffe and Tennyson: A_i represents atom i . The coordinates are given by $r_1 = A_2 - R$, $r_2 = A_1 - P$ and the angle $\theta = \angle A_1QA_2$. The geometric parameters are defined by $g_1 = \frac{A_3 - P}{A_3 - A_2}$; $g_2 = \frac{A_3 - R}{A_3 - A_1}$.

Jacobi coordinates can be obtained by setting the g parameters to:

$$g_1 = \frac{m_2}{m_2 + m_3}, \quad g_2 = 0, \quad (2.100)$$

whereas for Radau coordinates:

$$\begin{aligned} g_1 &= 1 - \frac{A}{A + B - AB}, \quad g_2 = 1 - \frac{A}{1 - B + AB}, \\ A &= \left(\frac{m_3}{m_1 + m_2 + m_3} \right)^{\frac{1}{2}}, \quad B = \frac{m_2}{m_1 + m_2}. \end{aligned} \quad (2.101)$$

This coordinate system is used in the Sutcliffe-Tennyson Hamiltonian [81] which is implemented in the DVR3D suite of codes. An overview of the main driving modules required for the work presented in this thesis will now be made.

2.4.3 The vibrational problem

The program uses a multidimensional DVR in scattering (Jacobi) or Radau coordinates. In scattering coordinates r_1 represents the ‘diatom’ distance between atom 2 and atom 3, and r_2 the separation of the atom 1 from the diatom centre of mass. The angle between r_1 and r_2 is θ . A formal definition of (r_1, r_2, θ) in Radau coordinates is given below. In FBR, the purely vibrational ($J = 0$) Hamiltonian matrix can be written as [10] :

$$\begin{aligned} \langle m, n, j | \hat{H}^{J=0} | m', n', j' \rangle &= \langle m | \hat{h}^{(1)} | m' \rangle \delta_{n, n'} \delta_{j, j'} \\ &+ \langle n | \hat{h}^{(2)} | n' \rangle \delta_{m, m'} \delta_{j, j'} \\ &+ \left(\langle m | \hat{g}^{(1)} | m' \rangle \delta_{n, n'} + \langle n | \hat{g}^{(2)} | n' \rangle \delta_{m, m'} \right) j(j+1) \delta_{j, j'} \\ &+ \langle m, n, j | V(r_1, r_2, \theta) | m', n', j' \rangle . \end{aligned} \quad (2.102)$$

Here, V is the potential, and the radial kinetic energy integrals are given by

$$\langle t | \hat{h}^{(i)} | t' \rangle = \left\langle t \left| \frac{-\hbar^2}{2\mu_i} \frac{\partial^2}{\partial r_i^2} \right| t' \right\rangle , \quad (2.103)$$

$$\langle t | \hat{g}^{(i)} | t' \rangle = \left\langle t \left| \frac{\hbar^2}{2\mu_i r_i^2} \right| t' \right\rangle , \quad (2.104)$$

where $|t\rangle = |m\rangle$ for $i = 1$ and $|t\rangle = |n\rangle$ for $i = 2$. μ_i are the appropriate reduced masses associated with the particular coordinate system used by [81] :

$$\begin{aligned} \mu_1^{-1} &= g_2^2 m_1^{-1} + m_2^{-1} + (1 - g_2)^2 m_3^{-1} \\ \mu_2^{-1} &= m_1^{-1} + g_1^2 m_2^{-1} + (1 - g_1)^2 m_3^{-1} , \end{aligned} \quad (2.105)$$

where the g factors are determined for Radau and Jacobi coordinates by Eq.(2.101) and Eq.(2.100), respectively.

The angular basis functions $|j\rangle$, when $J = 0$, are Legendre polynomials while the radial basis functions are Laguerre polynomials. These are either Morse oscillator-like functions or spherical oscillators. The Morse oscillator-like functions are defined as [82] :

$$\begin{aligned} |n\rangle = H_n(r) &= \beta^{\frac{1}{2}} N_{n\alpha} \exp\left(-\frac{y}{2}\right) y^{\frac{\alpha+1}{2}} L_n^\alpha(y) , \\ y &= A \exp[-\beta(r - r_e)] , \\ A &= \frac{4D_e}{\omega_e}, \beta = \omega_e \left(\frac{\mu}{2D_e} \right)^{\frac{1}{2}}, \alpha = \text{integer}(A) , \end{aligned} \quad (2.106)$$

where the parameters μ , r_e , ω_e and D_e are associated with the reduced mass, equilibrium separation, fundamental frequency and dissociation energy of the relevant coordinate respectively, and $N_{n\alpha}L_n^\alpha$ is a normalised associated Laguerre polynomial [10]. Note that the r_e , ω_e and D_e can be treated as variational parameters, which makes their association to physical quantities somewhat loose.

The spherical oscillator functions are particularly useful for systems which have significant amplitude for $r_2 = 0$, and also perform better when long inter-nuclear distances are needed to describe the system. These functions are defined by [83]:

$$\begin{aligned} |n\rangle &= H_n(r) = 2^{\frac{1}{2}} \beta^{\frac{1}{4}} N_{n\alpha+\frac{1}{2}} \exp\left(-\frac{y}{2}\right) y^{\frac{\alpha+1}{2}} L_n^{\alpha+\frac{1}{2}}(y) , \\ y &= \beta r^2 , \\ \beta &= (\mu\omega_e)^{\frac{1}{2}} . \end{aligned} \quad (2.107)$$

Here, (α, ω_e) are treated as variational parameters.

As explained in section 2.4, the three dimensional DVR of the Hamiltonian is obtained by applying the transformation $\mathbf{T}^T \mathbf{H} \mathbf{T}$. For $J = 0$, the transformed Hamiltonian can be written at the DVR grid points as:

$$\begin{aligned} {}^{(3D)}H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} &= K_{\alpha,\alpha'}^{(1)} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} + K_{\beta,\beta'}^{(2)} \delta_{\alpha,\alpha'} \delta_{\gamma,\gamma'} \\ &+ L_{\alpha,\alpha',\gamma,\gamma'}^{(1)} \delta_{\beta,\beta'} + L_{\beta,\beta',\gamma,\gamma'}^{(2)} \delta_{\alpha,\alpha'} \\ &+ V(r_{1\alpha}, r_{2\beta}, \theta_\gamma) \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} , \end{aligned} \quad (2.108)$$

The kinetic energy terms in Hamiltonian in Eq.(2.108), after application of the quadrature approximation become:

$$K_{\eta,\eta'}^{(i)} = \sum_{t,t'} T_t^n \langle t | \hat{h}^{(i)} | t' \rangle T_{t'}^{n'} \quad (2.109)$$

$$L_{\eta,\eta',\gamma,\gamma'}^{(i)} = J_{\gamma\gamma'} \sum_{t,t'} T_t^n \langle t | \hat{g}^{(i)} | t' \rangle T_{t'}^{n'} \quad (2.110)$$

$$\simeq \frac{J_{\gamma\gamma'} \hbar^2}{2\mu_i r_{i\eta}^2} \delta_{\eta\eta'} , \quad (2.111)$$

where:

$$J_{\gamma\gamma'} = \sum_j T_j^\gamma j(j+1) T_j^{\gamma'} . \quad (2.112)$$

2.4.3.1 Symmetry

Both Scattering and Radau coordinates can be used to exploit the C_{2v} (permutation) symmetry of an AB_2 system.

In the case of Jacobi coordinates, the $\mathbf{J}$ matrix of Eq.(2.112) becomes:

$$J_{\gamma\gamma'q} = 2 \sum_{j=0}^{N/2-1} T_{2j+q}^{\gamma'} (2j+q)(2j+q+1) T_{2j+q}^{\gamma} , \quad q = 0, 1 . \quad (2.113)$$

For problems including rotational excitation, this symmetry is preserved with the body-fixed z -axis placed either along either r_2 or r_1 .

In Radau coordinates, the permutation symmetry is carried by the radial coordinates. Symmetrising the DVR by taking suitable combinations of points in r_1 and r_2 , the new functions become:

$$|\alpha, \beta, q\rangle = [2(1 + \delta_{\alpha,\beta})]^{-\frac{1}{2}} \left(|\alpha, \beta\rangle + (-1)^{q+k} |\beta, \alpha\rangle \right) , \quad q = 0, 1 , \quad (2.114)$$

where $\alpha > \beta$ for $q + k$ odd or $\alpha \geq \beta$ for $q + k$ even. This definition of q identifies the ortho and para symmetry blocks for AB_2 molecules each by a single q value.

2.4.4 Rotational motion with standard embeddings

The rotational problem can be fully expanded in terms of a finite set of rotation matrices [84]. These functions are symmetrised to reflect the rotational parity of the system, given by $(-1)^{J+p}$ with $p = 0, 1$. They will be denoted $|J, k, p\rangle$. To deal with transitions from linear to non-linear geometries, these rotation matrices are k -dependent angular functions denoted $|j\rangle$ above [81]. The FBR Hamiltonian matrix for the fully coupled vibration-rotation problem can be expressed as:

$$\begin{aligned} \left\langle m, n, j, J, k, p \left| \hat{H} \right| m', n', j', J, k', p \right\rangle = \\ \delta_{k,k'} \left\langle m, n, j \left| \hat{H}^{J,k} \right| m', n', j' \right\rangle \\ - (1 + \delta_{k,0} + \delta_{k',0})^{-\frac{1}{2}} \delta_{k',k\pm 1} \left\langle t \left| \hat{g}^{(i)} \right| t' \right\rangle \delta_{j,j'} \delta_{s,s'} C_{J,k'}^{\pm} C_{j,k'}^{\pm} , \end{aligned} \quad (2.115)$$

where:

$$k = p, p+1, \dots, J , \quad p = 0, 1 . \quad (2.116)$$

If the body-fixed z -axis is taken parallel to r_1 then $|t\rangle = |m\rangle$, $s = n$ and $i = 1$; and if z is along r_2 , $|t\rangle = |n\rangle$, $s = m$ and $i = 2$. The angular factors are then given by:

$$C_{\ell,k}^{\pm} = (\ell(\ell+1) - k(k \pm 1))^{\frac{1}{2}}. \quad (2.117)$$

Using the solutions of the first step as a basis to expand the full problem causes the first term in Eq.(2.115) to become $\epsilon_h^{J,k}$ and the problem of constructing the Hamiltonian matrix reduces to the one of constructing the second, off-diagonal in k , term.

The quadrature approximation means that the matrix element $\langle t | \hat{g}^{(i)} | t' \rangle$ is diagonal in the DVR, which implies that the angular contribution is diagonal in the FBR. It is then possible to transform the DVR wavefunctions to an FBR in θ by doing:

$$\psi_{\alpha,\beta,j}^{J,k,h} = \sum_{\gamma} T_j^{\gamma} \psi_{\alpha,\beta,\gamma}^{J,k,h}. \quad (2.118)$$

This is referred to as the DVR² – FBR¹ representation. In it, the Hamiltonian matrix in terms of solutions of the first step is:

$$\begin{aligned} & \langle h, k, p | \hat{H} | h', k', p \rangle = \\ & \delta_{h,h'} \delta_{k,k'} \epsilon_h^{J,k} \\ & - (1 + \delta_{k,0} + \delta_{k',0})^{-\frac{1}{2}} \delta_{k',k \pm 1} \sum_{\alpha,\beta,j} \psi_{\alpha,\beta,j}^{J,k,h} \psi_{\alpha,\beta,j}^{J,k',h'} C_{J,k'}^{\pm} C_{j,k'}^{\pm} M_{\alpha,\alpha,\beta,\beta}^{(i)}. \end{aligned} \quad (2.119)$$

where:

$$k = p, p+1, \dots, J, \quad p = 0, 1,$$

and the M-matrix is given by:

$$M_{\alpha,\alpha'}^{(1)} = \sum_{m,m'} T_m^{\alpha} \langle m | \hat{g}^{(1)} | m' \rangle T_{m'}^{\alpha'} \simeq \delta_{\alpha\alpha'} \frac{\hbar^2}{2\mu_1 r_{1\alpha}^2}, \quad (2.120)$$

if $i = 1$ and z embedded along r_1 , when it is diagonal in β , and:

$$M_{\beta,\beta'}^{(2)} = \sum_{n,n'} T_n^{\beta} \langle n | \hat{g}^{(2)} | n' \rangle T_{n'}^{\beta'} \simeq \delta_{\beta\beta'} \frac{\hbar^2}{2\mu_2 r_{2\beta}^2}, \quad (2.121)$$

if $i = 2$ and z embedded along r_2 , when it is diagonal in α .

2.4.5 Rotational motion with a bisector embedding

In this representation, the Hamiltonian matrix in terms of solutions of the first step is [85]:

$$\begin{aligned}
\langle h, k, p, q | \hat{H} | h', k', p, q' \rangle = & \\
& \delta_{h,h'} \delta_{k,k'} \epsilon_h^{J,k} \\
& - (1 + \delta_{k,0} + \delta_{k',0})^{-\frac{1}{2}} \delta_{k',k \pm 1} \delta_{q',1-q} C_{J,k}^{\pm} \sum_{\alpha,\beta,\gamma,\gamma'} \psi_{\alpha,\beta,\gamma}^{J,k,h} \psi_{\alpha,\beta,\gamma'}^{J,k',h'} \\
& \times \left(M_{\alpha,\alpha,\beta,\beta}^{(1)} - M_{\alpha,\alpha,\beta,\beta}^{(2)} \right) J_{k \pm 1,k,\gamma,\gamma'}^{(1)} \\
& - (1 + \delta_{k,0} + \delta_{k',0})^{-\frac{1}{2}} \delta_{k',k \pm 2} \delta_{q',q} C_{J,k \pm 1}^{\pm} C_{J,k}^{\pm} \\
& \times \sum_{\alpha,\beta,\gamma} \psi_{\alpha,\beta,j}^{J,k,h} \psi_{\alpha,\beta,\gamma}^{J,k',h'} \left(\frac{1+\gamma}{1-\gamma} \right) \left(M_{\alpha,\alpha,\beta,\beta}^{(1)} + M_{\alpha,\alpha,\beta,\beta}^{(2)} \right) J_{k \pm 2,k,\gamma,\gamma'}^{(2)}, \quad (2.122)
\end{aligned}$$

where:

$$k = p, p+1, \dots, J, \quad p = 0, 1.$$

In Eq.(2.122), the angular integrals are obtained by quadrature in terms of basis functions and then transformed:

$$J_{k',k,\gamma,\gamma'}^{(1)} = \sum_{j,j'} T_j^{\gamma(k)} \left(\delta_{j,j'} + \left(\frac{k+k'}{2} \right) \left\langle j, k \left| \frac{(1+\cos\theta)}{\sin\theta} \right| j', k' \right\rangle \right) T_{j'}^{\gamma'(k')}, \quad (2.123)$$

$$J_{k',k,\gamma,\gamma'}^{(2)} = \sum_{j,j'} T_j^{\gamma(k)} \left(\delta_{j,j'} + \left\langle j, k \left| \frac{(1+\cos\theta)}{(1-\cos\theta)} \right| j', k' \right\rangle \right) T_{j'}^{\gamma'(k')}, \quad (2.124)$$

where the notation $\gamma(k)$ has been used to emphasise that the DVR points for the bra and ket are based on the Gaussian quadrature points of associated Legendre functions of different degrees.

2.4.6 Rotational motion with z-perpendicular embedding

The structure of the Hamiltonian matrix for the z -perpendicular embedding is somewhat different from the other cases since the couplings are between cases with $\Delta k = \pm 2$ only but there are additional couplings between blocks with positive and negative k . In this case the rotational parity, p , is given by the parity of k . To help define the matrix elements it is useful to define an extra quantum number, denoted s below, which depends on the sign of k and takes the value 0 or 1 [86].

The rotational kinetic energy operator also has a diagonal contribution as well

as coupling k blocks differing by two:

$$\begin{aligned}
& \langle Jksj | T^{\text{rot}} | Jk's'j' \rangle = \\
& - (1 + \delta_{0k})^{1/2} \frac{1}{2} M^+ \left\langle j \left| \frac{\cos \theta}{1 - \cos^2 \theta} \right| j' \right\rangle A_{Jk'}^\pm \delta_{k,k' \pm 2} \delta_{s,s'} \\
& + (1 + \delta_{0k})^{1/2} \frac{1}{4} M^- \langle j | \frac{1}{(1 - \cos^2 \theta)^{1/2}} | j' \rangle A_{Jk'}^\pm \delta_{k,k' \pm 2} \delta_{s,1-s'} , \quad (2.125)
\end{aligned}$$

where:

$$\begin{aligned}
A_{Jk}^\pm &= A_{J-k}^\mp = ([J(J+1) - k(k \pm 1)][J(J+1) - k(k \pm 3) - 2])^{1/2} , \\
M^\pm &= \frac{1}{2} \left[\frac{1}{m_1 R_1^2} \pm \frac{1}{m_2 R_2^2} \right] .
\end{aligned}$$

Finally the Coriolis kinetic energy operator couples terms diagonal in k but differing in s

$$\begin{aligned}
& \langle Jksj | T^{\text{cor}} | Jk's'j' \rangle = \\
& - \frac{k}{2} M^- \left(\left\langle j \left| - \frac{\cos \theta (1 + 2a + 2j')}{(1 - \cos^2 \theta)^{1/2}} \right| j' \right\rangle \right. \\
& \left. + \left\langle j \left| \frac{2(j' + a)}{(1 - \cos^2 \theta)^{1/2}} \frac{(h_{j'-1}^{ab})^{1/2}}{(h_{j'}^{ab})^{1/2}} \right| j' - 1 \right\rangle \right) \delta_{kk'} \delta_{s,1-s'} , \quad (2.126)
\end{aligned}$$

There is also a special case which occurs when $k = 1$, where there are extra terms both on the diagonal, augmenting $\langle Jkqs | T^{\text{vib}} | Jk's'j' \rangle$, and on the off-diagonal augmenting $\langle Jksj | T^{\text{cor}} | Jk's'j' \rangle$ so that:

$$\begin{aligned}
& \langle Jksj | T_{k=1}^{\text{vib}} | Jk'js'j' \rangle = \\
& \frac{(-1)^{1+s}}{4} J(J+1) M^+ \left\langle j \left| \frac{\cos \theta}{1 - \cos^2 \theta} \right| j' \right\rangle \delta_{k,1} \delta_{k',1} \delta_{s,s'} , \quad (2.127)
\end{aligned}$$

and

$$\begin{aligned}
& \langle Jksj | T_{k=1}^{\text{cor}} | Jk's'j' \rangle = \\
& \frac{(-1)^{s'+q}}{4} J(J+1) M^- \left\langle j \left| (1 - \cos^2 \theta)^{-1/2} \right| j' \right\rangle \delta_{k,1} \delta_{k',1} \delta_{s,1-s'} , \quad (2.128)
\end{aligned}$$

where q is the parity of the radial basis, see Eq.(2.114). The above matrix elements include a cancellation between vibrational and rotational terms which is potentially

singular at linear (i.e. $\theta = 0$ or π) geometries.

2.4.6.1 DVR3D suite Calculation Procedure

The calculation is generally set up as a series of diagonalisations and truncations [87]. Assuming a coordinate ordering such that γ is diagonalised first, then β and lastly ($\theta \rightarrow r_1 \rightarrow r_2$), the 1D problems that have to be solved for each α and β are given by

$$^{(1D)}H_{\gamma,\gamma'}^{\alpha,\beta} = L_{\alpha,\alpha,\gamma,\gamma'}^{(1)} + L_{\beta,\beta,\gamma,\gamma'}^{(2)} + V(r_{1\alpha}, r_{2\beta}, \theta_\gamma) \delta_{\gamma\gamma'}. \quad (2.129)$$

Amplitudes for the h^{th} level, with eigen-energy $\epsilon_h^{\alpha,\beta}$, are given at each grid point, α, β , by $C_{\gamma,h}^{\alpha,\beta}$.

The solutions with $\epsilon_h^{\alpha,\beta} \leq E_{max}^{1D}$ are then selected and used to solve 2D problems for each value of β . This gives

$$^{(2D)}H_{\alpha,\alpha',h,h'}^\beta = \epsilon_h^{\alpha,\beta} \delta_{\alpha\alpha'} \delta_{hh'} + \sum_{\gamma} C_{\gamma,h}^{\alpha,\beta} C_{\gamma,h'}^{\alpha',\beta} K_{\alpha\alpha'}^{(1)}. \quad (2.130)$$

Solutions for the l^{th} level, with eigen-energy ϵ_l^β are given by $C_{\alpha,l,h}^\beta$.

The solutions with $\epsilon_l^\beta \leq E_{max}^{2D}$ are then used to solve the full 3D problem of dimension N :

$$^{(3D)}H_{\beta,\beta',l,l'} = \epsilon_l^\beta \delta_{\beta\beta'} \delta_{ll'} + \sum_{\alpha,h,h'} C_{\alpha,l,h}^\beta C_{\alpha,l',h'}^{\beta'} \sum_{\gamma} C_{\gamma,h}^{\alpha,\beta} C_{\gamma,h'}^{\alpha,\beta'} K_{\beta\beta'}^{(2)}. \quad (2.131)$$

Solutions of this diagonalisation are the required eigen-energies, ϵ_i , and wavefunction coefficients $C_{\beta,i,l}$.

2.4.6.2 Wavefunctions and Matrix elements

The eigenvectors of the 3D Hamiltonian are obtained as coefficients of the intermediate basis. To perform the calculations presented in this thesis, these vectors are transformed so that they express the amplitude of the wavefunction at the DVR grid points. The wavefunction amplitude for the i^{th} eigenstate at the DVR grid points is then :

$$\Psi_{\alpha\beta\gamma}^i = \sum_{l,h} C_{\beta il} C_{\alpha lh}^\beta C_{\gamma h}^{\alpha\beta} = \sum_l C_{\beta il} \sum_h C_{\alpha lh}^\beta C_{\gamma h}^{\alpha\beta}. \quad (2.132)$$

The transformation back to FBR is done with the angular functions represented as a basis set of associated Legendre polynomials. The wavefunction then is written

as:

$$\Psi_{\alpha\beta}^{Ji} = \sum_{jk} d_{j\alpha\beta}^{Jki} |j\rangle . \quad (2.133)$$

The new coefficients, d^{Jki} , are obtained from the back transformation

$$d_{j\alpha\beta}^{Jki} = \sum_{\gamma} \Psi_{\alpha\beta\gamma}^i \omega_{\gamma}^{\frac{1}{2}} |j(\gamma)\rangle . \quad (2.134)$$

For the $J = 0$ case, the expectation values of geometrically defined operators can be computed in a straightforward manner using a DVR and the quadrature approximation simply by summing the square of the wavefunction and the operator over all grid points. In the case where $J > 0$ it is necessary to convert the DVR² – FBR¹ representation to a fully DVR common grid. This, is done using a similar transformation to that of Eq.(2.134), where new coefficients are obtained for a common DVR grid across all k blocks associated with the rotational excitation. This transformation was adapted from the line intensity calculation program in the DVR3D suite [10].

2.4.6.3 A Problem with the Quadrature Approximation

There is one particular failure of the quadrature approximation [37], which occurred when evaluating the r_2^{-2} integrals. In scattering coordinates, it is possible for the r_2 coordinate to be equal, or very close, to zero if this linear geometry is energetically accessible or favourable. It is desirable to use the spherical oscillator functions in this case. Under these circumstances it was found [37] that the quadrature approximation had to be abandoned for the r_2^{-2} integral because of its non-polynomial behaviour as $r_2 \rightarrow 0$.

An alternative procedure may be implemented which continues to use the quadrature approximation to construct $^{(1D)}\mathbf{H}$, and then constructs $^{(3D)}\mathbf{H}$ using the full-matrix transformation of the r_2^{-2} integrals, correcting for the fact that the quadrature approximation was used in $^{(1D)}\mathbf{H}$ [37]. So the formulation is:

$$^{(3D)}\tilde{H}_{\beta,\beta',l,l'} = ^{(3D)}H_{\beta,\beta',l,l'} + \sum_{\alpha,k,k'} C_{\alpha,l,k}^{\beta} C_{\alpha,l',k'}^{\beta'} (\tilde{M}_{\beta,\beta'}^{(2)} - M_{\beta,\beta'}^{(2)}) \sum_{\gamma,\gamma'} C_{\gamma,k}^{\alpha,\beta} C_{\gamma',k'}^{\alpha,\beta'} J_{\gamma\gamma'} , \quad (2.135)$$

where $^{(3D)}H_{\beta,\beta',l,l'}$ is defined by Eq.(2.131) and:

$$\tilde{M}_{\beta,\beta'}^{(2)} = \sum_{n,n'} T_n^{\beta} \langle n | \hat{g}^{(2)} | n' \rangle T_{n'}^{\beta'} , \quad (2.136)$$

and $M_{\beta,\beta'}^{(2)}$ is given by the approximation in Eq.(2.121). The FBR matrix elements above can be evaluated analytically, and are given by [82]:

$$\langle n | \hat{g}^{(2)} | n' \rangle = \frac{\hbar^2 \beta}{(2\alpha + 1)\mu_2} \left(\frac{n!}{n'!} \frac{\Gamma(n' + \alpha + \frac{3}{2})}{\Gamma(n + \alpha + \frac{3}{2})} \right)^{\frac{1}{2}}, \quad n \geq n'. \quad (2.137)$$

2.5 Conclusion

With the theoretical framework described in this chapter it should be possible to define an automatic procedure for the calculation of nuclear motion resonances from DVR wavefunctions obtained from the DVR3D suite of programs for the calculation of spectra of triatomic molecules. The introduction of a Complex Absorbing Potential in the dissociation coordinate as defined in the Jacobi coordinate system should permit the calculation of resonances using wavefunctions in a DVR and the formalism presented in section 2.3.5.4, associated with the simple integration techniques described in section 2.4.6.2.

In the following chapters, the necessary algorithms and software to achieve this goal will be presented.

Chapter 3

RES3D Implementation

In this section, the computational implementation of the CAP method is described, including the algorithmic techniques involved in automating the detection of resonant states using complex eigenvalue trajectories computed through the CAP method.

3.1 Resonance Detection and Consistency

In the previous chapter, the CAP method was described as well as a qualitative analysis of the connections between this method and other $\mathcal{L}^2$ methods. It was observed that this method has characteristics of both the smooth scaling the stabilisation methods. Effectively, by gradually perturbing the system's Hamiltonian with a smooth exterior-like function, one looks for stabilities in the resulting complex eigenvalues. These stabilities manifest themselves in the form of a reduced variation of the eigenvalues' position on the complex plane as the CAP is amplified. There is also the presence of curves and cusps that are consequence of the transition of dominance between two errors, one caused by the introduction of a CAP and other by the truncation of the basis set [88]. The point at which these errors cancel should indicate the correct resonant energy eigenvalue. These two factors – stability of the eigenvalue and error cancellation point – should coincide. The existence or absence of such coincidence should then be taken into account in an accurate calculation of resonances using the CAP method.

The choice of functional form in the CAP must also be addressed, as consistency dictates that results should be independent of the form of the CAP. What is observed in practice is that the CAP's functional form does have an effect on the detection of resonances, introducing a level of uncertainty that needs to be accounted for.

3.1.1 Independence or Resonances from CAP

Usually, the functional form employed in the definition of the CAP depends on a few parameters. Reasonable physical assumptions define a range of choices for those parameters. One of these assumptions is that CAP's starting point, r_{min} , should be relatively far inside the dissociation region in order to absorb only the continuum part of the wavefunction. However, the choice of parameters is mostly arbitrary, leading to a degree of uncertainty in the results which, to the author's knowledge, has not been properly quantified before.

Although some work has been done in establishing methods to produce “optimal” CAP's [67; 68; 69; 70; 71; 72], the fact remains that there is no fundamental physical reason for choosing a particular CAP other than setting its starting point, r_{min} , at some point inside the open dissociation channel, and its ending point, r_{max} , at the end of the wavefunction grid, as discussed in section 2.3.5.4. For this reason, those stabilities detected across different CAP forms that are not consistent to some degree should be treated as artifacts.

In this work both the GLM CAP and the monomial CAP with n set to 2, referred as the M2 CAP, described in section 2.3.5.5, were employed to test their effect on both the properties of the resonant states and the consistency of the results.

As will be demonstrated later, just using different r_{min} values for the same CAP functional form may be sufficient to generate inconsistent results in both the resonance positions and widths in some of the stabilities identified. This effect occurs in varying degrees for each detection, which naturally leads to the idea of an uncertainty that needs quantification. In an attempt to tackle this issue, a consistency check was implemented in the calculation. This check involves calculating the resonances for a set of CAPs, differing only in their r_{min} positions, probing the consequences of “absorbing” different regions of the continuum wavefunctions and quantifying the accuracy of the detections by having an uncertainty associated with them.

3.1.2 Automatic Resonance Detection

Successive diagonalisations with varying values of λ cause the eigenvalues of the perturbed Hamiltonian (2.88) to “travel” across the complex plane, each one with its own trajectory. These trajectories must then be inspected one by one. The main difficulty with this approach lies in the fact that to find resonant states one has to inspect thousands of plots and manually identify all the values of λ_{op} for a number of CAP parameters and functions. To alleviate these difficulties, an automated detection procedure that uses the graphical method criteria described above to detect

the existence of stability points and cusps was introduced.

The procedure consists of analysing the individual trajectories, obtained for a particular $W(R)$ function as values of λ increase. Each trajectory is scanned in a search for the nearby occurrence of three conditions. The first condition arises from the nearby existence of local maxima or minima in the complex energy, as generally occurs in the presence of a loop or a cusp. Secondly, the same trajectory is tested for the existence of stability regions where the density of points along the trajectory has a maximum. This can be stated as:

$$\frac{dN_E}{dl} = 0, \quad \frac{d^2N_E}{dl^2} < 0 \quad , \quad (3.1)$$

where N_E is the number of complex energy points per unit of trajectory length and l is the position along the trajectory. Finally, the existence of maxima in the trajectory's curvature is tested, with the curvature κ given by:

$$\kappa(\lambda) = \frac{|E'(\lambda)\Gamma''(\lambda) - \Gamma'(\lambda)E''(\lambda)|}{(\Gamma'(\lambda)^2 + E'(\lambda)^2)^{3/2}} \quad . \quad (3.2)$$

The next step is to identify which λ values satisfy all three conditions within a certain tolerance window. If all three conditions occur within that window, a successful identification of a stability point is flagged. Each successful detection is then recorded. With this information it is now possible to assess the uncertainty associated with the choice of r_{min} and identify which results are truly consistent.

3.1.3 Detection Consistency Analysis

Spurious identifications may arise in two situations. Firstly, if the CAP range Δr is insufficiently long, then the CAP functional form will be inadequately sampled, thus leading to the introduction of an error. Secondly, if Δr is too long, parts of the wavefunction that are close to the potential well will be over-absorbed by the CAP which will significantly affect the position and width of the detection.

To remove these spurious identifications, an iterative procedure removes all stability point detections that produce a large deviation from the average of the norm of the complex energy. The procedure goes as follows: the average of the stability points found over all tested r_{min} values is calculated; the deviation from the average for each stability point is computed; the average is recalculated excluding the stability point with largest deviation and that lies outside the tolerance window; the process is repeated until no stability points can be excluded; finally, the largest deviation from the average complex energy that lies inside the tolerance window is

given as the uncertainty, and a percentage of detection is then calculated from the fraction of points selected over all the tested r_{min} values.

The detailed algorithms of how these two procedures are implemented will be discussed in the following section.

3.2 RES3D development

3.2.1 General Approach

As described in section 2.3.5.4, the CAP method is relatively simple to implement once $\mathcal{L}^2$ eigenvectors with nuclear kinetic energies above the dissociation of the molecule under study have been calculated. There are three broad steps that need to be performed: CAP matrix construction; eigenvector trajectory construction through successive CAP matrix diagonalisations; and finally, the eigenvector trajectory analysis.

It is useful to separate these three parts due to reasons associated with the cost of accurate calculations. One reason is that it makes restarting an interrupted calculation easy since all procedures can be executed independently. This can simply be done by producing intermediate data that can be re-used. This re-usability is particularly useful when performing numerous calculations that need to be performed in a consistency analysis scheme.

When developing a new program that will be integrated with the DVR3D suite of codes it is important to consider the programming paradigm under which the suite was designed – simply modular FORTRAN 77 and FORTRAN 90. For a matter of consistency and to make the interoperability easier it would be convenient to program RES3D in the same language with interoperability in mind. However, the time span of development and programming approach have created considerable difficulties with maintenance and documentation the DVR3D source codes. This is understandable since this program suite has been developed by successive Ph.D. students and Post Doctoral researchers without specific guidelines from the programming standpoint, apart from the need to have programs that run efficiently on limited hardware. Although some attempts have been made to modernise the codes, these mainly consisted of introducing features to reduce implementation difficulties and increase scalability, such dynamic memory allocation – a new feature introduced with FORTRAN 90.

Undesirable side effects of this development method led to increased difficulties in extending program functionality and correcting errors. For example, variable naming schemes conditioned by memory constraints of very early development stages

were difficult to interpret. Also due to the understandable need to quickly produce results, documentation of new features and changes was not optimal. The cost of this immediate productivity is consequently passed on to later generations of graduates in the form of time consuming reverse-engineering of the code structure and functionality.

Elementary technical problems with variable naming schemes and documentation add to a more difficult conceptual problem that arises in what is called *Procedural Programming* (PP). In this programming paradigm, to which FORTRAN 77 is tightly bound, programmes are written to describe machine-procedure ideas as opposed to the ideas of the problem one is trying to solve, i.e., the mental focus of the programmer is on what the machine needs to do to solve the problem and not on concepts of the problem being solved, or *problem space*. This leads to difficulties in the interpretation of existing code since it requires the mental effort of analysing a succession of basic procedures until a picture of what the problem space ideas are is created. This is opposed to reading the problem idea and then looking at how the machine is instructed to solve it. To tackle this well known problem in computer science, the concept of *Object Oriented Programming* (OOP) was created.

In OOP, general ideas are called *Classes*. Classes are themselves composed of *Attributes* and *Methods*. Classes serve as general definitions of *Objects* – the actual entities that the program will manipulate. These are particular cases of classes in the sense that they become entities with defined attributes. Methods are procedures that can be performed on the object’s attributes, which may result in change in the object’s properties, or production of another object belonging to the same or other class. For example, methods can be defined to obtain information about an object (e.g., the number of dimensions in a coordinate system), for simple manipulation of the object attributes without returning any values (e.g. rotation in space of a coordinate system relatively to some referential), or to transform one object into another (e.g. transformation of Cartesian to spherical coordinates). It is then possible to write code that solves a particular problem using the problem-space ideas through objects and methods without losing track of the problem in machine-specific procedures. An example of OOP pseudo-code is (based on the coordinate system example):

```
/* read from some medium n and x(n) */
  read n
  do i from 1 to n
    read x(i)
/* create an object cart with dimensions
```

```

    n and coordinates x(n) */
    cart =: Cartesian.create(x,n)
/* perform a rotation in the coordinates */
    cart.rotate(euler angles)
/* if the dimensions are correct, convert to spherical*/
    if cart.dimensions == 3 then
        spher =: cart.tranformToSpherical
/* write the spherically represented object in some medium */
    spher.write

```

Notice how in this particular example the language employed in the code almost makes the comments redundant. This means that the code portrays almost exactly the concepts in problem space, significantly improving readability. What is missing in the pseudo-code is the definition of the data structures (attributes) and the functions that apply to them (methods) which define the object **cart** in this example. These would be packaged in program modules (Classes) that would define the details of the data structures and procedures in some programming language or machine specific way.

The main advantages of OOP can be summed up in the following:

- **Encapsulation** Hiding the implementation, beside improving readability dramatically, provides protection against unintended introduction of bugs in the code, for example, by eliminating the possibility accidentally changing the value of a variable affecting a separate procedure in the program. It tightly binds data to the procedures that act upon it.
- **Modularity** The code is clearly structured and can be separated into blocks. Debugging is made efficiently through location of particular activities. Testing methods can be defined within classes incrementally, reducing dramatically the number of bugs in large projects.
- **Inheritance** It is possible to clone and adapt classes with additional functionality, without having to re-write an entirely new class.
- **Polymorphism** This allows the writing of code that adapts the interface and functionality to different data types used as argument. It also leads to the idea of specialisation of classes from a more general concept, itself represented as a class.
- **Reusability** Classes are clearly defined in the way their are to be used (interface). Implementation of already debugged classes in new code is straight-

forward. Restructuring or extension of codes is also made much easier. Implementation and debugging productivity are dramatically increased. It should be noted that this feature is not specific to OOP, but it is facilitated through it.

3.2.1.1 Object Orientation through FORTRAN 95

FORTRAN 95 does not allow a full implementation of OOP. It lacks Inheritance (pointers may be used to alleviate this issue) and an efficient method to implement polymorphism, both of which are present in the new FORTRAN 2003. Nevertheless, Encapsulation is present in FORTRAN 95 (as well as Modularity - albeit not strictly an OOP feature). More serious difficulties arise because methods cannot be bound to objects as seen in the OOP pseudo-code above: FORTRAN 95 still uses the old “function” and “subroutine” modular procedure constructs that cannot be bound to a particular object. It is possible to work around these language limitations through the use of suitable naming schemes that label methods with the originating class (module in FORTRAN 95). For example, the pseudo-code:

```
cart.rotate(euler_angles)
```

can be replaced with the FORTRAN 95 construct:

```
call cartesian_rotate( euler_angles , cart ).
```

Doing this prepares the way for an easy conversion to FORTRAN 2003 (which the author believes is inevitable). The aim is to mimic OOP as closely as possible within the limitations of FORTRAN 95 to tap into some of its benefits. This approach is known as Object-Like Programming (OLP) [89].

Classes can be defined using FORTRAN 95 Modules. Objects can be constructed by associating derived data types to methods through appropriate naming functions and subroutines grouped inside Modules. Explicit declaration of interfaces (e.g. for operator overloading) can also be used inside Modules to mimic polymorphism through the Interface declaration. Modules also offer encapsulation through the *public* and *private* keywords.

A detailed characterisation of FORTRAN in terms of its suitability for OOP is outside of the scope of this work. Nevertheless it must be pointed out that languages such as C++, and more recently JAVA and Python, already benefit from the large library of algorithms efficiently implemented throughout the various versions of FORTRAN through binary linking. In hindsight, many of the difficulties that the author faced by doing OLP in FORTRAN could have been avoided through that route. It was in deed a miscalculated cost/benefit decision.

In order to understand and visualise the OOP concepts and algorithms used to

implement the CAP method and resonance analysis, the Unified Modelling Language (UML) will be used [90; 91]. UML provides a standardised diagrammatic representation of classes and objects and how they relate to each other. This facilitates both the design and development stages and also provides a very clear visual representation for documentation purposes.

3.2.2 Stages of RES3D Object Design

The first step is to break the problem down into ideas or concepts that will be mapped onto the object space. This is the initial analysis of the problem where the objects are discovered by looking for external factors and boundaries, duplication of elements in the system, and the smallest conceptual units. This is known as the *object discovery* stage. As objects are built, the requirements for object attributes and methods are identified and the internal needs of the objects may be realised through additional classes. This is known as the *object assembly*. Putting these objects together in the form of a system that produces the desired outcome leads to further iterations of the discovery and assembly stages in an evolutionary process. In particular, other helper classes may be required, to facilitate object interaction. This stage is called *system construction*. As new features are added to the system, one may discover that the system becomes progressively more difficult to extend. Restructuring parts of the system may be required to increase its scalability. This is called *system extension*. Finally, comes the *object reuse stage*. This is the real stress test for the classes generated during the previous design stages and it's one of the most beneficial outcomes of the adoption of Object Oriented Programming. More general definition of classes' and objects' principles may be required to produce true reusability in other problems.

It is interesting that these stages of development are not guidelines that must be strictly followed. They are the *natural design pattern* that emerges from the simple principles of OOP [91]. This pattern was also observed by the author in the development of the RES3D program.

3.2.2.1 Object Discovery

The more general and separately identifiable concepts that are involved in the calculation of resonant states are the Hamiltonian for the triatomic molecule perturbed by an imaginary CAP, the trajectories traced by the eigenvalues of this Hamiltonian as function of the CAP amplitude parameter, and the resonances that are to be detected at the loops and cusps of these trajectories. These concepts and their rela-

tionships can be readily mapped onto the object space through classes **ComplexH**, **Curves**, and **Resonances**. Fig. 3.1 shows the initial UML diagram describing these basic classes (ideas) and their relationships.

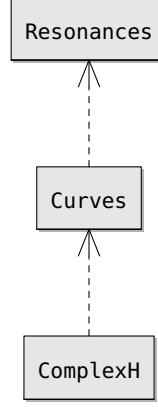


Figure 3.1: Resonance UML diagram at object the discovery stage. These are the most general ideas involved in the calculation of resonances.

In Fig. 3.1, the dashed line arrows indicate a dependency relationship, where the class to which the arrow points has a dependency on the attributes of the class the arrow points from. For example, the class **Curves** *uses* the class **ComplexH**. Fig. 3.1 describes the simple, rough ideas and their relationships in the form of generic classes. Their attributes and methods are not yet well defined at this stage and consequently are omitted from the class descriptors.

As stated in section 2.3.5.4, at the core of the calculation of resonant states is diagonalisation the complex perturbed Hamiltonian matrix, described in **ComplexH**, and with elements defined by:

$$\langle \phi_i | H' | \phi_j \rangle = E_j \delta_{ij} - i\lambda \langle \phi_i | W(R) | \phi_j \rangle. \quad (3.3)$$

This expression points to the class relationship between **ComplexH** and two other objects, namely the eigenvalues from the $\mathcal{L}^2$ nuclear motion calculation and the CAP potential matrix. These three objects are described by classes **Eigenvalues**, **Eigenvectors**, and **CAPMatrix**, respectively. The UML representation of the basic association of these classes is given in Fig. 3.2:

In the following section, other classes required to implement these general classes and their relationships will be defined in more detail.

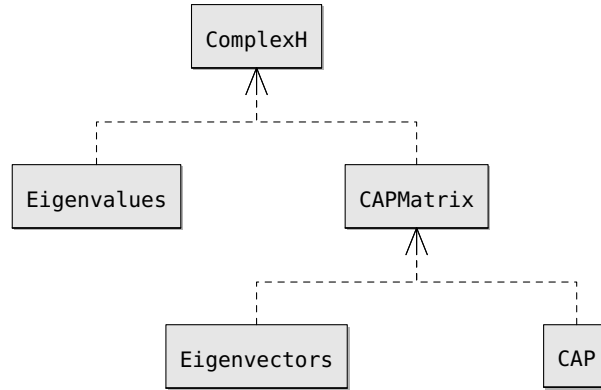


Figure 3.2: Simple UML representation of the perturbed Hamiltonian matrix with elements $\langle \phi_i | H' | \phi_j \rangle$ by the object **ComplexH**, which is dependent on the **Eigenvalues**, E_j and **CAPMatrix** with elements given by $\langle \phi_i | W(R) | \phi_j \rangle$. **CAPMatrix** depends on **Eigenvectors**, ϕ_j , and **CAP**, $W(R)$, for its construction.

3.2.2.2 Object Assembly

At this stage, the design constraints, such as the origin of data in the **Eigenvalues** and **CAPMatrix** classes and the topology of the hardware that will be used to perform the calculations are considered.

The first step in the calculation is to produce the eigenvalues E_i and respective eigenvectors ϕ_i from the nuclear motion Hamiltonian through the DVR3D and ROTLEV programs. The result is stored in a file that can readily be identified as an object, henceforth referred to as **WaveFile**, constituted of, among other properties, the arrays **Eigenvectors** and **Eigenvalues**. The UML representation of the **WaveFile** class and its relationship with the main classes is shown in Fig. 3.3:

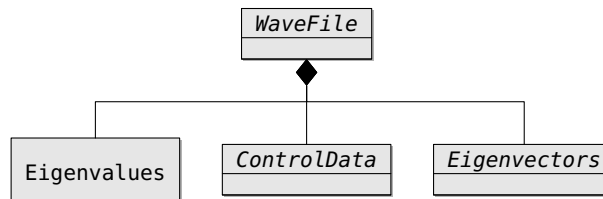


Figure 3.3: Simple UML representation of the class **WaveFile**, composed of **Eigenvalues** and **Eigenvectors**, as well as **ControlData**. The **Eigenvector**, and by association the **WaveFile** structure and attributes are dependent, among other things, on the type of coordinate system used, its embedding on the molecular coordinates, and quantum numbers of the system under analysis – all attributes of **ControlData**. For this reason these are defined as *abstract* classes.

In Fig. 3.3, the lines with diamond-shaped arrowheads indicate a component association, meaning that the class to which the arrow points is composed of the class the arrow points from. For example, the class **WaveFile** has classes **Eigenvalues** and **Eigenvectors** in its composition. **WaveFile** and **Eigenvector** are abstract

classes in the sense that their structure and methods are dependent on the specific type of calculation performed, be it purely vibrational, rotation-vibrational, in Radau or Jacobi coordinates, or other distinctive properties, such as the rotational quantum number J . Consequently, the methods used to build the **CAPMatrix** are also dependent on these characteristics. The class **ControlData** contains all these defining attributes. This is itself an abstract class because its attribute structure will also depend on the type of wavefunction.

As an example of the attribute dependency described above, building the **CAP-Matrix**, $\mathbf{W}(R)$, with elements defined by:

$$\{\mathbf{W}\}_{ij} = \langle \phi_i | W(R) | \phi_j \rangle , \quad (3.4)$$

requires an approximately exact integration using the eigenvector DVR, such that, in general:

$$\langle \phi_i | W(R) | \phi_j \rangle \approx \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}^i \Phi_{\alpha\beta\gamma}^j W(R_{\alpha\beta\gamma}), \quad (3.5)$$

where Φ a three dimensional DVR of ϕ with grid defined by $\{\alpha, \beta, \gamma\}_g$ in some coordinate system, g , and R is the Jacobi dissociation coordinate projected on that same g coordinate system grid. The specific way in which the integration will be performed depends on the coordinate system of the DVR3D calculation and on the symmetry of the molecule. Therefore, the requirement exists for an association class that implements these matrix element calculation methods. This class may be named **EigenvectorsToElements** and it will serve the role of defining the association between **Eigenvectors**, **CAP**, and **CAPMatrix**. This association is more clearly illustrated by the UML diagram in Fig. 3.4.

The next step in the calculation is to perform a succession of diagonalisations with increasing values of the CAP amplitude parameter, λ . This may be represented by an association class that will be responsible for the diagonalisation of the complex Hamiltonian represented by Eq.(3.3) and the consequent production of trajectories. Again, in the notation of UML, this can be viewed in Fig. 3.5.

Similarly there will be a class responsible for the association of the **Curves** and the **Resonances** class, as depicted in Fig. 3.6.

In particular, the **CurvesToResonances** class will incorporate the algorithms that are responsible for the detection of loops and cusps associated with the existence of a resonant state.

The class that will be responsible for the control of the program at its successive stages of execution is **Input**. This class is responsible for requesting user control

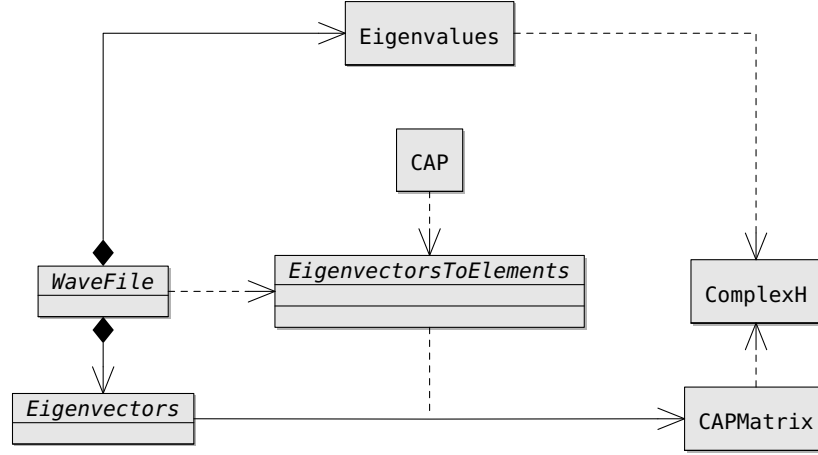


Figure 3.4: UML representation of the relationship between the **WaveFile** and **ComplexH** classes through the **Eigenvalues** class and the association class **EigenvectorsToElements**. It implements the integration in Eq.(3.4) of **Eigenvectors** with a **CAP** to generate the matrix elements in **CAPMatrix**. Note that **EigenvectorsToElements** depends class **WaveFile**'s attributes and therefore is an abstract class requiring **WaveFile** object-specific implementation of methods.

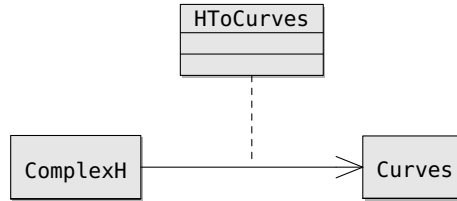


Figure 3.5: UML representation of the association of classes needed for the calculation of the eigenvalue trajectories that will be used to identify resonances. **HToCurves** is an association class that implements the calculation of objects in the **Curves** (trajectories) class.

input that will be stored in some of its attributes and generate the required control data with its methods. It will also be responsible for the majority of the checks that need to be performed to insure input consistency.

So far, the classes that have the role of performing calculations, i.e., evaluating the object attributes, are the association classes **EigenvectorsToElements**, **HToCurves**, and **CurvesToResonances**. This implies that these classes will require specific control data and will depend on an **Input** class. This dependency, although trivial, is has its UML representation in figure Fig. 3.7.

Assembling all the previous structure in one single UML diagram gives the preliminary representation of RES3D, as seen in Fig. 3.8. It will serve as the basis for the System Construction stage where auxiliary classes will be added.

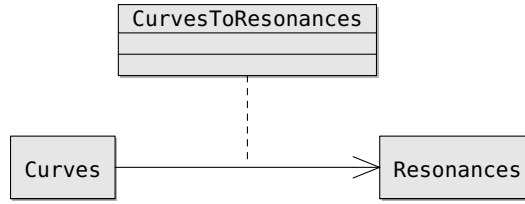


Figure 3.6: UML representation of the calculation of resonances from the curves generated through the successive diagonalisations of the complex Hamiltonian $\mathbf{H}'$. **CurvesToResonances** is an association class that implements this calculation using objects of class **Curves** to produce objects of class **Resonances**.

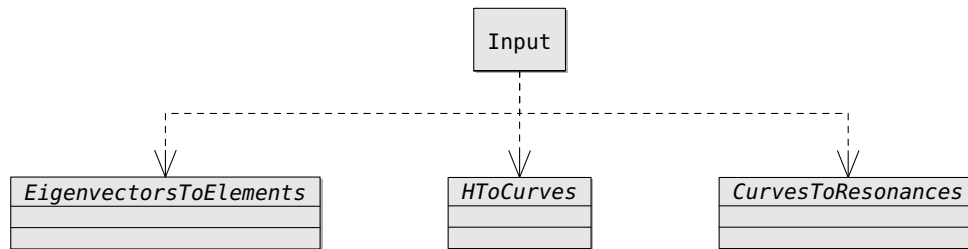


Figure 3.7: UML diagram representing dependency of the association classes **EigenvectorsToElements**, **HToCurves**, and **CurvesToResonances** on the class **Input**, which is responsible for providing control data to these classes.

3.2.2.3 System Construction

In the System construction stage, some attributes and methods will have already been defined and their classes tested. But as new methods are developed, some auxiliary classes are included to accomplish their desired functionality. Also, some of the classes need to be redefined due to either hardware constraints or implementation convenience, specially considering the OOP limitations in FORTRAN 95. For simplicity, classes are presented here without attribute or method specification. These will be described in detail later in this chapter with the final form of public methods and attributes.

One technically limiting aspect that needs to be considered is the size and number of eigenvectors needed to construct the matrix elements. These tend to be in the order of thousands, with the files required for this calculation weighing several Gigabytes. This represents a problem in terms of access to information in large, slow media, such as mechanical hard drives, particularly when the available RAM is a small fraction that required to perform the full calculation. In these cases, the program has to travel across the file multiple times in order to access each eigenvector, and more so for off diagonal matrix terms. A method involving direct access to a file and an optimal algorithm to minimise disk reads is necessary (the details of this are discussed later in this chapter). Unfortunately, the file structure in ei-

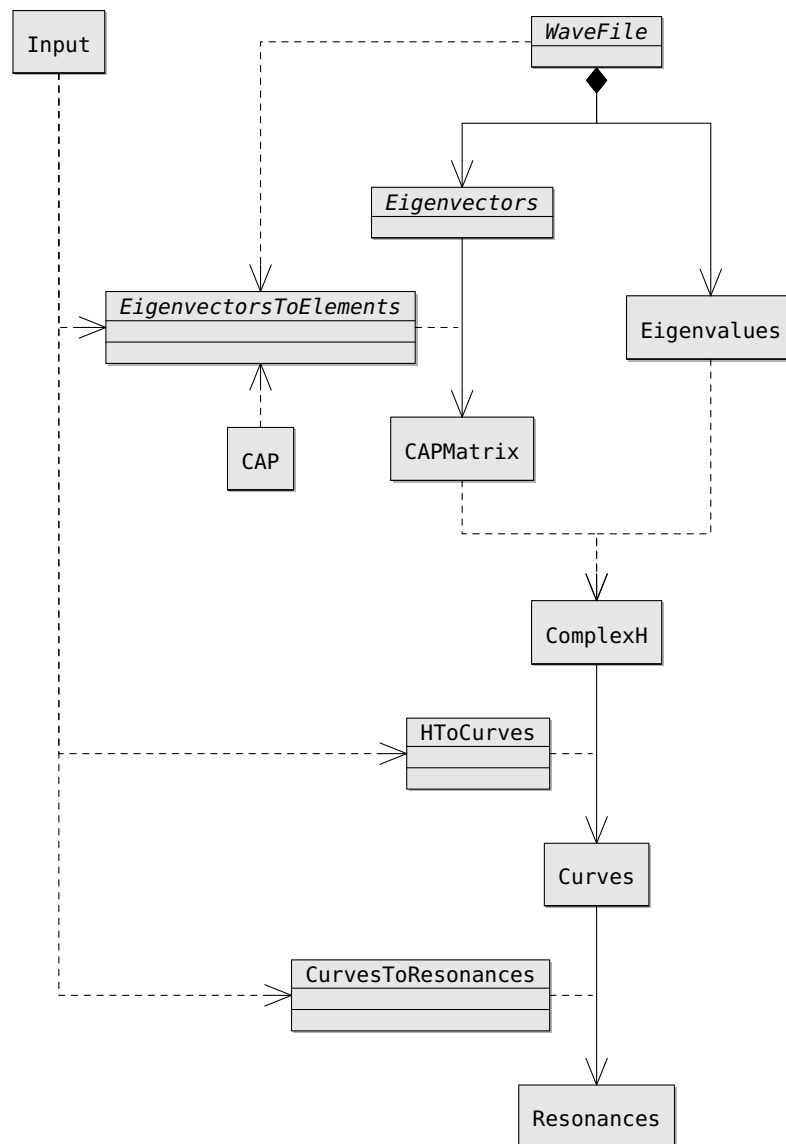


Figure 3.8: UML representation of the preliminary form of RES3D. The absence of detailed functionality is omitted for simplicity.

ther DVR3D or ROTLEV wavefunction files forbids the use of direct access reading schemes. To deal with these issues, a class has to be defined which will be responsible for the efficient file packing of the wave-function (eigenvector) data to enable direct access. This effectively requires the separation of the eigenvector part of the file from the remaining data. Since that eigenvector data is structured in terms of vibrational blocks with index k , this auxiliary class will be named **KBlock** and it will be composed of two parts: one named **KBlockHead**, containing **ControlData**, **DVRGrid**, and **Eigenvalues** (self-explanatory) classes; and the **KBlockTail**, con-

taining the **DVREigenvalues** for direct access. Access to these files on disk will be controlled through a set of methods here referred as **KBlockIO**. Fig. 3.9 illustrates the UML class diagram of this structure.

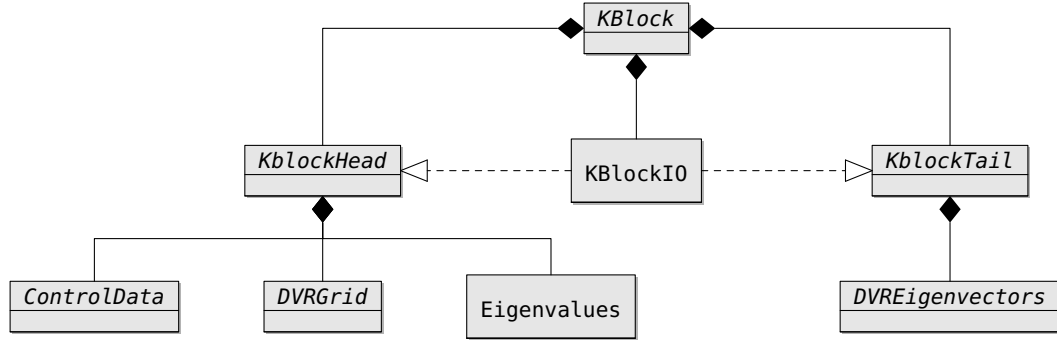


Figure 3.9: Class diagram of the **KBlock** class, composed of the **ControlData**, **Eigenvalues**, **DVREigenvalues**, and **DVRGrid** classes, as well as **KBlockIO**.

As mentioned earlier, the first stage in the program is effectively the calculation of the CAP matrix elements. In the case of $J = 0$ wavefunctions obtained from DVR3D, this can be readily performed from the data present in the wavefunction file. The full DVR of the wavefunctions permits a straightforward implementation of Eq.(3.5). In the $J > 0$ case this is no longer possible since the eigenvectors are stored in a DVR for the radial coordinates and in an FBR for the angular coordinates. Therefore, the eigenvectors need to be transformed back into a full DVR by recalculating the angular coordinate Gaussian quadrature grid points and performing the so-called back-transformation. A class of methods, henceforth referred to as **FBRToDVR**, is required to go from an FBR to a DVR in the angular coordinate. The new **KBlock** structure is ideally suited to accommodate the resulting transformed Eigenvectors, hence the **DVREigenvalues** class name.

The transformation involves the recalculation of Gaussian quadrature points with the orthogonal polynomials used in the angular coordinate basis, as discussed in section 2.4.1. This will be handled by a class named **DVRAngularGrid** containing the methods to generate these grid points and weights and the data structures to store these. For consistency, this class will be part of **DVRGrid** which thus contains the information about the full DVR grid as well as its defining characteristics, such as the coordinate system. In particular, the radial grid will be packed into a class appropriately called **DVRRadialGrid**. There will also be the need for a class that implements the coordinate transformations that are required to convert the intermediate coordinate systems – Radau, Jacobi, bond-length-angle, and bond-length. This realisation class will be referred to as **Geometry**. Fig. 3.10 succinctly

describes these relationships.

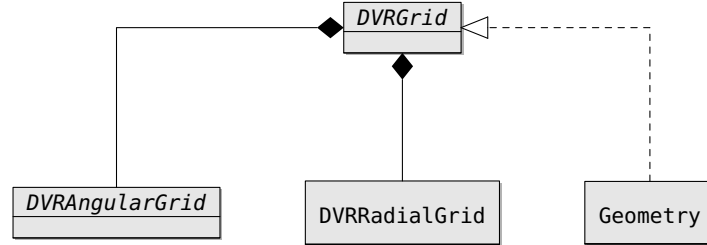


Figure 3.10: UML representation of the **DVRGrid** class, composed of the **DVRRadialGrid** and **DVRAngularGrid** classes, with the geometry transformation methods are implemented through the **Geometry** class.

The conversion of the wavefunction data from **WaveFile** to **KBlock** can now be fully described in detail (excluding methods and attributed for clarity) through Fig. 3.11.

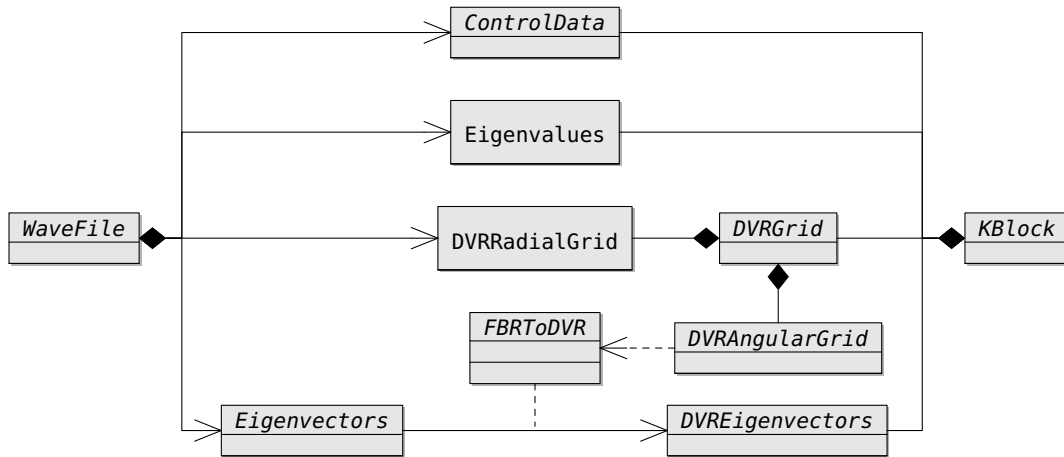


Figure 3.11: UML Class diagram representing the association between **WaveFile** to **KBlock**. The data structures contained in classes **ControlData**, **Eigenvalues**, **DVRRadialGrid**, and **Eigenvectors** are directly produced from the data in **WaveFile**. The class **DVRGrid** is composed of **DVRRadialGrid** and **DVRAngularGrid**. The latter contains the methods for creation of the Gaussian quadrature integration points, on which the association class **FBRTtoDVR** depends for the transformation of DVR-FBR eigenvectors packed in class **Eigenvectors** into the fully DVR eigenvectors in class **DVREigenvectors**. The internal structure of **KBlock** is omitted for simplicity.

The production of the elements in **CAPMatrix** can now be made using this new **KBlock** structure. The ideas are fundamentally the same as those presented in Fig. 3.4, but extra detail can now be presented with the introduction of the **DVRGrid** and **Geometry** classes. Fig. 3.12 depicts the class diagram relating the class **KBlock** to **ComplexH** using the classes described above in this section.

As mentioned before, the complex matrix stored in **ComplexH** has to be di-

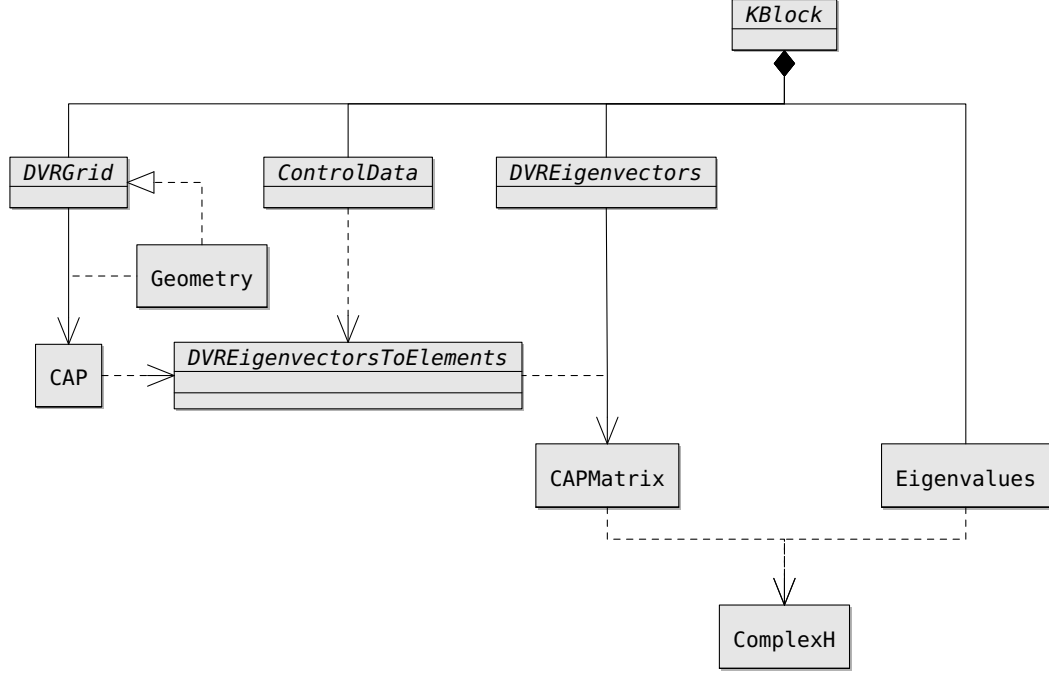


Figure 3.12: Class diagram representing the association between **KBlock** and **ComplexH**. Grid geometry information is passed to the **CAP** class through the methods in class **DVRGrid** which are realised by the association class **Geometry**. **DVREigenvaluesToElements** depends on class **CAP** and the internal choice of methods to perform the integration in Eq.(3.4) is dependent on the abstract class **ControlData**.

agonalised for successive values of the parameter λ in Eq.(3.3). The trajectories of the eigenvalues have to be tracked. Early in the development of the trajectory tracking methods that will be described later, it was observed that some of these trajectories crossed in such a way that would create tracking uncertainties. Failure to properly track trajectories could lead to the creation of false cusps or curves that could easily be confused with the stability points associated with resonances. These crossings manifest themselves through a swap in the ordering of eigenvalues between two consecutive λ points. To solve this problem, the ordering at every step of the diagonalisation should be preserved. This can be achieved by simply doing the dot product across all complex eigenvectors between two consecutive values of λ , verifying which pair more closely satisfied the condition:

$$|\Phi_j(\lambda_{i-1}) \cdot \Phi_k(\lambda_i)| \approx 1 , \quad (3.6)$$

where Φ_i is the i^{th} complex eigenvector. This is a reasonable assumption since the variations of λ should be small and no more than a negligible perturbation between each step of the calculation. After this, the data must be realigned by eigenvalue

order as opposed to diagonalisation order which is fairly trivial to perform.

It is thus necessary to elaborate on the description presented in Fig. 3.5 by refining classes and associations that deal with the diagonalisation of the complex Hamiltonian **ComplexH**, and its products – complex eigenvalues and eigenvectors. The diagonalisation is performed through the methods in class **ComplexDiag** which will be discussed later in this chapter. These methods require the storage of complex eigenvalues and eigenvectors in classes **CEValues** and **CEVectors**, respectively. Also, a class that implements the test of the condition in Eq.(3.6) is required, namely **EigenTest**. This class will generate sorted eigenvalues and eigenvectors, represented by classes **SortedCEVectors** and **SortedCEValues**, respectively. Class **SortedCEVectors** can be stored in a file to produce wavefunctions that may be used to calculate quantities like the dipole transition moments needed for the evaluation of spectral line intensities. Class **SortedCEValues** is simply reordered to represent trajectories of eigenvector positions on the complex plane as a function of λ and the curvature of these trajectories is calculated. The class **Curves** contains all this resulting information. It is this class that will be used to perform the automatic resonance detections. Fig. 3.13 describes the association relationship between these classes.

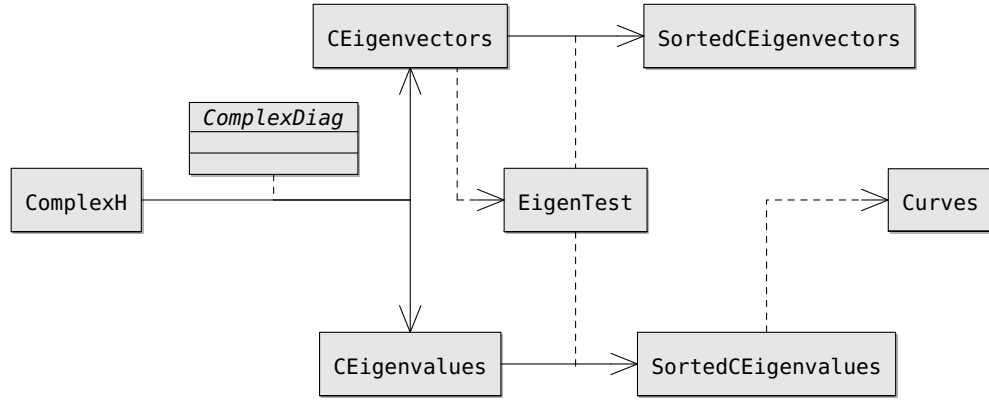


Figure 3.13: Class diagram of the association between **ComplexH** and **Curves** through intermediate classes. The abstract class **ComplexDiag** is responsible for the diagonalisation of **ComplexH** to produce **CEigenvectors** and **CEigenvalues**. The trajectories of individual eigenvalues on the complex plane are tracked through the association class **EigenTest**, which depends explicitly on the class **CEigenvectors** for its tracking methods. The result of **EigenTest** are the self-explanatory **SortedCEigenvectors** and **SortedCEEigenvalues**. The latter is used to produce the class **Curves**.

The final stage in the calculation is the analysis of the trajectories in search of resonance candidates. At this point only the heuristics system for identification of resonance candidates is discussed. The consistency analysis presented in section 3.1.3 requires a full system extension.

From the object orientation point of view, this stage is probably the simplest, since the problem that it needs to solve is fundamentally procedural – it is simply a method. Nevertheless, and as will be discussed later on, the introduction of a stack data structure class simplifies the procedure tremendously.

As mentioned earlier, the class **Curves** has self-evident classes **Trajectories** and **Curvatures** among its methods and attributes. These constitute the data that will be taken in by class **Resonances** which is responsible for the detection of resonances and for their storage for analysis. The class that greatly simplifies the procedure is class **Stash** which is no more than a stack/vector hybrid container, created by the author, that is inspired in the *vector* container which natively exists in JAVA, but absent in FORTRAN. It implements methods for stacking, indexing and sorting ordinal data. Fig. 3.14 describes the associations between these classes.

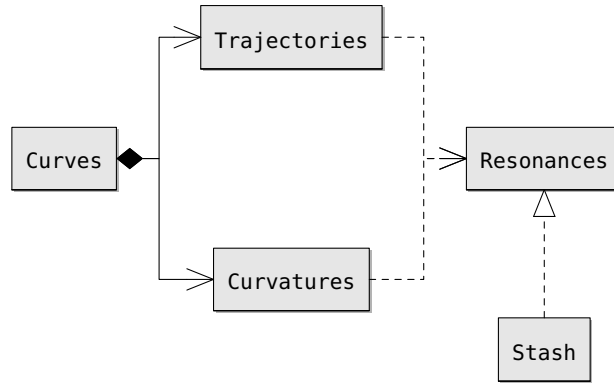


Figure 3.14: Class diagram of the association between **Curves** and **Resonances**. **Curves** is composed of **Trajectories** and **Curvatures** on which **Resonances** depends to produce the final results. **Resonance** uses **Stash** as an auxiliary class in the detection methods, appropriately represented by their realisation association.

There is still one feature that needs to be implemented but constitutes an extension of the system. As it is, the final step in the calculation cannot be implemented efficiently within the program. The final control class (controlling program execution from input) will also be defined when the final system extension is achieved.

3.2.2.4 System Extension

The traditional strategy for the calculation of resonances relies on the generic procedure described in Fig. 3.8. But as stated in section 2.3.5.4, the consistency of the identified resonances must be verified to quantify their accuracy. The straightforward way of doing this is to perform multiple calculations by setting properties of the CAP differently in each one. The issue is now one of establishing the best program structure to achieve this without unnecessary repetition of steps.

From the OOP point of view, the consistency analysis requires the program to produce a number of objects of the **CAPMatrix** class. These objects will then be used to generate the same number of complex perturbed Hamiltonian matrices, trajectory sets and resonance results. The consistency analysis is then performed by an additional class named **Consistency**. Based on Fig. 3.12, the UML class diagram in Fig. 3.15 describes the first of these steps in the production of **ComplexH** objects through association multiplicity. This multiplicity information reflects the

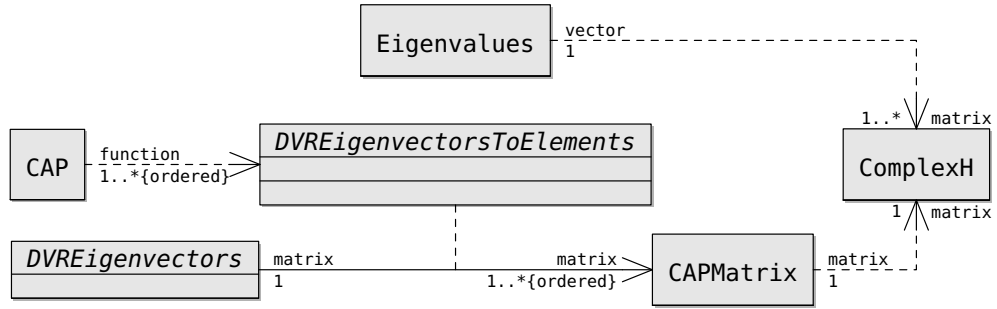


Figure 3.15: Class diagram representing the subset of the program structure responsible for the production of objects from the class **ComplexH**. The multiplicity numbers and descriptors at the association ends indicate the limits to the number of objects generated from the class at the respective association end.

extension of the program model needed to produce resonance consistency analysis data. In particular, the association between the class **CAP** and the association class **DVREigenvaluesToElements** is such that multiple ordered (distinguishable) CAP functions are used in a single association between one set of eigenvectors (packed in one single object) and a multiple number of objects of the class **CAPMatrix**. The relationship between these objects and the objects of the class **ComplexH** is of one to one, effectively meaning that there will be as many **CAPMatrix** as **ComplexH** objects. This extension required the reformulation of the methods in class **DVREigenvaluesToElements** so that they could calculate multiple elements associated with multiple operators simultaneously.

The association between the **ComplexH**, **Curves**, and **Resonances** is also uniquely defined in the same way as **CAPMatrix** is to **ComplexH** and without the need of further system extension other than execution control in the main class which at this point has not yet been defined and whose role in the previous stage has been left to the class **Input**.

Once a set of objects of the **Resonance** class has been produced, they are fed to class **Consistency**. Fig. 3.16 represents this relationship and the use of some auxiliary classes for method implementation purposes. These methods will be discussed in more detail later in this chapter. Again, multiplicity is used to illustrate

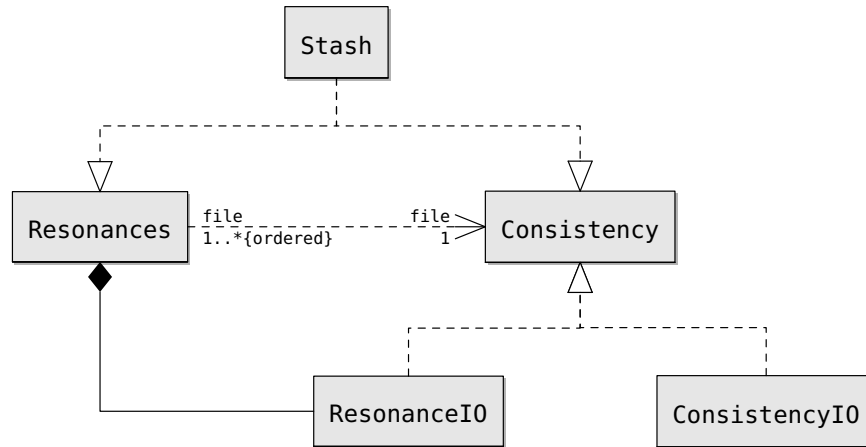


Figure 3.16: Class diagram representing the association between **Resonances** and **Consistency** through the use of auxiliary classes **ResonancesIO** and **ConsistencyIO** that serve as constructors of the file objects generated by both classes. In particular, to read the file **Resonances** files on which **Consistency** depends, the auxiliary class **ResonancesIO** implements the reading facilities. Also, the use of auxiliary class **Stash** is illustrated.

the association of objects, where multiple objects of class **Resonances** are passed on to the class **Consistency**. This in turn produces one single object file containing the results. It is important to note that both the file sets originated by **Resonances** and the single generated by **Consistency** are kept for final analysis.

Other parts of the system had auxiliary Input/Output classes are implemented in the same sense as those described above in order to keep data for analysis, as well as preserve data for the restart of calculations. This was done for classes **CAPMatrix** and **Curves**. Particularly important is the addition of plain text storage of trajectory and curvature data in ASCII format for visualisation purposes.

3.2.2.5 Object Reuse

There are several parts of the previously described system which are of significant value in terms of reusability for future applications. Some examples are: class **WaveFileToKBlock** can be reused in other applications to generate plots of wavefunctions as those presented in this document; class **Geometry** can be used also in plotting to improve the visualisation of wavefunctions that are in unintuitive coordinate systems such as Radau coordinates to, for example, the more intuitive Jacobi coordinate system; class **KBlockToElements** can be used to calculate diagonal elements, i.e., observables by using other real operators as functions; the class **Stash** can be used in many general applications that require the use of versatile stack and vector hybrids with built-in sorting facilities.

3.2.3 RES3D Algorithms

In the previous section, a black-box approach to describing the functionality of the RES3D program was made using UML class diagrams that for clarity and abbreviation contained only class descriptors without attributes or methods. In this section, a more detailed description of the most important classes will be made for some of their attributes and methods, as well as some of the activity describing procedures these methods use to achieve their functionality, mainly through UML activity and sequence diagrams.

3.2.3.1 CAP Matrix Construction

The first critical stage of the complete resonance calculation is the production of CAP matrices. As stated before, an accurate calculation involves a number of eigenvectors in the order of the thousands. Usage of memory buffering and direct access methods provide optimal IO and computation performance since these take full advantage of the available RAM and the disk devices' random access characteristics. These would be entirely lost if sequential reading procedures were implemented instead. Fig. 3.17 shows in detail the main attributes and methods involved in the **CAPMatrix** constructor method appropriately named *CAPMatrixBuild()*. The data in an object of class **Input**, passed as a method argument, is responsible for controlling the activity of the *CAPMatrixBuild()* method alongside with the properties of the wavefunction file stored as a **KBlock** object. Also, class **CAP** implements the operators used for the full consistency calculation through the obviously named interface class **Operators**. It also uses the information in the same **Input** object to determine which of the $\{cap1(), cap2(), \dots capN()\}$ functions compose the operator set and what their parameters are. An example of such parameters (and the one currently implemented) is the starting point of the CAP.

The method *CAPMatrixBuild()* uses in its procedures the *allElements()* method from class **DVREigenvectorsToElements** to calculate the elements of the CAP matrix. This is effectively the part of that calculation where the main optimisations reside, including the memory buffering strategy. As implied by Fig. 3.17, those methods rely on the IO methods in **KBlock** to achieve this. Fig. 3.18 exemplifies the construction of the CAP matrix using memory buffering and optimal file reading.

The first parts of the matrix to be built are the central triangular matrices which are shaded in Fig. 3.18. Because of symmetry, these blocks permit the fast sequential reading of contiguous eigenvectors to fill the memory buffer. Each of the greyed areas is the set of matrix elements produced with a single buffer fill. The



Figure 3.17: Class diagram representing the association of classes that lead directly to the construction of **CAPMatrix** objects. With the exception of class **CAP** only the public attributes and methods are displayed. All arguments in capitals with an asterisk are objects of the class with corresponding initials. The method `CAPMatrixBuild()` depends directly on the methods and attributes of **DVREigenvectorsToElements** and **Input**. The latter dependency is expressed through the declaration of an **Input** object as an argument of `CAPMatrixBuild()`. The interface required by **DVREigenvectorsToElements** for the `operators()` external function is defined by the interface class **Operators** and is realised by class **CAP**. The method `capSelect()` also depends on **Input** by passing its instantiation as an argument. The dependency of the methods of class **DVREigenvectorsToElements** on class **KBlock** is also illustrated.

remaining matrix can no longer be produced using the a simple sequential read due to the need to access very distinct parts of the wavefunction file to compute the elements. Both the triangular areas and the square areas are computed through trivial loops using the data in memory and the single element computation routines

depending on the number of CAPs and parameters tested. This is done using the IO methods in that same class class. Other features are implemented in the program such as the ability to skip the calculation of any CAP matrix files already present which can be used for restarting purposes or for increased versatility in checking consistency across many different calculations.

3.2.3.2 Complex Hamiltonian Diagonalisation

As shown before, building objects of the **ComplexH** class requires both **CAPMatrix** and **Eigenvalues** objects. The **KBlockHead** data structure, which now resides in a file, contains the data to form these objects. Fig. 3.20 illustrates how these classes and **ComplexH** methods are linked. The *buildComplexH()* method uses the file IO methods in classes **KBlock** and **CAPMatrix** to read the eigenvalue and CAP matrix data from their respective files. The eigenvalues will simply be added to the diagonal of the CAP matrix projected on the imaginary coordinate with intensity λ , as described by Eq.(3.3). The **CAPMatrix** object contains in its attributes the information about the eigenvector indices with which it was built, making the eigenvalue selection yet again trivial. A feature that was introduced in the code was the possibility of selecting a subset of the CAP matrix to produce a smaller complex Hamiltonian. This is useful for assessing the convergence of results with respect to this parameter without repeating the calculation of numerous CAP matrices. An example of such a subset is given in Fig. 3.21.

After the creation of the **ComplexH** object, the procedure moves on to the diagonalisation itself. The function that realises the *Diagonalise()* method is LAPACK's ZGEEV[92] complex non-symmetric matrix eigensolver. At the time of RES3D's writing, this was the only eigensolver that was able to perform the calculation reliably across multiple platforms.

As explained in section 3.2.2.3 and illustrated in Fig. 3.5, after each diagonalisation, the position of the eigenvalues on the complex plane must be tracked as they often change order, in what can be better understood as a trajectory crossing. For this, an initial control diagonalisation is made setting $\lambda = 0$, effectively nullifying the CAP matrix contribution. This will generate an initial set of eigenvectors that reflect the canonical eigenvalue ordering. From here on, the successive diagonalisations proceed by increasing the value of λ according to a λ -grid progression function given by:

$$\lambda(i) = h \frac{\chi^{i-1} - 1}{\chi - 1}, i = 1, \dots, N \quad (3.7)$$

whose parameters h and χ can be adjusted on input. To help explain the basic

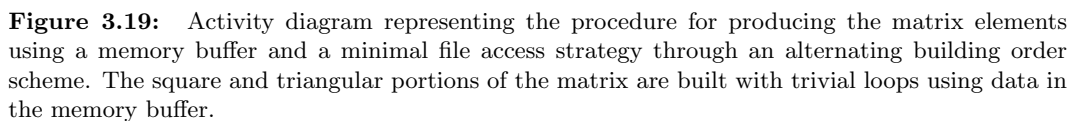




Figure 3.20: Class diagram representing the association of classes that lead directly to the construction of **ComplexH** objects. Only the public attributes and methods are displayed. All arguments in capitals with an asterisk are objects of the class with corresponding initials. The method *buildComplexH()* depends directly on the methods and attributes of **CAPMatrix** and **KBlock** and **Input**. The latter dependency is expressed through the declaration of an **Input** object as an argument of *buildComplexH()*. Note that **ComplexH** is an abstract class since it depends on external libraries such as LAPACK for the implementation of the *buildComplexH()* method.

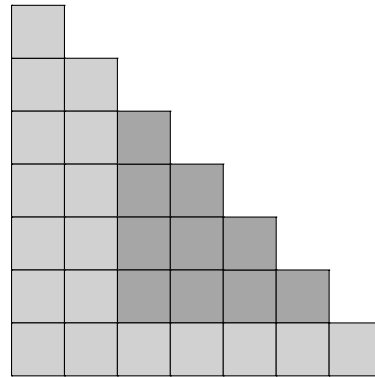


Figure 3.21: Representation of a square matrix of size seven from which a sub-matrix (in dark grey) of size four is selected. This approach is used in convergence of results relative to the complex Hamiltonian size parameter.

idea behind the procedure, Fig. 3.22 illustrates the central loop responsible for the sequence of diagonalisations through a UML sequence diagram. After the control

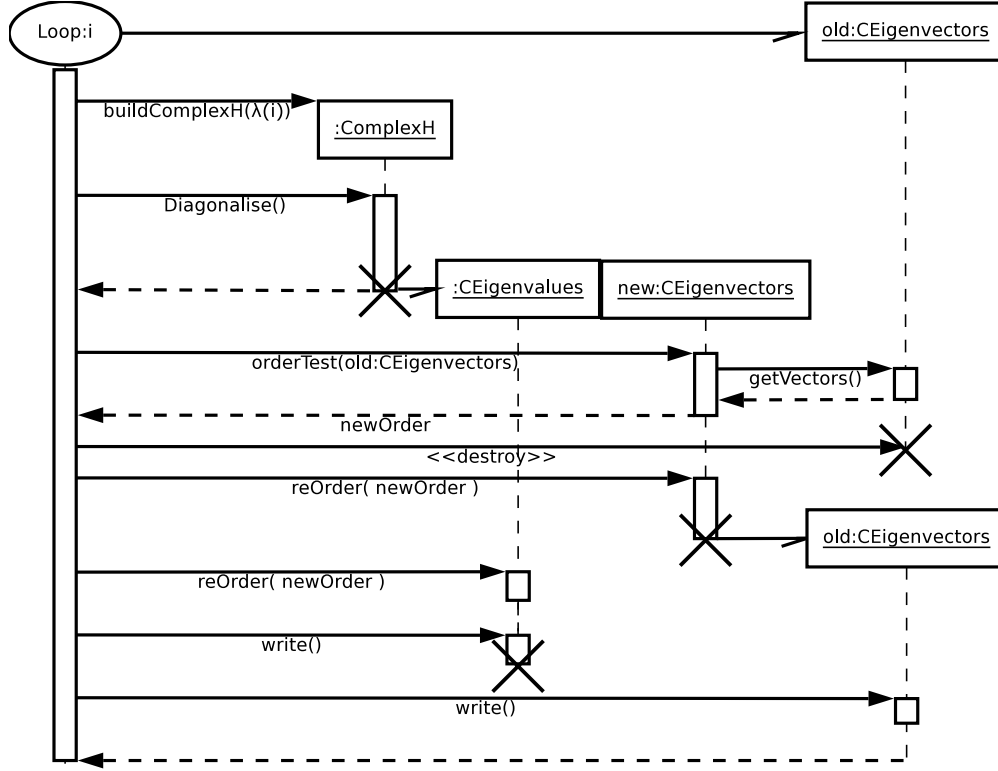


Figure 3.22: UML sequence diagram sketching the process of successive diagonalisation of the complex Hamiltonian matrix, here referred to as an instantiation of the class **ComplexH**. Note that the explicit dependency on $\lambda(i)$ is for clarity purposes only.

eigenvectors old:CEigenvalues are produced in the zero-*th* step, these are passed into the first loop iteration. The first object of class **ComplexH** is created with the respective $\lambda(i)$ parameter defined by Eq.(3.7) and the eigensolver is called. The successful diagonalisation results in the construction of an object of class **CEigenvalues** and the respective complex eigenvector container object new:CEigenvalues. The method *orderTest()* associated with the new:CEigenvalues is called with the previously generated old:CEigenvalues as argument. This will start the test for the condition in Eq.(3.6) between the old and new objects. The *orderTest()* call returns the integer vector newOrder containing the correlation between new and old indices and old:CEigenvalues is destroyed. The newOrder vector will be used to sort new:CEigenvalues using its *reOrder()* method, at the end of which the old:CEigenvalues is created from new:CEigenvalues and the latter is destroyed. Also, the **CEigenvalues** object is sorted with its internal method *reOrder()*. The final step in the loop is to use the IO methods in the **CEigenvalues** and **CEigenvalues** classes to write their contents to files. Later in this chapter, a

memory buffer strategy will be described that facilitates the parallelisation of this procedure.

The complex eigenvector files are stored for future usage in the construction of resonant wavefunctions and calculation of relevant quantities or plotting, whereas the complex eigenvalue files generated in the previously mentioned loop will be used to generate class **Curves** objects through a trivial rearrangement of the eigenvalue data, and the curvature of the trajectories is calculated. Again, **Curves** IO methods will save its contents to disk so that the trajectories can be analysed.

3.2.3.3 Eigenvalue Trajectory Analysis

As described in section 2.3.5.4, the trajectory analysis heuristics consist of the detection of the coincidence, within a tolerance window, of the following conditions: a stability of the grid points with respect to λ ; a minimum in the complex energy; and a peak in the trajectory curvature. All these must happen within an energy window given by a percentage of the maximum energy covered by a trajectory. The approach taken here is to stream the data from the **Curves** files through a test pipeline. The entire class **Resonances** consists on one single method *resonances_search()* that is responsible for this pipeline. It also depends on the auxiliary class **ResonanceIO**, declared in Fig. 3.16, which contains the usual read and write methods and on the **Stash** class for the identification algorithm. The resonance objects will simply be the files produced by the *resonances_search()* method. Fig. 3.23 illustrates the pipeline through which the trajectory data is streamed and how the detections are made and stored in the detection stacks.

Throughout the development of the resonance identification heuristics, a particularly significant difficulty emerged associated with the detection of the narrowest resonances, i.e., very small λ_{op} . The precision limits in the diagonalisation resulted in data contaminated with numerical errors to which peak detection based on differentiation is particularly sensitive. To solve this problem, an running average smoothing procedure was introduced that relies on neighbouring points within a trajectory segment, effectively cancelling out random fluctuations.

The detection of stability consists simply of finding points in each energy eigenvalue trajectory that satisfy the simultaneous condition:

$$\frac{\Delta E_n}{dn} = 0, \quad \frac{d^2 \Delta E_n}{dn^2} > 0 \quad (3.8)$$

where ΔE_n is the n th forward difference in the discrete complex energy trajectory E . In an effort to further remove spurious detections due to numerical noise, this is

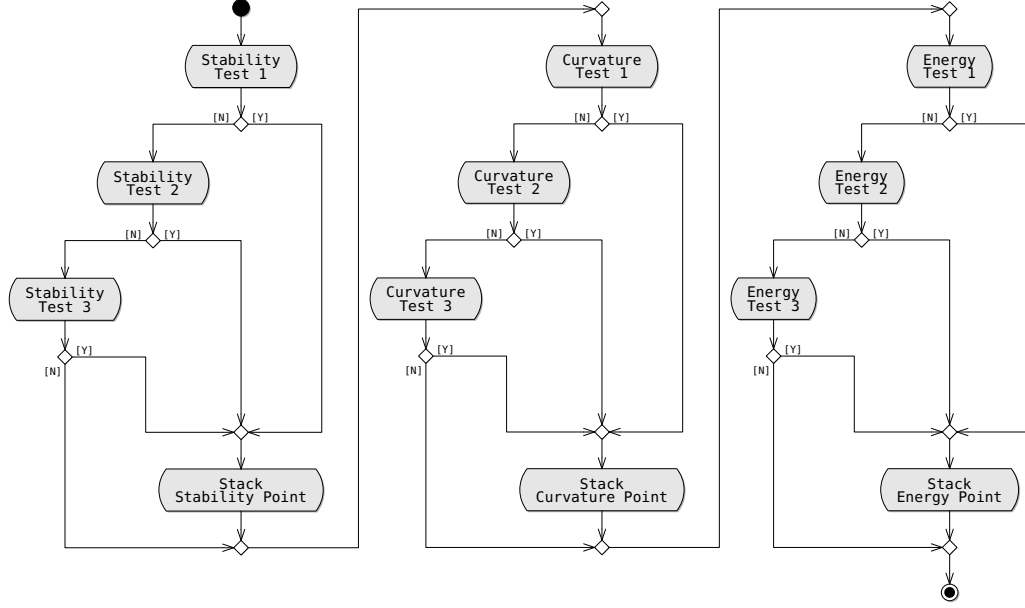


Figure 3.23: Activity diagram describing the testing procedure that stacks the points three conditions for resonance are detected. Test1 , Test2 and Test3 refer to different averaging window conditions in the maximum (minimum) detection.

implemented by logically checking the equivalent condition:

$$\Delta E_{n+M} > \dots > \Delta E_{n+1} > \Delta E_n < \Delta E_{n-1} < \dots < \Delta E_{n-M} \quad (3.9)$$

which, without smoothing, will be applied to $2M + 1$ points in the trajectory grid. This spatially broadened condition insures that the detected stability occurs over a relatively large range, hence reducing even further the possibility of interference by numerical noise. When averaging is applied, the number of logical tests remains effectively the same, but the number of points used increases by the amount included in the average, P , i.e., a total of $(2M + 1)P$ points. This is the case since the points taken for separate averages do not overlap. The averaged condition will then be

$$G_{n+MP} > \dots > G_{n+P} > G_n < G_{n-P} < \dots < G_{n-MP} \quad (3.10)$$

where G_n is the *moving average* along the trajectory given by:

$$G_n = \frac{1}{P} \sum_{i_0=0}^{P-1} \Delta E_{n+i_0}. \quad (3.11)$$

Since the tests are performed for a large number of λ grid points which undergo a large range of variation regimes defined by Eq.(3.7), three tests are performed, as

described in the activity diagram in Fig. 3.23. One is done using the condition in Eq.(3.9) without averaging, and the remaining two use averaging with arbitrary P sizes. It was verified that $P = M/3$ for the second and $P = M/10$ for the third tests provide ratios that work in most conditions

Similarly to this, the remaining two heuristics are tested. In the case of the minimum in the complex energy, both the imaginary and real parts of E are tested as expressed above, replacing ΔE with E_r and Γ respectively. Finally the curvature, calculated with the expression:

$$\kappa(\lambda) = \frac{|E'_r(\lambda)\Gamma''(\lambda) - \Gamma'(\lambda)E''_r(\lambda)|}{(\Gamma'(\lambda)^2 + E'_r(\lambda)^2)^{3/2}} . \quad (3.12)$$

This expression is implemented through a finite differences method. Due to the sensitivity of this method to numerical noise, the running average is particularly useful. Therefore, the same procedure described above is applied. The testing condition this time is:

$$\frac{d\kappa_n}{dn} = 0, \quad \frac{d^2\kappa_n}{dn^2} < 0 \quad (3.13)$$

meaning that maxima are sought. This was implemented testing the condition:

$$\kappa_{n+M} < \dots < \kappa_{n+1} < \kappa_n > \kappa_{n-1} > \dots > \kappa_{n-M} . \quad (3.14)$$

As mentioned before, these calculations are implemented in a stream that runs for each complex eigenvalue trajectory. The points in the trajectory for which these tests are positive are placed in a their respective stacks. These stacks are then processed in a series of loops to identify those points at which all the conditions are satisfied. To understand how the proximity condition is tested, refer to the UML activity diagram in Fig. 3.24.

In the event that any of all three heuristic conditions coincide within a user defined window, where the minimum in complex energy is taken as reference, the loop is exited an another trajectory is tested.

All the resulting coincident points are written to a file using **Resonances IO** methods. One such file is kept for each tested CAP, and the set is then passed to the **Consistency** class methods for the final analysis step.

3.2.3.4 Resonance Consistency Analysis

As with the resonance identification heuristics class **Resonance**, the **Consistency** class consists of one single method and uses the **Stash** class and the auxiliary IO class responsible for reading the detected resonances, **ResonanceIO**, as well as its

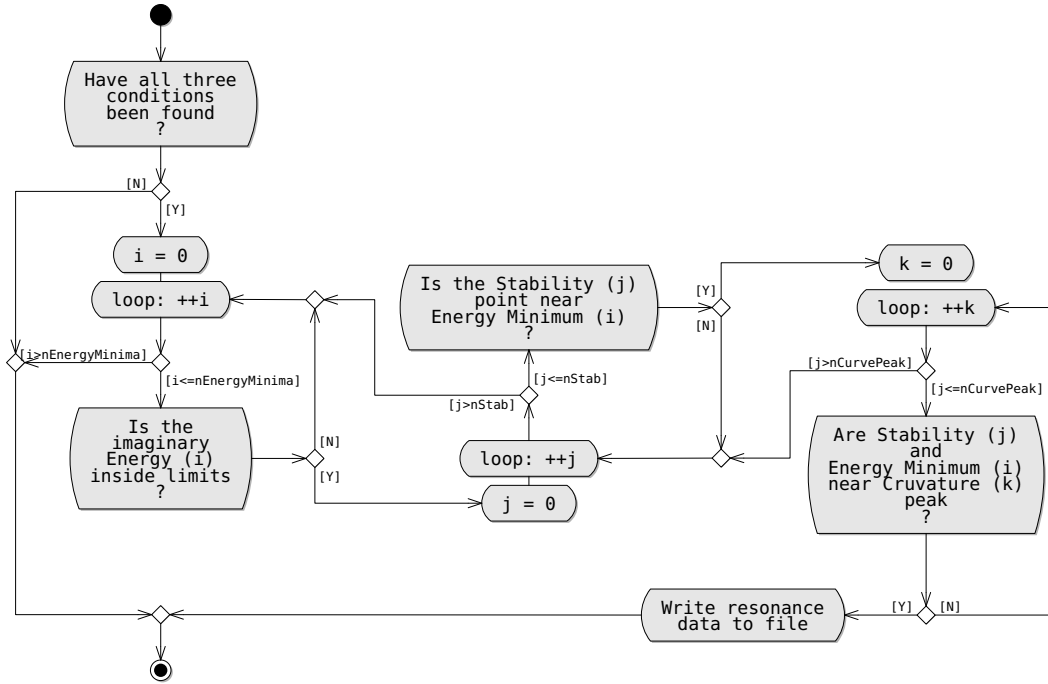


Figure 3.24: Activity diagram describing the testing procedure that tests the proximity of the points in the trajectory at which the three conditions for resonance were detected. The word “near” implies that the distance between the tested points lies within the tolerance window.

own ConsistencyIO.

The idea behind the consistency analysis and the algorithm that performs it is described in section 3.1.3. Fig. 3.25 depicts the algorithm used to remove spurious resonances identifications from the final consistency analysis.

A tolerance window in the complex plane is introduced, in which the identified resonance candidates must fall. This window depends on the average of these stability points. Therefore, once the spurious resonances are removed, the average must be recalculated. The process is repeated until no resonance is excluded upon an average recalculation. As a result, the average, maximum deviation from the average, and percentage of successful detections will be given. After all the stacks corresponding to individual eigenvalues with detected resonances are examined, the procedure simply writes the results to a file and the calculation is terminated.

Each activity described in the Fig. 3.25 may involve the addition, subtraction and sorting of elements in stacks. The use of stack objects simplifies these activities significantly due to well defined methods. They can simply be manipulated by “sending” messages to them. For example, to remove the largest deviation point from the stack, a sorting message is passed to it, indicating to do so in ascending deviation order; a stack pop message is passed to the stack, resulting in the removal

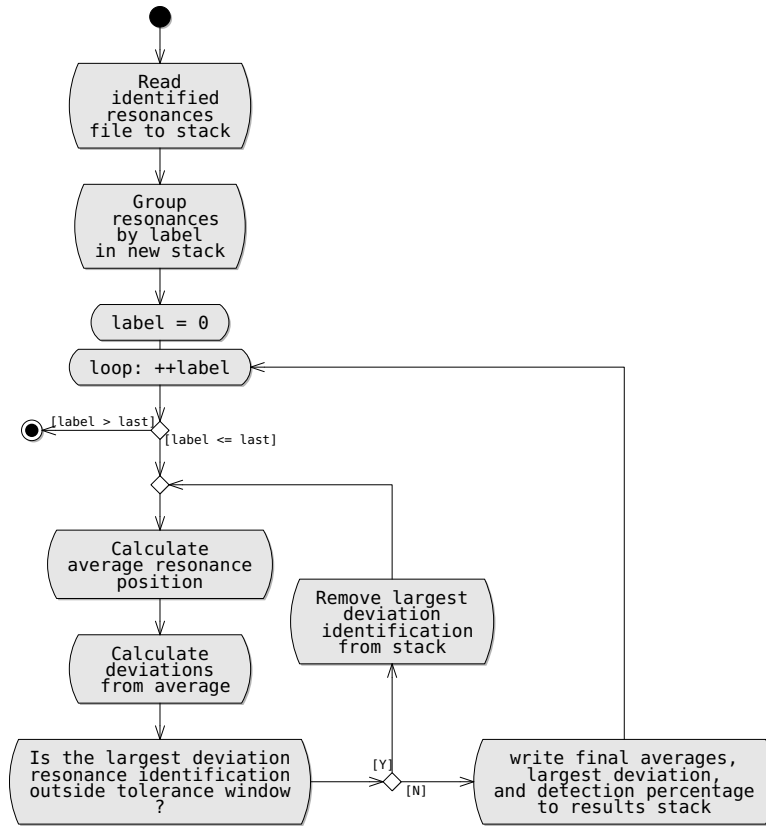


Figure 3.25: Activity diagram describing the removal of spurious resonances before the consistency analysis is performed.

of the last element.

3.2.4 Parallel Implementation

Recent developments in CPU architecture are forcing the need for the development code which is able to execute on multiple CPU “cores”. This is because current CPU manufacturing processes are reaching the physical limits of clock speed and transistor miniaturisation. Therefore, to take advantage of the full power available in today’s and future CPUs, programs must be written so that they can create threads that span across multiple processors in a shared memory environment.

There are no restrictions to the way parallelism is to be implemented in OOP. The case can be made for the development of OOP codes with parallelism in mind from the start, although the author believes that this leads to the same pitfalls of procedural programming, where the program is designed for machine architecture, rather than communicating effectively the problem that is being solved. Since the methods implemented RES3D rely mostly on independent iterations in loops,

parallelism can be easily implemented using OpenMP [93].

In essence, OpenMP is a set of language pre-processing commands that control the creation of so called *computing threads* – simultaneous sequential computations under the same process, or program. It provides facilities to parallelise and control the execution of loops and other program sections using a simple but powerful syntax. Another important feature of this language the internal availability of its libraries in latest versions of most FORTRAN and C++ compilers. This voids the need for installation at the operating system level such as that required by MPI (Message Passing Interface) libraries [94].

The two critical stages in terms of computational effort are the construction of the CAP matrix and its successive diagonalisation. The methods associated with these activities reside that reside in classes **DVREigenVectorsToElements** and **ComplexH**.

In section 3.2.3.1, more specifically in Fig. 3.19, the method **allElements()**, through which the CAP matrix is built, is detailed. In that scheme there are two private activities named “build triangle” and “build square” that are responsible for the calculation of the matrix elements in those regions, as illustrated in Fig. 3.18. These private activities contain *do loops* in which the **DVREigenVectorsToElements** methods are called. These loops were wrapped in the so called OpenMP “pragmas” (the OpenMP declarations), instructing the compiler to parallelise these sections of code. On execution, a number of threads, equal to the one present in operating system environment variable \$OMP_NUM_THREADS, is issued. It should be pointed out that the DVR integrals algorithm is itself a *do loop* to which the pragmas could have been applied. This was in fact attempted, but no significant gains were achieved since the calculations at that level are very fast. This means that the CPU overhead required to generate a new thread is of the same order of magnitude as, or larger than each iteration of the loop. Near linear scaling with the number of CPUs was obtained when the calculations were performed with parallelism one loop level above, i.e., at the *elements_triangle()* and *elements_square()* level.

In the stage of the calculation where the method *Diagonalise()* in class **ComplexH** becomes active, the numerous diagonalisations that need to be performed to generate the eigenvalue trajectories are virtually independent from each other. This can be verified by inspecting the algorithm described in Fig. 3.22. Therefore, there is the opportunity to use the OpenMP pragmas to parallelise that particular procedure. Unfortunately, a simple loop parallelisation will not work due to the object **old:CEigenVectors** that is passed from one loop iteration to the other. The way to solve this is to split the loop into two parts and, analogously to the method used

to build the CAP matrix, use a memory buffer in between the two now separate loops to pass the complex eigenvalues and eigenvectors across each diagonalisation iteration. This requires an additional outer loop that iterates through the number of memory blocks. Fig. 3.26 illustrates how this parallelisation was achieved. Further

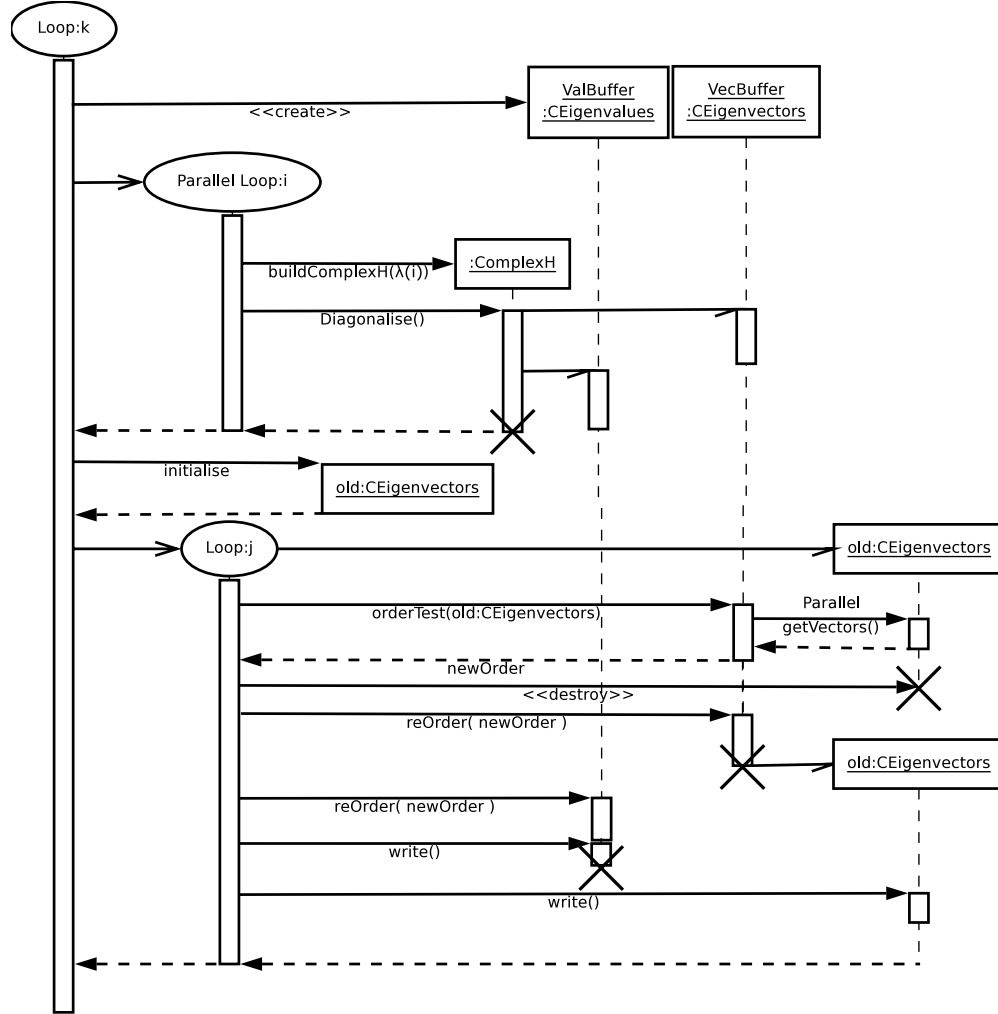


Figure 3.26: UML sequence diagram sketching the process of successive diagonalisation of the complex Hamiltonian matrix, here referred to as an instantiation of the class **ComplexH**. Here the original loop i is broken into one parallel loop i followed by a sequential loop j , both embedded in the sequential loop k . Loops i and j are linked through buffers **VecBuffer** and **ValBuffer**. The *orderTest()* is also parallelised.

savings can be made if the dot products performed in the *orderTest()* in the second loop are parallelised. Both these modifications were done with a perfect linear scaling with the number of CPUs used.

3.2.5 User Manual

In the previous sections, a technical exposition on the most important aspects of the RES3D implementation was made. Using that information, the input temporary and output files can now be discussed as well some of the functionality in RES3D that was not covered in previously.

The program requires at least one file to be present in the same directory as the executable. This file is the wavefunction file either from DVR3D or ROTLEV. The input file must be redirected to standard input and, as will be later explained, the wavefunction file name must be in one of the input file fields. RES3D will issue a number of parallel threads equal to the value set in the `$OMP_NUM_THREADS` operating system environment variable. If this variable is not set, the program defaults the number of threads to one. It is advisable that the number of threads be equal or less than the number of CPU's available.

Once the execution of the program starts, RES3D begins to convert the wavefunction file to the more workable "KBlock" file format. Each vibrational block of the wavefunction is then separated into a set of file pairs named `kblock***_head.bcs` `kblock***_tail.bcs`, with "***" being the block index digits, starting with zero (or one, depending on symmetry) to $2J + 1$, where J is the rotational quantum number in this calculation. An ASCII file named `kblock000_head_dump.bcs` is written to disk and the calculation is stopped. This file contains the kblock head file information and the the input data processing results. This gives the user the opportunity to verify the consequences of the input generated, such as the exact number of basis functions contained within the energy cut-offs and the positions of the outermost grid points in all dissociation channels. This is particularly useful when doing convergence tests where it is necessary to determine the size of matrices generated by the energy cut-offs on input.

Once KBlock files are generated, it is no longer necessary to have the original wavefunction files in the same directory as the RES3D executable. **Important note:** For the calculation to proceed, the dump file must be present in the same directory as the executable. Any file with that same name being present will allow the calculation to proceed.

Following the wavefunction file conversion, the calculation of the CAP matrices starts, generating sequentially a number of binary files called `cap**.bcs`, where "**" are two digits that index the file to increasing values of the CAP length Δr . The number CAP's tested, the smallest, the largest length and its functional form can be set on input. If the calculation is interrupted while building one particular CAP matrix, it is possible to resume it by removing the incomplete file, making sure that

the original input, KBlock files and already completed CAP files are in place.

After the all CAP matrix files are written, the complex Hamiltonian construction and diagonalisation process begins. This will generate sorted eigenvalue binary files named `eigs**.bcs`. Optionally, the sorted eigenvector binary files named `eig_vecs**.bcs` may also be generated. The eigenvalue files contain the intermediary data that will be used to generate the complex eigenvalue trajectories. These depend on the $\lambda(i)$ CAP amplitude function of Eq.(3.7), whose parameters must be assigned on input. Again, the creation of these files benefits from the same (limited) restart facility that is implemented for the CAP files

The rearrangement of the eigenvalue trajectories and the calculation of trajectory curvatures comes after the diagonalisation procedure. The files `curvs**.bcs` are generated, as well as the ASCII formatted file `deltar**curv_plot.bcs` containing useful information for plotting and analysis purposes.

Once the initial search for resonances on these trajectories is finished, files `res**.bcs` will be written, containing the resonance candidates in ASCII format. These files will be read in the last stage of the calculation.

Finally, the consistency analysis is performed on the `res**.bcs` file data and the results are written to a single ASCII file named `res_consist.bcs`.

3.2.5.1 Input

In section 3.2.2.2 it was noted that class **Input** is responsible for interpreting the input file and control the execution of the program, effectively linking the active classes. What will be discussed here is how the input file is structured as well as the description and functionality of its entries.

The file is divided in three regions all starting with empty lines that may be used to place comments, each associated with a different part of the RES3D's execution.

The first section is made of input lines that will provide all the information need to perform the CAP matrix construction. Likewise, the second and third regions are associated with the diagonalisation and resonance detection stages. Each line is defined as follows:

Line 1: a line for comments.

Line 2: `cap%molecule` - label with a maximum of seven characters

Line 3: `cap%capchoice` - maximum of 20 characters defining the choice of cap functional form. Currently implemented choices are: `manop`, `simple`, `simple3`, and `simple8` which indicate the GLM, and monomial CAPs of order two, three and eight, respectively.

- Line 4:** `cap%coord` - four characters indicating the dissociation channels to which the CAP will be applied to. The current options are, 1-23, 2-3, 3-12, 12-3, and 123, corresponding to placing the CAP in the dissociation coordinate of atom 1, 2, 3, both 1 and 2, and all, respectively.
- Line 5:** `cap%rmaxchoice` - in the case where the dissociation grid is not symmetric, chose in which maximum extent point the CAP. The options are, `long`, `short` and `adapt` (characters).
- Line 6:** `cap%drmin` , `c%drmax`, `c%ndr` - controls the shortest, longest and the number of CAP lengths (as measured from the CAP end) , respectively, calculated for consistency test purposes. The types are real, real and integer, respectively
- Line 7:** `cap%lowest_energy` , `c%highest_energy` - low and high energy cut-offs for selection of the vibration-rotation states' eigenvectors to be used in the CAP calculations (as measured from the ground state) in cm^{-1} . Both are real type
- Line 8:** `cap%ground_energy` - energy of the ground state as given by the DVR3D output in cm^{-1} . Real type
- Line 9:** `cap%wavefile` - wavefunction file name (max 200 characters).
- Line 10:** `cap%mem` - memory available to the program in MegaBytes. Real type.
- Line 11:** a line for comments.
- Line 12:** `diag%lowest_energy` , `diag%highest_energy` - low and high energy cutoffs for selection of a sub-matrix of the CAP for construction of the complex Hamiltonian (as measured from the ground state) in cm^{-1} . Both are real type.
- Line 13:** `diag%chi` , `diag%h` , `diag%nlambda` - parameters that calibrate the $\lambda(i)$ - grid progression function for χ , h , and the total number of grid points N . The types are real, real and integer respectively.
- Line 14:** `diag%ccnumber` , `diag%ecthres` - maximum number of allowed trajectory crossings and minimum threshold for the equivalence correlation two eigenvectors. The types are integer and real (between 0 and 1), respectively.

Line 15: `diag%outputvec` - logical value determining if the diagonalisation eigenvalues are printed or not (`.true.` or `.false.`).

Line 16: a line for comments.

Line 17: `resonance%resmode` - value of n in $(2n + 1)$ test points used in the heuristics for resonance identifications (typically 20). Integer type.

Line 18: `resonance%resupcut` , `r%reslocut` - upper and lower cut in the imaginary energy ($\Gamma/2$) of detected resonances in cm^{-1} . Both are real type.

Line 19: `resonance%re_thres` , `r%im\_thres` - real energy range in cm^{-1} and percentage of the total imaginary energy ($\Gamma/2$) that defines the tolerance window in detection and consistency, respectively. Both are real.

A sample input file follows:

```
---- comment line
MOLEC
simple3
1-23
adapt
2.0d0 4.0d0 3
0.0 999999999
0.0
path/to/wavefunction.file
6000
---- comment line
0.0 999999999
1.010 0.7d-5 500
100 0.8
.false.
---- comment line
20
100.0 2.0d-17
0.5 3.0
```

3.2.5.2 Output

There are five files that may be used for analysis of the calculation. These are:

- **kblock**_head_dump.bcs** - dumps the contents of the **kblock** file heads and the results of processing the input such as the total number of states used in the construction of the CAP, the number and index of states used in the complex Hamiltonian construction, the end position of the CAPs in the dissociation channels and other useful information.
- **deltar**curv_plot.bcs** - contains the trajectory, curvature, lambda function progression and derivatives information for plotting purposes. The following FORTRAN code describes the file structure:

```
do j = 1 , cap%nlambda
write(fileUnit,"(I4.4,1X,I5.5,5(1X,E22.15))")
i,j,lambda(j),realE(j,i),complexE(j,i), &
complexE'(j,i),curvature(j,i)
end do
write(fileUnit,*)
write(fileUnit,*)
end do
```

The file formatting above was design to be read by the GNUplot “plot” command. An extract from the GNUplot manual is given below.

GNU PLOT

Index

The index keyword allows only some of the data sets in a multi-data-set file to be plotted.

Syntax:

```
plot 'file' index <m>{{:<n>}:<p>}
```

Data sets are separated by pairs of blank records.

index m selects only set m;

index m:n selects sets in the range m to n;

and index m:n:p selects indices m, m+p, m+2p, etc.,

but stopping at n .

Following C indexing, the index 0 is assigned to the first data set in the file. Specifying too large an index results in an error message. If index is not specified, all sets are plotted as a single data set.

Example:

```
plot 'file' index 4:5
```

<http://www.gnuplot.info/demo/multimsh.html>

Using

The most common datafile modifier is using.

Syntax:

```
plot 'file' using {<entry> {:<entry> {:<entry> ...}}} {'format'}
```

If a format is specified, each datafile record is read using the C library's 'scanf' function, with the specified format string. Otherwise the record is read and broken into columns at spaces or tabs. A format cannot be specified this way for time-format data (instead use `set xdata time`).

Ideally this output file would be fed into a visual analysis module that would plot the trajectories and detected resonances.

- **res**.bcs** - this file contains the resonance detections for its equally indexed complex Hamiltonian. Every line of this file is structured according to the following FORTRAN code:

```
write(unit, "(I4.4,2X,F15.7,2x,G17.8,2(2X,D9.2),2(2X,D12.5))") &  
stateIndex, realEnergy, ImaginaryEnergy, realTolerance, &  
imaginaryTolerance, trajectoryLambdaValue, curvatureLambdaValue
```

The variable names in the code above should be self explanatory.

- **res_consist.bcs** - contains the resonance consistency analysis across all tested CAPs. Its lines are described by the following FORTRAN code:

```
write(10,'(i4.4,2x,f5.1,2x,f10.3,2x,G12.3,2x,f7.3,2x,E12.3)') &  
state, detectionPercentage, averageRealEnergy, &  
averageComplexEnergy, realUncertainty, complexUncertainty
```

Again, the variable names should be self explanatory.

- **std out** - Output of the consecutive stages of execution with warning and error messages in case of a diagnosed failure.

3.3 Conclusion

It is now possible to compute a very large number of resonant states and perform consistency tests in a massive scale without visual inspection and manual annotation of resonances. The program is still very basic in terms of its functionality and interface, but with the OOP approach it is much easier to maintain and to extend or reshape its functionality. This is the program used to produce the results in this document.

Chapter 4

Results and Discussion

In the previous chapter the basic theoretical and computational framework required to calculate both bound and quasi-bound vibration-rotation energy states of tri-atomic molecules was presented, as well as the development of a program named RES3D to calculate resonance positions and widths of triatomic molecules.

In this chapter, previously reported calculations of HOCl resonances are used in the validation of the methods implemented in RES3D. For the reasons described in section 1.3, these tests will be followed by the details to the calculation and study of vibrational states of D_2H^+ that constitute the basis for the calculation of resonances.

The D_2H^+ system will be used to study influence of the RES3D input parameters on the accuracy of the resonance results. This study will serve as a basis for the calculation of both D_2H^+ and H_3^+ resonances, as well as provide insight into what choice of parameters should be made to calculate resonances in other tri-atomic systems.

The final results and convergence characteristics of resonances for D_2H^+ and H_3^+ vibrational resonances as well as the first calculation of H_3^+ $J = 3$ resonances are presented and discussed.

4.1 RES3D HOCl Validation Tests

Although extensive tests have been made throughout the development of RES3D, the real test for its performance is its ability to reproduce resonance results from independently performed calculations. The ideal candidate molecule for this task is HOCl due to the availability of calculations from other groups [65], and more recently Tennyson’s group [14], both in good agreement with experimental data [66].

There are two main overarching groups of procedures that will be tested. Firstly, the production of a correct CAP matrix. This will put to the test all the integration routines, the application of the operator to the grid points and coordinate transformations, and matrix setup procedures. These will be tested by comparing the eigenvalue trajectories obtained from diagonalising two HOCl perturbed Hamiltonians. One perturbed by the CAP produced using a program developed independently by Mussa and Tennyson to perform his HOCl calculations [14], and another produced by the RES3D CAPMatrix methods using wavefunctions calculated with the parameters in reference. The trajectories will be compared directly without searching for any specific resonances. Matching trajectories should mean that the CAPs produced with RES3D are consistent, at least in this case, with those that led to successful calculations. Finally, the setup of the diagonalisation routines and trajectory tracking mechanisms, as well as the automatic detection system, will be tested. These modules working in conjunction should lead to the correct automatic identification all the resonances presented in references [14]. Any discrepancies should be easy to justify by the more restrictive identification criteria working in RES3D.

For simplicity, the tests presented here are those performed for the $J = 0$ case.

4.1.1 CAP Matrix construction Test

The RES3D CAP matrix construction class **CAPMatrix** described in section 3.2.3.1 was ostensibly tested against the DVR3D suite module XPECT3 using wavefunctions created for different molecules and rotational excitations, insuring that the method *CAPMatrixBuild()*, produced correct expectation values for different observables. The test presented here probes specifically the perturbed Hamiltonian matrix off-diagonal elements calculation.

4.1.1.1 Unperturbed Hamiltonian Eigenvectors

The calculations of these eigenvectors follow closely those produced using a parallel version of DVR3D tailored to perform calculations in Jacobi coordinates [95]. This program employs the three-dimensional DVR scheme, discussed in Section 2.4, to

solve the nuclear motion problem within the Born-Oppenheimer approximation for the ground electronic potential energy surface, using massively parallel computers.

HOCl PES:

The nuclear motion eigenvectors and eigenvalues of $J = 0$ HOCl, were produced using the potential energy surface of Skokov *et al.* [96]. This surface has a dissociation threshold of $D_0 = 19,289.2 \text{ cm}^{-1}$, which agrees well with the experimental value of $19,289.6 \text{ cm}^{-1}$ [97]. It supports about 800 vibrational states. Using this PES, Skokov *et al.* were able to reproduce the energies up to $21,716.33 \text{ cm}^{-1}$ which is well above its dissociation threshold. This makes the surface ideal for studying quasi-bound states in uni-molecular dissociation. The dissociation co-ordinate r_2 is defined as the distance between Cl and the centre of mass of OH, r_1 is the OH internuclear distance and θ is the angle between r_1 and r_2 .

Basis set:

The angular DVR functions are based on (associated) Legendre polynomials, and the radial DVR functions based on Morse oscillator-like functions, as discussed in section 2.4.3. The DVR basis size was defined by $N_{r_2} = 96$, $N_{r_1} = 45$, and $N_\theta = 60$, corresponding to a total basis size of 259,200, with a truncation to 14,400 final 3D Hamiltonian size, which convergence tests proved to be sufficient. The variational parameters of the Morse-like functions, r_e , ω_e and D_e were optimised for the two radial motions. For r_1 they were set to $4.8295 a_0$, $0.01654 E_h$, and $0.0023 E_h$, respectively; for r_2 to $8.980 a_0$, $0.00008 E_h$, and $0.0000554 E_h$. The r_2 grid was designed to extend significantly into the asymptotic region. This calculation was performed on 96 processors in the UCL’s Keter computing service to produce the unperturbed Hamiltonian eigenvectors and eigenvalues.

4.1.1.2 CAP parameters

To calculate the CAP matrix, a total of 2,400 eigenvectors were retained, of which 1,920 were used as a basis for the construction of the perturbed Hamiltonian matrix in Eq.(2.91), starting at the bound state 481 – bound states are included simply to reproduce Mussa’s calculation parameters exactly. The same functional form was used for the CAP as that of reference [14]. This was the order three monomial of Eq.(2.92), with starting position $r_{min} = 11.0 a_0$ and $r_{max} = 14.0 a_0$, as the grid is extended to a maximum in r_2 of $13.95 a_0$.

Another CAP matrix calculation was performed with the external independent routine, with the same parameters. The resulting matrix file was then “imported”

to a format readable to the CAPMatrix methods, including the eigenvalues and the grid data, and fed into RES3D for diagonalisation.

4.1.1.3 Eigenvector Trajectories

The eigenvalue trajectories were calculated with the successive diagonalisation technique described in section 3.2.3.2. To insure that the trajectories are independent of the grid distribution in Eq.(3.7) and that they are easy to differentiate, two sets of parameters were used. For the calculation using the “external” CAP, the λ grid parameters were set to $\chi = 1.01$, $h = 0.5 \times 10^{-5} E_h$, and $N_\lambda = 900$. The RES3D CAP was calculated using $\chi = 1.01$, $h = 1.0 \times 10^{-6} E_h$, and $N_\lambda = 400$. This last parameter was set simply to save computational resources.

4.1.1.4 Test Results

The plots in Fig. 4.1 were made choosing a random set of trajectories without looking for specific resonances. They are the trajectories of the complex eigenvalues obtained from the successive diagonalisation of the perturbed non-Hermitian Hamiltonian with the grids described above. Apart from very small discrepancies that may have their origin in numerical noise, the trajectories are remarkably close, which validates the integration procedures used to build the CAP.

4.1.2 Diagonalisation and Identification Test

This final validation test was carried out using the same parameters described above for the “external” CAP, but this time starting the complete calculation using the wavefunctions and eigenvalues produced by the calculation described in section 4.1.1.1. The resonance identification heuristics used a window of 0.5 cm^{-1} for the tolerance in the real energy (resonance position) and a tolerance window of 3% of the total covered complex energy ($\Gamma/2$). Due to the high compaction of the eigenvalue trajectory grid, the total number of points used to detect maxima in curvature and stability was set to 60. The detection cut-offs were set to 0 cm^{-1} at the minimum and 100 cm^{-1} at the maximum width.

Table 4.1 shows the comparison between the $J = 0$ resonances published in reference [14] and those calculated with RES3D. The similarity between the two sets of results is striking. The differences in positions are mostly negligible and within 0.01 cm^{-1} and the full widths Γ are all within the same order of magnitude, as evident by the differences in base 10 logarithms presented in the right-most column of table 4.1 – values greater than one would mean a difference of at least an order of

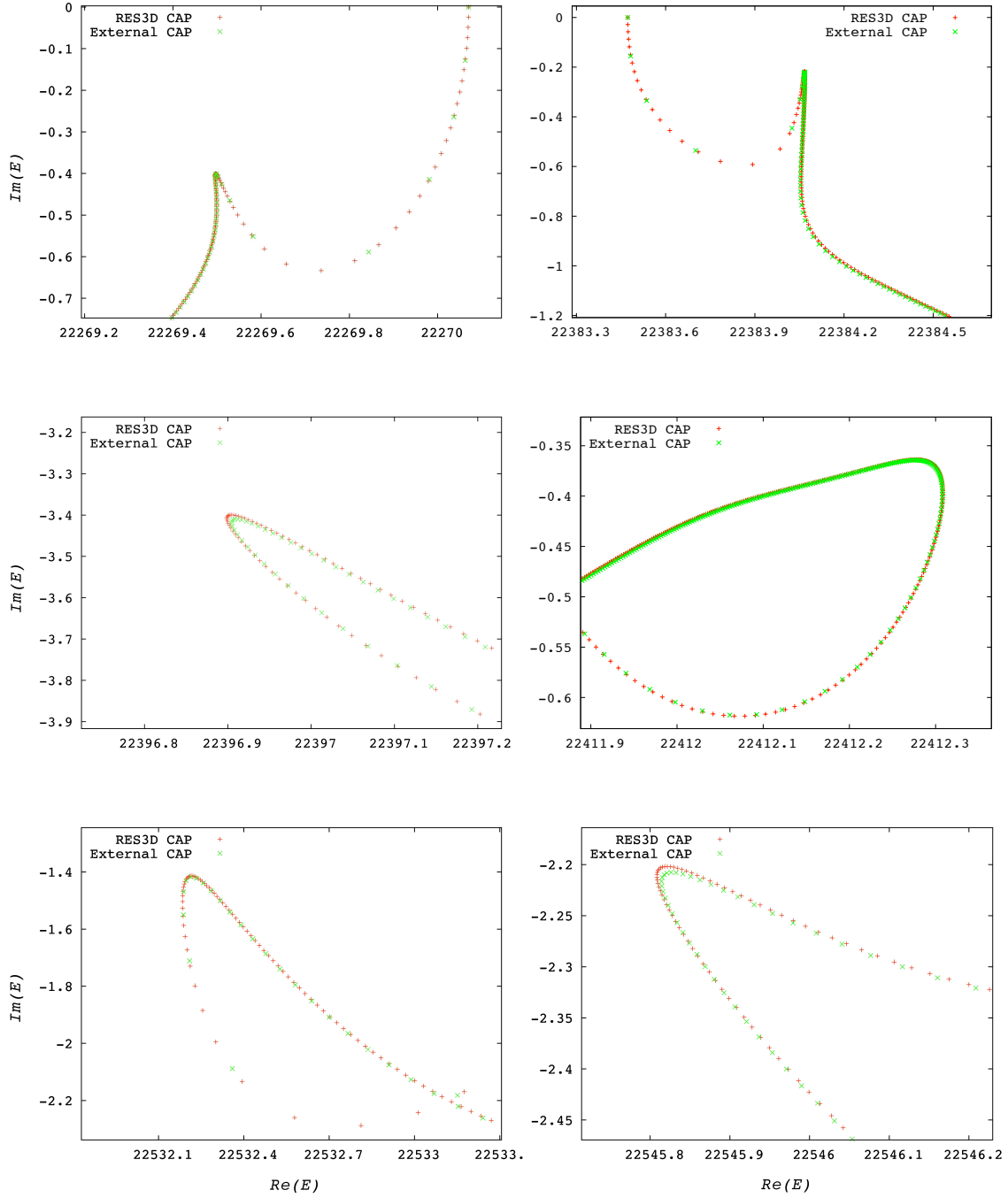


Figure 4.1: Trajectories of the n^{th} complex eigenvalues defined by $\epsilon_n(\lambda) = (E_n^R(\lambda) - i\Gamma_n(\lambda)/2)$ in cm^{-1} , with the abscissas corresponding to $E_n^R(\lambda)$ labelled as $Re(E)$, and the ordinates with $-\Gamma_n(\lambda)/2$ labelled as $Im(E)$. The trajectory labelled “External CAP” were produced by diagonalisation of a CAP produced using an independently written program, whereas the one labelled “RES3D CAP” was produced using the CAPMatrix class methods in RES3D. These trajectories were obtained with eigenvectors 379, 414, 422, 426, 463, and 469 in the basis order, all having starting energies at $\lambda = 0$ above the dissociation threshold of HOCl.

Table 4.1: Comparison between the vibrational resonances of HOCl calculated by Mussa and Tennyson (M&T), and those calculated using RES3D. E and Γ are the resonance positions and widths published by M&T. $\delta E = |E - E_R|$ and $\delta\Gamma = |\Gamma - \Gamma_R|$, where E_R and Γ_R the resonance positions and widths obtained through RES3D. $O(\delta\Gamma) = \log_{10} |\Gamma/\Gamma_R|$ gives the difference in order of magnitude between the widths published by M&T and those calculated with RES3D. The numbers in parenthesis indicate the power of 10. The resonance positions are relative to the ground state of HOCl.

E	Γ	δE	$\delta\Gamma$	$O(\delta\Gamma)$
19308.75	5.00(-03)	0.009	3.58(-03)	0.55
19335.86	6.40(-03)	0.009	2.00(-02)	0.62
19402.55	1.90(-03)	0.003	8.00(-06)	0.00
19424.37	8.60(-03)	0.006	2.60(-04)	0.01
19459.63	3.70(-02)	0.043	1.04(-02)	0.11
19554.98	7.20(-04)	0.006	1.74(-03)	0.53
19603.01	1.30(-02)	0.004	2.10(-03)	0.08
19605.92	4.40(-03)	0.009	4.00(-04)	0.04
19610.32	8.20(-03)	0.011	1.62(-03)	0.08
19616.07	9.90(-04)	0.008	1.64(-04)	0.08
19778.15	6.80(-03)	0.009	1.20(-04)	0.01
19848.38	1.00(-03)	0.005	6.00(-06)	0.00
19874.65	3.00(-02)	0.005	2.00(-04)	0.00
19905.91	7.10(-03)	0.009	2.00(-05)	0.00
19946.87	1.80(-03)	0.009	9.36(-04)	0.32
20170.56	5.20(-04)	0.004	1.00(-05)	0.01
20194.38	3.00(-05)	0.009	5.60(-06)	0.07
20291.82	1.40(-03)	0.007	5.00(-05)	0.02
20300.90	4.60(-02)	0.011	8.00(-04)	0.01
20573.13	8.00(-03)	0.004	4.00(-05)	0.00
20589.38	1.30(-03)	0.006	7.42(-04)	0.37
20602.18	5.60(-03)	0.003	4.80(-04)	0.04
20656.93	1.10(-03)	0.008	1.76(-03)	0.41
20868.53	6.80(-03)	0.008	8.00(-05)	0.01
20897.96	2.50(-03)	0.007	0.00(00)	0.00
20913.68	1.30(-04)			
20963.04	6.90(-04)	0.008	1.08(-03)	0.41
20984.56	1.40(-03)	0.008	1.05(-03)	0.60
21101.69	2.80(-04)	0.003	2.80(-05)	0.04
21279.43	3.40(-02)			
21332.86	1.50(-04)	0.012	6.00(-07)	0.00
21338.57	6.00(-04)	0.011	4.83(-04)	0.71
21376.02	4.40(-03)	0.001	2.00(-04)	0.02
21398.04	2.50(-03)	0.002	8.28(-03)	0.63
21464.91	5.40(-04)	0.008	3.20(-05)	0.03
21690.82	1.40(-04)			
21714.53	8.00(-03)	0.016	2.86(-03)	0.19

magnitude. However, there are three missed identifications. These can be attributed to the λ grid setup where the narrowest resonances did not have their signature trajectories effectively covered. Nevertheless, the success rate is very high.

It should be pointed out that the published results are identified “manually”, only taking into account the maxima and minima in the trajectories.

It is therefore safe to assume that all the methods from the CAP matrix construction up to the automatic resonance identification heuristics reproduce previous results obtained independently, and are therefore validated.

4.1.3 CAP consistency test

Since the HOCl calculations in reference [14] are presented without concrete consistency analysis data, there is no term of comparison that can be used to validate the CAP consistency procedures. Nevertheless, a thorough analysis of this algorithm will be presented in the following sections, in particular through the tests performed for the D_2H^+ resonance calculations.

4.2 D_2H^+ Bound Vibrational States

Munro *et al* [9] calculated vibrational states of H_3^+ up to, and beyond, the H_3^+ dissociation threshold. Their study of these states highlighted the characteristics of a particular set of states lying close to the dissociation limit, whose wavefunctions had a significant amplitude for large values of the dissociating coordinate. Those states were called asymptotic vibrational states (AVS). Using the optimal DVR3D input parameters established in those calculations, the vibrational states of D_2H^+ are calculated. The existence of AVS in D_2H^+ and is discussed, and their properties studied by the calculation of expectation values for a number of observables, including rotational constants.

4.2.1 H_3^+ Potential Energy Surface

As mentioned in Section 2.2.2, the Potential Energy Surface (PES) used in the calculation of H_3^+ and D_2H^+ bound states is the corrected PPKT2 potential. This is the fully *ab initio* PES of Polyansky *et al* [41] adjusted to remove a non-physical hump at large values of the dissociating coordinate [98; 29].

The minimum of the PPKT2 PES is given by an equilateral triangle of sides $1.65 a_0$. The classical dissociation channel opens at an energy of 37169.4 cm^{-1} above the minimum of the potential, and corresponds to a process of the kind $X_3^+ \rightarrow X_2 + X^+$, referring to this value as D_e . The asymptotic interaction between the diatom and the ion fragment is given, to first order [50], by the charge-induced dipole and charge-quadrupole, whose leading term is of the order $\approx 1/R^3$, where R is the Jacobi dissociation coordinate discussed in section 2.4.2.1. For D_2H^+ , due to the presence of two isotopic species, two different break-up processes can occur. Fig. 4.2 shows different cuts through the PES, and illustrates the break-up reactions possible. Those reactions have different quantum dissociation energies (D_0) as a result of the different zero-point energies of the diatomic fragments. The energy region between the opening of the dissociation channel and the zero-point energy of the diatomic fragment is very interesting: classical states in this energy range can dissociate but quantum mechanical states are bound by the zero-point energy of their constituents [11]. In this region the system does not have enough energy to dissociate, but its size could be very large as there is no potential barrier in the R coordinate. In fact one might expect the bound three-body states lying in this energy range to display strong features suggestive of dissociation, such as very extended wave functions.

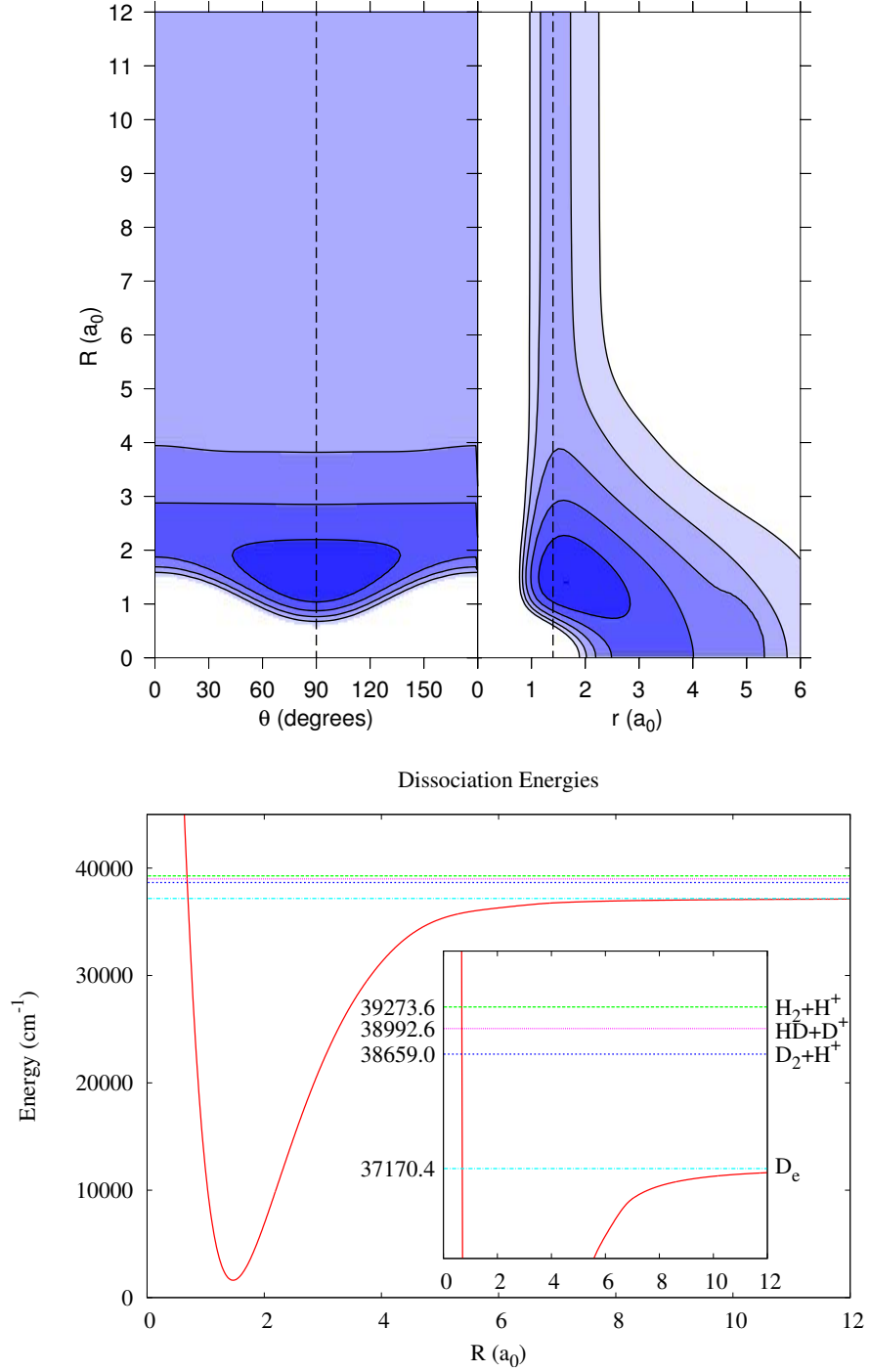


Figure 4.2: Cuts through the potential energy surface. The potential surface is represented for sake of clarity in Jacobi coordinates $\{r, R, \theta\}$, where r is the diatom distance, R is the distance between the third particle and the diatom centre of mass, and θ is the relative angle. In the left hand plot two three-dimensional cuts $V(r = 1.411a_0, R, \theta)$ and $V(r, R, \theta = 90^\circ)$ are presented, respectively. The depth of the potential is represented using contour lines of interval of 10^4 cm^{-1} . The dashed line represents the collocation of the two-dimensional cut of the right-hand picture. This left hand plot shows the dissociation channel $V(r = 1.411a_0, R, \theta = 90^\circ)$ of the PES along with the lowest dissociative path for both H_3^+ and D_2H^+ .

4.2.2 Calculations

In the calculations presented here, corrections to the non-relativistic Born-Oppenheimer approximation framework were neglected, as those corrections are likely to be much smaller than the residual error in the potential in the near-dissociation region, although it should be noted that the Born-Oppenheimer corrections for D_2H^+ have a lower symmetry than the potential [99]. The effects of these corrections were evaluated perturbatively and are discussed later in this section.

The calculation of the D_2H^+ $J = 0$ bound states uses the work of Munro *et al* [9] as a starting point. The two-body nuclear motion calculations were performed to characterise the zero-point energies of the various dissociation products using the LEVEL code [100]. To account for the inertia of electron motion as their orbitals are readjusted to the changing nuclear configurations, these and the remaining calculations were made using effective masses of 1.0075372 u and 2.013814 u for the H and D nuclei, as recommended in reference [101].

The three-body calculations were performed using PDVR3D, an adapted version of the DVR3D program [17; 9; 95]. This program employs the three-dimensional DVR scheme, discussed in Section 2.4, to solve the nuclear motion problem within the Born-Oppenheimer approximation for the ground electronic potential energy surface, using massively parallel computers.

To take advantage of the deuterium nuclei C_{2v} symmetry of D_2H^+ , Radau coordinates were used [81], as described in section 2.4.2.2, to parametrise the three internal degrees of freedom of the molecule. The associated DVR was based on spherical oscillators for the two radial coordinates (r_1, r_2) and Legendre polynomials for the angular coordinate α . However, for sake of clarity, Jacobi coordinates, described in section 2.4.2.1, are used in all the figures to represent the wavefunctions, as their physical interpretation is much more straightforward than for Radau coordinates.

To converge an extended number of levels for D_2H^+ (up to the lowest dissociation channel) a vast basis set is required. Like DVR3D, PDVR3D, can exploit the C_{2v} symmetry of the problem. Therefore, a complete calculation is done by indicating explicitly the symmetry of the diatom pair, which can be A_1 or B_1 , and then repeating the calculation for each symmetry. The final basis set included 120 points for each radial coordinate, and 96 points of the angular coordinate. The radial basis set was constructed from spherical oscillators [10] with $w_e = 0.004 E_h$, and $\alpha = 0$, and covers the range from $0.09 a_0$ to $12.80 a_0$. The convergence of results was checked against the variation of all the basis set parameters mentioned above, using converged parameter from previous calculations of H_3^+ vibrational states [9].

Whereas for the angular grid the range is fixed, for the radial grid number of points and the grid extension was varied, as shown in the footnote of table 4.2. The radial grid range is in Radau coordinates, and corresponds to a range of about 0-20 a_0 in the dissociating Jacobi coordinate R .

Table 4.2 shows the convergence for the highest 5 A_1 bound states as a function of the number of radial points N_r , angular points N_α and the 2D cutoff E_{2D} . The convergence is shown for the energy E , the rotational constant C , and the mean value of the dissociating coordinate $\langle R \rangle$. As expected for a (pseudo-)variational method, the convergence is much better for the energy than for the other observables. It is not simple to quantify the absolute precision of this calculation as it depends on the many factors mentioned above.

It can be noted from table 4.2 that the various errors tend to cancel each other. However, it can be said that the overall convergence of the energy averaged for all calculated levels is within 0.1 cm^{-1} , except for the last state (number 1209), for which the convergence is of the order 1 cm^{-1} . Due to the computational cost of each job a similar convergence study was not performed for the B_1 bound states. It was assumed that the basis set found to be the best for the A_1 states would provide a similar accuracy for the B_1 states, as there is a lower density of states for this symmetry. Convergence for the lower-lying states was found to be very significantly better than for the ones tabulated which are the highest considered in this study. This is a general feature of variational methods.

As a result, the final grid contained 696,960 points in the A_1 symmetry and 685,440 points in the B_1 symmetry. The implementation of the DVR method leads to the diagonalisation of a real symmetric matrix which characterises the eigenvalue problem. In order to obtain eigenvalues and eigenvectors of such a vast matrix a truncation-diagonalisation approach [102; 103] was used. For each angular point the associated 2D sub-matrix was diagonalised, and only those 2D eigenstates with energy less than a chosen cutoff E_{2D} were retained. The value of E_{2D} was then chosen to give a convergence error of less than 0.2 cm^{-1} . The dimension of the final 3D matrix was of 122,000 (17.5% of the original basis set), corresponding to $E_{2D} = 72689.84 \text{ cm}^{-1}$. The calculations were performed on the HPCx supercomputer at the Daresbury Laboratory, UK, and required 864 processors for 4 hours 13 minutes. The diagonaliser routine PDSYEVD from the ScaLAPACK library (<http://www.netlib.org/scalapack/>) was employed in this calculation.

The D_2H^+ problem proved to be numerically more demanding than H_3^+ ; this is due to the higher density of bound states of the former with respect to the latter. As an example, if one considers the energy range between D_e and dissociation, H_3^+

Table 4.2: Convergence of the energy E , the rotational constant C and the mean value of the dissociative coordinate $\langle R \rangle$ for the highest five even parity band origins (states 1205-1209) for D₂H⁺ with respect to changes in the basis set size and the cutoff parameter. The values in columns E , C and R refer to the basis sets described in the text, whereas the differences are the converged values minus the values with the indicated basis set. Units are cm⁻¹ for E and C , a_0 for R .

N_e	E	ΔE^a	ΔE^b	ΔE^c	C	ΔC^a	ΔC^b	ΔC^c	R	ΔR^a	ΔR^b	ΔR^c
1205	38632.901	-0.008	0.007	-0.130	7.984	0.007	0.009	0.018	4.578	0.003	0.005	0.010
1206	38633.914	-0.027	0.001	-0.081	9.334	-0.012	-0.001	-0.013	5.281	-0.006	0.000	-0.006
1207	38640.219	-0.011	0.028	-0.094	7.542	-0.022	0.034	-0.004	4.333	-0.013	0.019	-0.002
1208	38649.775	-0.151	0.242	-0.071	6.149	-0.227	0.380	0.017	3.536	0.128	0.343	0.137
1209	38655.445	-0.395	0.551	-0.052	6.266	-0.131	0.101	-0.026	3.581	-0.075	0.059	-0.015

^a $N_r=110$ (0.09 a_0 - 12.23 a_0) $N_\alpha=96$ $E_{2D}=72,689.84$ cm⁻¹.

^b $N_r=120$ (0.09 a_0 - 12.80 a_0) $N_\alpha=88$ $E_{2D}=72,689.84$ cm⁻¹.

^c $N_r=120$ (0.09 a_0 - 12.80 a_0) $N_\alpha=96$ $E_{2D}=70,577.38$ cm⁻¹.

has 120 states in an interval of $2,100\text{ cm}^{-1}$, whereas D_2H^+ shows 181 states in an interval of about $1,500\text{ cm}^{-1}$. A total of 2,287 bound states for D_2H^+ (1,209 A_1 , 1,078 B_1) was obtained, which represents, by the variational principle, a lower limit on the actual number supported by the PPKT2 potential. Equivalent calculations on H_3^+ gave a total of 859 states. This number is reduced with respect to D_2H^+ not only by mass effects but also by the higher symmetry of the H_3^+ isotopologue, as degenerate states are not counted twice. Figure 4.3 shows these effects by comparing the density of H_3^+ in the “proper” D_{3h} symmetry, H_3^+ in a C_{2v} symmetry, and D_2H^+ . Application of the Pauli principle would lead to a further reduction as H_3^+ states of A_1 symmetry are forbidden.

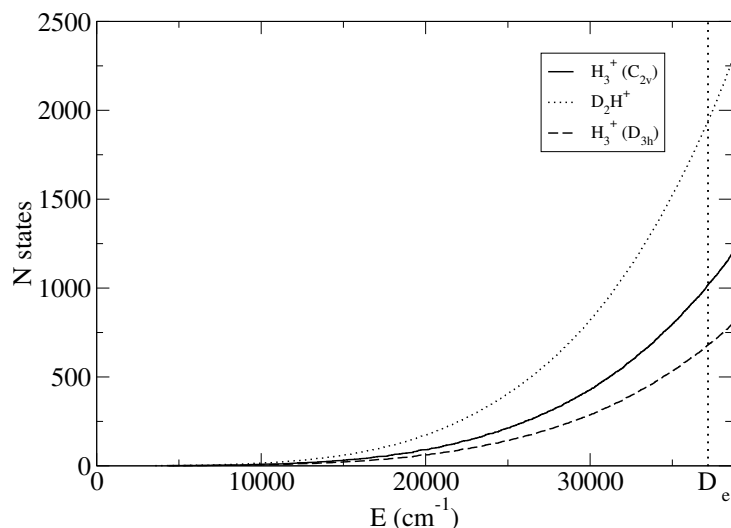


Figure 4.3: Cumulative number of vibrational bound states for H_3^+ with standard D_{3h} symmetry and lower (C_{2v}) symmetry, and D_2H^+ , up to dissociation given by $D_0(D_2H^+)$.

The DVR approach also gives an approximation for the wavefunction of all bound states as eigenvectors of the Hamiltonian matrix. Using these eigenvectors the mean value of a range of observables was calculated, including some geometric ones, such as the distance between the various particles, or the included angles, and kinetic ones, like the potential energy. Another observable of interest is the rotational constant C associated with the in-plane motion of the molecule. For the purposes of this analysis, this constant is defined by the mean value of the inverse of the molecules moment of inertia and computed using the method of Ernesti and Hutson [104], which is designed for floppy molecules. Such constants have been found useful for other floppy systems [105]. All the integrals associated with the calculation of the mean were evaluated using the DVR approximation.

4.2.3 Results

Tables 4.3 and 4.4 present the converged values of the energy for those levels above the D_e threshold, for levels of A_1 and B_1 symmetry, respectively. The mean values of the inter-diatom distance r and the diatom-ion distance R , where the diatom is constituted by D_2 , as well as the the D-H-D angle γ and the H-D-D angle β , are also shown to help in characterising the geometrical features of the states, as well as the rotational constant C , and the mean potential energy.

In order to show how the properties of high-lying states differ from those of lower-lying states, the tables also include results for the lowest 4 states for each symmetry and some of the intermediate states. There are several differences one can immediately recognise between the lower and upper part of the spectrum: The rotational constant for the high-lying states is less than half its value for the ground state. This last character is reflected in the mean inter-particle distance, which is much bigger in the higher energy states than in the lowest ones, giving a notion of how the dissociation wavefunctions are elongated by nature. This property of near-dissociation states can be highlighted by considering, besides the mean value of the various observables, also their root-mean-square deviation [106]. The latter is defined, if the observable x is considered, as $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$. For example, the ground state root-mean-square deviation of the inter-particle distance is about $0.2 a_0$, showing that the molecule is fairly stiff and the nuclei move only close to their average separation, which almost coincides with the minimum of the PES. Conversely, for the higher states this standard deviation is never smaller than $3 a_0$. Such values are typical of a very extended wavefunction, as can be seen from Figs. 4.4 and 4.6.

Among the levels closest to dissociation, it is possible to recognise two different classes of states: a first set of states, which have a compact geometry, and which will be referred to here as standard three-body states, and a second set of states called Asymptotic Vibrational States (AVS), which have been studied previously for H_3^+ [9]. The AVS have a strongly marked isosceles shape, where two particles are close to each other and form a diatom, and the third particle orbits around them at a large distance. This is reflected by the large value of the dissociative coordinate R and the small value of C , as well as in the mean values of the angles D-H-D and H-D-D. The diatom structure is less pronounced in H_3^+ than D_2H^+ , for reasons of symmetry.

Physically, one could interpret the AVS as weakly-bound ion-diatom states, where the diatom behaves as if the third particle were a small perturbation, and the ion then is bound to the diatom due to the weak charge-induced dipole and

charge quadrupole forces. However, in both molecules this interpretation is not completely satisfactory. In order to test the “2+1” interpretation of the AVS, one can compare the bond-length r of the diatom components with the equivalent distance in the free diatoms. Even for the states with the strongest AVS features one finds that this distance is larger than in the corresponding diatom, where $\langle r \rangle$ is $1.448 a_0$ for H_2 and $1.432 a_0$ for D_2 . Thus it must be concluded that the AVS states presented in table 4.3 can not be considered as pure “2+1” states, but rather as mixtures of “2+1” and standard three-body states. It is likely that the number of vibration band origins found is not exhaustive, and that if this study is extended to a larger range of the coordinates r, R more states will be found for both molecules. States that show stronger “2+1” characteristics could then be expected.

Fig. 4.4 and Fig. 4.6 show the probability density for several states for D_2H^+ of A_1 and B_1 symmetry, respectively. These figures give two different cuts through the 4-dimensional surface $|\psi(r, R, \theta)|^2$. These cuts are bound to be subjective and therefore different cuts could show other aspects of the problem. Nevertheless, a careful choice of cuts may provide some insight about properties of the wavefunctions. The first graph in Fig. 4.4 shows the probability density for the ground state of D_2H^+ , so to have a clear visual perception of how compact this state is, compared with the high-lying ones. In the same figure, the next two graphs show two states (number 1023 A_1 and 1025 A_1) below D_e but high in energy. Both show a very complex nodal structure in the intermediate region, possibly due to the requirement of orthogonality to the lower states. Among the higher-lying states, it is possible to recognise a number of AVS states of the D_2+H kind (1183 A_1 , 1204 A_1 , 1208 A_1 and 1209 A_1), similar to the ones found in H_3^+ , as well as standard three-body states (1206 A_1) or mixtures (1205 A_1 , 1207 A_1). It is also possible to recognise linear D-H-D configurations (1201 A_1 , 1186 A_1 and 1203 A_1).

The B_1 states shown in Fig. 4.6 are also interesting. Despite the high-energy of those levels, there are no AVS states of the D_2-H kind as in the other symmetry. This is due to the fact that the D_2 pair has the wrong (odd) inter-nuclear symmetry with respect to the ground vibrational D_2 state (which is even). It can be seen by comparing state 1074 B_1 in Fig. 4.6 with state 1204 A_1 in Fig. 4.4. On the other hand, the last state (1078 B_1) shows a clear DH-D character, where the two D nuclei are apart from each other and the H sits symmetrically on both of them.

4.2.4 Beyond the Born-Oppenheimer approximation

In these calculations for D_2H^+ , all effects beyond the non-relativistic BO framework have been neglected. In a previous ultra high accuracy study [54], Polyan-

Table 4.3: Energy levels of A₁ symmetry for D₂H⁺. Units are cm⁻¹ for energy, E , the rotational constant, C , and for the potential, V , a_0 for diatomic internuclear distance, r , and the Jacobi dissociation coordinate, R , and degrees for the H-D-D angle β and the D-H-D angle γ .

n	E	$\langle R \rangle$	$\langle r \rangle$	$\langle \beta \rangle$	$\langle \gamma \rangle$	C	$\langle V \rangle$
1	3561.76	1.49	1.70	60.53	59.90	12.96	1824.19
2	5529.21	1.46	1.79	58.90	63.87	12.32	2872.93
3	6299.46	1.55	1.72	61.22	58.81	12.58	3289.43
4	7381.59	1.44	1.87	57.53	67.41	11.75	3923.94
43	15777.81	1.58	2.04	58.55	68.50	10.06	8965.28
44	15825.30	1.92	1.76	70.98	47.43	9.98	9809.01
245	25600.81	1.82	2.29	63.08	67.49	7.94	15800.07
246	25603.88	2.03	2.11	67.44	55.90	8.51	15559.81
631	32846.80	2.25	2.40	67.71	60.65	6.47	20643.77
632	32849.30	2.22	2.44	67.92	59.64	6.51	20194.59
1179	38442.55	2.36	3.33	63.11	71.62	4.91	26437.55
1180	38453.76	2.75	2.58	69.31	59.69	5.20	25710.07
1181	38455.90	3.00	2.65	67.94	61.10	4.94	26463.06
1182	38474.41	2.53	2.56	68.30	59.81	5.70	24311.57
1183	38477.06	3.78	2.08	75.84	45.26	4.46	28608.72
1184	38490.37	2.33	2.77	65.20	66.59	5.67	24355.98
1185	38500.31	2.88	2.46	71.72	52.62	5.49	25053.40
1186	38502.57	2.71	2.72	67.58	62.14	5.24	25519.50
1187	38509.54	3.85	2.38	70.07	57.62	4.36	28538.70
1188	38515.71	2.55	2.89	65.13	66.54	5.22	25673.88
1189	38522.17	2.86	2.61	69.99	57.37	5.18	26029.17
1190	38525.52	2.41	2.72	65.38	66.04	5.55	24565.13
1191	38541.32	2.50	2.81	67.14	63.50	5.45	25072.30
1192	38547.08	2.38	2.82	65.53	64.98	5.54	24728.34
1193	38553.79	2.70	2.73	69.02	59.21	5.39	25387.13
1194	38557.44	2.68	2.98	68.17	61.11	5.06	26426.46
1195	38568.62	2.63	2.87	67.14	63.73	5.16	26163.17
1196	38571.35	2.71	3.17	63.31	70.84	4.83	26601.80
1197	38578.26	3.17	2.55	67.84	62.12	5.00	26131.52
1198	38582.38	3.17	2.39	71.89	53.23	5.33	25963.56
1199	38588.10	3.60	2.54	70.08	57.27	4.68	27342.11
1200	38596.62	2.43	2.70	65.58	65.49	5.53	24670.43
1201	38598.07	2.83	2.93	65.80	66.57	4.96	26045.55
1202	38610.92	3.14	2.63	69.53	57.78	5.20	26047.78
1203	38619.78	2.35	3.16	63.30	70.80	5.17	25793.78
1204	38623.80	4.73	2.42	73.44	51.16	4.14	28822.61
1205	38632.90	3.88	2.58	69.57	59.18	4.58	27479.89
1206	38633.91	2.35	2.95	61.90	73.61	5.28	25118.52
1207	38640.22	4.80	2.43	72.37	53.50	4.33	28209.45
1208	38649.78	6.51	2.40	73.92	51.52	3.54	30366.94
1209	38655.45	6.88	2.35	72.92	53.82	3.58	29850.34

Table 4.4: Energy levels of B₁ symmetry for D₂H⁺. Units are cm⁻¹ for E , C and V , a_0 for r and R , degrees for β and γ , all of which are defined in table 4.3.

n	E	$\langle R \rangle$	$\langle r \rangle$	$\langle \beta \rangle$	$\langle \gamma \rangle$	C	$\langle V \rangle$
1	5640.74	1.56	1.70	62.60	56.72	12.49	2953.82
2	7622.49	1.54	1.78	61.14	60.37	11.88	4006.11
3	8237.79	1.64	1.71	63.58	55.28	12.10	4422.24
4	9394.66	1.64	1.75	64.07	55.86	11.54	5131.94
37	16786.00	1.65	2.04	60.97	65.83	9.62	9695.39
38	16939.90	1.76	1.94	65.03	58.89	9.76	10038.75
181	25011.63	1.96	2.15	66.44	59.89	8.12	15280.12
182	25040.76	2.06	2.07	69.42	55.45	8.03	15340.59
439	31191.95	2.14	2.37	67.03	61.34	6.94	19357.70
440	31204.66	2.18	2.32	67.70	59.58	6.96	19196.46
1048	38419.38	2.46	3.03	66.00	65.49	5.23	25615.51
1049	38422.76	2.41	2.66	67.73	62.28	5.52	24504.47
1050	38435.72	2.40	2.68	66.40	63.24	5.55	24213.34
1051	38443.28	2.63	2.87	68.13	60.60	5.24	26123.34
1052	38447.58	2.78	2.60	69.23	58.58	5.30	25637.06
1053	38451.67	2.49	2.56	68.46	61.17	5.61	24290.03
1054	38462.02	2.28	2.86	64.81	68.41	5.46	24699.44
1055	38472.67	2.42	2.65	67.65	62.05	5.59	24492.90
1056	38476.47	2.61	2.51	70.69	54.99	5.67	24039.18
1057	38483.11	2.39	2.81	66.19	64.70	5.53	24952.42
1058	38485.80	2.31	2.72	65.57	66.31	5.58	24025.03
1059	38497.23	2.39	3.09	65.22	67.65	5.23	25247.23
1060	38511.47	2.52	2.99	66.44	64.10	5.28	25656.26
1061	38514.74	3.31	2.55	72.93	51.85	4.73	27853.90
1062	38520.27	2.81	2.51	72.35	51.89	5.47	25430.14
1063	38525.74	2.49	2.84	65.81	65.91	5.31	25473.81
1064	38532.24	2.37	3.04	63.08	69.96	5.42	25530.20
1065	38548.31	3.07	2.67	72.82	52.05	4.85	26969.61
1066	38556.76	2.24	2.98	62.07	72.61	5.28	24908.55
1067	38566.38	2.47	2.88	66.70	64.38	5.37	25188.84
1068	38579.87	2.91	2.42	70.69	55.98	5.22	25996.85
1069	38583.00	2.36	2.91	64.78	67.92	5.40	24914.41
1070	38587.78	2.52	3.12	64.43	69.50	4.96	26437.36
1071	38590.30	2.53	3.05	63.70	70.30	4.96	26357.06
1072	38596.81	2.43	2.76	66.37	63.96	5.49	24897.32
1073	38616.36	2.60	2.78	67.58	62.08	5.30	25500.54
1074	38622.05	3.29	2.35	74.20	48.49	5.02	27057.47
1075	38628.54	2.99	2.47	70.82	55.89	5.21	25585.60
1076	38646.92	3.18	2.64	71.44	54.28	4.96	26619.90
1077	38652.81	2.68	2.60	68.33	60.96	5.43	24979.71
1078	38655.33	2.76	2.86	64.56	68.34	5.03	26741.07

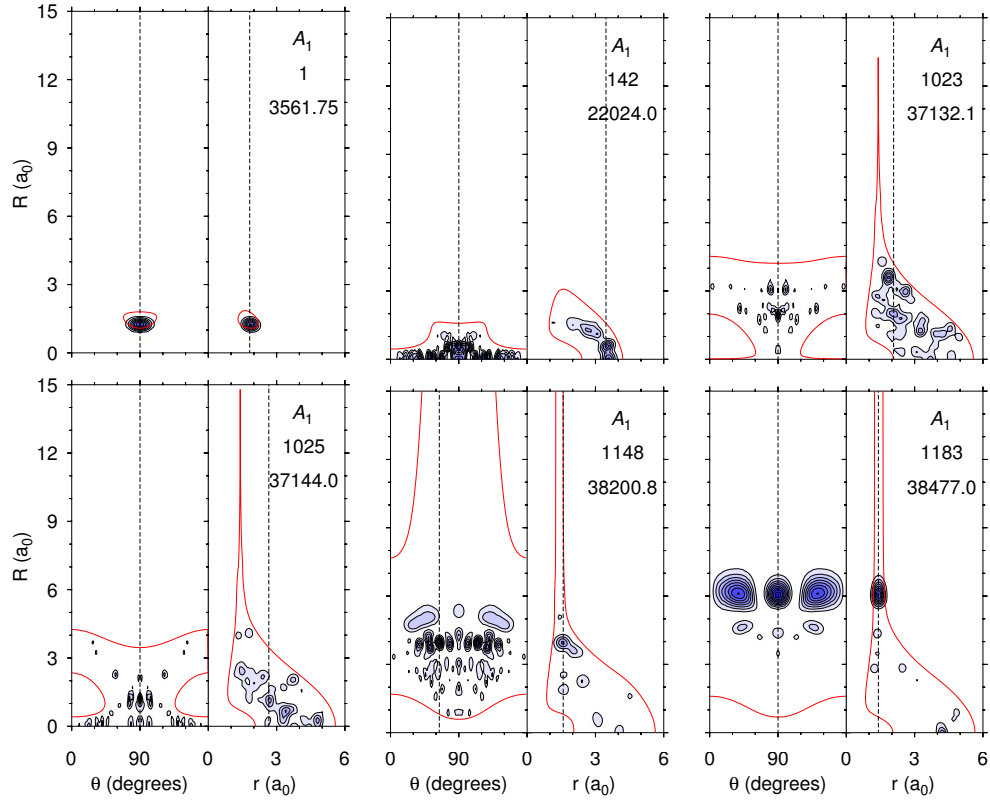


Figure 4.4: Two dimensional slices through the molecular probability density ψ^2 for several D_2H^+ states of A_1 symmetry. The density is normalised so that $\int \psi^2 dr_1 dr_2 d\alpha = 1$, where $\{r_1, r_2, \alpha\}$ are the Radau coordinates. For sake of clarity, however, the plots use Jacobi coordinates to parametrise the probability density. The left-hand part of the plot represents the cut $\psi(r_{\max}, R, \theta)^2$, whereas the right-hand part shows the cut $\psi(r, R, \theta_{\max})^2$. The probability is normalised so that $\Psi(r_{\max}, R_{\max}, \theta_{\max})^2 = 1$, where the point $\{r_{\max}, R_{\max}, \theta_{\max}\}$ is associated with the absolute maximum of the density, and the cuts are chosen so that this point is contained in both parts of plot. Contours represent steps of 10 % in probability. The continuous lines show the classical turning point.

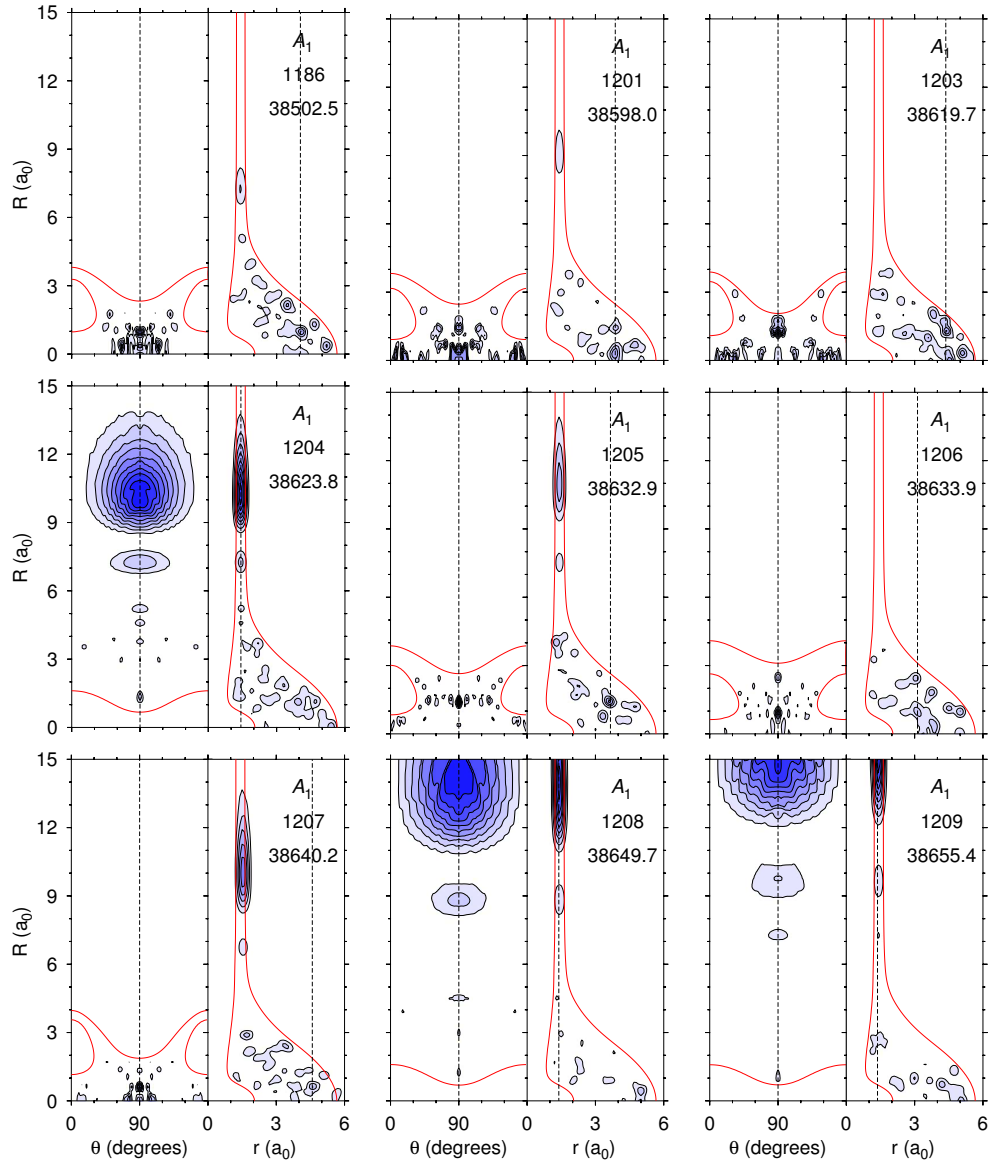


Figure 4.5: Figure 4.4, continued.

sky and Tennyson discussed the importance of some of the corrections to the non-relativistic BO approximation. Their work was limited to vibrational band origins below 10000 cm^{-1} . The relativistic and adiabatic BO corrections to the $1^1A'$ PES are reported in [54] as polynomial surfaces, whose coefficients are fitted to calculated data points. Unfortunately those surfaces are accurate in a range which is much smaller than the extent of the high-lying bound states of D_2H^+ , and therefore it is not meaningful to evaluate their effect on the calculated states. However, Polyansky and Tennyson concluded that the effect on the lowest states of the relativistic effect

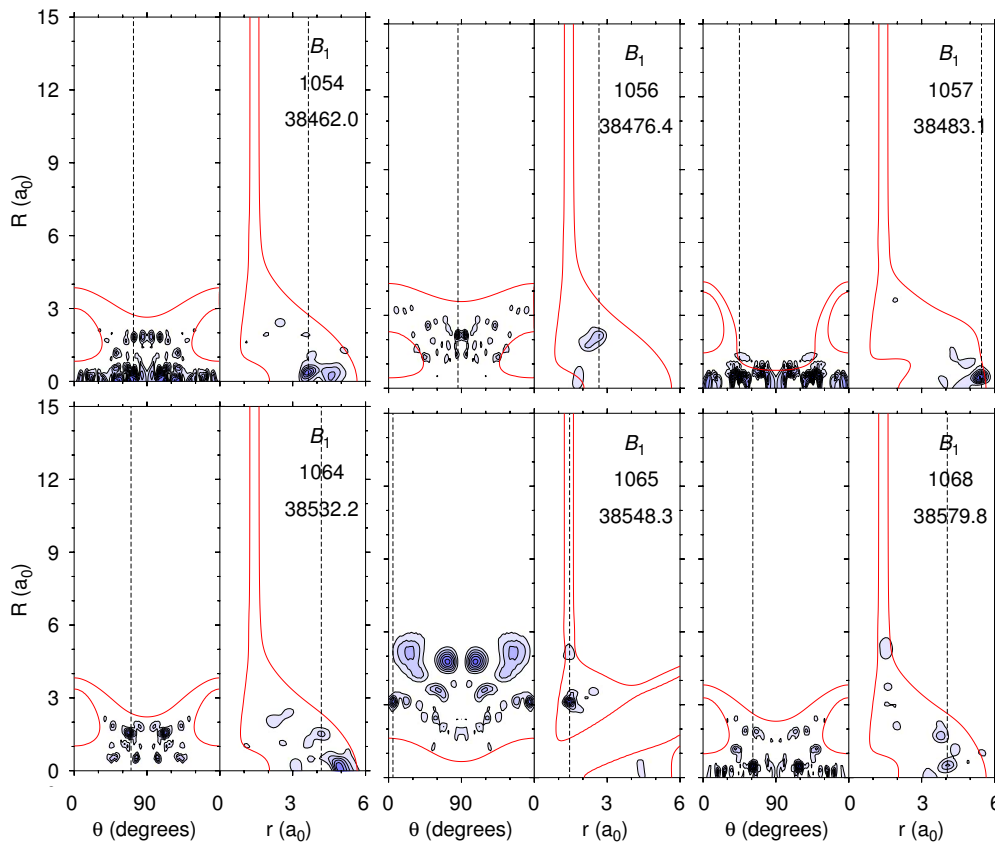


Figure 4.6: Two dimensional slices through the molecular probability density ψ^2 for several D_2H^+ states of B_1 symmetry. For explanation of the plots see the caption of Fig. 4.4.

is very small and of the adiabatic correction is of the order of 1 cm^{-1} .

The study of off-diagonal BO or non-adiabatic corrections is particularly demanding as it involves the calculation of all the PESs, their derivatives with respect to the nuclear coordinates, and the coupling between them. It is very difficult, even for systems as small as triatomics, to even evaluate these corrections approximately for low-lying states [107], and one generally has to resort to simple models instead.

It has been shown in previous works that those very complicated effects can be modelled effectively by allowing for the nuclear masses to be varied. This procedure is known as mass scaling and was firstly introduced by Bunker and Moss for diatomics [108]. Subsequently, Polyansky and Tennyson applied the same method to H_3^+ [101], where they showed that modelling the non-adiabatic corrections through this scaling significantly improves the first principles calculation of the rotation-vibration energies of H_3^+ . However, it is also important to note that this scaling may be less effective as the vibrational excitation increases [109].

Non-adiabatic corrections have been included in the nuclear problem by intro-

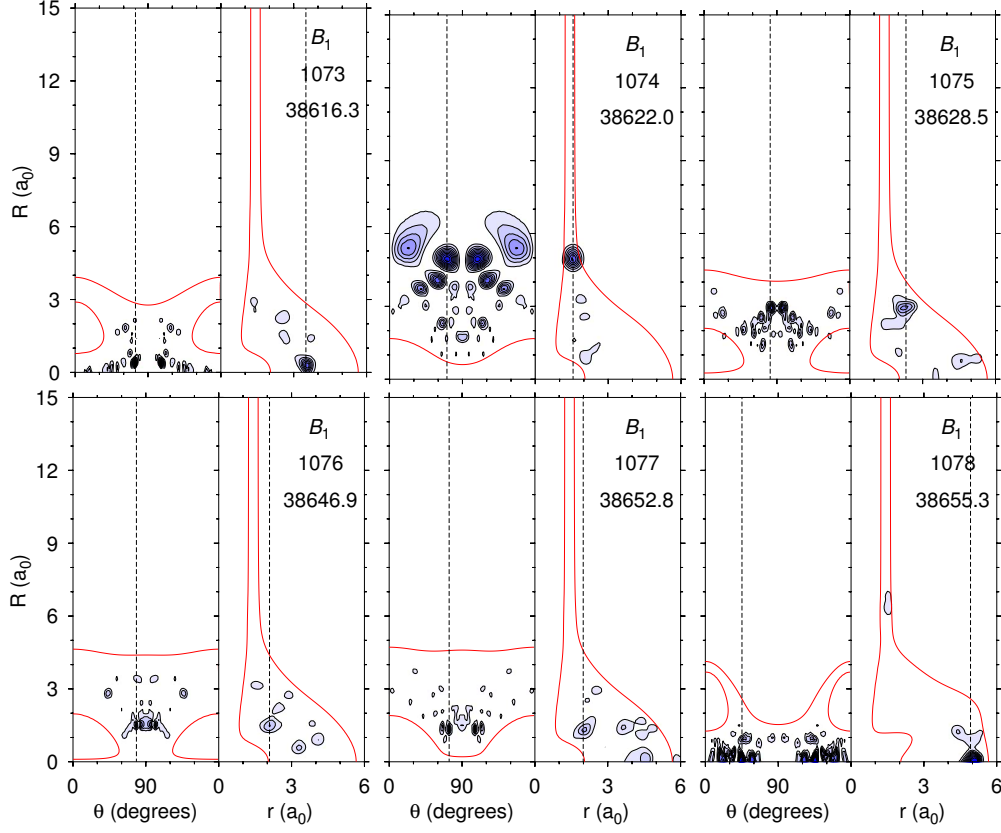


Figure 4.7: Figure 4.6, continued.

ducing a mass scaling for the H and D nuclear masses, using the same scaling relation as the one proposed by Polyansky and Tennyson [101]. The resulting masses, also referred to as *intermediate masses* are $m_H^{(i)} = 1.0075372$ u and $m_D^{(i)} = 2.0138140$ u, compared to the nuclear masses $m_H^{(n)} = 1.00727647$ u and $m_D^{(n)} = 2.0135532$ u. This correction is implemented by simply replacing the nuclear masses with the intermediate masses in the nuclear Hamiltonian.

The effect of this mass scaling on the energy levels was evaluated perturbatively. The system's kinetic energy for each calculated state v , K_v , is obtained as the difference between the total and potential energy:

$$K_v = E_v - \langle V \rangle_v, \quad (4.1)$$

where E_v is the energy of the v th state, and $\langle V \rangle_v$ is the mean value of the potential energy V for the same state.

The Kinetic Energy depends on the reduced mass μ , which is a function of the nuclear masses. μ then depends on the choice of coordinate system, and a general

expression is presented in [10]. In this specific case it was found that

$$\mu^{-1} = \frac{(1+g^2)}{m_D} + \frac{(1-g)^2}{m_H}, \quad (4.2)$$

where g is a function of the two nuclear masses:

$$g = \frac{1 - \sqrt{\frac{m_H}{m_H + 2m_D}}}{1 + \sqrt{\frac{m_H}{m_H + 2m_D}}}. \quad (4.3)$$

The Kinetic Energy is inversely proportional to μ :

$$K_v^{(0)} = \mu K_v, \quad (4.4)$$

therefore the non diagonal BO correction to the v th level ΔE_v can be evaluated using this method straightforwardly:

$$\Delta E_v = \left(\frac{1}{\mu^{(i)}} - \frac{1}{\mu^{(n)}} \right) K_v^{(0)} = \left(\frac{\mu^{(n)} - \mu^{(i)}}{\mu^{(i)}\mu^{(n)}} \right) K_v^{(0)} = \delta_\mu \frac{K_v^{(0)}}{\mu^{(i)}} = \delta_\mu K_v, \quad (4.5)$$

where $\mu^{(i)}$ and $\mu^{(n)}$ are the reduced masses calculated from Eq.(4.2) using intermediate and nuclear masses, respectively. Using the values for the nuclear masses indicated above, $\delta_\mu = -1.61 \cdot 10^{-4}$ was obtained, which justifies the perturbative approach adopted.

In this fashion the influence of the non-BO correction was calculated, for all levels, giving an average of 1.88 cm^{-1} with a maximum of 2.43 cm^{-1} for A₁ states, while for B₁ states the average energy difference was 1.68 cm^{-1} with a maximum difference of 2.47 cm^{-1} .

If such corrections were to be evaluated more carefully, one should consider the coupling among all the PESs. In particular, one expects the failures to the BO approximation to be more important for those vibrational states which have a significant amplitude in those regions of the nuclear geometries where two or more PESs come close to each other.

The H₃⁺ system has an avoided crossing between the 1¹A' ground state PES and the 2¹A' first excited state, which are associated with the X₂+X⁺ and X₂⁺+X dissociation channels, respectively. The crossing is located at configurations with $r \simeq 2.5 a_0$ and $R \geq 8.0 a_0$ [54] in dissociation coordinates where r is the distance between the X₂ diatom nuclei and R is distance from its centre of mass to the third nucleus. The crossing is caused by the fact that at large diatomic distances X₂⁺+X

becomes the lowest dissociation channel. However, at these nuclear configurations the bound states of D_2H^+ have a very low amplitude (as it can be seen from Fig. 4.4) because the dissociation energy of D_2H^+ for its lowest dissociation channel (D_2+H^+) is around 15000 cm^{-1} below the required energy to reach the avoided crossing. Fig. 3 in reference [54] depicts the potential region of the crossing in detail.

4.3 D_2H^+ Vibrational Resonances

In the previous section, a detailed description of the vibrational state calculations of D_2H^+ was presented. The basis set parameters used for the calculation of H_3^+ were used as the starting point for the D_2H^+ calculations, leading to a final 3D Hamiltonian size of 122,000, giving bound states converged within about 0.1 cm^{-1} . This level of convergence is significant since the density of states in D_2H^+ is approximately twice that of H_3^+ [110].

To improve upon those results and to provide a measure of convergence for the resonance calculations, two new calculations of D_2H^+ vibrational states were performed. The largest calculation of D_2H^+ at $J = 0$ was made increasing the radial grid size to 130 points and setting the final Hamiltonian to a size of 124,818. These calculations achieved an energy convergence to 0.05 cm^{-1} . These convergence results will determine the lower limit for the convergence of D_2H^+ states presented in table 4.8. An important side-effect of changing the the number of radial grid points is a change in the overall grid box size. Similarly in D_2H^+ , changing the number of radial grid points from 120 to 130 moved the furthest point, i.e., the furthest point in the Jacobi dissociation coordinate, R_3 , for any angle α , as given in Fig. 4.8, from 20.70 to $21.58 a_0$. Thus, the convergence results incorporate the effect of changing the grid box size. In the remainder of this section, Jacobi coordinates will be referred to in the notation of Fig. 4.8.

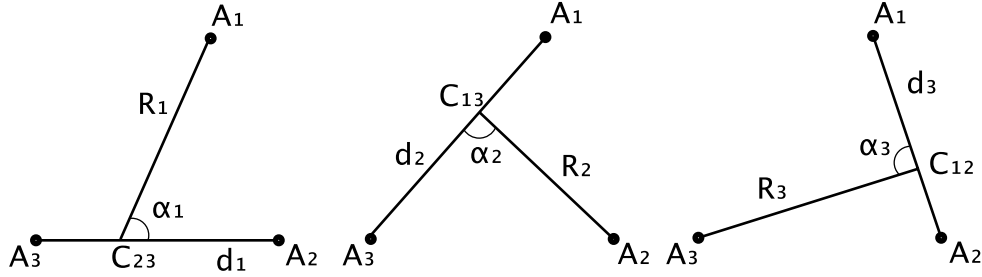


Figure 4.8: Diagram representing the three possible choices of the Jacobi coordinate system (d_i, R_i, α_i), where d_i is the diatom inter-nuclear distance, R_i the dissociation coordinate with origin at the diatomic centre of mass, C_i , and α_i is the dissociation angle.

These and the previously described eigenvectors can now be used to calculate the vibrational nuclear motion resonances of this system using RES3D, as described in section 3.2.5. But first, an analysis of the CAP method presented in section 2.3.5.4 will be made to assess the calculation parameters' impact on the resonance identifications.

4.3.1 CAP method parameter study

To assess how the CAP forms and parameters influence the results, tests were performed using D₂H⁺ eigenvectors primarily for two reasons. Firstly, this is probably one of the most challenging systems to perform calculations on due to the extremely high PES accuracy required and the extreme difficulty in producing converged bound state eigenvectors. Secondly, this system allows the study of both single and multi-channel dissociation through two contiguous energy regions, as illustrated in Fig. 4.2. Between 38,659 and 38,992 cm⁻¹ only dissociation of a proton can occur, with the dissociation coordinate being R_3 . Above 38,992 cm⁻¹, D₂H⁺ can dissociate into both D⁺+HD, through R_1 and R_2 , and H⁺+D₂ through R_3 . These tests were restricted to the calculation of resonances with A_1 symmetry since these are the hardest to converge.

In the case where the system has symmetry, the CAP is applied to all the symmetric channels by embedding the coordinate system appropriately, as illustrated in Fig. 4.8. In the case of H₃⁺, this is written as:

$$\hat{H}' = \hat{H} - i\lambda \sum_{i=1}^3 W(R_i) \quad , \quad (4.6)$$

where i runs over the number of symmetric channels, which is 3 for H₃⁺. In the D₂H⁺ case:

$$\hat{H}' = \hat{H} - i\lambda (W(R_1) + W(R_2) + V(R_3)) \quad , \quad (4.7)$$

where the potentials W and V have the same functional form but with different choices of the parameter r_{max} , according to the furthest grid points in their respective dissociation coordinates.

This approach leads to a question in the case where the representation of the wavefunction is made in a symmetry lower than that of the potential: for H₃⁺, which has D_{3h} symmetry, the dissociation of all three hydrogen atoms would be equally represented by the three possible Jacobi coordinate transformations. With a C_{2v} representation in Radau coordinates, the three transformations to Jacobi coordinates lead to shorter and sparser grids on two of the coordinate systems. For example, R_3 as described in Fig. 4.8, and with the wave-function parameters set for the calculation of highest convergence, a maximum of 21.56 a_0 was obtained where as for R_1 and R_2 , 18.64 a_0 was obtained. Because the difference in extent is only about 10%, the total CAP to r_{max} was set at 21.56 a_0 , and the same extent Δr was used for all channels.

4.3.1.1 λ grid

There is a clearly defined window for the lifetime of resonant states that may participate in the pre-dissociation spectrum that arises from the physical dimensions of the Carrington-Kennedy experimental apparatus. The lower and upper limit for the lifetimes are given by time the ions in these resonant states take to travel from their origin to the start and the end of the drift tube, respectively, since the drift tube is where the dissociation must occur to be detected. The time that an ion takes to travel from the ion source to the laser is of the order of 10^{-6} seconds [23]. This means that the initial state must have a maximum width of about 10^{-6} cm⁻¹. Detection of the dissociation products is sensitive to final states with lifetimes between 10^{-9} and 10^{-7} seconds respectively. This sets the final state resonance widths approximately between 10^{-5} and 10^{-3} cm⁻¹. Due to this broad width window, the λ grid must obey three constraints: it must cover all the relevant CAP intensities that map the positions of the stability points with Γ between 10^{-5} and 10^{-3} cm⁻¹; it must be sufficiently dense to describe the stability points in detail; the differences between the grid points must be small so that the eigenvectors can be matched at each step. This last point is particularly important since the eigenvalues often change their ordering as λ increases, reflecting the existence of crossings between trajectories. The trajectory tracking is achieved by doing a normalised scalar product between all the complex eigenvectors in every two successive λ steps, as discussed in section 3.2.2.3. It is desirable for all these constraints to be met with minimum computational cost.

As explained in section 3.2.3.2, to cover the resonance space appropriately at both low and high energy ranges and to allow for a finer control of the grid progression, an exponential function balanced by a fraction for λ , repeated here for convenience:

$$\lambda_n = h \frac{\chi^n - 1}{\chi - 1}, \quad n = 0, \dots, N \quad (4.8)$$

where h has units of energy and is used to establish the order of magnitude, χ is the progression parameter, and N is the number of grid points.

For both D₂H⁺ and H₃⁺, the parameters $\chi = 1.01$ and $h = 4.39 \times 10^{-2}$ cm⁻¹ were found to be suitable, giving a maximum amplitude of 2.41×10^5 cm⁻¹ at 1,100 points. These were sufficient to cover the complex plane for all the eigenvalues tested.

4.3.1.2 Automatic detection

The detection algorithm described in section 3.1.2 was calibrated by setting four parameters. The first two are the tolerance window for the occurrence of the different

detection stability point conditions. Since an accuracy of about 0.1 cm⁻¹ is desired, the maximum distance allowed between the existence of points that satisfy those criteria in the real axis was set to this value. The imaginary energy range covered by trajectories varies dramatically by orders of magnitude from eigenvalue to eigenvalue. For this reason tolerance for this component is given as a percentage of the total imaginary energy. As in the case of the RES3D validation tests in section 4.1.1.2 tolerance of 3% produces consistent results.

The second two parameters control the consistency tolerance between the different stability points detected across all the tested r_{min} values for a particular resonant eigenvalue, as discussed in the end of section 3.1.2. It was found that defining these parameters as 0.1 cm⁻¹ for the real part of the energy and 15% for the complex part was adequate to eliminate spurious detections.

4.3.1.3 CAP consistency

Two sets of consistency tests were performed: the first to verify that the results are actually consistent for different r_{min} positions, i.e., different CAP lengths, Δr , with a single functional form; the second to test the GLM against the M2 CAPs. All calculations in this section were performed using all the available continuum basis elements from the most converged vibrational D₂H⁺ calculation, described in the introduction to this section, in the interval 38,724 to 38,842 cm⁻¹ as well as a few bound-region basis elements for testing purposes. The r_{min} consistency tests are shown in table 4.5. These results indicate that for a particular number of states, changing the range covered by the complex absorbing potential has an effect on the detection of resonances. But more importantly, there is a high level of consistency across most detections.

The differences between consistent and inconsistent states can be better understood through Fig. 4.9 and Fig. 4.10, which illustrates the detection of trajectories in the complex energy plane using five GLM CAP with Δr values from 2 to 10 a_0 .

By simple visual inspection, it can be seen in case a) that the trajectories are consistent in the position of the stability points and peaks in curvature, whereas in case b) the position of the stability points and curvature peaks changes significantly with Δr , suggesting that this result may not be reliable. In fact the rate of detection given by the automated procedure is 77.8% in case a), whereas in case b) it was 44.4%, which is in accordance with these observations.

A common feature in these two cases is that the trajectory associated with $\Delta r = 4 a_0$ appears to have a much lower maximum curvature than other trajectories. This is also observed for all trajectories with $\Delta r \leq 4 a_0$ and for other eigenvalues as well.

Table 4.5: Sample of resonance positions, E , and half-widths, $\Gamma/2$, in cm^{-1} obtained directly from the automatic stability point detection method for the GLM CAP for a set of 5 Δr values, ranging from 4 to 8 a_0 with r_2 set at $21.58a_0$. Powers of ten are given in parenthesis.

$\Delta r = 4.0 a_0$		$5.0 a_0$		$6.0 a_0$		$7.0 a_0$		$8.0 a_0$	
E	$\Gamma/2$	E	$\Gamma/2$	E	$\Gamma/2$	E	$\Gamma/2$	E	$\Gamma/2$
		38729.28	2.95(-1)	38728.67	5.53(-1)	38724.69	3.15(0)	38724.83	3.16(0)
38739.99	9.33(-1)	38739.83	1.18(0)			38728.70	5.54(-1)	38728.70	5.73(-1)
38743.70	1.74(-1)	38743.68	2.12(-1)			38735.20	1.47(1)	38735.93	1.63(1)
		38753.23	7.31(-6)			38739.73	1.20(0)	38739.71	1.20(0)
		38760.54	1.80(-1)	38753.23	7.71(-6)	38743.67	2.16(-1)	38743.67	2.15(-1)
		38762.27	2.22(-1)	38760.55	1.76(-1)	38753.23	7.77(-6)	38753.23	7.94(-6)
38762.27	2.57(-1)	38773.68	9.28(-2)	38762.28	2.19(-1)	38760.55	1.76(-1)	38760.55	1.76(-1)
38773.53	2.49(-1)	38785.14	3.69(-1)	38773.50	2.62(-1)	38762.28	2.19(-1)	38762.28	2.19(-1)
38785.13	3.22(-1)	38791.87	2.77(-1)	38785.14	3.72(-1)	38773.50	2.61(-1)	38773.50	2.59(-1)
		38797.41	1.22(-1)	38791.88	2.79(-1)	38785.14	3.74(-1)	38785.13	3.74(-1)
		38804.61	1.16(0)	38797.41	1.22(-1)	38791.88	2.80(-1)	38791.88	2.81(-1)
		38811.89	2.82(-2)	38804.61	1.16(0)	38797.41	1.22(-1)	38797.41	1.22(-1)
38815.92	6.68(-1)	38815.89	6.88(-1)	38811.89	2.84(-2)	38804.61	1.15(0)	38804.61	1.16(0)
38820.23	7.42(-1)	38820.20	7.64(-1)	38815.88	6.95(-1)	38811.89	2.84(-2)	38811.89	2.90(-2)
		38830.02	4.89(-2)	38820.20	7.73(-1)	38815.88	6.94(-1)	38815.88	6.99(-1)
		38837.83	2.20(0)	38830.02	4.87(-2)	38820.19	7.74(-1)	38820.19	7.87(-1)
		38837.83	2.20(0)			38830.02	4.88(-2)	38830.02	4.86(-2)
38838.30	1.80(0)	38841.76	4.46(-1)	38837.88	2.18(0)			38838.22	2.10(0)
38841.61	3.45(-1)			38842.38	6.60(-1)	38837.92	2.22(0)	38845.48	8.97(-1)
						38843.47	1.01(0)		

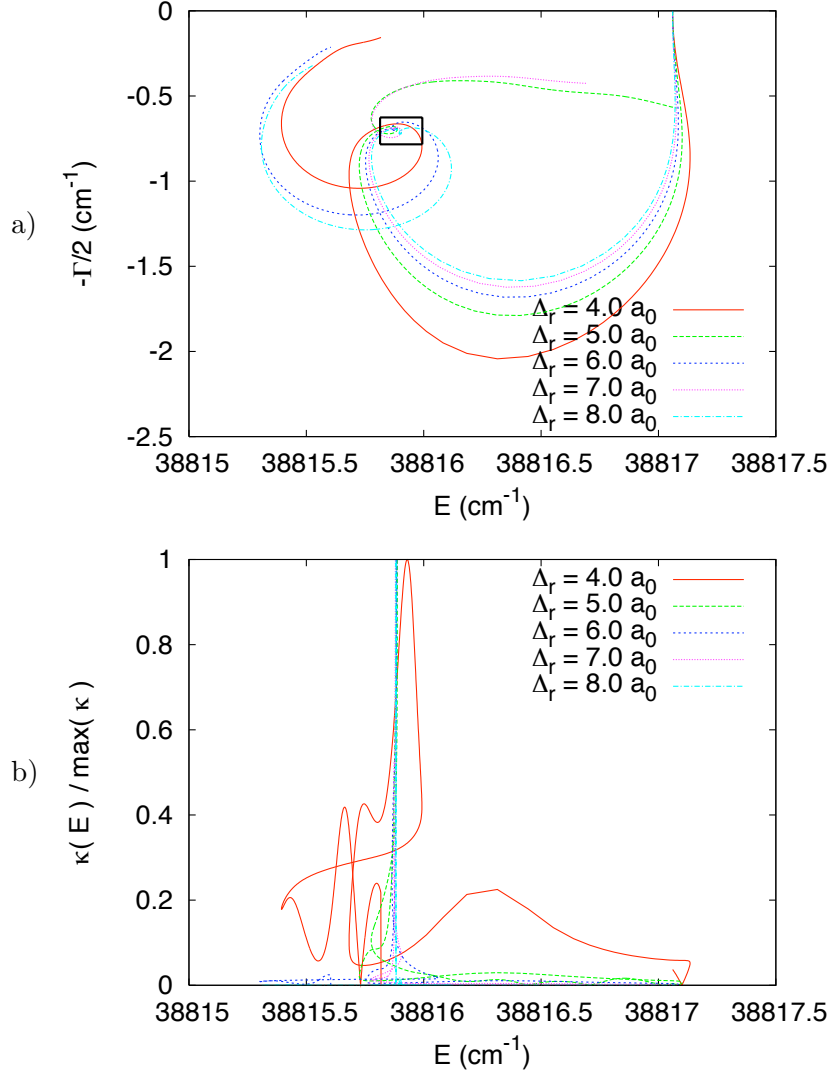


Figure 4.9: Sample of trajectories in the complex energy plane and their curvatures, generated using the GML CAP for A_1 basis elements, for Δ_r from 4 to 8 a_0 in steps of 1 a_0 , and with λ from 0 to $2 \times 10^5 \text{ cm}^{-1}$. The plots indicate: a) a resonance identification at $38,815.90 \text{ cm}^{-1}$ with $\Gamma/2 = 0.70 \text{ cm}^{-1}$; b) normalised curvature with respect to the resonant energy. The black squares are the detection results, centred at the averaged real and imaginary parts of the eigenvalue, with sides indicating the maximum deviation in the detected stability points for the total of five CAPs used. c) and d) are the respective . The detection percentage 77.8%.

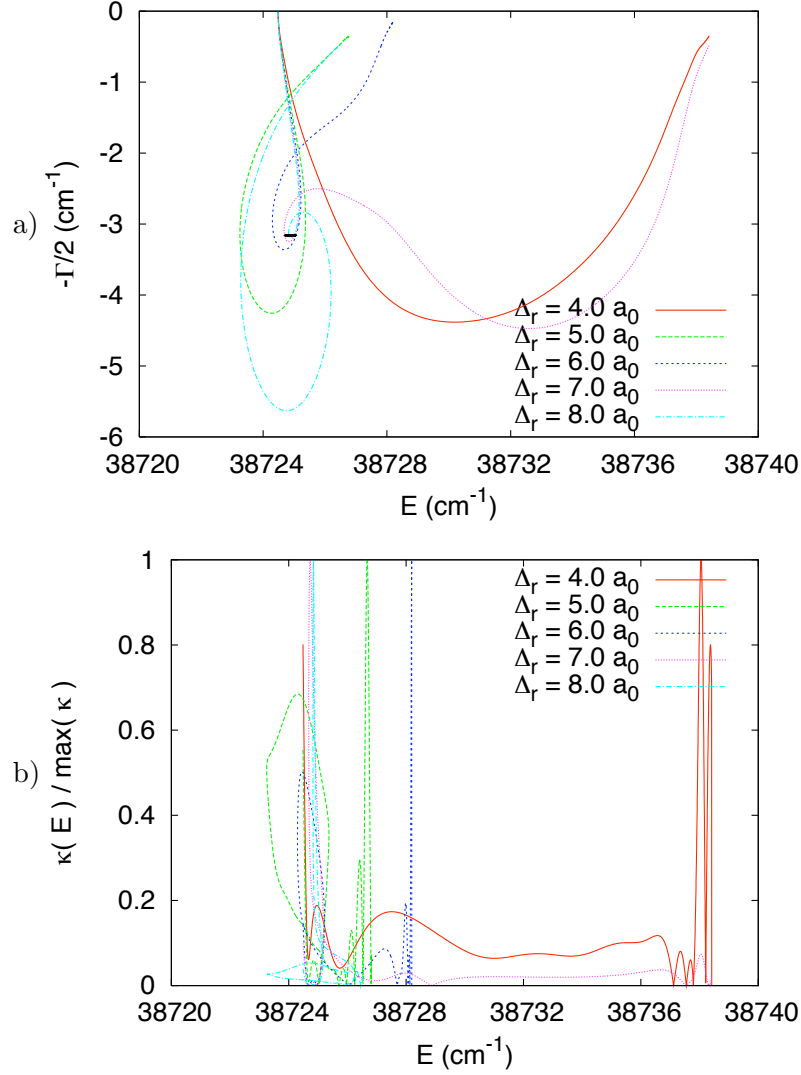


Figure 4.10: Sample of trajectories in the complex energy plane and their curvatures, generated using the GML CAP for A_1 basis elements, for Δ_r from 4 to 8 a_0 in steps of 1 a_0 , and with λ from 0 to $2 \times 10^5 \text{ cm}^{-1}$. The plots indicate: a) an inconsistent resonance identification at $38,724.87 \text{ cm}^{-1}$ with $\Gamma/2 = 3.16 \text{ cm}^{-1}$; b) normalised curvatures with respect to the resonant energy. The black squares are the detection results, centred at the averaged real and imaginary parts of the eigenvalue, with sides indicating the maximum deviation in the detected stability points for the total of five CAPs used. The detection was 44.4%.

This suggests that insufficient grid points are covered by CAPs with $\Delta r \leq 4 a_0$, i.e., the CAP is being sub-sampled, which causes the eigenvalue trajectory calculation to become inaccurate. An interesting example is that of the very narrow resonance positioned at 38,753.23 cm⁻¹, in table 4.5, which has a very consistent detection throughout all CAP's with $\Delta r > 4 a_0$, but apparently no detection for $\Delta r \leq 4 a_0$. As will be shown later in section 4.3.4, this is caused by the fact that the basis elements that contribute to this resonant state have amplitudes close to zero at large distance spatial grid points, thus introducing an additional numerical error for small Δr .

The consistency of results between the GLM and M2 CAPs was also tested. The results are shown in table 4.6 and indicate that, with the exception of state with energy 39,460 cm⁻¹ where the detection procedure converged to what appear to be local minima that were differently emphasised by each CAP, there is a remarkable consistency in both positions and widths of the calculated resonant states with energies up to 39,187 cm⁻¹. The GLM CAP has a slightly higher detection rate in most cases, giving results which are more consistent as a function of r_{min} . Also, its optimum transmission properties allow the use of a smaller λ range of values to build the trajectories that lead to detections. For these reasons, all final results were calculated using the GLM CAP.

4.3.2 D₂H⁺ Partial Widths

In the case of multi-dissociation channel systems such as D₂H⁺ the total reaction rate is the sum of the reaction rates through each open reaction channel, i.e., the total probability of dissociation is the sum of the probabilities of dissociation through all possible channels at a given energy. This would imply that the line widths associated with a particular dissociation channel at energies above the threshold should add up to the total line width of the system at that same energy. Verification of this property in these resonant calculations is an important indicator in the reliability of the method. To test this, a calculation was performed using a GLM CAP applied separately to the H⁺+D₂ and D⁺+HD dissociation channels. Δr was set to 6 a_0 and the basis functions have the same properties as described in the tests above. The results after matching closest resonance energies detected for each dissociation channel are presented in table 4.7.

From these results it can be seen that, in all except two cases, the sum of the partial widths equals the total width obtained using a single CAP for both dissociation channels to within about 30%. The resonance energies obtained vary by about 0.5 cm⁻¹. These discrepancies are probably due to the fact that the optimal λ

Table 4.6: Comparison of states with half-widths less than 0.15 cm⁻¹, obtained with the GLM and M2 CAPs for a common set of parameters for D₂H⁺ $J = 0$ A_1 symmetry calculations. “%” represents the percentage of successful detections over all the 9 values of Δr from $2a_0$ to $10a_0$. E and $\Gamma/2$ in cm⁻¹ are averages after removal of spurious detections. ΔE and $\Delta\Gamma/2$ are error in cm⁻¹ of energy and half-widths respectively. Powers of ten are given in parenthesis.

GLM					M2				
%	E	$\Gamma/2$	ΔE	$\Delta\Gamma/2$	%	E	$\Gamma/2$	ΔE	$\Delta\Gamma/2$
66.7	38685.19	5.34(-6)	0.00	3.93(-6)	77.8	38685.19	5.16(-6)	0.00	5.57(-6)
88.9	38753.24	6.88(-6)	0.00	3.01(-6)	55.6	38753.24	6.99(-6)	0.00	3.21(-6)
77.8	38797.41	1.24(-1)	0.01	8.24(-3)	66.7	38797.41	1.21(-1)	0.01	4.65(-3)
55.6	38811.89	2.71(-2)	0.00	5.83(-3)	77.8	38811.89	3.04(-2)	0.00	6.89(-3)
66.7	38830.03	4.76(-2)	0.01	3.81(-3)	77.8	38830.02	4.85(-2)	0.00	2.86(-3)
66.7	38891.22	8.17(-2)	0.02	1.03(-2)	44.4	38891.23	8.53(-2)	0.01	1.75(-2)
77.8	38918.41	1.22(-1)	0.05	1.69(-2)	88.9	38918.41	1.28(-1)	0.05	1.86(-2)
88.9	39058.55	1.47(-1)	0.01	4.73(-3)	77.8	39058.55	1.45(-1)	0.00	3.61(-3)
77.8	39074.43	1.77(-2)	0.00	1.73(-4)	77.8	39074.43	1.80(-2)	0.00	2.94(-3)
88.9	39119.14	4.08(-2)	0.00	2.06(-3)	88.9	39119.14	4.03(-2)	0.00	5.15(-3)
88.9	39129.46	1.96(-2)	0.00	4.67(-4)	77.8	39129.46	1.92(-2)	0.00	2.44(-3)
88.9	39186.83	8.43(-2)	0.00	3.92(-3)	77.8	39186.83	8.35(-2)	0.01	1.46(-3)
22.2	39291.15	5.87(-2)	0.06	1.86(-3)					
55.6	39460.37	1.20(-1)	0.00	2.19(-4)	88.9	39460.31	7.14(-2)	0.09	1.19(-2)
22.2	39927.57	1.39(-1)	0.00	1.03(-2)					

Table 4.7: Resonant energies and half-widths in cm^{-1} for the H⁺+D₂, D⁺+HD and total dissociation above the D⁺+HD threshold. This calculation was performed using the GLM CAP with $\Delta r = 6 \text{ a}_0$ for all dissociation channels and r_2 set to the grid limit of both H⁺+D₂ and D⁺+HD dissociation channels at 21.58 a_0 and 16.09 a_0 respectively. $\Delta\Gamma/2$ is the difference between the sum of the partial widths and calculated total width. Powers of ten are given in parenthesis.

H ⁺ +D ₂		D ⁺ +HD		All		
E	$\Gamma/2$	E	$\Gamma/2$	E	$\Gamma/2$	$ \Delta\Gamma/2 $
39019.59	1.15(0)	39019.89	3.02(0)	39018.01	4.00(0)	1.74(-1)
39022.70	1.64(0)	39022.89	2.68(-2)	39023.02	1.32(0)	3.44(-1)
39036.86	9.03(-1)	39035.42	1.46(0)	39036.53	3.34(0)	9.75(-1)
39074.43	1.78(-2)	39074.94	3.68(1)	39075.71	3.70(1)	1.69(-1)
39089.82	3.46(-1)	39089.08	2.17(-1)	39089.08	3.69(-1)	1.93(-1)
39097.50	2.30(0)	39095.36	1.01(0)	39098.00	3.62(0)	3.09(-1)
39125.95	8.93(-1)	39125.27	3.42(-1)	39125.44	1.50(0)	2.63(-1)
39136.19	6.69(-1)	39136.89	1.58(-1)	39136.08	9.11(-1)	8.31(-2)
39145.27	1.84(0)	39144.69	9.58(-3)	39144.72	1.24(0)	6.08(-1)
39170.62	4.23(-1)	39171.18	2.06(0)	39171.73	2.77(0)	2.91(-1)
39175.31	3.50(0)	39174.21	1.53(0)	39175.16	5.64(0)	6.08(-1)

value for each channel is coupled, as described by Eq.(4.7), leading to a mismatch between the stability points in the separate channels. Decoupling the λ parameter could possibly solve this problem. However, the implementation of this idea is computationally costly. When the CAP is applied solely to the D⁺+HD dissociation channel, some widths differ by orders of magnitude on changing the wavefunction basis from 120 to 130 radial grid points. This may be because Radau coordinates do not permit a complete sampling of the D⁺+HD dissociation regions of the potential, leading to difficulties in terms of convergence when adapting the CAP to all dissociation channels simultaneously. Nevertheless, acceptable results can be obtained by restricting Δr in the total CAP to lengths from 4 to 8 a_0 . This makes Δr large enough to cover sufficient grid points in the D⁺+HD channel and short enough not to go too close to the potential well.

4.3.3 The role of bound vibrational states

One of the key benefits of the CAP method is that eigenvectors used as basis for the construction of the Hamiltonian of Eq.(2.91) can be chosen neglecting nearly all the bound vibrational states, as their coupling with the resonant states will be negligible. This assumption needs to be tested, particularly because of the presence of asymptotic vibrational states (AVS) [9], which extend far into the dissociation region where the CAP is placed. In fact the effect of the AVS is negligible: only for one H⁺+D₂ resonant state the effect is significant, showing a difference of 0.16 cm⁻¹ in energy and 1.75×10^{-2} cm⁻¹ in width between the calculations with and without AVSs, while the remaining states differ by less than 0.01 cm⁻¹ in energy and 10% in width. This leads to the conclusion that, from the technical point of view of including these states in the CAP calculation, the AVS and all other bound states show negligible coupling to the resonant states and therefore are excluded from the final calculations. Nevertheless, it must be noted that a link of orthogonality between resonant states and AVS exists. In fact, the basis elements above dissociation depend strongly upon the convergence of the bound states for their position, and due to their extension, the AVS are particularly difficult to converge.

4.3.4 D₂H⁺ Vibrational Resonances

Apart from the technical issues inherent to the CAP method as described in section 4.3.1, there are two more aspects determining how accurate the results are for a given PES. The first aspect is the number of basis elements used to build the CAP matrix, and the second is the size of the basis set used to build these basis eigenvectors

themselves. The results presented here show how these two parameters influence the final resonance energies and widths. In terms of the CAP basis convergence, the smallest calculation only use basis elements that lie within the relevant resonance energy window, as discussed above, and the intermediate step will be half-way in between that number and the maximum available.

The final results for $J = 0$ D_2H^+ candidate resonances are presented in table 4.8 for both the $H^+ + D_2$ and $D^+ + HD$ dissociation channels as well as the convergence relative to the CAP basis and the wavefunction basis.

The results were obtained using 519 A_1 states and 485 B_1 states lying between 38,658 and 41,029 cm^{-1} . Due to the grid constraints imposed by the $D^+ + HD$ dissociation channel, as described in the end of section 4.3.2, five CAP's with the GLM functional form were used with Δr ranging from 4 to 8 a_0 in steps of 1 a_0 with r_{max} placed at the end of the grid of each respective channel.

A total of 384 candidate resonances with width less than 100 cm^{-1} were detected in the range 38,658 to 39,658 cm^{-1} , of which 131 have a consistency in Δr above 60%. Detections in the same energy range with half-widths narrower than 0.1 cm^{-1} are presented in Table 4.8. Table 4.8 shows that there are D_2H^+ resonant vibrational states narrow enough to play a role in the pre-dissociation spectrum for this system, which is somewhat surprising since these Feshbach-type resonance which arise through energy trapping in the asymmetric stretch and bending degrees of freedom, [58] are usually assumed to be broader [26; 111; 112].

As expected [14], the resonance widths systematically become narrower as either the CAP or wavefunction basis is increased. Two states in particular result in very narrow widths, namely states 3 and 11, both with A_1 symmetry. Very narrow widths in these states suggests that λ_{op} is very small, leading to wavefunctions that differ very slightly from the starting eigenvector ϕ . This is confirmed by examining the modulus of the coefficients $c_n^i(\lambda)$ in Eq.(2.90).

Table 4.9 shows the coefficients associated with resonant states, both labelled by the order of the original basis elements. States labelled 3 and 11 in table 4.8 are resonant states Ψ_5 and Ψ_{16} in table 4.9. It shows that the square modulus of the coefficients c_n^5 and c_n^{16} , associated with those particular resonant states, is particularly close to 1, where as the remaining coefficients are all very small.

To help visualise these resonances, Fig. 4.11 shows plots of the basis elements ϕ_5 and ϕ_{16} , associated with narrow resonances 3 and 11, respectively, along with basis element ϕ_3 which appears to be associated with resonance 2 in table 4.8, and basis element ϕ_{14} which has a relatively low association with Ψ_{14} , a broad A_1 resonance at 38,743.7 cm^{-1} with half-width of 0.21 cm^{-1} .

Table 4.8: Results and convergence for the D₂H⁺ candidate resonant states using a CAP adapted to both the H⁺+D₂ and D⁺+HD dissociation channels. The states that are within the lifetimes of the observed pre-dissociation spectrum are highlighted. The columns are, position of the resonance, E , uncertainty in the position due to consistency, ΔE , resonance half-width, $\Gamma/2$, uncertainty in half-width due to consistency, $\Delta\Gamma/2$, detection percentage, %. For the convergence of results, δE and $\delta\Gamma/2$ are the difference between the largest calculation and the respective lower convergence calculation for the energy and half-widths respectively: the subscript “a” indicates a CAP eigenvector cutoff at 40,765 cm⁻¹ and the subscript “b” indicates a cutoff at 40,500 cm⁻¹. Where there is no subscript, the difference is relative to the lower convergence wavefunction. S is the spatial symmetry of the state. The results are presented in cm⁻¹. Powers of ten are given in parenthesis.

Identified Resonances					CAP matrix convergence				Basis convergence		S	
E	$\Gamma/2$	ΔE	$\Delta\Gamma/2$	%	δE_a	δE_b	$\delta\Gamma_a/2$	$\delta\Gamma_b/2$	δE	$\delta\Gamma/2$		
1	38661.82	2.40(-2)	0.14	8.77(-3)	60	0.00	0.01	-1.30(-3)	-2.10(-3)	-0.12	-2.78(-2)	A ₁
2	38669.66	1.69(-2)	0.10	4.37(-3)	80	0.00	0.01	0.00(0)	-9.00(-4)	-0.01	-2.39(-6)	A ₁
3	38685.19	5.24(-6)	0.00	1.43(-6)	60	0.00	0.00	0.00(0)	-1.00(-8)	-0.01	-2.39(-6)	A ₁
4	38691.04	6.85(-2)	0.31	1.66(-2)	60	-0.20	-0.02	9.90(-3)	9.00(-3)	-0.18	-1.36(-1)	A ₁
5	38706.55	9.71(-4)	0.00	8.49(-4)	60	0.00	0.00	-5.90(-5)	-2.90(-5)	-0.01	-1.09(-4)	B ₁
6	38712.97	7.02(-3)	0.00	0.00(0)	20	-0.07	-0.06	-6.18(-3)	-7.18(-3)	-0.06	-4.68(-3)	B ₁
7	38722.37	9.95(-2)	0.32	1.59(-2)	40	0.28	-0.03	2.17(-2)	-2.50(-3)	0.37	-3.20(-1)	B ₁
8	38730.15	1.92(-2)	0.11	4.38(-3)	60	0.00	-0.01	-1.00(-4)	-7.00(-4)	-0.12	-5.60(-3)	B ₁
9	38738.25	4.38(-2)	0.00	0.00(0)	20	0.23	-0.32	-4.10(-2)	-8.80(-3)	0.04	-9.00(-4)	B ₁
10	38738.56	5.18(-2)	0.11	4.92(-3)	40	-0.03	0.00	-1.00(-3)	-1.00(-8)	-0.14	-1.23(-2)	B ₁
11	38753.24	8.13(-6)	0.00	5.55(-7)	60	0.00	0.00	-1.00(-8)	-1.00(-8)	0.00	-9.97(-6)	A ₁
12	38754.08	7.95(-3)	0.03	3.64(-3)	60	0.00	0.00	1.30(-4)	1.70(-4)	-0.01	8.80(-4)	B ₁
13	38754.50	6.13(-2)	0.50	6.48(-2)	80	0.03	0.04	-5.90(-3)	-4.40(-3)	-0.11	2.39(-2)	B ₁
14	38767.79	2.33(-3)	0.00	1.60(-3)	100	0.00	0.00	-3.80(-4)	-3.80(-4)	-0.01	-3.20(-4)	B ₁
15	38773.96	2.50(-2)	0.03	1.71(-2)	100	0.00	0.00	-8.00(-4)	-7.00(-4)	0.00	-1.20(-3)	B ₁
16	38778.59	2.65(-2)	0.10	1.56(-2)	80	-0.04	0.01	4.60(-3)	2.50(-3)	-0.04	-3.04(-2)	B ₁
17	38781.48	4.50(-3)	0.01	2.53(-3)	60	0.01	0.00	-8.40(-3)	-2.30(-4)	-0.02	-4.75(-3)	B ₁
18	38811.89	2.81(-2)	0.00	1.52(-3)	80	0.00	0.00	0.00(0)	0.00(0)	0.01	-8.00(-4)	A ₁
19	38830.02	5.01(-2)	0.00	3.39(-3)	80	0.00	0.00	0.00(0)	0.00(0)	-0.02	-3.00(-4)	A ₁
20	38887.53	5.64(-2)	0.00	1.35(-3)	60	0.00	0.00	1.40(-2)	1.00(-4)	0.01	-1.00(-2)	B ₁
21	38891.23	6.77(-2)	0.02	2.77(-2)	60	0.01	0.00	-1.38(-2)	-2.00(-4)	0.02	-1.42(-2)	A ₁
22	38918.44	8.61(-2)	0.04	4.00(-2)	40	-0.01	0.01	1.40(-3)	-2.00(-3)	0.13	-4.19(-2)	A ₁
23	38952.73	3.63(-2)	0.03	1.60(-2)	100	0.01	0.01	4.00(-3)	3.90(-3)	0.00	-1.20(-3)	B ₁
24	38978.91	2.58(-3)	0.00	1.58(-3)	60	0.00	0.00	-1.00(-5)	-2.00(-5)	-0.02	-1.42(-3)	B ₁

The basis elements ϕ_5 and ϕ_{16} , associated with 3 and 11 have almost no symmetric stretch excitation, a characteristic akin to the so called horseshoe states [26; 113] which fundamentally are high bending excitations. State 2 has basis element ϕ_3 associated with it through a coefficient $c_n^3 = 0.94541$, which is fairly high. It appears though that due to the presence of a symmetric stretch excitation, the half width of this resonant state is significantly larger than either 3 or 11. Basis element ϕ_{14} displays what appears to be a high symmetric stretch excitation and simultaneously is associated with a broad resonance with width of 0.21 cm^{-1} . These observations suggest that basis elements with low symmetric stretch excitations may provide an indication for the energy of resonant states, and a qualitative notion of their width.

A feature of the narrow resonances 3 and 11 is that they display a very good wavefunction convergence and very strong consistency in their detection. This can be easily explained by the low coupling that these states have with the remaining basis elements, as indicated by table 4.9.

It should be noted that there are no resonance widths narrower than 0.01 cm^{-1} above the $\text{D}^+ + \text{HD}$ dissociation threshold. This may be due to the fact that both $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{HD}$ channels are open, which naturally increases the probability of dissociation, reducing resonant life-times. However the behaviour of the resonance widths in this region suggests that the widths may be overestimated and may require larger CAP basis sets to fully converge them.

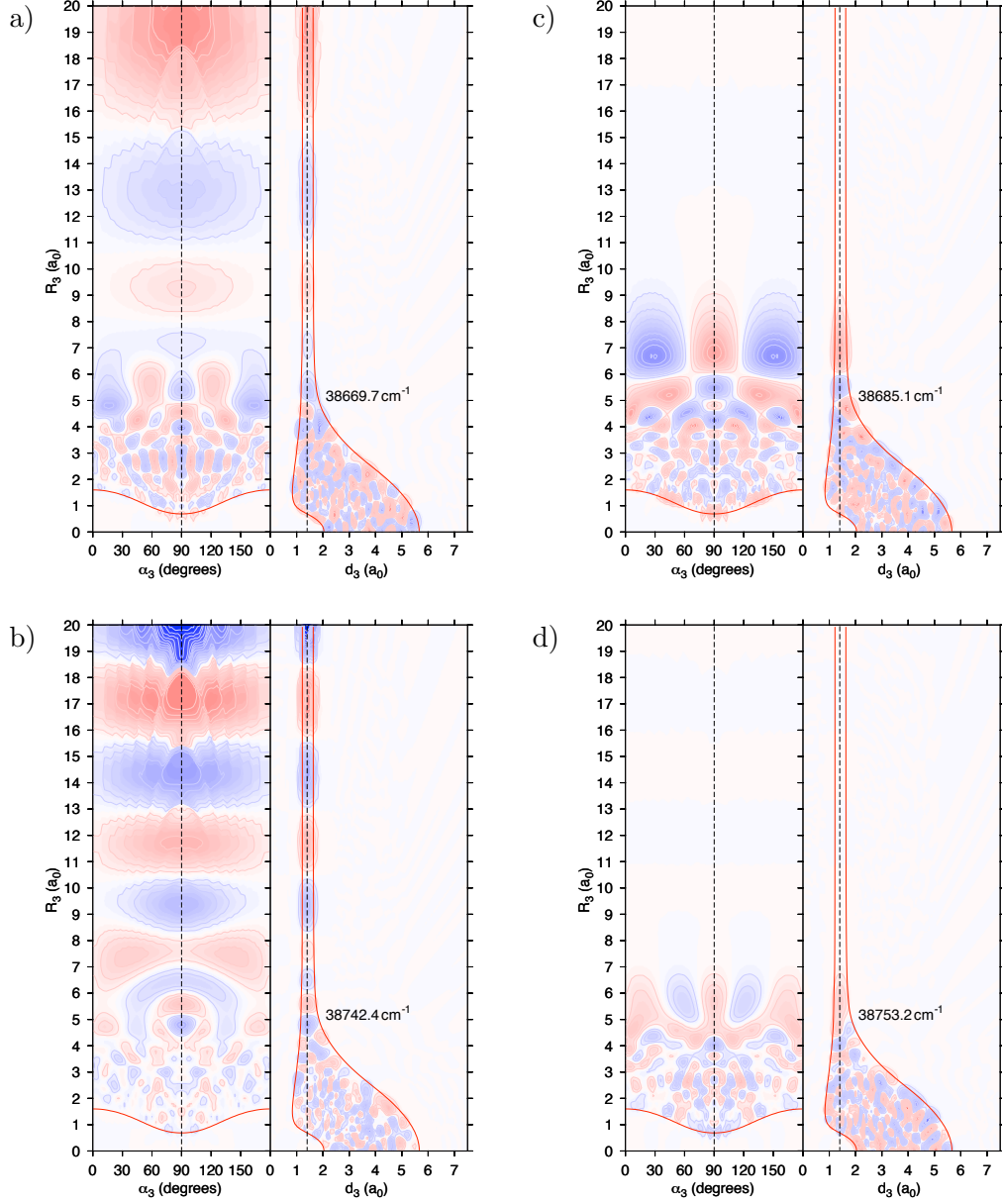


Figure 4.11: 2D plots of two sections of the of the A_1 D_2H^+ basis elements, ϕ_i , that correspond to: a) broad resonance 2 in tab. 4.8; b) narrow resonance 3 in tab. 4.8; c) broad resonance $E = 38743.7 \text{ cm}^{-1}$ and $\Gamma/2 = 0.21 \text{ cm}^{-1}$; d) narrow resonance 11 in tab. 4.8. These basis elements are associated with the coefficients c_n^3 , c_n^5 , c_n^{14} and c_n^{16} in table 4.9, respectively. The red contour shows the classing turning surface. Shades of red show the negative part of the eigenvector, the darker the deeper, whereas shades of blue the positive part. The amplitude of the eigenvector is normalised to one. In each plot, two panels show two different 2D cuts of the wavefunction, and the dotted line indicates where the two sections intersect. Oscillations in large R_3 regions are fitting artifacts due to the sparsity of the angular grid.

Table 4.9: Value of the coefficients c_n^i associated with basis elements ϕ_i of the resonant states $\Psi_n(\lambda = \lambda_{op})$. Four coefficients are chosen to be such that $\Psi_i(\lambda = 0) = \phi_i$ for $i = 3, 5, 14$ and 16 . Resonances Ψ_3 , Ψ_5 and Ψ_{16} correspond to resonances 2 3 and 11 in table 4.8, whereas Ψ_{14} is a broad resonance with $E = 38743.7 \text{ cm}^{-1}$ and $\Gamma/2 = 0.21 \text{ cm}^{-1}$. λ is given in cm^{-1} . Powers of ten are given in parenthesis.

	$\Psi_3(\lambda = 65)$	$\Psi_5(\lambda = 69)$	$\Psi_{14}(\lambda = 57)$	$\Psi_{16}(\lambda = 67)$
$ c_n^3 ^2$	0.94541(00)	0.85964(-09)	0.17066(-05)	0.44550(-10)
$ c_n^5 ^2$	0.81463(-01)	1.00000(00)	0.16052(-09)	0.38949(-14)
$ c_n^{14} ^2$	0.45854(-05)	0.21422(-09)	0.37914(-00)	0.16122(-07)
$ c_n^{16} ^2$	0.10713(-01)	0.45794(-15)	0.19894(-08)	1.00000(00)

4.4 H_3^+ Vibrational Resonances

4.4.1 H_3^+ bound state calculations.

Full diagonalisations of Hamiltonians for H_3^+ [9; 29] with angular momentum $J = 0$ and $J = 3$ also performed using PDVR3D [10] in Radau coordinates with the lab referential z axis perpendicular to the molecular plane [17; 40; 86]. The calculations were performed on HPCx [114] using the corrected PPKT2 PES[41; 9] that correctly describes the dissociation regions of the H_3^+ system. Although other promising PESs for this system H_3^+ have been reported,[55; 56] the availability of computational resources prevented the performance of comparative tests using these new surfaces.

Originally, the H_3^+ calculations were performed with a grid defined by 96 angular points and 120 radial points in Radau coordinates with C_{2v} , and not the natural D_{3h} spacial symmetry. This causes E states in the D_{3h} symmetry group to appear repeated as A_1 and B_1 states from the C_{2v} group. Note that, due to the Pauli principle, only the states in the B_1 symmetry block are physically allowed in H_3^+ with $J = 0$. The radial basis functions were constructed from spherical oscillators[10] with basis parameters $\alpha = 0$, $\omega = 0.004 \text{ E}_h$. In the final H_3^+ calculations the 3D Hamiltonian size was 79,091, with states converged within 1 cm^{-1} [9].

To improve upon the calculations in reference [9] and to provide a measure of convergence for the resonance calculations, two new calculations of H_3^+ vibrational states were performed. The largest vibrational H_3^+ calculations were performed with the radial grid size extended to 140 points and a final 3D Hamiltonian of 94,224, giving energy states converged to about 0.1 cm^{-1} . These convergence results will determine the lower limit for the convergence of H_3^+ resonant presented in table 4.10. As mentioned in section 4.3, an important side-effect of changing the the number of radial grid points is a change in the overall grid box size. In H_3^+ , changing the number of grid points from 120 to 140 moved the outermost grid point in R_3 from 19.91 to 21.56 a_0 .

4.4.2 H_3^+ vibrational resonances

The results for the H_3^+ vibrational resonances with half-width narrower than 0.1 cm^{-1} and respective convergence results are presented in table 4.10.

Table 4.10: Results and convergence of H_3^+ vibrational resonant states. Highlighted states are within the life-time range of the observed pre-dissociation spectrum. The columns are position of the resonance, E , resonance half-width, $\Gamma/2$, uncertainty in the position due to consistency, ΔE , uncertainty in half-width due to consistency, $\Delta\Gamma/2$, detection percentage, %, and the C_{2v} symmetry of the state, S . The results are presented in cm^{-1} . Powers of ten are given in parenthesis.

	Identified Resonances					CAP matrix convergence				Basis convergence		S
	E	$\Gamma/2$	ΔE	$\Delta\Gamma/2$	%	δE_a	δE_b	$\delta\Gamma_a/2$	$\delta\Gamma_b/2$	δE	$\delta\Gamma/2$	
1	39288.16	2.90(-2)	0.09	2.20(-2)	55.6	0.00	0.00	-1.00(-7)	-2.00(-7)	-0.16	-3.16(-5)	B_1
2	39288.21	3.50(-2)	0.00	7.74(-3)	22.2	0.00	0.00	0.00(0)	0.00(0)	-0.20	-1.30(-3)	A_1
3	39303.89	7.71(-2)	0.09	1.93(-2)	22.2	0.00	0.00	0.00(0)	0.00(0)			B_1
4	39342.65	9.77(-2)	0.00	1.75(-2)	22.2	-0.01	0.01	3.00(-4)	2.10(-3)			A_1
5	39344.07	5.42(-2)	0.02	3.94(-2)	22.2	0.00	0.00	0.00(0)	0.00(0)	-0.11	-1.27(-1)	B_1
6	39374.52	2.56(-3)	0.00	2.25(-3)	44.4	0.01	0.01	-1.40(-3)	-3.00(-3)	1.24	-1.13(-2)	A_1
7	39391.20	5.68(-2)	0.00	0.00(0)	11.1	0.00	0.00	-1.00(-5)	3.90(-4)	-1.23	-9.26(-1)	A_1
8	39396.39	2.83(-2)	0.00	0.00(0)	11.1	0.00	0.22	0.00(0)	5.07(-2)	-0.63	5.58(-2)	B_1
9	39397.27	8.12(-2)	0.01	2.88(-2)	44.4	-0.93	-0.07	-1.02(-1)	-1.36(-2)			B_1
10	39420.42	8.86(-2)	0.00	0.00(0)	11.1	0.00	0.01	-4.00(-4)	1.07(-2)	-1.62	-7.33(-1)	A_1
11	39431.44	2.91(-2)	0.01	1.29(-2)	22.2	1.06	0.01	-1.21(0)	-7.50(-3)			B_1
12	39435.86	6.77(-2)	0.00	3.12(-3)	22.2	0.00	0.01	0.00(0)	8.20(-3)	-0.14	6.76(-2)	B_1
13	39436.02	6.14(-2)	0.01	4.43(-3)	44.4	-0.14	0.00	6.27(-2)	0.00(0)	-0.19	1.09(-2)	B_1
14	39469.14	1.02(-2)	0.00	5.66(-3)	33.3	0.00	0.00	0.00(0)	1.30(-3)			A_1
15	39478.00	8.19(-2)	0.12	6.67(-2)	55.6	0.00	0.00	-4.00(-4)	-1.10(-3)	-0.05	-1.72(-1)	A_1
16	39488.00	9.07(-2)	0.07	6.07(-2)	55.6	0.01	0.01	-3.81(-2)	-2.30(-3)	-1.46	-5.16(0)	B_1
17	39503.97	6.65(-2)	0.05	2.65(-2)	33.3	0.02	0.00	-1.53(-2)	-5.00(-4)			B_1
18	39514.85	1.16(-3)	0.00	8.99(-4)	44.4	-0.02	-0.06	2.70(-3)	-1.38(-2)			A_1
19	39523.38	6.34(-2)	0.02	2.40(-2)	33.3	0.00	0.00	-3.00(-4)	-1.40(-4)	1.89	-1.57(0)	B_1
20	39552.30	2.01(-2)	0.00	6.78(-4)	22.2	0.00	0.02	-2.00(-4)	-9.80(-3)	-0.28	-7.84(-1)	A_1
21	39552.89	3.83(-3)	0.00	5.04(-4)	33.3	0.00	0.00	0.00(0)	5.50(-3)	0.77	-4.67(-1)	B_1
22	39571.29	2.06(-2)	0.01	1.27(-2)	33.3	0.00	0.00	3.00(-5)	-3.00(-5)	-0.04	-9.62(-2)	A_1
23	39604.79	1.15(-3)	0.00	1.52(-4)	33.3	0.00	0.00	-6.30(-3)	-1.33(-2)			B_1
24	39605.15	8.61(-2)	0.01	2.06(-2)	44.4	-0.80	0.00	-1.58(-1)	1.00(-5)	-0.50	-1.53(-1)	A_1
25	39667.57	9.75(-2)	0.00	1.28(-3)	33.3	0.00	0.00	0.00(0)	2.00(-4)	-2.76	-1.64(0)	B_1
26	39720.22	2.10(-2)	0.00	1.43(-2)	77.8	0.00	0.01	0.00(0)	2.29(-2)			B_1
27	39725.55	4.29(-2)	0.00	3.02(-2)	66.7	0.00	0.00	-2.10(-3)	0.00(0)	-0.20	-3.60(-2)	B_1
28	39744.32	2.75(-2)	0.00	1.94(-3)	55.6	0.00	0.00	-6.10(-3)	-6.00(-3)	1.19	-2.33(-1)	B_1
29	39745.83	3.92(-3)	0.00	2.41(-4)	33.3	0.00	0.00	-2.00(-4)	-7.00(-4)			A_1
30	39786.87	6.13(-2)	0.01	3.91(-2)	55.6	0.00	0.00	0.00(0)	-1.00(-5)	-1.64	-1.29(-1)	B_1
31	39850.87	3.09(-3)	0.00	2.59(-5)	22.2	0.00	0.00	-1.16(-2)	-9.50(-3)	-1.99	-2.66(-1)	B_1
32	39891.62	6.34(-2)	0.01	1.69(-3)	33.3	0.00	0.00	0.00(0)	-7.00(-5)			B_1
33	39926.18	7.14(-2)	0.00	1.06(-2)	33.3	0.00	0.01	-8.00(-4)	-1.80(-3)			A_1
34	39975.55	1.29(-2)	0.02	7.95(-3)	55.6	0.00	0.00	1.00(-4)	-5.00(-4)	0.96	4.51(-2)	B_1
35	40054.03	4.63(-2)	0.00	1.50(-3)	44.4	0.00	0.00	0.00(0)	-5.00(-4)	1.26	-3.73(-1)	B_1
36	40184.40	8.22(-2)	0.01	5.38(-3)	44.4	0.00	0.03	1.00(-4)	2.28(-2)	-0.15	-1.47(-2)	A_1
37	40325.60	3.42(-3)	0.00	3.29(-4)	44.4	0.00	0.00	4.00(-4)	1.50(-3)	0.99	-4.98(-1)	B_1

These were calculated using 592 basis elements for A_1 states and 570 basis elements for B_1 states, from the energy region 39,273 to 43,300 cm^{-1} . Nine CAP's with Δ_r ranging from 2 to 10 a_0 in steps of 1 a_0 were calculated, setting r_2 to 21.56 a_0 . A total of 252 candidate resonances was identified in the energy range 39,273 to 40,273 cm^{-1} , of which 48 have consistency in Δr above 60%. The wavefunctions with 120 radial points had the furthestmost grid point in the dissociation coordinate, R , at 19.91 a_0 . Therefore the same CAP parameters were maintained as with the largest calculation.

Unlike the resonances calculated for D_2H^+ , these resonances show larger widths and less consistency in the narrowest half-widths. The results appear to have worse wavefunction convergence than the ones obtained for D_2H^+ . This may be due to the large jump in wavefunction parameters between the largest and smallest H_3^+ calculation.

States pairs (1,2), (20,21) and (28,29) in table 4.10 appear to be degenerate pairs with E symmetry from the D_{3h} group which occur in both A_1 and B_1 symmetries of the C_{2v} group, as discussed in section 4.4.1. Because of the finite basis set, their energies are not quite identical. This energy splitting can also be used as a measure of convergence [37].

4.5 H_3^+ $J = 3$ Resonances

Similar calculations to the ones reported above were performed for H_3^+ at $J = 3$ using the same basis set parameters and size as the first $J = 0$ calculation, but at a very high computational cost: approximately 45,000 CPU hours[17]. This high cost prevented the calculation of other rotational states and the full convergence analysis of H_3^+ at $J = 3$. However, based upon the results for $J = 0$ it is probable that these states are converged to a similar level of accuracy.

4.5.1 H_3^+ $J=3$ resonance results

Table 4.11 presents results for $J = 3$ H_3^+ calculations including Coriolis coupling effects and using all the basis elements with corresponding eigenvalues between 39,273 and 43,300 cm^{-1} . The calculations were performed over all four C_{2v} group symmetries, resulting in a total of 893 candidate resonances in the energy range 39,273 to 40,273 cm^{-1} , 571 of which are consistent to more than 60% in Δr , defined by five values ranging from 4 to 8 a_0 . The resonance widths obtained in this case are of the same order of magnitude as the ones calculated at $J = 0$ due to their substantially Feshbach-type nature. For $J = 3$ the rotational barrier is not sufficiently high to trap shape resonances [26]. Nevertheless, the fact that some of these Feshbach-type resonances fall within the lifetimes observed in the pre-dissociation spectrum of H_3^+ indicates that states with low angular momentum must be studied to fully characterise this dense spectrum.

Table 4.11: Results for $J = 3$ H_3^+ resonant states in cm^{-1} . The columns are position of the resonance, E , resonance half-width, $\Gamma/2$, uncertainty in the position due to consistency, ΔE , uncertainty in half-width due to consistency, $\Delta\Gamma/2$, detection percentage, %, and S is the C_{2v} symmetry of the state. Powers of ten are given in parenthesis.

	E	$\Gamma/2$	ΔE	$\Delta\Gamma/2$	%	S
1	39280.05	4.82(-2)	0.12	2.52(-2)	60	A_2
2	39288.57	3.48(-2)	0.06	1.52(-2)	100	A_2
3	39293.63	1.23(-2)	0.00	0.00(0)	20	B_2
4	39299.35	1.08(-2)	0.01	5.36(-3)	80	A_2
5	39302.80	7.49(-3)	0.01	1.83(-3)	80	A_2
6	39327.05	1.73(-2)	0.01	1.14(-2)	100	A_2
7	39335.59	1.21(-2)	0.01	6.55(-3)	100	A_2
8	39339.51	3.70(-2)	0.03	1.89(-2)	80	A_2
9	39346.79	9.03(-3)	0.00	1.35(-2)	100	A_1
10	39354.59	4.33(-2)	0.03	2.77(-2)	80	A_2
11	39355.57	4.28(-3)	0.00	0.00(0)	20	A_2
12	39395.19	3.18(-4)	0.00	7.98(-6)	40	A_2
13	39399.53	2.63(-2)	0.00	7.63(-4)	40	A_2
14	39411.34	9.22(-2)	0.14	4.05(-2)	80	B_1
15	39438.28	6.45(-3)	0.00	2.63(-3)	80	A_1
16	39447.63	4.98(-2)	0.02	1.53(-2)	80	B_1
17	39456.76	4.22(-2)	0.00	7.40(-5)	40	A_2
18	39470.23	2.52(-2)	0.00	4.66(-4)	60	A_2
19	39475.83	3.39(-3)	0.00	0.00(0)	20	B_1
20	39495.56	4.37(-2)	0.01	3.91(-3)	40	A_2
21	39500.71	2.78(-2)	0.01	4.10(-3)	80	B_1
22	39501.64	1.65(-2)	0.00	2.50(-3)	60	A_2
23	39504.24	1.50(-2)	0.00	1.41(-3)	60	A_2
24	39511.78	1.61(-2)	0.00	1.13(-4)	40	A_2
25	39513.03	2.61(-2)	0.00	3.27(-4)	40	A_2
26	39534.13	9.38(-3)	0.00	9.49(-5)	40	A_2
27	39542.25	4.91(-2)	0.01	1.47(-2)	60	A_1
28	39547.30	5.40(-2)	0.08	1.21(-2)	80	B_1
29	39549.40	1.17(-2)	0.00	0.00(0)	20	A_1
30	39550.06	6.96(-2)	0.02	7.89(-3)	40	B_1
31	39553.74	2.91(-2)	0.00	1.69(-3)	60	A_2
32	39558.37	1.91(-2)	0.00	0.00(0)	20	A_1
33	39558.70	8.52(-3)	0.00	1.64(-5)	40	A_2
34	39575.62	2.05(-2)	0.00	4.51(-3)	60	A_2
35	39576.80	2.65(-2)	0.00	3.64(-3)	60	A_2
36	39584.40	1.30(-2)	0.00	4.20(-4)	40	A_2
37	39606.89	2.65(-2)	0.00	3.81(-3)	40	A_2
38	39615.16	1.83(-2)	0.00	1.73(-3)	60	A_2
39	39654.58	7.00(-2)	0.01	1.84(-2)	40	B_1
40	39795.06	4.80(-2)	0.20	1.22(-1)	100	A_1
41	40016.57	6.94(-2)	0.01	1.31(-2)	60	B_1
42	40309.21	4.94(-2)	0.01	1.71(-2)	40	A_2

Conclusion

5.1 On the calculation of D_2H^+ bound states

This work extended previous calculation for the vibrational band origins of H_3^+ to the less symmetric isotopologue D_2H^+ . The bound states of this molecule were computationally more difficult to converge as the spectrum is more dense. Sub-wavenumber convergence for 1209 A_1 and 1078 B_1 calculated band origins up to dissociation has been achieved.

At high energy, the bound states seem to show some interesting properties. In particular, there seems to be a class of states, named AVS previously [9], whose wavefunctions exhibit particularly large amplitude at large values of the ion-diatom dissociating coordinate. In order to obtain convergence for those extended states and the inner ones, a very large basis set is required, which results in a very expensive calculation. It is likely that the potential used will support further bound states which extend beyond the range of this DVR grid.

Following the work in [54] some corrections to the Born-Oppenheimer energies were evaluated. However, the correction surfaces available in [54] are only well defined in a range which is far smaller than the extent of the higher lying states, and therefore could not be used. It is expected that the combined relativistic and adiabatic corrections to the vibrational band origins to be of the order of magnitude of 1 cm^{-1} . Using the mass scaling model the non-adiabatic BO corrections were evaluated perturbatively. For D_2H^+ , those corrections have a lower symmetry than the potential, therefore are expected to be larger, however the simple model employed yielded an average correction of 1.79 cm^{-1} for all the calculated levels. It is expected that this model is correct to better than a factor of two, as the calculated

states have a particularly low amplitude in the area where the two lowest PESs come close to each other. Finally, it is known that the higher energy states are sensitive to details of the PES. Both the fitting error and the intrinsic accuracy of the electronic structure calculations are only about 5 cm^{-1} in this region [41]; these residual errors therefore remain more important than the corrections to the non-relativistic BO Hamiltonian.

In the literature [21; 25; 26; 30; 31; 32], semi-classical studies of the spectrum of D_2H^+ near its dissociation limit can be found, but to the author’s knowledge, no quantum mechanical studies were reported so far.

Heilliette and co-workers [115] studied NO_2 in the near dissociation region. They found, in addition to the strongly coupled three-body states, a family of states corresponding to orbiting motion of the two fragments around each other. They compared fully quantum-mechanical treatment with a semi-classical approach, and found that whereas for the 2D case, that is with diatom frozen, the two give similar results, the semi-classical approach fails completely in the proximity of the dissociation limit in the 3D case. This is because of the quantum character of the diatom fragment. However, as was shown, a full quantum mechanical treatment of the molecule in 3D near dissociation meets with great numerical difficulties and requires the use of powerful supercomputers.

Finally, it is interesting to discuss how this theoretical work relates to the spectra of Carrington *et al* [23]. Firstly, a large increase in density of states near dissociation is necessary to explain the exceptionally high number of lines recorded in the experiment. The low C rotational constant values could lead to significantly more AVS when rotations are considered [98]. It is possible that associated with the AVS states there will be a series of resonant states above dissociation. It is possible to study such states using $\mathcal{L}^2$ -methods such as the Complex Absorbing Potential method [14; 71] employed in this work.

5.2 On the calculation of resonances with RES3D

A new program for the calculation of resonant states in triatomics, RES3D, was developed. It employs a complex absorbing potential $\mathcal{L}^2$ method with a new automated procedure to find stability points in the complex plane associated with resonant states. This automation enables a consistency and uncertainty analysis of energies and half-widths to be performed for each candidate resonance by parametrically changing the extent of the complex absorbing potential (CAP).

Although the detection of resonances is automatic, the method requires calibra-

tion for the particular system under analysis. Particularly difficult to establish is the grid for the complex eigenvector trajectories. This grid is determined by the progression of the λ parameter in Eq.(4.8), as it sets the intensity of the CAP. This calibration is crucial both for the successful automatic identification of resonances through the heuristics described in section 3.2.3.3 and the complete coverage of the relevant width windows.

While studying the properties of resonances relatively to the trajectory grid parameters, it was observed that the narrowest widths were detected with lowest λ_{op} values, whereas the broadest widths were detected at higher λ_{op} . This indicates that the basis function at the root of the eigenvalue trajectory ($\lambda = 0$) correlates strongly with the wavefunction of the resonant state, as was observed in section 4.3.4. Conversely, broader widths will have stronger coupling with neighbouring basis functions. This suggests a future method whereby resonances are detected as the diagonalisation progresses. This could allow even greater time savings by, say, setting a threshold for a number of resonance detections or widths. However it is still difficult to predict how the λ progression parameters should be determined solely based on the properties of the system under analysis.

Similar difficulties occur when calibrating the automatic detection parameters related with tolerance. In particular, the number of grid points used by the search algorithm may be difficult to establish since it depends greatly on the resolution of stability points and curvatures, factors which are fundamentally dependant on the trajectory grid. Some level of trial and error is still needed.

Still, the benefits of the methods currently implemented in RES3D clearly outweigh any of the shortcomings mentioned above since for the first time it is possible to unambiguously and consistently identify resonances and quantify the uncertainties in the procedure.

It was also observed that the geometric properties of the CAP, specifically its extent as defined by the distance between its starting point inside the dissociation channel to the outermost grid point, $\Delta r = |r_{max} - r_{min}|$ has implications on the complex eigenvalue trajectories. Spurious resonance identifications may occur if the CAP does not cover a sufficient number of grid points, i. e., Δr is too small, or if the CAP covers regions of the potential well, i. e., Δr is too large. For this reason, an algorithm was implemented in RES3D that successfully eliminates identifications that are very much outside of the “core” identifications, thus avoiding result contamination. This elimination will still have consequences to the detection percentage, as discussed in section 3.2.3.4.

With the procedures discussed above, it is now possible to apply this analysis

to a large number of basis functions above dissociation. Studies of size and nature of the basis functions used in the definition of resonant wavefunctions in Eq.(2.90) through the construction and diagonalisation of the non-Hermitian Hamiltonian in Eq.(2.91), suggested that there is a variational-like behaviour in the resonance widths: the larger the basis size, the narrower the resonances become. It was also found that basis functions collected from bound states have a negligible coupling with resonances. This effectively means that all the information that is needed to calculate resonances resides in the eigenvectors above the dissociation threshold. The author speculates that the information about the potential is almost entirely transmitted to these eigenvectors by the orthogonality relations between these and bound state eigenvectors. This is partially evident in the convergence behaviour of resonances relatively to convergence from the DVR grid. Unfortunately, this measure of convergence is coupled to the box size of the problem, which does not permit a pure analysis of the bound state convergence effect. This is due to the increase in eigenvector density above the dissociation threshold as the box size increases.

Another interesting property of the CAP method is that the resonances that are both narrow and close to the dissociation threshold exhibit stability properties as the basis size changes which are akin of the stabilisation method discussed in section 2.3.5.1.

As it stands, RES3D can also produce the eigenvectors associated with resonant states. These may be utilised in the calculation of the dipole transition moments needed to determine line amplitudes. To do this, they have to be projected onto the original basis and generate wavefunctions in Eq.(2.90). These will be in the same DVR basis as the eigenvectors produced in the DVR3D or ROTLEV calculations [10]. But this creates a problem related to the nature of the complex perturbed Hamiltonian in Eq.(2.91): different resonances will have different λ_{op} values associated with them. This means that the Hamiltonian will be different **for each and every resonance**. The orthogonality relationship referred above will ensure that these states will be orthogonal to the bound states, but that may not be the case between resonances, implying that it may not be possible to compute dipole transition moments between resonant states. This is a matter that requires further study.

5.3 On the resonances of H_3^+ and D_2H^+

Using RES3D, a number of very well converged, narrow, Feshbach-type resonances for D_2H^+ with $J = 0$ and for H_3^+ with both $J = 0$ and $J = 3$ were found. This result is particularly surprising since it has been long assumed that Feshbach-type

resonances would be too short lived to play a role in the Carrington-Kennedy spectrum of H_3^+ and its isotopologues [26; 111; 112]. The present study suggests that all angular momentum quantum numbers that support bound vibrational states should be investigated to gain a full understanding of this spectrum. Also important to note is the observation that AVS states do not appear to couple significantly with continuum wavefunctions in the calculation of resonant states. Nevertheless, they are important theoretically since their convergence may impact the transmission of information about the potential from bound states to the eigenvectors used as basis for resonances. Physically, they are significant since they will undoubtedly participate in the state transitions that give rise to the Carrington-Kennedy spectrum.

5.4 Future work: H_2O

Recently, a remarkable spectroscopic experiment on water vapour at low pressure was performed by the Boyarkin and Rizzo group in Lausanne [116]. This very high resolution experiment involving the use of multi-stage laser excitations of the water vapour will potentially allow the complete description of the rovibrational spectrum of the H_2O molecule, including both bound and quasi-bound states [116; 117]. For this purpose, a collaboration with this group is under way to produce a high-accuracy potential energy surface for H_2O . This surface is being used to calculate all bound states of H_2O that participate in this spectrum [10; 118]. Through the same procedure used in the calculations presented here for H_3^+ and D_2H^+ , RES3D is now being actively used to test the potential energy surface through the calculation of resonant states. These will allow the full assignment of the continuum absorption lines, and consequently, the full spectrum of H_2O .

Bibliography

- [1] J. Tennyson, M. A. Kostin, H. Y. Mussa, O. L. Polyansky, and R. Prosmiti. H_3^+ near dissociation: theoretical progress. *Phil. Trans. R. Soc. Lond. A*, 358:2419–2432, 2000.
- [2] J. J. Thomson. *Philos. Mag.*, 21:225, 1911.
- [3] J. J. Thomson. *Philos. Mag.*, 21:209, 1912.
- [4] J. Tennyson. Spectroscopy of H_3^+ : planets, chaos and the Universe. *Rep. Prog. Phys*, 57:421–476, 1995.
- [5] J. O. Hirschfelder. The energy of the triatomic hydrogen molecule and ion, V. *J. Chem. Phys.*, 6(12):795–806, 1938.
- [6] M. J. Gaillard, D. S. Gemmell, G. Goldring, I. Levine, W. J. Pietsch, J. C. Poizat, A. J. Ratkowski, J. Remillieux, Z. Vager, and B. J. Zabransky. Experimental determination of the structure of H_3^+ . *Phys. Rev. A*, 17(6):1797–1803, Jun 1978.
- [7] T. Oka. Observation of the Infrared Spectrum of H_3^+ . *Phys. Rev. Lett.*, 45(7):531–534, Aug 1980.
- [8] A. Carrington, J. Buttenshaw, and R. A. Kennedy. Observation of the infrared spectrum of H_3^+ ion at its near dissociation limit. *Molec. Phys.*, 45:753, 1982.
- [9] J. J. Munro, J. Ramanlal, and J. Tennyson. Asymptotic vibrational states of the H_3^+ molecular ion. *New J. Phys.*, 7:196, 2005.
- [10] J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, O. L. Polyansky, J. Ramanlal, and N. F. Zobov. DVR3D: a program suite for the calculation of

- rotation-vibration spectra of triatomic molecules. *Computer Phys. Comm.*, 163:85, 2004.
- [11] M. Berblinger, E. Pollak, and C. Schlier. Bound states embedded in the continuum of H_3^+ . *J. Chem. Phys.*, 88(9):5643–5656, 1988.
 - [12] N. J. Wright and J. M. Hutson. Regular and irregular vibrational states: Localized anharmonic modes in Ar_3 . *J. Chem. Phys.*, 110(2):902–911, 1999.
 - [13] František Karlický, Bruno Lepetit, René Kalus, and Florent Xavier Gadéa. Calculation of argon trimer rovibrational spectrum. *J. Chem. Phys.*, 126(17):174305, 2007.
 - [14] H. Y. Mussa and J. Tennyson. Calculating quasi-bound rotation-vibrational states of HOCl using massively parallel computers. *Chem. Phys. Lett.*, 366:449–457, 2002.
 - [15] F. S. Pan and T. Oka. Calculated forbidden rotational spectra of H_3^+ . *Astrophys. J.*, 305(1):518–525, 1986.
 - [16] S. Miller and J. Tennyson. Calculated rotational and rovibrational transitions in the spectrum of H_3^+ . *Astrophys. J.*, 335(1):486–490, 1988.
 - [17] J. J. Munro. *Spectroscopy of H_3^+* . PhD thesis, University of London - Department of Physics & Astronomy, University College London, 2006.
 - [18] P. R. Bunker and P. Jensen. *Fundamentals of Molecular Symmetry*. NRC, Research Press, 2005.
 - [19] A. Carrington and R. A. Kennedy. Infrared predissociation spectrum of the H_3^+ ion. *J. Chem. Phys.*, 81:91–112, 1984.
 - [20] I. R. McNab. The spectroscopy of H_3^+ . *Adv. Chem. Phys.*, 89:1–87, 1995.
 - [21] M. Berblinger, J. M. Gomez-Llorente, E. Pollak, and C. Schlier. Photodissociation dynamics of the D_2H^+ molecular ion. *Chem. Phys. Lett.*, 146:353–357, 1988.
 - [22] A. V. Chambers and M. S. Child. Barrier effects on the vibrational predissociation of D_2H^+ . *Mol. Phys.*, 65:1337–1344, 1987.
 - [23] A. Carrington, I. R. McNab, and Y. D. West. Infrared predissociation spectrum of the H_3^+ ion. II. *J. Chem. Phys.*, 98:1073–1092, 1993.

- [24] M. S. Child. The estimation of vibrational predissociation lifetimes. *J. Chem. Soc. Faraday Trans. II, Molec. Chem. Phys.*, 82:1143–1149, 1986.
- [25] R. Pfeiffer and M. S. Child. Towards an understanding of the predissociation excitation spectrum of H_3^+ . *Mol. Phys.*, 60:1367–1378, 1987.
- [26] E. Pollak and C. Schlier. Theory of Unimolecular Dissociation of Small Metastable Molecules and Ions As Exemplified by H_3^+ . *Acc. Chem. Res.*, 22:223–229, 1989.
- [27] J.M. Gomez Llorente and E. Pollak. A classical trajectory study of the photodissociation spectrum of H_3^+ . *J. Chem. Phys.*, 90:5406, 1989.
- [28] C. R. Le Sueur, J. R. Henderson, and J. Tennyson. Gateway states and bath states in the vibrational spectrum of H_3^+ . *Chem. Phys. Lett.*, 206:429–436, 1993.
- [29] J. J. Munro, J. Ramanlal, J. Tennyson, and H. Y. Mussa. Properties of high-lying vibrational states of the H_3^+ molecular ion. *Mol. Phys.*, 104:115–125, 2006.
- [30] A.V. Chambers and M.S. Child. Barrier effects on the vibrational predissociation of HD_2^+ . *Mol. Phys.*, 65:1337–1344, 1988.
- [31] M. Berblinger, C. Schlier, and E. Pollak. Isotope effects in the photodissociation dynamics of the H_3^+ molecular ion. *J. Phys. Chem.*, 93:2319–2328, 1989.
- [32] J. M. Gomez Llorente and E. Pollak. A classical trajectory study of the photodissociation spectrum of H_3^+ . *J. Chem. Phys.*, 90:5406–5418, 1989.
- [33] S. Miller and J. Tennyson. Calculation of the high angular momentum dissociation limit for H_3^+ and H_2D^+ . *Chem. Phys. Lett.*, 145:117–120, 1988.
- [34] S. Carter and W. Meyer. A variational method for the calculation of vibrational energy levels of triatomic molecules using a Hamiltonian in hyperspherical coordinates. *J. Chem. Phys.*, 93(12):8902–8914, 1990.
- [35] W. Meyer, P. Botschwina, and P. Burton. *Ab initio* calculation of near-equilibrium potential and multipole moment surfaces and vibrational frequencies of H_3^+ and its isotopomers. *J. Chem. Phys.*, 84(2):891–900, 1986.
- [36] J. R. Henderson and J. Tennyson. All the vibrational bound states of H_3^+ . *Chem. Phys. Lett.*, 173:133–138, 1990.

- [37] J. R. Henderson, J. Tennyson, and B.T. Sutcliffe. All the bound vibrational states of H_3^+ : a reappraisal. *J. Chem. Phys.*, 98:7191–7203, 1993.
- [38] M. J. Bramley, J. W. Tromp, T. Carrington Jr, and G. C. Corey. Efficient calculation of highly excited vibrational-energy levels of floppy molecules - the band origins of H_3^+ up to 35000 cm^{-1} . *J. Chem. Phys.*, 100:6175, 1994.
- [39] V. A. Mandelshtam and Howard S. Taylor. The quantum resonance spectrum of the H_3^+ molecular ion for $J = 0$. An accurate calculation using filter diagonalization. *J. Chem. Soc., Faraday Trans.*, 93:847–860, 1997.
- [40] M. A. Kostin, O. L. Polyansky, J. Tennyson, and H. Y. Mussa. Rotation-vibration states of H_3^+ at dissociation. *J. Chem. Phys.*, 118(8):3538–3542, 2003.
- [41] O. L. Polyansky, R. Prosmiti, W. Klopper, and J. Tennyson. An accurate, global, ab initio potential energy surface for the H_3^+ molecule. *Mol. Phys.*, 98:261–273, 2000.
- [42] J. R. Henderson and J. Tennyson. Calculated spectrum for near-dissociation H_3^+ : a first attempt. *Mol. Phys.*, 89:953–963, 1996.
- [43] R. J. LeRoy and R. B. Bernstein. Dissociation energy and long-range potential of diatomic molecules from vibrational spacings of higher levels. *J. Chem. Phys.*, 52(8):3869–3879, 1970.
- [44] F. Luo, C. F. Giese, and W. R. Gentry. Direct measurement of the size of the helium dimer. *J. Chem. Phys.*, 104(3):1151–1154, 1996.
- [45] J. S. Briggs, S. Boonchui, and S. Khemmani. The derivation of time-dependent Schrödinger equations. *Journal of Physics A: Mathematical and Theoretical*, 40(6):1289–1302, 2007.
- [46] J. K. L. MacDonald. Successive Approximations by the Rayleigh-Ritz Variation Method. *Phys. Rev.*, 43(10):830–833, May 1933.
- [47] P. R. Bunker and P. Jensen. *Molecular Symmetry and Spectroscopy*. NRC, Research Press, second edition edition, 1998.
- [48] M. Born and R. Oppenheimer. Zur quantentheorie der molekeln. *Ann. Phys.*, 389:457–484, 1927.

- [49] H. Essén. The physics of the Born-Oppenheimer approximation. *Int. J. Q. Chem.*, 12:721–735, 1977.
- [50] C. F. Giese and W. R. Gentry. Classical trajectory treatment of inelastic scattering in collisions of H^+ with H_2 , HD, and D_2 . *Phys. Rev. A*, 10(6):2156–2173, 1974.
- [51] R. Schinke, M. Dupuis, and Jr. W. A. Lester. Proton- H_2 scattering on an ab initio CI potential energy surface. I. vibrational excitation at 10 ev. *J. Chem. Phys.*, 72(7):3909–3915, 1980.
- [52] R. Schinke. Proton- H_2 scattering on an ab initio CI potential energy surface. II. combined vibrational-rotational excitation at 4.67 and 6 ev. *J. Chem. Phys.*, 72(7):3916–3922, 1980.
- [53] M. J. Bramley, J. R. Henderson, J. Tennyson, and B. T. Sutcliffe. On the Meyer-Botschwina-Burton potential energy surface for h_3^+ . *J. Chem. Phys.*, 98(12):10104–10105, 1993.
- [54] R. Prosmiti, O. L. Polyansky, and J. Tennyson. An accurate, global, ab initio potential energy surface for the H_3^+ molecule. *Chem. Phys. Lett.*, 273:107–114, 1997.
- [55] A. Aguado, O. Roncero, C. Tablero, C. Sanz, and M. Paniagua. Global potential energy surfaces for the H_3^+ system. Analytical representation of the adiabatic ground-state $1^1A'$ potential. *J. Chem. Phys.*, 112:1240–1254, 2000.
- [56] L. P. Viegas, A. Alijah, and A. J. C. Varandas. Accurate ab initio based multisheeted double many-body expansion potential energy surface for the three lowest electronic singlet states of H_3^+ . *J. Chem. Phys.*, 126(7):074309, 2007.
- [57] P. W. Atkins and R. S. Friedman. *Molecular Quantum Mechanics*. Oxford University Press, 2001.
- [58] N. Moiseyev. Quantum theory of resonances: calculating energies, widths and cross-sections by complex scaling. *Phys. Rep.*, 302:212–293, 1998.
- [59] H. S. Taylor, G. V. Nazarov, and A. Golebiewski. Qualitative aspects of resonances in electron-atom and electron-molecule scattering, excitation, and reactions. *J. Chem. Phys.*, 45(8):2872–2888, 1966.

- [60] A. U. Hazi and H. S. Taylor. Stabilization method of calculating resonance energies: Model problem. *Phys. Rev. A*, 1(4):1109–1120, Apr 1970.
- [61] B. Simon. Quadratic form techniques and the Balslev-Combes theorem. *Commun. Math. Phys.*, 27:1–9, 1972.
- [62] N. Moiseyev and J. O. Hirschfelder. Representation of several complex co-ordinate methods by similarity transformation operators. *J. Chem. Phys.*, 88(2):1063–1065, 1988.
- [63] U. V. Riss and H. D. Meyer. Calculation of resonance energies and widths using the complex absorbing potential method. *J. Phys. B: At. Mol. Opt. Phys.*, 26:4503–4536, 1993.
- [64] N. Moiseyev, S. Friedland, and P. R. Certain. Cusps, theta trajectories, and the complex virial theorem. *J. Chem. Phys.*, 74(8):4739–4740, 1981.
- [65] S. Skokov, J. M. Bowman, and V. A. Mandelshtam. Calculation of resonance states of non-rotating HOCl using an accurate abinitio potential. *Phys. Chem. Chem. Phys.*, 1:1279 – 1282, 1999.
- [66] A. Callegari and T. R. Rizzo. State-to-state unimolecular reaction dynamics of highly vibrationally excited molecules. *Chem. Soc. Rev.*, 30:214–225, 2001.
- [67] B. Poirier and T. Carrington Jr. Semiclassically optimized complex absorbing potentials of polynomial form. I. Pure imaginary case. *J. Chem. Phys.*, 118(1):17–28, 2003.
- [68] B. Poirier and T. Carrington Jr. Semiclassically optimized complex absorbing potentials of polynomial form. II. Complex case. *J. Chem. Phys.*, 119(1):77–89, 2003.
- [69] D. E. Manolopoulos. Derivation and reflection properties of a transmission-free absorbing potential. *J. Chem. Phys.*, 117(21):9552–9559, 2002.
- [70] T. Gonzalez-Lezana, E. J. Rackham, and D. E. Manolopoulos. Quantum reactive scattering with a transmission-free absorbing potential. *J. Chem. Phys.*, 120:2247, 2004.
- [71] J. G. Muga, J. P. Palao, B. Navarro, and I. L. Egusquiza. Complex absorbing potentials. *Physics Reports*, 395:357–426, 2004.

- [72] O. Shemer, Da. Brisker, and N. Moiseyev. Optimal reflection-free complex absorbing potentials for quantum propagation of wave packets. *Phys. Rev. A*, 71(3):032716, 2005.
- [73] Z. Bačić and J. C. Light. Theoretical methods for rovibrational states of floppy molecules. *Annual Review Of Physical Chemistry*, 40:469–498, 1989.
- [74] J. C. Light and T. Carrington. Discrete-variable representations and their utilization. *Adv. Chem. Phys.*, 114:263–310, 2000.
- [75] J. C. Light, I. P. Hamilton, and J. V. Lill. Generalized discrete variable approximation in quantum mechanics. *J. Chem. Phys.*, 82(3):1400–1409, 1985.
- [76] A. S. Dickinson and P. R. Certain. Calculation of matrix elements for one-dimensional quantum-mechanical problems. *J. Chem. Phys.*, 49(9):4209–4211, 1968.
- [77] J. Tennyson. Why calculate the spectra of small molecules. *J. Chem. Soc. Faraday Trans.*, 88(22):3271–3279, 1992.
- [78] R. B. Walker and J. C. Light. Reactive molecular collisions. *Ann. Rev. Phys. Chem.*, 31(1):401–433, 1980.
- [79] R. Radau. *Ann. Sci. Ecole Normale Superior*, 5:311, 1868.
- [80] H. Wei and Jr. T. Carrington. The discrete variable representation of a triatomic Hamiltonian in bond length–bond angle coordinates. *J. Chem. Phys.*, 97(5):3029–3037, 1992.
- [81] B. T. Sutcliffe and J. Tennyson. A general treatment of vibration-rotation coordinates for triatomic molecules. *Int. J. Quant. Chem.*, XXXIX:183–196, 1991.
- [82] J. Tennyson and B. T. Sutcliffe. The *ab initio* calculation of the vibrational-rotational spectrum of triatomic systems in the close-coupling approach, with KCN and H₂Ne as examples. *J. Chem. Phys.*, 77(8):4061–4072, 1982.
- [83] J. Tennyson and B. T. Sutcliffe. Variationally exact ro-vibrational levels of the floppy CH₂⁺ molecule. *J. Mol. Spectrosc.*, 101(1):71 – 82, 1983.
- [84] D. M. Brink and G. R. Satchler. *Angular Momentum*. Clarendon Press, Oxford, 1979.

- [85] J. Tennyson and B. T. Sutcliffe. Dcretization to avoid singularities in vibration-rotation hamiltonians: A bisector embedding for AB₂ triatomics. *Int. J. Quant. Chem.*, 42(4):941–952, 1992.
- [86] M. A. Kostin, O. L. Polyansky, and J. Tennyson. Calculations of rotation-vibration states with the z axis perpendicular to the plane: High accuracy results for H₃⁺. *J. Chem. Phys.*, 116:7564–7573, 2002.
- [87] J. R. Henderson, C. R. Le Sueur, S. G. Pavett, and J. Tennyson. Coordinate ordering in the discrete variable representation. *Comp. Phys. Comms.*, 74(2):193 – 198, 1993.
- [88] U. V. Riss and H. D. Meyer. The transformative complex absorbing potential method: a bridge between complex absorbing potentials and smooth exterior scaling. *J. Phys. B: At. Mol. Opt. Phys.*, 31(10):2279–2304, 1998.
- [89] Ed Akin. *Object-Oriented programming via FORTRAN 90/95*. Cambridge Press, 2003.
- [90] James Rumbaugh, Ivar Jacobson, and Grady Booch. *The Unified Modeling Language Reference Manual*. Addison-Wesley, second edition, 2005.
- [91] Bruce Eckel. *Thinking in C++*. Prentice Hall, second edition, 2000.
- [92] E. Anderson, Z. Bai, C. Bischof, S. Blackford, J. Demmel, J. Dongarra, J. Du Croz, A. Greenbaum, S. Hammarling, A. McKenney, and D. Sorensen. *LAPACK Users’ Guide*. Society for Industrial and Applied Mathematics, Philadelphia, PA, third edition, 1999.
- [93] B. Chapman, G. Jost, R. van der Pas, and D. J. Kuck. *Using OpenMP: Portable Shared Memory Parallel Programming*. MIT Press, 2007.
- [94] *Open MPI: A Flexible High Performance MPI*, Poznan, Poland, September 2005.
- [95] H. Y. Mussa and J. Tennyson. Bound and quasi-bound rotation-vibrational states using massively parallel computers. *Computer Phys. Comm.*, 128:434–445, 2000.
- [96] S. Skokov, K. A. Peterson, and J. M. Bowman. An accurate ab initio HOCl potential energy surface, vibrational and rotational calculations, and comparison with experiment. *J. Chem. Phys.*, 109(7):2662–2671, 1998.

- [97] R. J. Barnes, G. Dutton, and A. Sinha. Unimolecular Dissociation of HOCl Near Threshold: Quantum State and Time-Resolved Studies. *J. of Phys. Chem. A*, 101(45):8374–8377, 1997.
- [98] J. Tennyson, P. Barletta, J. J. Munro, and B. C. Silva. The role of asymptotic vibrational states in H_3^+ . *Phil. Trans. R. Soc. Lond. A*, 364:2903, 2006.
- [99] B. M. Dinelli, C. Ruth Le Sueur, J. Tennyson, and R. D. Amos. Ab initio ro-vibrational levels of H_3^+ beyond the born-oppenheimer approximation. *Chem. Phys. Lett.*, 232:295, 1995.
- [100] R. J. Le Roy. LEVEL 7.5: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels. Chemical physics research report, University of Waterloo, 2005.
- [101] O. L. Polyansky and J. Tennyson. *Ab initio* calculation of the rotation-vibration energy levels of H_3^+ and its isotopomers to spectroscopic accuracy. *J. Chem. Phys.*, 110:5056–5064, 1999.
- [102] J. C. Light and Z. Bačić. Adiabatic approximation and nonadiabatic corrections in the discrete variable representation: Highly excited vibrational states of triatomic molecules. *J. Chem. Phys.*, 87(7):4008–4019, 1987.
- [103] J. R. Henderson and J. Tennyson. Very highly excited vibrational states of LiCN using discrete variable representation. *Mol. Phys.*, 69:639–648, 1990.
- [104] A. Ernesti and J. M. Hutson. On the rotational constants of floppy molecules. *Chem. Phys. Lett.*, 222:257–262, 1994.
- [105] D. J. Nesbitt and R. Naaman. On the apparent spectroscopic rigidity of floppy molecular systems. *J. Chem. Phys.*, 91(7):3801–3809, 1989.
- [106] A. Messiah. *Quantum Mechanics*. Dover Publications, Inc., New York, 1999.
- [107] D.W. Schwenke. Beyond the potential energy surface: Ab initio corrections to the born-oppenheimer approximation for H_2O . *J. Phys. Chem. A*, 105(11):2352–2360, 2001.
- [108] P. R. Bunker and R. E. Moss. The breakdown of the born-oppenheimer approximation: the effective vibration-rotation hamiltonian for a diatomic molecule. *Mol. Phys.*, 33:417–424, 1977.

- [109] R. E. Moss and L. Valenzano. Adiabatic and non-adiabatic corrections to properties of the hydrogen molecular cation and its isotopomers: dissociation energies and bond lengths. *Mol. Phys.*, 100:649–654, 2002.
- [110] P. Barletta, B. C. Silva, J. J. Munro, and J. Tennyson. *Ab initio* spectroscopy of D_2H^+ near dissociation. *Molec. Phys.*, 104:2801–2814, 2006.
- [111] G. Drolshagen, F. A. Gianturco, and J. P. Toennies. Vibrational breakup of triatomic collision complexes - a model study for $\text{H}+\text{H}_2$. *Israel J. Chem.*, 29:417–425, 1989.
- [112] C. Schlier and U. Vix. Lifetimes of triatomic collision complexes. *Chem. Phys.*, 95:401–409, 1985.
- [113] J. Tennyson and J. R. Henderson. Highly excited rovibrational states using a discrete variable representation: The H_3^+ molecular ion. *J. Chem. Phys.*, 91(7):3815–3825, 1989.
- [114] M. Ashworth, I. J. Bush, M. F. Guest, A. G. Sunderland, S. Booth, J. Hein, L. Smith, K. Stratford, and A. Curioni. HPCx: towards capability computing. *Concurrency Computat.: Pract. Exper.*, 17:1329–1361, 2005. Computer hardware reference.
- [115] S. Heilliette, A. Delon, R. Jost, S. Y. Grebenshchikov, R. Shinke, B. Abel, and J. C. Rayez. *J. Phys. Chem.*, 8:1069, 2001.
- [116] P. Maksyutenko, T. R. Rizzo, and O. V. Boyarkin. A direct measurement of the dissociation energy of water. *J. Chem. Phys.*, 125(18):181101, 2006.
- [117] P. Maksyutenko, J. S. Muentner, N. F. Zobov, S. V. Shirin, O. L. Polyansky, T. R. Rizzo, and O. V. Boyarkin. Approaching the full set of energy levels of water. *J. Chem. Phys.*, 126(24):241101, 2007.
- [118] A.D. Bykov, N.N. Lavrentieva, T.P. Mishina, L.N. Sinitsa, R.J. Barber, R.N. Tolchenov, and J. Tennyson. Water vapor line width and shift calculations with accurate vibration-rotation wave functions. *J. Quant. Spectr. Rad. Trans.*, 109(10):1834 – 1844, 2008.