Resonances in electron molecule scattering

An approach for their identification and a study of dissociative electron attachment to \( \text{H}_2 \) and \( \text{SO}_2 \)

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Abstract

This thesis investigates the role of resonances in electron-molecule scattering with a particular focus on their facilitation of dissociative electron attachment (DEA). It examines the resonances in electron scattering from H₂ and SO₂ and explores, both through application and implementation, methods for their identification and characterisation.

We present an implementation of a technique for the identification and characterisation of resonances based on the analytical continuation of the Jost function. Tests are carried out using analytical and molecular R-matrix data sets in order to investigate the strengths and limitations of the technique.

Scattering calculations are carried out for H₂ and SO₂ using the R-matrix method to allow: i) application of various existing techniques to identify and characterise the resonances in these systems; ii) identification of links from the resonances to DEA and other experimental works.

Velocity slice imaging (VSI) experiments of electron scattering from H₂ have revealed asymmetries in the momentum distributions of dissociated hydrogen anions at energies around 15 eV. In order to investigate this time-delays are used for the identification and characterisation of 35 resonances (∼30 are newly discovered) between bond lengths of 1.1 to 4.0 a₀ for energies from 12 to 15 eV. None of our calculated resonances could reproduce the asymmetries in the momentum distributions using a simple two resonance model provided in the literature.

For electron scattering from SO₂ there are inconsistencies between the resonances reported in the experimental and theoretical literature. To provide a more accurate and definitive description of the resonances time-delays and eigenphase sums are used for the identification and characterisation of six resonances at equilibrium geometry for energies up to 10 eV. A major finding is that even with 300 target states included in the calculation the results are not converged. Analysis shows our results are potentially compatible with experiment, although further work is still required.
To Eric, Norah and Hugo
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Utmost thanks to Prof Jimena Gorfinkiel, for granting me this opportunity, despite all the risk involved with a part time PhD. For all your attentiveness, guidance, knowledge and solid feedback throughout.

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Chapter 1

Introduction

Scattering is a process which occurs throughout nature and within man-made environments, affecting the world around us, as well as how we interact with it. From the seemingly simple act of looking at something, where photons are scattered from the observed objective; to the electron-molecule scattering experiments of interest to this thesis, there is often the same general motivation at play when humans (or other sentient beings) are involved: finding out about the target (or objective) from which we are scattering. In the electron-molecule scattering experiment we usually want to map the internal structure of the target or study its reactions with the scattering electron. These experiments, although performed under laboratory conditions, and the corresponding theoretical findings, often relate to interesting processes occurring, without direct intervention, in nature. We will discuss some of these in more detail shortly.

The topic of interest to this thesis is electron-molecule scattering and, in particular, the formation of resonances and the associated reactions which can occur in these systems. In this thesis a resonance is mostly regarded as a temporary electronic state in the continuum. It usually indicates an increased likelihood of a reaction or interaction being observed or a reaction which would otherwise not occur without the resonance state. We will describe the physics relating to the resonance more fully later but for now note that the resonant reactions of interest occur predominantly at low scattering electron energies (approximately below the ionisation thresholds of the molecule).

Although there are several electron-molecule scattering processes which can be considered as being enabled or enhanced by resonances (we will detail them below) one particular process, dissociative electron attachment (DEA), has been the subject of intense theoretical and experimental study over many decades. The reason for this interest is the consequence of the reaction: DEA results in molecular fragmentation, at energies below the ionisation thresholds, into atoms and/or molecules, with the incident electron remaining attached to one of the fragments.

Therefore in order to better understand reactions such as DEA, it is vital that we understand resonances in electron-molecule scattering so that we can develop more sophisticated means of identifying and characterising them from our computational scattering data. The modelling of these processes, as we will discover shortly, is of importance to other scientific fields, some of which are practically relevant, such as radiation biology. In addition, resonances are also interesting as a topic of purely theoretical study, as they are a phenomenon arising from the quantum nature of the electron-molecule system.

The main work of this thesis is an implementation of a new method for the identification and characterisation of resonances and a study of DEA to H$_2$ and SO$_2$. 
1.1 Overview of Electron-Molecule Scattering

At high enough energies (well above the ionisation threshold) the incident electron essentially interacts with a "snapshot" of the molecule, where the electronic and vibrational/rotational motions of the nuclei can be assumed as fixed in space over the period of interaction. At these energies, the Hamiltonian describing the scattering can be formed using an average effective field for the electrons (we'll discuss a general approach to how the motions of the nuclei are handled shortly).

For low energy electron-molecule scattering (below the ionisation threshold) the electronic degrees of freedom must be accounted for to provide a good description of the effects arising from the interactions between the individual electrons, such as exchange and polarisation. The techniques used at these energies which properly account for the low energy electron interactions are referred to as \textit{ab initio}.

The intermediate energy regime (just above the ionisation threshold) presents its own set of computational difficulties: at these energies (where the incident electron energy straddles the molecular ionisation potential) the higher angular momenta and increased number of scattering channels make the \textit{ab initio} computations too complicated for completion in reasonable time frames. However, the electron energies are insufficiently high to use the more approximate high energy approaches [1].

For all the energy regimes in electron-molecule scattering the Fixed-Nuclei approximation is often applied, where the nuclei are assumed to be static over the period of interaction. Here, the scattering problem can be solved separately for different geometries of the target molecule. Modelling in this manner provides an initial analysis of the resonances and is usually sufficient when the motions of the nuclei are not of concern. For a treatment of electron-molecule collisions accounting for the vibrational nuclear motion (which are a requisite for a proper description of DEA) theoretical approaches such as the local complex potential must be used [2].

In this thesis we studied resonances in low energy electron-molecule scattering within the Fixed-Nuclei approximation using the R-matrix method [1], with sufficiently detailed target and scattering descriptions for good modelling of the exchange and polarisation effects. The R-matrix method is one of several used to perform \textit{ab initio} calculations to model low energy electron collisions. Other techniques are available, such as the Kohn and Schwinger variational methods [3, 4, 5]. The R-matrix method will be described in detail and its advantages highlighted in chapter 2.

1.1.1 Resonance Enhanced and Enabled Scattering Processes

During the formation of a resonance the incident electron is temporarily captured by the target. Most simply, a resonance can result in an increase to the elastic scattering cross section around the vicinity of the resonance energy (resonance enhanced elastic scattering). Other processes can also be enhanced by the presence of resonances, such as electronic excitation. Additionally, some scattering processes are enabled by resonant states, such as DEA, as already mentioned. With $A$ and $B$ representing atomic or molecular fragments and $i$, $j$, $k$ electronic, vibrational and rotational excitation states respectively we can represent the molecular processes\textsuperscript{1} that either occur or are significantly enhanced by resonances as follows:

\textsuperscript{1}We consider here only reactions involving an initially neutral molecule.
Elastic scattering:
\[ AB + e^- \rightarrow AB + e^- \]  \hspace{1cm} (1.1)

Electronic, vibrational and/or rotational excitation (with primes representing excitations):
\[ AB(i, v, j) + e^- \rightarrow AB(i', v', j') + e^- \]  \hspace{1cm} (1.2)

Electron impact dissociation:
\[ AB + e^- \rightarrow A + B + e^- \]  \hspace{1cm} (1.3)

Dissociative electron attachment:
\[ AB + e^- \rightarrow AB^-* \rightarrow A + B^- \]  \hspace{1cm} (1.4)

The intermediate \( AB^-* \) system shown for DEA is a temporary (indicated with the *) anion or quasi-bound or resonance intermediate state, where the electron can be considered as temporarily attached to the molecule \( AB \). This state may also form for the other reactions but is nearly always a necessary step for DEA to occur. In addition, this state may be excited if the incident electron energy is sufficient.

1.2 Resonances

We started with an initial definition of a resonance as being a temporary electronic state in the continuum. In this section we discuss resonances from a more fundamental perspective. Resonances are a phenomena which can arise from interactions with any system displaying wave-like properties. As quantum mechanics is a theory which, by design, accounts for the wave-like nature of matter, resonance behaviour is to be expected in the systems which it describes. For a simple illustration we briefly consider the steady-state solutions of the one dimensional TISE for a particle in a square well of depth \( V_0 \) and half-width \( a \), centered about the origin. Here the total energy can be written in terms of the wavevector \( k \) as:
\[ E = \frac{\hbar^2 k^2}{2m} + V \]  \hspace{1cm} (1.5)

where \( m \) is the particle mass, \( \hbar \) the Plank constant and \( V \) the potential (with \( V = 0 \) over the interval of the well and \( V = V_0 \) outside the interval of the well). The solutions of the TISE outside the well are:
\[ \psi(x) = \begin{cases} 
A e^{ikx} + B e^{-ikx} & x < -a \\
C e^{ikx} + D e^{-ikx} & x > a 
\end{cases} \]  \hspace{1cm} (1.6)

where \( A, B, C \) and \( D \) are constants which can be determined on application of the appropriate boundary conditions. Applying these boundary conditions allows solving for the transmission probability, \( T \) [6]:
\[ T = \left[ 1 + \frac{V_0^2 \sin^2(ka)}{4E(E-V_0)} \right]^{-1} \]  \hspace{1cm} (1.7)

Then perfect transmission occurs when the fractional term becomes zero, which for real energies above the well \( (E > V_0) \), is dependent on the \( \sin^2(ka) \) term and occurs when \( ka = n\pi \) (as illustrated
1.2 Resonances

in figure 1.1, where perfect transmission can be seen to occur at the energy peaks where \( T = 1 \). These peak energies are a result of constructive interference between waves reflected internally at the boundaries of the well, resulting in perfect transmission through the well. Additionally, at these peak energies, there is a whole number of wavelengths between \(-a\) and \(+a\), meaning the incident particle beam at these energies behaves in the same manner as if the well wasn’t there. Between the peaks are minimums, caused by destructive interference between the internally reflected waves.

It’s also interesting to note that the scaling of the occurrence of the zeros of \( \sin^2(ka) \) is with \( E^2 \), meaning that the resonance will widen (and thus its “effect” lessen) approximately with the energy squared and the classical, zero-resonance limit approached as the particle energy tends to infinity (see figure 1.1, in particular the change to the spacing of the peaks).

![Figure 1.1: Transmission probability, T, as given by equation (1.7), when scattering from a square well potential for \( \frac{mV_0a^2}{\hbar^2} = 40 \) as a function of \( E/V_0 \).](image)

This is a basic illustration of the resonance as arising from the wave-like nature of quantum particles. We will also consider in chapter 2 resonances in the case of trapping potentials (which, as we’ve just seen, isn’t a necessary condition for a resonance) and how resonances relate to poles in the scattering quantities.² These poles occur not just for resonances but for bound and virtual states as well and arise as a result of the required constraints for proper asymptotic solutions of the TISE.

An important property of a resonance state is its lifetime. In the picture above when the particle is within the region of the well it can experience reflections at the boundaries, meaning the particle effectively becomes trapped over the interval of the well for a period of time. Generally, resonances have an energy width, \( \Gamma \), which is related, via the uncertainty principle to their lifetime, \( \tau \):³

\[
\tau \simeq \frac{\hbar}{\Gamma}
\]  

(1.8)

The initial one dimensional picture discussed is a very simple one and if anything, can only really be applied as an analogy to scattering from targets with a simple internal structure. Targets with more complicated internal structures, which are outside the scope of this simple picture, are what give rise to the novel resonance enabled processes in electron-molecule scattering, such as DEA.

²Although it is possible to construct potentials with resonance effects but no associated poles [7] this isn’t of interest to this work.

³It’s interesting to note that the resonant state is considered to have a finite energy uncertainty yet arises from the solutions to the TISE (where \( \Delta E = 0 \)).
As already mentioned, we will develop this fundamental picture of the resonance further in chapter 2, turning the current discussion back to how the resonance affects the observables relevant to electron-molecule scattering. Resonances in scattering experiments are, in the simplest case, observed as peaks centred around an energy in the resultant spectra. In molecular experiments these peaks can be observed in scattering cross sections or ion yields measured across a range of incident electron energies. It’s worth mentioning that many resonances are so wide as to have no significant effect on the experimental observables and that not all resonances lead to DEA (more on this latter point below).

Over the course of the collision changes to the target state can occur, such as electronic or vibrational excitation, which in turn will influence the interaction. The state of the target on temporary attachment of the scattering electron is referred to as the parent state. Resonances can be classified on both the parent state and the energy of the parent state relative to that of the resonant state. More generally, a resonance can be associated with more than one parent state. This classification is well described in the literature [8, 9, 10] and includes:

- **Shape resonances.** This is the simplest form of resonance. It occurs when an incident electron attaches to the target in its ground electronic state. In other words, shape resonance have the ground electronic state of the target as parent.

- **Core-excited resonances.** These resonances occur when an incident electron electronically excites the target molecule and then attaches to an empty orbital. There are two types depending on whether the resonance energy is below or above that of the excited parent state.
  - Electronic Feshbach resonances: When the energy of the resonance is below that of the parent state energy.
  - Core-excited shape resonances: When the energy of the resonance is above that of the parent state energy.

- **Vibrational Feshbach resonances.** When the incident electron energy is very low, the electron can attach to the ground state of the molecule forming a dipole-bound state, whose energy is slightly lower than that of the ground state of the neutral. The electron energy is transferred to molecular vibrations and it is these anion vibrational states that are resonant.

### 1.3 Dissociative Electron Attachment

DEA is a prevalent enough reaction to require consideration in many physical environments involving electron-molecule collisions, such as plasmas, the interstellar medium (ISM) and atmospheres (including our own) and surface physics etc. DEA is one of the reactions responsible for the breakup of DNA, via low energy electrons liberated from other nearby atoms and/or molecules [11] via processes such as photoionisation. In the field of medicine this DEA induced damage of DNA is an important when considering the effects of radiation therapy and imaging on the human body. The recent review by Fabrikant et. al [12] provides a good summary for DEA across relevant fields.

We now give a brief overview of the DEA process and how it links to resonant states, as well as other processes competing with DEA. A more detailed description of the DEA process can be found in recent reviews [11, 14, 12]. Following formation of the temporary anion, its decay mechanism is dependent on what routes are energetically available and the lifetime (width) of the resonance state. In some cases auto-detachment of the electron will occur, accompanied by decay of the target to an
energetically accessible vibrational and rotational state of the ground or parent electronic state. Here
the resonance state will not lead to DEA. Sometimes decay to the parent state is not energetically
possible (which is the case for Feshbach resonances); the auto-detachment process in these cases will
occur via decay to electronic states lower in energy than the parent state, (again into an energetically
accessible vibrational and rotational state). Since the target will need to effectively rearrange itself
from the parent state to the energetically accessible state the lifetimes of Feshbach resonances are
typically longer lived than shape and core-excited resonances. If the temporary anion is sufficiently
vibrationally excited for dissociation to occur and the molecule fragments before the electron can
auto-detach then DEA will have occurred and in this case the scattering electron will remain attached
to one of the dissociated fragments. Figure 1.2 shows how these processes relate to the potential
energies of the ground, anionic and resonance states for the variation of the nuclear separation of a
diatomic molecule. This figure also shows how the ion yield as a function of the scattering electron
energy relates to the potential energies of the ground and anionic states for the variation of the nuclear separation of a diatomic molecule.

Typically, shape and core-excited shape resonances have shorter lifetimes (and are therefore wider) than Feshbach resonances. This is because (for shape and core-excited shape resonances) the decay mechanism is directly into the ground state or parent state, which is usually a relatively quick process. With Feshbach resonances decay to the parent state is not available [14].

It’s possible that a single DEA process can proceed via more than one resonance. As the molecular nuclei move relative to one another the DEA path can switch from one resonance to another. Additionally resonances which are close enough and/or with widths high enough to be considered as overlapping can result in superposition effects.

Experimentally, DEA has traditionally been studied using negative ion mass spectrometry [15, 16]. A more recent technique, velocity slice imaging (VSI), allows the angular distributions of the DEA produced anions to be obtained [17, 18, 19]. Insight into anionic resonant states, including those not leading to DEA, can also be gained from experimental studies such as electron energy loss spectra. Several techniques have been developed allowing measurements such as cross sections [20, 21] and current transmissions [22] to be obtained. In many case cases the measurements relating to vibrational excitations of the neutral molecule occur via an intermediate state of the anionic resonance of interest, which may or may not be vibrational depending on whether the resonance supports vibrational excitations from the ground state or not.

1.4 Identification and Characterisation of Resonances

Several theoretical techniques currently exist to facilitate identifying and characterising resonances. Many of these approach the problem by attempting to fit a physically meaningful function of energy in the vicinity of the resonance. The usual form of the fitted function is a Lorentzian (or related Breit-Wigner form [7]) with a background polynomial, which can be applied to the cross section, K-matrix, eigenphase sum (the multi channel phase shifts induced by the scattering event) or the time-delay. Whether a resonance is present or not is usually decided on the basis of a least squares difference between the fitted and the real data. However, as the resonance contribution becomes small in comparison with the background contributions, the quality of any fit will deteriorate to the point where it’s impossible to confidently identify the resonance. These background contributions can become relatively significant as the resonance widens, overlaps with other resonances or moves close to thresholds.

The aforementioned time-delay provides a powerful mechanism for analysis, allowing extraction of the resonance parameters from the eigenvalues of the Q-matrix. The time-delay can be interpreted as the additional time spent by the scattering particle in the vicinity of interaction due to the influence of the target potential. The Q-matrix is the multi-channel representation of the time-delay and once diagonalised effectively separates the resonances (and also the non-resonant contributions) across its eigenvalues. Although fitting is also carried out to Lorentzians plus a polynomial background (as with the previously mentioned scattering quantities), in general better fits will be achieved, especially for the case of overlapping resonances. Several studies have shown the time-delay technique locates resonances more conclusively than the eigenphase method [23, 24].

There are many other techniques for the identification and characterisation of resonances. Part of the work for this thesis was an implementation of one such approach based on a technique devised by
1.5 Electron Scattering from the H$_2$ and SO$_2$ Molecules

Rakityansky et al. [25]. The method makes use of Padé approximants to allow analytical continuation of a discretely valued S-matrix into the complex plane. The motivation for this work was the unreliability of the available techniques for characterising "difficult" resonances: those which are overlapping, very wide, or close to threshold (see [26] for an example). However, as we will see in chapter 3, Rakityansky et al.’s technique has its own drawbacks.

1.5 Electron Scattering from the H$_2$ and SO$_2$ Molecules

A major part of the work presented in this thesis involves R-matrix calculations for electron scattering from the H$_2$ and SO$_2$ molecules and the identification and characterisation of the resonances in these systems. These are both molecules of scientific interest, H$_2$ is a cosmically abundant molecule [27]. Both H$_2$ and SO$_2$ are molecules constituting interstellar mediums [28, 29] and planetary atmospheres [30, 31] (including our own) and are process gases for plasmas [32]. SO$_2$ is also a cause of acid rain [33].

Although both H$_2$ and SO$_2$ are relatively simple, there still remains contradictory and unexplained experimental findings around the resonant states in the anions formed from these molecules. For the energy regimes of interest to available DEA experiments there has been insufficient theoretical calculations to be confident that all resonances (or at least those associated with DEA) have been identified, which is especially true for H$_2$ [19, 34, 35]. For SO$_2$ particularly, there are some conflicts between the resonances reported in the different theoretical and experimental studies [18, 36, 37, 38, 22]. Therefore, the motivation in looking at these molecules was the need to identify and better characterise the resonances in these systems, over energy intervals of interest to experiment. We aimed to connect our identified resonances with the DEA (and for SO$_2$, vibrational spectroscopy) findings in the experimental literature. For the reasons which will be given later, our approach for resonance identification and characterisation based on Rakityansky et al.’s technique was not applicable to these molecules and more traditional approaches were used, in particular those based around the time-delay and eigenphase sum.

1.6 Objectives and Layout of the Thesis

This thesis is concerned with electron scattering from molecules with a particular focus on resonances and related processes, such as DEA. The objectives were:

1. To implement and apply, for the first time, a technique for the identification and characterisation of resonances based on analytical continuation of the S-matrix.

2. To use traditional mechanisms for the identification and characterisation of resonances to provide insight into:

   (a) DEA to H$_2$. In particular the VSI experiments which have shown an asymmetry in the angular distributions of the dissociated H$^-$ ions.

   (b) DEA to SO$_2$. In particular the resonances identified in prior experimental and theoretical works and the discrepancies on the symmetry assigned to the resonances for anion production around 7.5 eV.
1 INTRODUCTION

Following this introduction, chapter 2 presents a theoretical overview of scattering theory and resonances in scattering systems, as well as the R-matrix and quantum chemistry relevant to electron-molecule scattering. This is then followed in chapter 3 by a description of the implementation and application of a new approach for the identification and characterisation of resonances, based the technique by Rakityansky et al.. The main focus in chapter 3 is on the method of extraction and its implemenation, with little effort placed on physical analysis or even detailed presentation of the results. Chapters 4 and 5 look at the identification and characterisation of resonances in the H$_2$ and SO$_2$ molecules using more traditional methods for resonance identification and characterisation. The work presented in these two chapters involved performing R-matrix calculations. In contrast to chapter 3 emphasis is given to the application of the extraction techniques and the presentation of the resonance data obtained.
Chapter 2

Theoretical Methods

This chapter mainly presents the pre-existing theory and computational methods which form the foundation for the work presented in the subsequent chapters. This work can be roughly broken down into the following three components:

- The \textit{ab initio} scattering calculations from which we extract the resonance data. These were carried out using the R-matrix approach.
- The use of existing techniques for characterising resonances.
- The implementation and application of an alternative approach of characterising resonances based on the work of Rakityansky et al..

Section 2.1 presents a basic overview of scattering theory in order to give a common background for all three components in the list above. Primarily, the S-matrix and other useful scattering quantities are obtained. Section 2.2 then builds on these fundamentals by describing the various methods which exist for the identification and characterisation of resonances from the scattering quantities obtained in the first section.

Following this initial overview of general scattering theory and resonances, section 2.3 presents the time-independent Schrödinger Equation describing the electron-molecule scattering systems investigated. Section 2.4 discusses the R-matrix approach, which was used for our scattering calculations. Details on the methods for constructing the multi-electronic basis functions used to express the Hamiltonian (and subsequently obtain the wavefunctions through its diagonalisation) are given in section 2.5.

Finally section 2.6 gives an overview of the UKRmol+ software suite, the molecular R-matrix implementation used for the scattering calculations throughout this work.

2.1 Fundamental Scattering Theory

In this section we will introduce some fundamental concepts and ideas relating to scattering theory. This will lay a foundation for the theoretical methods discussed in the subsequent sections. Atomic units are used throughout.

We begin by considering a fairly general scattering experiment, described at asymptote in terms of an in-going state $|\psi_{\text{in}}\rangle$ and an out-going state $|\psi_{\text{out}}\rangle$. We now define an operator $S$ [7], such that:
2 THEORETICAL METHODS

\[ |\psi_{\text{out}}\rangle = S |\psi_{\text{in}}\rangle \] (2.1)

and consider the application of this expression to the TISE:

\[ H |\Psi\rangle = E |\Psi\rangle \] (2.2)

where \( E \) is the total energy of the system, \( |\Psi\rangle \) is the state vector and \( H \) is the Hamiltonian given by:

\[ H = T + V \] (2.3)

where \( T \) is the kinetic energy operator and \( V \) the potential energy operator. In order to simplify the problem we consider a position basis representation:

\[ \Psi(r) = \langle r | \Psi \rangle \] (2.4)

In this representation the Hamiltonian takes the following form:

\[ H\Psi(r) = E\Psi(r) \] (2.5)

and the potential energy operator in (2.3) takes the general form of the vector potential \( V(r) \). We now further simplify the problem [7] by reducing this potential to a radial potential \( V(r) \) which tends towards zero at infinity. Under these conditions, if the sets of \( |\psi_{\text{in}}\rangle \) and \( |\psi_{\text{out}}\rangle \) are solutions of (2.2) then we can expand both states in the orthonormal basis \( |\psi_j\rangle \), such that:

\[ |\psi_{\text{in}}\rangle = \sum_j \alpha_j |\psi_j\rangle \quad \text{and} \quad |\psi_{\text{out}}\rangle = \sum_j \beta_j |\psi_j\rangle \] (2.6)

where \( \alpha_j \) and \( \beta_j \) are complex coefficients. Inserting these into (2.1):

\[ \sum_j \beta_j |\psi_j\rangle = S \sum_j \alpha_j |\psi_j\rangle \]

Multiplying both sides by a basis bra:

\[ \sum_j \langle \psi_k | \psi_j \rangle \beta_j = \sum_j \langle \psi_k | S |\psi_j\rangle \alpha_j \quad \Rightarrow \quad \beta_k = \sum_j S_{kj} \alpha_j \]

where \( S_{kj} = \langle \psi_k | S |\psi_j\rangle \) is a complex number. We can rewrite the expression above by defining the vectors \( \alpha \) and \( \beta \) containing the coefficients:

\[ \beta = S\alpha \] (2.7)

where \( S \) is the S-matrix, relating the coefficients of the out-going and in-coming states. An important property of the S-matrix, arising from the consequence of the conservation of probability, is that it is unitary, i.e.:

\[ S^\dagger S = I \] (2.8)

where \( I \) is the identity matrix.
2.1 Fundamental Scattering Theory

2.1.1 Partial Wave Expansion

We now use the method of partial wave analysis [39] to obtain an S-matrix and other related scattering quantities. This will work by separating the wavefunction into its angular momentum components. We start by considering the TISE for a radial potential tending to zero at infinity:

$$\left(-\frac{1}{2}\nabla^2 + V(r)\right)\psi(r) = E\psi(r)$$  \hspace{1cm} (2.9)

We now write the asymptotic solutions as $\psi_A(r)$ (where the subscript $A$ indicates asymptotic). These solutions represent both the incident and scattered waves, having plane and spherical forms respectively. For convenience we set the $z$-axis to be along the direction of propagation of the incoming plane wave. Then:

$$\psi_A(r) = \lim_{r\to\infty} \psi(r) \propto e^{ikz} + \frac{e^{ikr}}{r} f(\theta)$$  \hspace{1cm} (2.10)

where $k$ is the wavenumber of the particle and is related to its energy by $E = \frac{1}{2}k^2$; $f(\theta)$ is the scattering amplitude, with the polar angle $\theta$ the scattering angle between the incident and scattered wavevectors (the azimuthal angle $\phi$ has no effect for an incident plane wave due to the symmetry of the radial potential, as is apparent in figure 2.1).

![Figure 2.1: Polar coordinates around a scattering center, O, orientated with respect to a plane wave incident along the z-axis. The position of the point, P, can be fully specified using the two angles $\theta$ and $\phi$ and the radius $r$.](image)

The scattering amplitude, $f(\theta)$, must be determined in order to calculate the observable quantities. One method of determining $f(\theta)$ is partial wave analysis, which begins by considering the solutions to (2.9), which take the following form in spherical polar coordinates:

$$\Phi(r)Y_{l,m}(\theta, \phi)$$  \hspace{1cm} (2.11)

where $Y_{l,m}(\theta, \phi)$ are the spherical harmonics, $l$ and $m$ the angular momentum and magnetic quantum numbers respectively and $\Phi(r)$ the radial solutions. We will account for the angular symmetry implied by $f(\theta)$ in equation (2.10) and illustrated in figure 2.1 later. Expressing the radial solutions in reduced form $u(r) \equiv r\Phi(r)$, we obtain the reduced radial equation [39]:

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(r) + E \right] u(r) = 0$$  \hspace{1cm} (2.12)

It is useful to consider three regions when examining the solutions to (2.12):
2 THEORETICAL METHODS

- Target region \((r \leq r_t)\): A sphere of radius \(r_t\) inside of which both \(V(r)\) and the centrifugal term \(l(l+1)/r^2\) must be taken into account.
- Intermediate region \((r > r_t)\): assuming that \(V(r)\) falls off faster than \(1/r^2\), the effect from \(V(r)\) becomes negligible and only \(l(l+1)/r^2\) will have effect.
- Asymptotic region \((r \to \infty)\): when the particle is essentially free from any influence of the target and both \(V(r)\) and \(l(l+1)/r^2\) become negligible.

In the intermediate region (indicated with an \(I\)) the general solutions are:

\[
\Phi_I(r) = A(k, r) j_l(kr) + B(k, r) n_l(kr) \tag{2.13}
\]

or, in reduced form:

\[
u_I(r) = r \Phi_I(r) \tag{2.14}
\]

where \(j_l\) and \(n_l\) are the spherical Bessel and Neumann functions of order \(l\) [40]. What we require are linear combinations to represent the scattered waves at asymptote as included in (2.10). These combinations are the spherical Hankel functions, which, as functions of \(kr\) are:

\[
h^{(1)}_l(kr) \equiv j_l(kr) + i n_l(kr) \quad \text{and} \quad h^{(2)}_l(kr) \equiv j_l(kr) - i n_l(kr) \tag{2.15}
\]

of the first and second kind respectively. In the asymptotic region, the first kind takes the following form:

\[
h^{(1)}_l(kr) \propto (-i)^{l+1} \frac{e^{ikr}}{kr} \tag{2.16}
\]

We now express the radial part of the scattered component in (2.10) as a linear combination of asymptotic Hankel functions of the first kind along with spherical harmonics for the angular part (from analogy to (2.11)) as:

\[
\psi_A(r, \theta, \phi) \propto e^{ikz} + \sum_{l,m} C_{l,m} (-i)^{l+1} \frac{e^{ikr}}{kr} Y_{l,m}(\theta, \phi) \tag{2.17}
\]

where \(C_{l,m}\) are constants. This allows us to write the scattering amplitude as:

\[
f(\theta, \phi) = \frac{1}{k} \sum_{l,m} C_{l,m} (-i)^{l+1} Y_{l,m}(\theta, \phi) \tag{2.18}
\]

which, since our potential is spherically symmetric, reduces to:

\[
f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (-i)^{l+1} \sqrt{\frac{2l+1}{4\pi}} C_l P_l(\cos \theta) \tag{2.19}
\]

where \(P_l\) are the Legendre polynomials of degree \(l\). The \(C_l\) coefficients are in general functions of \(k\). The above is often rewritten in the following form:

\[
f(\theta) = \sum_{l=0}^{\infty} (2l+1) a_l P_l(\cos \theta) \tag{2.20}
\]

Finally, we expand the incident wave, \(e^{ikz}\), in a form that satisfies the solutions of (2.12) in the
2.1 Fundamental Scattering Theory

intermediate region. Spherical Bessel functions of the first kind, \( j_l(kr) \), are appropriate here, as they are finite valued at the origin. We thus end up with the following form for the asymptotic wavefunction:

\[
\psi_A(r, \theta) \propto \sum_{l=0}^{\infty} i^l(2l + 1) \left[ j_l(kr) + ika_l h^{(1)}_l(kr) \right] P_l(\cos\theta) \tag{2.21}
\]

which we have expressed using the Hankel functions of the first kind (as given by equation (2.16)). Hence, the scattering amplitude and therefore the wavefunction (including both incident and scattered waves) at asymptote can be expressed as a series of spherical waves with increasing angular momentum, usually referred to as partial waves.

2.1.2 Scattering Quantities

We now show the relationship between the S-matrix (2.7) and the scattering amplitude for elastic scattering from a central field given by (2.20).\(^4\) We begin by considering that the conservation of particle flux means that \( A \) and \( B \) in (2.13) can only differ by a phase shift \( \delta_l(k) \) \(^4\). Then, noting that (2.12) is homogeneous so that \( Nu(r) \), for arbitrary \( N \), is also a solution, (2.14) can be written as \(^1\):

\[
u_I(r) = Nr \left[ j_l(kr) + n_l(kr) \tan\delta_l(k) \right] \tag{2.22}
\]

If we now set \( N = -2ik\cos\delta_l e^{i\delta_l} \) and use the asymptotic forms \( j_l(kr) = \frac{1}{kr} \sin(kr - \frac{1}{2} l\pi) \) and \( n_l(kr) = \frac{1}{kr} \cos(kr - \frac{1}{2} l\pi) \) we obtain:

\[
u_A(r) = e^{-i\delta_l} - e^{i\delta_l} e^{2i\delta_l(k)} \quad \text{where:} \quad \theta_l = kr - \frac{1}{2} l\pi \tag{2.23}
\]

Then, considering how the S-matrix relates the coefficients of the incoming and outgoing states at asymptote and that for partial wave scattering the S-matrix will be diagonal due to conservation of angular momentum \(^4\), the S-matrix can be expressed in terms of the phase shift as:

\[
S_l(k) = e^{2i\delta_l(k)} \tag{2.24}
\]

It is also useful to define the K-matrix:

\[
K_l(k) = \tan\delta_l(k) \tag{2.25}
\]

and the T-matrix:

\[
T_l(k) = S_l(k) - 1 \tag{2.26}
\]

Also, using (2.23), (2.20) and (2.10), it can be shown that \( a_l = \frac{1}{2\pi} \left( e^{2i\delta_l(k)} - 1 \right) \), thus allowing the scattering amplitude to be written in terms of the S-matrix \(^4\):

\[
f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l + 1) P_l(\cos\theta) (S_l - 1) \tag{2.27}
\]

We can now determine a quantity for the scattering wave intensity into a solid angle \( d\Omega = \sin\theta d\theta d\phi \) \(^4\).

\(^4\)For the case of elastic scattering from a central field, the S-matrix (2.7) will be diagonal. See discussion in section 2.1.4.
This is the angular differential cross section, \( d\sigma \) and is given by:\(^5\)

\[
d\sigma = |f(\theta)|^2 \sin \theta d\theta d\phi
\]

The integral cross section, \( \sigma \), is then the integral of \( d\sigma \) over the entire sphere surrounding the scattering region and gives the total probability that a particle undergoes scattering:

\[
\sigma = \int \int |f(\theta)|^2 \sin \theta d\theta d\phi = 2\pi \int |f(\theta)|^2 \sin \theta d\theta
\]

Then using (2.27) to replace \( f(\theta) \) above, the total cross section can be written in terms of the S-matrix as:

\[
\sigma = \frac{1}{k^2} \sum_{l=0}^{\infty} (2l + 1) |1 - S_l|^2
\]

### 2.1.3 Poles of the S-matrix

We will now explore the S-matrix in a little more detail, in particular looking at how it behaves at energies corresponding to bound, resonant and virtual states of the scattering system. We begin with a representation of the S-matrix given in [7], originally based upon work by Jost [44]. It considers the asymptotic radial solutions of the TISE as a regular solution\(^6\) of (2.12) expressed as a linear combination of spherical Hankel functions:

\[
\Phi_A(r) = F_l^{(in)}(k) h^{(1)}_l(kr) - F_l^{(out)}(k) h^{(2)}_l(kr)
\]

where the \( F_l \) indicate the Jost functions, with \( F_l^{(in)}(k) \) describing the amplitude of the incoming wavefunction and \( F_l^{(out)}(k) \) that of the outgoing one. Then, once again considering how the S-matrix relates the coefficients of the incoming and outgoing states at asymptote, and the fact that the S-matrix will be diagonal shows that the S-matrix can be written in the following fractional form:

\[
S_l(k) = \frac{F_l^{(out)}(k)}{F_l^{(in)}(k)}
\]

The Jost functions can be related to the asymptotic forms of \( A \) and \( B \) in the intermediate region solution (2.13). First consider, as implied by equation (2.23), that \( A \) and \( B \) are functions only of \( k \) (and not \( r \)) at asymptote. By then equating the amplitudes of \( j_l \) and \( n_l \) in (2.13) with (2.31), we obtain:

\[
F_l^{(in)}(k) \xrightarrow{r \to \infty} \frac{1}{2} [A(k) - iB(k)]
\]

\[
F_l^{(out)}(k) \xrightarrow{r \to \infty} \frac{1}{2} [A(k) + iB(k)]
\]

A pole in the S-matrix is said to exist where the S-matrix becomes equal to \( \pm \infty \) at some complex value of the wavenumber. We can see that poles will occur when the \( F_l^{(in)}(k) \) in equation (2.32) becomes equal to zero.

---

\(^5\)If the wavefunction is normalised such that it describes a flux of particles, this can be interpreted as the ratio of the number of scattered particles per unit time, \( dn(\theta, \psi) \), within a solid angle, \( d\Omega \) and the incident particle flux, \( F \).

\(^6\)A regular solution is zero at the origin.
2.1 Fundamental Scattering Theory

We now give a simple illustration of how these poles relate to the bound, resonant and virtual states of the scattering system by looking again at the behaviour of the wavefunction at asymptote for a 1D potential well of width width $2a$ centred about $x = 0$ and with $V_0$ the potential of the top of the well, as illustrated in figure 2.2(A). A more detailed discussion is given in [45].

![Figure 2.2](image)

Figure 2.2: Three simple systems used to illustrate the correlation between S-matrix poles and bound and resonant states. The dotted lines show the $x$ and $V$ axis, the solid lines the value of the potential as a function of $x$. System A is a square well potential, which can support bound, virtual and resonant states [46]. System B is a double barrier potential, which supports only resonant states. System C is a double delta potential, which can support only bound states. See [45, 47, 48] for details of the double delta potential.

The general solutions [6] to this 1D potential well outside the well are:

$$
\psi(x) = \begin{cases} 
Ae^{ikx} + Be^{-ikx} & x < -a \\
Ce^{ikx} + De^{-ikx} & x > a 
\end{cases}
$$

This is a repeat of (1.6), except here we are working in atomic units using hartrees, so that:

$$
k = \sqrt{2(E - V_0)}
$$

(2.35)

where $E$ and $V_0$ can be interpreted as the total and potential energies outside the well. The constants $A$, $B$, $C$ and $D$ can be determined analytically, where $A$ and $D$ can be regarded as the amplitudes of the incoming waves and $B$ and $C$ those of the outgoing, at asymptote. Irrespective of the form of the potential inside the well the S-matrix for this system satisfies:

$$
\begin{bmatrix}
B \\
C
\end{bmatrix} = \begin{bmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{bmatrix}
\begin{bmatrix}
A \\
D
\end{bmatrix}
$$

(2.36)

When $E > V_0$, $k$ is real and the asymptotic solutions are imaginary exponentials and thus oscillatory. However, when $E < V_0$, $k$ is imaginary and thus the asymptotic solutions are real exponentials. This means that in order for the wavefunction to be normalisable both $A$ and $D$ must be zero, since these belong to exponentials increasing with $|x|$. Therefore:

$$
\begin{bmatrix}
B \\
C
\end{bmatrix} = \begin{bmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{bmatrix}
\begin{bmatrix}
0 \\
0
\end{bmatrix}
$$

(2.37)

$E < V_0$

The trivial solutions where $B$ and $C$ are also zero in (2.37) cannot hold physically for bound states, since the wavefunction describing these states must be non-zero at $|x| = a$. Therefore, $B$ and $C$ are
non-zero and finite only in the indeterminate limit\(^7\) to some bound state energy, \(E_b\), for when there are \(S\) elements which are infinite. Or, in other words, the energy of the bound state pole is equal to the energy of the bound state, \(E_b\), where \(A\) and \(D\) become zero and the \(S\) element/s infinite.

For resonant states, the asymptotic form of the wavefunction is not zero by definition \[8\]; these states are not discrete in nature like bound states. To illustrate the relationship between resonance states and their associated poles we consider a particle temporarily trapped within a potential barrier, as illustrated in figure 2.2(B). By examining how the position of the poles behave as the potential barriers tend towards delta functions a simple relationship (for the case here) between poles and the nature of the potential can be appreciated \[45\].

For finite \(V_0 > E\) (figure 2.2(B)), we can solve for the S-matrix by applying the usual boundary conditions at \(x = \pm a\). We consider here the positive parity (indicated with the +) solutions and simplify by setting \(a = 1\) and assume that the barrier widths are negligibly narrow:

\[
S_+ = e^{-2ik} \frac{(k - iV_0)e^{ik} - iV_0e^{-ik}}{(k + iV_0)e^{-ik} + iV_0e^{ik}}
\] (2.38)

which has poles at:

\[
e^{2ik} = \frac{ik}{V_0} - 1
\] (2.39)

For the case \(V_0 = \infty\) the barriers are delta functions as shown in figure 2.2(C), the particles incident from the left will interact with the delta function at \(x = -a\) as if it was an impenetrable barrier and as such will be completely reflected. Between the two barriers, there will be bound states, with solutions identical to those for an infinite square well:

\[
S_+ \xrightarrow{V_0 \to \infty} e^{-2ik}
\] (2.40)

which has discrete solutions (poles) at \(k = (n + \frac{1}{2})\pi\) where \(n \geq 0\).

An interesting question to then ask, when \(V_0 > E\), what happens to the S-matrix poles that were associated with the bound states when \(V_0 = \infty\)? This question can be answered by assuming the following form for a given pole:

\[
k_{\text{pole}}^{\text{res}} = k_{\text{pole}}^{\text{bound}} + \gamma - i\delta
\] (2.41)

where \(k_{\text{pole}}^{\text{res}}\) is the position of the pole associated with a resonant state (when \(V_0 > E\)) expressed as some deviation \(\gamma - i\delta\) away from a real bound state wavenumber (eg at \(k = \frac{\pi}{2}\)), when \(V_0 = \infty\). If we insert this expression into (2.38) and solve for the \(\gamma\) and \(\delta\) corresponding to the pole, we find that the pole has moved away from the real bound state wavenumber and become complex. At this complex wavenumber, corresponding to the resonance pole, the system will behave in a manner very similar to that for the bound state described by (2.37), i.e. it will be entirely composed of outgoing waves, with \(A\) and \(D\) equal to zero.

A third type of state associated with S-matrix poles are virtual states, which can be understood by considering the multivalued relationship between \(k\) and \(E\) in (2.35), which forms a Riemann surface.\(^8\) When \(E - V_0 < 0\) we considered bound states as being associated with positive imaginary values

\(^7\)Of the form \(0 \times \infty\).

\(^8\)It is sufficient for this work to simply regard the Riemann surface as that formed from plotting some complex function \(f(z)\) against some complex variable \(z\).
of \( k \). Virtual states occur in the case where \( k \) is negative imaginary, which also satisfies (2.35) when \( E - V_0 < 0 \).

An example of the distribution of the poles associated to the three types of states in the \( k \) and \( E \) planes is shown in figure 2.3.

![Figure 2.3: S-matrix pole positions on the \( E \), left panel, and \( k \), right panel, planes for: bound states (red dots), a virtual state (yellow dot) and resonances (green dots). The physical and non-physical regions are used to identify the different sheets on the Riemann multi-surface. These are defined in section 2.1.5. The three types of states are determined by where they are located on the \( E \) or \( k \) plane and are discussed further in the text. Adapted from [7].](image)

For all three types of states; bound, virtual and resonance, it’s not always necessary (or possible) to have scattering data (either calculated or experimental) in the vicinity of the state pole in order to obtain information on the state, such as its position or width (1.8). However, it’s possible to obtain these states from scattering data at energies outside the region of interest through analytic continuation of the experimental (or theoretical) scattering data to the energy region containing the poles [8]. For example, with inelastic scattering experiments bound states are usually detected from the loss of energy in the scattering electron through induced transitions between the bound and/or continuum states. However, it’s possible to analytically continue experimental, elastic scattering data to negative energies and locate the bound states [8]. Another example, of more relevance to this thesis, is the analytical continuation of S-matrix data calculated at real energies to the complex energy regions for the location of resonant states. Generally speaking, if there is enough scattering data of sufficient accuracy, it is possible to analytically continue this data to locate bound, virtual and resonance states with a parameterised, analytic form of the S-matrix. We will discuss such a form in section 2.2.2 of this chapter.

Now that we have illustrated how poles relate to the bound, resonant and virtual states of the scattering system we return to (2.31). In this equation, when \( F_j^{(in)}(k) \) is zero, we can readily see from (2.32) that a pole will exist in the S-matrix [7]. It can also be shown, from the analytic properties of the Jost functions and S-matrix in equation (2.31) [1], that the poles associated with resonances appear in pairs. From figure 2.4 we can see that if a zero exists for \( F_j^{(in)} \) at a \( k = a + ib \), then another one will also exist at \( k = -a + ib \). This is important to the work presented in chapter 3, where a method for locating the resonance poles is detailed.
2 THEORETICAL METHODS

Figure 2.4: Symmetry of the Jost functions (2.33) and (2.34). The dashed lines connect the points (black dots) on the $k$-plane at which the values or conjugate values (indicated with *) are equal. Taken from reference [49].

2.1.4 Multi Channel Scattering

For the case of elastic scattering from a central field it was shown that the S-matrix is given by a series of $l$ uncoupled equations (2.24). This results in the S-matrix given by (2.7) being diagonal, with an element exclusively for each of the partial waves given by $l$, representing $l$ number of incoming and $l$ number of outgoing channels. For the case of a single partial wave of $l = 0$, known as S-wave scattering, the S-matrix reduces to a scalar quantity. Since, as discussed, the S-matrix relates the incoming and outgoing asymptotic wavefunctions, then these channels can initially be thought of as referring to the uncoupled states of the system at asymptote. For elastic scattering from a central field, the channels are uncoupled, so that any particle entering in incoming channel $l$ must exit in outgoing channel $l$.

For a more general multi channel scattering system (such as will be considered for the work presented in this thesis) the wavenumber, $k_n$, is related to the threshold energies, $E_{th}^n$, where $n$ is the channel number, by:

$$k_n = \pm \sqrt{2(E - E_{th}^n)}$$ (2.42)

with $E$ the total energy of the scattering system. The channel threshold energies, $E_{th}^n$, are regarded as the energies where the channels become energetically accessible. For the multi channel case transitions can occur between the channels which are energetically accessible (open channels). For these cases the off diagonal elements of the S-matrix will be non-zero, meaning that the amplitudes of the wavefunctions are coupled between the incoming and outgoing channels of different $n$. Channel transitions are often linked to inelastic collisions but, for the case of non-radial potentials (eg molecules), elastic transitions can occur between channels with different $l$ values.

Figure 2.5 and table 2.1 illustrate, for a two channel process and assuming that the total energy of the system remains conserved, the possible incoming and outgoing channels and the corresponding changes in the potential and kinetic energies of a scattered particle. In the given two channel illustration, a particle is initially in one of the two incoming channels on the left and then leaves via either of the two outgoing channels on the right. There are therefore four possible paths through the system.
2.1 Fundamental Scattering Theory

Figure 2.5: Schematic using the representation in [7] illustrating the paths through a two channel scattering system. The incident particle can enter the scattering process through either of the two channels. It can then exit through either of channels if energetically viable.

<table>
<thead>
<tr>
<th>Matrix Element</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ch</td>
<td>KE</td>
</tr>
<tr>
<td>[1,1]</td>
<td>1</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>[1,2]</td>
<td>1</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>[2,1]</td>
<td>2</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>[2,2]</td>
<td>2</td>
<td>$\epsilon$</td>
</tr>
</tbody>
</table>

Table 2.1: Table showing the kinetic (KE) and potential (PE) energies associated with a two channel scattering system and associated S-matrix elements $S_{ij}$, with $i$ and $j$ indicated in the first column of the table. Channel (Ch) 1 has a threshold energy $E_{1}^{th} = 0$ and Ch 2 $E_{2}^{th} = 2$. Note the changes to the incident electron kinetic energy ($\epsilon$) for the non-diagonal matrix elements.

The multi channel equivalent to equation (2.12) is given by:

$$\frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2 u_i(r) = 2 \sum_{j=1}^{n_{ch}} V_{ij}(r) u_j(r)$$  \hspace{1cm} (2.43)

where $n_{ch}$ is the total number of channels and $V_{ij}$ the potential coupling term, given by:

$$V_{ij}(r) = \int Y_{l_i,m_i}^*(\theta, \phi) U_{ij}(r) Y_{l_j,m_j}(\theta, \phi)$$  \hspace{1cm} (2.44)

where $i$ and $j$ label the channels and $U_{ij}(r)$ contains the channel and channel-coupling potentials.

In a similar manner to the relationships between the asymptotic scattering quantities given in section 2.1.2 we can state here the following relationships. The S and T-matrices are related to the K-matrix by:

$$S = \frac{1 + i K}{1 - i K}$$  \hspace{1cm} (2.45)

$$T = \frac{2i K}{1 - i K}$$  \hspace{1cm} (2.46)

The eigenphase sum $\delta_{sum}$, which is the multi channel analogue of the inverse form of equation (2.25), is given by:

$$\delta_{sum} = \sum_{i=1}^{n_{ch}} \tan^{-1}((K_D)_{ii})$$  \hspace{1cm} (2.47)

where $K_D$ is the diagonalised K-matrix.

2.1.5 Multi Channel S-matrix

In a manner similar to section 2.1.3 we now express the multi channel S-matrix in a fractional form to allow a better understanding of its poles. Due to the multivalued relationship between the energy and channel wavenumber given by (2.42), in the multi channel case it is convenient to express the S-matrix
and Jost matrices as functions of energy:

\[ S_l(E) = \frac{F_{l\text{out}}^*(E)}{F_{l\text{in}}^*(E)} \]  

(2.48)

In order to obtain the Jost functions as functions of energy we can start with the multi channel wavefunction in the intermediate region as the energy analogue of (2.13) and, since in general the solutions are coupled, we use matrix notation:

\[ \Phi_I(r) = J_l(Er)A(E,r) - N_l(Er)B(E,r) \]  

(2.49)

where \( A, B \) are unknown matrices. For an \( N \) channel system:

\[ J_l(kr) = \text{diag}\{j_{l_0}(k_0r), j_{l_1}(k_1r), ..., j_{l_N}(k_Nr)\} \]  

(2.50)

and:

\[ N_l(kr) = \text{diag}\{n_{l_0}(k_0r), n_{l_1}(k_1r), ..., n_{l_N}(k_Nr)\} \]  

(2.51)

where \( l_0, l_1, ..., l_N \) and \( k_0, k_1, ..., k_N \) refer to the angular momentum quantum number and wavenumber respectively in the indicated channel, 1, 2, ...\( N \).

Considering the asymptotic behaviour of the wavefunction in analogy to the discussion given in section 2.1.3 we can write the asymptotic solutions in terms of the spherical Hankel and Jost functions:

\[ \Phi_A(E, r) = H_{l}^{(1)}(E, r)F_{l\text{in}}^*(E) - H_{l}^{(2)}(E, r)F_{l\text{out}}^*(E) \]  

(2.52)

where:

\[ H^{(1/2)}(kr) = \text{diag}\{h_{l_0}^{(1/2)}(k_0r), h_{l_1}^{(1/2)}(k_1r), ..., h_{l_N}^{(1/2)}(k_Nr)\} \]  

(2.53)

We then arrive at the analogues to (2.33) and (2.34):

\[ F_{l\text{in}}^*(E) \xrightarrow{r \to \infty} \frac{1}{2} [A(E) - iB(E)] \]  

(2.54)

\[ F_{l\text{out}}^*(E) \xrightarrow{r \to \infty} \frac{1}{2} [A(E) + iB(E)] \]  

(2.55)

By substituting the reduced form of (2.49) (see single channel equivalent equation (2.14)) into the TISE (2.43) for \( u_j(r) \) and considering the asymptotic behaviours it can be shown [50] that the following system of coupled first order differential equations is obtained:

\[ \begin{cases} 
\frac{\partial}{\partial r} A = -K^{-1}NV(JA - NB) \\
\frac{\partial}{\partial r} B = -K^{-1}JV(JA - NB)
\end{cases} \]  

(2.56)

where \( K = \text{diag}\{k_1, k_2, ..., k_N\} \) is a diagonal matrix containing the channel wavenumbers and \( V \) the matrix constructed from the potential coupling terms, \( V_{ij} \), as given in equation (2.44).

It can be shown [25] that the Bessel and Neumann functions in equation (2.49) can have the odd powers of \( k \) factored out. If these factorised forms of the Bessel and Neumann functions are substituted
2.1 Fundamental Scattering Theory

into (2.56), then after some algebra [25], using (2.54) and (2.55), the Jost functions can be expressed as explicit functions of the odd $k$-factors:

$$
F_{mn}^{out/in}(E) = \frac{1}{2} \left[ \frac{k_{ln}^{l+1}}{k_{lm}^{n+1}} A_{mn}(E) \pm i k_{lm}^{n+1} B_{mn}(E) \right]
$$

(2.57)

where $m$ and $n$ refer to the matrix elements corresponding to the initial and final channels. The $\tilde{A}$ and $\tilde{B}$ refer to the factorised $A$ and $B$ matrices, such that:

$$
A_{mn} = \frac{k_{ln}^{l+1}}{k_{lm}^{n+1}} \tilde{A}_{mn}, \quad B_{mn} = k_{lm}^{n+1} \tilde{B}_{mn}
$$

(2.58)

Figure 2.6: Physical and unphysical sheets of the Riemann surface of (2.42) for the single channel case. The upper two plots show the mapping of the real and imaginary parts of the energy on the physical sheet to the imaginary and real $k$ values. The bottom two plots show the same mapping but for the unphysical sheet. Shown are bound states (red dots), a virtual state (orange filled square) and resonances (yellow filled circles). The labels of the form -Im and +Re etc indicate the sheets form from the ± signs of (2.42). Note that for the resonances only a single pole from the conjugate pair is shown.

In equation (2.57) the wavenumbers $k_n$ are related to the energy $E$ via the multi-valued relationship (2.42). This relationship forms a complex surface, whose nature must be considered when searching it for the energies of the S-matrix poles. There will be multiple surfaces per channel relating the $k$
and $E$ values; a total of $2^N$ values of (2.57) for a $N$ channel system at an energy $E$. The scattering literature (eg [42, 7, 1, 43]) handles the complications relating to the multi-valuedness of (2.42) by firstly defining the following sheets:

- Physical sheet: where the imaginary component of $k$ is positive or, if the imaginary component is zero, the real component of $k$ is positive.
- Unphysical sheet: where the imaginary component of $k$ is negative.

The poles associated with states of a scattering system can be found as follows:

- Bound states: on the physical sheet along the real energy axis below the channel threshold.
- Virtual states: on the unphysical sheet along the real energy axis below the channel threshold.
- Resonances: on the unphysical sheet above the thresholds at complex energies.

These are all illustrated for the simple case of zero threshold (i.e. $E^{th} = 0$ in equation (2.42)) in figure 2.6. Here we can see that there is a branch point\(^9\) at the origin and a cut in the imaginary sheet from the branch point to positive infinity. For the case of several channels with differing thresholds, all channel surfaces are superimposed with each branch point displaced from the origin by a real energy equal to the channel threshold. In this case the energy can be above the threshold of one channel and below the threshold of another. The correct sheets can be chosen by enforcing the analytic properties of the S-matrix, including the unitary property [1].

### 2.1.6 Time-Delay and Q-matrix

This section describes another two scattering quantities, the single channel time-delay and the multi channel equivalent, the Q-matrix. The Q-matrix is a quantity which is particularly useful (as we will see in section 2.2) for the identification and characterisation of resonances and is used extensively in chapter 4. We start by considering the time-delay as was originally defined by Eisenbud [51, 52].

\[
\Delta t = \frac{d\delta}{dE} \tag{2.59}
\]

where $\delta$ is the phase shift (see section 2.1.2).

A derivation of this formula is given in appendix A. The generalisation of (2.59) to the multi channel case was given by Smith, who defined the lifetime or Q-matrix [51] as being related to the average time that a particle spends near the scattering center for the different scattering channels. He showed that the lifetime, $Q_{l,l}$, for elastic scattering is related to the angular momentum states $l$ and is equivalent to the time-delay calculated for the $\delta_l$ phase shift with respect to change in energy, as per equation (2.59). The proof is obtained by considering the excess number of particles within the region of interaction divided by the asymptotic total flux either towards or away from the scattering region. For the more general inelastic case, the unitary property of the S-matrix is utilised. The general expression arrived at for the Q-matrix is:

\[
Q = iS \frac{dS^\dagger}{dE} \tag{2.60}
\]

An important result is that when the Q-matrix is diagonalised the eigenvalues, when much larger than $1/E$, can indicate the presence of a resonance. For resonances, the profile of the time-delay

\(^9\)A branch point is a point on the Riemann surface where there is a discontinuity on a full rotation around it.
2.2 Identification and Characterisation of Resonances

eigenvalue will, in the ideal case, be Lorentzian, whose width is related to the lifetime of the resonance via equation (1.8).

An important property of the Q-matrix [1], relating it to the form (2.59) is:

\[ \text{Tr} Q = 2 \delta_{\text{sum}} \sum dE \]  

(2.61)

where \( \delta_{\text{sum}} \) is the eigenphase sum as defined by equation (2.47).

2.2 Identification and Characterisation of Resonances

As explained in the Introduction, resonances play an important role in electron-molecule scattering and are responsible for enhancing or causing several processes. Since a resonance can manifest itself in several forms depending on what observable or other quantity is used to describe the scattering process, it should be of little surprise that many methods have been developed for the extraction of their parameters. We categorise these methods as follows:

- **Breit-Wigner Based Fit Techniques.** In which the resonances are identified and characterised from fits of expected forms to the scattering data as a function of real energy.
- **Analytic Continuation.** In which the scattering data as a function of real energy is used to form the basis for an analytical continuation into the complex energy plane, where the resonances are located.
- **Others.** Techniques which don’t fall into the above two categories.

The first two categories are discussed in this section, with some examples. The Breit-Wigner based fit techniques encompass some very common approaches to the identification and characterisation of resonances, two of which, fitting to the eigenphase sums and to the eigenvalues of the Q-matrix, have been used for the results presented in this thesis. Although there are several scattering quantities which qualify for analytic continuation and also differing techniques for carrying out the continuation, we have chosen here to focus on a particular method and quantity: analytic continuation of the Jost Function, which was used for the work presented in chapter 3 of this thesis. Other approaches for analytic continuation and also some techniques which are neither Breit-Wigner based or analytic continuation are briefly discussed in appendix B.

2.2.1 Breit-Wigner Based Fit Techniques

How a resonance manifests in the ideal case (which we will define shortly) in different scattering quantities as a function of energy or momentum we refer to as the ideal resonance profile. A number of approaches based around these ideal profiles have been developed for the detection and characterisation of resonances in atomic and molecular scattering, some of which are widely used (see for example [53, 54, 55, 23, 56, 24]). In this section we give an overview of these ideal resonance profiles and some of the techniques based around them.

Breit and Wigner [57] showed that the form of a resonance in the cross section can often be well approximated with a simple formula, the Breit-Wigner formula, by considering the probability
amplitudes and transitions between the continuum and certain nuclear states. Derivations of the Breit-Wigner formula using these approaches and others are detailed in the literature [8, 1, 42, 7]. Related forms can be derived also for the other scattering quantities; we will be considering the eigenphase sum and the Q-matrix below. Additionally, Hazi showed that the formula is also valid in the multi channel case [58].

By first considering that the pole associated with a resonance occurs at the following complex energy:

\[ E_{res} = E^R - \frac{i\Gamma}{2} \]  

(2.62)

where \( E^R \) is the resonance position and \( \Gamma \) the resonance width, the Breit-Wigner formula can be written for the eigenphase sum as:

\[ \delta_{\text{sum}}(E) = \delta_b(E) + \delta_r(E) = \delta_b(E) + \sum_{i=1}^{N} \tan^{-1} \frac{\Gamma_i/2}{E^R_i - E} \]  

(2.63)

for a system of \( N \) resonances of positions \( E^R_i \) and widths \( \Gamma_i \). The splitting of the eigenphase sum into background, \( \delta_b(E) \) and resonant, \( \delta_r(E) \) components is a consequence of the approximation and allows us to see that \( \delta_r(E) \) will undergo a rapid shift of \( \pi \) radians as the energy increases past the resonance. However, this approximation will hold only when the background contribution is a slowly varying function of the energy, otherwise the Breit-Wigner form will become non-unitary. Some situations where the approximation will break down (or at least become numerically intractable) are when the resonance is too [1]:

- close to channel threshold/s.
- overlapped with other resonance/s.
- wide in relation to the background behaviour.

When close to a threshold, the wider the resonance, the more the threshold will essentially be inside the profile of the resonance. Similarly, when overlapping with another resonance, the degree of overlap will increase with the width of either or both of the overlapping resonances.

When sufficiently outside of these circumstances, the approximation provides an accurate means to identify resonances and/or extract their parameters by attempting to fit a calculated eigenphase sum with expression (2.63) using some representation for the background contribution. For example, the RESON program [59], part of the UKRmol+ suite (see Section 2.6) uses a power series, typically linear or quadratic, for the background. Possible resonances are located by looking for a sign change to the second derivative of the eigenphase sum as a function of energy and then a least squares fit is carried out.

The Breit-Wigner formula or a related form can also be used to express the scattering amplitude [7], the S-matrix [60], K-matrix [61], cross sections [7] and, as we’ll see, the trace of the Q-matrix. Fitting to the Q-matrix eigenvalues has proven especially effective [24] for the identification and characterisation of resonances, primarily due to the separation of the resonances over the Q-matrix eigenvalues. This is often referred to as the time-delay method (for reasons apparent in section 2.1.6) and was used for the study of resonances in chapter 4.
2.2 Identification and Characterisation of Resonances

Differentiating the Breit-Wigner eigenphase sum (2.63) and using equation (2.61) yields a Lorentzian form for the trace of the Q-matrix near \( N \) resonances:

\[
\text{Tr} Q = \sum_{i=1}^{N} \left( \frac{\Gamma_i}{(E - E_i^R)^2 + (\Gamma_i/2)^2} + 2 \frac{d\delta_{bg}}{dE} \right)
\]  

(2.64)

This expression tells us that the sum of eigenvalues of the Q-matrix can be expressed as a sum of Breit-Wigner terms plus a background.

Implementations of the time-delay method include the TIMEDEL [62] and the updated TIMEDELn [63] programs. These programs calculate the Q-matrices as given by (2.60) from inputted K-matrices. S-matrices are obtained from the K-matrices using equation (2.45) and then differentiated numerically. TIMEDEL then fits to the largest eigenvalue of the Q-matrix while the improved TIMEDELn fits to multiple eigenvalues and tracks the resonances across the different eigenvalues as the energy changes, improving the detection for overlapping resonances. TIMEDELn has also improved performance over TIMEDEL by parallelising across geometries of the molecule and the derivative calculations in equation (2.60). One shortcoming when using the time-delay over the eigenphase sum is the difficulty of obtaining accurate derivatives close to the channel thresholds, potentially increasing the detection difficulty for resonances close to thresholds.

As mentioned, the time-delay method has the significant advantage that resonances can be separated, from one another and from the background, across the eigenvalues of the Q-matrix. This advantage is demonstrated in [63] and in chapter 4, where TIMEDELn was used to characterise resonances in the \( \text{H}_2 \) molecule; the separation of the resonances across the different eigenvalues is clearly seen (in contrast, the eigenphases obtained in chapter 3 and shown in figure 3.7 show no such separation). Although the separation of the Q-matrix eigenvalues offers significant advantages, within each eigenvalue we can expect similar limitations as encountered when fitting the eigenphase sum using Breit-Wigner fits. This is because (2.64) is obtained directly from (2.63), which, since it is the result of a linear approximation, must therefore be subject to similar limitations.

We end this section by again mentioning that the expression of the resonance contribution to the different scattering quantities (e.g., the eigenphase sum and the Q-matrix eigenvalues) as a sum of Breit-Wigner terms is subject to limitations. One of these limitations is the loss of unitarity when the resonances are overlapping. This is of importance since the unitarity condition is a requirement for the accurate calculation of resonance parameters. Considering partial wave scattering [60], the Breit-Wigner form of the partial wave amplitude for a single resonance is initially considered without the background:

\[
f(E) = \frac{\Gamma/2}{(E - E^R) + i\Gamma/2}
\]  

(2.65)

where, as usual, \( \Gamma \) is the width and \( E^R \) the energy of the resonance. The unitary condition can be shown [64] for partial-waves to be:

\[
\text{Im} f(E) = |f(E)|^2
\]  

(2.66)

from which we can show that (2.65) is unitary. However, for the case of the amplitude of \( N \) overlapping
resonances expressed as a sum of Breit-Wigner profiles:

\[ f(E) = \sum_{i=1}^{N} \frac{\Gamma_i/2}{(E - E_i^R)^2 + i\Gamma_i/2} \]  

(2.67)

the unitary condition can be seen to break down when:

\[ N > 1 \quad \text{and} \quad |E_R^1 - E_R^2| \lesssim \Gamma_1 + \Gamma_2 \]  

(2.68)

for any two resonances. For this reason there has been significant work to obtain analytical forms for the amplitudes and K- and S-matrices that are unitary for both multiple channels and multiple resonances. Some of these techniques have been reviewed in [60], although no citations relating to atomic or molecular studies could be found. However, a later study by Shimamura et al [65] derives a unitary form for fitting two overlapping resonances in the eigenvalues of the Q-matrix. The positronium negative ion was used as the test system and accurate fits were obtained using their derived form.

2.2.2 Analytic Continuation of the Jost Function

The coincidence principle tells us that if we are able to sufficiently approximate a function which is analytic over some segment in the complex plane then we should be able to analytically continue the function throughout its defined domain, with an achieved accuracy depending on the quality of the initial approximation. This means that we can obtain data points in a region where the calculations are relatively simple (i.e. scattering data in the physical region) and then continue the function into the region of interest. In the case of S-matrix poles associated with resonances, this corresponds to the unphysical region.

There are many methods which apply this principle to S-matrix data and other scattering data for the identification of resonances from the corresponding poles in the complex plane; a summary of the field is given in appendix B. Here we concentrate on methods for the analytical continuation of the Jost function developed by Rakityansky et al. [49, 25] which were used as the basis for the software implementation presented in chapter 3. The technique has the advantage of allowing continuation of the Jost Function from any S-matrix poles associated with resonances, this corresponds to the unphysical region.

Rakityansky et al. [49] describe a method to approximate an S-matrix, \( S_l(k) \), using a Padé approximation for the single channel case. After considering the S-matrix property of tending to unity as the energy tends to infinity and also the symmetry of the Jost functions, the approximated S-matrix takes the following form:

\[ S_l(k) = \frac{1 + \sum_{\mu=1}^{M} a_{\mu} k^{\mu}}{1 + \sum_{\mu=1}^{M} (-1)^{\mu+1} a_{\mu} k^{\mu}} \]  

(2.69)

which can be rearranged to form the following linear system:

\[ \sum_{\mu=1}^{M} \left[ 1 + (-1)^{\mu+1} S_l(k) \right] k^{\mu} a_{\mu} = S_l(k) - 1 \]  

(2.70)

from which \( M \) coefficients can be obtained using \( S_l(k) \) values at \( M \) different \( k \) points. The poles can then be found as the roots of the polynomial comprising the denominator of (2.69). Generally, not all
2.2 Identification and Characterisation of Resonances

$M$ roots associated with this polynomial can be considered as true poles of the S-matrix. However, those roots that do represent the true S-matrix poles will converge with increasing $M$ and those that do not will move about in a much more erratic manner \cite{25}. Therefore the true poles can be extracted with an algorithm based upon this behaviour. Those which converge and lie on the unphysical sheets of the S-matrix will correspond to the resonances.

The extension of this technique to the multi channel case is described in \cite{25, 66, 67, 68}. The method adopted in \cite{25} expands $\tilde{A}$ and $\tilde{B}$ as the following power series:

$$\tilde{A}(E) = \sum_{\mu=0}^{M} \alpha^{(\mu)} E^\mu \quad \text{and} \quad \tilde{B}(E) = \sum_{\mu=0}^{M} \beta^{(\mu)} E^\mu$$

(2.71)

where $E$ is the energy and $\alpha$ and $\beta$ matrices of coefficients. Inserting these expansions into the factored Jost function (2.57), forming the S-matrix (2.48) and then simplifying by enforcing the following behaviour of the S-matrix elements at zero energies (with $O$ the big-O Landau Symbol and $k_m$ defined by equation (2.42)):

$$S_{mm}(E) \xrightarrow{k_m \to 0} 1 + O(k_m^q), \quad q \geq l + 1$$

$$S_{mn}(E) \xrightarrow{k_m \to 0} O(k_m^q), \quad m \neq n, q \geq l + \frac{1}{2}$$

(2.72)

the following linear system is obtained:

$$\sum_{\mu=1}^{M} \left[ \frac{k_{m+1}}{k_m} \left( S_{mm}(E_i) - 1 \right) \alpha^{(\mu)}_{mn} - ik_m k_n^{l+1} (S_{mm}(E_i) + 1) \beta^{(\mu)}_{mn} \right] k_m^{l+1} k_n^{l+1} \alpha^{(\mu)}_{jn} - ik_m k_n^{l+1} \beta^{(\mu)}_{jn} \right] E_i^\mu = \delta_{mn} - S_{mn}(E_i)$$

(2.73)

which can be solved for the coefficients $\alpha_{mn}$ and $\beta_{mn}$ assuming a sufficient number of S-matrix data at energies $E_i$ (see chapter 3 for more details), from which the Jost matrices can be constructed by considering that from (2.71) and (2.57) the matrix elements of $F_{i}^{in}(E)$ are given by:

$$F_{mn}^{in}(E) = \frac{1}{2} \sum_{\mu=0}^{M} \left[ \frac{k_{m+1}}{k_m} \alpha^{(\mu)}_{mn} - ik_m k_n^{l+1} \beta^{(\mu)}_{mn} \right] E^\mu$$

(2.74)

The poles of the S-matrix can then be obtained from the root sets of the determinant of $F_{i}^{in}(E)$. i.e. where:

$$\text{det} \left[ F_i^{in}(E) \right] = 0$$

(2.75)

Chapter 3 describes the implementation of this technique and its application to electron-molecule scattering.
2 THEORETICAL METHODS

2.3 The Electron-Molecule Scattering Hamiltonian

In this brief section we introduce the Hamiltonian describing electron-molecule scattering. Since we are working in the fixed-nuclei approximation (as discussed in the introduction) we solve the electronic part of the problem separately for each molecular geometry.

We work throughout in an \( N + 1 \) electron coordinate basis,\(^\text{10}\) with \( N \) referring to the \( N \) target electrons and the \( +1 \) to the additional scattering electron. The Hamiltonian describing the \( N + 1 \) system is labelled \( H_{N+1} \). The operator \( H_{N+1} \) commutes with the molecular point-group symmetry operators so we can write the TISE separately for each of the irreducible representations, \( \Gamma \), of the point group the molecule belongs to as:

\[
H_{N+1} \Psi^\Gamma(x_1, \ldots, x_{N+1}) = E \Psi^\Gamma(x_1, \ldots, x_{N+1}) \tag{2.76}
\]

which is an analogue to equation (2.5), with \( x \) referring to the space and spin coordinates of an electron, where the space coordinates, \( r \), are defined in figure 2.7.

\( H_{N+1} \) in (2.76) can be decomposed into:

\[
H_{N+1} = H_N + H_{\text{int}} \tag{2.77}
\]

with \( H_N \) the target molecule Hamiltonian, accounting for both the nuclear repulsion and the interactions of the \( N \) target electrons with one another and the nuclei:

\[
H_N = \sum_{i=1}^{N} \left( \frac{-1}{2} \nabla_i^2 - \sum_{k=1}^{\text{Nuclei}} \frac{Z_k}{\rho_{k,i}} \right) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{r_{i,j}} + \sum_{k=1}^{\text{Nuclei}} \sum_{l=k+1}^{\text{Nuclei}} \frac{Z_k Z_l}{R_{k,l}} \tag{2.78}
\]

and \( H_{\text{int}} \) accounting for the interactions of the scattering electron with the target electrons and nuclei:

\[
H_{\text{int}} = \frac{-1}{2} \nabla_{N+1}^2 - \sum_{k=1}^{\text{Nuclei}} \frac{Z_k}{\rho_{k,N+1}} + \sum_{i=1}^{N} \frac{1}{r_{i,N+1}} \tag{2.79}
\]

In the above equations the indices \( i \) and \( j \) refer to the electrons and \( k \) and \( l \) the nuclei. \( R, r \) and \( \rho \) refer to the nuclei-nuclei, electron-electron and nuclei-electron separations respectively (see figure 2.7). \( Z \) refers to the nuclear charge. As mentioned, since we are working in the fixed-nuclei approximation, only the kinetic energy terms for the electrons have been included, those for the nuclei have been ignored.

2.4 R-matrix Theory

In this section we give a derivation of the R-matrix theory, adapted from [24]. The main idea with the R-matrix method is that configuration space is split into three regions: inner, outer and asymptotic, via spheres of radii \( a \) and \( a_p \) (typically centered on the molecular center of mass). Within the inner region (\( r < a \)) electron exchange and correlation between the scattered electron and \( N \)-electron target system are important. In the outer region (\( a \leq r < a_p \)) these effects may be neglected and the electron can be considered as moving in the target’s long-range multipole potential. In the asymptotic region (\( r \geq a_p \)) the scattering electron can be regarded as being fully freed from the influence of the target and the wavefunction in the outer region can be matched to the forms at the asymptotic boundary. The

\(^{10}\) i.e. from the state vector expansion \( \vert \Psi \rangle = \sum_k A_k \vert \psi_k \rangle \), the wavefunction is \( \Psi(x_1, \ldots, x_{N+1}) = \sum_k A_k (x_1, \ldots, x_{N+1} \vert \psi_k \rangle \)
2.4 \textit{R}-matrix Theory

Figure 2.7: Molecular coordinates (bold, black) and distances separating the various constituents (orange) for a triatomic molecule. The nuclei are represented with the large green and blue circles. Two of the electrons are represented with the small red circles. Although 2D is sufficient to fully represent a planar molecule, a full 3D treatment must be used to realistically describe non-planar molecules and the motions of the electrons. 2D is used here as a simplification for purpose of clarity.

The main advantage of this approach is that the more complex problem of the inner region only needs to be solved once in order to formulate the boundary conditions between the inner and outer regions. The $\Psi^\Gamma(x_1, ..., x_{N+1})$ in equation (2.76) are expanded as

$$\Psi^\Gamma(x_1, ..., x_{N+1}) = \sum_k A_k^\Gamma(E) \psi_k^\Gamma(x_1, ..., x_{N+1})$$

(2.80)

where the expansion coefficients, $A_k^\Gamma(E)$ will be a function of the total energy of the system for which (2.76) is solved and are implicitly linked to the boundary conditions between the inner and outer regions [1]. Once these boundary conditions, as a function of energy, have been established the system can be solved separately for each energy using the much simpler outer region equations. Again, since we are working within the fixed-nuclei approximation, the system is solved separately for each different set of fixed nuclear coordinates.

2.4.1 Inner Region

Typically, in quantum mechanics, having setup the electron-molecule scattering Hamiltonian (2.77) the next step towards solving the system is to chose an appropriate basis set, $\psi_k^\Gamma$, for the expansion of the wavefunction in the $N + 1$ electron coordinate basis (2.80). A common choice for these types of calculations, irrespective of the method used, is the close-coupling expansion of $\psi_k^\Gamma$:

$$\psi_k^\Gamma(x_1, ..., x_{N+1}) = A \sum_{i=1}^{n} \sum_{j=1}^{n_c} a_{ijl} \Phi_i(x_1, ..., x_N) u_{ij}(x_{N+1}) + \sum_{i=1}^{m} b_{ik} \chi_i^\Gamma(x_1, ..., x_{N+1})$$

(2.81)

where $A$ is the antisymmetrisation operator. The functions, $\Phi_i$, $u_{ij}$ and $\chi_i$ are respectively the target wavefunctions, the continuum orbitals and the $L^2$ configurations. The summations run over the number, $n$, of target states, the number, $n_c$, of continuum orbitals and $m$, the number of $L^2$ configurations. In
the first term, the product of the target state, $\Phi_i$, and the continuum orbital set, $u_{ij}$, must be such that the resultant symmetry is $\Gamma$. The coefficients, $a_{ijk}$ and $b_{ik}$, are determined, when using the R-matrix method, through the diagonalisation of a Hermitian Hamiltonian, which we will derive shortly.

Equation (2.81) is crucial to the physics of the calculation, as it provides the description of the $N + 1$ electron system in the inner region. The construction of the functions $\Phi_i$, $u_{ij}$ and $\chi_i$ is discussed separately in section 2.5; here we want to examine the behaviour of (2.81) at the R-matrix radius $a$. We start by considering the form of the continuum orbitals, $u_{ij}$, which describe the unbound (or "scattering") electron. Since the inner region accounts for electron exchange and correlation, $a$ must be chosen such that the target wavefunctions are effectively fully contained within the inner region. This means at the R-matrix boundary the target orbitals must effectively vanish and the continuum orbitals reduce to a pure partial-wave expansion (see analogous form (2.17)):

$$u_{ij}(x_{N+1})|_{r_{N+1} \rightarrow a} = c_{ij} \frac{F_{ij,m_{ij}}(r_{N+1})}{r_{N+1}} Y_{l_{ij},m_{ij}}(\hat{r}_{N+1}) \Xi_{ij}(\sigma_{N+1})$$

(2.82)

which consists of chosen continuum bases for the radial expansion, $F_{ij,m_{ij}}(r_{N+1})$, sets of spherical harmonics $Y_{l_{ij},m_{ij}}$ and electron half spin functions $\Xi_{ij}$ of electron spin coordinate $\sigma_{N+1}$. As mentioned above, there will be a set of continuum orbitals for each target state symmetry, such that all irreducible representations, $\Gamma_s$, for the molecular point group are formed from the products.

When solving (2.76) in the inner region using the expansions (2.80) and (2.81) the effect of the finite region of space is to render the Hamiltonian non-Hermitian. It can be easily shown for a one dimensional case [24] that the non-Hermicity is due to boundary terms which arise from the basis function expansion at the R-matrix boundary when evaluating the matrix elements of the Hamiltonian. The Bloch operator [1, 10] can be applied to compensate for these boundary terms and restore Hermicity to the problem. However, in (2.82) we have surface terms on the R-matrix sphere arising from evaluations of the radial part only. In order to isolate these radial parts so that they can be compensated for using the Bloch operator we first need to remove the zero valued (at $a$) target functions in the products formed in the first expansion in (2.81)\(^{11}\) and also remove the angular and spin parts of (2.82). The radial terms can be removed by projecting the $|\psi_k\rangle$ onto the multi-electron basis set:\(^{12}\)

$$|\tilde{\Phi}_j \mathcal{Y}_j(\tilde{x}_i)\rangle \quad \text{where} \quad \tilde{\Phi}_j \equiv \tilde{\Phi}_j(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{N+1})$$

(2.83)

and we’ve introduced $\mathcal{Y}$ to collect the angular and spin dependency of the $i$th electron, such that:

$$\mathcal{Y}_j(x_i) \implies \mathcal{Y}_j(\hat{r}_i, \sigma_i) = Y_{l_{ij},m_{ij}}(\hat{r}_i) \Xi_j(\sigma_i)$$

(2.84)

Then the Bloch operator can now be written as:

$$L = \frac{1}{2} \sum_{i=1}^{N+1} \sum_{j=1}^{n_{ch}} |\tilde{\Phi}_j \mathcal{Y}_j(\tilde{x}_i)\rangle \delta(r_i - a) \left( \frac{d}{dr_i} - \frac{b-1}{r_i} \right) \langle \tilde{\Phi}_j \mathcal{Y}_j(\tilde{x}_i)|$$

(2.85)

where $b$ is some constant. Before applying the form of the Bloch operator given by equation (2.85) we first consider its addition to the Hamiltonian (2.2) (dropping $\Gamma$ for brevity):

\(^{11}\)Otherwise everything will reduce to zero on evaluation of the inner product.

\(^{12}\)We use terminology here where the form of the expansion in the coordinate basis is often implied in the bras and kets, for example $|f_j(x)\rangle \implies |x\rangle \langle x|f_j(x)\rangle$ where $\langle x|f_j(x)\rangle = f_j(x)$, so that $\langle f_i(x)\rangle \langle f_j(x)\rangle \implies \int dx \langle f_i(x)|x\rangle \langle x|f_j(x)\rangle = \int dx \sum_{j} f_i^*(x) f_j(x) = b_{ij}$ where the last Kronecker delta implies orthonormality of the basis functions $f_j(x)$.
2.4 R-matrix Theory

\[(H + L) |\Psi\rangle = (E + L) |\Psi\rangle \quad \Rightarrow \quad (H + L - E) |\Psi\rangle = L |\Psi\rangle \quad (2.86)\]

We now introduce the \(|\psi_k\rangle\); a complete, normalised set of linearly independent eigenfunctions of \(H + L\). Using the fact that \(|\psi_k\rangle \langle \psi_k| = 1\) we can write (2.86) as:

\[\sum_k (H + L - E) |\psi_k\rangle \langle \psi_k| = L |\Psi\rangle \quad (2.87)\]

Then, evaluating the \(H + L\) \(|\psi_k\rangle\), applying \(|\psi_k]\langle \psi_k|\) to both sides and some algebra:

\[|\Psi\rangle = \sum_k (E_k - E)^{-1} |\psi_k\rangle \langle \psi_k| L |\Psi\rangle \quad (2.88)\]

The \(E_k\) (known as the R-matrix poles) can be determined by diagonalising the left-hand side of:

\[\langle \psi_k| H + L |\psi_{k'}\rangle_a = E_k \delta_{kk'} \quad (2.89)\]

where the \(a\) subscript specifies the radial limits of the integral formed on the inner product. The \(E\)s can be obtained with:

\[\langle \phi_k| H |\phi_{k'}\rangle_a = E \delta_{kk'} \quad (2.90)\]

where \(|\psi_k\rangle\) and \(|\phi_k\rangle\) are potentially different orthonormal and complete basis expansions.

We now define the scattering electron channel functions as:

\[|\Phi_i Y_i(\hat{x}_{N+1}) \frac{1}{r_{N+1}} \rangle \quad (2.91)\]

which is a set of basis states representing the coupling of the target states, \(\Phi_i\), with the angular and spin functions of the continuum electron, \(Y_i\). By projecting the wavefunction (2.88) onto these states we obtain:

\[\langle \Phi_i Y_i(\hat{x}_{N+1}) \frac{1}{r_{N+1}} | \psi_k \rangle_a = \sum_k (E_k - E)^{-1} \langle \Phi_i Y_i(\hat{x}_{N+1}) \frac{1}{r_{N+1}} | \psi_k \rangle_a \langle \psi_k | L |\Psi\rangle_a \quad (2.92)\]

where the \(E_k\) and \(E\) are obtained from equations (2.89) and (2.90) respectively. The inner product \(\langle \Phi_i Y_i(\hat{x}_{N+1}) \frac{1}{r_{N+1}} | \psi_k \rangle_a\) reduces to the radial functions of the \(N + 1\) electron.\(^{13}\) By defining the reduced radial wavefunctions:

\[F_i(a) = \langle \Phi_i Y_i(\hat{x}_{N+1}) \frac{1}{r_{N+1}} | \Psi\rangle_a \quad (2.93)\]

\(^{13}\)Antisymmetrisation of the wavefunction means that each of the terms in \(\psi_k\), given by (2.81), will be composed of a product of \(N + 1\) sets of functions, with each set consisting of functions of the space and spin coordinates of one of the \(N + 1\) electrons. When forming the inner product for each of the wavefunction terms a reduced expression will be obtained due to orthonormality (and considering that that integrals for the space, angular and spin coordinates for all of the electrons are evaluated independently of one another). When the inner product of \(\Phi_i Y_i(\hat{x}_{N+1}) \frac{1}{r_{N+1}}\) and \(\psi_k\) is formed, all of the space and spin parts, as well as the angular and spin parts of the \(N + 1\) electron and the \(\frac{1}{r_{N+1}}\) (included in \(u_{ij}\)) of the product terms will reduce to unity, since they are parallel. All that will remain are the radial functions of the \(N + 1\) electron and any coefficients.
and boundary amplitudes:

\[ w_{ik}(a) = \langle \Phi_i \mathcal{Y}_j(\hat{x}_{N+1}) \frac{1}{r_{N+1}} | \psi_k \rangle_a \]  

(2.94)

we can then write (2.92) as:

\[ F_i(a) = \sum_k \frac{w_{ik}(a)}{E_k - E} \langle \psi_k | L | \Psi \rangle_a \]  

(2.95)

To evaluate \( \langle \psi_k | L | \Psi \rangle_a \) we first consider \( \langle \psi_k | L | \Psi \rangle \) and apply the form of the Bloch operator given by equation (2.85):

\[
\langle \psi_k | L | \Psi \rangle = \frac{1}{2} \sum_{j=1}^{N+1} \sum_{\ell=1}^{n_{eh}} \langle \psi_k | \tilde{\Phi}_j \mathcal{Y}_j(\hat{x}_\ell) \rangle \delta(r_i - a) \left( \frac{d}{dr_i} - \frac{b-1}{r_i} \right) \langle \tilde{\Phi}_j \mathcal{Y}_j(\hat{x}_\ell) | \Psi \rangle
\]

(2.96)

where the multi-electron expansion given by equation (2.83) results in the summation reducing to a function of a single electron radial coordinate only (as we required earlier when introducing the expansion (2.83)).

Now evaluating the inner product in the inner region:

\[
\langle \psi_k | L | \Psi \rangle_a = \frac{1}{2a} \sum_{j=1}^{n_{eh}} \omega_{jk}(a) \left( a \frac{dF_j}{dr} \bigg|_a - bF_j(a) \right)
\]

(2.97)

Inserting into (2.95):

\[ F_i(a) = \frac{1}{2a} \sum_{j=1}^{n_{eh}} \sum_k \frac{w_{ik}(a)\omega_{jk}(a)}{E_k - E} \left( a \frac{dF_j}{dr} \bigg|_a - bF_j(a) \right) \]  

(2.98)

Then the R-matrix is defined such that it relates the reduced radial wavefunction at the boundary to its differential via the boundary amplitudes:

\[ F_i(a) = \sum_{j=1}^{n_{eh}} R_{ij}(E) \left( a \frac{dF_j}{dr} \bigg|_a - bF_j(a) \right) \]  

(2.99)

where

\[ R_{ij}(E) = \frac{1}{2a} \sum_k \frac{\omega_{ik}(a)\omega_{jk}(a)}{E_k - E} \]  

(2.100)

and the \( E_k \) determined using equation (2.89).

\[ ^{14} \text{Also see relevant details from footnote } ^{13}. \text{ The expansion } \tilde{\Phi}_j \mathcal{Y}_j(\hat{x}_\ell) \text{ is composed of a series of similar terms to those in the expanded } \psi_k, \text{ except only the angular and spin parts are included for the } i \text{th electron (see equivalence (2.83)). When the inner product of } \tilde{\Phi}_j \mathcal{Y}_j(\hat{x}_\ell) \text{ and } \psi_k \text{ is formed, the only terms from } \psi_k \text{ to survive are the ones where } N \text{ product functions and coordinates match. The other terms disappear due to orthogonal functions for the same space and spin coordinates zeroing. For the term with matching functions, } N \text{ product pairs will disappear, since they are parallel with a product of unity. For the } i \text{th coordinate in expansion (2.83) the angular pair for the } i \text{th coordinate will also disappear since the product is unity. Thus, only the radial part from the } \psi_k \text{ term is left, which results in each matrix element being a function of a single electron radial coordinate only.} \]
2.4 R-matrix Theory

2.4.2 Outer Region

In the outer region the scattering wavefunction is written as:

$$\psi_k(x_1, ..., x_{N+1}) = \sum_{j=1}^{n_{ch}} \Phi_j(x_1, ..., x_N) Y_j(\hat{x}_{N+1}) \frac{F_j(r_{N+1})}{r_{N+1}}, \quad r_{N+1} \geq a$$ (2.101)

Note firstly the absence of the antisymmetrisation operator $A$, which is no longer required as this region of space is considered as only occupied by the scattering electron. Also note that, unlike the inner region wavefunction (2.81), there are no coefficients in this expansion, as these arise implicitly when solving for $F$ using the boundary conditions imposed from the inner region solution. In the simpler outer region the reduced radial functions $F_j(r_{N+1})$ satisfy equation (2.43):

$$\left[ \frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2 \right] F_i(r_{N+1}) = 2 \sum_{j=1}^{n_{ch}} V_{ij}(r) F_i(r_{N+1})$$ (2.102)

where the channel threshold energies, $k_i^2$, correspond to the energies of the included target states, with $k_i = \sqrt{2(E - E_{th}^i)}$ the channel momenta (see equation (2.42)).

The coupling potentials, $V_{ij}(r)$, are given by:

$$V_{ij}(r) = \langle \Phi_i Y_i(\hat{x}_{N+1}) \left| \sum_{p=1}^{N} \frac{1}{r_{p(N+1)}} - \sum_{k=1}^{N_{ele}} \frac{Z_k}{\rho_k(N+1)} \right| \Phi_j Y_j(\hat{x}_{N+1}) \rangle$$ (2.103)

which describes the potential in terms of the multipole moments of the target electronic states (permanent when $i = j$ and transition when $i \neq j$). These can be expressed as the following expansion [10, 24]:

$$V_{ij}(r) = \sum_{\lambda=0}^{\infty} a_{ij\lambda} r^{-\lambda - 1}, \quad i, j = 1, ..., n_{ch}, r \geq a$$ (2.104)

Inserting this expression for $V_{ij}(r)$ in (2.102) gives:

$$\left( \frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2 \right) F_i(r) = 2 \sum_{j=1}^{n_{ch}} \sum_{\lambda=0}^{\infty} a_{ij\lambda} r^{-\lambda - 1} F_j(r)$$ (2.105)

This set of multi channel, coupled equations describes the scattering electron moving in the long ranged potential resulting from the polarisation and multipole effects of the molecule. It can be solved to give $F_i(r)$ from the boundary conditions provided by the R-matrix at $r = a$. In the next section we discuss how the K-matrix and other asymptotic scattering quantities can be obtained from these solutions.

2.4.3 Propagation and Asymptotic Expansion

In order to obtain the scattering quantities, the solutions, $F_i(r)$, in the outer region must be matched to those at asymptote, where the effects of the long range potentials are considered to be negligible. At asymptote the radial wavefunctions for neutral targets can be written as follows:
2 THEORETICAL METHODS

\[ F_i(r)_{r \to \infty} = \sum_j \left( R_i^j(r) + K_{ij} R_c^j(r) \right) \]  

(2.106)

where:

\[ R_i^j(r) = \frac{1}{\sqrt{k_i}} \sin(k_i r - \frac{\pi}{2} l_i) \]  

(2.107)

and:

\[ R_c^j(r) = \frac{1}{\sqrt{k_i}} \cos(k_i r - \frac{\pi}{2} l_i) \]  

(2.108)

representing the incoming and scattered waves respectively and \( K_{ij} \) are the K-matrix elements. For non-neutral targets additional terms are included in the two trigonometric functions above [10]. Since the work presented in this thesis is concerned only with scattering from neutral target we omit these details here.

In order to obtain the \( K_{ij} \) in equation (2.106) the \( F_i(r) \) must be first obtained from (2.105) in the asymptotic region. Equation (2.105) is a second order coupled differential equation, to which several common methods can be applied for solution. For example Numerov’s method is applicable to differential equations of the second order without a first order term. With Numerov’s method the starting point would be the R-matrix sphere and the technique would move out step-by-step until the asymptotic region is reached. However, the wavefunction is typically rapidly varying across the outer region and noise growth as the calculation moves outwards would require a large computational resource to achieve reliable results. Also, solutions would have to be independently obtained for each energy of interest.

To avoid the inefficiency of Numerov’s method propagation techniques are used [69]. With these techniques the region of space between the R-matrix boundary, \( a \), and the asymptotic region, \( a_p \), is subdivided into a number of subregions. The Hamiltonian is then diagonalised across each region in turn, in a manner analogous to that described for the inner region: a Bloch operator is added to the Hamiltonian to restore Hermicity and the propagated R-matrix obtained on the next subregion boundary. Propagation techniques have the advantage that, as already explained for the R-matrix approach, a significantly complex part of the calculation, the diagonalisation of the Hamiltonian, can be completed independent of specific scattering energies.

In practice, the R-matrix is propagated to a large \( r \) and the \( F_i(r) \) matched to the asymptotic form given by (2.106). For each energy (and associated channel \( k_i \)) as per equation (2.42) equation (2.106) is solved for the K matrix, which, in turn, allows calculation of the other scattering matrices and quantities described in section 2.1.4. Details of the asymptotic expansion and the calculation of its coefficients can be found in [70].
2.5 Construction of the Inner Region Wavefunction

This section discusses the construction of the R-matrix basis functions (2.81), which we reproduce here:

\[ \psi^\Gamma_k(x_1, \ldots, x_{N+1}) = A \sum_{i=1}^{n_c} \sum_{j=1}^{n_e} a_{ijk} \Phi_i(x_1, \ldots, x_N) u_{ij}(x_{N+1}) + \sum_{i=1}^{m} b_{ik} \chi^\Gamma_i(x_1, \ldots, x_{N+1}) \]

The set of \( \Phi_i(x_1, \ldots, x_N) \), as mentioned, are the wavefunctions describing bound target states. In the R-matrix method, each of these multi-electron states is typically constructed from a set of single-electron wavefunctions (or spin-orbitals). Different methods, with varying degrees of accuracy are available for construction of these functions. The choice and construction of the spin-orbitals, along with the method used to represent the electronic states constitutes the target model.

The continuum orbitals, \( u_{ij} \) describe the scattering electron in the inner region. The main consideration when running an R-matrix calculation, with regards to the continuum, is the choice of the radial basis, \( F_{ij,m} \) in equation (2.82) and the maximum partial wave included.

The \( L^2 \) configurations are usually constructed with at least all of the molecular orbitals used to build the target states except in this case these are occupied by all \( N+1 \) electrons. They’re required because the continuum functions, \( u_{ij} \) are unable to accurately model the scattering electron in the molecular orbital states due to its necessary orthogonality with the target orbitals [1]. They are also crucial to properly describe short-range electron correlation effects and polarisation.

The scattering model consists of the \( L^2 \) configurations, the continuum used, and the number of and method for calculating the target states. The options and approaches adopted for both the target wavefunctions and the scattering model will determine the quality of the scattering results obtained and the computation time required for their calculation [10]. The remainder of this section will discuss the options and approaches used for the R-matrix scattering calculations presented in this thesis.

2.5.1 Target Wavefunctions

The methods for the determination of the target wavefunctions used for the work presented in this thesis follow well established techniques. Here we provide a brief overview. The Born-Oppenheimer approximation is assumed throughout.

In order to determine the target wavefunctions, \( \Phi_j \), a basis set is first chosen for the creation of the molecular orbitals, with each molecular orbital, \( \omega_j \), taking the following general form:

\[ \omega_j = \sum_{k=1}^{n} c_{jk} \chi_k \]

(2.109)

where \( \chi_k \) are a set of basis functions and the coefficients \( c_{jk} \) are to be determined. In quantum chemistry, for these expansions Slater-type orbitals (STOs) or Gaussian-type orbitals (GTOs) can be used but GTOs are preferred. Each orbital is centered on one of the nuclei.

In order to account for the electron spin the orbitals are used to build the spin-orbitals. Since electrons are fermions the the Pauli exclusion principal (PEP) must be satisfied. This is achieved with a wavefunction which is anti-symmetric with respect to particle exchange, which, for an \( N \) electron system, will result in a linear combination of products of \( N \) spin-orbitals. Considering that each spin-orbital is a function of the space and spin coordinates, \( x \), of a single electron we can write the
ground state wavefunction, $\Phi_0$, of an $N$ electron system as a Slater determinant:

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \omega_1(x_1) & \omega_2(x_1) & \ldots & \omega_N(x_1) \\ \omega_1(x_2) & \omega_2(x_2) & \ldots & \omega_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \omega_1(x_N) & \omega_2(x_N) & \ldots & \omega_N(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} |\omega_1 \omega_2 \ldots \omega_N| \tag{2.110}$$

where $N$ is the number of molecular electrons. It can be easily seen on expansion of the above determinant that the anti-symmetrical properties of the wavefunction are satisfied on exchange of electron label. Since this is the ground state wavefunction the $N$ spin-orbitals are the lowest energy spin-orbitals which can be occupied without violating the PEP. In order to determine the coefficients in equation (2.109), assuming the wavefunction (2.110) the Hartree-Fock self-consistent field (HFSCF) approximation is used, where the electrons are treated as moving independently of one another in a net potential, considered as arising from the average effect of the other electrons in the system and the nuclei. The coefficients in (2.109) are found through the variational procedure applied to:

$$E_{HF} = \frac{\langle \Phi_0 | H_N | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} \tag{2.111}$$

The Hartree-Fock energy $E_{HF}$ will then provide an upper-bound to the ground state energy. In other words, the optimal coefficients for a given basis set are those which minimise (2.111).

The main problem at this point is that the approximated net potential is usually unknown. Therefore to solve (2.111) a guess is made for the potential, usually from considering the charge distributions of the nuclei centered spin-orbitals with starting values for the coefficients. This starting potential is then used as input to the Hartree-Fock equations [71] and a new set of coefficients solved for. The process is continued until the coefficients converge to a value and the self-consistent field is obtained.

The HF-SCF approach does not account for the full electron correlation, leading to a higher than exact energy. In order to better describe the electron correlation an approach know as Configuration Interaction (CI) can be used. In this approach a linear combination of Slater determinants is formed, usually starting from the HF ground state configuration adding determinants corresponding to the possible excitations of the system (i.e. with electrons occupying spin-orbitals unoccupied in the ground state configuration), including both single and multiple excitations. CI therefore results in the following linear combination:

$$\Phi = C_0 \Phi_0 + \sum_{a,p} C^p_a \Phi^p_0 + \sum_{a<b} C^{pq}_{ab} \Phi^{pq}_{ab} + \sum_{a<b<c} C^{pqr}_{abc} \Phi^{pqr}_{abc} + \ldots \tag{2.112}$$

The final three terms in the summation represent all possible single, double and triple excitation configurations respectively. When all possible excitations of all electrons in the target to all available spin-orbitals are included in the expansion, the approach is referred to as full-CI. Note that another set of coefficients have been introduced, $C$, in addition to those for the molecular orbital expansion (2.109). These additional coefficients are found through diagonalisation of the molecular Hamiltonian, $H_N$, with (2.112) as basis and $H_N$ given by (2.78). This CI approach is regularly used in quantum chemistry calculations.

Typically a better approach is to use the Complete Active Space Self Consistent Field (CASSCF)
2.5 Construction of the Inner Region Wavefunction

The main advantage of CASSCF is that it can approach the quality of full-CI but with a much smaller calculation. The reduction comes about mainly from a full CI on a chosen subset of spin-orbitals, the active orbitals, leading to fewer configurations. The orbitals not included in this CI are those which are always occupied, known as frozen orbitals; and those which are always unoccupied, known as virtual orbitals. Careful choice of the active and frozen orbitals will minimise the size of the calculation while maintaining accuracy. CASSCF optimises both the basis expansion coefficients (2.109) and the CI coefficients (2.112) simultaneously. Although this simultaneous coefficient optimisation is expensive, with the choice of a sensible active space, this cost is usually mitigated.

The set of equations formed from the CASSCF wavefunction and the Hamiltonian, $H_N$, is solved iteratively until convergence is attained, with minimisation carried out on each iteration. The minimisation is usually in one of two modes: state-specific mode, where a single state is minimised and state-averaged mode, where the (optionally weighted) average of a set of selected states is minimised. For the calculations in this thesis it was preferable to have better optimisation, on the whole, over a number of states and thus state-averaged mode was used.

2.5.2 Scattering Models

The scattering model, as mentioned, is defined by the choice of the number and type of target wavefunctions (as stated in the previous section), along with the $L^2$ configurations. In this section we describe the scattering models which were used to obtain the results presented in this thesis, as well as some other common approaches. Static Exchange (SE) is the simplest scattering model used in scattering calculations. It comprises a ground state target wavefunction and $L^2$ configurations with the first $N$ electrons confined to the ground state configuration, and the scattering electron allowed to occupy a selected set of virtual orbitals. The ground state target is described at the Hartree-Fock level and therefore correlation between the target electrons is not well described; however it is accounted for to a degree between the target and the scattering electron, due to the scattering electron being able to occupy multiple virtual orbitals. As the target is unable to change state (relax) in response to the effect of the incoming electron, polarisation is not described by this model. Additionally, SE is only able to model shape resonances; core-excited resonances cannot be described with SE. This is because it’s not possible to excite any of the target electrons with this description.

Static Exchange plus Polarisation (SEP) retains the same Hartree-Fock target descriptions as SE but extends the $L^2$ configurations to allow promotion of a single target electron from valence orbitals into one of the selected set of virtual orbitals. The valence orbitals are a selected subset of the spin-orbitals occupied in the ground state configuration from which promotion is allowed. The ground state orbitals not in this valence subset are the core orbitals, which are doubly occupied and frozen. SEP enables description of the polarisation of the molecule by the incoming electron as well as allowing some modelling of core-excited resonances. The major drawback of SEP is that these additional $L^2$ configurations describe correlation effects which aren’t included in the target description. Since the target states included in the calculation define the channel functions (2.91) the $L^2$ states describing the excited states of the molecule plus the scattering electron in a valance orbital aren’t adequately represented in the outer region. This leads to a tendency for an increased probability distribution in the vicinity of the molecule compared to the outer and asymptotic regions. This is similar to the behaviour.

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15With the exception of small molecules, where full-CI can be practically employed.
2 THEORETICAL METHODS

linked to resonances, but in this case the resultant peaks in the scattering observables are non-physical. These artificial peaks, resulting from omission of the necessary channel functions in the outer region, are usually very narrow and are known as pseudoresonances.

The issue of pseudoresonances in the SEP approach can be mitigated with the Close-Coupling (CC) model, where additional target states are included in the scattering wavefunction expansion. This allows modelling of the target excitations in the inner region and also provides the appropriate channels for these states in the outer region. As well as addressing the problem of the pseudoresonances, the inclusion of excited states in the CC model allows more explicit modelling of core-excited resonances, since the parent states of these resonances are now included. To avoid pseudoresonance all excited states which are energetically accessible must be included in the CC expansion.

In order to achieve an accurate calculation when working with the CC model the description of the N-electron target must be close to the quality of the description of the N+1-electron system. In this work we have used the CASSCF technique. Here the first step is to ensure that an active space has been chosen which sufficiently models the target wavefunction. The usual approach is then to choose $L^2$ configurations such that the additional electron is allowed to occupy the same valence space as set for the target.

2.5.3 Continuum Description

The continuum in the inner region is described by the $u_{ij}(x_{N+1})$ in (2.81); their form at the R-matrix boundary is shown in equation (2.82). These functions are comprised of a partial wave expansion with some chosen basis for the radial part. In practice, there will also be some contribution from the target orbitals, which we will discuss shortly.

The choice of the functions for the radial part of the expansion is between Gaussian type orbitals (GTOs) or B-spline orbitals (BTOs) or a combination of both. BTOs have more linear independence than GTOs and also give a much better reproduction of the continuum’s oscillatory nature, which is especially true for bigger R-matrix radii. When both are used GTOs are used to describe the continuum close to the target and BTOs further away.

The radial part of a GTO expansion takes the following form:

$$\Psi_{i,j}^G(r) = \sum_{i,j} c_{i,j} e^{-\alpha_{i,j} r^2}$$

(2.113)

The $\alpha$ exponents are optimised according to the selected R-matrix radius and for each of the angular momenta. This is done by fitting to the solutions of the radial SE, i.e. Bessel functions [72].

BTOs, being recursively generated piecewise polynomials [73], are much more generic in nature than GTOs; hence the increased ability to better reproduce the continuum. This comes at the cost of increased computational demands due to the integrals requiring more numerical work (the GTO integrals are mostly analytical, with only the ‘tails’ requiring a numerical contribution). A B-spline set is formed over a closed interval $[a, b]$ from a set of pre-defined knot points\(^{16} t_m \) where $t_{m+1} \geq t_m$. So that the B-spline set of order $n$ is generated recursively by:

$$B_{m,1}(x) = \begin{cases} 
1 & t_m \leq x < t_{m+1} \\
0 & \text{otherwise}
\end{cases}$$

(2.114)

\(^{16}\)Knot points connect the pieces of the piecewise polynomial.
and

\[ B_{m,n}(x) = \frac{x - t_m}{t_{m+n-1} - t_m} B_{m,n-1}(x) + \frac{t_{m+n} - x}{t_{m+n} - t_{m+1}} B_{m+1,n-1}(x) \]  \hspace{1cm} (2.115)

The radial part of a BTO expansion takes the following form:

\[ \Psi_{i,j}^B(r) = \sum_{i,j} c_{i,j} B_{j,n}(r) \]  \hspace{1cm} (2.116)

Once an appropriate basis is chosen for the radial part, the full set of continuum orbitals are Gram-Schmidt orthogonalised to the target orbitals and symmetrically orthogonalised amongst themselves. In practice it’s not usually possible to have a perfectly complete basis set describing the continuum in the inner region as there will be some linear dependence between it and the target orbitals. This linear dependence means that the eigenvectors of the overlap matrix\(^{17}\) corresponding to overlapping orbitals will have significantly small eigenvalues. To address this, as part of the orthogonalisation procedure, continuum orbitals corresponding to eigenvalues of the overlap matrix which are less than some selected threshold are removed from the calculation. However, care must be taken so that the resultant set of continuum orbitals are sufficiently complete to allow accurate calculations. Accounting for orthogonalisation and the removal of the overlapping continuum orbitals the full form of (2.82) throughout the inner region is given by:

\[ u_{ij}(x_{N+1}) = N_{ij} \left( \sum_{i',j'} c_{ij,i',j'} \frac{F_{i',j',m_{i'},m_{i'}}(r_{N+1})}{r_{N+1}} Y_{i',j',m_{i'},m_{i'}}(\theta_{N+1}, \phi_{N+1}) + \sum_k d_{ijk} \omega_k(x_{N+1}) \right) \]  \hspace{1cm} (2.117)

where the additional summations involving target orbitals, primed indices and the normalisation term \(N_{ij}\) all arise from the orthogonalisation procedure.

### 2.6 UKRmol+ Software Suite

The R-matrix results presented in this thesis were obtained using the UKRmol+ suite of codes [74], of which we give a brief overview here. This software suite is an implementation of the R-matrix approach as applied to electron and positron scattering from, as well as photoionization of, molecules. UKRmol+ is a completely re-engineered version of an older suite, UKRmol [75], adding support for photoionisation, as well as providing increased capabilities such as higher precision and improved parallelisation. In addition UKRmol+ added support for B-spline based continuum and larger number of partial waves. The B-spline based continuum is of particular importance to the study of scattering from H\(_2\) presented in chapter 4.

#### 2.6.1 Target and Inner Region

The target calculation begins with MOLPRO [77], a quantum chemistry package used for performing electronic structure calculations for molecules. It takes as main input a specification of the molecular geometry and the type of basis set to be used for the molecular orbital expansions. From this it outputs the HF and CASSCF orbitals, with the later requiring specification of the active space and the state averaging as additional input. This output is then used by SCATCI_INTEGRALS to calculate the

\(^{17}\)The overlap matrix \(O_{\alpha\beta} = \langle \alpha | \beta \rangle\).
one and two electron integrals required for evaluation of (2.89), as well as the boundary amplitudes. The two electron integrals come about from the electron-electron Coulombic term in equation (2.78), the one electron (and overlap) integrals from the other terms in equations (2.78) and (2.79). As part of the inner region calculation SCATCI_INTEGRALS also constructs the continuum orbitals using the method described in section 2.5.3. This is done according to the chosen basis; either GTO, BTO or both, along with the number of specified partial waves for that basis. For the orthogonalisation, continuum orbitals are removed with eigenvalues of the overlap matrix smaller than a deletion threshold both for the orthogonalisation between target and continuum orbitals and also for orthogonalisation amongst the continuum orbitals only. For the case of orthogonalisation between target and continuum orbitals the deletion threshold is configured via user input.

In order for the method to provide accurate calculations in efficient timeframes the radius of the R-matrix sphere must be optimised; large enough that the amount of charge from the target electrons in the external region is negligible, but small enough for the calculation times to not become unnecessarily long. Additionally, with continuum GTOs, linear dependence problems will be encountered for large R-matrix radii (> 18\(a_0\) [78]). To assist with the optimisation of the R-matrix radii the UKRmol+ suite has the program RADDEN, which calculates and outputs the radial charge densities of the target orbitals.\textsuperscript{18}

The configuration state functions (CSF) (as described for the \(N\) electron system in section 2.5.1)

\textsuperscript{18}this is also calculated by SCATCI_INTEGRALS.
are generated by CONGEN and are used, along with the output from SCATCI_INTEGRALS, as input to SCATCI, which constructs and then diagonalises the Hamiltonian matrices. There are two successive runs of both CONGEN followed by SCATCI: once for the $N$ electron system and then for the $N + 1$ electron system. The calculated target states from the $N$ electron SCATCI run (the $\Phi_i$ in (2.81)) are also used as input to the $N + 1$ electron SCATCI calculation (this is required for consistency checking and is discussed in more detail in [74]).

The final target calculation program is DENPROP, which calculates the target properties required for the outer region calculations from the $N$ electron SCATCI output, specifically the dipole and quadrupole permanent and transition moments. This, along with the target and scattering states and the boundary amplitudes (from the SCATCI_INTEGRALS output) are passed to the outer region calculation.

### 2.6.2 Outer Region

![Diagram of the sequence of programs for a UKRmol+ outer calculation.](image)

**Figure 2.9:** The sequence of programs for a UKRmol+ outer calculation. Taken from [76], which in turn is an adaption from [74]. The green boxes indicate final scattering result outputs, see figure 2.8 for further details on the legend. † RSOLVE is called recursively by RESON.

The first outer region program to run, SWINTERF, collects outputs from the target and inner region calculations and performs some preliminary calculations. Specifically it uses the boundary amplitudes along with the eigenvalues and eigenvectors of the R-matrix basis functions to create the surface amplitudes (2.94) and channel data. It also uses the dipole and quadrupole permanent and transition moments to calculate the coefficients of the coupling potential in equation (2.104) using...
equation (2.103). These coefficients, along with the surface amplitudes and channel data are outputted for input to the RSOLVE routine, which then propagates the R-matrix to the asymptotic region (at the propagation radius, \( a_p \)) as described in section 2.4.3. It then calculates and outputs the K-matrices. Optionally (and not used for the work in this thesis) the BOUND program runs off the SWINTERF output to calculate the bound states of the \( N + 1 \) system.

Following the RSOLVE calculation various options are available for determining the scattering quantities and the detection and characterisation of resonances, depending on the needs of the user. The calculated K-matrices can be used by the TMATRX program to calculate T-matrices, which can then be used by either or both the DCS\(^{19} \) and IXSECS programs to produce differential and integral cross sections respectively. The K-matrices can also be used by EIGENP and TIMEDEL to calculate the eigenphase sums and time-delays. The program RESON automates resonance detection using the eigenphase sums from EIGENP as explained in section 2.2.1. Also used for detection of resonances is the external (to the UKRmol+ suite) program TIMEDELn [63]; this was used to obtain the results in chapter 4 and was discussed in a little more detail in section 2.2.1. Zdeněk Mašín’s time-delay program was also used to obtain plots of the time-delay eigenvalues; no further functionality is provided by this program and it was mainly used as a consistency check against time-delay eigenvalues obtained using TIMEDELn.

\(^{19}\)An external program, POLYDCS is also regularly used.
Chapter 3

Identification and Characterisation of Resonances Using an Implementation Based on the Continuation of the Jost Function

As highlighted in section 2.2 of the previous chapter, identification and characterisation of resonances can often be difficult when the resonances are very wide, overlapping or close to channel threshold/s. As an attempt to provide a more reliable means for locating these difficult resonances, we created implementations of methods for the identification and characterisation of resonant, bound and virtual states proposed by Rakityansky et al. [25, 49]. These methods are based around a technique where the S-matrix describing the scattering system is expressed in a rational form; two variants exist, the single channel case, which can be used for elastic scattering only, and the more general multi channel case, which can be used for both elastic and inelastic scattering (scattering channels are defined in chapter 2). Based on the multi channel method, a code, reskit [79], was created and released, of which details and usage can be found in appendix C. To the author’s knowledge, this is the first time that a code has been released based on this method. In this chapter, we give an overview of the implemented procedures based on Rakityansky’s methods and present results from the application of the procedures to analytically solvable systems and several electron molecule scattering systems.

This chapter is adapted from a related publication [79] and the Probation Report produced as part of the requirements for this PhD.

3.1 Method for Obtaining the Physical Poles of a Parameterised S-matrix

Section 2.2.2 of the previous chapter proposed rational forms for the single and multi channel S-matrix using a Padé approximant and simple power series expansions, respectively. It was also shown that these single and multi channel rational S-matrices can be arranged into linear systems, which can be solved by providing fit data from several previously calculated S-matrices as input. Then, using the obtained coefficients, an approximated, rational form of the S-matrix can be constructed, whose denominator can be used to determine the S-matrix roots. Following this, a general approach (for both single and multi channel cases) can be used to locate the roots which are candidates for the physical poles of the S-matrix. Finally, these candidate poles can be assigned indicators of confidence (or quality indicators - QIs) on their correspondence to the true, physical poles of the S-matrix. The remainder of this section gives more details on the various procedural steps.
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

3.1.1 Terminology and Notation

Since this chapter introduces a unique set of terminology we provide table 3.1 as an overview and reference of the non-standard terms used to describe the procedures in this chapter. These non-standard terms mainly relate to two parts of the procedure. Firstly, the comparison tests used to determine candidate S-matrix poles from the roots extracted from rationalised Jost functions. Then, the determination and assignment of the QIs used to indicate the confidence that these candidate poles are true physical poles of the S-matrix. Full descriptions of the terminology and procedures will be given throughout this section.

<table>
<thead>
<tr>
<th>Symbol / Term</th>
<th>Definition</th>
</tr>
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| fit point     | $k$, $S_l(k)$ pair (single channel) or $E$, $S_l(E)$ pair (multi channel)
| fit set       | Set of fit points used as input to the routines |
| $M$           | Maximum power of a rationalised Jost function |
| $m$           | Index of a series of rationalised Jost fit calculations (the "fit") with increasing $M$ |
| $M_m$         | $M$ for fit $m$ |
| $M_{max}$     | Highest power in a series of fits |
| $O$           | Number of pre-calculated S-matrices |
| $P$           | Number of fit points used for a fit selected from the $O$ pre-calculated S-matrices |
| $P_m$         | $P$ for fit $m$ |
| $P_{max}$     | Highest number of fit points used in a series of fits |
| $R_m$         | Root set for the fitted Jost function at index $m$ |
| $R_m[i]$      | Referencing complex root $i$ in root set $R_m$ |
| $R_m[i][R, I]$| Referencing real ($R$) or imaginary ($I$) components of root $R_m[i]$ |
| $r_{diff}_{R, I}$ | Relative difference of the real ($R$) or imaginary ($I$) components between two roots |
| $a_{diff}_{R, I}$ | Absolute difference of the real ($R$) or imaginary ($I$) components between two roots |
| $z_k$         | Value below which can be considered small enough for a root to be set to zero |
| $d_k$         | Threshold value used for a comparison test |
| comparison test | Test to determine if $r_{diff}$ (or potentially $a_{diff}$) for two roots $R_m[i]$ and $R_m[j]$ is less than a threshold $d_k$ |
| $c_f$         | Number of successive $m$ pairs a comparison test is applied to |
| QI            | Quality indicator |
| $\forall d_k$| QI relating to the precision of candidate poles |
| $\Sigma M$    | QI relating to the number of successful $c_f$ comparison tests |

Table 3.1: Table defining the terminology and symbols used in the procedures for identifying candidate poles from a rationalised S-matrix and the assignment of the 'quality indicators' (QIs). One based indexing is used, where relevant.

$k$ is used to specify single channel scattering data ranges. Since for the multi channel case $k$ can be ambiguous (see equation (3.3)), the multi channel scattering data ranges are always specified using $E$.

3.1.2 Solving for the Coefficients and Finding the Roots

For the single channel case, recall from chapter 2, section 2.2.2 the rationalised form of the S-matrix:

$$S_l(k) = \frac{1 + \sum_{\mu=1}^{M} a_{\mu} k^{\mu}}{1 + \sum_{\mu=1}^{M} (-1)^{\mu} a_{\mu} k^{\mu}}$$  \hspace{1cm} (3.1)
3.1 Method for Obtaining the Physical Poles of a Parameterised S-matrix

from which the following linear system was obtained:

$$\sum_{\mu=1}^{M} \left[ 1 + (-1)^{\mu+1} S_l(k) \right] k^{\mu} a_\mu = S_l(k) - 1$$  \hspace{1cm} (3.2)

For this single channel case the number of fit points, \( P \), required to solve (3.2) is equal to the maximum power, \( M \); i.e. \( P=M \). Once (3.2) has been solved and the coefficients, \( a_\mu \), determined, the roots can then be obtained, using well known numerical methods \([80, 81, 82]\), from the simple polynomials comprising the denominator of equation (3.1).

The multi channel case, in general, is more complicated since the wavenumber is now defined in terms of the channel threshold energies, discussed in chapter 2, section 2.1.4 and given by equation (2.42), which we repeat here:

$$k_n = \pm \sqrt{2(E - E_n^{th})}$$  \hspace{1cm} (3.3)

This complication results in the S-matrix denominator, \( F_{out}^l(E) \), in equation (2.48):

$$S_l(E) = \frac{F_{out}^l(E)}{F_{in}^l(E)}$$

no longer being a simple polynomial, making the roots much harder to obtain reliably. As an initial approach this was simplified from a general multi channel system to an elastic channel system by setting all the threshold energies in equation (3.3) to zero. This simplification results in a decoupled series of channels for the angular momenta, \( l \), and allows equation (2.74) to be expressed as:

$$F_{mn/ln}^{out/in}(k) = \frac{1}{2} \sum_{\mu=0}^{M} \left[ \alpha_{mn}^{(\mu)} k^{l_n-l_m+2\mu} \pm i \beta_{mn}^{(\mu)} k^{l_n+l_m+1+2\mu} \right]$$  \hspace{1cm} (3.4)

which is a polynomial function of a single \( k \) only and can be solved for the roots using the same methods as for the single channel case. This allowed us to obtain entire root sets\(^20\) and thus more reliably detect the physical S-matrix poles.

However, before finding the roots the coefficients must first be obtained; this is done in the same manner, whether or not the simplification leading to (3.4) is in place or not. \( M \) is the maximum power in the expansion of the elements of the coefficient matrices, \( \alpha \) and \( \beta \), in equation (3.4). This requires a total of \( 2(M+1) \) coefficient matrices, which reduces on application of the zero energy enforcement (2.72), so that only \( P=2M \) unique S-matrices must be provided in order to solve equation (2.73) for the elements of the coefficient matrices \( \alpha^{(\mu)} \) and \( \beta^{(\mu)} \). These coefficient matrices will then allow determination of the elements \( F_{mn/ln}^{in/out}(E) \) of \( F_{in/out}^l(E) \), which in turn will allow the parametrised S and Jost matrices to be obtained.

The polynomial obtained on insertion of (3.4) into equation (2.75) and expansion of the resultant determinant dictates the total number of roots. Thus the total number of roots will depend on \( M \) as well as the angular momenta and number of channels of the scattering system being investigated.

\(^20\)Most polynomial root finding methods guarantee to find all of the roots (see for example implementations of Laguerre’s method). This guarantee does not hold for non-polynomials (see for example Muller’s method [83] or Delves method [84], where only single roots or a set of roots over some pre-defined, finite region of the Riemann surface can be obtained, at best).
We now describe a comparison test to be applied across \( cf \) number of successive \( Ms \) (i.e. for each \( m: M_m, M_{m+1}, ..., M_{m+cf}, n \) in equation (3.5) is each of \( m + 1, ..., m + cf \)). The test is applied between all possible pairs of roots in \( R_n \) and \( R_{n-1} \) for each successive \( M \). It is carried out completely separately for the real and imaginary components, i.e. the \( \mathbb{R}, \mathbb{I} \) subscripts in the procedure below indicate either \( \mathbb{R} \) or \( \mathbb{I} \) throughout. It proceeds as follows:

- If both \( R_n[i]_{\mathbb{R},\mathbb{I}} \) and \( R_{n-1}[j]_{\mathbb{R},\mathbb{I}} \) are less than or equal to \( zk \) the relative difference, \( rdiff_{R,\mathbb{I}} \), between them is considered exactly zero.
- If only one of \( R_n[i]_{\mathbb{R},\mathbb{I}} \) and \( R_{n-1}[j]_{\mathbb{R},\mathbb{I}} \) is less than or equal to \( zk \) then that one is set to \( zk \), with the other one remaining unchanged. The relative difference, \( rdiff_{R,\mathbb{I}} \), is then calculated using equation (3.5).
- If both \( R_n[i]_{\mathbb{R},\mathbb{I}} \) and \( R_{n-1}[j]_{\mathbb{R},\mathbb{I}} \) are greater than \( zk \) the relative difference, \( rdiff_{R,\mathbb{I}} \), is then calculated with equation (3.5).

Then, if both \( rdiff_{\mathbb{R}} \) and \( rdiff_{\mathbb{I}} \) are less than a comparison threshold \( dk \) (note that the same \( dk \) is used for both real and imaginary components), the comparison test passes. At a given \( m \) the comparison test is first applied to determine the energy positions of the roots in \( R_{m+1} \) which are within real and imaginary energy thresholds from the energy positions of any of the roots in \( R_m \). The roots satisfying this are flagged as possible poles. If, for any particular \( R_m[i] \), there is more than one root in \( R_{m+1} \) satisfying the comparison test then whichever of these roots (in \( R_{m+1} \)) is closest to \( R_m[i] \) is used as the value of the possible pole. After this first application of the comparison test:

- If \( cf = 1 \), the test has completed and the possible poles are returned as the candidate poles.
- If \( cf > 1 \), the possible poles are then carried forward to the next \( M \) step where they are tested in a similar manner against those in \( R_{m+2} \). The set of possible poles are then replaced with those passing this second comparison test. This process will continue for steps of increasing \( M \) until the designated \( cf \) steps are reached. Then the set of possible poles from the final comparison against the root set \( R_{m+cf} \) are returned as the candidate poles.

### 3.1.4 Quality Indicators for the Candidate Poles

In this section we outline the calculations of the 'quality indicators' (QIs), used to quantify the likelihood that the candidate poles returned from the location routine just described are true poles of...
3.2 Systems Examined

the S-matrix. The basic idea is to apply the location routine across a number of successive ranges of
M values, up until some specified value $M_{\text{max}}$ is reached. This is then repeated by decreasing $dk$ until
it becomes so small that no candidate poles are returned from the location routines. Based on this, we
define $\varpi_{dk}$ and $\Sigma M$ QIs as:

- $\varpi_{dk}$: lowest value of $dk$ at which the candidate pole was identified. This is closely related to the
  converged precision of the pole for increasing $M$. Lower values are better.
- $\Sigma M$: for all the $M$ ranges for all the $dks$ the count of how many times a particular candidate
  pole was located. Higher values are better.

These QIs can be used to help provide confidence on whether or not a candidate pole is a true pole
of the S-matrix, as well as provide some information on the quality of the reported values for the real
and imaginary values of pole. There will be some dependence of the reported QIs on the chosen values
for $zk$ and the starting $dk$. The precision of the input data set is also expected to have a significant
influence on the reported QIs.

3.2 Systems Examined

In this section we give an overview of the systems used to test our procedure. The test systems can be
divided into two categories: those which are analytically solvable and the molecular-scattering systems
from which K-matrices were obtained using the UKRmol+ codes. We give a brief description of the
systems from which we derived input to our procedure.

3.2.1 Analytically Solvable Systems

As an initial test system for the single channel procedure we considered the simple square well. Here
the potential is described by:

$$V(x) = \begin{cases} 0 & -a \leq x \leq a \\ V_0 & |x| > a \end{cases}$$

where $x$ is the translational coordinate of the particle, $V_0$ the depth of the well and $2a$ its width.

The solutions to the TISE for this potential are known and can be found in many basic quantum
mechanics textbook (eg [6] but also see equations (1.6), (2.35) and figure 2.2 A). By matching the
forms and the derivatives of the general solutions at the boundaries, $\pm a$, two sets of transcendental
equations are obtained, one for each of the parities of the wavefunction, which can be solved graphically
(or iteratively) for the bound state energies. We first tested the single channel pole locating routines
using a potential well of half width $a = 2.0 \ a_0$ and depth $V_0 = 0.5 \ Ha$. From this well we iteratively
obtained from the analytical solutions a value of -0.050887684 Ha for the first bound state (accurate
to the number of shown decimal places), which we used to compare to that obtained using the pole
locating routines. Following this simple test we then looked at the performance of the routines in
detecting the first bound state of the well as the well depth, $V_0$, was increased. The bound state
behaviour from the first three negative parity solutions is shown in figure 3.1. In this figure it can be
seen that, as the depth of the well is increased, the bound state energy decreases. Thus by deepening
the well we can examine the performance of the pole locating routines as the bound state is moved
further from a static fit set formed at positive energies. It is worth mentioning that there are more
elaborate treatments of this seemingly simple model case in the literature, since they could form the basis of a follow up study in the future. Zavin and Moiseyev [46] have looked in detail at the behaviour of bound, virtual and resonant states as the depth of the well is varied.

For the initial test of the multi channel implementation (reskit) we used the 2 channel radial well as described in [42]. This popular test system was also used by Rakityansky et al. to test their implementation of the Padé fit method [25]. We give a brief overview of the well here, based on the treatment in [85], and how we arrived at our analytical test quantities.

When we consider s-wave scattering, the 2 channel radial well reduces to a single dimensional problem of the translational coordinate \( r \), which, unlike \( x \) in equation (3.6), is always greater than or equal to zero. The general form of the potentials used in our tests have the following form:

\[
V_{mn}(r) = \begin{cases} 
0 & r > a \\
 v_{mn} & r < a 
\end{cases}
\]  

(3.7)

where \( v_{11} \) and \( v_{22} \) are the channel potentials and \( v_{12} = v_{21} = -0.5 \) Ha the coupling potentials. The Hamiltonian elements for a scattering system with these potentials is given by:

\[
H_{mn} = -\frac{1}{2} \frac{d^2}{dr^2} \delta_{mn} + V_{mn}(r) + E_{th}^n \delta_{mn}
\]  

(3.8)

where the channel potentials are shifted by the channel thresholds, \( E_{th}^n \). The wavenumber is then expressed as equation (3.3).

The solutions of the 2 channel radial well are given in [42] and take the form of the following functions for each of the S-matrix elements:

\[
S_{1,1} = \frac{g(-k_1, k_2)}{g(k_1, k_2)} e^{-2iak_1}, \quad S_{2,2} = \frac{g(k_1, -k_2)}{g(k_1, k_2)} e^{-2iak_2}, \quad S_{1,2} = S_{2,1} = \frac{h(k_1, k_2)}{g(k_1, k_2)} e^{-iak_1+k_2}
\]  

(3.9)
where \( h \) and \( g \) are both functions of the wavenumbers, \( k_1 \) and \( k_2 \), in each of the channels. Note that that each of the elements share the same denominator \( g(k_1, k_2) \).

We first examined the simple elastic case, with \( v_{11} = v_{22} = -2.0 \) Ha, channel thresholds, \( E_{1}^{th} = E_{2}^{th} = 0 \) Ha and with a well of radius \( a = 1.0 \) \( a_0 \). We then proceeded as follows:

- To identify and characterise the resonances, we used an iterative search routine to locate the zeros of \( g(k_1, k_2) \) on the complex-energy plane. These are shown graphically in figure 3.2 and are discussed in section 3.5.1.

- For the bound states, we found the zeros of \( g(k_1, k_2) \) using algebra. The energy of the bound states can be expressed as a transcendental equation in energy, as for the single channel case. This equation was solved graphically. By doing this we obtained two bound states, at \(-0.0307\) and at \(-0.4657\) Ha (with decimal precision here dictated by that of the graphing tool used).

We also briefly looked at inelastic scattering from the 2 channel well system and tested our results by comparing visually to the cross sections presented in [85, 86]. Our results for this system are discussed in section 3.6. They were obtained with \( v_{11} = v_{22} = -2.0 \) Ha, \( a = 1.0 \) \( a_0 \) and thresholds \( E_{1}^{th} = 0 \) Ha and \( E_{2}^{th} = 2 \) Ha.

Figure 3.2: Resonances for the 2 channel elastic square well, represented by plotting the reciprocal of the S-matrix denominator, as derived analytically in [42]. Resonances occur in closely spaced pairs, shown in the zoomed image for those close to the point \( 24 + 15i \). The four resonances around the points \( 6.2 \pm 6.5i \) (see table 3.6) are not evident from this figure.

### 3.2.2 Molecular Systems

For the molecular system tests, the starting points were elastic scattering K-matrix data sets obtained using the UKRmol scattering codes as mentioned in section 2.6, chapter 2. The sets were obtained from UKRmol calculations performed on the pyrazine, uracil, Para-benzoquinone (PBQ) and CO\(_2\) molecules. The characteristics of the calculations performed for each of these molecular systems are shown in table 3.2, which includes: the scattering model used for the construction of the inner region wavefunction (see section 2.5, chapter 2), the irreducible representation of the data investigated \( \Gamma \) (section 2.5), the number of channels in the calculation for that irreducible representation (section 2.1.4) and the number of different geometries of the molecule studied.
Table 3.2: Overview of the electron-molecule scattering systems used to test our procedures for the identification of candidate poles from a rationalised S-matrix. The R-matrix method was used to obtain K-matrices describing electron scattering from the molecules listed, from which a subset of K-matrices were then used as input to the procedural fit routines. Although Carbon dioxide belongs to the $D_{\infty h}$ point group, the R-matrix calculations were carried in the lower symmetry $C_{2v}$ point group.

### 3.3 Choice of Input Data

For each of the systems studied the approach was to calculate the parametrised S-matrix by fitting to 

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Scattering Model</th>
<th>Point Group</th>
<th>Symmetry</th>
<th>Number of Channels</th>
<th>Number of Geometries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrazine $C_2N_2H_4$</td>
<td>SEP</td>
<td>$D_{2h}$</td>
<td>$^2A_u$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Uracil $C_4N_2O_2H_4$</td>
<td>SE</td>
<td>$C_4$</td>
<td>$^2A''$</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^2A'$</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Parabenzoquinone (PBQ) $C_6H_4O_2$</td>
<td>SEP</td>
<td>$D_{2h}$</td>
<td>$^2B_{2u}$</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Carbon Dioxide CO$_2$</td>
<td>SE</td>
<td>$C_{2v}$ ($D_{\infty h}$)</td>
<td>$^2A_1$</td>
<td>9</td>
<td>1</td>
</tr>
</tbody>
</table>

For the single channel square well, fits were calculated for $P$s in the range $[2, 8]$, each over the $k$ interval $[0.01, 1.0] a_0^{-1}$, such that the step, $\Delta k$, between successive $k$s ensured that the range $[0.01, 1.0] a_0^{-1}$ was always closed.

For all of the other systems (the multi channel radial well and the single and multi channel molecular cases) the fit set was constructed from a pre-existing set of $O$ number of points, such that $O \geq P_{\text{max}}$. A consequence of selecting the fit points from some pre-existing set is that when the $P - 1$ number of steps across the fit range is not an integer factor of the $O - 1$ number of steps across the pre-existing set then the $k$ or $E$ interval will not be closed. In these cases the final point was chosen to be as close to the end of the calculated set as possible.

We illustrate this by considering the 2 channel radial well. Here fits were carried out for $P$s = 4, 8, 16, 32, 64. These fit points were spread evenly over a pre-existing set of 1001 energies, themselves spread evenly in the $E$ range $[1.0, 8.0]$ Ha. The fit points were selected such that the first fit point was always at $E = 1.0$ Ha and the final fit point as close to $E = 8.0$ Ha as possible. For example, with $P = 16$, the final energy point is calculated as:

$$E_{\text{max}} = \text{START}_\text{ENERGY} + \text{STEP}_\text{SIZE}_\text{ENERGY} \times \text{NUM}_\text{STEPS} = 1.0 + \left( \frac{1001 - 1}{16 - 1} \times \frac{8.0 - 1.0}{1001 - 1} \right) \times (16 - 1) = 7.930 \text{ Ha}$$

It should be mentioned that since we are doubling $P$ in this example, the same closed energy interval can be satisfied for all $P$s, by choosing a pre-existing set such that the number of steps across it is a multiple of the number of steps across the $P_{\text{max}}$ fit points (which is 63 steps). However, for the molecular systems we found that doubling $P$ required excessively long calculation times for convergence of the poles to be observed; for these cases we increased $P$ linearly. This meant we...
3.4 **Single Channel Results**

couldn’t always have the same closed interval for the fit sets for each of the Ps, although our tests found that for large enough pre-existing sets the slight variation in end point energy made little difference to the calculations.

For the molecular data sets, $P$ was each of the integers in the range $[2, P_{max}]$ for the single channel case and the even integers in the range $[4, P_{max}]$ for the multi channel cases, with $P_{max}$ given in table 3.3 for each of the molecules. The initial data set used for the selection of the $P$ fit points was a set of K-matrices outputted from the UKRmol suite for the given test molecule. This set of K-matrices was then truncated over the energy range of interest for the test, with the truncated range then converted to S-matrices values using (2.45). This truncated and converted set of O S-matrices then comprised our selection set for the fit routines from which $P$ fits point were selected for each $P$ in the specified ranges up until $P_{max}$. As for the 2 channel radial well the final fit point from a given $P$ selected fit points was chosen such that it was as close to end of the selection set of O points as possible, in a manner analogous to the illustration (3.10) above. Table 3.3 summarises for each of the molecules the data points provided from the UKRmol code, the sub-range fitted to and the $P_{max}$ used.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>UKRmol data set (Ry) $E_{min} E_{max}$ interval</th>
<th>Fit set (Ry) $E_{min} E_{max}$</th>
<th>$P_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrazine 1ch</td>
<td>7.35e-4 1.4703675 3.675e-4</td>
<td>7.35e-4 0.184485</td>
<td>11</td>
</tr>
<tr>
<td>pyrazine 3ch</td>
<td>7.35e-4 1.4703675 3.675e-4</td>
<td>7.35e-4 0.441368</td>
<td>48</td>
</tr>
<tr>
<td>uracil 6ch</td>
<td>7.35e-4 0.882 7.35e-4</td>
<td>7.35e-4 0.882</td>
<td>40</td>
</tr>
<tr>
<td>uracil 10ch</td>
<td>7.35e-4 0.882 7.35e-4</td>
<td>7.35e-4 0.882</td>
<td>40</td>
</tr>
<tr>
<td>PBQ 3ch</td>
<td>7.35e-4 0.366765 1.470e-3</td>
<td>7.35e-4 0.366765</td>
<td>48</td>
</tr>
<tr>
<td>CO$_2$ 9ch</td>
<td>7.35e-4 0.734265 1.470e-3</td>
<td>7.35e-4 0.732795</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 3.3: Energy ranges of the *ab initio* data sets and subsets used as fit data to determine the parametrised S-matrix. The first column indicates the molecular data set and number of channels in the calculation, the second group of columns (UKRmol data set) describes the raw K-matrix data range as outputted from the UKRmol routines. The third group of columns (Fit set) specifies the sub-range of data (with respect to the UKRmol data set) used for testing our procedure. Also shown in the final column is the $P_{max}$ used for each of the molecules.

For both the analytical and molecular systems the $P$ S-matrix fit points were used to find the coefficients and roots as described in section 3.1.2 of this chapter.

### 3.4 Single Channel Results

In this section we present results from the single channel implementation of the method for the identification and characterisation of resonant, bound and virtual states proposed by Rakityansky et al. and discussed in section 2.2.2 of the previous chapter.

#### 3.4.1 Potential well

We started by looking at single channel scattering from the one dimensional square well, as illustrated by equation (3.6) with $a = 2.0 \, a_0$ and $V_0 = 0.5 \, \text{Ha}$. Table 3.4 shows the convergence of the root corresponding to the first bound state energy for increasing number of fit points $P$. With the
parametrised S-matrix we matched this bound state energy to five decimal places for $P = 5$ and nine decimal places for $P = 7$.

<table>
<thead>
<tr>
<th>$P$</th>
<th>$\text{Re } k (a_0^{-1})$</th>
<th>$\text{Im } k (a_0^{-1})$</th>
<th>$\text{Re } E \text{ (Ha)}$</th>
<th>$\text{Im } E \text{ (Ha)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0.399605936</td>
<td>-0.079842452</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.320232959</td>
<td>-0.051274574</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.318808343</td>
<td>-0.050819379</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0.319011597</td>
<td>-0.050884199</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1e-14</td>
<td>0.319022729</td>
<td>-0.050887750</td>
<td>3e-15</td>
</tr>
<tr>
<td>7</td>
<td>1e-14</td>
<td>0.319022522</td>
<td>-0.050887684</td>
<td>3e-15</td>
</tr>
<tr>
<td>8</td>
<td>3e-14</td>
<td>0.319022524</td>
<td>-0.050887685</td>
<td>1e-16</td>
</tr>
<tr>
<td>Analytical</td>
<td>0</td>
<td>0.3190225</td>
<td>-0.050887684</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.4: Convergence of the pole corresponding to the negative parity bound state of the single channel well with $a = 2.0 \ a_0$ and $V_0 = 0.5 \text{ Ha}$ identified using our implementation of the single channel variant of the Rakityansky et al. procedure. This was generated using $P$ fit points evenly across the $k$ interval $[0, 1.0] \ a_0^{-1}$. The analytical value of the pole is shown in the last row for comparison.

In order to investigate the effect of increasing energy distance between the fit set and the bound state of interest we ran calculations using the single channel procedure for increasing well depth. As shown in figure 3.1, increasing the depth of the well lowers the energy for all bound states. Figure 3.1 shows that the behaviour of the bound state energies for increasing well depth is the same for all bound states; upon manifesting, the bound state energies initially move relatively slowly down into the well as the depth increases. This speeds up until they appear to keep pace with the decreasing bottom of the well. Since the fit data is all in the positive energy region then, as the depth of the well is increased, a larger extrapolation is required to reach the expected value of the first bound state.

Figure 3.3 shows the effect of increasing the well depth (and therefore the energy distance between the fit set and the first bound state) has on the accuracy of the single channel procedure for locating the first bound state. The vertical axis of Figure 3.3 corresponds to the energy of the first bound state. We studied the accuracy of the fit as the depth of the well is increased in steps of 0.2 from 0.01 to 2.401 Ha. Since we expected the results to deteriorate with increasing well depth we chose a much higher number of fit points, $P = 65$, than used to obtain the results in table 3.4. At all well depths fits were made over a range of $k_{\text{min}} = 0.01 \ a_0^{-1}$ up until the value of $k_{\text{max}}$ shown on the horizontal axis. Following each fit, the roots of the denominator of equation (3.1) were obtained. If any of these roots were within $\pm 0.03$ Ha from the analytically obtained bound state then the state was considered as having been located by the routine; these points correspond to the Xs in figure 3.3. Although the value of $\pm 0.03$ Ha for the threshold appears quite relaxed, when the range over which most of the 65 roots appeared is taken into account, the probability of randomly obtaining a root within this threshold is low. On inspection of the roots nearly all of them were found within the range $[-10, 30] + [-20, 25]i$ Ha. Then, assuming that the roots are uniformly distributed within this range, the probability of randomly selecting a value within the threshold is approximately 1 in 7500.
3.4 Single Channel Results

Figure 3.3: 3D plot showing detection of the first bound state energies of a square well of half width $a = 2.0 \, a_0$ for different fit ranges ($k_{\text{max}}$) using the parameterised S-matrix. The multiple values for the first bound state energies, as apparent on the y-axis, were achieved by changing the depth of the well (see figure 3.1). The 'X's indicate the $k_{\text{max}}$ values for which the first bound state energies were identified, where the threshold criteria to qualify for identification was ±0.03 Ha from the values obtained by solving the TISE graphically using the analytical solutions. $P = 65$ fit points were used in all cases, evenly spaced over the interval from $k_{\text{min}} = 0.01 \, a_0^{-1}$ up until $k_{\text{max}}$. There are also a number of 'gaps' evident in the figure (eg at $k_{\text{max}} = 10 \, a_0^{-1}$ and a bound state energy of ~1.3 Ha), where, for a particular $k_{\text{max}}$, the bound state was discovered for energies both above and below the 'gap'. These arose from numerical problems with the matrices and were not investigated in any detail.

Since the fit points all lie in the positive energy region finding a bound state is essentially an exercise in extrapolation of which figure 3.3 illustrates the following (for a given $P$):

- As the known bound state moves down into the well it will fail to be detected (to within a preset precision: ±0.03 Ha in this case) after some depth.

- For a given well depth the pole will be detected (to an acceptable precision) only for a given range of $k_{\text{max}}$.

To compensate for longer extrapolations and sub-optimal $k$ ranges, $P$ can be increased. However, this will come at the cost of increased computation time as well as degradation of the results due to what we assume is increased numerical error propagation with the higher powered polynomials.

3.4.2 Pyrazine

We performed these calculations using a data set consisting of 4000 K-matrices generated with the UKRmol suite for scattering from pyrazine in $2A_u$ symmetry. The range of this data set, as well as the truncated range used in our calculation, is shown in the first row of table 3.3. Note that, as mentioned, each set of $P$ fit points up until $P_{\text{max}} = 11$ are selected from the truncated data set for input to the parametrised S-matrix fit. A single resonance at ~0.07693±0.00065i Ry had been previously located
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

from this data set using RESON [87]. This shape resonance is well understood and documented in the literature [88, 89, 90].

Again, as for the analytical well, we obtained good convergence to the known resonance value. This is evident in table 3.5, which shows that by \( P = 11 \) fit points we have located the pole to match that obtained with the RESON program to a precision of about three and five decimal places for the real and imaginary components respectively. Relatively this corresponds to a 0.38% and 0.18% deviation respectively.

<table>
<thead>
<tr>
<th>( P )</th>
<th>Real ( k )</th>
<th>Imag ( k )</th>
<th>Real ( E ) (Ry)</th>
<th>Imag ( E ) (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.42951</td>
<td>7E-10</td>
<td>0.18448</td>
<td>-6e-10</td>
</tr>
<tr>
<td>3</td>
<td>-0.19073</td>
<td>-0.002586</td>
<td>0.03637</td>
<td>0.000986</td>
</tr>
<tr>
<td>4</td>
<td>-0.29130</td>
<td>-0.001577</td>
<td>0.08485</td>
<td>0.000919</td>
</tr>
<tr>
<td>5</td>
<td>-0.27828</td>
<td>-0.001153</td>
<td>0.07744</td>
<td>0.000642</td>
</tr>
<tr>
<td>6</td>
<td>-0.27737</td>
<td>-0.001175</td>
<td>0.07693</td>
<td>0.000651</td>
</tr>
<tr>
<td>7</td>
<td>-0.27780</td>
<td>-0.001172</td>
<td>0.07717</td>
<td>0.000651</td>
</tr>
<tr>
<td>8</td>
<td>-0.27769</td>
<td>-0.001093</td>
<td>0.07711</td>
<td>0.000607</td>
</tr>
<tr>
<td>9</td>
<td>-0.27759</td>
<td>-0.001182</td>
<td>0.07705</td>
<td>0.000656</td>
</tr>
<tr>
<td>10</td>
<td>-0.27735</td>
<td>-0.001177</td>
<td>0.07692</td>
<td>0.000653</td>
</tr>
<tr>
<td>11</td>
<td>-0.27736</td>
<td>-0.001176</td>
<td>0.07693</td>
<td>0.000652</td>
</tr>
<tr>
<td>RESON</td>
<td>-0.2768</td>
<td>-0.00117</td>
<td>0.07664</td>
<td>0.00065</td>
</tr>
</tbody>
</table>

Table 3.5: Convergence of the pole corresponding to the known resonance for single channel pyrazine in \( ^2A_u \) scattering symmetry. The fit was obtained from the specified \( P \) fit points spread evenly across the energy interval of 7.35E-3 Ry to approximately 1.84485 Ry. The value of the pole obtained with the RESON program is shown in the final row.

In figure 3.4 we show the single channel cross section, \( \sigma \), for scattering from pyrazine in \( ^2A_u \) symmetry, calculated from the parametrised S-matrix using:

\[
\sigma(E) = \pi \frac{k^2}{E} |1 - S(E)|^2
\]

where \( S(E) \) is the S-matrix value at a particular energy \( E \). The cross-section shown in figure 3.4 was obtained from an S-matrix determined using \( P = 65 \) fit points spread evenly across the energy interval of 7.35E-3 to approximately 1.84485 Ry. Also shown in figure 3.4 is the cross-section calculated directly from the ab initio K-matrices.

There are two main points to make about the comparison between these two cross sections; firstly, we see on the inset very strong agreement between the original and the fitted data (the slight deviations which are apparent arise due to the use of different discrete energy sets for the two plots). Secondly, the resonances occurring above an energy of around 0.8 Ry are not apparent in the fitted data, which we explain from their position being well outside the set of fit points (shown with red crosses) and their widths being much narrower than the known resonance at 0.077 Ry. It’s worth mentioning that these are unphysical resonances (due to the limitations of the SEP model as discussed in section 2.5.2). However, we would expect that whether or not a resonance is physical should have little impact on the ability of the procedure to detect it or not.

For examination of the automatic pole detection described in section 3.1.3 we tested using a value of 0.0001 \( a_0^{-1} \) for the comparison threshold, \( dk \). This resulted in the pole / conjugate pole pair
3.5 Multi Channel Results

3.5.1 Potential well

As for the single channel case, we used a potential well to test the multi channel case. Table 3.6 shows the closest roots to the known states as described in section 3.2 for a 2 channel, elastic square well with $a=1.0 \, \text{a}_0$, $v_{11}=v_{22}=2.0 \, \text{Ha}$. For the reskit calculation, even $P$ were used by fitting $P=2M$ fit points in the interval 1.0-8.0 Ha, with a starting $dk$ of $10^{-4} \, \text{a}_0^{-1}$ and testing across 3 successive $M$ (i.e. number of steps, $cf=2$). The $P$ fit points were selected from a set of $O = 1000$ evenly spaced energy points for which the S-matrix was calculated using the functional form given in [42]; 100 decimal places were used throughout these calculations.

The first two poles in table 3.6 correspond to bound states while all the others correspond to
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

Table 3.6: S-matrix poles for a 2 channel, elastic radial square well of width $a=1.0 \, a_0$ and depth $v_{11}=v_{22}=2.0 \, H\alpha$. The two column groups list the real and imaginary components of the energy of the poles obtained numerically from the exact solutions given in [42] (left group) and those located using reskit (right group). The right group shows the QIs, $\varpi dk$ and $\Sigma M$, for two values of $M_{\text{max}}$. A hyphen indicates that no pole was identified. For the real and imaginary components a decimal precision of three digits has been used throughout, which is the approximate precision of the functional method used for the left group. Note that the real and imaginary components in the right group are shown as obtained from the $M_{\text{max}} = 20$ calculation, although these were nearly identical, to three decimal places, to those obtained with $M_{\text{max}} = 15$. Also note that the precision shown here is much lower than that obtained from the reskit calculation (which is much higher than we have room to represent in this table, see table 3.7 for a representation of the decimal precision).

<table>
<thead>
<tr>
<th>$M_{\text{max}} = 15$</th>
<th>$M_{\text{max}} = 20$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varpi dk$</td>
<td>$\varpi dk$</td>
</tr>
<tr>
<td>$\Sigma M$</td>
<td>$\Sigma M$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Functional E (H\alpha)</th>
<th>Parametrised E (H\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real</td>
<td>Imag</td>
</tr>
<tr>
<td>-0.4657</td>
<td>0</td>
</tr>
<tr>
<td>-0.0307</td>
<td>0</td>
</tr>
<tr>
<td>6.131</td>
<td>5.940</td>
</tr>
<tr>
<td>6.129</td>
<td>-5.940</td>
</tr>
<tr>
<td>6.482</td>
<td>7.130</td>
</tr>
<tr>
<td>6.480</td>
<td>-7.130</td>
</tr>
<tr>
<td>53.041</td>
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<td>-24.572</td>
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<tr>
<td>53.168</td>
<td>27.347</td>
</tr>
<tr>
<td>91.663</td>
<td>35.372</td>
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<tr>
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<td>-35.372</td>
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<tr>
<td>91.726</td>
<td>38.952</td>
</tr>
<tr>
<td>91.726</td>
<td>-38.952</td>
</tr>
</tbody>
</table>

Table 3.7: Convergence of the pole near 6.13 H\alpha in table 3.6 for increasing $M$.

<table>
<thead>
<tr>
<th>$M$</th>
<th>$\text{Real } E (\text{H}\alpha)$</th>
<th>$\text{Imag } E (\text{H}\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.947548796707301856015280400671</td>
<td>0.265748262516494625022746083132</td>
</tr>
<tr>
<td>3</td>
<td>0.137528668651726452078587289159</td>
<td>2.333754499518979210913580125889</td>
</tr>
<tr>
<td>4</td>
<td>6.105231600017854127389513402724</td>
<td>5.940297892975684034502238988090</td>
</tr>
<tr>
<td>5</td>
<td>11.1461162888606028783996046546</td>
<td>5.941232293795682020948957147385</td>
</tr>
<tr>
<td>6</td>
<td>13.1507564769439283260313036</td>
<td>5.940191201112208768288824174064</td>
</tr>
<tr>
<td>7</td>
<td>13.1497980760253892033660974623</td>
<td>5.94022373957829569731962652009</td>
</tr>
<tr>
<td>8</td>
<td>13.1497977768742537429753059739</td>
<td>5.94022383472942139796505014326</td>
</tr>
<tr>
<td>9</td>
<td>13.1497977999105847638466698984</td>
<td>5.940223835529722433870519755797</td>
</tr>
<tr>
<td>10</td>
<td>13.14979799878582791881404577</td>
<td>5.94022383552942360668159225567</td>
</tr>
<tr>
<td>11</td>
<td>13.1497979987877434690863840223</td>
<td>5.940223835529423904158295614678</td>
</tr>
<tr>
<td>12</td>
<td>13.149797998787743384742378356</td>
<td>5.940223835529423904169672091908</td>
</tr>
<tr>
<td>13</td>
<td>13.149797998787743384779192569</td>
<td>5.940223835529423904169648952163</td>
</tr>
<tr>
<td>14</td>
<td>13.149797998787743384779503703</td>
<td>5.940223835529423904169648154793</td>
</tr>
<tr>
<td>15</td>
<td>13.1497979987877433847795037177</td>
<td>5.940223835529423904169648154758</td>
</tr>
</tbody>
</table>
3.5 Multi Channel Results

Figure 3.5: Effect of width on quality indicator $\Sigma M$ for a potential well of width $a=1.0 \; a_0$. The different resonance widths were achieved by varying the depth of the well ($v_{11}$ and $v_{22}$) from 0 to 10 Ha. The fit set was chosen over a range of 7.0 Ha centred around the real part of the resonance energy. A starting $dk$ of $10^{-4} \; a_0^{-1}$ was used, with $cf=2$.

resonances: both the resonance pole and its conjugate pole are tabulated. Three things are immediately clear from the table: i) the method identifies poles well outside the range of the real energies for which S-matrix data is provided; ii) the QIs get worse (that is, $\sqrt{dk}$ increases and $\Sigma M$ decreases), as the method ‘extrapolates’ further away from the data provided; iii) use of a larger value for $M$ (in the same energy range) enables the identification of poles further from the energy range of the input data set as well as improving the QIs for the poles already identified.

Figure 3.5 and table 3.6 clearly show, for a potential well of width $a=1.0 \; a_0$, that the QIs get worse as poles move further away from both the real axis and the (real) energies for which the S-matrix data is provided. In figure 3.5 $\Sigma M$ can be seen to decrease (worsen) as the imaginary part of a given pole (i.e. the width of the resonance it corresponds to) increases for deepening of the well. The data in figure 3.5 corresponds to a specific resonance as the depth of the well is varied. In order to eliminate the effect of extrapolating the real component of the energy, the calculation for each depth was done by shifting the energy range of the fit set, so that the real part of the pole energy was located approximately in its centre. Unsurprisingly, $\Sigma M$ decreases as the width of the resonance increases, even though all the poles identified by reskit are true poles of the system. This example demonstrates that bad QIs (lower $\Sigma M$ and higher $\sqrt{dk}$) are to be expected for wider resonances. In other words, if the resonance is wide with bad QIs this should not necessarily be taken to indicate the pole identified is not a true pole of the system. Table 3.6 tabulates located poles for a particular well, for $v_{11}=v_{22}=2.0$ Ha. Again we can see that the $\Sigma M$ and $\sqrt{dk}$ of the located poles worsen as the imaginary part of the pole increases.

Finally, as an illustration of the convergence of a root, for increasing values of $M$, table 3.7 shows the value of the roots converging to the third pole listed in table 3.6. It can be seen that, in this calculation, both real and imaginary components of the pole converge to a precision of more than 20 decimal places. As we will see, this is not the case when $ab\; initio$ S-matrix data is used.
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

3.5.2 Pyrazine

This is an example of locating poles corresponding to resonances from \textit{ab initio} K-matrix data. This data corresponds to 3 channel elastic electron scattering from the pyrazine molecule in $^2A_u$ symmetry. For the calculation, even $P$ were used in the interval $7.35 \times 10^{-4}$ to $0.441368$ Ry, with a starting $dk$ of $10^{-4}$ $a_0^{-1}$, $cf = 3$ and $M_{\text{max}} = 20$. The energy interval encompasses the well known shape resonance around 0.077 Ry [88, 89, 90] (as already mentioned for the single channel case). For this 3 channel case the resonance was detected by RESON at $0.07664 \pm 0.00065i$ Ry.

Table 3.8 summarizes the candidate poles. It is immediately clear that the QIs in this calculation are, in general, poorer than for the case of the square well, even though the real component of all the candidates poles is inside the energy range of the initial S-matrix data. The candidate pole with the best QIs (labelled 1, with the smallest $\sqrt{dk}$ and largest $\Sigma M$) corresponds to the known resonance of the system. This resonance is visible in the elastic cross section plotted in figure 3.6. Figure 3.6 shows that the S-matrix obtained using Padé approximants (with $M = 10$) describes the scattering process very well within the region of the fit points provided: the agreement between the cross sections obtained from both original and fitted S-matrices is excellent.

The other pole / conjugate pole pairs in table 3.8 have significantly poorer QIs. Two of them (labelled 2 & 3) have relatively large imaginary components. The last three poles (labelled 4 & 5) have an extremely small $\Sigma M$ and a negative real component: the pair with a non-zero imaginary component is clearly non-physical (bound states have zero imaginary components) and we shall not discuss it further.

The issue to address is whether the candidate poles are true poles of the system or not. We note here that it is possible for poles of the S-matrix of a system not to manifest themselves in physical observables. Therefore it is possible that, even if no resonance (or virtual state) has been identified in a certain energy region by scattering calculations or experiments, a true pole of the S-matrix is present in that region.

<table>
<thead>
<tr>
<th>Label</th>
<th>Real $E$ (Ry)</th>
<th>Imag $E$ (Ry)</th>
<th>$\sqrt{dk}$</th>
<th>$\Sigma M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.076641</td>
<td>6.5298e-4</td>
<td>1e-11</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>0.076641</td>
<td>-6.5298e-4</td>
<td>1e-11</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>0.068281</td>
<td>0.17860</td>
<td>1e-5</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.068281</td>
<td>-0.17860</td>
<td>1e-5</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>0.30872</td>
<td>0.24350</td>
<td>1e-5</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>0.30872</td>
<td>-0.24350</td>
<td>1e-5</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>-0.05360</td>
<td>0.09512</td>
<td>1e-4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>-0.05360</td>
<td>-0.09512</td>
<td>1e-4</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>-0.09335</td>
<td>0</td>
<td>1e-4</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.8: Real and imaginary components of the poles and QIs for 3 channel elastic scattering from pyrazine in $^2A_u$ symmetry obtained with reskit using $M_{\text{max}} = 20$ in the energy interval $7.35 \times 10^{-4}$ to 0.441368 Ry, a starting $dk$ of $10^{-4}$ $a_0^{-1}$ and $cf=3$. Any quantity whose absolute value is less than $10^{-20}$ is regarded, and tabulated, as zero. Note that the poles are listed in order of deteriorating QIs, not in energy order.

The candidate poles labelled 2, 3 & 5 have not been identified in the literature [88, 89, 90] as resonances nor do they seem to have an effect in the elastic cross section. Their poor QIs could be due, as was shown in the case of the radial square well, to the fact that these poles lie further away from the...
3.5 Multi Channel Results

real axis. However, their QIs do not improve significantly when $M_{\text{max}}$ is increased to 48, whereas $\Sigma M$ increases significantly (to 80) for the first pole / conjugate pole pair.

Also, for the candidate pole labelled 5, the imaginary component is zero which corresponds to a bound/virtual state of the anion $\text{C}_4\text{N}_2\text{H}_4^-$. However, the cross section obtained from this calculation does not show the behaviour expected in the presence of a virtual state. It is possible here, since the QIs are so low, that this is a spuriously reported pole. By chance, two random roots from successive $M$ can have energies less than $dk$ apart and be identified as the same (stable) root. This will be much more likely to be a possibility for lower QIs. Also, larger values of $dk$ (but less so for bigger $cf$) will increase the likelihood of a spuriously reported pole. The higher the number of channels, the more roots of the S-matrix (for a specific number of fit points), again increasing the likelihood of random roots being identified as candidate poles. It is also possible that this is a genuine pole but is a non-physical artefact of the R-matrix calculation.

![Figure 3.6: $2\text{A}_u$ contribution to the elastic cross section for 3 channel scattering from pyrazine. 'Original' indicates the cross section obtained from the \textit{ab initio} S-matrix, 'Fitted' corresponds to the cross section obtained from the rational S-matrix and the 'Fit points' ($P=20$) are those used in the fit. Inset shows a zoomed plot in the vicinity of the $\sim 0.077$ eV resonance.](image)

One way of helping establish confidence whether a candidate pole is physical and not arising through coincidence (that the roots for successive $M$s are close in energy through chance) is to perform the calculations changing the range of energies for which the \textit{ab initio} data is provided [49]. This will entail either changing the starting energy, the energy range or both. In the case of scattering from pyrazine, both variations of the starting energy and the range were investigated, with the constraint that the energy range of the fit set always encapsulated the real values of the poles in table 3.8. We found that the first pole pair at the top of table 3.8 (labelled 1) was detected for all our variations of the starting energy and the energy range. The other poles with low QIs in the table were not consistently detected for our variation test sets, i.e. would sometime be and sometimes not be detected. We therefore take a sceptical approach and deem that the candidate poles with poor QIs ($\forall dk \geq 10^{-5}$)
cannot be designated true poles of the S-matrix with confidence. We feel it’s clear that the pole labelled 1 in table 3.8 is physical.

The poorer QIs for this example compared to those for the radial square well can probably be attributed to the precision of the input data provided. Whereas in the case of our radial square well calculations the S-matrix data was determined to 100 decimal places, the \textit{ab initio} R-matrix calculations have significantly lower precision. For the radial square well, resonances with a real component far from the energy range of the input S-matrices are identified with high QIs. However, our tests showed that this is not the case when (less precise) \textit{ab initio} data is used. Therefore, the energy range for the inputted S-matrices when using \textit{ab initio} (or lower precision) scattering data should be chosen more carefully.

### 3.5.3 Uracil 6 channel

In this example, K-matrix data from a calculation of 6 channel elastic electron scattering from uracil in $^2A''$ symmetry is used. The \textit{ab initio} data has again been obtained using the UKRmol suite. The calculations were performed at the SE level and, in order to reduce the number of channels, only partial waves up to $l=3$ were included (for details of the calculation on which this one was based see [55]). Unlike pyrazine, uracil is a polar molecule (its dipole moment is around 4.4 D); this means that a long range interaction affects the scattering process. It is well known [91, 55] that this system possesses three shape resonances. At the SE level Kossofski et al. [92] found resonances at 0.17, 0.30 and 0.59 Ry. The resonances detected (with RESON) in the UKRmol SE calculation used in this test are shown in table 3.9.

![Table 3.9](image)

Table 3.9: Poles and goodness indicators for 6 channel elastic scattering from uracil at the equilibrium geometry in $^2A''$ symmetry obtained using the RESON program from UKRmol calculated K-matrices. These three resonances have been identified by a number of scattering calculations.

![Table 3.10](image)

Table 3.10: Poles and QIs for 6 channel elastic scattering from uracil in $^2A''$ symmetry at the equilibrium geometry obtained using the reskit routines with $P = 4 \rightarrow P = 40$ fit points spread evenly across the energy interval of 7.35E-3 to approximately 0.882000 Ry.
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Figure 3.7: $^2A''$ eigenphase sum for 6 channel elastic scattering from uracil at the equilibrium geometry. The eigenphase sum as calculated directly from the UKRmol produced K-matrices is shown in green. Superimposed (in red, blue, purple and orange) are least squares minimisation fits for each of the resonances using the Breit-Wigner resonant profile given by equation (2.63), along with a quadratic background, using the positions and widths of the four resonances in table 3.10. The labels shown for each of the resonances correspond to those in table 3.10.

For our calculation, even $P$ were used in the interval $7.35 \times 10^{-4}$ to $\sim 0.8820$ Ry, with a starting $dk$ of $10^{-4}$ $a_0^{-1}$, $cf = 3$ and $M_{max} = 20$. Table 3.10 summarises the candidate poles found, which show poorer QIs than for both the radial square and the 3 channel pyrazine. Performance was likely worse for uracil than for pyrazine due to the increase in the number of channels from 3 to 6. The first three candidate pole / conjugate pole pairs (labelled 1, 2 & 3 in table 3.10) correspond to resonances identified using the RESON program, as can be seen by comparing to the values in table 3.9. It’s interesting to note here that the final resonance fitted by RESON in table 3.9 has a goodness indicator of 0.38e-02, which is high enough to, in practice, qualify it as poorly identified. The fact that we have independently detected what seems to be the same resonance using reskit (labelled 2 in table 3.10) makes this much more likely to be an actual resonance, rather than a spurious report by RESON.

The last pole / conjugate pole pair (labelled 4 in table 3.10) would describe a rather wide resonance. This resonance has relatively poor QIs, which is in line with the previous discussion; resonances with large imaginary components will generally have poorer QIs. However, it is hard to say for sure whether or not this is a true pole of the S-matrix, as it is not, to the author’s knowledge, reported in the literature. Additionally, as shown in figure 3.7, resonance 4 has no discernible effect on the eigenphase sum, although this might be expected, given the high width of this resonance.

Also shown in figure 3.7 are fits for each of the detected resonances in table 3.10, made using the pole positions and widths as input to equation (2.63) with $N = 1$, along with a quadratic background. With reference to the labels and values specified in table 3.10, figure 3.7 shows that a good fit is obtained with the positions and widths of pole 3 as input to equation (2.63). Poles 1 and 2 clearly show worsening fit quality, although there is still a matching of trend and clear association between
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

the original and fitted curves. Pole 4 however, clearly does not produce a fit matching anything like the original curve. Considering figure 3.6, where a near perfect fit was obtained to the elastic cross section for 3 channel scattering from pyrazine, we emphasise the difference in fit method here: the pyrazine cross section was calculated directly from the parametrised S-matrix, whereas in figure 3.7 we have fitted each resonance individually using the resonance positions and widths, without accounting for influence from the surrounding resonances. In retrospect, better fits may be possible by simultaneously fitting all three or four resonances (depending on whether resonance 4 exists or not) using equation (2.63). However, it needs to be noted that the unitary breakdown condition given by equation (2.68) is well satisfied for resonances 1 and 4 and also 2 and 4 (but not 1 and 2).\textsuperscript{21} It can then be hypothesised that the deterioration in quality of the fits using the positions and widths of resonances 1 and 2 is due to their overlap with resonance 4 (which could imply the existence of resonance 4 if the hypothesis holds true).

Figure 3.8 shows the $^2A''$ contribution to the cross section obtained from the original \textit{ab initio} S-matrix and the rational one. Once again the agreement between the two is excellent, but only down to around 0.07 Ry. Below that energy, the cross section obtained from the rational S-matrix shows unphysical peaks. We believe this behaviour is related to the enforcement of the condition that the S-matrix becomes the identity matrix when $k \to 0$ to obtain the system of equations (2.73) not being appropriate for polar molecules in the fixed-nuclei approximation. Clearly, this problem does not prevent the identification of poles at higher energies, but we would expect that it will prevent the identification of poles in the low energy range. We suspect that this is a contributing factor to the low QIs obtained for resonance 3 in table 3.10.

![Graph of cross section vs energy](image)

Figure 3.8: $^2A''$ contribution to the cross section for 6 channel elastic scattering from uracil. 'Original' indicates the cross section obtained from the \textit{ab initio} S-matrix, 'Fitted' corresponds to the cross section obtained from the rational S-matrix and the 'Fit points' ($P^2=20$) are those used in the fit.

\textsuperscript{21}We note that the condition (2.68) is also satisfied between resonance 3 and 4 but only marginally.
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3.5.4 Uracil 10 channel

We now describe the results for 10 channel elastic scattering for three geometries of the uracil molecule in \( ^2A' \) symmetry. As discussed in the introduction, DEA occurs when a scattering electron attaches to a molecule in a resonant state with sufficient total vibrational energy and long enough lifetime to allow dissociation to occur with an electron remaining attached to one of the dissociated fragments. It is therefore important to understand how the position and width of a resonance changes as the bond length increases from the equilibrium geometry to the dissociation limit (see chapter 1 section 1.3). The resonance widths allow determination of an effective lifetime over the range of bond lengths.

Table 3.11 shows the energies and widths obtained at equilibrium geometry using the RESON program and table 3.12 the poles located using the reskit routines for the three geometries.

### Table 3.11: Poles and QIs for 10 channel elastic scattering from uracil at the equilibrium geometry in \( ^2A' \) symmetry obtained using the RESON program.

<table>
<thead>
<tr>
<th>Lbl</th>
<th>Equilibrium D0 Geometry</th>
<th>D1 Geometry</th>
<th>D2 Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Real ( E ) (Ry)</td>
<td>Imag ( E ) (Ry)</td>
<td>Goodness Indicator</td>
</tr>
<tr>
<td>1</td>
<td>0.635</td>
<td>-0.0113</td>
<td>1e-06</td>
</tr>
<tr>
<td></td>
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<td>0.0113</td>
<td>1e-06</td>
</tr>
<tr>
<td>2</td>
<td>0.682</td>
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<td>1e-06</td>
</tr>
<tr>
<td></td>
<td>0.682</td>
<td>0.0420</td>
<td>1e-06</td>
</tr>
<tr>
<td>3</td>
<td>0.815</td>
<td>-0.0477</td>
<td>1e-05</td>
</tr>
<tr>
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<td>0.815</td>
<td>0.0477</td>
<td>1e-05</td>
</tr>
<tr>
<td>4</td>
<td>0.789</td>
<td>-0.0807</td>
<td>1e-04</td>
</tr>
<tr>
<td></td>
<td>0.789</td>
<td>0.0807</td>
<td>1e-04</td>
</tr>
</tbody>
</table>

Table 3.12: Poles and QIs for 10 channel elastic scattering from uracil in \( ^2A' \) symmetry obtained with \( P = 4 \rightarrow P = 40 \) fit points spread evenly across the energy interval of 7.35E-3 to approximately 0.882000 Ry.

Figure 3.9 shows the equilibrium geometry cross section obtained directly from the \textit{ab initio} R-matrix data and also from the parametrised S-matrix. As usual there is good correspondence between the two, except for the low energies. These low energy deviations occur for the same reasons given in the previous section discussing the 6 channel uracil tests. It’s evident from figure 3.9 that there are three resonances present. Also evident from the figure and the results shown in table 3.12 is that the lowest and highest energy pole / conjugate pole pairs in table 3.12, (labelled 1 & 3) both overlap (i.e. satisfy the inequality (2.68)) with the central one (labelled 2).

Four pole / conjugate pole pairs have been located by reskit, which is more than the three resonances apparent in the cross section (figure 3.9) and eigenphase sum (not shown). Possible explanations for this are that one of the reskit located resonances is spurious or that it is otherwise
unobservable in the cross section and eigenphase sum.\textsuperscript{22} If unobservable, it would be due to a combination of background effects and overlap with surrounding resonances. The pole / conjugate pole pairs labelled 3 and 4 (in table 3.12) have the lowest quality indicators (and highest widths) and are both close to one another and peak 3 in figure 3.9, whereas the pole pairs labelled 1 and 2 each appear to be associated exclusively with a single peak (peak1 and peak2 respectively in figure 3.9). Therefore, we suspect that either one of the pole pairs labelled 3 or 4 is the "unobservable" resonance. It is difficult to be certain which of these (either 3 or 4) would be more likely to be the resonance "unobservable" in the cross section and eigenphase sum. This is primarily due to the fact that the detected resonances are overlapping, as per the condition (2.68), making distinguishing them from one another difficult in quantities such as the cross section and eigenphase sum. It’s possible that they may appear separated (assuming that neither are spurious) in the time-delay (see chapter 2, section 2.1.6) but this was not examined in this work.

We can see from table 3.11 that the goodness indicators obtained for the resonances with the RESON program are much worse for the 10 channel $^2A'$ case than for the 6 channel $^2A''$ case. Possible reasons for the deterioration in goodness indicators are the closer proximity of the resonances to one another and a more complex or prominent background in the 10 channel results, as is apparent when comparing figures 3.8 and 3.9.

The RESON detected resonance at 0.631 Ry has a goodness indicator approximately 100 times

\textsuperscript{22}It’s also possible that multiple resonances can manifest as a single peak but we think this is of minor consequence here.
Multi Channel Results

3.5 Multi Channel Results

higher (worse) than the other two. We suspect that this is a spurious detection by RESON, since the RESON detected resonance at 0.635 Ry has a nearly identical position and width to the reskit detected resonance at the same energy (labelled 1 in table 3.12). Since there is no equivalent detection to the RESON 0.631 Ry resonance in the reskit results and that this 0.631 Ry resonance is below peak1 in figure 3.9, to which the 0.635 Ry has already been associated, then there is no apparent feature in the cross section or eigenphase sum to which this resonance can be linked. The question then arises as to why RESON didn’t detect three non-spurious resonances linked to the three peaks in the cross section.23 A detailed investigation was not carried out but an explanation could be due to the background and overlap effects previously discussed, especially when considered alongside the fact that RESON will attempt to fit a maximum of two overlapping resonances [59].

We now discuss the significant deterioration of the QIs when compared to those obtained for the 6 channel \(^2A''\) shown in table 3.10. Although these are different resonances obtained for a different symmetry, the most prominent poles (with best QIs, labelled 1) in both tables have similar widths and are therefore good candidates for comparison. The prominent pole for the 10 channel \(^2A'\) symmetry has a \(\Sigma M\) about half that of the prominent pole for the 6 channel \(^2A''\) symmetry and the \(\vee dk\) are 3 orders of magnitude lower than for the 6 channel case. We first dispel the possibility that this could be related to the fact that the resonances are overlapping in the the \(^2A'\) case. According to [60] the most rigorous approach for analysis of overlapping resonances is to consider them as manifesting from poles located on the Riemann surface. Assuming that they are not so close as to be indistinguishable to numerical techniques, then two poles close to one another on the Riemann surface will manifest as distinct roots of \(F^m\), equation (3.4). Although their close proximity may have a degrading effect on the numerical routines for determining the coefficients and roots of the rational S-matrix we expect this to be much less than the degrading effect when attempting Breit-Wigner fits to overlapping resonances in quantities defined on the real energy axis. Therefore we do not expect the fact that the resonances are overlapping to be the reason for the deterioration of the results. Instead we propose that the likely main reason we see the deterioration of the QIs for the 6 and 10 channel uracil calculations is that the additional number of channels has increased the effect of numerical error propagation, as more operations are required to compute the roots.

Finally we draw attention to the relationship between the deterioration of the QIs and the increase in width which is evident from table 3.12. Here we can observe a clear deterioration of the QIs as the width increases moving down the table 3.12. Note that we were unable to make this observation with the results from uracil 6 channel \(^2A''\) symmetry due to the low energy pole in these results and the associated issue linked to dipolar molecules at low energies (as discussed earlier).

In order to investigate the ability of the procedure to follow resonances for changes to the molecular geometry two other uracil geometries were examined. Following resonances for changing geometry is important for the reasons given at the start of this section. The studied geometries were obtained by stretching the N-H bond, indicated with a small arrow in figure 3.10, by 0.1 \(a_0\) (D1) and 0.2 \(a_0\) (D2). The results obtained using the reskit routines are shown for these geometries, in addition to the equilibrium one, in table 3.12. The dependence of the real and imaginary parts of the poles on the geometry are shown in figure 3.11. It’s hard to draw a definitive conclusion when attempting to correlate the small changes of the positions and widths shown in the figure 3.11 (and table 3.12) with

23 Although besides the discussion point here we mention that no shape resonances of \(^2A'\) symmetry were reported in [55] or in any other literature which we are aware of.
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

Figure 3.10: Chemical structure of the uracil molecule. The white circles represent hydrogen atoms, orange carbon atoms, blue nitrogen atoms and red oxygen atoms. The green arrow indicates the bond stretched to produce the results for the three geometries in table 3.12. Picture adapted from [24].

the slight changes in the QIs in table 3.12. Some of the behaviour may appear contrary to that discussed so far; for example, from D0 to D1 the pole / conjugate pole labelled 4 in table 3.12 shows a 10-30% increase in the width but with improved QIs. However, the energy position also increases, which moves the real part of the pole towards the center of the fit set, a behaviour expected to improve QIs.

We now return to discuss the two pole / conjugate pole pairs whose existence and peak association in the cross section (figure 3.9) is unclear (those labelled 3 and 4 in table 3.12). We note that these two pole pairs are present in all three geometries, which gives weight to the possibility that these pole pairs are at least inherent in the system represented by the ab initio R-matrix data, if not physical. We mention again that if the spurious (i.e. those not associated with a true pole of the S-matrix) roots move about randomly as described in [49] then we would not expect to see them for all geometries. Here we are seeing repetition of the pole / conjugate pole pairs labelled 3 and 4, not in different subsets from the same ab initio R-matrix data set but across data sets from separate calculations involving slightly different geometries of the molecule. This is in line with the conjecture in section 3.5.2, which stated "it is possible for poles of the S-matrix of a system not to manifest themselves in physical observables".

Finally, with respect to the study of DEA, it’s clear from the analysis here that it’s possible to track both the position and widths of resonances for changing bond length using the reskit routines. A full study of the potential for our four identified resonances to result in DEA is outside the scope of this work, with conclusions only likely with calculations involving a wider range of bond lengths and a more elaborate scattering model. The reader is again referred to the comprehensive work on which this study was based [55]. We do note here that our results show that for $^2A'$ symmetry there are three shape resonances, possibly four, one of which has relatively long lifetimes across the three geometries studied.

3.5.5 Carbon Dioxide

We also investigated 9 channel elastic scattering from CO$_2$ in the $^2A_1$ symmetry using the reskit routines. For this molecule no $^2A_1$ resonances are known to exist in the scattering energy range between 7.35E-4 and 0.732795 Ry and our results did not contradict this; nothing was found at any of the $dk$s (1e-4, 1e-5, 1e-6 and 1e-7) or $cs$s (2 and 3) examined. However, there is a known virtual state of the CO$_2$ molecule [93], which has not been located by the reskit routines. The reason for the
3.5 Multi Channel Results

Figure 3.11: Real and imaginary components of the poles (legend corresponds to the labels in table 3.12) for 10 channel elastic scattering from uracil in $^2A'$ symmetry at equilibrium (D0), D1 and D2 geometries.

non-detection of virtual states with our procedure is likely due to the $z k$ preventing determination of the QIs close to the origin. We will discuss this deficiency in more detail in section 3.7 and propose a rectification.

3.5.6 Para-benzoquinone

Finally we apply our technique to K-matrices for 3 channel elastic scattering from the non-polar molecule PBQ in the $^2B_{2u}$ symmetry, the results of which are shown in table 3.13. The eigenphase sum from the R-matrix calculations shows the presence of a very narrow resonance that RESON was unable to identify (it is too narrow for the program to detect the sign change in the second derivative of the phase shift with respect to the energy, although a finer energy grid may have helped). A very narrow $^2B_{2u}$ resonance is also mentioned in the study of Loupas and Gorfinkiel [94], at an energy of 1.70 eV and width 8E-4 eV, obtained from their close-coupling calculation.

<table>
<thead>
<tr>
<th>Real $E$ (Ry)</th>
<th>Imag $E$ (Ry)</th>
<th>$\nu dk$</th>
<th>$\Sigma M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.29108</td>
<td>-7.5356e-6</td>
<td>1e-08</td>
<td>46</td>
</tr>
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<td>0.29108</td>
<td>7.5356e-6</td>
<td>1e-08</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 3.13: Poles and QIs for the $^2B_{2u}$ contribution to 3 channel elastic scattering from PBQ with $P = 4 \rightarrow P = 4$ fit points spread evenly across the energy interval of 7.35e-3 to approximately 0.366765 Ry. The $M$ range used to generate this table is the same as that used for the 3 channel elastic scattering from the pyrazine molecule in $^2A_u$ symmetry shown in table 3.8 with which we compare results.

So far in our analysis we’ve seen that the QIs deteriorate both for increasing width and increasing number of channels in the calculation. However, the quality indicators shown in table 3.13 are significantly worse, even though the widths are smaller, than those for the pole associated with the known pyrazine resonance (labelled 1 in table 3.8), which were obtained for the same number of
channels and across the same $M$ range. We believe that in both cases the reported values of the poles have reached the maximum possible precision available from the limited precision of the input data set. To show this we first consider the widths of the resonances along with the $\sqrt{dk}$ for the 3 channel PBQ and 3 channel pyrazine cases. Then we use equation (3.5) to convert the $\sqrt{dk}$ from an indication of highest relative precision to an indication of highest absolute precision. The poles in the two cases are then shown to have converged to within the following decimal precisions:

PBQ: $7.5 \times 10^{-13} > adiff > 7.5 \times 10^{-14}$  
pyrazine: $6.5 \times 10^{-14} > adiff > 6.5 \times 10^{-15}$

These ranges for the $adiffs$ are both close to one another and to the precision of the input K-matrix data of approximately 14 decimal places.

The lower (worse) $\Sigma M$ obtained for the detected PBQ pole / conjugate pole pair in table 3.13 compared to the pyrazine $\Sigma M$ for pole / conjugate pole pair 1 in table 3.8 are simply due to the fact that the $\Sigma M$ QI relates to the number of successful $cf$ comparison tests; there are no comparison tests executed for $dk$s less than $\sqrt{dk}$.

3.6 Inelastic Scattering and Core-excited Resonances

The present implementation, although based on a general methodology, currently only works for systems in which all the channels have the same energy (i.e. for elastic scattering). For inelastic scattering, locating the roots of the S-matrix is much harder, since the $F^{\text{in}}$, equation (3.4), is no longer a simple polynomial. Iterative techniques such as Muller’s method [83] can at best only locate a single root at a time, given a starting guess. The more elaborate Delves method [84] (which uses Muller’s method), which is designed to attempt to return all of the roots within a closed contour defined in the complex plane, can also be employed. Initial tests for the square well and some $ab initio$ data using the Delves technique showed some potential but further refinement to the routines would be required when applied to the $ab initio$ data, especially for the case when resonances are close to threshold/s. Figure 3.12 shows cross sections calculated directly from the analytical S-matrix given in [42] and from the parameterised S-matrix using Rakityansky et al.’s method. For both cases the cross sections were calculated from the S-matrices using the following formula [85]:

$$\sigma_{mn} = \frac{\pi}{k_n^2} |\delta_{mn} - S_{mn}|^2 \quad (3.12)$$

As evident from figure 3.12, excellent correspondence was achieved between the cross sections obtained from the analytical solutions and those from the parameterised S-matrix, obtained from the 2 channel inelastic radial well described in section 3.2 (channel potentials $v_{11} = v_{22} = -2.0$ Ha, width $a = 1.0$ a$_0$ and thresholds $E_{1}^{th} = 0$ Ha and $E_{2}^{th} = 2$ Ha). However, no root finding is required to obtain the cross sections in figure 3.12, which is the major technical hurdle in implementing the methods for finding the poles associated with an S-matrix describing inelastic scattering.

Finally, we note that, although we did not encounter the problem, it looks likely that we would be forced to adopt the Delves method for certain elastic cases as well, since certain expansions of $|F_{mn}^{(\text{in})}|$ can lead to negative exponents depending on the channel angular momenta.
3.7 General Discussion

We have implemented the methods of Rakityansky et al. for parameterising and locating the poles of an S-matrix for both the single and multi channel cases. For the multi channel case we have developed two QIs, $\vartheta dk$ and $\Sigma M$, to convey confidence in candidate poles identified from the roots obtained from the denominators of the parametrised S-matrices. The $\vartheta dk$ can be interpreted as the relative precision of the converged poles and $\Sigma M$ the number of times the converged pole was detected using all of the root sets from the fitted S-matrices.

These QIs have been used to analyse the quality of the S-matrix poles obtained using these methods from several systems. The data was obtained from analytically solvable systems and from ab initio R-matrix calculations for several molecules, for both single and multi channel cases. In particular the following systems were examined: the square and radial potential wells, pyrazine, uracil, PBQ and CO$_2$ molecules, in various symmetries. We now summarise the general behaviour of the procedure proposed in section 3.1 observed from this analysis, as well as its benefits and limitations. With regard to the quality of bound, virtual and resonance state detection we observed the following behaviours:

![Figure 3.12: Analytical and rational cross sections for a 2 channel, inelastic square well of width, $a = 1.0 \, \text{a}_0$, depths $v_{11} = v_{22} = -2.0 \, \text{Ha}$ and thresholds $E_{1}^{th} = 0 \, \text{Ha}$ and $E_{2}^{th} = 2 \, \text{Ha}$, as described in section 3.2. The different coloured lines indicate the matrix elements of cross section as given by equation (3.12).](image)
3 IDENTIFICATION AND CHARACTERISATION OF RESONANCES USING AN IMPLEMENTATION BASED ON THE CONTINUATION OF THE JOST FUNCTION

1. Deterioration with increasing number of channels. Illustrated by the QIs associated with the poles obtained in the 3 channel pyrazine and 6 and 10 channel uracil tests.

2. Deterioration with increasing width of the resonance. Observed with most of the test systems (see behaviour 6 for the exception case), both single and multi channel. Figure 3.5 shows the effect of the width for the two channel radial well. This behaviour is also illustrated for the molecular case in table 3.8, which shows the detected poles for 3 channel pyrazine.

3. Deterioration as the bound state energy or resonance position (real part of the pole) moves away from the center of the input data set energy range, regardless of any change or not to the width (imaginary part of the pole). Figure 3.3 demonstrates this behaviour for a bound state in a single channel square well.

4. Improvement for increasing \( M \). This behaviour is shown explicitly for the radial well in table 3.6. It can also be inferred from the inverse correlation between the \( \Sigma M \) and \( \sqrt{dk} \) QIs.

5. Sensitivity to the energy grid of the input data set. This behaviour is shown from the tests for the variation of the square well depth in table 3.3. The behaviour can also be inferred from the inverse correlation between the \( \Sigma M \) and \( \sqrt{dk} \) QIs.

6. For narrow enough resonances, deterioration with decreasing width of the resonance. This was seen, with some justification, for the behaviour of the narrow resonance detected for PBQ, discussed in section 3.5.6.

7. The achieved precision of the detected bound states and resonances will decrease with decreasing precision of the input data set.

The first of these behaviours can likely be attributed to the increasing size of the calculation with increasing channels; a higher number of arithmetic operations (to calculate the parameterised S-matrix) increases the effect of numerical noise propagation. The second is a consequence of the physical characteristics of the system and is a behaviour observed in all (author known) resonance detection techniques: as a resonance increases in width it becomes more difficult to detect (assuming it’s not too narrow to begin with - see behaviour 6). From a general perspective the wider a resonance is, the smaller the resonance effect will be in proportion to the background contribution. We consider that, as applied to the technique discussed in this chapter, the background effect arises from the extrapolation region on the Riemann surface between the S-matrix fit data (defined only at real energies) and the resonance pole position.

The second behaviour along with the third are both extrapolation related (since both consider the detection of the resonance on the Riemann energy surface with respect to a set of S-matrix data defined only at real energies). Therefore confidence can be increased in reported results by more effectively positioning the input data set relative to the real position of the resonance. However, since the input data set is for real energy values, very little can be done in this respect for increasing widths (once the data set is centered about the real value of the pole). What can otherwise be done is increasing \( M \) at the cost of computational time (the effect of which is shown in figure D.1 in appendix D) or optimising the step size of the input data set (which is behaviour 5). Also for the case of very wide resonances, additional calculations can be carried out with small energy displacements in the input data set to see if poles with low QIs can be reproduced, thus building confidence in whether or not they are physical.

Behaviour 6 is a limitation arising from the precision of the input data set. However, the current QIs do not readily reflect, or account for this numerical limitation, due to the use of a relative comparison
3.8 Conclusions

A procedure has been developed based on a technique presented by Rakityansky et al. [25] to allow the analytical continuation of a parameterised Jost function from a discrete set of elastic, multi channel S-matrix data determined at real energies into the complex plane. In addition to performing the continuation and the subsequent location of a set of candidate poles, the procedure also provides quality indicators for each of the candidate poles. These quality indicators can be used as a measure of confidence for whether a located pole is physical or not and also to provide an accuracy for the energy positions and widths of the located poles.

The procedure has been applied to a number of test systems. For the analytically solvable ones, tests showed that the accuracy in the location of the bound states was dependent on their energy within the well; as the energy of the bound states was lowered and they moved away from the fit set (composed of S-matrix values determined at real energies above the well) the accuracy in their reported values degraded. However, bound states close enough to the top of the well were identified to a high degree of accuracy. Also, for the 2 channel radial well, a number of resonance states were also identified using the procedure, again with decreasing accuracy as the resonances moved away from the fit set, both from increasing width and/or from changing position.

For the tests performed on the molecular UKRmol ab initio data sets all resonances previously reported in the literature were located using our procedure, as well as some resonances previously unreported in the literature. For the molecular data sets the QIs of the detected resonances were, in general, much worse than for the resonances reported for the analytically solvable systems. This is likely due to the smaller number of significant figures of the ab initio data. We also observed the same relationship between QIs and widths as for the analytically solvable systems; that generally, the QIs are worse for wider resonances. Since we tested several molecular data sets with differing number of channels we were additionally able to see that the QIs generally degrade as the number of channels increase.

The present implementation, although based on a general methodology, currently only works for systems in which all the channels have the same energy (i.e. for elastic scattering). For inelastic scattering, additional methods for root location will be required. The present implementation is also ineffective for polar molecules at very low energies.
Chapter 4

Temporary States of $H_2^-$ Investigated using a Technique based on the Time-delay

In this chapter we present resonance potential energy curves and widths from calculations of electron collisions with molecular Hydrogen around the $H(1s) + H(2l)$ dissociation limit obtained using the R-matrix method. This work was motivated by recent velocity slice imaging (VSI) experiments, which revealed in the angular distributions of the dissociated $H^-$ ions a lack of symmetry not consistent with dissociation via a single resonant state [19].

4.1 Introduction to $H_2^-$ and DEA

$H_2$ is the simplest neutral molecule; being diatomic it’s linear with a center of inversion and therefore belongs to the $D_{\infty h}$ point group. DEA to $H_2$ results only in an $H^-$ and a neutral hydrogen atom. The first two DEA dissociation limits with $H^-$ in the ground state are $H(1s) + H^-(1s^2)$ at 3.67 eV and $H(2l) + H^- (1s^2)$ at 13.88 eV (unless noted otherwise, these and other energies in this chapter are relative to the ground vibrational state of neutral $H_2$ in the ground electronic state). Although $H^-$ doesn’t support singly excited bound states, there is a series of doubly excited resonance states starting at $\sim 10$ eV above the $H^-$ ground state [96]. These lead to a series of $H(1s) + H^{**}$ dissociation limits starting at 14.00 eV (with $H^{**}$ representing an anion in a doubly excited resonant state), which is very close to the $H(2l) + H^- (1s^2)$ dissociation limit at 13.88 eV. Therefore both the $H(2l) + H^- (1s^2)$ and the $H(1s) + H^{**}$ dissociation limits can be considered as possible DEA outcomes for energies around the $H(1s) + H(2l)$ dissociation limit at 14.68 eV. However, due to their instability, any $H^{**}$ produced via DEA is unlikely to be detected by the experiments typical to the study of DEA.

The experimental DEA cross sections for production of $H^-$ at energies around these dissociation limits show three peaks at $\sim 3.75$, $\sim 10$ and $\sim 14$ eV (see [97] for an early review). The first two peaks are understood to arise from DEA into $H(1s) + H^- (1s^2)$ and are well understood [35]; the $\sim 3.75$ eV peak can be associated with a wide $^2\Sigma_u^+$ shape resonance and the second, $\sim 10$ eV peak, with a wide $^2\Sigma_g^+$ core-excited resonance.

The work in this thesis was focused on identifying and characterising the resonances which result in $H(2l) + H^- (1s^2)$ and a DEA peak at $\sim 14$ eV. Our intention was to use these results to investigate the hypothesis put forward by Krishnakumar et al. [19], that the DEA occurs via coherent superposition of two, $^2\Sigma_g^+$ and $^2\Sigma_u^+$, resonances. In the Krishnakumar et al. [19] paper this hypothesis has been examined with a simple model allowing calculation of an asymmetry parameter. They used as input to their model the $^2\Sigma_g^+$ potential curve from [98] and an "average lifetime" calculated using the width at 14 eV reported from an early work [21], however for the $^2\Sigma_u^+$ resonance no real resonance data
was used, rather shifted target energies and estimated widths were employed as a substitute due to (we assume) the authors identifying no adequate candidate resonances in the literature. A range of autodetachment lifetimes for the simulated $^2\Sigma_u^+$ resonance was used, which allowed an asymmetry parameter matching that from the VSI experiments to be obtained empirically [19].

4.2 Previous Studies

One of the earliest experimental observations of the effect of the $\sim 3.75$ eV $^2\Sigma_u^+$ resonance comes from peaks in the vibrational cross sections obtained by Ramien [99] in 1931, although little explanation was given for these findings at the time. A subsequent theoretical work by Taylor and Harris [100] attributed a $^2\Sigma_u^+$ shape resonance as the cause of the $\sim 3.75$ eV peak, which was corroborated by the subsequent experiments of Schultz and Asundi [15]. Two experimental DEA studies provided early evidence of the $\sim 10$ eV ($^2\Sigma_u^+$) and $\sim 14$ eV resonances, those of Schultz [101] and of Rapp [102]. Both these experiments obtained DEA cross sections from about 6 to 20 eV, showing prominent peaks at $\sim 10$ and $\sim 14$ eV. Other early experiments [103, 104, 21] obtained elastic and inelastic electron scattering measurements, providing additional evidence of the H$_2^-$ resonances responsible for the $\sim 10$ and $\sim 14$ eV peaks in the DEA cross sections. A few years after these experiments, in 1973, Schultz’s review [97] attributed the $\sim 10$ eV peak in the DEA cross section as arising from a $^2\Sigma_g^+$ resonance.

The two lower energy peaks in the DEA cross section are well understood, with each peak attributed to a single resonance only and each resonance associated with a single parent state over the entire range of bond lengths from equilibrium up until the dissociation limit. Although both of the resonances are relatively wide, they are well separated energetically from any surrounding resonances. This is not the case for the $\sim 14$ eV peak; around these energies there is a large number of target states dissociating to H(1s) + H(2l) and several resonances identified in a recent theoretical study [35]. Early experiments by Schultz [101] and Rapp [102] looking at absolute cross sections for H$^-$ production both describe the $\sim 14$ eV peak as being associated with dissociation into H(2l) + H$^-$ (1s$^2$). The peaks in the cross section are reported at similar energies in the two studies, however Schultz’s reported peak value is approximately 50% higher than Rapp’s. More recent velocity map imaging (VMI) experiments by Krishnakumar et al. [105] have provided momentum distributions of the DEA produced H$^-$ ions as well as absolute cross sections for H$^-$ production, with a $\sim 14$ eV peak value close to that obtained by Rapp. Both VMI and VSI yield additional information relating to the momentum distributions of the ejected anions, which in turn can be related to the symmetry of the resonant state.

The Taylor and Harris study [100] was one of the first theoretical treatments of H$_2$ negative ion resonances. A more comprehensive study by Eliezer et al. [106] followed, which additionally reported three core-excited shape resonances of $^2\Sigma_g^+$ symmetry leading to dissociation into H(2l) + H$^-$ (1s$^2$), with parent states $c^3\Pi_u$, $C^1\Pi_u$ and $EF^3\Sigma_g^+$. A more recent R-matrix study$^{24}$ was carried out by Stibbe and Tennyson (hereafter S&T) [35], which obtained potential energy curves, widths and branching ratios for several resonances. This brought further clarification to the resonant behaviour for energies below 13 eV and also highlighted that several of the resonances have more than one parent state. They additionally made the observation that Eliezer’s resonances are in fact “manifestations of the same resonance”. Another relatively recent theoretical work by Celiberto et al. [34] used S&T’s second $^2\Sigma_g^+$ resonance (located at $\sim 12$ eV at equilibrium geometry) only and the local complex potential approximation to calculate the cross section of the Schultz and Rapp experiments. Although they

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$^{24}$Using an old diatomic version of the UK Molecular R-matrix Codes [107].
produced results close to those of these experiments (seemingly contradicting the later experiment by Krishnakumar et al. [105]) the authors themselves state that "a multichannel formalism for calculating the DEA cross section in the energy region around 14 eV, which includes all the possible resonances with parent states that correlate to the H(n=2) + H(1s) asymptotic states would certainly provide a more complete description of the underlying dynamics".

4.3 Characteristics of the Calculation

As mentioned, H₂ is a linear molecule with a centre of inversion and therefore belongs to the D_∞h point group. Since the UKRmol+ software suite only supports 1D representations, the calculations were carried out in the D_2h point group with the molecular axis aligned along z. Obtained resonance positions are presented, following conversion, in the following D_∞h symmetries: \(2\Sigma^+\), \(2\Sigma^-\), \(2\Pi\), \(2\Delta\), \(2\Sigma^+\), \(2\Sigma^-\), \(2\Pi\) and \(2\Delta\) for bond lengths from 1.1 a₀ to 4.0 a₀ in steps of 0.1 a₀. The equilibrium bond length of H₂ in its ground state is 1.4011 a₀.

4.3.1 Target Model

Despite its simplicity, H₂ has a complex structure of excited states, the study and characterisation of which has been ongoing for at least a century, likely driven by both the simplicity of the molecule and also its cosmic abundance and importance within many physical fields. A review of the early work can be found in [98], which details both experimental and theoretical potential energy curves for several of the states. From a theoretical perspective, data for the H₂ states has been produced by a number of authors, mainly Kolos, Wolniewicz and collaborators [108, 109, 110, 111] and, more recently, Corongiu et al. [112, 113, 114]. Very recently a comprehensive work by Nakashima and Nakatsuji [115] determined accurate energies for a large number of states. Since these states include all of those used in our calculations, we have used Nakashima and Nakatsuji’s work as a benchmark for our target model.

Again, due to the simplicity of the molecule we were able to use full CI for the target description, with a d-aug-cc-pVTZ basis set. The choice of d-aug-cc-pVTZ followed from tests at equilibrium geometry with several Dunning [116] type cc-pV basis sets: cc-pVTZ, aug-cc-pwCVTZ, aug-cc-pVQZ-f, aug-cc-pwCV5Z, d-aug-cc-pVDZ, d-aug-cc-pVQZ, d-aug-cc-pV5Z. We now discuss the results of these tests.

Use of augmented basis sets had a dramatic effect on the description of the electronic states of H₂; with no augmentation we calculated the third lowest state, the \(a^3\Sigma^+_g\) at \(~2.5\) eV higher than the equivalent results in Nakashima and Nakatsuji [115]. Single augmented bases greatly improved the results, especially for lower excited states but not to a sufficient degree for the higher energies. Doubly augmented produced acceptable results for the higher energy states, in all likelihood due to their more diffuse nature.

Tests of the number of functions describing the valence orbitals showed less of an effect on the target description. Testing with double augmented sets we saw significant improvement moving from double to triple zeta but after that the degree of improvement greatly diminished. We therefore judged the d-aug-cc-pVTZ basis set to offer adequate target quality with a reasonable computational effort and have used this for the results presented in this chapter. Ground state and vertical excitation energies for the equilibrium geometry obtained using the d-aug-cc-pVTZ and d-aug-cc-pVQZ basis sets, along with the results of Nakashima and Nakatsuji [115] are shown in table 4.1. With the d-aug-cc-pVTZ
4.3 Characteristics of the Calculation

basis set we obtained an absolute ground state energy at equilibrium geometry 0.05 eV higher than Nakashima and Nakatsuji’s.

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<th>Label</th>
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<tr>
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<td>15.1046</td>
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<tr>
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<td>15.8235</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>2 $^1\Pi_u$</td>
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<td>16.3026</td>
<td>14.9858</td>
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</tbody>
</table>

Table 4.1: Absolute ground state and vertical excitation energies of H$_2$, in eV, at the equilibrium bond length 1.4011 $\text{a}_0$ calculated at full CI level using the basis sets indicated. The results of Nakashima and Nakatsuji [115] are also included. Note that the states are listed in the order in which they appear in our calculations.

Figure 4.1 shows a comparison of our energy curves, obtained using the d-aug-cc-pVTZ basis set, with those of Nakashima and Nakatsuji. Panel (a) in figure 4.1 shows good agreement between the two calculations for the states converging on the H(1s) + H(1s) dissociation threshold. At equilibrium geometry the $b^3\Sigma_u^+$ excitation energy is 0.03 eV lower in our calculation. Panel (b) shows potential parent states for the resonances of interest in this study: H$_2$ states dissociating to H(1s) + H(2l) inside the energy range of interest to this study. Agreement is also good for most of these states. The exceptions are the high energy $m^3\Sigma_u^+$ state (0.07 eV higher in our calculations) and the two $\Pi_g$ states (0.17 eV higher). Away from the equilibrium geometry deviations between our results and [115] approximately carry across the range of bond lengths for all but three states converging on H(1s) + H(2l). The $h^3\Sigma_g^+$ and $\text{GK}^3\Sigma_g^+$ state deviations significantly increase at higher bond lengths, with maximum deviations of 0.12 eV at a bond length of 3.2 $\text{a}_0$ for $h^3\Sigma_g^+$ and 0.23 eV at a bond length of 2.4 $\text{a}_0$ for $\text{GK}^3\Sigma_g^+$. The description of the $m^3\Sigma_u^+$ state, which has a deviation of 0.07 eV at equilibrium bond length, improves significantly at the higher bond lengths.

Panel (c) in figure 4.1 shows the states converging on thresholds higher than H(1s) + H(2l). It’s quite clear here that the quality of the target description has deteriorated. However, the H(1s) + H(3l) threshold energy is $\sim$2.5 eV above the H(2l) + H$^-(1s^2)$ dissociation limit of interest to our study.
Figure 4.1: Energies for $H_2$ as a function of internuclear separation, calculated with the d-aug-cc-pVTZ basis set (full lines) and those of Nakashima and Nakatsuji [115] (crosses). Energies are shown relative to the ground state at equilibrium geometry and are distributed in the three panels according to the adiabatic dissociation limits of the states shown: (a), $H(1s) + H(1s)$; (b), $H(1s) + H(2l)$; (c), $H(1s) + H(1s^2)$. Lines are coloured according to state symmetry and styled according to state number.

and as such we deemed these states less likely to be parents of resonances converging on the $H(2l) + H^-(1s^2)$ dissociation limit. Use of the d-aug-cc-pVQZ basis set in this energy region did bring some improvement: for example the difference between our and Nakashima and Nakatsuji’s threshold energy for the $2\Sigma^+ u$ state at equilibrium was reduced from 1.8 eV to 1.3 eV (see Table 4.1).

4.3.2 Scattering Model

We included 29 target states belonging to the irreducible representations of $D_{2h}$ in our calculations. They correspond to 21 states in the $D_{\infty h}$ point group. These include all states dissociating to the $H(1s) + H(1s)$ and $H(1s) + H(2l)$ thresholds. Tests with 50 target states for the equilibrium geometry made little difference to the scattering results in our energy region of interest.

An R-matrix radius of 40 $a_0$ was necessary, as confirmed using RADDEN, to ensure all the target orbitals for the d-aug-cc-pVTZ basis sets had negligible amplitude at the boundary. The largest value of the probability density of an orbital at 40 $a_0$ for the d-aug-cc-pVTZ basis sets was $4.5 \times 10^{-7}$.

As $H_2$ is a two electron, diatomic molecule, we were able to use a BTO-only basis to describe the continuum. This basis was comprised of 30 BTOs of order 9 along with partial waves up to $l=6$. Increasing the number of BTOs or the number of partial waves above these values made only negligible difference to the scattering results. A deletion threshold of $10^{-4}$ was used for the orthogonalisation of the continuum orbitals.

A propagation radius of 200 $a_0$ was often sufficient to obtain good scattering results at most bond lengths. However, at bond lengths where some target states were energetically very close, greater propagation radii were required for converged results. This was the case for bond lengths around 1.9 $a_0$,
where both the $c^3\Pi_u$ and $a^3\Sigma^+_g$ states and the $C^1\Pi_u$ and $GK^1\Sigma^+_g$ states are very close to one another, as well as around 2.9 $a_0$, where the $C^1\Pi_u$ and $GK^1\Sigma^+_g$ thresholds are very close to one another. In these cases, propagation radii up to 1100 $a_0$ were used. Despite this, our results around 1.9 $a_0$ still showed the presence of unphysical spikes in the time-delays and cross sections.

4.4 Identification and characterisation of the Resonances

Resonance identification and characterisation was, in nearly all circumstances, carried out using techniques based on the time-delay, as discussed in section 2.1.6. Both the TIMEDELn software package and Zdeněk Mašín’s time-delay program (both mentioned in chapter 2, sections 2.2.1 and 2.6) were used. Additionally, some special scripts were created, based around the python numpy package, which allowed interactive fits to be carried out on the TIMEDELn obtained Q-matrix eigenvalues. As mentioned, the bond lengths from 1.1 $a_0$ to 4.0 $a_0$ in steps of 0.1 $a_0$ were searched for resonances, with energy ranges sufficiently wide to include all of the target states in panel (b) in figure 4.1 plus an additional amount to be confident of detecting any resonances around the outermost target states.

We now discuss in more detail our approach for the location and characterisation of the resonances. Both the time-delay program and TIMEDELn calculate a specified number of eigenvalues of the Q-matrix across the specified energy range. The time-delay program offers no further calculation and was therefore only used as a consistency check against the TIMEDELn calculated Q-matrix eigenvalues. TIMEDELn does provide additional functionality and was the primary program for locating the resonances in this work. Having calculated the Q-matrix eigenvalues, TIMEDELn then proceeds to attempt to locate any resonances by fitting Lorentzians plus a linear background to the calculated Q-matrix eigenvalues. However, since the time-delay associated to a resonance can be distributed over several eigenvalues, TIMEDELn first executes its EIGSORT routine to track the resonances as they switch between the eigenvalues whenever there is an avoided crossing between them. The ideal output of this routine is a single set of data per resonance containing as much of the Lorentzian-like profile in the vicinity of the resonance as is present and distinguishable across all the eigenvalues. This output is then used as input to the subsequent fit routines.

There are two main configuration options to be considered when setting up a TIMEDELn calculation. The first is whether to use a static or dynamic energy grid and the second is whether the routines take into consideration the channel thresholds or not. The grid mode selects whether to calculate the eigenvalues for a static, predefined set of energy points or to dynamically calculate them using a variable grid spacing based on the emerging characteristics of the resonance, effectively zooming the grid in for narrow resonances until sufficient energy points have been calculated to allow a reliable fit. When the channel thresholds are considered, the routines will run independently between the thresholds i.e. the routines will not attempt to perform fits across the thresholds. We ran TIMEDELn calculations with two configurations using as input our UKRmol+ produced scattering data: the first with a dynamic grid and accounting for the thresholds and the second a static grid and ignoring the thresholds. The static grid used an energy interval of 0.002 eV, which was sufficiently fine to describe adequately all of the resonances reported in our results. From the dynamic grid results we were confident we hadn’t missed any narrower resonances.

Typically, both of our configurations resulted in calculations which worked very well for resonances associated with a clearly-defined Lorentzian-like form in the time-delays (which we consider as one where the resonance is visibly and smoothly Lorentzian-like in the time-delays over an energy range
extending approximately between the two energies corresponding to the two values at one quarter peak maximum). For bond lengths around \(1.9 \text{ a}_0\) where we experienced unphysical spikes in the time-delays (as described in section 4.3.2), both of our TIMEDELn calculations, in most cases, resulted in no attempt to fit to any resultant unphysical spikes in the time-delays. In some cases, though, no distinction (by the routines) appeared to be possible between these unphysical spikes and physical resonances, resulting in spurious resonances being reported. Also with both configurations, cases where there were outlying points in an otherwise well-defined Lorentzian-like profile did not appear to have the outliers discarded by the fit routines with the result that the quality of the fit was degraded. These outliers could arise from threshold effects (discussed in more detail below). Another problem which we observed with both configurations was a failure to properly track the resonance to the correct eigenvalue, resulting in a discontinuity in the input data. This could have a dramatic effect on the resonance to be fitted, depending on where in the profile the discontinuity was located. An example can be seen in figure 4.5 just before 12.90 eV. For this case there was little effect on the resultant fit, since the discontinuity was located far from the Lorentzian maximum.

Two main behaviours were observed, across the thresholds, in the time-delays. In some cases the Q-matrix eigenvalues would be truncated by the threshold, resulting in an apparent discontinuity, and in other cases they would cross the threshold practically unperturbed. For both these cases different fits were obtained depending on whether the channel thresholds were considered or not when fitting. For the case where the threshold had little effect on the resonance, ignoring the threshold when fitting typically obtained better fits, since more input data was available to the fit routine. An example of the case for a truncated resonance is illustrated in figure 4.4. This figure shows that when the threshold is considered, only the calculated Q-matrix eigenvalues on the side of the threshold with the Lorentzian maximum were used for input fit data, resulting in the orange fitted curve. Conversely, when the threshold isn’t considered the calculated Q-matrix eigenvalues on both sides of the threshold were used for input, resulting in the blue fitted curve. It’s debatable which of these curves best represents the resonance. In this work we have reported the positions and widths taking into account the thresholds. This has a caveat: the reported values are for a fit which effectively ignores the effect of the truncation.

It’s also important to note that, for the calculations not fitting across the threshold, when the resonance structure in the Q-matrix eigenvalues was truncated to the extent that no maximum of the Lorentzian-like form was present (only the 'tail') no resonance was detected at all. In the calculations fitting across the threshold, the routines appeared to detect the 'peak' formed from the threshold induced discontinuity in the eigenvalue curve (see figure 4.6) and fits were obtained, although these were typically inaccurate.

Our approach was therefore to use the TIMEDELn fit routines to provisionally locate the resonances, removing any spurious resonances arising from numerical noise, as well as manually checking for any potential resonances missed by TIMEDELn. Following this we then obtained more accurate fits of the provisional resonances using our interactive fit method. This had an identical fit model to that used by TIMEDELn but additionally allowed us to remove any outlying points, correct for any discontinuities arising from the EIGSORT routine, choose the optimal range to fit over and handle the thresholds according to their effect on the relevant Lorentzian-like structures. However, even when fitting interactively, we would encounter resonances which we couldn’t reliably fit; these fell into two broad categories: those without a maximum in the Lorentzian-like time-delay profile (i.e. with just a Lorentzian-like ‘tail’) and those with a maximum but with profiles which were quite non-Lorentzian in
4.5 Results

form (which usually resulted in a fitted peak energy which was significantly deviated from the peak in the calculated Q-matrix eigenvalues). For both these cases, if there was sufficient evidence at the surrounding bond lengths that this was indeed a structure associated to a resonances (i.e. acceptable fits were obtained), we provided only an estimated position and no width, showing as a dotted line in our PE diagrams.

4.5 Results

Our results are presented below in separate subsections for each of the following seven D_{2h} symmetries: 2\Sigma^+, 2\Sigma^-, 2\Pi, 2\Delta, 2\Sigma^+_u, 2\Pi_u and 2\Delta_u. No evidence of 2\Sigma_u resonances was found in the energy region of interest.

The resonance parameters were obtained from the time-delay as discussed in section 4.4. Due to the very close proximity of several target states at 1.9 a_0 we were not always able to obtain fits to the resonance peaks at this bond length. No attempt was made to fully determine parent states of the resonances via reduced state calculations, instead likely parent states have been inferred from inspection of the resonance energy curves and the neighbouring target states. They should only be taken as indicative.

We note as well that very narrow resonances close to the excitation thresholds are hard to distinguish from threshold effects and may have therefore been missed.

4.6 2\Sigma^+_g Resonances

Evidence was found of ten resonances of 2\Sigma^+_g symmetry with possibility of converging on the H(2l) + H^- (1s^2) dissociation limit. Their energy as a function of bond length is shown in figure 4.2. Two of these resonances, 1^2\Sigma^+_g and 2^2\Sigma^+_g are documented in S&T and the remaining, to our knowledge, are undocumented in the current literature.

In S&T and [117] resonance 1^2\Sigma^+_g is shown, using reduced state calculations, to have parent states a^3\Sigma^+_g, EF^1\Sigma^+_g, c^3\Pi_u and C^1\Pi_u. Figure 4.2 shows our resonance at the lower bond lengths lying below these four parent states. At bond length 1.1 a_0 it’s relatively wide (\Gamma \sim 0.4 eV) and, as a result, the right hand side of the Lorentzian-like structure in the time-delay is truncated by the a^3\Sigma^+_g target state, possibly affecting the quality of the fit. As the bond length increases the separation between 1^2\Sigma^+_g and the higher lying target states increases, such that by 1.2 a_0 its associated Lorentzian-like time-delay is relatively uninterrupted by any surrounding thresholds and very good fits are obtained. Except for the B^1\Sigma^+_u and EF^1\Sigma^+_g target state crossings, which we’ll discuss shortly, this separation between the resonance and closest target states is maintained over the remaining range of calculated bond lengths. Figure 4.3 shows the near perfect Lorentzian-like form of the time-delay associated with the 1^2\Sigma^+_g resonance and the obtained fits at a bond length of 1.5 a_0.

Resonance 1^2\Sigma^+_g crosses two target states over its detection range: B^1\Sigma^+_u just before 2.1 a_0 and EF^1\Sigma^+_g just after \sim 3.5 a_0. Its width decreases for increasing bond length by about a factor of 25 from 1.1 a_0 to the first crossing point at \sim 2.1 a_0, after which the width begins to increase. This behaviour is also documented in S&T, although the increase in the width is more noticeable in our results. The second crossing induces a jump both in the width and in the energy curves, although this time the increase in width is smaller in our results than in S&T’s. Overall, comparison of our results for this resonance to those of S&T [35] show an average difference of 0.063 eV in the positions and 0.021 eV in the widths. Our positions (relative to the ground state at equilibrium) are higher throughout, except
Figure 4.2: The left hand panel shows $^2\Sigma_g^+$ resonance (thick black lines) and target state energies (coloured lines) as a function of inter-nuclear separation. The right hand panel shows the corresponding resonance widths. The numbers in the two panels label the resonances as referenced in the text. The target state are those converging on the H(1s) + H(2l) dissociation threshold, with the exception of the $^2\Pi$ and $HH$ states, which converge on the H(1s) + H(3l) threshold. On the left hand panel, dashed black lines are used where we were unable to obtain reliable fits; here, positions from manual inspection of the time-delay eigenvalues are used instead (no widths are provided for these bond lengths). Energies are relative to the ground state at equilibrium bond length.

at 3.9 $a_0$ and 4.0 $a_0$. The widths are higher at the middle bond lengths (2.1 $a_0$ to 3.2 $a_0$) and lower for bond lengths outside this range.

Based on S&T’s assignment of the $B^1\Sigma_u^+$ state as its parent, resonance $^2\Sigma_g^+$ is core-excited shape in character in the narrow range of bond lengths where it was successfully fitted (3.7 - 4.0 $a_0$ by S&T; 3.9 and 4.0 $a_0$ in this work). Both calculations show a rapidly decreasing width for increasing bond length in this range, with our results lower in position and higher in width. Even when successful fits were obtained there was still a high degree of truncation to the Lorentzian-like form of the time-delay associated with the resonance: figure 4.4 shows this at the highest calculated bond length of 4.0 $a_0$. It also shows fits obtained using time-delay input data over two different energy ranges: one spanning across the threshold and the other from the high side of the threshold, where the Lorentzian-like peak associated with the resonance is present. It is clear from the figure that attempting to fit across the thresholds results in higher calculated positions and lower widths.

The maximum in the time-delay associated with resonance $^2\Sigma_g^+$ at bond lengths shorter than the 4.0 $a_0$ in figure 4.4 (specifically <3.7 $a_0$) is heavily affected by the $B^1\Sigma_u^+$ state threshold and can’t
4.6 $^2\Sigma_g^+$ Resonances

Figure 4.3: Largest Q-matrix eigenvalues (in black) in the vicinity of the $^1\Sigma_g^+$ resonance at a bond length of 1.5 $a_0$. Also shown, in orange, is the fitted curve using our interactive fit scripts. The fit here is good enough to nearly completely hide the original Q-matrix eigenvalue curve. Energies are relative to the ground state at a bond length of 1.5 $a_0$.

be fitted; the resonance positions here have been obtained from visual inspection. Evidence for the resonance at lower bond lengths is from Lorentzian-like 'tails' clearly visible right down to 2.3 $a_0$. For bond lengths lower than this (2.3 $a_0$) the resonance is likely (based on the previous trend) quite wide and is perhaps drowned out by the nearby $^1\Sigma_g^+$ resonance. It’s therefore possible that this resonance may continue to even smaller bond lengths, since there are visible maxima in the time-delays above the $B^1\Sigma_u^+$ state at bond lengths 1.9, 1.8 and 1.7 $a_0$ (and possibly even shorter bond lengths); this raises the possibility that this and resonance $^4\Sigma_g^+$ are actually one resonance. However, this is quite speculative and as such we consider the resonance as convincingly identified between 2.3 and 4.0 $a_0$.

Just above the $c^3\Pi_u$ target state, between 2.1 $a_0$ to 4.0 $a_0$, a truncated Lorentzian-like form of the time-delay provides evidence of resonance $3^2\Sigma_g^+$. This resonance appears likely to be core-excited shape in character with $c^3\Pi_u$ as parent. Between 2.1 $a_0$ and 2.8 $a_0$, just about half of the Lorentzian-like form is present in the time-delay; at higher bond lengths this proportion lessens and, combined with the increasing width, results in failure to successfully fit the time-delay by 2.9 $a_0$.

At 1.1 $a_0$, resonance $^4\Sigma_g^+$ is positioned slightly (~0.007 eV) above the $B^1\Sigma_u^+$ state, its likely parent, making it core-excited shape in character. It then quickly moves even closer to the $B^1\Sigma_u^+$ state and after 1.3 $a_0$ no reliable fits could be obtained.

Starting at the initial bond length, 1.1 $a_0$, with a Lorentzian-like profile significantly truncated by the $EF^1\Sigma_g^+$ threshold, by 1.5 $a_0$ the $5^2\Sigma_g^+$ resonance has moved sufficiently away from the threshold for the maximum to be visible and successful fits obtained. This is a relatively narrow resonance ($\Gamma \sim 0.008$ eV throughout). The width increases slowly until ~3.1 $a_0$ where it drops and the resonance is 'absorbed' into the $EF^1\Sigma_g^+$ threshold; the resonance is no longer observed for the higher bond.
TEMPORARY STATES OF $H_2^+$ INVESTIGATED USING A TECHNIQUE BASED ON THE TIME-DELAY

Figure 4.4: Largest Q-matrix eigenvalues (solid and dashed black lines) in the vicinity of the $2^3\Sigma_g^+$ resonance at a bond length of 4.0 a$_0$. The threshold for target state $B^1\Sigma_u^+$, the only one within the plotted energy range, is indicated with a vertical line in the figure. This is an example of a Lorentzian-like resonance profile truncated by a threshold. In order to illustrate the effect of the truncation on resultant fits, two fits are shown: The blue curve corresponds to a fit obtained using input data from both sides of the threshold (both solid and black curves). The orange curve corresponds to a fit obtained using input data from above the threshold (solid black curve only). Energies are relative to the ground state at a bond length of 4.0 a$_0$.

lengths. This is likely a Feshbach resonance with $EF^1\Sigma_g^+$ as its main parent state.

$6^2\Sigma_g^+$ is a relatively wide core-excited shape resonance (assuming $a^3\Sigma_g^+$ is its parent state) first appearing around the bond length where $EF^1\Sigma_g^+$ drops below the $a^3\Sigma_g^+$ state. It is detected up to 4.0 a$_0$.

Resonance $7^2\Sigma_g^+$ is present below target state $e^3\Sigma_u^+$ (likely its parent state) for bond length 1.1 a$_0$ and has a width of $\sim$0.046 eV. This width changes little until, at $\sim$1.9 a$_0$, the resonance crosses state $e^3\Sigma_u^+$ and the width starts to increase while the resonance moves away from the $e^3\Sigma_u^+$ state. At $\sim$3.2 a$_0$, just after the $GK^1\Sigma_g^+$ state drops below the $e^3\Sigma_u^+$ state, there is a small reduction in the width. If $e^3\Sigma_u^+$ is assumed to be its parent state, the resonance changes from Feshbach at the lower bond lengths to core-excited shape at the higher ones.

Resonance $8^2\Sigma_g^+$ is first evident at $\sim$2.0 a$_0$, lying between the $h^3\Sigma_g^+$ and $B'^1\Sigma_u^+$ target states. The largest Q-matrix eigenvalues associated with this resonance are shown in figure 4.5, as well as the calculated fit used for characterisation of the resonance. This figure shows that the associated Lorentzian-like form is interrupted by both the $h^3\Sigma_g^+$ and $B'^1\Sigma_u^+$ states on the high and low energy sides of the maximum respectively, although much more so by the closer $h^3\Sigma_g^+$ state. Additionally, at 2.0 a$_0$, as the energy decreases from the maximum of the resonance Lorentzian-like profile towards the lower $B'^1\Sigma_u^+$ state a discontinuity occurs in the time-delay due to EIGSORT having switched to another eigenvalue. Also apparent from figure 4.5 is that the energy range of the input K-matrices
4.6 \(2\Sigma_g^+\) Resonances

Figure 4.5: Q-matrix eigenvalue curve (solid and dashed black curves) in the vicinity of the \(8^2\Sigma_g^+\) resonance at a bond length of 2.0 \(a_0\) and an accompanying fit (orange curve). Also shown, as vertical coloured and dashed lines, are the target thresholds for the states indicated in the legend. This is an example of a Lorentzian-like resonance profile interrupted both by a threshold spike and by a discontinuity where EIGSORT has jumped to another eigenvalue. The fit was obtained using only the data between these two interruptions (solid black curve only). The high time-delay point on the high energy side of the \(h^3\Sigma_g^+\) threshold, we believe, is a threshold effect and not a direct continuation of the curve from the low energy side of the threshold. Energies are relative to the ground state at a bond length of 2.0 \(a_0\).

Figure 4.5: Q-matrix eigenvalue curve (solid and dashed black curves) in the vicinity of the \(8^2\Sigma_g^+\) resonance at a bond length of 2.0 \(a_0\) and an accompanying fit (orange curve). Also shown, as vertical coloured and dashed lines, are the target thresholds for the states indicated in the legend. This is an example of a Lorentzian-like resonance profile interrupted both by a threshold spike and by a discontinuity where EIGSORT has jumped to another eigenvalue. The fit was obtained using only the data between these two interruptions (solid black curve only). The high time-delay point on the high energy side of the \(h^3\Sigma_g^+\) threshold, we believe, is a threshold effect and not a direct continuation of the curve from the low energy side of the threshold. Energies are relative to the ground state at a bond length of 2.0 \(a_0\).

used for fitting this resonance was between the discontinuity in the time-delay up until just before interruption by the \(h^3\Sigma_g^+\) state. As the bond length increases from \(\sim 2.0\ a_0\), state \(B'^1\Sigma_u^+\) moves away and the resonance narrows, such that by \(\sim 2.8\ a_0\) its Lorentzian-like form is nearly fully visible. As the bond length increases further, the resonance begins to move closer to the \(h^3\Sigma_g^+\) state so that only a Lorentzian-like ‘tail’ is present up to at least 3.7 \(a_0\), as illustrated in figure 4.6. \(h^3\Sigma_g^+\) appears to be the parent state, making the resonance Feshbach in character.

Resonance \(9^2\Sigma_g^+\) is fitted only for the two lowest bond lengths, where it’s located below \(B'^1\Sigma_u^+\), its likely parent state, and is thus Feshbach in character. At 1.5 \(a_0\) it becomes very hard to distinguish due to the large number of surrounding target states. There is some inconclusive evidence in the time-delays that the resonance follows its parent at the higher bond lengths after the crossing of the \(B'^1\Sigma_u^+\) and \(h^3\Sigma_g^+\) target state; resonance ‘tails’ can be observed around the \(B'^1\Sigma_u^+\) state up until \(\sim 2.8\ a_0\).

Resonance \(10^2\Sigma_g^+\) is located below the \(GK^1\Sigma_g^+\) target state (its likely parent) up until \(\sim 2.5\ a_0\), at which point the \(GK\) energy curve turns downwards, due to an avoided crossing. The nearby \(I^1\Pi_g\), \(i^3\Pi_g\) and \(h^3\Sigma_g^+\) states, as well as resonance \(8^2\Sigma_g^+\) make it difficult to determine whether the resonance continues or not to higher bond lengths. \(10^2\Sigma_g^+\) is likely Feshbach with \(GK^1\Sigma_g^+\) as parent.
Figure 4.6: Q-matrix eigenvalue curve in the vicinity of the $8^2\Sigma^+_g$ resonance at a bond length of 3.2 $a_0$. The threshold for target state, $h^3\Sigma^+_g$, within the plotted energy range, is indicated in the figure. This is an example where a Lorentzian-like resonance profile has been truncated by a threshold to the extent that only the Lorentzian-like 'tail' is visible. We were unable to get reliable fits for this and other cases where the maximum of the Lorentzian-like structure was not visible. Energies are relative to the ground state at a bond length of 3.2 $a_0$.

4.7 $2\Sigma^-_g$ Resonances

Figure 4.7: The left hand panel shows the $2\Sigma^-_g$ resonance (thick black lines) and target state energies (coloured lines) as a function of inter-nuclear separation. The right hand panel shows the corresponding resonance widths. Other details as in Figure 4.2.
4.8 $^2\Pi_g$ Resonances

Only one $^2\Sigma_g^-$ resonance was detected with confidence. This is a relatively wide resonance ($\sim 0.36$ eV), that appears below the $^3\Sigma_u^+$ target state and above the $g^3\Sigma_u^+$ and $HH^1\Sigma_u^+$ states (see Figure 4.7). After 1.8 $a_0$ no widths are provided; this is due to the unphysical spikes at 1.9 $a_0$, discussed in section 4.3.2, but also due to an issue encountered with TIMEDELn not properly tracking the eigenvalue associated with the resonance. This TIMEDELn issue, which didn’t affect all of the bond lengths above 1.9 $a_0$, was observed as an abrupt jump to an adjacent eigenvalue not leaving enough of the eigenvalue for reliable fitting (a less extreme example of this issue can be seen in figure 4.5). Time prevented us from fixing this, either in the code or manually in the outputted data. After $\sim 3.3$ $a_0$ the resonance is barely discernible from the background, so fits would not have been possible even without the TIMEDELn issue.

4.8 $^2\Pi_g$ Resonances

![Figure 4.8: The left hand panel shows $^2\Pi_g$ resonance (thick black lines) and target state energies (coloured lines) as a function of inter-nuclear separation. The right hand panel shows the corresponding resonance widths. Other details as in Figure 4.2.](image)

We have confidently identified four resonances of $^2\Pi_g$ symmetry with possibility of converging on the H(2l) + H$^-$ (1s$^2$) dissociation limit. These are shown in figure 4.8.

Resonance $^2\Pi_g$ is observed between 1.5 $a_0$ and 4.0 $a_0$. Although a Lorentzian-like structure in the time-delay is quite clear at the initially detected bond lengths, by 1.7 $a_0$ and 1.8 $a_0$ the proximity of the $a^3\Sigma_g^+$ threshold and the increase in resonance width (by 1.8 $a_0$ $\times 5$ the width at 1.5 $a_0$) prevent reliable fits from being obtained. For higher bond lengths the dramatic widening of the resonance
means the threshold for the $B^1\Sigma^+_u$ state increasingly affects its profile in the time-delay and, by 2.2 $a_0$, we were unable to produce reliable fits and report only estimates of the positions. The resonance is likely core-excited shape in character with $B^1\Sigma^+_u$ as parent.

At the initial bond length of 1.1 $a_0$, resonance $2^2\Pi_g$ is below state $e^3\Sigma^+_u$, its likely parent, which would make it Feshbach in character. By 1.3 $a_0$ the resonance has become so close to threshold that only a ‘tail’ is present in the time-delays preventing fits from being obtained for the remainder of the bond lengths. At $\sim$1.5 $a_0$ the ‘tail’ appears to shift from being predominately on the low energy side to the high energy side; perhaps suggesting a change in character from Feshbach to core-excited shape. These low and high energy ‘tails’ around the $e^3\Sigma^+_u$ state at 1.5 $a_0$ can be seen in figure 4.9. Not apparent from the plot (due to the limited range used in the plot for the time-delay) is that there is no smooth Lorentzian-like peak present, due to the truncation by the $e^3\Sigma^+_u$ threshold.

Figure 4.9: Q-matrix eigenvalue curves in the vicinity of the $2^2\Pi_g$, $3^2\Pi_g$ and $4^2\Pi_g$ resonances at a bond length of 1.5 $a_0$. Also shown, as vertical coloured and dashed lines, are the target thresholds for the states indicated in the legend. The time-delay associated with the $2^2\Pi_g$ resonance at this bond length shows only a ‘tail’, due to truncation by the $e^3\Sigma^+_u$ threshold. The time-delay for the $3^2\Pi_g$ resonance is truncated by the $h^3\Sigma^+_g$ threshold at an energy above the peak. The time-delay for the $4^2\Pi_g$ resonance crosses the $GK^1\Sigma^+_g$ threshold near to its peak but with minimal disruption to its associated Lorentzian-like form. Energies are relative to the ground state at a bond length of 1.5 $a_0$.

Resonance $3^2\Pi_g$ is initially detected at 1.1 $a_0$, below target state $B^1\Sigma^+_u$. As the bond length increases up until $\sim$1.6 $a_0$ the resonance both narrows and moves closer to both the $B^1\Sigma^+_u$ and $h^3\Sigma^+_g$ states. As shown in figure 4.9 it is still sufficiently lower in energy than both these states ($B'$ and $h$) to allow for a clearly distinguishable peak and provide good fits. As the bond length continues to increase the $h^3\Sigma^+_g$ state moves rapidly upward, away from the vicinity of the Lorentzian-like peaks associated with the $3^2\Pi_g$ resonance. The resonance does, however, continue to both narrow and move closer to the $B^1\Sigma^+_u$ state, until at 2.6 $a_0$ it can no longer be reliably fitted. There is no convincing evidence of the resonance after 2.8 $a_0$, when the $GK^1\Sigma^+_g$ target state drops below the $B^1\Sigma^+_u$. The $B^1\Sigma^+_u$ state is a
likely parent state of the resonance and the resonance Feshbach in character.

Resonance $4^2\Pi_g$ follows closely the $GK^1\Sigma_g^+$ target state over the range of bond lengths where it is detected. This state has little effect on the resonance profile in the time-delay (it is neither skewed or truncated by it), as can be seen for $1.5 \, a_0$ in figure 4.9. The resonance has several target states very close in energy making it impossible to assign it a specific parent state: $B'^1\Sigma_u^+$ and $h^3\Sigma_g^+$ at the lower bond lengths and $i^3\Pi_g$ and $i^1\Pi_g$ states at the higher ones. The width increases from a value of $\sim 0.11 \, \text{eV}$ at $1.1 \, a_0$ to a maximum of $\sim 0.14 \, \text{eV}$ at $1.6 \, a_0$ and then decreases again to $\sim 0.11 \, \text{eV}$ at $2.0 \, a_0$. At higher bond lengths, up to around $2.5 \, a_0$ there is still some evidence of the resonance from Lorentzian-like ‘tails’, however it’s impossible to provide an accurate estimate of the resonance position.

In addition to these $2\Pi_g$ resonances, there is some evidence of other resonances in the time-delay, in the form of Lorentzian-like ‘tails’: firstly, around the $e^3\Pi_u$ and $C^1\Pi_u$ targets states over nearly the entire range of calculation bond lengths in both cases; also above the $a^3\Sigma_g^+$ target state running from $2.0 \, a_0$ to $4.0 \, a_0$; finally, just above the $GK^1\Sigma_g^+$ (but below the $e^3\Sigma_u^+$) target state from $3.3 \, a_0$ to $4.0 \, a_0$ and around the $C^1\Pi_u$ state over the entire range of calculation bond lengths.

4.9 $2\Delta_g$ Resonances

The energy curves for the resonances of $2\Delta_g$ symmetry are plotted in Fig. 4.10. Resonance $1^2\Delta_g$, Figure 4.10: The left hand panel shows $2\Delta_g$ resonance (thick black lines) and target state energies (coloured lines) as a function of inter-nuclear separation. The right hand panel shows the corresponding resonance widths. Other details as in Figure 4.2.
TEMPORARY STATES OF $H_2^+$ INVESTIGATED USING A TECHNIQUE BASED ON THE TIME-DELAY

located between the $a^3\Sigma_g^+$ and $c^3\Pi_u$ target states, is clearly identifiable in the time-delay. Its energy closely follows that of state $c^3\Pi_u$, making it potentially its parent and the resonance Feshbach in character. As the bond length increases from 1.1 $a_0$, the resonance narrows rapidly and the $a^3\Sigma_g^+$ and $c^3\Pi_u$ thresholds get closer; however, the narrowing occurs at a greater rate (than the encroachment of the targets) and by $\sim 1.7$ $a_0$ nearly the entire peak of the Lorentzian-like form is visible in the time-delay, with little interruption from the surrounding target states. The $B^1\Sigma_u^+$ energy also rapidly drops in energy, crossing the $c^3\Pi_u$ state at $\sim 1.4$ $a_0$ and the $a^3\Sigma_g^+$ state at $\sim 1.6$ $a_0$. At 1.5 $a_0$ the $B^1\Sigma_u^+$ threshold is nearly exactly on top of the Lorentzian-like peak associated with the $1^2\Delta_g$ resonance. However, as can be seen from figure 4.11, this appears to have little effect on the resonance’s time-delay. At $\sim 1.9$ $a_0$, where the $a^3\Sigma_g^+$ and $c^3\Pi_u$ cross, the resonance can no longer be followed with any degree of certainty. It is therefore not possible to ascertain whether the $2^2\Delta_g$ is a continuation of this resonance.

Figure 4.11: Two Q-matrix eigenvalue curves in the vicinity of the $1^2\Delta_g$ and $3^2\Delta_g$ resonances at a bond length of 1.5 $a_0$. Only the eigenvalues relevant to the $1^2\Delta_g$ and $3^2\Delta_g$ resonances are shown. Also shown, as vertical coloured and dashed lines, are the target thresholds for the states indicated in the legend. The $1^2\Delta_g$ resonance profile to the left appears relatively unscathed by the $B^1\Sigma_u^+$ and $c^3\Pi_u$ thresholds but there’s a clear truncation by the $a^3\Sigma_g^+$ threshold, although this is far enough away from the peak to have minimal effect on the quality of the time-delay fit for this resonance. The $3^2\Delta_g$ resonance to the right has been truncated by both the $C^1\Pi_u$ and $EF^1\Sigma_g^+$ thresholds. Energies are relative to the ground state at a bond length of 1.5 $a_0$.

Resonance $2^2\Delta_g$ is first evident at 2.1 $a_0$ (some inconclusive evidence is visible at 2.0 $a_0$ and even shorter bond lengths where the crossing of the $a^3\Sigma_g^+$ and $c^3\Pi_u$ target states complicates the time-delay). The resonance lies above the $c^3\Pi_u$ state and is therefore likely core-excited shape in character. As the bond length increases the resonance moves away from its parent, first widening and then, after $\sim 3.1$ $a_0$, narrowing. At $\sim 3.4$ $a_0$, the $EF^1\Sigma_g^+$ state crosses both the resonance and state $c^3\Pi_u$, and the resonance again begins to widen.

Resonance $3^2\Delta_g$ is sandwiched between states $EF^1\Sigma_g^+$ and $C^1\Pi_u$; the associated time-delays are
4.9 $^2\Delta_g$ Resonances

Figure 4.12: Q-matrix eigenvalue curve (solid and dashed black lines) in the vicinity of the $^3\Sigma_g^+ \rightarrow ^3\Pi_u$ resonance and an accompanying fit (orange curve) at a bond length of 1.5 $a_0$. Also shown, as vertical coloured and dashed lines, are the target thresholds for the states indicated in the legend. This is the heavily truncated resonance profile shown to the right in figure 4.11. The fit was obtained using data only from the central, non-truncated region of the time-delay (solid black curve). Energies are relative to the ground state at a bond length of 1.5 $a_0$.

shown in figure 4.11 for a bond length of 1.5 $a_0$. Similarly to resonance $^1\Delta_g$, it narrows rapidly for increasing bond length and appears to vanish after the surrounding states cross. Although significantly truncated on both sides of the Lorentzian-like peak in the resonance’s associated time-delay, there was still enough of the remaining Lorentzian to allow fits to be obtained, as shown for 1.5 $a_0$ in figure 4.12.

Resonance $^4\Delta_g$ is a higher energy, relatively wide, resonance. It was clearly evident in the time-delays from 2.0 $a_0$ up until 2.6 $a_0$. It may continue to the lower bond lengths but the large number of target states in close proximity made this impossible to ascertain with confidence. The energy curve of this resonance behaves quite differently to those of the nearby target states but more similarly to that of the $^3\Sigma_g^+$ or $^3\Sigma_u^+$ states; we therefore assume these latter are the more likely possible parent states.

The highest energy and widest resonance, $^5\Delta_g$, sits just above the $^3\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ and $^3\Pi_u$ states at the lower bond lengths (only the latter converging on the H(2l) + H$^-$ (1$s^2$) limit). The resonance moves slowly away from these states with increasing bond lengths. By 1.9 $a_0$ its Lorentzian-like form in the time-delay is barely discernible and as such, widths cannot be provided. The resonance does not have obvious parentage.

In addition to the resonances reported, inconclusive evidence of a resonance (a Lorentzian-like ‘tail’ on the high-energy side in the time-delay) above the $^3\Pi_u$ target state running from $\sim$2.1 $a_0$ to at least 3.2 $a_0$ is visible.
4 TEMPORARY STATES OF H$_2$ INVESTIGATED USING A TECHNIQUE BASED ON THE TIME-DELAY

4.10 \$2\Sigma_u^+$ Resonances

The energy curves of the nine resonances identified and characterized for the \$2\Sigma_u^+$ symmetry are shown in figure 4.13. \$1\Sigma_u^+$ is documented in S&T. The remaining eight resonances are, to our knowledge, undocumented in the current literature. S&T document another \$2\Sigma_u^+$ resonance following the \$b^3\Sigma_u^+$ target state, which we also see evidence of in our time-delays. However, since the \$b^3\Sigma_u^+$ target state dissociates to H(1s) + H(1s), the associated \$2\Sigma_u^+$ is outside the scope of this study and has been excluded from figure 4.13.

Resonance \$1\Sigma_u^+$ is likely Feshbach in character and was identified for the whole range of calculated bond lengths, although at 1.1 a$_0$ it is too close to state \$a^3\Sigma_g^+$ to obtain reliable fits. However, evidence of this resonance is clear in the eigenphase sum, with a jump of approximately $\pi$ around the \$a^3\Sigma_g^+$ threshold. As the bond length increases the energy gap between the \$1\Sigma_u^+$ resonance and state \$a^3\Sigma_g^+$ increases and the width rapidly decreases. At $\sim$1.6 a$_0$ the \$B^1\Sigma_u^+$ state drops below the \$a^3\Sigma_g^+$ state and approaches the resonance (this is illustrated in figure 4.14): by 2.5 a$_0$ the resonance is nearly on top of this state and its width has decreased by a factor of ten. From this bond length up until 3.8 a$_0$, we were unable to reliably fit the resonance, although the ‘tails’ of the Lorentzian-like profile are clearly visible in the time-delay. Successful fits aren’t obtained again until 3.8 a$_0$, at which point the resonance is moving away from the \$B^1\Sigma_u^+$ state and its width increases with bond length.

As mentioned, the \$1\Sigma_u^+$ resonance has previously been documented by S&T and, as such, provided
4.10 $^2\Sigma_u^+$ Resonances

a useful comparison for our calculations. The results agree well; our positions (relative to the ground state equilibrium energy) are slightly higher for bond lengths < 2.9 a₀ and slightly lower for ≥ 2.9 a₀. The maximum deviation is ~ 0.12 eV, although this is much lower for the central bond lengths, with an average deviation of ~ 0.02 eV. The widths also follow the same trends, but the differences are higher: ~ 40% and ~ 7% (our results relative to S&T) for the biggest and smallest values of the widths respectively. We note that S&T experienced the same issues when fitting their time-delays for this resonance at the central bond lengths. In S&T and [117] it’s shown, using reduced state calculations, that the parentage is shared by both $B^1\Sigma_u^+$ and $a^3\Sigma_g^+$ states, with $B^1\Sigma_u^+$ dominating at the higher bond lengths and $a^3\Sigma_g^+$ at the lower.

Between 2.0 a₀ and 2.8 a₀, sandwiched by the $C^1\Pi_u$ (above) and $EF^1\Sigma_g^+$ (below) states, we found evidence of the relatively narrow (~ 0.01 eV to ~ 0.02 eV) $2^2\Sigma_u^+$ resonance. Outside of this range (where the $EF^1\Sigma_y^+$ lies above the $C^1\Pi_u$ state) there was no definitive evidence of the resonance: Lorentzian-like 'tails' can be observed in the time-delay near the $EF^1\Sigma_y^+$ threshold until this state crosses below the $a^3\Sigma_g^+$ threshold but we deemed this to be insufficient evidence.

Resonance $3^2\Sigma_u^+$ is evident from the time-delay from 3.4 a₀ to 4.0 a₀. The resonance is wide enough such that its Lorentzian is truncated by the nearby $GK^1\Sigma_g^+$ state, which is its likely parent. The avoided crossing between the $EF^1\Sigma_y^+$ and $GK^1\Sigma_g^+$ states seems to cause the lack of continuation of this resonance to the lower bond lengths.

![Figure 4.14](image-url)

Figure 4.14: Q-matrix eigenvalue curve, associated with the $1^2\Sigma_u^+$ resonance, showing the effect of the $B^1\Sigma_u^+$ threshold (vertical purple line) for increasing bond length. Fits were obtained for the first three bond lengths but not at 2.5 a₀, as only a 'tail' of the Lorentzian-like profile is present. Energies are relative to the ground state at the indicated bond lengths.

The $e^3\Sigma_u^+$ target state is associated with (and is likely parent of) two resonances at the lower bond lengths. Resonance $4^2\Sigma_u^+$ is the narrower of the two with a width decreasing from ~ 0.035 eV at 1.1 a₀ to ~ 0.02 eV at 1.4 a₀. After 1.4 a₀ the resonance moves closer to the $e^3\Sigma_u^+$ target state and no quality
Figure 4.15: Q-matrix eigenvalue curves in the vicinity of the $4^2\Sigma_u^+$, $5^2\Sigma_u^+$ and $6^2\Sigma_u^+$ resonances at a bond length of 1.4 $a_0$. The time-delay peaks for $4^2\Sigma_u^+$ and $6^2\Sigma_u^+$ are both truncated and only a ‘tail’ is present on the high energy side of the $B^2\Sigma_u^+$ threshold for resonance 6. Since the maximum was present for $4^2\Sigma_u^+$, fits to the time-delay associated with this resonance were obtained. However, since there is no discernible peak for $6^2\Sigma_u^+$ no fits were attempted for this resonance at this bond length. Energies are relative to the ground state at a bond length of 1.4 $a_0$.

Fits could be obtained (although a Lorentzian-like ‘tail’ is present throughout the remainder of the calculated bond lengths on the low energy side of the $e^3\Sigma_u^+$ threshold). The resonance appears to be Feshbach in character, with $e^3\Sigma_u^+$ as its parent state. Figure 4.15 shows the resonance at 1.4 $a_0$ as it approaches, for increasing bond length, the $e^3\Sigma_u^+$ target state. The second resonance associated with target state $e^3\Sigma_u^+$, $5^2\Sigma_u^+$, appears to be core-excited shape and is wider: $\sim$0.05 eV at 1.1 $a_0$, increasing to $\sim$0.24 eV at 1.6 $a_0$. Shortly after this bond length, as the resonance widens, evidence of its presence gradually diminishes until it is no longer discernible from the background.

For bond lengths below 1.5 $a_0$ resonance $6^2\Sigma_u^+$ is only evidenced by a Lorentzian-like ‘tail’ on the high energy side of the $B^1\Sigma_u^+$ threshold, as shown in figure 4.15 for 1.4 $a_0$. At 1.5 $a_0$ the resonance displays a clear Lorentzian-like peak in the time-delay, which is unaffected by the crossing of the $h^3\Sigma_g^+$ state at $\sim$1.55 $a_0$. The resonance follows the $B^1\Sigma_u^+$ target state, sitting above it, until the $GK^1\Sigma_g^+$ state crosses them both from above at just under 2.9 $a_0$, after which no evidence of the resonance can be found in the time-delay. The resonance is likely core-excited shape in character. The resonance width increases from $\sim$0.04 eV at 1.5 $a_0$ to a maximum of $\sim$0.13 eV at 2.6 $a_0$ before decreasing again.

In addition to the resonances mentioned, there is some evidence in the time-delay of other possible resonances: i) above the threshold of state $a^3\Sigma_g^+$ over the entire range of calculated bond lengths a Lorentzian-like ‘tail’ is observed; ii) running above the $I^1\Pi_g$ and $\beta\Pi_g$ thresholds and below the $g^3\Sigma_g^+$ and $HH^1\Sigma_g^+$ from 1.1 $a_0$ to $\sim$2.0 $a_0$ is the peak of what looks like a resonance that is much wider than the energy difference between thresholds; iii) from 1.1 to $\sim$2.9 $a_0$ there is a Lorentzian-like ‘tail’ on the low energy side of the $B^1\Sigma_u^+$ threshold.
4.11 $^{2}\Sigma_{u}^{-}$ Resonances

There was no conclusive evidence of any resonances of $^{2}\Sigma_{u}^{-}$ symmetry within the investigated bond length and energy ranges. However, there was some indication of possible resonances in the time-delays that could not be fitted: above the $B^1\Sigma_u^+$ and $c^3\Pi_u$ target states between 1.1 a$_0$ and $\sim$1.7 a$_0$, above the $a^3\Sigma_g^+$ state between $\sim$1.7 a$_0$ and at least 3.1 a$_0$ and also above the $EF^1\Sigma_g^+$ state from $\sim$1.7 a$_0$ to $\sim$2.8 a$_0$. Some further indication of resonances in the shape of ‘tail’s on the higher energy side of the $I^1\Pi_g$ and $f^3\Pi_g$ thresholds was also visible.

4.12 $^{2}\Pi_u$ Resonances

We found strong evidence of seven resonances of $^{2}\Pi_u$ symmetry. Their energies and widths are shown in figure 4.16.

Resonance $1^2\Pi_u$, which was also documented by S&T, has a distinct maximum in the time-delay between the bond lengths of 1.2 and 3.4 a$_0$. At 1.1 a$_0$ the Lorentzian-like form is truncated by the $a^3\Sigma_g^+$ threshold and no reliable fits could be obtained. For the higher bond lengths, up until 3.4 a$_0$, the resonance position is sufficiently far from the surrounding thresholds to allow good fits with provision of reliable widths. The width at 1.2 a$_0$ is $\sim$0.027 eV, which decreases to a minimum at $\sim$1.8 a$_0$ of $\sim$0.0076 eV, just after the $B^1\Sigma_u^+$ state drops below the resonance. After this, the width increases to $\sim$0.1 eV at 3.4 a$_0$. It’s unclear whether the resonance continues for bond lengths above 3.4 a$_0$; there is

Figure 4.16: The left hand panel shows $^{2}\Pi_u$ resonance (thick black lines) and target state energies (coloured lines) as a function of inter-nuclear separation. The right hand panel shows the corresponding resonance widths. Other details as in Figure 4.2.
a 'tail' on the high energy side of the $EF^1\Sigma_g^+$ threshold for bond lengths greater than 3.4 $a_0$, however for the lower bond lengths, where the resonance has been detected well separated from the $EF^1\Sigma_g^+$ threshold, this 'tail' is also present (on the high energy side of the $EF^1\Sigma_g^+$ threshold). We therefore believe there wasn’t enough evidence in our results that this resonance is "sitting" on the $EF^1\Sigma_g^+$ threshold at the higher bond lengths as proposed by S&T. Agreement with the results of S&T for this resonance is poorer than for the $2\Sigma_g^+$ and $2\Sigma_u^+$ ones. Although the trends in the width are roughly the same, with a minimum at $\sim 1.8$ $a_0$, there is significant difference in the positions and the widths. Our widths are much smoother in variance across the bond lengths than those reported by S&T: a large number of 'jags' in the widths of S&T are not evident at all in our results. Our relative positions are higher throughout with an average absolute difference of $\sim 0.077$ eV. For the widths, the average absolute/relative difference is $\sim 0.013$ eV/ 55%, with our results higher throughout, except at the lowest bond lengths. A possible source for the differences between the data is the better modelling of the polarisation effects provided in our work from the use of the d-aug-cc-pVTZ basis set (S&T acknowledges that their calculations "included no \( \delta \) or higher orbitals located on the target").

S&T assign $a^3\Sigma_g^+$, $c^3\Pi_u$ and $EF^1\Sigma_g^+$ as parent states of this resonance. Our results also suggest the $a^3\Sigma_g^+$ and $c^3\Pi_u$ states as parents for bond length 3.4 $a_0$ and shorter. Here the resonance sits below both of these states throughout, immediately below the $a^3\Sigma_g^+$ state at lower bond lengths and immediately below the $c^3\Pi_u$ state at the higher ones (the $a^3\Sigma_g^+$ and $c^3\Pi_u$ states cross one another at $\sim 1.9$ $a_0$), making the resonance Feshbach in character.

Evidence of a relatively wide ($>0.2$ eV), core-excited shape resonance, $2^2\Pi_u$, was found above the $c^3\Pi_u$ target state (its likely parent) at the lower bond lengths. Reliable fits were only obtained for 1.7, 1.8 and 1.9 $a_0$. For shorter bond lengths, although the maximum in the Lorentzian-like form associated with the resonance was sometimes visible in the time-delay, attempted fits were too poor to provide reliable values for the positions and widths. Below 1.4 $a_0$ a maximum was not visible in the time-delays due to truncation by the $c^3\Pi_u$ target state. The resonance is no longer present in our data after the $a^3\Sigma_g^+$ target state crosses the $c^3\Pi_u$ state from below, at $\sim 1.9$ $a_0$.

Although relatively wide (0.1-0.2 eV), resonance $3^2\Pi_u$ is sufficiently far from the surrounding thresholds at 4.0 $a_0$ to manifest as a nearly complete Lorentzian-like structure in the time-delays, as is shown in figure 4.17. However, as the bond length shortens the resonance gradually approaches the $a^3\Sigma_g^+$ threshold from below, until at a bond length of 2.5 $a_0$, the maximum is no longer discernible in the time-delay and only a 'tail' on the low energy side of the $a^3\Sigma_g^+$ target state indicates its presence. It may also be linked to a (seemingly separate) 'tail' on the high energy side of the $a^3\Sigma_g^+$ state running from 1.5 $a_0$ (or lower; the presence of the $1^2\Pi_u$ resonance makes it hard to tell) to at least 1.7 $a_0$ (the many close lying target states around this bond length makes it impossible to track the 'tail' here). It’s hard to know for sure this high-energy 'tail' is connected to $3^2\Pi_u$; if it is, then this would extend the bond length range of the $3^2\Pi_u$ resonance to potentially the entire range of calculated bond lengths. The width, throughout the range where we obtained fits, increases from $\sim 0.14$ eV at 2.6 $a_0$ to a maximum value of $\sim 0.19$ eV at 3.3 $a_0$ (just after the resonance crosses the descending $EF^1\Sigma_g^+$ state). After this the width decreases to a value of $\sim 0.1$ eV at 4.0 $a_0$. For most of the bond length range, $3^2\Pi_u$ appears to be Feshbach in character with the $a^3\Sigma_g^+$ target state as parent.

Although the Lorentzian-like peak in the time-delay associated to resonance $4^2\Pi_u$ is truncated on the low energy side, as shown in figure 4.18, it is well fitted at the initial bond length of 1.1 $a_0$,
4.12 $^2\Pi_u$ Resonances

which yields a width of $\sim 0.05$ eV. However, as the bond length increases, the resonance rapidly widens to $\sim 0.22$ eV at 1.4 $a_0$, the final fitted bond length. Above this bond length, although the time-delay profile has a distinct maximum, it is asymmetrically skewed by the (lower lying) $e^3\Sigma_u^+$ target state and achieving reliable fits is impossible. However, it’s clear from visual inspection of the time-delays that the resonance continues to widen, such that by 2.8 $a_0$ it’s barely discernible from the non-resonant background. It’s highly likely that the resonance is core-excited shape in character with $e^3\Sigma_u^+$ as parent.

Figure 4.17: Q-matrix eigenvalue curve in the vicinity of the $3^2\Pi_u$ resonance at a bond length of 4.0 $a_0$. The Lorentzian-like structure is affected by two target thresholds (shown with vertical lines) but at sufficient distance from the maximum of the resonance peak to allow a well discerned Lorentzian-like profile. Energies are relative to the ground state at a bond length of 4.0 $a_0$.

For the first bond lengths, 1.1 $a_0$ and 1.2 $a_0$, resonance $5^2\Pi_u$ is located above the $h^3\Sigma_g^+$ and below the $B'^1\Sigma_u^+$ target states. Its width is much higher than that of the surrounding resonances ($4^2\Pi_u$ and $6^2\Pi_u$), as is clear from figure 4.18. In the time-delay, the associated Lorentzian-like form is ‘tail’-less due to the influence of these two surrounding resonances. Good fits to the central section of the profile are achievable however, which provided a width of $\sim 0.17$ eV at 1.1 $a_0$. At around 1.3 $a_0$ the resonance moves below the $h^3\Sigma_g^+$ state where it remains for increasing bond length. After this and up until the final fitted bond length, 1.6 $a_0$, the resonance narrows slightly (to $\sim 0.17$ eV at 1.6 $a_0$). By $\sim 1.6$ $a_0$ the $h^3\Sigma_g^+$ target state crosses the $B'^1\Sigma_u^+$ target state from below and continues to move away from the resonance. The resonance appears (from visual inspection of the time-delays) to continue to the higher bond lengths as a ‘tail’ on the low energy side of the $B'^1\Sigma_u^+$ state that continues to be present even as the $h^3\Sigma_g^+$ and $B'^1\Sigma_u^+$ states move apart from one another. By 2.2 $a_0$ and higher bond lengths the ‘tail’ is barely or not discernible. We thus consider the $5^2\Pi_u$ resonance as Feshbach in character with the $B'^1\Sigma_u^+$ state as parent, although there may be some contribution to parentage from the $h^3\Sigma_g^+$ state at the shorter bond lengths.
4 TEMPORARY STATES OF H\textsubscript{2} INVESTIGATED USING A TECHNIQUE BASED ON THE TIME-DELAY

Figure 4.18: Q-matrix eigenvalue curves in the vicinity of the 4\textsuperscript{2}\Pi\textsubscript{u}, 5\textsuperscript{2}\Pi\textsubscript{u} and 6\textsuperscript{2}\Pi\textsubscript{u} resonances at a bond length of 1.1 \(a_0\). Target thresholds are shown as vertical lines. Fits were obtained for all three resonances shown here. Energies are relative to the ground state at a bond length of 1.1 \(a_0\).

Resonance 6\textsuperscript{2}\Pi\textsubscript{u} is detected at 1.1 \(a_0\) as a relatively narrow (~0.017 eV) resonance, truncated on the low energy side by the \(B'\Sigma\textsubscript{u}^+\) target state (and also on the high energy side but to a much lesser extent). Truncation below the maximum can be seen in figure 4.18. As the bond length increases the resonance widens, to ~0.09 eV at 1.6 \(a_0\) (just after the \(B'\Sigma\textsubscript{u}^+\) and \(h\Sigma\textsubscript{g}^+\) states have crossed). At 1.7 \(a_0\), we were unable to get a reliable fit; however, for the higher bond lengths, up until 2.8 \(a_0\), acceptable fits were obtained. After 1.7 \(a_0\) there’s an initial (quite dramatic) drop in the width to ~0.06 eV, after which the width increases to a maximum of ~0.11 eV at 2.6 \(a_0\). Above 2.6 \(a_0\), where the avoided crossing between states \(GK\Sigma\textsubscript{g}^+\) and \(EF\Sigma\textsubscript{g}^+\) starts to play a role, the resonance appears to narrow until its final reported bond length, 2.8 \(a_0\), where it is crossed by the \(GK\Sigma\textsubscript{g}^+\) state.

Resonance 7\textsuperscript{2}\Pi\textsubscript{u} becomes apparent in the time-delays just after the \(GK\Sigma\textsubscript{g}^+\) state crosses below the \(B'\Sigma\textsubscript{u}^+\) state at 2.9 \(a_0\). As the bond length increases and the \(GK\Sigma\textsubscript{g}^+\) state moves away from it, the resonance narrows quickly to a minimum at ~3.1 \(a_0\) and then slowly widens over the remaining bond lengths where it was detected, so that at 4.0 it has a width of ~0.43 eV. This is the widest of all the \(2\Pi\textsubscript{u}\) resonances confidently detected. It’s likely that this resonance has \(B'\Sigma\textsubscript{u}^+\) as parent and is core-excited shape in character. There’s a possibility that resonance 7\textsuperscript{2}\Pi\textsubscript{u} is a continuation of resonance 6\textsuperscript{2}\Pi\textsubscript{u} but the complexity of the time-delays around the bond lengths where the \(GK\Sigma\textsubscript{g}^+\) target state crosses both the resonance and the \(B'\Sigma\textsubscript{u}^+\) target states make this difficult to determine with reasonable certainty.

Also in the region of the \(h\Sigma\textsubscript{g}^+\) and \(B'\Sigma\textsubscript{u}^+\) target states is another possible resonance, which we don’t show in figure 4.16 as no distinct maximum can be fitted at any of the bond lengths where it is evident. The resonance first appears as a ‘tail’ on the high energy side of state \(h\Sigma\textsubscript{g}^+\) just after it crosses the \(B'\Sigma\textsubscript{u}^+\) state. The ‘tail’ is present up until at least 3.0 \(a_0\), even after the avoided crossing mentioned above. After this, the close proximity of the \(I^1\Pi\textsubscript{g}\) and \(i^3\Pi\textsubscript{g}\) thresholds make the ‘tail’ impossible to
discern confidently. Additionally, there were several large 'tails' around many of the target states; we note the more distinctive ones here. In addition to the already mentioned $EF^1\Sigma_g^+$ 'tail' at the higher bond lengths, another 'tail' can be seen on the low energy side of the $C^1\Pi_u$ target state from $\sim 1.9$ a$_0$, where the target states crosses below the $EF^1\Sigma_g^+$ state, to 4.0 a$_0$. This 'tail' has relatively large time-delay values, depending on the bond length; at 2.6 a$_0$, as example, it comprises the largest values in the time-delay over the entire calculated energy range for this bond length. Another large 'tail' is seen on the high energy side of the $EF^1\Sigma_g^+$ state from 1.1 a$_0$ to before it crosses above the $C^1\Pi_u$ state at $\sim 1.9$ a$_0$. Also a smaller 'tail' is seen above the $GK^1\Sigma_g^+$ target state, which is most significant after the $GK^1\Sigma_g^+$ crosses under the $B^1\Sigma_u^+$ state. At the higher energies, for the $2\Pi_u$ resonances, many of the target states have an associated 'tail'. The most notable are probably two 'tails' on both the low and high energy side of the $h^3\Sigma_g^+$ target state running from after it crosses from below the $B^1\Sigma_u^+$ state, at $\sim 1.5$ a$_0$, to the final calculated bond length (although the 'tails' become harder to discern as the $h^3\Sigma_g^+$ state approaches higher lying threshold at the longer bond lengths, $\sim 3.1$ a$_0$).

4.13 $2\Delta_u$ Resonances

Figure 4.19: The left hand panel shows $2\Delta_u$ resonance (thick black lines) and target state energies (coloured lines) as a function of inter-nuclear separation. The right hand panel shows the corresponding resonance widths. Other details as in Figure 4.2.

Figure 4.19 shows the two resonances of $2\Delta_u$ symmetry we have identified. Both were detected across the entire range of bond lengths and are core-excited shape in character: the parents are the $e^3\Sigma_u^+$ state for $1^2\Delta_u$ and the $B^1\Sigma_u^+$ state for $2^2\Delta_u$. The widths of both resonances increase for increasing bond length, with $2^2\Delta_u$ being the narrower of the two throughout.

We were unable to fit resonance $2^2\Delta_u$ at 2.9 a$_0$, although a Lorentzian-like 'tail' was still visible in the time-delays. There is a small step down in the width of resonance $1^2\Delta_u$ for increasing bond
4 TEMPORARY STATES OF $H_2^-$ INVESTIGATED USING A TECHNIQUE BASED ON THE TIME-DELAY

length at 3.7 $a_0$, which is very likely numerical rather than physical: due to threshold effects more data points were available to the fit routines for the higher bond lengths.

In addition to these resonances, we found some potential evidence of other resonances of $^2\Delta_u$ symmetry: above the $C^1\Pi_u$ threshold across all the bond lengths, above $e^3\Pi_u$ at the lower ones and above $a^3\Sigma_g^+$ at the higher bond lengths.

4.14 Discussion of the VSI Asymmetric $H^-$ Momentum Distributions around 15 eV

As mentioned in the introduction, the recent VSI experiments by Krishnakumar et al. revealed a symmetry loss in the momentum distributions of the produced anions from DEA to $H_2$ for electron scattering energies around 15 eV [19]. Having defined a measure of the asymmetry, $\eta$, in terms of the integral of the signal strength over both the forward ($I_F$) and the backward ($I_B$) directions (with respect to the incident electron beam), as:

$$\eta = \frac{I_F - I_B}{I_F + I_B}$$

(4.1)

Table 4.2: Values of the asymmetry parameter $\eta$ (4.1) obtained by Krishnakumar et al. [19] from their experimental momentum distributions of anions produced from DEA of $H_2$.

<table>
<thead>
<tr>
<th>Electron energy (eV)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.5</td>
<td>-0.19±0.02</td>
</tr>
<tr>
<td>15</td>
<td>-0.17±0.02</td>
</tr>
<tr>
<td>15.5</td>
<td>-0.12±0.02</td>
</tr>
</tbody>
</table>

Krishnakumar et al. reported values of $\eta$ for incident electron energies of 14.5 eV, 15 eV and 15.5 eV, as shown in table 4.2. The values in this table show a greater integrated signal strength in the backward direction for all three electron energies, with the asymmetry highest at 14.5 eV, lessening for increasing electron energy. Since momentum distributions of anions dissociating via a single resonant state all display forward-backward symmetry, the asymmetry observed in Krishnakumar et al.’s distributions reveals that the DEA must be occurring via more than one resonant state. As mentioned in the introduction, this suggestion that the DEA around 15 eV is multi-resonant in nature is also made by Celiberto et al. [34] in their recent theoretical study into DEA of $H_2$.

The Krishnakumar et al. paper [19] includes an attempt to empirically reproduce the asymmetry in the VSI images by considering the superposition of gerade ($g$) and ungerade ($u$) resonances in terms of

- $\tau_g$ and $\tau_u$; the average autodetachment lifetimes.
- $t_g$ and $t_u$; the dissociation times along the resonance potential energy curves, $V_g(R)$ and $V_u(R)$.

and assuming equal capture cross sections for both the gerade and ungerade resonances. They then express $\eta$ as:

$$\eta = a_t \cos \delta$$

(4.2)

where $a_t$ is a time-dependent term composed from the average autodetachment lifetimes and dissociation times, given by:

$$a_t = \sqrt{3} \frac{\exp \left[-\left(\frac{t_g}{2\tau_g} + \frac{t_u}{2\tau_u}\right)\right]}{\exp \left[-\left(\frac{t_g}{\tau_g}\right)\right] + \exp \left[-\left(\frac{t_u}{\tau_u}\right)\right]}$$

(4.3)
and $\delta$ is the relative phase between the two dissociation paths given by:

$$
\delta = \frac{1}{\hbar} \int_{R_e}^{\infty} \left[ \sqrt{2\mu(E - V_u(R))} - \sqrt{2\mu(E - V_g(R))} \right] dR + \frac{\pi}{2} \tag{4.4}
$$

with $E$ the electron energy, $\mu$ the reduced mass of the system and $R_e$ the bond length at which capture takes place. We have taken $R_e$ to be the equilibrium geometry of the ground electronic state, approximately $R_e = 1.4 \ a_0$.

As input to their model, for the gerade resonance Krishnakumar et al. used one of the two closely lying $^2\Sigma_g^+$ resonances\textsuperscript{25} reported in Eliezer’s early work \cite{106} (they don’t indicate which one), and assumed an average autodetachment lifetime of 8 fs (or a width of 0.082 eV). For the ungerade they don’t use any of the resonances reported by S&T \cite{35}; rather they use the $^2\Pi_u$ target state energies shifted by an unspecified amount, which we assumed must be equal to the difference between the H(2l) + H\textsuperscript{−} (1s\textsuperscript{2}) and H(1s) + H(2l) energies.\textsuperscript{26} For the average ungerade autodetachment times, results were obtained over a range from 1 to 50 fs and empirically compared with experiment. For the dissociation times the author informed us via private communication that 10 fs was used, which we assumed was for both the gerade and ungerade resonances. Figure 4.20 shows shifted versions of the the Eliezer resonances, the shifted $^2\Sigma_u^+$ and $^2\Pi_u$ target state energies, as well as resonances obtained in our and S&T’s work. Figure 4.21 shows the modelled asymmetries obtained by Krishnakumar et al. for the shifted $^2\Sigma_u^+$ and $^2\Pi_u$ target states; they deemed the asymmetries obtained using the $^2\Pi_u$ shifted target in better agreement to those obtained from their VSI experiments (table 4.2).

We first attempted a reproduction of Krishnakumar et al.’s empirically obtained values of $\eta$. Using the shifted target states for the ungerade resonance, the communicated 10 fs dissociation times and testing both of the options for the $^2\Sigma_u^+$ resonance given in Eliezer’s work we failed to reproduce their results (first two rows in figure 4.22). Shifting the Eliezer resonances down by 0.25 eV produced better results (rows three and four in figure 4.22). For a simulated $^2\Sigma_u^+$ following the $^2\Pi_u$ shifted target (right hand column in figure 4.22), using a dissociation time of 25 fs for both the gerade and ungerade resonances and a shifted lower energy $^2\Sigma_u^+$ ($\epsilon^2\Pi_u + \epsilon$) resonance reported in \cite{106} (final row in figure 4.22) we came closest to reproducing the Krishnakumar et al. results. For a simulated $^2\Sigma_u^+$ following the $^2\Sigma_u^+$ shifted target (left hand column in figure 4.22), either the third or final row could be considered as the best reproductions. The 0.25 eV shift applied to the Eliezer resonances was proposed in an early review by Schulz \cite{97} which states "when one arbitrarily adds 0.25 eV\textsuperscript{27} to Eliezer’s calculated values excellent agreement exists between theory and experiment" but we do not know for sure whether this was applied by Krishnakumar et al.. We suspect that the 25 fs dissociation time is closer to the one used to obtain the results in Krishnakumar et al.’s work than the 10 fs privately communicated. This is because, for a given $\delta$ in equation (4.2), the change in $\eta$ with variation of $\tau_u$ will be dependent only on $\tau_g$, $t_u$ and $t_g$ (and independent of the resonance potential curves).\textsuperscript{28} Assuming that the 8 fs stated in the Krishnakumar et al. paper \cite{19} for $\tau_g$ was used in the model to produce their reported results, then the only single remaining, uncertain, variable is the value used for both $t_u$ and $t_g$.

\textsuperscript{25}S&T \cite{35} purposed that these two resonances are "manifestations of the same resonance”.

\textsuperscript{26}An upward shift, such as applied in Weingartshofer et al.’s work \cite{21} for their high energy $^2\Sigma_u^+$ resonance, would move the dissociation level above the ~14 eV DEA peak and is thus not applicable here.

\textsuperscript{27}Whether up or down in energy is not specified.

\textsuperscript{28}This can be most easily observed by choosing an electron energy where $\delta = 1$ (i.e. the darkest red) and comparing the values from the attempted reproduction with the plots in figure 4.21 when moving vertically up the plot with changing $\tau_u$. 

100
Using 25 fs for this came much closer to the results in [19] then 10 fs.

We note that although the shifted $^2\Sigma_g^+ (c^3\Pi_u + e)$ resonance gave us the closest results to Krishnakumar et al.
this resonance is further from our $^1\Sigma_g^+$ resonance than Eliezer’s $^2\Sigma_g^+ (C^1\Pi_u + e)$ resonance. However, as can be appreciated from figure 4.22 both Eliezer’s resonances with the -0.25 eV offset produced results much closer to Krishnakumar et al. than the same two resonances without the offset applied.

Figure 4.20: Target state (thin, translucent lines) and resonance (full and dashed bold lines) energies of H$_2$ obtained from various works, relative to the first vibrational state of the electronic ground state. The target state data is from this work. The solid and dotted black lines are resonances documented in Eliezer’s work [106] both unshifted (opaque) and shifted down by 0.25 eV (translucent). The bold, solid, coloured lines are the $^1\Sigma_g^+$, $^2\Sigma_g^+$, $^3\Sigma_g^+$ and $^1\Sigma_u^+$ resonances obtained in this work (only the resonances close in energy to those from the other works are shown). The dotted version of the respective colours are from S&T’s work, shown for comparison (S&T did not document any resonance close to our $^3\Sigma_g^+$ resonance). The shifted target states used to simulate the ungerade resonance in the Krishnakumar et al. [19] model are shown as dashed black lines. With the exception of the $^2\Sigma_g^+$ and $^3\Sigma_g^+$ resonances all of the resonances have been used for various calculations of $\eta$ using equation (4.2).
Figure 4.21: The modelled forward-backward asymmetry in the momentum distributions of H\(^-\) obtained by Krishnakumar et al. [19]. The model is given by equation (4.2), with the colour showing the value of \(\eta\) as a function of electron energy and average lifetime of the \(^2\Sigma^+_u\) resonance. The two plots show \(\eta\) for the two shifted target states (\(B^1\Sigma^+_u\) and \(C^1\Pi_u\)) used by Krishnakumar et al. to simulate the unknown \(^2\Sigma^+_g\) resonance. Figure adapted from [19].

The simulated results for \(\eta\) reported by Krishnakumar et al. using their empirical approach with the \(C^1\Pi_u\) shifted target state energy closely matched those of their experiment. However, the \(C^1\Pi_u\) shifted target state energy does not coincide with any resonance of \(^2\Sigma^+_u\) or other symmetry obtained in this work. Therefore, on this basis, it seems unlikely that this shifted target state energy corresponds to a resonance of \(^2\Sigma^+_u\) symmetry. This can be appreciated from figure 4.20, which shows that the two shifted target states (\(B^1\Sigma^+_u\) and \(C^1\Pi_u\)) are not close to any of our calculated \(^2\Sigma^+_u\) resonances for nearly all of the bond lengths. The shifted \(B^1\Sigma^+_u\) target state is between 0.5 eV and 0.7 eV from any calculated resonance of \(^2\Sigma^+_u\) symmetry for all bond lengths above \(\sim 1.9\ a_0\). The shifted \(C^1\Pi_u\) target state is closer to the nearest \(^2\Sigma^+_u\) resonance than the shifted \(B^1\Sigma^+_u\) state up until \(\sim 2.8\ a_0\). After this it moves away from the nearest \(^2\Sigma^+_u\) resonance rapidly, until, at \(4.0\ a_0\) it’s more than 1 eV away. As an example, the lack of correspondence between the shifted states and our results is illustrated with respect to the time-delays in figure 4.23 at \(1.9\ a_0\). At this bond length we consider the correspondence between the shifted target states and the nearest \(^2\Sigma^+_u\) resonance to be poor; for bond lengths longer than \(1.9\ a_0\) the correspondence only worsens. Additionally, both our \(1^2\Sigma^+_g\) and \(1^2\Sigma^+_u\) resonances and S&T’s equivalent resonances cross one another at \(\sim 2.0\ a_0\); there is no such crossing between any of the Eliezer gerade resonances and the shifted targets used as inputs by Krishnakumar et al. to their model.

Krishnakumar et al. discarded the S&T data for the \(1^2\Sigma^+_g\) (Res 2) and \(1^2\Sigma^+_u\) (Res 6) resonances (our labels, S&T in parenthesis) on the basis that "the overlap of these curves with the Franck–Condon region is below the energy range of interest here, even after taking their widths into account" [19]. However, it’s apparent from the potential energy diagrams\(^{29}\) that many vibrational states of the two resonances with energy sufficient for dissociation (i.e. above the dissociation threshold) should be accessible from the ground state. As discussed in the introduction to this chapter the dissociation thresholds for resonances of interest to Krishnakumar et al.’s VSI experiments, around 14 eV, are

\(^{29}\)See for example Res 2 and Res 6 in figures 2 and 4 in S&T [35] (their labels).
4 TEMPORARY STATES OF $H_2^-$ INVESTIGATED USING A TECHNIQUE BASED ON THE TIME-DELAY

Figure 4.22: Various attempts to reproduce the modelled forward-backward asymmetry in the momentum distributions of $H^-\text{obtained by Krishnakumar et al. [19]}$ as shown in figure 4.21. The model is given by equation (4.2), with the colour showing the value of $\eta$ as a function of electron energy and average lifetime of the $^2\Sigma^+_g^+$ resonance. Each row has plots for the two shifted target states obtained for different combinations (shown to the right of each row) of: i) the Eliezer resonance used for the $^2\Sigma^+_g^+$; ii) whether or not a -0.25 eV was applied to this resonance (see text) and iii) the dissociation time used for the $^2\Sigma^+_g^+$ and $^2\Sigma^+_u^+$ resonances.
4.14 Discussion of the VSI Asymmetric $H^-$ Momentum Distributions around 15 eV

Figure 4.23: Time-delays for $^2\Sigma_u^+$ symmetry at a bond length of 1.9 $a_0$. The prominent structures are the Lorentzian-like form at $\sim 10.7$ eV and the threshold spike at $\sim 10.8$ eV. Marked with arrows are the positions of the shifted target states used in the work of Krishnakumar et al. [19] to simulate a hypothetical $^2\Sigma_u^+$ resonance. All time delays for the other ungerade symmetries are close to zero with no features over this energy range.

either the 13.88 eV threshold for dissociation into H(2l) + H$^-$($1s^2$) or the series of doubly excited anion states, H(1s) + H$^{--*}$, starting at 14.00 eV. Nonetheless, using either our calculated positions and widths, or those of S&T for the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ resonances we were unable to reproduce the $\eta$ observed in the Krishnakumar et al. VSI experiments. We also unsuccessfully attempted to reproduce the $\eta$ using our $^2\Sigma_g^+$ and $^2\Sigma_u^+$ resonances (not shown in figure 4.20, although both closely follow the $^3\Sigma_u^+$ state shown in the upper part of this figure); since these resonances are close enough to one another in energy to overlap. At this point we decided that confidently reproducing the Krishnakumar et al. experimental $\eta$ results was not possible due to the likely limitations in our calculated results when used as input to the Krishnakumar et al. model and also perhaps due to some deficiencies in the Krishnakumar et al. model itself (which we will discuss in more detail shortly).

Limitations in our results are a consequence of the relatively short cut-off point for the bond length in our calculations. In order to provide the values for $V_u(R)$ and $V_g(R)$ in (4.4) a significant extrapolation of the resonance potential energy curves was required. We noticed that these extrapolations were not very numerically stable, with small changes to the input data resulting in quite large changes to the calculated $\eta$. The cause of this instability was very likely the large extrapolations required to reach the dissociation limits. The short cut-off point for the bond length in our calculations also affected the number of widths available for calculating the average values of $\tau_g$ and $\tau_u$ in equation (4.2). Although not directly relevant to the calculation of $\eta$, it’s worth mentioning that the short cut-off point removes certainty on whether our resonances dissociate to H(2l) + H$^-$($1s^2$) or H(1s) + H$^{--*}$. Since only the former are likely to be able to potentially contribute to the observed asymmetry in the Krishnakumar et al. VSI experiments we cannot be sure that any candidate resonance used as input to Krishnakumar et al.’s model is relevant to their DEA experiments.

However, we suspect that, even without these limitations in our calculated results, Krishnakumar
### Table 4.3: Values, calculated by us, for $a_t$ in Krishnakumar et al.’s asymmetry model (equation (4.2)) using resonance widths and lifetimes from various works. All times are in fs. The labels used for the resonances are those from the respective works. For the calculations based on the resonances in our and S&T’s works the autodetachment lifetimes are the average of the lifetimes calculated from the resonance widths at the bond lengths investigated in the respective works. For the case of Krishnakumar et al. the autodetachment lifetimes were taken directly from their work; for $\tau_g$ Krishnakumar et al. “used an average lifetime of 8 fs for the $2\Sigma^+_g$ based on the reported width of 90 meV at 14 eV [21]”; for $\tau_u$ we have tested with two values, which appear to most closely match the results from their empirical model, shown in figure 4.21, for the $C^1\Pi_u + \Delta$ modelled resonance. $a_t$s calculated with the lifetimes are shown for both 10 and 25 fs dissociation times for the two resonances. The $a_t$s provide upper and lower bounds for the forward-backward asymmetry as given by $\eta$ in equation (4.2); all of Krishnakumar et al.’s measured asymmetries given in table 4.2 are within these bounds.

<table>
<thead>
<tr>
<th>Work</th>
<th>Resonance</th>
<th>$\tau_g$ (fs)</th>
<th>$\tau_u$ (fs)</th>
<th>$a_t$ (fs)</th>
<th>$t_{g/u}=10$</th>
<th>$t_{g/u}=25$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eliezer (shifted) widths from [21]</td>
<td>$2\Sigma_g (c^3\Pi_u + e)$</td>
<td>8</td>
<td>3.5</td>
<td>0.65</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>$7^2\Sigma^+_g$</td>
<td>8.98</td>
<td>23.55</td>
<td>0.82</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1^2\Sigma^+_g$</td>
<td>15.38</td>
<td>30.54</td>
<td>0.85</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>S&amp;T [35]</td>
<td>Res 2</td>
<td>17.43</td>
<td>26.41</td>
<td>0.86</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>S&amp;T [35]</td>
<td>Res 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Examination of $a_t$, equation (4.2), is more straightforward, since this is independent of the resonance potentials and is somewhat useful since it provides upper and lower bounds to the $\eta$. Our calculated values for $a_t$ are shown in table 4.3 for i) Krishnakumar et al.’s dissociation times and those calculated using ii) the $1^2\Sigma^+_g / 1^2\Sigma^+_u$ and iii) $7^2\Sigma^+_g$ / $4^2\Sigma^+_u$ resonance pairs from this work, as well as iv) S&T’s Res 2 and Res 6. Results are shown for both 10 and 25 fs dissociation times. Most noteworthy is that Krishnakumar et al. measured asymmetries in table 4.2 are within all calculated $a_t$ in table 4.3. We also note that the lifetime of 9 fs calculated for our $7^2\Sigma^+_g$ resonance is close to that of 8 fs Krishnakumar et al. used for Eliezer’s $c^3\Pi_u + e$ resonance. However, both values were calculated differently; the Krishnakumar et al.’s 8 fs was "based on the reported width of 90 meV at 14 eV [21]" and the 9 fs was obtained by averaging the lifetimes of the $7^2\Sigma^+_g$ resonance over the calculated bond lengths.
4.15 Summary and Conclusions

Potential energy curves and widths have been obtained for 35 resonances formed during electron scattering from $\text{H}_2$ around the energy of the $\text{H}(1s) + \text{H}(2l)$ dissociation limit (from about 12 eV to 16 eV at equilibrium geometry) over the H-H bond length range of 1.1 to 4.0 $\text{a}_0$. The calculations were carried out using full CI for the target wavefunction, with a d-aug-cc-pVTZ basis set for the molecular orbitals and a B-spline basis set for the description of the continuum. This was sufficient to provide accurate modelling of all the $\text{H}_2$ target states dissociating to $\text{H}(1s) + \text{H}(2l)$ inside the energy range of interest to this study. Character (whether Feshbach or core-excited shape) has been inferred for most of these resonances when the parent state seemed quite clear from inspection of the potential energy curves. Most of the resonances are, to our knowledge, unpublished, although some of the lower energy ones were previously documented by S&T.

The time-delay was used for the identification and characterisation of the resonances. We found that this method provided good results for reasonable computational resource, with the main benefit coming from the separation of the resonances across the time-delay eigenvalues. The limitations encountered when using the time-delay approach were mostly related to the large number of target thresholds in the energy region of interest and the fact that many resonances had associated Lorentzian-like peaks in the time-delays close enough to these thresholds to be truncated or otherwise deformed by their presence. Our approach for these cases was to fit using input data only in the region where the Lorentzian-like peak was well defined (see figures 4.5 and 4.12 for two examples). However, although we usually obtained good fits using this approach, it must be considered that we have effectively just ignored the threshold in order to obtain the resultant fitted parameters.

Unfortunately, an approach using reskit, based on the methods discussed in chapter 3, would have been completely unfeasible with respect to computational resource. This is due to the large number of channels involved in the calculation. Even if this wasn’t the case, the current state of the reskit code doesn’t provide a straightforward treatment for inelastic scattering systems.

An important motivation for this work was investigating the asymmetries in the angular distributions of the dissociated $\text{H}^-$ ions encountered in recent DEA VSI experiments [19]. This was attempted using the model provided in the experimental work. We were unable to reproduce the experimental results using this model, in part, due to the calculations not being performed to sufficiently long H-H bond lengths. However, we believe that successful reproduction of the asymmetries in the angular distributions of the dissociated $\text{H}^-$ ions will also need to account for threshold effects and more than two resonances and possibly provide a full treatment of the nuclear dynamics [118, 34].
Chapter 5

Temporary States of \( \text{SO}_2^- \) Investigated using techniques based on the Eigenphase and Time-delay

In this chapter, we present an investigation of the electronic resonances in electron scattering from \( \text{SO}_2 \) at equilibrium geometry, over a range of incident electron energies from 0.1 to 10 eV. We provide a discussion of the related literature, particularly on the topics of experimental DEA and vibrational spectroscopy, as well as recent related theoretical works. This discussion will highlight apparent disparities in the assignment of symmetries for some of the resonances in both the experimental and theoretical literature. These discrepancies are the motivation for our work.

\( \text{SO}_2 \) is a cause of acid rain [33] and can be found in interstellar mediums [29] and planetary atmospheres [31]. It is a triatomic molecule, of \( C_{2v} \) symmetry, occurring most stably in a bent geometry, with an S-O bond length of 1.432 Å and O-S-O angle of 119° [119]. \( \text{SO}_2 \) contains 32 electrons, 18 of which are valence with the remaining 14 occupying the \( 1s^2 \) orbitals of the O atoms and the K(n=1), L(n=2) orbitals of the S atom. Its ground state configuration is: \( 1a_1^2 \), \( 1b_1^2 \), \( 2a_1^2 \), \( 3a_1^2 \), \( 2b_2^2 \), \( 1b_1^2 \), \( 4a_1^2 \), \( 5a_1^2 \), \( 3b_2^2 \), \( 6a_1^2 \), \( 4b_2^2 \), \( 7a_2^2 \), \( 2b_1^2 \), \( 5b_2^2 \), \( 1a_2^2 \), \( 8a_2^2 \). It has a dipole moment of 1.6331 D and polarisability of 3.882 Å\(^3\) [119].

There are a number of DEA thresholds of \( \text{SO}_2 \), arising from the four possible anionic fragments, \( \text{O}^- \), \( \text{SO}^- \), \( \text{S}^- \) and \( \text{O}_2^- \) and accompanying neutral fragments. The lowest dissociation threshold for DEA is for \( \text{S}^- \) formation at 3.9 eV. Energies and fragments constituting the other dissociation channels can be found in [37].

5.1 DEA and Vibrational Excitation Experiments on \( \text{SO}_2 \)

For energies \( <10 \text{ eV} \), the experimental total DEA cross section from the ground state of \( \text{SO}_2 \) shows two prominent peaks, one at \( \sim 4.5 \text{ eV} \) and the other at \( \sim 7.5 \text{ eV} \). The lower peak is composed mainly of contributions from the partial cross sections for both \( \text{O}^- \) and \( \text{SO}^- \) formation, with \( \sim 50\% \) higher contribution from \( \text{O}^- \) and is agreed in the literature to occur via a resonance of \( ^2A_1 \) symmetry [37, 18, 36, 120, 38]. The higher energy peak (\( \sim 7.5 \text{ eV} \)) is nearly all from \( \text{O}^- \) formation, with a much smaller contribution from \( \text{SO}^- \) formation [36]. \( \text{S}^- \) provides a contribution to the \( \sim 4.5 \text{ eV} \) and \( \sim 7.5 \text{ eV} \) peaks, although this is more than an order of magnitude lower than the combined contributions for both \( \text{O}^- \) and \( \text{SO}^- \) formation [36]. As we will detail below, there is contention in the literature for symmetry assignment to the resonances responsible for the \( \sim 7.5 \text{ eV} \) DEA peak. Combinations of \( ^2A_1 \), \( ^2B_1 \) and \( ^2B_2 \) symmetries have been proposed in the various works ([37, 18, 36, 120, 38]) as being associated with the resonances responsible for this DEA peak. A very small peak is also present at \( \sim 9 \text{ eV} \) in partial cross section for \( \text{S}^- \) formation, proposed as arising from a resonance of \( ^2A_1 \), \( ^2B_1 \) or
5.1 DEA and Vibrational Excitation Experiments on SO$_2$

$^2$B$_2$ symmetries [36].

DEA to SO$_2$ was first studied experimentally in the early 1970s. Initial experiments by Rallis and Goodings [16] and Harland et al. [121] obtained negative ion signals for O$^-$ formation, revealing the two low energy peaks (at $\sim$5 eV and $\sim$7.5 eV). The later work by Abouaf and Fiquet-Fayard [122] also included negative ion signals for SO$^-$ and S$^-$ formation for the $\sim$4.5 eV peak.

Later work by Krishnakumar et al. [18, 36] obtained partial and total cross sections for DEA to both the ground and excited states of SO$_2$. Their velocity slice imaging (VSI) experiments also allowed identification of the the negative ion resonance symmetries from consideration of the selection rules around the orientation and initial electronic states of the molecule with respect to the incident electron momentum vector. For the two lowest energy peaks (at $\sim$4.5 eV and $\sim$7.5 eV) this analysis resulted in $^2$A$_1$ and $^2$B$_2$ for the negative ion symmetries respectively. For the peak at $\sim$9 eV their analysis resulted in any of $^2$A$_1$, $^2$B$_1$ or $^2$B$_2$ as allowed negative ion symmetries. Their total DEA cross sections from the $1^1B_1$ (with possible admixture of the $1^3B_1$ state) excited state revealed a lower energy peak at $\sim$0.5 eV. This $\sim$0.5 eV peak has a major contribution from O$^-$ formation and a $\sim$7 times smaller contribution from SO$^-$ formation; there was no apparent contribution from S$^-$ formation. From their analysis of the selection rules and results from their molecular orbital calculations they assigned the same $^2$A$_1$ resonance associated with the $\sim$4.5 eV peak to the $\sim$0.5 eV peak. The more recent study by Nandi and Krishnakumar [123] in 2010 involves measurements of the kinetic energies of the fragmented anions. Their analysis of these KE measurements showed that the two peaks (at $\sim$4.5 eV and $\sim$7.5 eV) in the DEA cross sections from the ground state share the same O$^-$ dissociation limit.

Recent experiments on DEA to SO$_2$ have been performed using the VSI and VMI techniques, which have allowed analysis of the anion resonances via the anion momentum distributions obtained using these methods. Gope et al. in 2017 [37] obtained momentum distributions of the fragment anions for O$^-$, SO$^-$ and S$^-$ formation for scattering electron energies between 2 and 10 eV. Around the vicinity of the second SO$^-$ peak, at $\sim$7.5 eV, they noticed an asymmetry in the momentum distribution, which they explained via a coherent superposition of anion resonances of $^2$B$_1$ and $^2$B$_2$ symmetries. For S$^-$ formation at 4.9 eV Gope et al. found O$_2$ was produced predominantly in the ground state, with the excess energy resulting in its vibrational excitation.

Between 2018 and 2020, Jana and Nandi performed a detailed study of O$^-$, S$^-$ and SO$^-$ formation from DEA to SO$_2$ using the VSI technique [120, 38, 124]. From their obtained angular distributions they attributed a resonance of $^2$A$_1$ symmetry for the O$^-$ peak at $\sim$4.5 eV. In the latter publication Jana and Nandi [124] examine the VSI results for O$^-$, S$^-$ and SO$^-$ formation around the $\sim$7.5 eV peak under consideration of the axial-recoil approximation [125]. Under the axial-recoil approximation, the resonance symmetry can be determined from the VSI images if the molecule undergoes no rotation or other structural changes during the dissociation process. For the case of DEA to SO$_2$ Jana and Nandi [124] report the axial-recoil approximation holds for O$^-$ and SO$^-$ formation but completely breaks down for S$^-$ formation. This means that the combination of $^2$A$_1$ and $^2$B$_1$ resonance symmetries for O$^-$ and SO$^-$ formation is a valid picture for the dissociation but no such picture in terms of resonance symmetry can be obtained from the VSI images for S$^-$ formation. Jana and Nandi also noted a slight asymmetry in the momentum distributions for S$^-$ formation.

To summarise: there isn’t agreement on the resonance symmetries associated with DEA via the

Since Krishnakumar is listed as one of the co-authors of Gope et al.’s work [37], we regard Gope et al.’s symmetry assignments for the resonances associated with the $\sim$7.5 eV DEA peak as superceding those in the earlier two works involving Krishnakumar [18, 36], discussed in the previous paragraph.

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5 TEMPORARY STATES OF SO$_2^-$ INVESTIGATED USING TECHNIQUES BASED ON THE EIGENPHASE AND TIME-DELAY

~7.5 eV peak in the literature; Gope et al. [37] propose a superposition of resonances of $^2$B$_1$ and $^2$B$_2$ symmetries for the SO$^-$ contribution and Jana et al. [120, 38] a combination of $^2$A$_1$ and $^2$B$_2$ symmetries for the SO$^-$ and O$^-$ contributions.

There have also been a number of experimental studies of low energy vibrational excitation of SO$_2$ [22, 126, 20, 127]. These experiments are potentially examining the same resonances leading to DEA and can provide resonance energies which are more in-line with the energies obtained from our calculations. In the vibrational excitation experiments, energies are measured for the transitions from the electronic and vibrational ground state of SO$_2$ to the vibrational states of the resonance. In contrast, our scattering calculations determine the vertical transition energies from the electronic ground state of SO$_2$ to the resonance state. As is discussed in section 5.6.3 it’s not straightforward to accurately correlate these energies.

Electron transmission spectroscopy was used in the 1973 work of Sanche and Schultz [22], where the derivative of the transmitted current versus the incident electron energy was measured. This shows a series of vibrational levels between incident electron energies of 2.87 and 3.8 eV. Above these energies, up until the limit of their measurements at 6 eV, the series appears to continue but is perturbed with another series of peaks. The two vibrational series were considered by the authors as being associated with two resonant states of SO$_2^-$. The lower series, they proposed as being a resonant state of either shape or core-excited character. For the case of core-excited character they suggested a state of $^2$A$_2$ symmetry; for the shape character no symmetry was proposed. There was no analysis or discussion around the higher vibrational series (>3.8 eV) in their results. Following from this work, Simon et al. [126] obtained energy loss spectra for the scattering of electrons from SO$_2^-$, corroborating Sanche and Schultz’s results for the lower energy vibrational series. Although stating that "a detailed analysis including angular distributions is in progress" they agreed with Sanche and Schultz’s assignment of $^2$A$_2$ symmetry for the anion state associated with the vibrational series, suggesting the resonance is core-excited on the basis that "if the $^2$B$_1$ ground state of SO$_2^-$ was involved one would expect strong excitation of bending modes as the apex angles are quite different for the ground states of SO$_2$ and SO$_2^-$. Moreover, if the lowest shape resonance becomes observable at 2.8 eV and higher, and gives a boomerang effect [128] in this energy region, one would expect to observe sharp peaks below 2.8 eV as the width of the barrier varies continuously with energy".

A later work by Andrić et al. [20] also obtained energy loss spectra for the scattering of electrons from SO$_2$ around incident electron energies sufficient for investigation of the resonance associated with the lower vibrational series reported by Sanche and Schultz (2.5 to 4.5 eV). They also matched the angular behaviour of their differential excitation cross sections to Read’s angular correlation theory [129] for "a resonant transition between an A$_1$ ground state and an intermediate B$_1$ or B$_2$ state with the participation of only the first allowed partial wave". Based on the molecular orbitals of SO$_2^-$ and their associated symmetries they suggested that the low energy resonance is of $^2$B$_2$ symmetry. Later experiments by Gulley et al. [127] examined a wider range of incident electron energies, between 1 and 30 eV. Although Gulley et al. provided no analysis of the resonance symmetries their cross sections were in reasonable agreement with those in the Andrić et al. study, for electron energies between 2.5 to 4.5 eV. The assignment of symmetries to the resonances discussed in this section is summarised in table 5.4.
There are significantly fewer theoretical studies of electron scattering from $\text{SO}_2^-$ reported in the literature than experimental ones. Gupta and Baluja [130] presented results of electron scattering from $\text{SO}_2^-$ at equilibrium geometry calculated using the R-matrix method with a DZP basis set. Three calculations were performed with different scattering models: SE, SEP and CC using HF orbitals of $\text{SO}_2$. As well as a bound state of $\text{SO}_2^-$ of $^2\text{B}_1$ symmetry, they reported a number of resonances. Calculations using an SE model showed shape resonances of $^2\text{A}_1$ and $^2\text{B}_2$ symmetries at energies of 5.20 and 6.00 eV respectively. From their SE calculation they obtained widths for these resonances of $\sim$4.50 eV. From their CC calculation they reported: two shape resonances of $^2\text{A}_1$ and $^2\text{B}_2$ symmetries and two core-excited resonances of $^2\text{A}_2$ and $^2\text{B}_1$ symmetries (reproduced in table 5.1).

Vinodkumar et al. [131] presented results from an R-matrix calculation showing evidence of five resonances. Similar to Gupta and Baluja they used a DZP basis set and a CC scattering model. Three resonances were discussed by them: of $^2\text{A}_1$ symmetry at 3.4 and 8.17 eV and of $^2\text{A}_2$ symmetry at 5.1 eV. Although not discussed in their text, resonances of $^2\text{B}_1$ and $^2\text{B}_2$ symmetries are apparent in their eigenphase sums at energies of $\sim$8 and $\sim$9 eV respectively. Vinodkumar et al.’s results are shown alongside Gupta and Baluja’s in table 5.1.

A theoretical work by Basumallick et al. [132] studied exclusively two $^2\text{A}_1$ resonances using the correlated independent particle Fock space multi-reference coupled cluster method augmented by complex absorption potential with a aug-cc-pVTZ basis set. They reported energies and corresponding widths (in parenthesis) for the two $^2\text{A}_1$ resonances of 4.45 (0.007) and 6.56 (0.017) eV. However, the energies correspond to non-vertical transitions from the ground state to the resonances state at their respective equilibrium geometries.

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Table 5.1: Resonance positions from CC calculations of electron scattering from $\text{SO}_2$ reported by Gupta and Baluja [130] and Vinodkumar et al. [131]. The energies correspond to vertical attachment from the electronic ground state at its equilibrium geometry. The Vinodkumar et al. $^2\text{B}_1$ and $^2\text{B}_2$ resonances are not explicitly mentioned in [131] but are apparent from the included eigenphase sums.

Since Gupta and Baluja’s results do not account for nuclear dynamics and only apply to the equilibrium geometry, as for all studies with these limitations, exact correspondence cannot be expected between the theoretical resonance positions and the peaks in the experimental DEA cross section; at best only rough correspondence can be made. The first shape resonance identified in their work, $^2\text{A}_1$, is extremely likely to be the resonance responsible for the DEA formation of $\text{O}^-$, $\text{S}^-$ and $\text{SO}_2^-$ for scattering electron energies around the peak at $\sim$4.5 eV. The $^2\text{A}_1$ symmetry of this resonance corresponds to that reported, without contention, in the DEA experiments discussed in the previous section. Their second shape resonance, $^2\text{B}_2$, likely corresponds to the $^2\text{B}_2$ resonance.
TEMPORARY STATES OF $\text{SO}_2^-$ INVESTIGATED USING TECHNIQUES BASED ON THE EIGENPHASE AND TIME-DELAY

symmetry proposed as either solely [36] or as a contributor [37, 120] to the $\sim 7.5 \text{ eV}$ peak for DEA to $\text{SO}_2$. However, no resonances of the $^2\text{B}_1$ [37] and $^2\text{A}_1$ [120] symmetries proposed in the experimental works as contributing to anion formation around the $\sim 7.5 \text{ eV}$ peak were reported by Gupta and Baluja. Additionally, an $^2\text{A}_2$ resonance, as reported by Gupta and Baluja for the resonance at $6.25 \text{ eV}$, was not identified in any of the experimental DEA works. For the $\sim 9 \text{ eV}$ peak, the $^2\text{B}_1$ resonance reported at $9.58 \text{ eV}$ by Gupta and Baluja could be one of the $^2\text{A}_1$, $^2\text{B}_1$ or $^2\text{B}_2$ resonances proposed (seemingly tentatively) by Krishnakumar et al. [36] for DEA via this peak. None of the Gupta and Baluja resonances are likely candidates for Krishnakumar et al.’s proposed $^2\text{A}_1$ and $^2\text{B}_2$ resonance symmetry for the $\sim 9 \text{ eV}$ peak.

5.3 Characteristics of the Calculation

5.3.1 Target Model

State-averaged CASSCF calculations were performed with $\text{SO}_2$ in the equilibrium bent geometry (as described in the introductory paragraph of this chapter) using the MOLPRO package, with a CAS(18,12) model. This model was constructed as described in chapter 2, section 2.5.1. Briefly, the main considerations for a SA-CASSCF calculation are; the basis set, the active space and the selected states for averaging. The active space, containing the 18 valence electrons, was chosen to consist of the $5\text{a}_1$, $6\text{a}_1$, $7\text{a}_1$, $8\text{a}_1$, $9\text{a}_1$, $2\text{b}_1$, $3\text{b}_1$, $3\text{b}_2$, $4\text{b}_2$, $5\text{b}_2$, $6\text{b}_2$ and $1\text{a}_2$ molecular orbitals. Since the excitations of the remaining 14 electrons were assumed to play little role in scattering for the energies of interest in this study they were confined to the frozen core. This was the same active space used in Gupta et al.’s study [130].

Following the setup of the active space we carried out tests for different basis sets and state averaging. Table 5.2 shows the absolute energy of the ground state, the dipole moments and the first 17 excitation thresholds obtained for cc-pVTZ and DZP basis sets with four, five and eight state averaging (the specific states used are given in the caption of table 5.2). It’s apparent from table 5.2 that the cc-pVTZ basis set, with eight state averaging, produces more accurate energies for the lower lying states. However, the energies of primary interest to this study are around the 7.5 eV peak in the DEA cross-section; here the DZP basis set delivers much better results, as well as a dipole moment much closer to the experimentally obtained values (Experimental: 1.6331 D [119]; DZP with five state averaging: 1.7834 D). We used a DZP basis set with five state averaging for our scattering calculations.

Also shown in table 5.2 are results from other calculations for the ground and excited state energies of $\text{SO}_2$. Of the four, that of Palmer et al. [133], using large scale CI, report the lowest excitation thresholds of the four works. Their ground state energy is more than 10 eV lower than the one used for our scattering calculations (from DZP with 5 state averaging). Gupta and Baluja [130] used a very similar target model to our own work, the DZP basis set and an identical active space. The primary difference from our work is their use of HF instead of SA-CASSCF orbitals. This difference likely explains why their ground state energy is 1.5 eV higher than ours and all of our excitation thresholds lower. Comparision of ours, Vinodkumar et al.’s and Gupta’s excitation thresholds to experiments is not straightforward due to the high variance of the reported experimental measurements over the

31Table 5.2 shows that a DZP basis set with eight averaging states is marginally better than the DZP with five averaging states. However the DZP basis set with eight averaging states was tested near the end of the work, at which point most of our scattering calculations had been completed.
The states are ordered according to the energies obtained from the DZP-S single calculation (the one used to obtain our experimental results). The energies are taken from the NIST standard reference database [119]. The states are ordered according to the energies obtained from the DZP-S single calculation (the one used to obtain our experimental results).

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Table 2: Absolute energies of the ground state (in eV) and bond moments of the ground state (in D).
5 TEMPORARY STATES OF SO$_2^-$ INVESTIGATED USING TECHNIQUES BASED ON THE EIGENPHASE AND TIME-DELAY

four works included in table 5.2 and, to a lesser extent, neglect of the vibrational states in the three theoretical works. Overall, our ground state energies and excitation thresholds are lower than both Gupta and Baluja’s and Vinodkumar et al.’s, and we are higher than most of the experimentally reported excitation thresholds. Grein doesn’t report a ground state energy; Elliott et al. do and it’s the lowest of all four pre-published theoretical works. Both Grein and Elliott et al. have excitation thresholds which are both lower and higher than ours, depending on the particular state.

Our calculated dipole moment is significantly closer to the experimental measurement [119] than the values reported by Gupta and Baluja (and also Vinodkumar et al.). Neither of the other two works, Grein [134] (using CCSD(T) and DFT) and Elliott et al. [135] (using the MRCI) report a dipole moment.

5.3.2 Scattering Model

For our scattering calculations we used an R-matrix radius of 10 a$_0$, which resulted in $\sim 10^{-8}$ for the largest value of the radial probability density across all the target orbitals used in the calculation. We deemed this low enough to consider the target charge density to be sufficiently contained inside the R-matrix sphere. A propagation radius of 80 a$_0$ was used throughout our calculations.

For the continuum, GTOs were used with six partial waves (or a maximum angular momentum of $l_{\text{max}}=5$). We found little difference between the cross-sections calculated with five partial waves to those calculated with six. For the orthogonalisation of the continuum orbitals a deletion threshold of $2 \times 10^{-7}$ was used. Most of our calculations were on an energy grid running from 0.1 to 10 eV in steps of 0.005 eV, which we deemed sufficient to be able to detect any resonance structure of interest. Calculations were performed using SE, SEP and CC scattering models.

For the SE and SEP models, HF orbitals were used with the 35 lowest energy orbitals used for the virtual space. For the SEP model, with respect to the L$^2$ configuration, we froze 14 electrons in the 7 lowest energy orbitals.

For the CC calculations, as mentioned in chapter 2, section 2.5.2, a good balance between the target (N electron) description and the scattering (N + 1 electron) description is required for accurate calculations. Our CC approach was CAS; here the $L^2$ configurations were constructed to allow the scattering electron, along with the 18 target valence electrons, to occupy the previously described active space.

For the CC calculations, tests for convergence of the cross sections were carried out for the following number of states included in the close-coupling expansion: 16, 31, 43, 54, 68, 104, 150, 200 and 300. As is shown in figure 5.1 the cross sections do not appear to have converged even for 300 states. This appears to be especially true of the resonant contributions to the cross sections. We did not have the available computational resource to run the calculations for larger numbers of target states. For the 150, 200 and 300 state calculations the grid was limited to run from a starting energy of 2.5 eV, since we’d identified no resonances below this energy for the calculations including lower numbers of target states. The 16 state calculation was performed to allow better comparison with the results of Gupta et al. [130].

5.4 Identification and characterisation of the Resonances

Our initial method for identifying and characterising the resonances was using the RESON software as described in chapter 2, section 2.2.1. Unfortunately, we encountered, on several occasions, RESON
failing to detect resonances which were obvious from visual inspection of the accompanying eigenphase sums and cross sections. For example, values for the $^2A_1$ resonance were reported by RESON for the calculation including 43 target states but not for many of the calculations with a higher number of target states. No attempt was made to determine whether this unreliability of RESON was linked to the grid size.

For the cases where RESON did successfully detect resonances we found that reliable values for the positions and widths were obtained (again determined from both the RESON goodness indicators and against visual inspection of the accompanying eigenphase sums and cross sections). This is in contrast to some of the resonances discussed for H$_2$ in chapter 4, where close proximity to other resonances and thresholds made it much more difficult to obtain reliable positions and widths for the resonances using the time-delays.

Since our results were not fully converged and calculations were performed for an increasing number of target states, we have used plots of the cross sections to illustrate the changing properties of the resonances as the number of included target states is increased (see figure 5.1). As is apparent in the figure, nearly all of the resonances manifest as well defined lorentzian, or inverse lorentzian, like structures in the cross sections.

We found that using the same interactive fit method which was used for the H$_2$ study applied to our time-delays proved to be the most reliable way to characterise resonances for this study. We therefore used this method to obtain the positions and widths of the resonances reported in this work for all of our scattering models.

The main aim in this section is to label and characterise the resonances identified in our results in order to facilitate subsequent discussion and comparison to other calculations and experiments. We discuss the elastic and total inelastic cross sections shown in figure 5.1, obtained from our CC calculations for 16, 31, 43, 54, 68, 104, 150, 200 and 300 target states included in the expansion; the time-delays shown in figure 5.2, obtained from our CC calculations with 300 target states; and the eigenphase sums and time-delays, obtained from our SE, SEP and CC calculations, shown in figures 5.4 and 5.5 respectively. Plots are shown for each of the four scattering symmetries, $^2A_1$, $^2A_2$, $^2B_1$, $^2B_2$. The starting energy for the calculations was 0.01 eV for the SE and SEP models and the CC calculations including 104 states and below. For the CC calculations including 150, 200 and 300 states a higher starting energy of 2.5 eV was used. The CC cross sections, eigenphase sums and time-delays were calculated up to an energy of 10 eV (except for the $^2B_2$ symmetry of the CC calculation including 16 target states, which was ran to slightly higher energies) and the SE and SEP ones up to 20 eV. The energy positions of the resonances obtained from our CC calculation with 16 and 300 target states are shown in tables 5.3 and 5.4; the first of these tables compares to the resonance positions obtained from our SE calculations and the second table to the resonances obtained in other works.

The results from our CC calculations show strong evidence of six resonances in the energy range from 0 to 10 eV. The resonances are especially clear in the time-delays (figure 5.2), where they all manifest as Lorentzian-like structures, very pronounced and distinct from the surrounding background. From the cross sections (figure 5.1) it’s quite clear that none of the resonances obtained from our CC calculations have fully converged in energy, with all resonances moving to lower energy and (at least initially) narrowing in width as the number of target states is increased. It’s expected that
Figure 5.1: Contributions from the four irreducible representations to the elastic and total excitation cross sections for electron scattering from SO$_2$. The total excitation cross section is the sum over all the excited states included in the calculation. The cross sections were calculated using the CC model described in the text. Cross sections are shown for different numbers of target states included in the calculation. The numeric labels for the resonances are shown in black, bold text. Note that the energy range on the x-axis is different for the elastic and inelastic cross sections. Also note that the effect of the $1^{2}B_2$ resonance (labelled 1) is barely discernible in the elastic cross section.
5.5 Scattering Results and Detected Resonance and Bound States

Figure 5.2: Time-delay (largest eigenvalues of the Q-matrix) for the four irreducible representations for electron scattering from SO$_2$, calculated using the CC model described in the text with 300 target states. Labelling is the same as in figure 5.1. The much smaller, unlabelled spikes are due to the excitation thresholds.

lower energies and widths are obtained for calculations including a higher number of target states due to the better description of polarisation. However, if the $N + 1$ scattering states become better represented than the $N$ electron target states, this can result in the polarisation being over described and the resonance energies being too low (over-correlation). We were unable to determine directly from the calculation whether or not this was the case but some insight was obtained from comparison of our calculated resonance positions to the experimental results. This insight is provided in the later sections. The lack of convergence is also highlighted in figure 5.3, which shows resonance positions as a function of the number of states used in the CC expansion. Figure 5.3 also indicates that the higher energy resonances appear to be closer to convergence than those at lower energies.

It is difficult to see, in figure 5.4, evidence of resonances in the eigenphase sum obtained using the SE model, due to the common scale used to show the eigenphase sums obtained from all three models (SE, SEP and CC). On close inspection a wide resonance in the SE eigenphase sum for $^2B_2$ symmetry is apparent. At a more appropriate scale and in the SE time-delays shown in figure 5.5 several peaks are evident. Positions and widths of those peaks which we believe arise from physical resonances and correspond to those from our CC calculations are tabulated in 5.3. The other peaks are either: potentially non-physical, we observed a dependency of the peak maximum on the quality of the continuum used in the calculation; and/or are outside the energy range (>10 eV) to be confidently able to make correspondence with the CC calculations. The continuum dependency was especially the case for the $^2A_2$ peak but also, to a much lesser extent, the $^2B_1$ peak and the high energy $^2A_1$ peak.

Figure 5.4 also shows eigenphase sums obtained using the SEP model. Some evidence of a wide phase shift in the SEP eigenphase sum is evident just below 4 eV for $^2A_1$ symmetry, perhaps corresponding to the wide peak in the $^2A_1$ SE time-delay. The wide $^2B_2$ phase shift evident in the SE eigenphase is also evident in the SEP eigenphase. There is some ambiguity for the $^2A_1$ and $^2B_2$ symmetries on whether the low energy, narrow SEP phase shifts or the much wider SEP phase shifts and peaks also evident in the SE calculations correspond to the low energy resonances obtained from our CC calculations. Since it’s not possible to confidently distinguish physical resonances from
Table 5.3: Calculated resonance positions for electron scattering from SO$_2$ obtained using the SE and CC models described in the text.

<table>
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<th>CC 16 states</th>
<th>CC 300 states</th>
<th>SE</th>
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<td>$E(eV)$</td>
<td>$\Gamma(eV)$</td>
<td>$E(eV)$</td>
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<tr>
<td>$1^{2}A_1$</td>
<td>4.24</td>
<td>0.19</td>
<td>3.06</td>
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<tr>
<td>$1^{2}B_2$</td>
<td>5.26</td>
<td>0.25</td>
<td>4.12</td>
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<tr>
<td>$1^{2}A_2$</td>
<td>5.60</td>
<td>0.42</td>
<td>4.42</td>
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<tr>
<td>$1^{2}B_1$</td>
<td>9.40</td>
<td>0.75</td>
<td>7.62</td>
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<tr>
<td>$2^{2}A_1$</td>
<td>9.93</td>
<td>0.56</td>
<td>7.96</td>
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<tr>
<td>$2^{2}B_2$</td>
<td>9.95</td>
<td>0.49</td>
<td>8.33</td>
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We now discuss our results in some detail. For each resonance discussed below an energy range is given for the CC resonances, the higher energy from the 16 state calculation and the lower from the 300. The resonance energies obtained from calculations performed with the other target state numbers are all between these energy positions and energy ordered with respect to decreasing state number. The six main resonances identified in this work are all clearly present in both the CC time-delays and the inelastic CC cross sections. All six resonances are also evident in the elastic CC cross sections but with varying degree of prominence.
5.5 Scattering Results and Detected Resonance and Bound States

Figure 5.4: Eigenphase sum for the four irreducible representations for electron scattering from SO$_2$. These were calculated using the SE, SEP and CC models described in the text. CC included 300 states with calculations performed from 2 to 10 eV. SE and SEP calculations are shown from 0 to 15 eV.

Resonance $1^2A_1$ appears over the energy range 3.06 to 4.24 eV in the CC time-delays. For the CC model, as the number of target states increase the resonance moves below the $3^2B_2$ excitation threshold at 3.607 eV, at which point it is only really apparent in the $2^2A_1$ elastic cross section in figure 5.1. Since there is a corresponding peak in the SE time-delay (figure 5.5) we deem this resonance shape in character. The higher $2^2A_1$ resonance is positioned between 7.96 and 9.93 eV in the CC calculation (figure 5.1). Its character is hard to determine with certainty. If the higher energy peak in the $2^2A_1$ SE time-delay is physical and associated with the $2^2A_1$ resonance (and not another unknown resonance at an energy $>$ 10eV in the CC results) then it’s shape in character. Otherwise this is likely a core-excited shape resonance.

There is a single resonance of $2^2A_2$ symmetry evident in our results, which appears between energies 4.42 and 5.60 eV in the CC time-delays. It contributes strongly to both the elastic and total inelastic cross sections. We therefore designate the $1^2A_2$ resonance as likely core-excited in character.

The single $2^2B_1$ resonance evident in our results, occurs in the CC time-delays for energies between 7.62 and 9.40 eV. If the $2^2B_1$ peak in the SE time-delay is physical, then it’s very likely associated
with the $1^2B_1$ resonance and the resonance character is shape. Otherwise the $1^2B_1$ resonance is core-excited.

We believe we have confidently detected two resonances of $2^B_2$ symmetry; a very narrow one at lower energies and another narrow one at higher energies. The low energy resonance, $1^2B_2$, appears for energies between 4.12 and 5.26 eV in the CC time-delay. If it’s associated with the resonance evident in the SE time-delay just above 5 eV then it will be shape in character. However, it’s also possible that the very wide peak apparent in the $2^B_2$ CC elastic cross section is linked to the very wide phase shifts in the $2^B_2$ SE and SEP time-delays and eigenphase sums. If this is the case then the $1^2B_2$ will be of core-excited shape character, with a small possibility of a Feshbach character if including more than 300 target states would bring it below the $3^B_1$ excitation threshold at 3.607 eV. However, an expected accompanying phase shift in the CC eigenphase sum for this case is absent, although it’s possible that this could be a result of the more detailed form for the CC eigenphase sum, likely due to the thresholds included for this calculation.

The higher energy $2^B_2$ resonance, $2^2B_2$, occurring for energies between 8.33 and 9.95 eV in the CC time-delays, is clearly core-excited in character, due to its contribution to the inelastic cross section and absence from the SE eigenphase sum.

Finally we mention the indication of a bound state of SO$^-_2$ for the $2^B_1$ irreducible representation. Figure 5.6 shows that for this symmetry the lowest R-matrix pole is below the ground state energy for calculations including 16, 43, 54, 68, 104, 150 and 200 target states (no examination was performed for the calculations including 31 and 300 target states).

### 5.6 Comparison of Present Results with Other Works

We now compare and propose possible connections between our results and those of other theoretical works, as well as the vibrational spectroscopy and DEA experiments. Much of this discussion is summarised in table 5.4.
### Table 5.4: Resonance symmetries, energies and widths (eV), using the CC model described in the text and those from the theoretical studies of Gupta et al. [130], Vinodkumar et al. [131] and Basumallick et al. [132]; the vibrational spectroscopy experiments of Sanche and Schultz [22], Simon [126] and Andric et al. [20]; and the DEA experiments of Krishnakumar et al. [18,36], Gope et al. [37] and Jana and Nandi [120,38]. Our results are from calculations using 16 and 300 target states.

Note that the energies have different meanings for theory and the two types of experiment: for the theoretical works the energies, with our work, Gupta et al. [130] and Vinodkumar et al. [131], are the vertical transition energies from the electronic ground state at equilibrium geometry to the electronic resonance at the equilibrium geometries of each state. For the DEA spectroscopy experiments the energies are for the two lowest accessible vibrational states of the resonance (relative to the ground vibrational state of the neutral). The DEA of Krishnakumar et al. [18,36], Gope et al. [37] and Jana and Nandi [120,38] are the energies from calculations using 16 and 300 target states and with symmetries of each state. For Basumallick et al. [131] and Andric et al. [20] are the vertical transition energies from the electronic ground state at equilibrium geometry to the electronic resonance at the equilibrium geometries of each state. For the experiment of Krishnakumar et al. [18,36], Gope et al. [37] and Jana and Nandi [120,38], the energies are the approximate peak positions in the total (for all dissociated fragments) DEA cross sections. Any empty cell means outside (or probably outside) the experimental energy range and symmetries of the study. A * indicates that the value was not reported in the work but rather has been taken from another related work. An empty cell means either not observed or observed but with no symmetry assignment.

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| 120  | [37] |       | | 37   |       | | 18,36|       | | 36   |       | | 30   |       | | 12  |       | |
| 122  | [132]|       | | 132  |       | | 131  |       | | 131  |       | | 130  |       | | 120  |       | |

| This work | 16 states | 300 states | |
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5 TEMPORARY STATES OF SO$_2^-$ INVESTIGATED USING TECHNIQUES BASED ON THE EIGENPHASE AND TIME-DELAY

Figure 5.6: Lowest R-matrix poles (solid lines) for the four symmetries with 16, 43, 54, 68, 104, 150 and 200 target states included in the calculation. Also shown is the ground state energy of SO$_2^-$ (dashed line). It’s evident from the figure that there’s a bound state of SO$_2^-$ for the $^2B_1$ irreducible representation with a binding energy of $\sim0.05$ eV for the 200 state calculation.

5.6.1 Comparison with Theoretical Works

We begin with a comparison of the results obtained from our 16 state calculation to those of Gupta et al. [130]. Our 16 state CC calculation was closest to Gupta et al.’s results, which was also performed with 16 target states in the CC expansion. The differences with their calculations is the $l_{\text{max}}=4$ they used for the continuum GTO basis, their lower R-matrix propagation radius of 50 a$_0$ and their use of HF-SCF orbitals for the representation of the target states. The active space, R-matrix radius and deletion threshold were the same for the two calculations. The absolute differences in positions (shown in table 5.4) and relative differences in the widths (in parenthesis) between the two works are: $^2A_1$, 0.26 eV (2.68); $^2B_2$, 0.57 eV (1.56); $^2A_2$, 0.65 eV (1.33); $^2B_1$, 0.18 eV (1.11), with all our positions and widths lower than those of Gupta et al.. We consider, that, on the whole, the results from the two calculations are similar. Since we’d noted little difference when calculating with $l_{\text{max}}=5$ for the continuum GTO basis our lower positions and widths could be due to the more accurate excitation thresholds obtained with our target model due to the orbital used, as discussed in section 5.3.1.

We now discuss how each of the resonances obtained with our 300 state calculation compare to the equivalent resonances of Gupta et al. [130], Vinodkumar et al. [131] and Basumallick et al. [132], where applicable. From this point on, unless otherwise indicated, the stated energies and widths from our work are those obtained for the calculation performed with 300 states.

All three R-matrix studies ([130], [131] and ours) detect a resonance of $^2A_1$ symmetry at energies 4.5, 3.4 and 3.1 eV (respective to the cited works). Vinodkumar et al. don’t report a width, the width given by Gupta et al. of 0.51 eV is significantly higher than our width of 0.068 eV. The position reported by Vinodkumar et al. for this $^2A_1$ resonance is lower than that reported by Gupta et al. and much closer to the position obtained from our 300 state calculation. As can be seen from table 5.4, this ordering of the positions and widths also applies to the other resonances reported by Vinodkumar et al. and Gupta et al..

The low energy $^2A_1$ resonance position reported by Basumallick et al. [132] of 4.45 eV corresponds to the difference between the ground state and resonance energies at the respective equilibrium geometries of the two states. The fixed-nuclei resonance energy is always equal or greater than that of the energy difference between the respective equilibrium geometries. Therefore, since their reported
energy position is still significantly larger than our positions obtained for all our CC calculations, we can state their energy for the $^2A_1$ resonance corresponds to an energy larger than ours for the fixed-nuclei resonance position.

A higher energy $^2A_1$ resonance was identified by both Vinodkumar et al., Basumallick et al. and in this work but not by Gupta et al.. We discuss this "non-reported" Gupta resonance later and focus here on the works were it was identified. In contrast to the low energy $^2A_1$ resonance Basumallick et al. reported a lower adiabatic energy than all the other works and all our CC calculations including the different numbers of target states for the higher energy $^2A_1$. The position reported by Vinodkumar et al. of 8.17 eV, most closely matches the position calculated with our 150 state calculation of 8.18 eV. We note that the 3.31 eV position obtained for the lower energy $^1A_1$ resonance with our 150 states calculation is also very close to the Vinodkumar et al. reported value of 3.4 eV, although we obtained a slightly closer position of 3.39 eV with the 104 state calculation. This indicates that for the Vinodkumar et al. calculation there is likely to be some aspect other than the number of included target states which has resulted in them obtaining lower energies for their resonances (compared to ours and Gupta et al.’s 16 state calculations). It was not clear from their publication and our attempt to reproduce their results what this could be.

Our attempt to reproduce Vinodkumar et al.’s calculation was based on their reported methodology and used; a DZP basis set, the specified active space, 8 target states, an R-matrix radius of 10 a₀, a propagation distance of 100 a₀ and GTOs with $l_{max}$=4 for the continuum. This resulted in (Vinodkumar et al.’s reported values in parenthesis); a ground state energy of -547.24 Ha (-547.20 Ha) and a dipole moment of 2.09 D (2.1 D). We considered our reproduced ground state energies and dipole moments close enough to those reported in Vinodkumar et al.’s paper to be confident that we had obtained a very similar target description. However, the resultant energy position of the lower $^2A_1$ resonance obtained from the scattering calculation was 4.75 eV, which is significantly higher than the reported 3.4 eV in Vinodkumar et al.’s paper.

A single $^2A_2$ resonance was detected in all three works at energies, 6.25, 5.1 and 4.42 eV respectively. A single resonance was also detected for $^2B_1$ symmetry in all three works, with reported energy positions, 9.58, ~8.0 and 7.62 eV, in the usual order and also showing decreasing energies across the three works as was described for the other resonances. For the widths, Gupta was higher again for both the $^2A_2$ and $^2B_1$ resonances, this time by a factor of just under 5.

From figure 5.1 and table 5.4 the low energy $^1B_2$ resonance appears mostly (with the calculations with higher numbers of target states) as a very narrow spike and may on first consideration appear too narrow to correspond to Gupta’s $^2B_2$ resonance (at an energy of 5.83 eV and width 0.39 eV). Although it’s clear from the discussion so far that the results are not converged for any of our resonances, the narrowing of the $^1B_2$ resonance for increasing number of target states is especially dramatic. For our 16 target state calculation, we obtained a $^2B_2$ resonance at an energy of 5.26 eV and a width of 0.25 eV, which we consider close enough to Gupta’s reported values to be confident that this is the same resonance. It’s clear from figure 5.7 that our 16 state $^2B_2$ resonance corresponds to the much narrower resonances detected for the calculations including higher numbers of target states. There was no clear evidence of a $^1B_2$ resonance in Vinodkumar et al.’s work.

We observe a higher energy $^2B_2$ resonance at 8.33 eV, previously reported only by Vinodkumar et al., at energies of ~9.0. We now discuss all three higher energy resonances; the $^1B_1$ resonance,
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Figure 5.7: Contributions from the $^2B_2$ symmetry to the total excitation cross sections for electron scattering from SO$_2$ in the vicinity of the $^1D_B$ resonance for different numbers of target states included in the calculation.

We now present some possible interpretations of the results from the vibrational spectroscopy and DEA experiments using our results, making it clear from the start that attempts to match our resonances with those responsible for the experimental observations are speculative. Ion yield due to dissociation via a negative ion resonance can only occur above the associated dissociation thresholds (for the different
5.6 Comparison of Present Results with Other Works

Figure 5.8: Elastic and excitation cross sections from the $X^1A_1$ ground state of SO$_2$ to the states indicated in the legends for our calculations including the number of states shown in parenthesis. Resonance labels are shown for the 300 state calculation in the elastic and the top and bottom panels for the excitation cross sections. Note that the excitation peak associated with the $1^2B_2$ resonance is barely discernible in the elastic cross section.
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5.6.3 Comparison with Vibrational Spectroscopy Experiments

We begin by attempting to obtain bounds for the fixed-nuclei resonance positions corresponding to the vibrational spectroscopy experiments of Sanche and Schultz [22]. We start by considering figure 4 in Andrić et al.’s publication [20], which shows the excitation functions at $20^\circ$ for the vibrational levels of the ground electronic state of $\text{SO}_2$. The shape of the enveloping profile in the three excitation functions in this figure indicate that the equilibrium geometries of the electronic ground state and the resonance state are displaced from one another [140]. According to the analysis in [140] (under the approximation of a harmonic oscillator potential) the peak energy of the enveloping profile, $\omega$ in this situation is given by:

$$\omega = \omega_{eg} + D\omega_0$$  \hspace{1cm} (5.1)

where $\omega_{eg}$ is the fixed-nuclei resonance position at the ground state equilibrium geometry, $\omega_0$ the vibrational spacing of the ground electronic and resonant states and $D > 1$ a dimensionless constant, which can be obtained from the width of the enveloping profile. However, the analysis in [140] i) is...
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under the assumption of an harmonic potential, which may not necessarily hold true, especially if the vibrational states of the resonance are significantly above the ground vibrational state of the resonance; ii) accounts only for vibrational excitations to the resonant state and not the subsequent decay back down to the ground electronic state. Therefore we can only approximate that $\omega_{eg}=3.30$ eV is an upper bound to any fixed-nuclei resonance position for correspondence with the vibrational spectroscopy experiments of Sanche and Schultz\textsuperscript{33} but that the actual position may be several vibrational states below this.

Having made clear the limitations imposed on our analysis we now consider how our results compare to those of the vibrational spectroscopy experiments. The three resonances in the results from our CC calculations (for all numbers of included target states), which are closest to the starting energies (2.87 and 3.8 eV) of the two vibrational resonance series initially observed and reported by Sanche and Schultz [22] are the $1^2A_1$, $1^2A_2$ and $1^2B_2$ resonances (for all our CC calculations with the different number of target states). The experimental literature suggests conflicting symmetries for the resonances associated with the two vibrational series: Sanche and Schultz [22] and Simon [126] both propose $^2A_2$ symmetry and Andrić et al. [20] $^2B_2$. There is perhaps some, non-conclusive, indication from our results that our $1^2B_2$ resonance may be responsible for the lower vibrational series, since it’s lower than the $1^2A_2$ by $\sim0.3$ eV in all our CC calculations for the different numbers of target states. However, we point out that this $\sim0.3$ eV spacing between the $1^2B_2$ and $1^2A_2$ resonances is significantly less than both the energy differences between the observed starts of the two vibrational series in the Sanche and Schultz experiments and the positions of the peaks of the enveloping profiles for the two series, which are $\sim1$ eV and $\sim2.5$ eV respectively. This could come about (at least with respect to the overlapping harmonic potential model [140]) from different values of $D$, in equation (5.1) associated with vibrational excitations to the two resonant states; arising from different vibrational spacings of the resonances linked to the two series and/or different widths of the enveloping profiles. In fact, it’s possible for a higher fixed-nuclei resonance position to be associated with a lower vibrational series. We therefore conclude that our results provide no clear resolution to the conflicting symmetries for the resonances associated with the two vibrational series.

If both the $1^2A_2$ and $1^2B_2$ resonances described by our calculations happen to be responsible for the two experimentally observed vibrational series, the question arises as to why the $1^2A_1$ is not visible in the vibrational spectroscopy experiments. We consider that, as discussed in section 5.1, the $^2A_1$ symmetry is universally associated with the DEA peak at $\sim4.5$ eV and that examination of the DEA peak as obtained by Krishnakumar et al. [36] for the different anions shows that DEA begins to noticeably take place at energies between 2.5 and 3.5 eV, depending on the fragment anion. Consider both that the starting energy range for DEA is mostly below the 3.30 eV upper bound for the fixed-nuclei resonance position corresponding to the first vibrational series and that the resonance states observed in the Sanche and Schultz vibrational spectroscopy experiments correspond to dominant modes of the symmetric stretch type [22, 20] and extend up to at least 6.2 eV. We can then deem it very unlikely that the $1^2A_1$ resonance can support sufficient vibrational states at the energies of the vibrational spectroscopy experiments. For the energy range of the vibrational spectroscopy experiments it would appear more likely for the $^2A_1$ resonance to dissociate to O\textsuperscript{−} than to support a symmetric

\textsuperscript{33}A linear regression of the peak maximum energies of the three excitation functions in Andrić et al.’s figure 4 to the ground state gives 3.25\pm0.05 eV. The upper bound is then obtained by considering case $D=1$, with a vibrational spacing of $\sim0.1$ eV for the low energy resonance (of the experimentally relevant mode) [22] and that the ground vibrational state of SO\textsubscript{2} in its electronic ground state is $\sim0.2$ eV above its electronic potential energy at equilibrium geometry [119].
stretch mode of the two O atoms about the S atom.

However, since the $^1A_2$ resonance is the only resonance with calculated energies below the $\omega_{eg}=3.30$ eV upper bound for the fixed-nuclei resonance position corresponding to the first vibrational series, it’s still worth considering its association with this vibrational series. If it is associated then the 3.06 eV obtained with our 300 state calculation would indicate a value of $\sim 2.4$ for $D$ in equation (5.1).

The more likely case, that the $^1A_2$ and $^1B_2$ resonances are associated with the two vibrational series, indicates that our 300 state results are still not converged. This is because the fixed nuclei positions obtained (respectively 4.42 and 4.12 eV) are still significantly above the 3.30 eV upper bound for the fixed-nuclei resonance position corresponding to the first vibrational series.

5.6.4 Comparison with DEA Experiments

In this section we provide analysis of the DEA experiments discussed in section 5.1 with consideration of our results. It seems very likely that our $^1A_1$ resonance is responsible for the low energy peak at $\sim 4.5$ eV, as $^2A_1$ symmetry has been assigned, without contention, to this resonance in the literature. We believe the resonance positions obtained from our CC calculations for all numbers of included target states are compatible with DEA via the $\sim 4.5$ eV peak. However, the lower resonance positions obtained from the calculations with the higher number of included target states could indicate a minimum in the potential energy surface with support for vibrational states. Since Krishnakumar et al.’s DEA measurements [36] showed contributions to the first DEA peak from O$^-$, S$^-$ and SO$^-$ fragments then this resonance is certainly associated with all three of these dissociation channels and is unlikely to be associated with any of the other DEA peaks. There has been no proposal in the literature that the $\sim 4.5$ eV DEA peak is associated with either of the two other low energy $^1A_2$ and $^2B_2$ resonances, suggesting that the dissociation limits of the $^1A_2$ and $^1B_2$ resonances are too high to be associated with the first DEA peak or that these resonances do not lead to dissociation (eg have a lifetime which is too short compared with the dissociation time$^{34}$).

Jana and Nandi [120] suggested a combination of $^2A_1$ and $^2B_2$ resonances responsible for the DEA peak at $\sim 7.5$ eV. They were able to show this is the case for production of O$^-$ and SO$^-$ fragments “where the axial-recoil approximation is seen to be valid” [124]. However, due to the breakdown of the axial-recoil approximation they were unable to assign resonance symmetries for S$^-$ production. $^2B_2$ was additionally proposed by Gope et al. [37] as being associated with the $\sim 7.5$ eV peak. The CC energy positions of our $^1B_2$ resonance are all compatible for association with the $\sim 7.5$ eV DEA peak, especially on consideration that if its proposed link to one of the two series observed in the vibrational spectroscopy experiments holds true then at least one of the dissociation channels can support vibrational states up until at least 6 eV, which is both approximately the limit of Sanche et al.’s experiments [22] and also the approximate energy where DEA around the $\sim 7.5$ eV peak begins [36]. For the lower energy series in Sanche et al.’s experiments this consideration applies only to the O$^-$ and S$^-$ dissociation channels, due to their assignment of the symmetric stretch mode to this vibrational series.

It’s unlikely that the $^1A_1$ resonance is associated with the $\sim 7.5$ eV peak since it’s already responsible for O$^-$, S$^-$ and SO$^-$ dissociation via the $\sim 4.5$ eV DEA peak. For the $^2A_1$ and $^2B_2$ resonances are associated with the two vibrational

$^{34}$Although the widths of the $^1A_2$ and $^1B_2$ resonances are less than the width of the $^1A_1$ resonance, we have only obtained the widths at the equilibrium geometry and it’s impossible to predict the behaviour of these widths for changing geometry.
resonances to be considered candidates for the $\sim$7.5 eV DEA peak, a decrease to their energies (expected for calculations including more than 300 target states) of at least $\sim$0.5 eV and $\sim$0.8 eV respectively would be required. Assuming we are converging onto the correct energies for the resonances, this would be borderline possible considering figure 5.3. If we are converging onto too low an energy this would make resonances $2^2A_1$ and $2^2B_2$ unlikely candidates for association with the $\sim$7.5 eV peak.

$2B_1$ was suggested by Gope et al. [37] as being the symmetry of one of the resonances associated with the $\sim$7.5 eV DEA peak. Energetically, our $1^2B_1$ resonance, at a energy of 7.62 eV from our 300 state calculation is very well positioned to be considered as potentially contributing to DEA via this peak. Figure 5.3 shows that the $1^2B_1$ resonance could be converging to an energy close to 7.5 eV and thus one of its dissociation channels could allow DEA at $\sim$7.5 eV, satisfying Gope et al.’s symmetry suggestion. Again, this depends on our calculations not converging onto too low an energy.

The DEA peak at $\sim$9 eV has been suggested as being linked to resonances of $2B_1$, $2B_2$ and/or $2A_1$ symmetries [36]. Our $2^2A_1$, $1^2B_1$ and $2^2B_2$ resonances are obvious candidates here. The lower lying resonances are not as likely to be linked to the $\sim$9 eV peak since all three DEA peaks are associated with production of $S^-$, either in whole ($\sim$9 eV) or in part ($\sim$4.5 eV and $\sim$7.5 eV). In other words, if our $1^2B_2$ resonance is linked to the $S^-$ production from the $\sim$9 eV DEA peak, then one of the high energy resonances ($2^2A_1$, $1^2B_1$ and $2^2B_2$) would then have to be linked to $S^-$ production from the $\sim$4.5 eV DEA peak. This could be possible if there is an avoided crossing at longer bond lengths of the vibrational mode associated with the $S^-$ production.

The $2^2A_2$ resonance reported in all three theoretical works considered here ([130], [131] and ours) does not seem to be associated with DEA by any experimental work. This could be for two reasons: the dissociation limits for this resonance are all above 10 eV or the autoionisation lifetimes are too short to lead to dissociation. As has been mentioned, since all three works only characterise the $2^2A_2$ at equilibrium geometry, further calculations are required to confirm which, if any, of these possibilities holds true.

### 5.6.5 General Discussion

We now attempt to ascertain whether the resonance positions from our CC results obtained for the different numbers of target states are approximately equal to, under or over the "exact" resonance positions. And also, when relevant, whether the converged positions are approximately equal to, under or over the "exact" resonance positions. Since the plots shown in figure 5.3 appear to indicate the resonances obtained with the 300 target state calculation, especially the lower energy ones, are still far from their final, converged, positions it may be tempting to assume that all of our 300 state positions are too high. Although this may be the case, it is prudent to analyse, as far as possible, whether this assumption holds in the light of the results from the other theoretical and experimental works.

Since the $1^2A_1$ resonance is below the lowest 4.5 eV DEA peak, even for 16 states, we cannot really use this resonance to determine the whether our CC or converged resonance positions are equal to, under or over the "exact" resonance positions. If this resonance is associated with the lower vibrational series observed in the vibrational spectroscopy experiments, this would imply, at the very least, our calculation including higher numbers of target states are over-correlated. However, we believe that it’s very unlikely the $1^2A_1$ resonance is linked to the lower vibrational series.

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$^{35}$Or more, although Gope et al. only associated the $^2B_1$ with the $SO^-$ channel.
If the $1^2B_2$ and $1^2A_2$ resonances are, as has been suggested, responsible for the two vibrational series observed in the vibrational spectroscopy experiments, we can gain some insight by comparing the two resonance positions with the upper bound of 3.30 eV obtained earlier for the fixed-nuclei resonance position corresponding to the lower vibrational series. All of our calculations for the different number of target states result in positions for both the $1^2B_2$ and $1^2A_2$ resonances higher than 3.30 eV. The fixed nuclei positions obtained from the 300 state calculation (4.12 and 4.42 eV respectively for the two resonances) suggest that this calculation is under-correlated. Since the convergence plots shown in figure 5.3 are approximately decreasing linearly for the higher (>100) state numbers it’s not possible to ascertain any convergence limit.

We have suggested our $1^2B_1$ resonance may be responsible for DEA at around ∼7.5 eV, as proposed by Gope et al. [37] and/or at around ∼9 eV, as proposed by Krishnakumar et al. [18, 36]. The latter association, with the ∼9 eV peak, does not indicate whether our 300 state $1^2B_1$ position or a final converged $1^2B_1$ position is higher or lower than the exact position. From figure 5.3 it appears that the $1^2B_1$ resonance is converging to an energy very close to ∼7.5 eV. If the $1^2B_1$ resonance is associated with the ∼7.5 eV peak then this indicates that the final converged position of our model may be well correlated to the exact resonance position, since this aligns well with the ∼7.5 eV DEA peak (although this assumes that the DEA peak corresponds to a dissociative vibrational state close to the fixed-nuclei resonance position).

Our two highest energy resonances, $2^2A_1$ and $2^2B_2$, are most likely to be associated with the ∼9 eV DEA peak. Since they are currently below the peak energy we are unable to use them to help use determine correlation of our results or convergence. To be associated with the ∼7.5 eV peak the final converged resonance positions would need to drop by ∼0.5 eV and ∼0.8 eV respectively. Considering figure 5.3 this would likely mean that a model with sufficient target states for convergence would result in resonance position higher than the exact positions. This is especially true for the case of the $2^2B_2$ resonance (since it’s at a higher energy than the $2^2A_1$ resonance).

5.7 Summary and Conclusions

We have calculated resonance positions and widths for electron scattering from SO$_2$ for energies between 0.1 and 10 eV. The R-matrix approach was used, with the target modeled using the state-averaged CASSCF approach, a DZP basis set and GTOs for the continuum.

Calculations were performed with SE, SEP and CC models. Results obtained using the CC model for 16, 31, 43, 54, 68, 104, 150, 200 and 300 states included in the close-coupling expansion showed that even for 300 target states the results were not converged. It’s hard to be certain whether our current results or converged results will be over-correlated or not. If we assume that a peak in the DEA cross section corresponds to a dissociative vibrational state close to the fixed-nuclei resonance position then our DEA resonances suggest that a converged calculation will be close to correlated or over-correlated. It’s more difficult to ascertain correlation from the vibrational spectroscopy experiments but there is a suggestion that we are close to correlated or under-correlated.

Although higher in energy, our results indicate either $2^2A_2$ or $2^2B_2$ for the symmetry of the resonance responsible for the first series observed in the vibrational spectroscopy experiments, matching proposals in the experimental literature. We believe that running calculations with a higher number of states included in the close-coupling expansion (and possibly for different geometries) may allow one of these symmetries to be assigned to the resonance associated with the first vibrational series. However,
5.7 Summary and Conclusions

this requires that our model is well-correlated and we are not completely certain whether this is the case or not.

Experimental assignments of resonance symmetry, both vibrational spectroscopy and DEA, are potentially consistent with our calculations. We say "potentially", since some ambiguity remains in our results and thus further work is required.

A definitive interpretation of the \( \text{SO}_2 \) DEA experiments is difficult, as we have obtained data for the equilibrium bond lengths only and cannot be sure if our results are correlated. To be able to confidently match our resonances with those responsible for the DEA peaks would require a more comprehensive study of the resonances as a function of molecular geometry, as well as obtaining results sufficiently converged and correlated.
Chapter 6

Conclusions

The main focus of this thesis has been the resonances which form in electron-molecule scattering systems and the processes related to these resonances, in particular DEA. Various pre-existing methods were used for the identification and characterisation of the resonances as well as a technique implemented as part of this work. Resonances were calculated and analysed for electron scattering from H\textsubscript{2} and SO\textsubscript{2}.

The implemented method for the identification and characterisation of the resonances was based on the analytic continuation of the Jost function as proposed by Rakityansky et al. [25]. For the H\textsubscript{2} and SO\textsubscript{2} works existing methods for resonance identification and characterisation were used, based on the time-delay and eigenphase sum (and to a lesser extent the cross section). Our calculations and subsequent analysis of the identified and characterised resonances provide original insight into the physics associated with resonance states for electron scattering from H\textsubscript{2} and SO\textsubscript{2}.

This chapter first summarises and provides outlook for the work carried out in this thesis; the implementation of Rakityansky et al.’s technique and the studies of electron scattering from H\textsubscript{2} and SO\textsubscript{2}. A discussion comparing the different techniques for resonance identification and characterisation then follows.

6.1 Summary and Outlook of Work

Our work on the implementation of a method for the identification and characterisation of resonances based on the analytic continuation of the Jost function (reskit) was primarily motivated by the desire for a more reliable approach to the more difficult to detect resonances. These include resonances which are wide, overlapping other resonances and close to thresholds.\textsuperscript{36} We also developed, as part of reskit and from first principles, a mechanism for assignment of quality indicators to the detected resonances. We consider these quality indicators essential, as without them there would be no direct indication of the confidence that the reported poles are true poles of the S-matrix. Using reskit we were able to successfully detect all known resonances in a number of scattering data sets, as well as previously unknown resonances. reskit performed especially well when applied to our 10 channel uracil test with three overlapping resonances. However, the main conclusion from this work is that, for the case of wide resonances, methods based on analytic continuation of the Jost function (and likely continuation of other scattering functions as well) suffer a loss in reliability and accuracy for increasing resonance width. This is a similar issue to that with the existing methods but we believe that the decrease in reliability and accuracy with increasing width is more rapid with the method based

\textsuperscript{36}There are also the very narrow resonances but these were of less relevance and were touched upon only briefly. We will mention these later in the conclusion, in a slightly different context.
on the eigenphase sum than our method based on the analytic continuation of the Jost function. The basis for this is that with the later approach, several very wide resonances were detected in our test systems which weren’t detected using the method based on the eigenphase sum (although we were unable to ascertain for sure whether these very wide resonances were genuine resonances or not).

Although we did compare the performance of reskit with a method based on the eigenphase sum (chapter 3, sections 3.4 and 3.5), more formal comparisons could be undertaken in the future, as well as to other currently available methods, such as those based on the time-delay. The approach based on the time-delay could help confirm that the very wide resonances which we only detected with our implemented approach were indeed genuine or not. This would show, nearly beyond doubt, that our approach performed better for these resonances than the method based on the eigenphase sum. On the other hand, if the approach based on the time-delay was unable to detect these very wide resonances then we would need to seek out or develop another approach to find this assurance.

As mentioned above, resonances which are difficult to detect and characterise include those which are wide, overlapping other resonances and close to thresholds. Since the case of inelastic scattering was not fully implemented as part of this work (as will be discussed shortly) the performance of reskit could only be analysed for the first two types of difficult resonance (wide and overlapping), since there are no thresholds in elastic scattering. Further work could therefore be undertaken to extend reskit to fully implement the method to include treatment of inelastic scattering. Another major limitation of reskit is the required computational resource when applied to large, many-channel, scattering systems. On a positive note, our routines can potentially be used for location of virtual states [95], those study usually entails calculations with a much lower number of channels. However, a deficiency in how the quality indicators are calculated close to the threshold branch points limit their application to virtual states. We believe, though, that addressing this matter is trivial and is something which could be rectified, without much effort, in the future.

The emphasis of chapter 3 was around the analytic continuation of the Jost function, resonance theory and techniques for the identification and characterisation of resonances. We will return to this discussion shortly, turning our attention now to chapters 4 and 5, whose topics were, respectively, electron resonances in H_2 and SO_2. This part of the work placed much more emphasis on the physics related to resonances in electron-molecule scattering. For these cases the resonances were identified and characterised using existing techniques.

We performed calculations of electron scattering from H_2 in order to investigate asymmetries observed in the anion momentum distributions in recent VSI DEA experiments. Our calculations were carried out for energies between \( \sim 11 \) eV to \( \sim 15.5 \) eV over the bond length range from 1.1 a_0 to 4.0 a_0. This range of energies is expected to encompass all anion states dissociating to H(2l) + H^\-(1s^2) at 13.88 eV, the limit believed to be associated with the experimental DEA peak in the anion yields observed at \( \sim 14 \) eV. The initial challenge was to identify which of these anion states could be responsible for the observed asymmetries in the anion momentum distributions at 14.5 eV, 15 eV and 15.5 eV incident electron energies observed by Krishnakumar et al. in their DEA experiments [19].

With full CI and a d-aug-cc-pVTZ basis set we calculated excitation thresholds, within the energy range of interest, close to those reported by Nakashima and Nakatsuji [115]. Using a B-spline basis set for the continuum, we were able to identify and characterise 35 resonances over our energy and bond length ranges. Four of these resonances, at the lower end of our investigated energy range, agree fairly well with those previously identified in the earlier work of Stibbe and Tennyson [35].
6 CONCLUSIONS

The method used for the identification and characterisation of resonances in the H$_2$ study was based on the time-delay (using the TIMEDELn software). As expected, good separation was achieved between overlapping resonances, although there were some cases when this wasn’t quite the case (see figure 4.18 in chapter 4 for an example). Difficulties arose from the close proximity of target thresholds to several of the resonances, which often resulted in truncation and other deformities of the Lorentzian-like profiles in the time-delays. This presented ambiguity when fitting for the resonance energies and widths and/or decreased the accuracy of the fitted values. We will return to discuss the effect of thresholds on resonances shortly.

To summarise, we found that using the time-delay allowed identification and characterisation of resonances in reasonable times. reskit, our implementation based on the analytic continuation of the Jost function, was not applicable to our H$_2$ study for two reasons: the large number of outer region channels resulting from the H$_2$ scattering model would have resulted in unacceptably long calculation times; also, reskit cannot currently be applied to inelastic systems. It’s worth noting that the automated reporting of resonances by the TIMEDELn package did not produce consistent enough results to be completely reliable and that, in order to get more accurate results, an additional manual approach was required.

We were unable to reproduce the asymmetries measured by VSI using the model provided in Krishnakumar et al.’s DEA paper [19] with our resonance data. We believe that this was due to a number of false assumptions inherent in the model. These result in the model not accounting for more than two resonances and the effects of nearby thresholds on the resonances. It’s also quite clear that our resonance energies and widths were not obtained to sufficiently high bond lengths in our calculations to provide accurate input to the model. We also suggest that a full understanding of the DEA around 14 eV will likely require a treatment inclusive of the nuclear degrees of freedom [141].

Our study of electron scattering from SO$_2$ was motivated by apparent inconsistencies in the literature around the DEA [18, 36, 123] and vibrational spectroscopy [22, 126, 20] experiments and the corresponding theoretical studies [130, 131]. Our aim was to perform a sufficiently accurate calculation and to then link our identified resonances to those responsible for the vibrational spectroscopy and DEA observations in order to resolve these inconsistencies. Our calculations were performed using the DZP basis set and the state-averaged CASSCF method at the equilibrium geometry only. We deemed our target model sufficiently accurate for investigation of the resonances of interest to this study.

We investigated the effect of adding more target states into the close coupling expansion. Analysis of our calculated SO$_2$ elastic and total excitation cross sections for an increasing number of target states showed that, even for 300 target states, the cross sections had not reached convergence. Unfortunately, we had insufficient computational resource and time to be able to run for higher numbers of target states. Comparison of our results with those from vibrational spectroscopy and DEA experiments does not provide a clear answer on whether the results from converged calculations would be correlated.

The 300 target state calculation results show potential alignment with most of the vibrational spectroscopy and DEA experiments in the literature. Two of our detected low lying resonances (the three mentioned in the previous paragraph) are likely responsible for the two vibrational series observed by Sanche and Schultz’s [22] electron transmission spectroscopy experiments and also later works [126, 20]. However, we can’t be confident (due to the non-convergence and perhaps non-correlation) that we can resolve the dispute over which of the resonance symmetries can be assigned to the lowest vibrational series. Our results also potentially correspond to the various (and, in some
cases, contradicting) symmetries proposed as being associated with the resonances responsible for the three DEA peaks \([18, 36, 37, 120, 38]\): \(2A_1\), \(2B_1\) and \(2B_2\), symmetries for both the two higher peaks. Our detected \(2A_2\) resonance, has not been proposed in the literature as associated with any DEA peak. We have suggested that this may be due to too short an average lifetime over the dissociating geometries or dissociation limits much greater in energy than that of the highest DEA peak at \(\sim 9\) eV.

Since our proposals for correspondence with the DEA experiments depend on speculations for the dissociation limits and resonance changes with geometries, calculations for the different stretch modes to establish these limits and characteristics would be required in order to confirm whether these speculations hold true or not. Running the calculations with more target states to potentially obtain converged resonance data may also be helpful (if not essential) in resolving the conflicts in the experimental literature. Also, a means to confidently determine the correlation of our results is required. Although our calculations do not account for the nuclear motions or otherwise attempt to include the vibrational states, it may be possible to obtain results to a sufficient accuracy to: i) assign the equilibrium resonances to the different dissociation limits and ii) determine the symmetries of the resonances responsible for the two vibration series observed in the spectroscopy experiments.

In the case of \(\text{SO}_2\) we also (in addition to \text{TIMEDELn}) used the RESON program, which is based on the eigenphase sum, for resonance identification and characterisation. This is a much more straightforward approach, primarily since fits are made to only a single quantity (the eigenphase sum), rather than the multiple eigenvalues of the Q-matrix, as is the case when using the time-delay approach. Since we were only searching for resonances at a single geometry and none of the resonances were overlapping or (bar one or two perhaps) too wide or close to threshold, we found that RESON would probably be adequate for the needs of this work. However, the RESON package which we used did not always reliably detect the same resonance for increasing number of target states. This is most likely due to issues with the routines or the input used for the routines, rather than inherent limitations of the underlying method. For this reason we used manual fits to the time-delay to obtain the reported resonance positions and widths, in a similar manner to the \(\text{H}_2\) work.

6.2 Discussion of the Methods for Identification and Characterisation of Resonances

As mentioned, techniques based on four different scattering quantities were used for identifying and characterising resonances for the works forming this thesis; the eigenphase sum, the time-delay, the Jost function and the cross sections (to a lesser extent). We will now give some final remarks on the first three of these techniques. We approach this discussion from the high level down; beginning more practically, with some considerations around automated resonance detection and performance before outlining some more fundamental considerations based on the scattering quantities. This will remove from the discussion factors we feel are linked to the higher level implementations, allowing a tighter focus on the more fundamental concepts.

The techniques based on the eigenphase sum (RESON program), the time-delay (\text{TIMEDELn} program) and analytic continuation of the Jost function (\text{reskit} program) provide mechanisms for automated detection of resonances. In practice, based on the work carried out for this thesis, we found\(^{37}\) that our results are calculated for equilibrium geometry only, for a given resonance it is not known which (if any) of the three dissociation peaks it could be associated with. Since our results are not fully converged it is possible that the associated DEA peak may be lower in energy than that calculated at equilibrium geometry.

\(^{37}\)For example, considering that our results are calculated for equilibrium geometry only, for a given resonance it is not known which (if any) of the three dissociation peaks it could be associated with. Since our results are not fully converged it is possible that the associated DEA peak may be lower in energy than that calculated at equilibrium geometry.
the main issue with RESON and TIMEDELn programs was the lack of reliability. This was especially true for RESON, which in some cases, even for resonances with quite well defined Lorentzian-like profiles in the cross section, would fail to identify a resonance. This may of course be rectifiable, either with an improvement to the detection routine or with an adjusted input configuration. However, after using an interactive method for fitting the time-delays, it became the preferred approach for resonance characterisation. This was for three main reasons: i) it avoided the reliability issues with the RESON and TIMEDELn programs; ii) fine tuning the fits resulted in better ones, overall; iii) visual inspection is required with the interactive approach for determination of the bounds and initial values for the fit. Of course, since this was a manual process, it was more time consuming (and tedious) but certainly not (in the author’s opinion) to any unworkable degree.\(^\text{38}\)

We suspect our reskit routines, for the elastic implementation, can achieve a higher degree of reliability than RESON and TIMEDELn. The basis for this is around the fact that the reskit QI routines are applied to sets of roots obtained using well established polynomial root finding algorithms. These root finding algorithms are well known to guarantee the location of all roots for a given polynomial. Although reskit performed well in all our test systems we still feel there is more scope for reliability testing here, since RESON also performed well in most of these test systems. We do not have this confidence in the reliability of a more general approach capable of application to inelastic systems. For our initial tests for automated root detection with extension of reskit to the inelastic case we were unable to implement the Delves method \(^\text{39}\) so that it operated in a reliable manner, returning all roots of the polynomial. With further work it may be possible to increase this reliability.

Unfortunately, any increase in reliably with the reskit routines is vastly overshadowed by its performance requirements. As shown in appendix D, the time required for reskit to calculate the QIs scales dramatically with the number of channels, such that even for a relatively small 10 channel scattering system completion time is on the order of days on a 3.60GHz Intel i7-3820 using cpython implementation.\(^\text{40}\) The time is mostly needed for the formation of the Jost determinant (2.75) but the root detection for a high number of fit points, \(P\), was also a contributing factor.\(^\text{41}\)

Both the TIMEDELn and RESON programs completed within reasonable time frames for both the \(\text{H}_2\) and \(\text{SO}_2\) studies in this thesis, although TIMEDELn is typically the more time expensive of the two. Both techniques have a time factor primarily affected by the required diagonalisations of the \(Q\) and \(K\) matrices respectively (although the \(K\)-matrices are the basic scattering quantities returned by the UKRmol+ suite, so these are usually calculated anyway). We believe the main criteria for selecting between the two programs is on the expected nature of the resonances. Ignoring automation and issues relating to reliability, if the resonances are well separated and unaffected by thresholds (as was the case for \(\text{SO}_2\)) then the eigenphase sum is sufficient for resonance analysis, otherwise the time-delays are probably a better choice, due to the separation of the resonances across the multiple \(Q\)-matrix eigenvalues. The main drawbacks with using TIMEDELn are the greater operational complexity

\(^{38}\)Fitting the approximately 400 \(\text{H}_2\) resonances took about 10 hours.
\(^{39}\)Required, since the expanded determinant of the Jost function is no longer a simple polynomial for the inelastic case.
\(^{40}\)cpython has a GIL and reskit does not support multi-process parallelisation.
\(^{41}\)The python sympy package was used for some of these operations, due to its ability to algebraically form the determinant, allowing for application of the robust polynomial root-finding routines. This package is implemented purely in python and is likely to be much slower than the python numpy libraries, which are just wrappers around the fortran BLAS and LAPACK libraries. Therefore there are potential performance improvements if a purely numerical approach can be realised for finding the roots of the Jost determinant.
6.2 Discussion of the Methods for Identification and Characterisation of Resonances

(primarily arising from the multiple eigenvalues) and also the difficulty in detection of resonances close to the excitation thresholds.

We now discuss the eigenphase sum, time-delay and Jost function with respect to using them for identification and characterisation of overlapping resonances. Since the eigenphase sum is a scalar function of the electron energy, with resonances ideally manifesting as \( \pi \) increases, then resonances which are close to one another will superimpose in the eigenphase sum resulting in detection difficulties (RESON will attempt to fit a maximum of two overlapping resonances using an analogous form of equation (2.67) with a linear or quadratic background). Both the time-delay and the Jost function provide better mechanisms for identification and characterisation of overlapping resonances; with the time-delay overlapping resonances are separated (to a high degree) across the Q-matrix eigenvalues; with the Jost function the overlapping resonances are associated with different roots of the determinant of the Jost function. Based on the discussed limitation of the reskit routines, the TIMEDELn program is currently the most applicable approach for cases of overlapping resonances in large, inelastic scattering systems.

For the identification and characterisation of wide resonances, we believe, again, that methods based on the time-delay and Jost function are likely to be superior to those based on the eigenphase sum (ignoring relative calculation times). With the time-delay, the separation of the Q-matrix eigenvalues will be more likely to isolate the wider resonance from the background, making detection easier. Things are harder to qualify for approaches based on the Jost function; although it might appear that the location of the roots of the determinant of the Jost function are independent of the background, the presence of a significantly varying background is likely to affect the ability to extrapolate from the S-matrix data comprising the fit (at real energies) to the root. It’s worth mentioning the relevance and necessity to identify and characterise very wide resonances, at least with respect to the physics of electron scattering, in particular DEA. Since, as given by equation (1.8) the lifetime is inversely proportional to the resonance width, the potential for DEA to occur solely via a very wide resonance diminishes with increasing width. However, it’s possible that DEA can occur initially via a very wide resonance, which then, very quickly, decays into a longer lived resonance. For these cases the ability to identify and characterise wide resonances may be useful.

When fitting resonances close to threshold a method based on the time-delay will suffer due to the complete loss of the kinetic energy of the scattering electron energy at the threshold energies, resulting in an infinite time-delay. Hypothetically, the reskit program may perform better for these cases, although, in addition to incorporating a more generic root finding routine (eg Delves) the program would require extension to deal with the multi-surface nature of the S-matrix around the threshold branch points.

We mention, mainly for completeness, the observed relationship of the precision of the resonances detected with reskit with the precision of the input data set. It’s fairly obvious that the resonance precision should decrease with decreasing precision of the input data set and that this should also hold for resonance detection with the RESON and TIMEDELn programs. However, no efforts were made to attempt to quantity the relationships in detail or otherwise compare performance of the three programs in this respect.

One area where an approach based on the Jost function may excel in comparison to the other approaches is for the location of discrete states: bound and virtual. Since these don’t manifest as Lorentzians or phase shifts (although there may be other indirect effects) in the time-delays and
eigenphase sums respectively, TIMEDELn and RESON, are unable to detect these types of states. Chapter 3 demonstrates, for the single channel case, that an approach based on the Jost function works well for bound states. However, reskit (in its state at time of writing) requires some minor adjustments for the QI routines to perform adequately close to the elastic threshold.

6.3 Final Remarks

It’s apparent from the work in this thesis that without an accurate description of the resonances it is not possible to gain a complete understanding of the DEA mechanism. The scope of this thesis was the study of resonances within the confines of the fixed-nuclei approximation, which although not accounting for the dynamics of the nuclei, still allowed us to gain some insight into the nature of resonances potentially linked with DEA to H₂ and SO₂. Generally speaking, to provide insight into the DEA process using R-matrix data, whether by investigating the resonances themselves or performing dynamics studies, requires: i) appropriate target and scattering models and an understanding of their strengths and limitations; ii) for given models, resonance data over a appropriate range of energy and sufficient geometries and iii) techniques for the identification and characterisation of the resonances from the scattering data, which are appropriate for the characteristics of the resonances of interest.

The calculated scattering quantities and extracted resonance descriptions from our H₂ and SO₂ studies allowed us to gain significant new insight into resonances potentially linked to DEA in these systems. However, we highlight here the limitations of both these studies (within the scope of an R-matrix study), to illustrate where future work could improve and bring further clarity to the DEA in these systems. For SO₂ the main limitations of our calculations were the lack of convergence and inability to determine the accuracy of the correlation and polarization as described by our CAS scattering model and also that they were only performed at the equilibrium geometry. For H₂, although we had much better convergence of the resonance positions and calculations at a number of bond lengths, obtaining data for higher bond lengths will certainly facilitate a more detailed understanding of the DEA.

With respect to the techniques for the identification and characterisation of resonances, we found that the regularly employed ones performed very well for the SO₂ study. However, the implementation and testing of reskit and the H₂ study highlighted some areas where there is room for improvement beyond the currently available techniques. These are when the resonances are very wide and/or close to threshold. In particular, for the H₂ study, improved characterisation of the resonances close to threshold will also likely be required for more accurate modelling of the DEA.

For the case of very wide resonances, currently employed techniques suffer from what appears to be an intrinsic relationship between the width of the resonance and the confidence in its detection. This relationship was also apparent from our test results obtained with reskit.

Our work on electron scattering from H₂ involved a number of resonances which were, at many of the bond lengths studied, overlapping and/or very close to threshold. The time-delay approach worked well for identifying and characterising the resonances which were overlapping. For the resonances close to threshold, we encountered deformation of the Lorentzian-like resonance profiles in the Q-matrix eigenvalues and/or ambiguities around fitting them. Although untested, we suspect that the identification of these resonances using analytical continuation of the Jost function could yield accurate energies for their related S-matrix poles. However, obtaining the resonance lifetimes from

\[ \text{As there is no inelastic implementation.} \]
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these close-to-threshold poles is unlikely to be as straightforward as for the case of ideal, Breit-Wigner like resonances.

As is apparent from this discussion, there are a range of techniques for the identification and characterisation of resonances, each with their own degrees of reliability, applicability, ease of use and execution times. Currently there is no one ultimate technique; different systems with different resonances warrant different and perhaps multiple approaches. Also, for the case of resonances close to thresholds, no approach known to the author can resolve the associated detection and interpretation ambiguities and also, for high enough widths and overlaps all existing techniques have their limits. Therefore, due to the room for developing improved and alternative techniques and the role of resonances in important physical processes, such as DEA, it’s very likely that methods for the identification and characterisation of resonances will continue to be an active area of research.
The time-delay can be derived using a simple one dimensional picture \[142, 143, 51\] of which we provide an adaption here. In this picture the scattering is from a finite ranged potential with the time-independent wavefunction taking the following form at asymptote:

\[ \psi(x) \xrightarrow{x \to \infty} \psi_A(x) = N \left[ e^{-ikx} - e^{i(kx+\delta)} \right] \]

(A.1)

where the first term represents incoming particles at \( t < 0 \) and the second outgoing particles at \( t \geq 0 \). \( N \) is the normalisation constant, determined using the standard process for normalising a particle beam; its evaluation is not relevant for the following discussion. Time dependence is added by adopting plane waves and wavepackets constructed by considering a superposition of two of these plane waves for both the incoming and outgoing waves:

\[ \psi(x, t) \xrightarrow{x \to \infty} \psi_A(x, t) = N \left[ e^{-i(k_1x-\omega_1t)} + e^{-i(k_2x-\omega_2t)} + e^{i(k_1x+\omega_1t+\delta_1)} + e^{i(k_2x+\omega_2t+\delta_2)} \right] \]

(A.2)

where \( \omega \) is the angular frequency. By then considering the means and differences of the parameters for the two waves:

\[ \omega = \frac{\omega_1 + \omega_2}{2}, \quad k = \frac{k_1 + k_2}{2}, \quad \delta = \frac{\delta_1 + \delta_2}{2} \]

and

\[ \Delta \omega = \frac{\omega_1 - \omega_2}{2}, \quad \Delta k = \frac{k_1 - k_2}{2}, \quad \Delta \delta = \frac{\delta_1 - \delta_2}{2} \]

(A.4)

we can write:

\[ \psi_A(x, t) = N \left[ e^{-i(kx+\omega t)} \cos(\Delta k x + \Delta \omega t) - e^{i(kx-\omega t+\delta)} \cos(\Delta k x - \Delta \omega t + \Delta \delta) \right] \]

(A.5)

where the first term on the right hand side represents the incoming wave and the second the outgoing wave. The probability distribution of the scattered wavefunction as given by the second term in (A.5) is:

\[ P_A(x, t) = |\psi_A(x, t)|^2 = N^2 \cos^2(\Delta k x - \Delta \omega t + \Delta \delta) \]

(A.6)

A picture of the outgoing wavepackets and probability distribution is shown in figure A.1, which illustrates the spatial forms at two different times for a zero potential (i.e. with a phase term \( \delta = 0 \)). The modulation effect of the cosine term on the outgoing term in equations (A.5) and (A.6) can be appreciated. The effect of adding a phase shift is to displace the wavepackets along the x-axis.
The time-dependent positions of the peaks of this probability distribution can then be found by locating the zeros of the first differential with respect to $x$, i.e., when:

$$\cos(\Delta{k}x - \Delta{\omega}t + \Delta{\delta})\sin(\Delta{k}x - \Delta{\omega}t + \Delta{\delta}) = 0 \quad (A.7)$$

or:

$$x_{\text{max}} = \frac{1}{\Delta{k}} \left[ (n + 1/2, n)\pi + \Delta{\omega}t - \Delta{\delta} \right] \quad (A.8)$$

The difference between the position of the peak of the probability distribution when a potential is present and when it is not (i.e., with $\delta = 0$) is equal to:

$$\Delta{x} = \frac{1}{\Delta{k}} \left[ (n + 1/2, n)\pi + \Delta{\omega}t - \Delta{\delta} \right] - \frac{1}{\Delta{k}} \left[ (n + 1/2, n)\pi + \Delta{\omega}t \right] = \frac{\Delta{\delta}}{\Delta{k}} \quad (A.9)$$

The velocity of the peaks of the probability distribution can be obtained by differentiating (A.8) with respect to $t$ to give:

$$v = \frac{\Delta{\omega}}{\Delta{k}} = \frac{\Delta{x}}{\Delta{t}} \quad (A.10)$$

where the rightmost equality is true for all $t$ since the velocity is constant. Then, since $\Delta{E} = \Delta{\omega}$ and from (A.9):

$$\Delta{t} = \frac{\Delta{\delta}}{\Delta{k}} \frac{\Delta{k}}{\Delta{\omega}} = \frac{\Delta{\delta}}{\Delta{\omega}} \frac{\Delta{\delta}}{\Delta{E}} \quad (A.11)$$

Finally, we express this in general form by performing $\lim_{\Delta{E} \to 0}$:

$$\Delta{t} = \frac{d\delta}{dE} \quad (A.12)$$

which shows that the time-delay is equal to the energy derivative of the phase shift.
This appendix gives a very brief overview of some of the other methods available for the identification and characterisation of resonances in atomic and molecular physics.

An alternative to the general approaches discussed in chapter 2, section 2.2 is to perform fits to channel-specific data. For example, fitting to a K-matrix element (as implemented by the RESFIT program [61]). The concept of fitting to channel-specific data is discussed in [7], where the following behaviour of the scattering amplitude in the region of the a multi channel resonance is assumed:

\[
f_{mn}(E) = \frac{\gamma_m \gamma_n^* / 2}{(E - E_R) + i \Gamma / 2}
\]  

(B.1)

where the \( m \) and \( n \) are the channel indices and the \( \Gamma_\alpha = |\gamma_\alpha|^2 \) the partial widths, referring to the channel-specific widths. The total width corresponds to:

\[
\Gamma = \sum_n |\gamma_n|^2
\]  

(B.2)

i.e. the total width is equal to the sum of the partial widths in the individual scattering channels. With this assumed form, the peaks corresponding to a particular resonances in each of the scattering channels will differ in height but their positions will coincide in energy. However, as for the single channel case, this assumption has limitations. These are discussed following from a more formal definition of (B.1) in [42] and are in part dependent on the relative behaviour of the background. This method is not as commonly used as fitting to the eigenphase sum or time-delay.

When solving the scattering system via the Lippmann-Schwinger equation [144, 8, 7] there are some intrinsic methods for the identification and characterisation of resonance. We start by describing very briefly here the Lippmann-Schwinger approach before mentioning some of the related resonances techniques.

Beginning with a definition of the following Green’s operators or resolvents:

\[
G_0(z) \equiv \frac{1}{z - H_0} \quad \text{and} \quad G(z) \equiv \frac{1}{z - H}
\]  

(B.3)

where \( z \) is valid for any real or complex value wherever the inverses exist. The free resolvent, \( G_0(z) \) is constructed from the free Hamiltonian \( H_0 \). \( G(z) \) includes the interaction potential \( V \) in the total Hamiltonian, \( H = H_0 + V \). The following eigenvalue equation can then be derived for the \( l \)-th partial
where $\eta_{nl}(k)$ are the Hilbert-Schmidt eigenvalues and $V_l$ the $l$th partial wave potential. The following relationships with the Jost functions and S-matrix can then be obtained:

$$F_l(k) = \prod_n \left(1 - \eta_{nl}(k)\right)$$  \hspace{1cm} (B.5)

$$S_l(k) = \frac{F_l(-k)}{F_l(k)} = \prod_n \frac{1 - \eta_{nl}(-k)}{1 - \eta_{nl}(k)}$$  \hspace{1cm} (B.6)

The first method dealing with resonances within the Lippmann-Schwinger formalism is Feshbach projection. This was developed over a number of publications, of which [145, 146] are considered key and is described in the textbooks [42, 8, 1] and reviewed and extended to shape resonances in [147, 148]. It is quite popular for the analysis of resonances in atomic and molecular scattering [149, 150, 151, 152].

The method initially considers the resolvent operator from (B.4), $G_0(z)$ and expresses it in terms of the total Hamiltonian $H$ projected into two mutually orthogonal subspaces, $\mathcal{H}_P$ and $\mathcal{H}_Q$, via the projection operators $P$ and $Q$ so that:

$$G_P = P \left(z - PHP\right)^{-1} P \quad \text{and} \quad G_Q = Q \left(z - QHQ\right)^{-1} Q$$  \hspace{1cm} (B.7)

where $G_P$ and $G_Q$ are resolvents in the two subspaces and the projectors are defined in the standard manner [153] such that:

$$P + Q = 1, \quad PQ = QP = 0, \quad P^2 = P, \quad Q^2 = Q, \quad P^\dagger = P, \quad Q^\dagger = Q$$  \hspace{1cm} (B.8)

By then considering $\mathcal{H}_P$ to be finite dimensional the resolvent can be expressed as:

$$G = G_Q + (1 + G_QH) D (1 + HG_Q)$$  \hspace{1cm} (B.9)

where $D = P \left[P \left(z - H - HG_QH\right) P\right]^{-1} P$.

As for the case when analytically continuing the Jost function, and as described in section 2.1.5, the resonant roots must be discovered on the unphysical sheets. This requires that $G_Q(z)$ is first established within the physical region. To do this we can assume that the total wavefunction $\Psi$ describing the interaction between the scattering electron and molecule can be represented by a close coupling expansion (which is discussed in section 2.5), such that $P\Psi$ projects onto the open channel space. Using the projector operator properties (B.7) it can be shown that, to determine $P\Psi$, a set of integral equations must be solved. Once $P\Psi$ has been determined, $QHQ$ can then be calculated and hence $G_Q(z)$ established. At this stage $G_Q(z)$ either as an operator or its matrix elements can be continued to the unphysical regions and the poles established as the roots of the determinant of the denominator part of $D$.

The second method based on the Lippmann-Schwinger formalism considers the analytic continuation of the Hilbert-Schmidt eigenvalues in (B.6) [8, 7, 144]. Here the S-matrix poles occur for the values:

$$\eta_{nl}(k_0) = 1$$  \hspace{1cm} (B.10)
B APPENDIX: OTHER METHODS FOR THE IDENTIFICATION AND CHARACTERISATION OF RESONANCES

Solving for the $\eta_{nl}(k)$ in the region $E < 0$ is relatively simple because, as shown in [8], the $\eta_{nl}(k)$ are real for the bound states in this region. By numerically obtaining discrete sets of $\eta_{nl}(E_i)$ a Padé approximation can be constructed and analytically continued to the unphysical region where the resonances may be located.

A third method we mention briefly is the recent [154, 155] effort in combining R-matrix theory with the Feshbach projection method to facilitate the study of resonances. Although the connection between these two theories has long been known (discussed by Feshbach [145] in 1962), it is only recently that their practical application has been pursued in atomic and molecular physics.

Moving away from the Feshbach projection methods, we mention an approach based on the analytic continuation of the coupling constant (ACCC) [156]. It considers the analytic continuation of a coupling constant $\lambda$ as introduced into the radial TISE describing the interaction between two spinless particles. For the $l$th partial wave we have, from equation (2.12):

$$\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \lambda V(r) - k^2(\lambda) u_\lambda(k_l, r) = 0$$  \hspace{1cm} (B.11)

such that, similarly to equation (2.32) and by exploiting some analytical properties of the Jost function and S-matrix [1]:

$$S_l(k_l) = \frac{F_l(\lambda, -k_l)}{F_l(\lambda, k_l)}$$  \hspace{1cm} (B.12)

[42] shows the following representation of the Jost function:

$$F_l(\lambda, k_l) = (a_0 + a_2 k_l^2 + a_4 k_l^4 + \ldots) + ik_l^{2l+1} (b_0 + b_2 k_l^2 + b_4 k_l^4 + \ldots)$$  \hspace{1cm} (B.13)

where the $a_i$ and $b_i$ are expansion coefficients and:

$$k_l(\lambda) = \sum_{j=1}^{l} A_j x^{2j-1} + \sum_{j=2l}^{\infty} B_j x^j \quad \text{where} \quad x = \pm \sqrt{\lambda - \lambda_0}$$  \hspace{1cm} (B.14)

Here $A_j$ and $B_j$ are expansion coefficients and $\lambda_0$ is some fixed threshold value between the bound-state region ($\lambda > \lambda_0$) and the resonance-region ($\lambda < \lambda_0$). The nature of $\lambda_0$ can be appreciated further [8] if one considers $\lambda_0$ as defining a point $\zeta$ on the imaginary axis. Then, as $\lambda$ decreases towards $\lambda_0$, poles paired on the imaginary axis about $\zeta$ will move towards and then merge at $\zeta$ when $\lambda = \lambda_0$. As $\lambda$ continues to decrease the pole / conjugate pole pair will bifurcate, with each pole moving apart symmetrically about the real axis. This essentially means that the $k_l(\lambda)$ can be obtained in the physical region for some $\lambda > \lambda_0$ and then analytically continued into the non-physical regions $\lambda < \lambda_0$ and the resonance poles located. In practice, a Padé approximation is used for the expansion (B.14). In terms of application within atomic and molecular physics this technique has not been as widely used as the method of Feshbach projection. However, there are a number of studies that have utilised it for the calculation of resonance positions and widths, for example [157, 158, 159].

Another method is the method of complex absorbing potentials [160]. Here the problem of the non-quadratically integrable resonant state is dealt with via a complex valued modification of the Hamiltonian. It has the advantage of allowing standard basis expansions to be used, therefore more readily supporting a quantum chemical approach. The shooting method [161] refers to the location of
the pole via an iterative procedure. This starts with an initial guess for the resonance position from which the Siegert states \[8\] are constructed. It then attempts to improve it using the documented iterative procedure \[161\], until it converges onto the S-matrix pole. This particular method has been recently incorporated into the UKRmol+ software suite \[162\], which was used to obtain scattering data for the results presented in this thesis and is discussed in section 2.6.

The methods discussed so far allow identification and characterisation of resonances without having to account for the asymptotic behaviour of the wavefunction. For a finite potential, the asymptotic wavefunction corresponding to an S-matrix pole has the form:

\[ \psi \sim e^{ikr} \]  

which tends to zero for \( r \to \infty \) for bound states since \( k \) is positive imaginary. However, for resonances and virtual states this diverges; for resonances \( k \) is complex and for virtual states \( k \) is negative imaginary.

One method to deal with the divergence for resonances is the stabilisation method \[8, 163, 164\] which considers that a resonant state, when narrow enough, is localised to a high degree within the potential barrier and that its corresponding wavefunction can be treated as zero outside the barrier, i.e. as a bound state. This approximation allows the wavefunction describing the system to be expanded in quadratically integrable basis functions. As the size of the basis is increased, the eigenvalues that remain stable are considered to correspond to the resonance states; these eigenvalues are real in value and thus the approximation does not provide the widths of the resonances.

Finally, the complex rotation approach \[8, 165\] deals with the divergence problem by utilising the fact that for the coordinate transformation:

\[ r \to re^{i\theta} \]  

and some real value of the complex polar angle \( \theta \), the product \( kr \) in (B.15) remains real. Thus integrals along the direction \( \theta \) will remain finite. This will allow a numerically stable way of calculating the Jost functions with consideration of asymptotic forms of the wavefunctions.
This appendix provides, from the following page onwards, a description of the reskit python package as it appeared in its related CPC publication [79]. The package has been published to the CPC code repository and to the author’s personal github account [166].

The original method section has been included to allow easier reference to the equations as they are mentioned in the software overview sections. It’s similar to that given in chapter 2 section 2.2.2 and at the start of chapter 3 in this thesis. The references to other works in the paper map to the references in this thesis as shown in table C.1:

<table>
<thead>
<tr>
<th>reskit CPC Paper [79]</th>
<th>This thesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4]</td>
<td>[42]</td>
</tr>
<tr>
<td>[12]</td>
<td>[25]</td>
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<td>[14]</td>
<td>[167]</td>
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<td>[15]</td>
<td>[80]</td>
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<tr>
<td>[16]</td>
<td>[81]</td>
</tr>
<tr>
<td>[17]</td>
<td>[82]</td>
</tr>
</tbody>
</table>

Table C.1: Table showing the mapping from references in the reskit CPC paper [79] to those in this thesis. The section of the reskit paper containing these references is shown over the next number of pages.

There’s a single known error in the included sections of the reskit CPC paper (page 278, right hand column). The term ”antipole” is used incorrectly. The intended term here was conjugate pole. This also applies throughout the whole of the paper, in those sections not included in this thesis. Thanks to Tom Rivlin for pointing this out.
overlap, when a resonance is very close to a channel threshold or when the resonance is very wide. In the latter case the problem is that it is very difficult to separate the resonant and the non-resonant (background) contribution to the eigenphase sum. There have been attempts to address the shortcomings of using the Breit–Wigner formula through the development of more elaborate approaches [6], although the authors are not aware of any publicly available computational implementations of the improved approaches. An alternative technique for identifying and characterising resonances is based on the analysis of the time-delay [7]. Resonances can be located by analysing the eigenvalues of the time-delay matrix. This technique is particularly effective for overlapping resonances. Computational implementations of the technique are available [8,9]. We note that a number of approaches, not based on scattering methods, have been developed for the identification of resonances. These are based on conventional bound state methodologies, stabilisation techniques, complex absorbing potentials, etc. One of them is based on the analytical continuation of the electron affinities of the target molecules in the presence of a perturbation potential [10,11]. In this method, known as the regularised method of analytic continuation, conventional quantum chemistry calculations are employed to determine the real energies of the system in the presence of a perturbation. The results are then analytically continued into the complex energy plane.

Rakinyansky et al. [12] have proposed an approach that takes advantage of the fact that resonances are associated with poles of the S-matrix [4,5] and that the S-matrix in Jost form can be expressed as the product of a matrix and the inverse of a related matrix. Analytical continuation is achieved by expressing this Jost form using Padé approximants. By fitting to S-matrix data for sufficiently discrete values along the real energy axis the coefficients of the Padé expansions can be found. The roots of the polynomial expansion of the determinant of the matrix that is inverted will correspond to the poles of the rational S-matrix. Since bound and virtual states are also associated to these poles (that are generally located on different sheets of the Riemann surface), the method actually enables the identification of all these types of states of a system. In addition, the rational S-matrices can be used to determine quantities like the cross section, time-delay, etc.

In this paper, we present a python toolkit, res kit, based on the approach of Rakinyansky et al. The toolkit provides the routines necessary to perform the S-matrix fit and the pole determination for cases in which all the channels involved in the process have the same energy, i.e. for an elastic process. Rakityansky and collaborators proposed approaches to both elastic [13] and inelastic [12] cases. In our software, we have implemented the more general inelastic case although, at the moment, the implementation only works for elastic cases for which the complexities of dealing with Riemann sheets are avoided. An implementation for the inelastic cases is expected to follow.

2. Method

We begin our discussion of the theory presented in [12] by considering an N channel scattering system involving both elastic and inelastic channels. For the purpose of discussion and because the tests presented and analysed in Section 5 correspond to electron–molecule scattering we will talk in terms of an electron as the incident particle. The technique (and the derived software) can be applied to any non-relativistic scattering system, provided that sufficient S-matrix data has been obtained.

A channel refers to a discrete state of the scattering system at asymptote and, in electron–molecule scattering, it is normally defined by the angular momentum of the scattering electron and the internal state of the target molecule. A channel, labelled n, is considered open if it is energetically accessible at asymptote, i.e. if the total energy of the system, E, is greater than or equal to its energy $E_n$.

We note that it is customary in electron scattering studies to take the lowest (ground) internal state of the target to correspond to the zero of energy. In this case $E_n=0$ for all channels associated to this internal state and the $E_m$ for all other channels become threshold energies.

2.1. Parametrised S and Jost matrices

The multi-channel S-matrix can be written in terms of matrices of the out and in Jost matrices as the product:

$$ S(E) = F_{\text{out}}(E)F_{\text{in}}(E)^{-1} $$

(1)

For an N-channel scattering problem the Jost matrices can be expressed in the following form:

$$ F_{\text{in}}^{\text{out}}(E) = \frac{1}{2} [A_{nm}(E) \pm iB_{nm}(E)] $$

(2)

where m and n are the channel indices over the range 1, 2, . . . , N. The quantities $A_{nm}$ and $B_{nm}$ can be regarded as the coefficients when the waveform at asymptote is expanded in terms of the Riccati–Bessel and Riccati–Neumann functions.

We now apply the technique presented in [12] to obtain parametrised forms of (1) and (2). Considering the channel momenta:

$$ k_n = \pm \sqrt{E - E_n^\text{th}} $$

(3)

and channel angular momenta $l_m$, Ogibda and Rakityansky show [12] that when no Coulomb (long range) interaction is present between the particles [14] the coefficients in (2) can be written in the factorised form:

$$ A_{nm} = \frac{k_{m+1}^n}{k_{m}^n} A_{mn}, \quad B_{nm} = \frac{k_{m+1}^n}{k_{m}^n} B_{mn} $$

(4)

We expand $\tilde{A}_{nm}$ and $\tilde{B}_{nm}$ as a power series:

$$ \tilde{A}(E) \approx \sum_{\mu=0}^{M} \alpha^{(\mu)}(E)^{\mu}, \quad \tilde{B}(E) \approx \sum_{\mu=0}^{M} \beta^{(\mu)}(E)^{\mu} $$

(5)

where $\alpha^{(\mu)}$ and $\beta^{(\mu)}$ are matrices of coefficients. Using (4) and (5) and inserting them into (2) will give the form of the Jost matrices in terms of the coefficients $\alpha^{(\mu)}$ and $\beta^{(\mu)}$. These can then be inserted into (1) which will then, after some algebra and enforcement of the zero energy behaviour [4] $S_{nm}(E) \xrightarrow{E \to 0} \delta_{mn} + O(k_n^2)$, yield the following linear system:

$$ \sum_{\mu=1}^{M} \left[ \frac{1}{k_{m+1}^{n}} (S_{nm}(E_i) - 1) \alpha^{(\mu)}(E_i) - i k_{m+1}^{n} a_{mn} \right] E^{\mu} = \delta_{mn} - S_{nm}(E_i) $$

(6)

where $S_{nm}(E_i)$ are the elements of an S-matrix obtained by some computational method for a discrete set of energies ($E_i$).

$M$ as defined in Eq. (5) is the maximum power of the two expansions, for which there will be a total of $2(M+1)$ unknown coefficients. However, since the zeroth coefficients are given by the zero energy enforcement, the S-matrix elements must be provided for $N_{\text{pts}} = 2M$ unique energy points in order to solve (6) and calculate the elements of $\alpha^{(\mu)}$ and $\beta^{(\mu)}$. This will allow the elements $f_{nm}^{\text{out}}(E)$ of $F_{\text{out}}^{\text{in}}(E)$ to be determined and thus the parametrised $S$ and Jost matrices obtained.
The first release of our software considers application to multi-channel, elastic systems only. Here all the thresholds can be set to zero and, using Eq. (4), Eq. (2) can be expressed purely in terms of a single $k$ as:

$$F_{mn}^{\text{out}}(k) = \frac{1}{2} \sum_{\mu=0}^{M} \left( a_{mn}^{\mu}k_{\mu}^{-2\mu/2} + i p_{mn}^{\mu}k_{\mu}^{-1/2(\mu+1)+2M} \right)$$

(7)

Since $F_{mn}^{\text{out}}(k)$ is a polynomial function of $k$, and the coefficients have been obtained solving equation (6), we can utilise well known numerical methods for the solving of polynomial systems [15–17].

2.2. Locating the S-matrix poles

The S-matrix poles are obtained by first finding the roots of:

$$\text{det}(\mathbf{F}(k)) = 0$$

(8)

The total number of roots will be dictated by the degree of the polynomial obtained after insertion of (7) into (8) and the subsequent expansion of the determinant. This means it will depend on the system that we choose to solve: the number of channels, their angular momenta and, of course, $M$. Generally not all of these roots correspond to true poles of the S-matrix. However, as pointed out in [12], the roots corresponding to the true poles can be expected to converge onto the ‘true’ value as $M$ increases while the other roots will move about in a random manner. Therefore, locating the poles involves comparing the roots across a range of increasing values of $M$.

To assist in the understanding of the following, more detailed, description of the routines involved in this task, we introduce the following notation:

- The increasing $M$ sequence is indexed using $m$.
- The set of roots found at a particular $M_m$ is labelled $R_m$.
- Root $i$ within the root set $R_m$ is denoted $R_m[i]$
- The number of steps across successive $M_m$ for which a comparison test will be applied is denoted by $c_f$.
- Real and imaginary components of the root are indicated using $\Re$ and $\Im$ subscripts respectively.

The procedure will use a comparison test (explained below) to determine, for each root in $R_m$, if any of the roots in $R_{m+1}$ is close enough to it. Those in $R_{m+1}$ that pass the comparison test (and are thus designated close) are flagged as possible poles. If a root in $R_m$ is close to more than one in $R_{m+1}$ then the root in $R_{m+1}$ that is closest to the root in $R_m$ is used. At this point if $c_f = 1$ then the test is complete and the flagged roots are designated as candidate poles.

If $c_f > 1$ then the flagged roots in $R_{m+1}$ are used to test against all of those in $R_{m+2}$ in a manner analogous to that just described, with the flagged roots updating those in $R_{m+2}$ that passed the comparison test. This continues until $c_f$ steps are reached, at which point the final set of flagged roots in $R_{m+c_f}$ are designated as candidate poles. At this point the routine described in Section 2.3 is executed to assign quality indicators to each of the candidate poles. Before discussing this we first describe the comparison test.

The comparison test is applied to all possible pairs of roots for successive $M_m$. The test is applied separately to the real and imaginary components:

- If the component is greater than a zero value $zk$ for both $M_m$ then $c_{diff}$ is calculated using:

$$c_{diff} = \frac{|R_m[\Re] - R_{m+1}[\Re]|}{\max(|R_m[\Re]|, |R_{m+1}[\Re]|)}$$

(9)

- If the component is smaller than or equal to $zk$ for one of the two $M_m$ then it is set to $zk$ for that step and $c_{diff}$ is calculated using expression (9).

- If the component is smaller than $zk$ for both $M_m$ then it will be set to $zk$ and $c_{diff}$ will also be set to zero.

If both $c_{diff}$ and $c_{diff}$ are less than a respective comparison threshold $dk$ (note that the same value is used for both real and imaginary components) then the comparison test passes and the root is flagged as a candidate pole.

2.3. Assessing the quality of the candidate poles

The identification of a candidate pole in a single application of a location test will therefore depend on $dk$, $zk$ and $M$. In practice, the location test is applied for a range of $dk$ and $M$ as determined by the input provided by the user; $zk$ is also an input parameter in reskit. We note that the number of significant figures in the input data (given by the method and computational approached used to generate it) will have an effect on the identification of poles (see below).

Unfortunately, not all candidate poles are true poles of the system, so a way of quantifying the likelihood that these poles are true poles is required. We do this by defining, and calculating, some ‘quality indicators’ (QI). This involves applying the location routine repeatedly across a range of $M$ values for decreasing $dk$. The QI are determined in the following way:

- The routine keeps count of how many times a particular candidate pole is located over the $M$ ranges for all of the $dk$s. This value defines the first QI, $\Sigma M$.
- The second QI is the lowest $dk$ for which a candidate pole is identified and is referred to as $\sqrt{dk}$.

These QI should provide the user with a mechanism to ascertain the confidence that a candidate pole is a true pole of the system, particularly when compared to any others also discovered in the same data set. However, care must be exercised when choosing the starting value of $dk$ and the value assigned to $zk$, especially with respect to the precision and size of the input data.

3. Using the software

The software to locate S-matrix poles using the method described in Section 2 is made available either from a number of independent python packages or via an encapsulating python package named reskit, all of which are installable via provided distutils setup.py scripts. In addition, a pip requirements.txt is provided with reskit containing specific version numbers for the known working reskit dependencies. We recommend installing into an isolated python environment using, for example, the virtualenv tool.

As well as pulling together the underlying packages (referred to as the reskit Utilities) reskit has also been designed to provide archiving of results, handling of low-level parameters and numeric type abstraction. Since it has a modular design, new techniques can be easily constructed using the Utilities and added as what is referred to as a Tool.

As a way of introducing the package and its use, we present and discuss an example program that uses reskit to find S-matrix poles using an ab initio data set as input; the program shown is a simplification of the test code included with the reskit release. The poles are found using the MCSMatFit Tool.
# Read in the K-matrix data

```
kmadict, kmatdict = rmol.read_Kmata("kmatrix_input_pyrazine.txt")
```

# Get a calculator with units and channel angular momenta

```
calc = rk.get_any_calc(rk.rydbergs, [3,5,5])
```

# Initialise the data into the required container

```
dkmat = rk.get_dmat_from_discrete(rk.kmat, kmatdict, calc, "pyrazine")
```

# Slice the data set (optional)

```
dkmat2 = dkmat[0:1200]
```

# Performance of the calculation of the poles and the quality indicators

```
sfittool = rk.get_tool(rk.mcsmatfit, dkmat2, "results")
```

```
cfins = sfittool.get_elastic_Fins(range(2,32,2))
```

# Find the stable Smat poles for the scattering data

```
sfittool.find_stable_Smat_poles(cfins)
```

To begin, the required modules are imported: reskit, channelsutil and ukrmolmatreader. The ab initio K-matrix data is read using the ukrmolmatreader (line 9). Further details of this data set, obtained for the pyrazine molecule can be found in Section 5. The ukrmolmatreader parser is specific to the particular file structure of our input data but all that is required by reskit is a python dictionary of either S-, K- or T-matrices keyed by energy (translation to the required S-matrix will be done internally if required). reskit supports both python types using numpy operations (default) or the arbitrary precision offered by the mpmath python library. Line 6 specifies to use mpmath with 100 decimal places.

The angular momenta, spin (for the calculation of the cross section) and energy units are provided by the user and then contained as an AsymCalc (asymptotic calculator) object, which is returned from the get_asym_calc function (line 12). In our example, it specifies that the unit of energies are Rydberg (Ry) and that there are three channels of angular momenta 3, 5 and 5.

The call to get_dmat_from_discrete in line 14 translates the user's scattering data, stored in kmadict, into a reskit compatible container type. Here, the first argument specifies the scattering matrix type of the user data, the scattering matrix itself is supplied as the second argument. The third argument is the AsymCalc instance, calc, that was returned in line 12. The "pyrazine" argument is a string given to describe the data set, which is used to build the path for saving and loading the results.

An accompanying function to get_dmat_from_discrete, which is called get_dmat_from_continuous, exists for the situation when the scattering data is given by a functional expression.

After creation of the reskit compatible container, it is reduced in size in line 16. This reduction is carried out using the python dictionary interface, in this case taking the first 1200 energy points only.

The first argument of the rk.get_tool function in line 18 is specifying the required Tool (MCSMatFit), the second is the reskit container created above, dkmat2. The third argument specifies a path into which any results (for example the coefficients calculated by MCSMatFit) generated by the Tool can be saved; if it is not supplied then the Tool will only programmatically return the generated results without any writes to disk. More is said on the storage of results at the end of this section.

rk.get_tool has an optional fourth parameter, param_file_path to allow overriding the default arguments for the low level routines. These include additional parameters for the numpy and mpmath routines, as well as more advanced reskit related parameters. By convention, each Tool provides a default.yaml file containing a set of default arguments. The user can supply their own arguments by passing a path argument for param_file_path, specifying the location of their overriding yaml file. Any user provided yaml file should match the structure and naming of the default yaml it is overriding.

Finally Lines 21 and 22 call the functions that perform the actual calculation. get_elastic_Fins accepts a range of \( N_{\text{pts}} \) and returns a list of \( F^m \) (see Eq. (2)) for each of the supplied \( N_{\text{pts}} \) (in this case the list returned from the range function inclusively contains \( N_{\text{pts}} \) from 2 to 30 with a step of 2). It does this by solving equation (6) for the coefficients and then using expansion (7). The \( F^m \) (contained in the list cfins) are then passed to the find_stable_Smat_poles function which locates the poles and calculates the QIs as described in Sections 2.2 and 2.3.

As mentioned, results from the calculations are written to disk if a results path has been specified in the call to the get_tool function. reskit provides a 'smart archive'. In that results are written to a location depending on the supplied data, the arguments of the calculation and whether numpy or mpmath types are used. This means that any result written into the archive will have enough accompanying information to allow it to be easily reproduced and to allow correct loading of any intermediate calculation results if available and required. All of the results are written relative to the path supplied to the get_tool function. As an example, the path to the find_stable_Smat_poles results in our example will look like:

```
results/pyrazine/mpmath_100/0,1200,None)/mcsmatfit/poles/default/[2,4,6,8,10,12,14,16,18,20,22,24,26,28,30]
```

The names results and pyrazine are provided by the user as the example above shows. \((0,1200,None)\) refers to the reduction of the data set in line 16, \(mnpmath_100\) and mcsmatfit to the types and Tool used in the calculation and default to the yaml file containing the Tool arguments. The list of numbers in square brackets are the \( N_{\text{pts}} \) used in the calculation. Similar paths will exist for the coefficients and roots obtained during the calculation, so that, for example, if the user decides to rerun the calculation including \( N_{\text{pts}} = 32 \) with no other changes, the existing coefficients and roots (i.e. those for values of \( N_{\text{pts}} \) already used) will be loaded from the archive. The final results will then be stored in an alternative folder at the end of the above path named \((2,4,6,8,10,12,14,16,18,20,22,24,26,28,30,32)\).

## 4. reskit package

Fig. 1 shows the architecture of reskit. At the lowest level is the Utilities group. This group encompasses a set of python packages which provide numerical operations and other fundamental functionality. The Tools, of which there are currently two, are dependent on the Utilities and are shown along with their public interfaces.

The reskit package file __init__.py provides access to the Tools and other general functionality, such as the initialisation of data into the required containers and type configuration. Also shown in Fig. 1 are two classes used to obtain the data for the examples provided (Ancilliary Example Modules) as well as the external packages required by reskit.

The typical user is not required to have any knowledge of the packages contained within the Utilities group; the more advanced user can refer to the detailed documentation provided within each of the package folders. This documentation provides instructions for using each Utility package either as a standalone entity or for building Tools and/or other Utilities that can interact with or be integrated into reskit. The remainder of this section will provide a brief overview of the various Utility packages before presenting a more detailed reference of the reskit and Tools interfaces.
4.1. reskit Utilities

The Utilities group contains the building blocks of reskit. It includes numerical routines that are used internally by the Tools, as well as the containers that are returned to the user from the reskit interface (e.g., from the get_dmat_from_discrete function called in the example program given in Section 3) and are used throughout the reskit software.

The pynumwrap package wraps the two different numeric types, standard python and mpmath, supported by reskit behind a common interface. The user can specify what types they want to work with by calling the use_python_types() or use_mpmath_types(dps) function. The latter of these functions offers arithmetic to a specified number of decimal places (dps) and as such allows more accurate (but slower) calculations to be carried out.

The matfuncutil package provides containers for the discrete and continuous representations of data that are typically associated with a scattering problem. The discrete containers for matrix, vector and scalar types are named dMat, dVec and dSca respectively and provide functionality for charting and operations such as slicing and selection of the fit data, as well as useful functions such as eigenvalues() and gradient(). Operating on a container will transform the dMat (or dVec or dSca) into an appropriate container containing the results of the operation.

The analogous matfuncutil continuous containers are named cMat, cVec and cSca. The main purpose here is to wrap a provided function reference and to allow easy discretisation to an appropriate discrete container. In addition, the cMatSympyPoly and cScaSympyPoly continuous containers are provided as extensions of the cMat and cSca to further represent symbolic matrices and scalars via the popular sympy python package. These symbolic
containers provide a simple interface for determinant and root finding.

tisutil provides extension of the matfuncutil containers to the various scattering representations: dSmat, dKmat, dTmat, cSmat, cKmat and cTmat. These containers are returned from the get_dmat_from_discrete and get_dmat_from_continuous functions and passed to the get_tool function in the reskit _init_.py package file. They are also returned from the functions in the urkommatreader and twochanradialwell example modules. These containers provide functionality for converting between the various scattering representations, routines for the calculation of cross sections (dXSmat) and eigenphase sums (dEPhsesScat), as well as the interface for the matfuncutil discrete containers. cMatSympypolyk is also provided as an extension of the matfuncutil cMatSympypolyk container, to allow parametrisation of a symbolic matrix by energy using the AsymCalc. The cFinMatSympypolyk, returned from get_elastic_Fin, is a MatSympypolyk.

The implementation of the technique described in Section 2 for the location of S-matrix poles is mainly contained in the param and stelempy Utility packages. param is responsible for solving Equation (6) for the $a^{(n)}$ and $p^{(n)}$ coefficients and using them to form the Jost functions as given by Equation (7). For the location of the S-matrix poles, a list of $F^m$ are first returned as cFinMatSympypolyk containers. The roots of the $F^m$ are then found using the cMatSympypolyk.find_roots function and passed to the stelempy package. stelempy was designed to find and quantify stable elements over a number of sets and allows the S-matrix poles to be identified using the technique described in Sections 2.2 and 2.3. The comparison test, summarised by Eq. (9), is implemented as the RationalCompare1 class in the pynumutil package.

channelutil contains the AsymCalc class containing the channel information, such as threshold energies, angular momenta and spin as well as functions to convert between energy and momentum. The reskit _init_.py file provides the helper function get_asym_calc to return an AsymCalc.

4.2. reskit Interface

The interface to reskit is through the _init_.py package file shown in Fig. 1. This section provides a summary of the available functions. Some of these are employed when a discrete set of scattering data (generated by other codes) is used and some when a functional expression is provided for these data. The parameters of each of the functions are listed and described.

get_asym_calc: Returns an AsymCalc for converting from momentum to energy.
- units (int): Specification of the energy units. Available options are reskit.rydbergs, reskit.hartrees and reskit.ev.
- amngms (list of ints, optional): Specification of the angular momenta in each of the channels. Defaults to zero in all channels.
- tot_spin (float, optional): Specification of the total spin of the system. Defaults to $\frac{1}{2}$. Only required for calculation of cross sections.
- targ_spins (float or list of floats, optional): Specification of the spin of the target electronic state associated with each of the channels. Defaults to zero in all channels. Only required for calculation of cross sections.

get_dmat_from_discrete: Converts discrete energy dependent scattering data into a reskit compatible container (i.e. dSmat, dTmat or dKmat). Types must match those specified using the use_python_types or use_mpmath_types functions.
- mat_dict (energy dict of scattering matrices): Scattering data to be used in the calculation. Can be either floats or mpmath types.
- asymcalc (AsymCalc): As returned from the get_asym_calc function.
- source_str (str): String provided to uniquely identify the scattering data. Will be used in the archiving of results.

get_dmat_from_continuous: Discretises continuous energy dependent scattering data into a reskit compatible container (i.e. dSmat, dTmat or dKmat). Types must match those specified using the use_python_types or use_mpmath_types functions.
- mat_type (int): As for get_dmat_from_discrete.
- fun_ref (function with float parameter): An energy function describing the elements of the scattering matrix. Can be either python float or mpmath.mpf type.
- asymcalc (AsymCalc): As for get_dmat_from_discrete.
- start_ene (float): Start energy for the discretisation.
- end_ene (float): End energy for the discretisation.
- num_points (float): Number of energy points for the discretisation.
- source_str (str): As for get_dmat_from_discrete.

get_tool: Initialises and returns a Tool.
- data (list of cFinMatSympypolyk): String provided to uniquely identify the scattering data. Will be used in the archiving of results.
- archive_root (str, optional): Specification of the location into which reskit will write its results.
- param_file_path (str, optional): Location of an existing yaml file containing overrides for the more advanced routine parameters.
- silent (bool, optional): Switch determining whether to suppress output to console.

use_python_types: Specifies to use python types.
- use_mpmath_types: Specifies to use mpmath types.
- dps (int): Specifies the mpmath precision.

4.3. Tools

In this section we describe the functionality provided by the Tools. MCSMatFit performs the analytic fit and pole identification whereas Chart provides functionality for the basic plotting of data.

4.3.1. MCSMatFit

These routines perform the fit and identify the poles as described in Section 2.

get_elastic_Fins: Performs $F^m$ fits using the specified list of fit points and returns a list of cFinMatSympypolyk.
- Npts_list (list of ints): List of Npts to be used for successive fits.

find_Fin_roots: Returns the roots of a list of parametrised $F^m$ as a list of python complex or mpmath.mpc types. There are additional advanced parameters supplied via the Tool yaml file.
- cfins (list of cFinMatSympypolyk): List of parametrised $F^m$.

find_stable_Smat_poles: Finds the S-matrix poles by identifying stable roots. The input can be either a list of roots or the $F^m$ themselves. There are additional advanced parameters supplied via the Tool yaml file.
• cfins_or_roots (list of either cfInMatSymppolyk or list of floats): As returned from either get_elastic_Fins or find_Fin_roots.

get_elastic_Smat: Performs an S-matrix fit using the specified number of fit points and returns a cSmat.
• Npts (int): Number of points to use in the fit. Must be an even number.

plot_Smat_fit: Plots the specified matrix element(s) of the original and rational S-matrices and the fit points used. There are additional advanced parameters supplied via the Tool yaml file.
• csSmat (cSmat): Rational S-matrix returned from get_elastic_Smat.
• num_plot_points, units, i, j, logx, logy, imag: Refer to the chart Tool for description.

plot_XS_fit: Plots the cross sections obtained from the original and rational S-matrices along with the fit points used. There are additional advanced parameters supplied via the Tool yaml file.
• csSmat (cSmat): Rational S-matrix returned from get_elastic_Smat.
• num_plot_points, units, logx, logy: Refer to the chart Tool for description.

4.3.2. Chart

plot_raw, plot_Smatrix, plot_Kmatrix, plot_Tmatrix, plot_UnitOpSMat, plot_EphaseSum, plot_XS: Plot various scattering related quantities. A png image of the plot will be automatically saved into the archive.
• start/end (int or float, optional): Indicates the start/end index (if int) or the nearest start/end energy (if float).
• num_plot_points (int, optional): The number of points to plot, evenly distributed between start and end.
• units (int, optional): If specified, then will convert to these units prior to plotting. Available options are reskit. rydbergs, reskit. hartrees and reskit. evs.
• logx (bool, optional): Switch to turn on x-axis log plotting.
• logy (bool, optional): Switch to turn on y-axis log plotting.
• imag (bool, optional): For complex quantities, switch to plot the imaginary component. By default just plots the real component.
• i (int, optional): Zero-based row index to plot. Default is to plot all rows.
• j (int, optional): Zero-based column index to plot. Default is to plot all columns.

The i and j parameters are only available when the quantity to plot is a matrix (i.e. not for plot_Ephase and plot_XS).

5. Example runs

In this section, we present some results obtained with the reskit package and discuss how to interpret them, in particular what the values of the QI say about the likelihood that candidate poles identified in the calculations are true poles of the system. The calculations correspond to the test runs that are provided in the code release and the figures presented have been created using the charting functionality provided by reskit. Atomic units are used throughout.

5.1. Square well

A simple test system is the elastic s-wave scattering two-channel radial square well for which the interaction potential

\[ V_{nm}(r) = \begin{cases} 
0 & r > a \\
V_{nm} & r < a 
\end{cases} \]  

(10)

where \( V_{nm} \) is a 2 × 2 matrix containing the channel potentials, \( v_{11} \) and \( v_{22} \), and a coupling factor \( \lambda \): \[ v_{nm} = \begin{pmatrix} v_{11} & 0.5\lambda v_{22} \\
0.5\lambda v_{22} & v_{22} \end{pmatrix} \] (11)

Here \( v_{11}, v_{22} \) and \( \lambda \) are constants. The exact solution for the S-matrix for this system is known [4].

Table 1 compares the values of the S-matrix poles obtained using reskit with those obtained numerically1 from the exact solutions given in [4] for a well with \( a = 1.0 \) and \( \lambda = 10.0 \) for the \( \text{reskit} \) calculation, even \( N_{00} \) points were used by fitting \( N_{00} = 2M \) points in the interval 1.0–8.0 Ha, with a starting \( dk \) of \( 10^{-4} \) and testing across 3 successive \( M \) (i.e. \( cf = 2 \)). The \( N_{00} \) points were selected from a set of 1000 evenly spaced energies points for which the S-matrix was calculated using the functional form given in [4]; 100 decimal places were used throughout these calculations.

The first two poles in the table correspond to bound states while all the others correspond to resonances: both the resonance pole and its corresponding antipole [5] are tabulated. Three things are immediately clear from the table: (i) the method identifies poles well outside the range of the real energies for which S-matrix data is provided; (ii) the QI get worse (that is, \( \sqrt{dk} \) increases and \( \Sigma M \) decreases), as the method ‘extrapolates’ further away from the data provided; (iii) use of a larger value for \( M \) (in the same energy range) enables the identification of poles further from the energy range of the input data set as well as improving the QI for the poles already identified.

Table 1 shows clearly that the QI gets worse as poles move further away from both the real axis and the (real) energies for which the S-matrix data is provided. To further illustrate the effect of ‘extrapolating’ away from the real axis, Fig. 2 shows how one of the QI, \( \Sigma M \), changes as the imaginary part of a pole (i.e. the width of the resonance it corresponds to) increases. The data corresponds to a specific resonance as the depth of the wells is varied. In order to eliminate the effect of extrapolating the real component of the energy, the calculation for each depth was done by shifting the energy range for which the S-matrices are provided, so that the real part of the pole energy is located approximately in the centre of the data set. Unsurprisingly, \( \Sigma M \) decreases as the width of

1 The exact solutions given in [4] describe scattering from a general two channel radial well. For the bound states the poles were located graphically from a transcendent equation derived from these solutions by the authors. For the resonances, they were obtained using the secant method to locate the zeros of the denominator of the S-matrix
In this section we discuss computational limitations encountered when running the routines. Discussions are all based on results obtained using a single 3.60GHz Intel i7-3820 core.

First and foremost the compute time required by the routines is very high. For some of the higher channel systems the norm was to wait a week for results. Scaling is most likely polynomial, since the main performance bottle-neck is the expansion of the determinant of the denominator of (2.48), using the Berkowitz routine [168]. Figure D.1 shows the measured time taken by the calculation for different numbers of channels.

Some investigation is required to determine if the time complexity can be lowered. The Berkowitz routine has a low time complexity and is considered relatively optimal. However, there are improvements to this mentioned in the literature [169] but it is certainly beyond the scope of the project to implement these, regardless of whether the improvement would be significant or not. Other aspects of the routine could be optimised; for example the calculations are currently carried out using purely python types. This is because high precision types were required and as such the numpy C library wrappers were not an option. Still, there may be other compiled libraries offering what we require and their integration into the current routines may be worth consideration. Unfortunately this is likely to reduce only by a constant factor, which ill compares to the time complexity of the Berkowitz.

What could also cause issues is increased error propagation for larger numbers of channels. Currently we were forced to use python types for arbitrary precision but since the molecular input data has a set precision we expect to reach a limit in how high we can go with the current data sets.
Figure D.1: Time taken by \texttt{reskit} including calculation of coefficients, expansion of determinant and solving for roots as a function of different numbers of fit points $P$ and channels. All times are cumulative in that the time taken for a given $P$ includes the time taken for all previous $P$s, so that the chart show total times for calculations up until a given $P$. Based on results obtained using a single 3.60GHz Intel i7-3820 core.
REFERENCES

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