R-matrix calculations of vibrationally resolved electron collisions with molecular hydrogen

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Abstract

Electron-H₂ is the most basic, fundamental system for the study of electron collisions with molecules and has many interesting features. In particular, at low energy there is a shape resonance associated with the ground state and at higher energy a resonance associated with a dissociative target state. In the region of 10-15 eV there is an enormously complicated resonance structure due to the forest of electronically excited target states present, many of which have associated resonances. Despite a large number of experimental and theoretical studies, many ambiguities remain over the designation, symmetry assignment, parentage and behaviour of different isotopes of these '10 eV' resonances.

The purpose of this work is to develop a full description of electron hydrogen molecule collisions at energies up to 14 eV with particular emphasis placed on the troublesome '10 eV' resonances.

*Ab initio* fixed-nuclei scattering calculations have been performed for electron-H₂ collisions as a function of H₂ bond length using the R-matrix method, up to 2Φ₉ total symmetry. The calculations include the seven lowest target states of H₂ which are represented by full CI wavefunctions.

The time-delay method of fitting has been developed during the course of this work. The use of this method has allowed the tracking of resonance positions and widths, and hence the production of resonance potential curves, where previous methods (most notably the fitting of the eigenphase sum) have failed due to problematic background variation.

Several resonances in the 10-14 eV region have been found to be associated with multiple 'parent' target states and in some cases can swap parents as a function of bond length. These phenomena provide an explanation for the inconsistencies in previous assignments of resonances in this region and other anomalies.

Vibrational energy levels have been found from the resonance potential curves and compared with experimental studies for H₂, D₂ and HD. The excellent agreement has allowed the production of a complete theoretical description of all the low-lying resonances. The agreement also provides corroboration of the multiple parent state/parent state swapping phenomena.
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Chapter 1

Introduction

1.1 Motivation

In all phases of matter, in all areas of the universe, electrons are in great abundance and are highly reactive. The scattering of electrons from molecules is important in many natural processes in a variety of areas of physics and underlies the development of many new technologies.

In CO$_2$ and other molecular lasers, the energy necessary for population inversion is provided by the excitation of vibrational and rotational states of the CO$_2$ molecule through electron impact. Other molecules can also be included in the laser to tune its operating characteristics. A detailed knowledge of the electron vibronic collision cross sections for all the species involved is therefore required in order to optimize the laser performance (Demaria 1973).

Collisions of electrons with molecules and molecular ions play a crucial role in the physics of the interstellar medium and planetary atmospheres. For example, rotational electron excitation of interstellar molecules is a significant mechanism in the cooling down of electrons. This mechanism will also establish the populations of rotational states and hence determine the intensities in the emission lines of the molecules (see, for example, Dalgarno & McCray (1972), Dickinson, Phillips, Goldsmith, Percival & Richards (1977)). In the earth’s ionosphere, the electron impact resonant vibrational excitation of N$_2$ is similarly an important electron cooling mechanism (Hines, Paghis, Hartz & Fejer 1965). In the thermosphere of the outer planets, H$_2$ is in great abundance and a knowledge of electron collisions with H$_2$ is necessary to model the conductivity in order to study the interaction of the magnetosphere and the atmosphere (Strobel & Atreya 1983).
In the biological and life sciences, knowledge of electron-molecule collisions is required to model the indirect effects of radiation on cells. When ionizing radiation passes through matter it will excite and liberate electrons. Along with damage caused directly by the radiation, these energetic electrons can themselves collide with molecules and cause damage to cells and may play a part in genetic mutation (Green 1997). Electron collision may also be important in the treatment of cancerous tumours through radiation therapy.

One of the processes involved in the electrical breakdown of air is the ionization of air molecules through electron impact (see, for example, Okada, Sakai, Tagashira, Nakagami & Watanabe (1996)). An understanding of this process is required in the design of high voltage transmission systems. One of the byproducts of such a breakdown is ozone and this has been used as a method for generating ozone. However, collisions between electrons and ozone will limit the amount of ozone produced (Mason 1997a).

Electron scattering is used in material science to probe the structure of materials such as molecular crystals (Dorset 1996). Electron collision cross section data is required for the design and optimisation of processes involving plasmas, such as plasma etching (Pearton & Ren 1994), magnetohydrodynamic power production (Spence & Phelps 1976), and thin film chemical vapour deposition techniques (Springer, Cameron & Reeves 1997).

In many of the areas mentioned above, the data required for the models has not been found by experiment with sufficient accuracy. There is therefore a very practical reason for theoretical calculations of electron molecule scattering - to provide data where experiment cannot. More fundamentally, the electron molecule system with its many degrees of freedom provides a challenging test of current quantum mechanical methods and promotes the development of new techniques.

Resonances, temporary pseudostates of the molecule-plus-electron system, have a major effect on any process involving the electronic excitation of a molecule. They also play a significant role in the dissociation of the molecule and can enhance rovibronic cross sections by an order of magnitude (Schultz 1973). Most molecules, have a forest of electronically excited states some 6–12 eV above their electronic ground states (see figure 1.1 for the potential curves of H$_2$). Collisions with electrons at this energy are often dominated by multiple resonance series which are difficult to disentangle experimentally or to model theoretically (Schultz 1973).

Even with a target of the simplest, most fundamental neutral molecule, H$_2$, there is a tremendously complicated resonance series structure in the 10–15 eV region along with further resonances lower in energy. Over the last thirty years there have been a large number of determinations, both experimental and theoretical, of this structure and an almost equal number of
Figure 1.1: Potential curves of the first seven states of H₂
differing conclusions reached about the nature of the resonance series.

Because of its simplicity, $\text{H}_2$ is often used as the prototypical molecule when studying new systems. It is vital to our understanding of resonance phenomena in molecules generally that we are able to understand the specific structure seen in this molecule.

### 1.2 The electron-molecule scattering problem

When an electron collides with a neutral atom, there are only three likely outcomes: i) the electron scatters elastically off the atom leaving the atom in its original electronic state; ii) the electron excites the atomic electrons leaving the atom in an excited state; iii) the electron has sufficient energy to remove an electron from the atom, leaving it positively ionized. Additionally, the electron can be captured by the atom to form a negative ion but this requires an extra process such as the emission of a photon.

When an electron collides with a neutral diatomic molecule, however, the story is far more complicated. Firstly, the molecule has vibrational and rotational degrees of freedom which can be excited with little energy. Any of the above outcomes of electron-atom collisions can occur along with rotational and/or vibrational excitation of the molecule. Secondly, the interaction between electron and molecule is multicentred and non-local which leads to a coupling between states. Thirdly, the molecule can break up in a variety of different ways through dissociation, dissociative attachment and dissociative ionisation (see figure 1.2).

It is clear that classical mechanics cannot hope to approximate anything more than the most basic elastic scattering and the system must be treated quantum mechanically. As with all quantum mechanical problems, this entails the solution of the Schrödinger equation, but because of the size of the system involved there is no question of being able to solve the equation exactly. The different methods of electron-molecule scattering are characterized by the different approximations they make in their attempt to solve the problem as accurately as possible.

The physics behind low-energy electron molecule scattering and the different theories which can be implemented for its solution have been excellently reviewed by Morrison (1993). Details of modern computational methods used can be found in Huo & Gianturco (1995).

For the electron molecule system, the Hamiltonian can be written in the molecular frame as:

$$\mathcal{H} = \mathcal{H}_m(x) + \tilde{T}_e(\gamma) + \tilde{V}_{\text{int}}(x, \gamma),$$

(1.1)
where \( \mathbf{x} = (\mathbf{r}, \mathbf{R}) \) includes both the electronic and nuclear coordinates of the molecule, and \( \gamma \) is the scattering electron coordinate. \( \mathcal{H}_m(\mathbf{x}) \) is the molecular Hamiltonian including all the kinetic and potential terms of the target electrons and the nuclei, \( \hat{T}_e(\gamma) \) is the kinetic energy operator of the scattering electron and \( \hat{V}_{\text{int}}(\mathbf{x}, \gamma) \) is the interaction energy between the scattering electron and the molecule. As a simplification, explicit spins have not been included.

The solution for a neutral molecular target assuming no ionization or dissociation must satisfy the asymptotic boundary condition

\[
\Psi(\mathbf{x}, \gamma) \sim \exp(i\mathbf{k}_0 \cdot \gamma)\psi_0(\mathbf{x}) + \frac{1}{\gamma} \sum_n \exp(i\mathbf{k}_n \cdot \gamma)f_{n0}(\mathbf{k}_n, \mathbf{k}_0)\psi_n(\mathbf{x}),
\]

where \( \psi_n \) is the wave function of the \( n_{th} \) unperturbed target state, \( \mathbf{k}_0 \) and \( \mathbf{k}_n \) are the initial and energetically allowed final momenta of the scattered electron and \( f_{n0} \) is the scattering amplitude. Clearly the first term represents an initial plane wave incident on the ground state and the second consists of a superposition of outgoing waves associated with each of the energy accessible target states.

The interaction energy \( V_{\text{int}}(\mathbf{x}, \gamma) \) in equation 1.1 can be further split into two parts:

\[
V_{\text{int}} = \hat{V}_{\text{nuc-elec}} + \hat{V}_{\text{elec-elec}}
\]

\textbf{Figure 1.2:} The different possibilities for the break up of a diatomic molecule due to electron impact

---

\[ V_{\text{int}} = V_{\text{nuc-elec}} + V_{\text{elec-elec}} \]
where $V_{\text{nuc-elec}}$ is the potential between the nuclei and the scattering electron and $V_{\text{elec-elec}}$ is the repulsion between the target electrons and the scattering electron.

The potential $V_{\text{nuc-elec}}$ introduces a coupling between the nuclear and electronic motions which makes the resulting equations extremely difficult to solve. It is therefore usual to invoke the Born-Oppenheimer approximation (Born & Oppenheimer 1927, Morrison, Estle & Lane 1977) which assumes that the electrons travel so quickly that they can react instantaneously to the motion of the nuclei. This makes the wavefunction separable into a nuclear part and an electronic part, which can be solved separately.

It has also been common practice to invoke the fixed-nuclei approximation where the nuclei are considered to remain stationary, simplifying the Hamiltonian even further. If required, it is often possible to approximate nuclear motion post facto (Morrison 1993) given a series of fixed-nuclei calculations as a function of bond length.

The potential energy $V_{\text{int}}(x, \gamma)$ can be expressed semi-classically to demonstrate explicitly the interactions involved.

$$V_{\text{int}} = V_{\text{scatelec-target}} + V_{\text{exch}} + V_{\text{polar}}.$$  \hspace{1cm} (1.4)

In this formulation, the first term of the potential is the static interaction of the scattering electron in the electric field of the target molecule $V_{\text{scatelec-target}}$. The other terms, $V_{\text{polar}}$ and $V_{\text{exch}}$, take into account the effects of the scattering electron on the molecular charge cloud.

Since the electrons are indistinguishable, the Pauli exclusion principle requires that the total wavefunction be antisymmetric with respect to exchange of label. This requirement can be imagined as an 'exchange force' which prevents the electrons sharing the same space. In some methods it is modelled explicitly as the exchange potential $V_{\text{exch}}$ (Morrison 1993). Since this effect is non-local, it results in a coupling between states, and hence introduces a coupling between equations which complicates their solution for certain methods. Close-coupling methods (discussed below) treat exchange implicitly by forcing each of the components of the (N+1) wavefunction to be antisymmetric.

Classically, polarization and correlation effects ($V_{\text{polar}}$) arise from the distortion of the target molecule charge cloud due to the electric field of the scattering electron. Quantum mechanically they arise through virtual excitation into energetically inaccessible excited electronic states. In some methods, such as those using a single centred expansion (Gianturco, Thompson & Jain 1995), polarization/correlation is treated explicitly by the use of a model potential. In close-coupling methods (discussed below) it is treated implicitly by including so-called $L^2$ configurations in the (N+1) wavefunction for which all electrons are placed in target
molecular orbitals.

The scattering problem can be treated at different levels, depending on which, and to what extent, these effects are to be included in the calculation. The different levels used by electronically elastic calculations are as follows:

- **Static**
  
  At this level, the scattering electron is deemed to be a separate entity from the target molecule. The exchange is taken as zero and it is assumed that the target itself remains undistorted by the approaching electron, i.e. the polarization is also zero. Treating the problem at this level has the advantage that the equations are easily solved. It has the disadvantage that the answers will be wrong quantitatively and, more often than not, even qualitatively.

- **Static exchange (SE)**
  
  In this approximation, exchange is included either implicitly or explicitly. However, the target molecule is not allowed to be perturbed, assuming again that the polarization is zero. Since polarization is the major cause of Feshbach resonances, any resonant region will not be well modelled.

- **Static exchange plus polarization (SEP)**
  
  In this case, along with exchange, the target is allowed to be perturbed through the inclusion of polarization and correlation effects.

For electronically inelastic calculations, close-coupling methods (of which the R-matrix method is one) are used. These involve the expansion of the (N+1) wave function over configurations made of target eigenfunctions multiplied by one-particle scattering functions. Such calculations will be at the SE or SEP level since, as mentioned previously, exchange is included implicitly by forcing the configurations to be antisymmetric. Polarization can be included through the addition of $L^2$ terms as described above.

1.3 **Previous calculations of $\text{H}_2^-$ resonances**

Since $\text{H}_2$ is the simplest neutral molecule, there have been a very large number of calculations of $e$–$\text{H}_2$ collisions over many years. All calculations pre-1980 were extensively reviewed by
Lane (1980) and this has been complemented by the review by Domcke (1991). Early calculations, performed at the static exchange level, did not explicitly see Feshbach resonances. This is understandable as polarization effects are the major contributor to the potential that traps the scattering electron in a pseudostate.

Electronic structure calculations (Schaefer III 1984) with three electrons are capable of modelling bound states very accurately. However, they cannot be used unadapted to find resonances. Step-by-step improvements in such calculations result in the improvement of the continuum into which the electron disappears. Techniques such as stabilization (Eliezer, Taylor & Williams 1967) have been used to try and get round this problem.

There have been a few \( \text{H}_2^- \) electronic structure calculations. One of the earliest as a function of geometry was that of Taylor & Williams (1965) which used a quasiviariational method to find a single \( 2\Sigma_g^+ \) resonance in agreement with the recently found experimental result of Kuyatt, Simpson & Mielczarek (1964). A later experiment (Kuyatt, Simpson & Mielczarek 1966) found two and not one resonance, and a further calculation (Eliezer et al. 1967) which added stabilization to the original quasiviariational method then found two \( 2\Sigma_g^+ \) Feshbach resonances with parents \( e^3\Pi_u \) and \( C^1\Pi_u \). It has since been shown that the second resonance seen experimentally (series \( c \)) is in fact \( 2\Pi_u \) and not \( 2\Sigma_g^+ \) symmetry (Comer & Read 1971, Schultz 1973). Eliezer et al. (1967) also calculated an \( a^1\Sigma_g^+ \) shape resonance but only for a single bond length and then postulated a potential curve based on that of the parent for limited bond lengths. These extra resonances are possibly 'phantom' resonances and are discussed in section 6.3.

Bardsley, Herzenberg & Mandl (1966) performed a simple variational calculation using a summation of valence-bond orbitals (for reasonable representation at long bond length) and molecular orbitals (for short bond length) in their \( (N+1) \) wavefunction and included outgoing-wave boundary conditions to allow for decay of the resonance. They looked at the lowest two \( \text{H}_2^- \) shape resonances: the \( 2\Sigma_u^+ \) ground state shape resonance and the \( 2\Sigma_g^+ \) core-excited shape resonance with parent \( b^3\Sigma_u^- \). Their trial wavefunctions were of such a simple form, however, that the detailed behaviour of the resonances as a function of bond length later proved to be inaccurate.

Buckley & Bottcher (1977) used a Feshbach projection operator technique with configuration interaction to look at resonances below 12 eV. In this method, the CI space is partitioned into a resonance and a continuum subspace. The Hamiltonian within each subspace is diagonalized separately to find the resonance states and the continuum states. The interaction between these states is then calculated.

The basis set used was an orthonormal set of hydrogen molecular ion \( \text{H}_2^+ \) orbitals which
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were linear combinations of atomic orbits (LCAO MO) with no attempt at optimization. Partly because of this lack of optimization but mainly due to the lack of valence-bond orbitals, the wavefunction is less and less well represented as the bond length is increased. Buckley and Bottcher saw a host of resonances including ones of $^2\Delta_g$, $^2\Pi_u$ and $^2\Sigma_g^+$ symmetry. One of the $^2\Sigma_g^+$ resonances had a double minimum in the $H_2^-$ potential curve due to an apparent avoided crossing. Only their $b\ ^3\Sigma_u^+$ shape resonance fits qualitatively with other theoretical or experimental determinations. Their simplistically represented wavefunctions and the method used, result in phantom resonances and incorrect asymptotic behaviour. However, they did note that the idea of a single parent might not always be meaningful although this has since been ignored, possibly because of their unphysical results.

A year later, Bardsley & Cohen (1978), with a basis of Slater type orbitals and elliptical orbitals, performed a series of variational calculations which involved adding sets of configurations one at a time to try and look at the interactions between $H_2^-$ states. They modelled the $^2\Sigma_g^+$ shape resonance with parent $b\ ^3\Sigma_u^+$ fairly successfully and found evidence for resonances of symmetry $^2\Sigma_g^+$, $^2\Pi_u$ and $^2\Delta_g$. However, this calculation is severely limited by the arbitrariness with which configurations are chosen and the size of the basis set used. Definitive identification of these resonances with experimental series is impossible. Notably, for $^2\Sigma_u^+$ symmetry, the variational procedure collapsed and so no evidence for the series $b$ could be seen.

DeRose, Gislason, Sabelli & Sluis (1988) studied the first three $^2\Sigma_u^+$ states of $H_2^-$ using a variation of the Feshbach projection operator technique. Here, the property used to separate CI space into the resonance and continuum subspaces was the electronic expectation value $<z^2>$. This was effected by finding the eigenvalues and vectors of the $<z^2>$ matrix. Eigenvectors with arbitrarily low eigenvalues are considered as resonance states, and with high eigenvalues as continuum states. The lowest resonance they found, the ground state $X\ ^1\Sigma_g^+$ shape resonance, fits fairly well with other determinations. The other two resonances, however, bear no relation to any resonances seen by others either experimentally or theoretically. This method relies on the hand picking of the CI states used in describing each resonance. The arbitrariness of this procedure and various approximations used in this method are likely to cause these spurious resonances.

Aside from electronic structure calculations, there have been a number of scattering calculations which have looked explicitly at the resonances.

da Silva, Lima, Brescansin & McKoy (1990) used the Schwinger multichannel method (a close-coupling SEP method) to study the effects of the series $a$ Feshbach resonance on elastic
and electronic cross sections in e–H\textsubscript{2} collisions. This method, developed by Takatsuka & McKoy (1981) and based on the Schwinger variational method (Schwinger 1947), incorporates the correct boundary condition automatically by using Green’s functions and so can use an $L^2$ basis without the need to tailor it for particular boundary conditions. The multichannel method was explicitly designed to treat the multicentre nature of the scattering problem. It has the advantage that by choosing Gaussian functions for the $L^2$ basis and plane waves for the incoming electron, all two-electron integrals can be calculated analytically. Another advantage is that the variational trial function does not have to be asymptotically correct and need only be a good approximation to the exact function in the region where the potential is effective. As the method uses plane waves to represent the incoming electron instead of the usual partial wave expansion\textsuperscript{1}, it produces T-matrices using a linear momentum instead of an angular momentum representation.

The da Silva et al. calculation included four target states plus the inner E region of the E,F $^1\Sigma_g^+$ state in a fairly basic (SCF) representation of the target. They did not include the c $^3\Pi_u$ and C $^1\Pi_u$ target states which, it has been shown in this work, contribute towards the parentage of the resonance. All calculations were performed at the equilibrium bond length only, but did manage to give a qualitative feel for the effect of the resonance.

Branchett & Tennyson (1990) studied resonances with 2, 4 and 6-state R-matrix calculations similar to those used in this work, also at the equilibrium bond length. They correctly assigned several of their resonance features but were unable to assign several others and did not see evidence for the series $b$, $d$ or $e$ resonances (Comer & Read 1971). Branchett, Tennyson and Morgan (1990, 1991) used a 7-state model to compute eigenphase sums and total cross sections (1990) and differential cross sections (1991), and looked explicitly at the resonance effects.

There have been many calculations of cross sections in e–H\textsubscript{2} scattering that have not looked explicitly at the resonance series, a few of which are discussed here.

The electronic transition between the ground state X $^1\Sigma_g^+$ and the b $^3\Sigma_u^+$ excited state is dipole forbidden and the states are only coupled through the exchange force. The transition thus provides an excellent test of different scattering methods. Three studies of this transition performed at the equilibrium fixed nuclear separation were reported simultaneously in 1985. All three calculations are 2-state calculations at the SCF level. The (N+1) wavefunctions contained $L^2$ or ‘correlation’ terms (all three electrons in target molecular orbitals – see equation

\textsuperscript{1}The partial wave expansion expresses a wavefunction as a sum over radial functions to take advantage of the spherical nature of the problem in the region far from the molecule
2.10) which allow for the relaxation of orthogonality conditions and polarisation.

Schneider & Collins (1985) used the linear algebra method. This employs the Feshbach (1958) projection operator description to formulate the separable optical potential form of the scattering equations. The resultant equations can be reduced to a set of radial, coupled integro-differential equations which are solved by means of the linear algebraic technique (Schneider & Collins 1981, Collins & Schneider 1981). Lima, Gibson, Huo & McKoy (1985) used the Schwinger multichannel variational method (described earlier) which also employs the projection operator formalism. Baluja, Noble & Tennyson (1985) used the R-matrix method in a similar formulation to that used in this work.

All three calculation produced very similar cross sections with those of Lima et al. (1985) particularly close to those of Schneider & Collins (1985). This is not surprising given the similarity of the (N+1) wavefunction for all three and the similarity of the methods of the latter two. There was good qualitative agreement with experimental integral cross sections.

Parker, McCurdy, Rescigno & Lengsfield III (1991) employed the complex Kohn variational method (Miller & Jensen op de Haar 1987, McCurdy, Rescigno & Schneider 1987) in a four-state calculation to generate integral and differential cross sections for excitation from the ground X $^1\Sigma^+_u$ to the b $^3\Sigma^+_u$, a $^3\Sigma^+_g$ and c $^3\Pi_u$ states. This method was developed from the Kohn variational method (Collins & Robb 1980) in an attempt to avoid anomalous singularities in the K-matrices suffered by that method. It uses a close-coupling expansion, similar to that used in other methods, and employs Feshbach partitioning to define an effective Hamiltonian. T-matrices are calculated from the matrix elements of this effective Hamiltonian to produce integral and differential cross sections.

More recently, Celiberto & Rescigno (1993) used the impact-parameter method to look at excitation cross sections from the ground state to the B $^1\Sigma^+_u$ and C $^1\Pi_u$ states. They studied both H$_2$ and D$_2$ molecules and found cross sections as a function of vibrational quantum number from threshold to 200 eV. Celiberto, Capitelli & Janev (1996), employing the same method and energy range, reported a scaling law for the electronic excitation cross sections of vibrationally excited diatomic molecules using H$_2$ and D$_2$ as examples. The impact-parameter method is useful in the higher energy regime but cannot be used for accurate determination of cross section in the highly resonant region studied in this work.
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1.4 Experimental determinations of resonance series

Resonance activity in the 0–15 eV region of e–H₂ scattering has been known for many years. Early experiments have been reviewed by Schultz (1973) with a more recent review by Trajmar, Register & Chutjian (1983). Many e–H₂ experiments have been performed which did not look explicitly at the resonance series, but these are not considered here.

The first experiments to tabulate resonance series vibrational level positions appear to have been those of Kuyatt et al. (1964, 1966). They looked at the transmission of electrons passing through H₂ (1964, 1966) and HD and D₂ (1966 only). In their earlier experiment they saw only a single resonance although in the later they saw two resonances, now believed to be series \( a \) and \( c \) (Schultz 1973). However, their absolute energy positions and, occasionally, vibrational spacings do not fit very well with those of other experiments and are considered unreliable.

Weingartshofer, Ehrhardt, Hermann & Linder (1970) performed energy loss experiments to look at decay into both the \( b \: ^3\Sigma_u^+ \) dissociative channel and the elastic channel. They saw three resonance series, the highest of which starts at 13.6 eV and is above the range addressed in the calculations presented here. The other two, starting at 11.3 and 11.5 eV, they named series I and II respectively. The energy range of these experiments was extended in a later experiments (Weingartshofer, Clarke, Holmes & McGowan 1975) and resonances at even higher energies were seen.

The most comprehensive analyses of resonances in H₂ and D₂ were completed by Comer & Read (1971) and later Joyez, Comer & Read (1973) who looked at decay into vibrational levels of the ground state. They recorded three resonance series. To the first, series \( a \), they managed to assign the symmetry and fitted its vibrational levels successfully to a Morse function to estimate the potential curve. However, they had difficulty deciding on a parent state. The second, series \( b \), they only saw in high vibrational levels of the ground state \((v \geq 8)\) in the first experiment and this resonance has been seen in only one experiment since (Huetz & Mazeau 1983). They assigned it a symmetry and a parent state but found when they tried to fit the levels to a Morse potential, that the fit was extremely poor. It was so poor, in fact, that they could not decide how many missing levels there were. The third series, \( c \), suffered from the same problem when trying to fit it to a Morse potential. Additionally, even the assignment of symmetry was uncertain and they could not decide which of two target states was the parent.

The resonance series I and II of Weingartshofer et al. (1970) were of very similar energy to Comer and Read’s series \( a \) and \( c \) resonances. When the latter reanalysed the former’s angular distribution data, they concluded that the series I and II must be of different symmetry to the
series \( a \) and \( c \) and renamed them series \( d \) and \( e \). However, in their later paper (Joyez et al. 1973), they suggested that series II and \( c \) were in fact the same.

Sanche & Schultz (1972) performed transmission experiments to look at the series \( a \) and \( c \) resonances. Their results for series \( a \) agree perfectly with the inelastic channel results of Comer & Read (1971) and Weingartshofer et al. (1970) but disagree with the transmission experiments of Kuyatt et al. (1966). They also tabulated two higher resonances: one starting at 13.66 eV similar to that seen by Kuyatt et al. (1966) (series \( f \)) and a further resonance series \( (g) \) starting at 15.09 eV, both outside the range considered here.

Elston, Lawton & Pichanick (1974) studied series \( a \) and \( c \) by monitoring resonance decay into the \( B \, ^1\Sigma^+_u \) (u.v. emitting) and the metastable \( c \, ^3\Pi_u \) states. Their results for series \( a \) agree well for the two channels and well with other experiments. Their results for series \( c \) are slightly different in absolute energy for the two channels and only in reasonable agreement with other experiments

Esaulov (1980) performed a differential time-of-flight energy loss study of \( \text{H}^- \) scattering by \( \text{D} \) (and vice versa) to examine electron detachment and charge exchange. Esaulov found evidence of decay of the core-excited shape resonance \( B \, ^2\Sigma^+_g \) into its parent \( b \, ^3\Sigma^+_u \) target state and concluded that it should lie around 0.8 ± 0.3 eV above its parent.

Hall & Andric (1984) studied the effect of the two lowest resonances on the vibrational excitation of \( \text{H}_2 \) and \( \text{D}_2 \). These resonances are the ground state shape resonance, \( X \, ^2\Sigma^+_u \), and the resonance associated with the \( b \, ^3\Sigma^+_u \) target state, the \( B \, ^2\Sigma^+_g \), which is a core-excited shape resonance in the Franck-Condon region. They found that the \( X \, ^2\Sigma^+_u \) resonance greatly enhanced the vibrational excitation cross section at 5 eV. At 10 eV, the \( X \, ^2\Sigma^+_u \) was the main contributor to the \( v = 1 \) vibrational level cross section but that as the value of \( v \) increases, the \( B \, ^2\Sigma^+_g \) became the dominant contributor.

Mason & Newell (1986) observed resonance vibrational levels in the electron impact total excitation cross section of the \( c \, ^3\Pi_u \, (v = 0) \) \( \text{H}_2 \) state and in the differential emission cross section of the \( B \, ^1\Sigma^+_u \) \( \text{H}_2 \) state. Their series \( a \) results agreed with all other experiments although their series \( c \) results appeared to disagree with those of Comer & Read (1971), probably because of a disagreement in the numbering of the vibrational levels. In a later experiment, Furlong & Newell (1995) looked at decay into the metastable \( c \, ^3\Pi_u \) for \( e-\text{H}_2 \), \( \text{HD} \) and \( \text{D}_2 \) scattering. Their results for series \( a \) are in reasonable agreement with other experiment for \( \text{H}_2 \), but disagree with the results of Kuyatt et al. (1966) (the only other results available) for \( \text{HD} \), although, as mentioned previously, those results are considered unreliable. Series \( a \) was not discernible in \( \text{D}_2 \). Their series \( c \) results for \( \text{H}_2 \) are fairly close to other experiments, again disagree for \( \text{HD} \).
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and, once a misnumbering of their vibrational levels is rectified (see chapter 5), agree fairly well for \( D_2 \).

1.5 Objectives

The experiments and theoretical calculations of the last 30 years, described in the previous two sections, have failed to come up with a consistent description of the \( H_2^- \) resonances. In an attempt towards a complete theoretical model, the objectives of this work are as follows:

- The assignment of symmetry to each of the \( H_2^- \) resonance series
- The assignment of parent states to each of the resonance series
- To confirm or disprove the existence of resonance series \( b \)
- To confirm or disprove that resonance series \( a \) and \( c \) are the same as series \( d \) and \( e \) respectively
- To provide an explanation for the difficulties encountered by experimentalists in fitting their data to a standard potential
- To provide an explanation for the disagreements and contradictions among and between experiment and theory regarding the assignment of resonances

1.6 Method

This study employs the R-matrix method to perform a series of fixed-nuclei electron–\( H_2 \) \textit{ab initio} scattering calculations over a range of bond lengths. Seven target states, with which the resonance series under consideration are known to be associated, are included in the calculation and the lowest eight total symmetries are considered.

For every symmetry, at each bond length in turn, resonances are searched for and parameterized using the time-delay matrix method and/or the eigenphase sum method. The resonances are assigned target state parents through various methods. These include comparing \( H_2^- \) resonance potential curves (found by tracking each resonance across bond length) with target state potential curves, examining branching ratios and performing calculations with a reduced number of target states.
From the $\text{H}_2^-$ potential curves, vibrational energy levels are found which can be compared directly with experimental results to identify positively the resonances seen experimentally.

### 1.7 Layout of the thesis

In chapter 2, the adiabatic molecular R-matrix theory of electron-molecule scattering is introduced. The computer codes used to implement the theory (written by the UK Molecular R-matrix group and additional codes written during the course of this work) are described.

Chapter 3 describes the utilisation of the codes for the system under consideration here, electron–$\text{H}_2$ scattering. The calculations are considerably complicated by the fact that they must be performed over a range of bond lengths and the various tests and optimizations and other adjustments that this necessitates are outlined.

In chapter 4, resonances and the parameterizing of resonances are discussed. The time-delay matrix method of fitting resonances is introduced and compared with the eigenphase sum method which has been used commonly in the past.

Chapter 5 is the main results chapter and describes all the resonances found for the lowest eight total symmetries as a function of bond length. Parental assignments are made and the resonances vibrational series compared with previous experiment. The phenomena of multiple parent states of resonances and parent state swapping of resonances as a function of bond length are noted.

In chapter 6, these phenomena are explored in detail. It is shown how they can explain many of the difficulties encountered by experimentalists in assigning parent states to resonances and in fitting standard potential curves to experimental data.

In the conclusion (chapter 7), the results are summarised and suggestions for improvements to the calculation are given. Possible future directions for the work are described.
Chapter 2

Adiabatic molecular R-matrix theory and implementation

In the first half of this chapter, the theory behind the adiabatic molecular R-matrix method is introduced. In the second, the UK molecular R-matrix group computer codes developed to utilize the method are described.

2.1 Overview

Adiabatic R-matrix theory is based on the splitting of configuration space into two regions by a spherical R-matrix boundary at \( r = a \) centred at the molecular centre of mass (figure 2.1). The boundary is placed so that the inner region just contains the electronic charge distribution of the target molecule. The contributions dominating the Hamiltonian are different in the two regions.

In the inner region \((r < a)\), the scattered electron lies within the molecular charge cloud and exchange, polarization and correlation must be taken into account. The target molecule plus scattering electron behave analogously to a bound state, and rigorous quantum chemistry methods can be used to find the wavefunctions. In the outer region \((r > a)\), where exchange and correlation are negligible, the scattering electron moves in the long-range multipole potential of the target and a single-centre expansion of the wavefunction can be used.

In the inner region, a set of energy independent eigenfunctions and eigenvalues are found for the \((N+1)\) system using a close-coupling expansion. The final inner region wavefunction is a linear combination of these with the coefficients found by matching with the computed outer
Figure 2.1: Splitting of configuration space in the adiabatic model
region functions at the boundary using the R-matrix. This is a sum of quantities related to the overlap integral of the internal and external wavefunctions at the boundary and the eigenenergies of the internal states (Burke, Mackey & Shimamura 1977).

The R-matrix is propagated outwardly (Morgan 1984) until it can be matched with asymptotic solutions. Asymptotic expansion techniques (Noble & Nesbet 1984) are used to find the K-matrix (related to the asymptotic solutions of equation 1.2 and described later) from which eigenphase sums can be calculated. Physical observables such as cross sections can be derived from the T-matrix which is found trivially from the K-matrix.

The development of the R-matrix approach to electron molecule scattering is well documented by Burke & Berrington (1993).

2.2 The inner region

In the inner region, scattering energy-independent target plus scattering electron (N+1) eigenfunctions are found by diagonalizing the inner region Hamiltonian using Configuration State Functions (CSFs) as the basis in a close-coupling expansion. The CSFs are built up by distributing the (N+1) electrons among orthogonalized target molecular orbitals and continuum molecular orbitals in all possible configurations within the constraints of the total symmetry under consideration.

2.2.1 Target molecular orbitals

The target molecular orbitals use a basis set of Slater-type atomic orbitals (STOs) (Slater 1960). These are of the form:

$$\psi_{ik}(n, l, m, \zeta_i) = \sqrt{\frac{(2\zeta_i)^{2n+1}(2n)!}{2^n}} r_{k}^{n-1} e^{-\zeta_i r_{k}} Y_{lm}(\hat{r}_{k})$$

where $i$ is the orbital index, $k$ is the nuclear centre index, $n$, $l$ and $m$ have their usual meanings, $\zeta_i$, the orbital exponent, can be varied to provide optimum representation, and the $Y_{lm}$ are complex spherical harmonic functions.

The target molecular orbitals, $\gamma_i$, are linear combinations of these atomic orbitals (LCAO),

$$\gamma_i = \sum_{l} D_{li} \psi_{l},$$

with the coefficients $D_{li}$ found through a self-consistent field (SCF) or Hartree-Fock calculation (see, for example, Bransden & Joachain (1983)).
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The electrons are placed in certain combinations of these target molecular orbitals multiplied by spin functions to produce configuration state functions (CSFs) \( \phi_i^N \) of different total symmetries. In the case of \( \text{H}_2 \), as it is a small molecule, all possible combinations can be used. For larger molecules, the number of configurations is too great for all of them to be considered and only certain combinations are chosen. The target molecular wavefunctions \( \psi_i^N \) are linear combinations of all the CSFs of the wavefunction's symmetry in a configuration interaction (CI) expansion.

\[
\psi_i^N = \sum_i c_{i\ell} \phi_i^N.
\]  

(2.3)

The coefficients \( c_{i\ell} \) are found by diagonalizing the \( N \)-electron target Hamiltonian matrix given by

\[
< \phi_i^N | H_N | \phi_j^N >,
\]  

(2.4)

using the configuration state functions as a basis.

2.2.2 Continuum molecular orbitals

The target molecular orbitals are supplemented with a set of continuum orbitals which describe the scattering electron in a partial wave expansion (Salvini & Burke 1984). These are centred on the centre of mass of the molecule and take the form:

\[
\eta_{i\ell}(r_G) = \frac{1}{r_G} u_{i\ell}(r_G) Y_{l,m}(\hat{r}_G)
\]

(2.5)

where the \( Y_{l,m} \) are complex spherical harmonics and the \( u_{i\ell} \) are effective atomic orbitals found by solving the model, single channel scattering problem:

\[
\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2V(r) + k_i^2 \right] u_{i\ell}(r) = 0
\]

(2.6)

subject to the boundary condition

\[
u_{i\ell}(0) = 0
\]

(2.7)

and the logarithmic boundary condition

\[
\frac{1}{u_{i\ell}} \left. \frac{du_{i\ell}}{dr} \right|_{r=a} = b.
\]

(2.8)

In equation 2.6, \( k_i^2 \) are the eigenenergies in Rydbergs, \( V_0 \) is an arbitrary potential and \( b \) is an arbitrary constant taken to be zero in this work.

Since only a finite number of terms can be used in the expansion of the R-matrix, the artificial boundary condition 2.8 necessitate a correction to the R-matrix known as the Buttle
correction which is added to the diagonal elements of the matrix (Buttle 1982). It is discussed further in section 2.2.4.

The continuum functions may be Lagrange orthogonalized to several of the target molecular orbitals (Tennyson, Burke & Berrington 1987) and then all the orbitals are Schmidt orthogonalized. The final continuum orbitals are therefore of the form:

$$
\xi_j(r_G) = \sum_i \frac{1}{r_G} u_{ij}(r_G) Y_{i,m_i}(\hat{r}_G) + \sum_i \rho_i A B_{ij} + \sum_i \rho_i B C_{ij}
$$

where $A$ and $B$ are the two nuclear centres.

### 2.2.3 Inner region (N+1) eigenfunctions

The inner region scattering energy-independent eigenfunctions of the target molecule plus scattering electron system are represented by:

$$
\psi_{k}^{N+1} = A \sum_{I} \psi_{I}^{N} (X_1, \ldots, X_N) \sum_{j} \xi_{j}(X_{N+1}) a_{I,jk} + \sum_{m} \chi_{m}(X_1, \ldots, X_N, X_{N+1}) b_{mk},
$$

where $A$ is the anti-symmetrization operator, $X_n = (r_n, \sigma_n)$ with $r_n$ the spatial coordinate and $\sigma_n$ the spin state of the $n^{th}$ electron. $\xi_j$ is a continuum molecular orbital spin-coupled with the scattering electron.

The first summation runs over CI target states. It accounts for one electron in a continuum state with the remaining electrons in a target state, known as a ‘target+continuum’ configuration.

The second term summation runs over configurations $\chi_m$ in which all the electrons are placed in target molecular orbitals and are known as $L^2$ functions. This provides a relaxation of orthogonality conditions introduced by the orthogonalization of the continuum orbitals to the target orbitals and accounts for polarization and correlation. Scattering calculations with larger molecules cannot use full CI due to computational limitations. This complicates the situation for the $L^2$ functions in these cases and there are different types of $L^2$ functions depending on whether the electron is placed in unoccupied virtual orbitals or in occupied orbitals (Gillan, Tennyson & Burke 1995).

The coefficients $a_{I,jk}$ and $b_{mk}$ are found through diagonalization of the relevant Hamiltonian matrix. This is constructed by first finding the individual matrix elements appropriate to the target configurations $\phi_i^N$ of which the CI target states $\psi_l^N$ are a summation (equation 2.3). These are then combined together using the coefficients of the target configurations $c_{i,l}$ calculated in the CI calculation, in a step known as the CI contraction.
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The Hamiltonian matrix elements can be divided into three groups: i) elements between two target+continuum configurations, ii) elements between a target+continuum configuration and an \( L^2 \) configuration and iii) elements between two \( L^2 \) configurations. Clearly no reduction in matrix size will be made by the CI contraction for case iii), but considerable savings are made for i) with smaller savings for ii) (Tennyson 1996a).

In early R-matrix calculations (such as those of Branchett & Tennyson (1990), Branchett, Tennyson & Morgan (1990), Gillan, Noble & Burke (1988)), a problem arose at this point due to inconsistencies in the phase of CI coefficients. The signs of each of the coefficients of the target CI expansion (the \( c_{il} \) in equation 2.3) obtained explicitly when generating the target \( \psi_i^N \) can differ from those obtained implicitly when generating the \((N+1)\) eigenfunctions \( \psi_k^{N+1} \) (Tennyson 1997). The most likely reason for this is the ordering of spin-orbitals within a configuration. The ALCHEMY configuration generator (Liu & Yoshimine 1981), adapted for use in the UK R-matrix codes and used here, orders by symmetry and index. For \( \text{H}_2 \) (\( D_{\infty h} \) symmetry) this ordering is \( 1\sigma_g, 2\sigma_g, 1\sigma_u, 2\sigma_u, ..., 1\pi_u, 2\pi_u, ..., 1\pi_g, 2\pi_g, ... etc. \)

Tennyson (1997) considered an \( \text{H}_2 \) target of \( ^1\Pi_u \) symmetry of which two typical configurations are \( 1\sigma_g 1\pi_u \) and \( 1\sigma_u 1\pi_g \). If the total \((N+1)\) symmetry is \( ^2\Sigma^+ \), the appropriate \((N+1)\) configurations would be \( 1\sigma_g 1\pi_u j\pi_u \) and \( 1\sigma_u 1\pi_g j\pi_u \) with \( j \) denoting the index of a continuum orbital. The first configuration is in the correct spin-orbital ordering but the second needs to be rewritten as \( 1\sigma_u j\pi_u 1\pi_g \). This interchange causes a change of sign in the Slater determinant and hence an inconsistency with the target CI coefficient.

This problem was tackled in the early part of this project by using a dummy continuum electron in an \((N+1)\) calculation immediately following the target CI calculation. All integrals related to this electron were set to zero so that the \((N+1)\) calculation simply reproduced the target CI vectors but with the necessary sign changes to particular coefficients that would make them consistent with the real \((N+1)\) calculation (Gillan 1994, Orel, Rescigno & Lengsfield III 1991).

However, this method is inefficient as it requires a repeat diagonalization of the target Hamiltonian. It also does not ensure that the sign of off-diagonal transition moments in the outer region is the same as the implicit sign in the internal region which can lead to problems (Tennyson 1997). A new solution has been realized by Tennyson (1997) which is based on the analysis of configurations. When an \((N+1)\) configuration is generated, a phase factor is calculated for that configuration by finding the number of swaps required to reorder the spin-orbitals correctly. This is then multiplied by the relevant coefficients. This is the method used for all the calculations reported here.
Chapter 2: Adiabatic molecular R-matrix theory and implementation

Sec. 2.2

Since the target molecular functions are considered zero at the distance of the R-matrix boundary, the logarithmic boundary condition on the continuum functions (equation 2.8) also holds for the (N+1) total wavefunction, i.e.:

\[ \frac{1}{\psi^{N+1}} \frac{d\psi^{N+1}}{dr} \bigg|_{r=a} = b \]  \hspace{1cm} (2.11)

This logarithmic boundary condition has the effect of making the Hamiltonian hermitian by cancelling out surface terms which arise from the scattering electron kinetic energy operator (Oberoi & Nesbet 1973, Oberoi & Nesbet 1975).

As an alternative, the Hamiltonian can be made hermitian through the use of the Bloch operator, \( L_{N+1} \) (Block 1957) which can be added to the Hamiltonian and which cancels the surface terms. The Bloch operator is of the form:

\[ L_{N+1} = \frac{1}{2} \sum_{i=1}^{N+1} \sum_{j} |\psi^N_j \rangle Y_{l_j m_j} \langle \hat{r}_i | \delta (\hat{r}_i - a) \left( \frac{d}{dr_i} - \frac{b}{r_i} \right) < \psi^N_j Y_{l_j m_j} (\hat{r}_i) | \]  \hspace{1cm} (2.12)

The coefficients in 2.10 are found by diagonalization of the modified inner region (N+1) Hamiltonian,

\[ < \Omega^N_{p} | H_{N+1} + L_{N+1} | \Omega^N_{p'} > \]  \hspace{1cm} (2.13)

where the \( \Omega^N_{p} \) are the basis configurations, to obtain the inner region (N+1) eigenfunctions \( \psi^N_{K} \).

2.2.4 Generation of the R-matrix

Once the energy-independent inner region eigenfunctions have been found, it is necessary to find the energy dependent R-matrix in order to match the inner and outer region wavefunctions.

The general Schrödinger equation for the system is

\[ H_{N+1} |\Psi >= E |\Psi >, \]  \hspace{1cm} (2.14)

where \( \Psi \) is the total (N+1) wavefunction and \( E \) is the total energy of the system, incorporating the scattering energy. By adding and subtracting the operator \( L_{N+1} \) and rearranging this becomes:

\[ (H_{N+1} + L_{N+1} - E) |\Psi >= L_{N+1} |\Psi > \]  \hspace{1cm} (2.15)

By multiplying each side by the inverse of the left hand side operator this becomes:

\[ |\Psi >= (H_{N+1} + L_{N+1} - E)^{-1} L_{N+1} |\Psi > . \]  \hspace{1cm} (2.16)
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Remembering that the inner region \( \psi_{k}^{N+1} \) are eigenfunctions of the \((H_{N+1} + L_{N+1})\) Hamiltonian with eigenvalues \( e_k \), the inverse operator can be rewritten as an expansion over these functions to obtain

\[
|\Psi> = \sum_{k} \frac{\psi_{k}^{N+1} <\psi_{k}^{N+1}|L_{N+1}|\Psi>}{(e_k - E)}. \tag{2.17}
\]

The reduced radial functions \( F_i \) and the surface amplitudes \( f_{ik} \) are defined as:

\[
F_i(r) = <\psi_{i}^{N}Y_{l_{i}m_{i}}|\Psi>, \tag{2.18}
\]

\[
f_{ik} = <\psi_{i}^{N}Y_{l_{i}m_{i}}|\psi_{k}^{N+1}>, \tag{2.19}
\]

where \( <\psi_{i}^{N}Y_{l_{i}m_{i}}| \) are channel functions. By substituting in the Bloch operator (equation 2.12), it can be shown that at the R-matrix boundary (Gillan et al. 1995):

\[
F_i(r) = \sum_{k} f_{ik}(E) \left( \frac{dF_j}{dr} - bF_j \right)_{r=a} \tag{2.20}
\]

in which the R-matrix is defined as

\[
R_{ij}(E) = \frac{1}{2a} \sum_{k} f_{ik}(a)f_{jk}(a) \frac{1}{e_k - E} \tag{2.21}
\]

The summation in equation 2.21 is over the surface amplitudes \( f_{ik} \) and hence in turn over the \((N+1)\) eigenfunctions \( \psi_{k}^{N+1} \). Clearly it is necessary to truncate this expansion at some point to include only a finite number of terms \( N_l \) for each value of \( l \). The error from this truncation is exacerbated by the boundary conditions at the R-matrix sphere given in equations 2.7 and 2.8 and is known as the Gibbs phenomenon (Gillan et al. 1995). As mentioned previously, in order to correct at least partially for this, a ‘Buttle correction’ (Buttle 1982, Shimamura 1978) is added to the diagonal terms of the R-matrix and takes the form:

\[
B_{ii}(E) = \frac{1}{2a} \sum_{i=N_{l_{i}}+1}^{\infty} \frac{|u_{ii}(a)|^2}{\frac{1}{2}k_{ii}^2 - E} \tag{2.22}
\]

where \( k_{ii}^2 = 2e_{ki} \) with \( u_{ii} \) and \( e_{ki} \) the eigenvector and eigenvalues respectively of equation 2.6.

The Buttle correction is evaluated as part of the continuum numerical function generation.

### 2.3 Inner region program modules

The UK Molecular R-matrix scattering package has been developed over many years by a variety of people. The inner region code was originally based on the quantum chemistry package ALCHEMY (McLean 1971, Noble 1982a) developed by IBM in the 1970s with many modifications to make it suitable for the scattering problem.
Figure 2.2: Flow diagram of the inner region target state calculation. Red arrows indicate input required by the scattering calculation, green arrows indicate input required by the outer region codes.
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Sec. 2.3

**Figure 2.3:** Flow diagram of the inner region (N+1) scattering calculation. Green arrows indicate input required by the outer region codes.
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The flow diagram for the inner region calculation of the target is shown in figure 2.2 and for the (N+1) calculation in figure 2.3

**INTS** is the integral generator that produces 1-electron, 2-electron and property integrals. It has been modified to restrict the range of the radial coordinate to within the R-matrix boundary (Noble 1982a). Its first task is in providing the necessary integrals to be used by the **SCF** module in setting up the target. It is later used to provide the integrals for the (N+1) calculation.

**SCF** performs a self consistent field (Hartree-Fock) calculation to produce target orbitals \( \gamma_i \) (equation 2.2), from linear combinations of atomic orbitals.

The module **NUMBAS** (Salvini & Burke 1984) generates continuum orbitals of the form of equation 2.5 in accordance with equations 2.6, 2.7 and 2.8. It is possible to specify different potentials \( V_0 \) either by inputting a potential or by allowing the module to work out a potential from the SCF vectors. The Buttle correction (equation 2.22) is also calculated by this module although for file handling reasons it is passed down to be outputted by **MOS**.

The module **MOS** initially takes as its input the target orbitals from **SCF** to output molecular orbitals used in the target CI calculation. In the scattering calculation it takes both the target orbitals and the continuum orbitals from **NUMBAS** and outputs orthogonalized molecular orbitals. It has options to Schmidt orthogonalize all the orbitals and to Lagrange orthogonalize the continuum orbitals to a specified number of target orbitals (Tennyson et al. 1987). The purpose of the latter is to eliminate linear dependence between the continuum and the target orbitals. Each time a Lagrange orthogonalization is performed, the linear combinations of continuum orbitals most linearly dependent on a target orbital are removed. **MOS** also computes the amplitudes of the continuum orbitals on the R-matrix boundary.

Module **TRANS** takes atomic integrals produced by **INTS** and multiplies them by combinations of molecular orbital coefficients to transform them into molecular integrals which are required for the construction of the Hamiltonian.

The module **CONGEN** generates configuration state functions (CSFs) with appropriate spin and symmetry couplings. The molecular orbitals to be included are hand picked by the user. It is used initially to produce CSFs for the target and then later for the target plus scattering electron (N+1) system. When a CSF is generated, the module also computes a phase factor to keep the phases between the target and (N+1) system consistent (Tennyson 1996a). **CONGEN** has been adapted for scattering calculations to allow explicit coupling of the continuum electron to individual target states (Noble 1982b).

**SCATCI** (Tennyson 1996a) performs the configuration interaction calculation first for the
target and then for the (N+1) system. It takes the configurations generated by CONGEN and the molecular integrals supplied by TRANS to build up the Hamiltonian matrix. In the case of the (N+1) system, the matrix is first contracted using the target eigenstate vectors. For both the target and (N+1) system, the matrix is then diagonalized to find all the eigenvectors and eigenvalues.

The module DENPROP (Gillan 1992) calculates dipole and quadrupole moments of the target from the target CI vectors produced by CI and the property integrals produced by INTS. The moments are used in the outer region calculation.

### 2.4 The outer region

As mentioned in the overview, in the outer region, exchange and correlation between the scattering electron and the target electrons are ignored. The wavefunction is expanded in a close-coupling expansion over target states (Gillan et al. 1995):

\[
\Psi = \sum_i \hat{\phi}_i(x_1 ... x_N, \sigma_{N+1})r_{N+1}^{-1} F_i(r_{N+1}) Y_{i,m_i}(\hat{r}_{N+1}),
\]

(2.23)

where \(x_j=(\hat{r}_j, \sigma_j)\), the position and spin of the \(j\)th target electron, the functions \(\hat{\phi}_i\) are formed by coupling the scattering electron spin \(\sigma_{N+1}\) with the target state \(\phi_i\), and the \(F_i\) are reduced radial wavefunctions.

Substituting this equation into the Schrödinger equation and projecting onto the channel functions \([\hat{\psi}_i Y_{i,m_i}]\) in a similar procedure to that used in the inner region, gives a set of coupled, homogeneous differential equations for \(F_i\):

\[
\left(\frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2\right) F_i(r) = 2 \sum_j V_{ij}(r) F_j(r),
\]

(2.24)

where \(V_{ij}\) is the potential matrix in the outer region which describes the coupling between the channels \(i\) and \(j\) and

\[
k_i^2 = 2(E - \epsilon_i),
\]

(2.25)

with \(\epsilon_i\) the eigenenergy of target state \(\phi_i\) and \(E\) the total energy of the system.

The reduced radial functions \(F_i\) of equation 2.23 in the limit \(r \to \infty\) have asymptotic solutions \(j\) for each open channel \(i\) of the form:

\[
F_{ij} \sim \frac{1}{\sqrt{k_i}} \left( (\sin(k_ir - \frac{1}{2}l_i\pi)\delta_{ij} + \cos(k_ir - \frac{1}{2}l_i\pi)K_{ij}) \right)
\]

(2.26)
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and \( F_{ij} \sim 0 \) for closed channels. Equation 2.26 defines the K-matrix elements \( K_{ij} \), which contain all the scattering information.

Equation 2.24 is solved by first propagating the R-matrix (Baluja, Burke & Morgan 1982, Morgan 1984) from the boundary to the asymptotic region (in this work taken as \( r = 150 \ a_0 \)). Gailitis (1976) asymptotic expansion techniques are then used to solve for the outer region functions (Noble & Nesbet 1984).

The eigenphase sum, \( \delta \), which can be used for the detection and parametrization of resonances can be found directly from the diagonalized K-matrix \( K_{ii}^D \):

\[
\delta = \sum_i \arctan(K_{ii}^D), \tag{2.27}
\]

where the sum is over the open channels.

The scattering matrix \( S \) is a transformation of the K-matrix,

\[
S = (1 + iK)(1 - iK)^{-1}. \tag{2.28}
\]

The time-delay matrix \( Q \) is related to the energy derivative of the S-matrix (Smith 1960):

\[
Q = -i\hbar S^* \frac{dS}{dE}. \tag{2.29}
\]

where \( S^* \) is the complex conjugate of \( S \).

The time-delay, which is also used for parametrizing resonances, is then the largest eigenvalue of the Q-matrix. Further details of both the time-delay and eigenphase sum can be found in chapter 4.

The T-matrix which is formed trivially from the S matrix, \( T = 1 - S \), can be used to derive physical observables such as integral and differential cross sections. For example, the integral cross section for excitation from state \( i \) to \( i' \) is (Burke 1982):

\[
\sigma(i \rightarrow i') = \frac{\pi}{k_i^2} \sum_S \frac{(2S + 1)}{2(2S_i + 1)} \sum_{\Lambda \ell' r} |T_{i' \ell' r} S_i \rangle |^2, \tag{2.30}
\]

where \( S_i \) is the spin angular momentum of the \( i_{th} \) target state, \( S \) is the total spin angular momentum and \( \Lambda \) is the total electronic angular momentum projected onto the molecular axis.

2.5 Outer region program modules

A flow diagram for the outer region codes used in this work is shown in figure 2.4. Unless otherwise stated, the codes have been developed by Morgan.
Figure 2.4: Flow diagram of the outer region scattering calculation. See text for details.
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**INTERF** provides the interface between the inner and outer regions. It takes the boundary amplitudes and CI vectors generated in the inner region to construct the surface amplitudes $f_{ik}$ of equation 2.18 and adds the Buttle correction to the diagonal of the R-matrix. It also passes on target and channel data.

**RSOLVE** takes the output of **INTERF** and uses subroutines RPROP (Baluja et al. 1982, Morgan 1984) to propagate the R-matrix to the asymptotic region and CFASYM (Noble & Nesbet 1984) to solve the wavefunctions in this region and hence to calculate K-matrices.

**EIGENP** takes the K-matrices and produces eigenphase sums using equation 2.27.

**RESON** (Tennyson & Noble 1984) is a program for automatically detecting and parameterizing resonances by fitting a standard Breit-Wigner (1936) form to the eigenphase sum. It is described further in chapter 4.

**TIMEDEL** was written for this work to calculate the time-delay and is documented in appendix A. This was needed for the parameterization of difficult resonances. The evaluation of the Q-matrix (equation 2.29) requires the energy derivative of the S-matrix. **TIMEDEL** uses routines in **RSOLVE** to find the K-matrix (and through transformation, the S-matrix) at energies $E + \frac{\Delta E}{2}$ and $E - \frac{\Delta E}{2}$ where $E$ is the scattering electron energy and $\Delta E$ is an arbitrarily small energy separation.

The Q-matrix is calculated and then diagonalized to produce its eigenvectors and eigenvalues. The largest eigenvalue is found and identified as the time-delay. The branching ratios of decay into the continuum of different target states are given by the square of the relevant component of the corresponding eigenvector. The module outputs the time-delay and branching ratios as a function of energy.

**FITLOR** fits a Lorentzian form to a hand-picked segment of the time-delay outputted from **TIMEDEL**. More sophisticated versions are currently under development and should automatically detect and parameterize resonances. The time-delay method for fitting resonances is more fully described in chapter 4.

**TMATRIX** transforms K-matrices into T-matrices. For adiabatic vibrational calculations, it has the option to average a set of T-matrices at different bond lengths over vibrational functions which are inputted separately, although this has not been used in the present work.

The T-matrices (vibrationally averaged or otherwise) can then be used by modules such as **IXSECS** and **DCS** (Malegat 1990) which calculate integral and differential cross sections respectively.
Chapter 3

Electron–H₂ calculations over a range of bond lengths

In this chapter, the general methods of the previous chapter are discussed for the specific case of the electron–H₂ collision calculations performed in this work. Various optimizations and tests undertaken to allow the most accurate calculation given limited computing power are described, as are the difficulties encountered and overcome in the implementation of the calculation.

3.1 Introduction

The previous chapter gave an overview of the theory and implementation of a general scattering calculation using the R-matrix method. As described in chapter 1, the purpose of this work is to examine the many resonances below 13 eV, and in particular the series a to e resonances described by Comer & Read (1971) and Schultz (1973). These resonances are known to be associated with the low-lying H₂ target states and in this calculation, the first seven states are explicitly considered: X ¹Σ⁺, E, F ¹Σ⁺, B ¹Σ⁺, b ³Σ⁺, a ³Σ⁺, c ³Π, C ¹Π. In order to include a reasonable number of vibrational levels, calculations were performed over a range of bond lengths from 0.8 to 4.0 a₀ on a grid of 0.1 a₀.

Extending calculations from a single bond length to a range of bond lengths complicates matters considerably. The basis functions that represent the target and continuum orbitals may work well at one particular bond length but might be very poor at another. The phases of the molecular orbital vectors are arbitrary and can jump around from bond length to bond length.
Their ordering can also change with bond length as their energies cross. These will both affect certain vibrational calculations. Additionally, at different bond lengths, the effects of higher target states not considered in the calculation might be significant.

To ensure continuity of the quality of the calculations across bond length, a great deal of time was spent on testing and optimizing the calculation for the range considered.

### 3.2 Choice of basis STOs

The quality of the calculation rests to a large part on the quality of the target, and hence on the quality of the basis set used to represent it. Given a basis set, it is possible to determine the errors in target state energy as a function of bond length by comparing the energies obtained using that basis with ‘exact’ energies. These ‘exact’ energies are taken from the following quantum chemistry structure calculations which used very large basis sets: $X^1\Sigma^+_g$, $b^3\Sigma^+_u$ from Kolos & Wolniewicz (1965); $B^1\Sigma^+_g$, $C^1\Pi_u$ from Wolniewicz & Dressler (1988); $E,F^1\Sigma^+_g$ from Wolniewicz & Dressler (1985); $C^3\Pi_u$ from Kolos & Rychlewski (1977); $a^3\Sigma^+_g$ from Kolos & Rychlewski (1995).

As mentioned previously, the basis used in this calculation is a set of Slater-type orbitals (STOs) of the form shown in equation 2.1. The criteria determining the choice of the STOs are that the basis be small enough to be manageable but flexible enough to be able to represent the target sufficiently at all the bond lengths used. The set taken as a starting point was that used by Branchett, Tennyson & Morgan (1991) which has 13 STOs and is shown in table 3.1.

This set had been optimized at the SCF level for the lowest seven target states at the single equilibrium geometry of $R = 1.4 \text{ a}_0$. The energy errors using this basis are shown in figure 3.1a.

The task of optimization here is a more complicated one, and requires the optimization of the energy at the CI level over a range of 33 bond lengths for all seven target states.

Any rigorous mathematical method for optimizing the 13 exponents of the basis set for all the different target symmetries over all the internuclear separations would be impossible if the $\zeta$ variables are taken as coupled. The first assumption is thus that each $\zeta$ exponent can be optimized independently of the rest. Even assuming this, changing the value can improve the representation at certain bond lengths but worsen it at others. A degree of arbitrariness is also therefore required in deciding the optimum value.
Chapter 3: Electron–H₂ calculations over a range of bond lengths

Sec. 3.2

Figure 3.1: Error in the target state energies as a function of bond length using a) the original basis set of Branchett et al. (1991) and b) the basis set optimized and used in this calculation.
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<table>
<thead>
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<th>Exponent</th>
<th>Orbital</th>
<th>Exponent</th>
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<td>1sσ₂ₚ</td>
<td>1.081</td>
</tr>
<tr>
<td>2sσ₂ₕ</td>
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<td>2sσ₂ₚ</td>
<td>0.800 → 0.700</td>
</tr>
<tr>
<td>2sσ₂ₚ</td>
<td>0.600 → 0.500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2pσ₂ₕ</td>
<td>1.820 → 1.300</td>
<td>2pσ₂ₚ</td>
<td>1.820</td>
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</tr>
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<td>3dπ₂ₕ</td>
<td>1.511</td>
<td>3dπ₂ₕ</td>
<td>2.470</td>
</tr>
</tbody>
</table>

Table 3.1: The ζ exponents of the STOs used by Branchett et al. (1991) with the changes made for this calculation in bold. The orbitals are denoted g or u to show the symmetry of the two-centred orbitals they are used to create.

Taking each STO in turn, a series of target CI calculations was performed, varying the ζ exponent of the STO about its original value and the internuclear separation over the range under consideration. The target threshold energies from these calculations were compared with the ‘exact’ values to give an energy error of the target thresholds for every value of ζ at each internuclear separation. These were then plotted for all eight total symmetries. From each graph, the ζ which best minimises the energy for that symmetry can be found.

In most cases, changing a particular ζ affected only one target state and so the best value for that target state could be taken. However, there were problems with interdependency between two states. For example, figures 3.2a and 3.2b show plots of the effect of varying the ζ of the 2sσ₂ₚ STO on the energy error for the B ¹Σ⁺ₚ and b ³Σ⁺ₚ symmetries respectively. The first graph would suggest an optimum exponent of around 0.60 whereas for the second graph, a value of around 0.75 is preferable. Other symmetries are also affected.

In order to combat this problem, an attempt was made to add an extra, diffuse 2sσ₂ₚ STO into the basis set. Unfortunately, the two 2sσ₂ₚ orbitals were too similar and could not be orthogonalized satisfactorily. The overlap integral between the functions was too great and despite extensively varying the exponents, it was not possible to eradicate the linear dependence. The extra STO was dropped and a compromise value of ζ = 0.65 for the 2sσ₂ₚ STO was used.

It was found that the B ¹Σ⁺ₚ and E,F ¹Σ⁺ₕ symmetries were considerably improved by reducing the exponent of the 2pσ₂ₕ orbital from 1.82. However the exponent could not be reduced to less than 1.30 as it would have worsened the ground state energy to too great an extent.

In order to stop the orbitals from leaking out of the R-matrix boundary, it was necessary to prevent them from becoming too diffuse. The 2sσ₂ₕ, although it gave better values for the
Figure 3.2: Error in energy of the a) $\Sigma^+_u$ excited state and b) $\Sigma^+_u$ excited state as a function of bond length and of the $\zeta$ exponent of the $2s\sigma_u$ STO
energy of the E,F \( 1\Sigma_g^+ \) symmetry at all geometries when its exponent was lowest, could not be allowed a value of \( \zeta \) less than 0.50.

The final basis set used is given, along with the original, in table 3.1. The errors in the target state energies using the final basis are shown in figure 3.1b.

### 3.3 Continuum molecular orbitals

In previous, fixed-nuclei, calculations, the arbitrary potential \( V_0 \) used in the calculation of the continuum orbitals (equation 2.8) has often been taken as an expansion of the isotropic parts of the SCF wavefunction potential (e.g. Branchett et al. (1990), Gillan, Nagy, Burke, Morgan & Noble (1987)). However, in this calculation, \( V_0 \) was taken as zero, resulting in bond length-independent continuum functions. At the equilibrium bond length of 1.4 \( \text{a}_0 \), there was a negligible difference in the results of calculations using the different orbital sets suggesting that the numerical flexibility of the functions was, in this case, sufficient to cope with the reduced physicality of the model.

The effect of changing the number of continuum functions was also tested. Increasing the maximum eigenenergy of the orbitals increases the number of possible continuum functions, the number of available channels and hence the size of the calculation. When this energy was increased from 5 eV to 8 eV there was a large increase in the total number of continuum orbitals from around 270 to 370 although only a subset of these orbitals are used for each total symmetry. The increased number of orbitals only had a very small effect on the final eigenphase sum (see figure 3.3).

In order to test the effect of increasing the maximum allowed eigenenergy to a region in which there is resonance activity, two state calculations (X \( 1\Sigma_g^+ \) + B \( 1\Sigma_u^+ \)) with maximum values of 6 eV and 12 eV were performed. As will be seen later, there is a resonance of \( 2\Sigma_g^+ \) symmetry at around 10 eV. Figure 3.4 shows that increasing the maximum value makes very little difference to the eigenphase sum even in a resonance region.

A maximum energy of 6 eV (with 307 orbitals made up of 58 \( \sigma_g \), 42 \( \sigma_u \), 42 \( \pi_u \), 42 \( \pi_g \), 42 \( \delta_g \), 27 \( \delta_u \), 27 \( \phi_u \) and 27 \( \phi_g \) orbitals) was taken as a compromise.

The continuum orbitals are initially Lagrange orthogonalized to several target molecular orbitals to alleviate linear dependence problems. This procedure in effect removes continuum orbitals that are too close to target molecular orbitals. In this calculation the continuum orbitals were orthogonalized to the lowest two \( \sigma_g \), one \( \sigma_u \), two \( \pi_u \) and one \( \pi_g \) target orbitals.
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Sec. 3.4

Figure 3.3: Effect of increasing the maximum allowed eigenenergy (and hence the number) of the continuum orbitals from 5 (solid) to 8 eV (dashed)

Figure 3.4: Effect of increasing the maximum allowed eigenenergy (and hence the number) of the continuum orbitals from 6 (solid) to 12 eV (dashed) in a resonance region
3.4 Effect of increasing the number of target states

Previous coupled state calculations have been performed only at the H\(_2\) equilibrium bond length. At this bond length there is a gap in energy between the first seven and the next highest energy level of around 1.6 eV. However, at the extremes of the bond lengths considered in this work, the higher target states are much nearer in energy. It was therefore decided to determine the effects of increasing the number of target states included in the calculation to thirteen. It was found that going up in energy, the representation of the target states became more and more unphysical. This can be put down to the fact that the STO basis set is very compact and has been optimized for the first seven states. To model the higher states properly, a larger basis set including more diffuse functions would be required. These diffuse functions would be likely to leak out of the R-matrix sphere and require such an increase in its size to contain the functions that many of the efficiencies gained from using the R-matrix method would be lost.

The effect of increasing the number of target states to 13 on the \(^2\Sigma_g^+\) symmetry eigenphase sum up to 13.5 eV can be seen in figure 3.5. At the equilibrium bond length of 1.4 a\(_0\), as expected, the additional states made very little difference. At a bond length of 4.0 a\(_0\), it began to make a difference at energies over around 10 eV. Given the unphysicality of the extra states and since the energy region at the bond length where the effect is important is not sampled, it was decided to leave the extra states out of the calculation.

3.5 Phase matching and smoothing over geometries

Performing scattering calculations across a range of bond lengths introduces additional vector consistency complications not seen in the single fixed nuclei calculation. These are of four types. Firstly, the phase of the SCF vectors (virtual and occupied) are arbitrary and their ordering can change due to energy crossing. Secondly, the phase of the molecular orbitals (from which boundary amplitudes are calculated) are arbitrary due to Lagrange orthogonalization and again the ordering can change due to energy crossing. Thirdly, the phases of the target CI vectors are arbitrary to a sign and, fourthly, the phases of the (N+1) CI vectors are arbitrary.

In order to perform non-adiabatic vibrational calculations, it is necessary to ensure that the sign of the phase of all these vectors at neighbouring bond lengths remains consistent and that the SCF and molecular orbital vectors vary smoothly with bond length, with no swapping of order.

The molecular orbital vectors were smoothed by a new subroutine SANIT written into the
Figure 3.5: Effect of increasing the number of target states in the calculation from 7 (blue) to 13 (red) for a) the equilibrium bond length $R = 1.4 \ a_0$ and b) the most extreme bond length used in this calculation, $R = 4.0 \ a_0$. 
MOS module, replacing an earlier routine which smoothed only phases (Sarpal, Tennyson & Morgan 1994). The SCF vectors were smoothed with a standalone program using the same SANIT routine.

As the bond length is changed by a small amount, all the vectors will change by only a small amount, but the positions of the new vectors and/or their phase might have changed. Starting with the equilibrium bond length \( R = 1.4 \ a_0 \) as the original set, the new (next bond length) vector set is smoothed to the original set. It is then taken as the original set for the next smoothing, i.e. the \( R = 1.5 \ a_0 \) is smoothed to the 1.4, then the 1.6 is smoothed to the 1.5 etc.

The smoothing is executed by taking the scalar product of each of the vectors in a new (next bond length) set with an original vector to identify the new equivalent vector. The scalar product between an original vector and its equivalent new vector will be approximately 1 (or -1 in the case of a phase swap) and the original vector with all non-equivalent vectors should be approximately zero.

Once the new equivalent vector has been indentified, it is then replaced in the same position within the new set as the original vector and a sign change made if necessary.

For this calculation, however, a problem was encountered. At the grid separation of 0.1 \( a_0 \), it was found for the SCF vectors that the scalar product of neighbouring bond length equivalent vectors was often very different to 1 and between neighbouring non-equivalent vectors was far from zero. This was particularly true if two target states crossed between grid points. This meant it was impossible to track definitely each vector between two bond lengths. To counteract this, the sets of SCF vectors were calculated on a finer grid of 0.02 \( a_0 \), which proved sufficient to track the vectors. In the case of the molecular orbital vectors, the calculation of which requires far more computer time, a finer grid was used only when found to be necessary.

The phase of the target CI vectors is smoothed by taking the scalar product of each new vector with the equivalent old vector and swapping the sign if the product is -1 and leaving the sign if it is 1. The phase of the (N+1) CI vectors are smoothed automatically in the INTERF module.

### 3.6 Swapping of target state potential curves

A further complication arising from performing calculations as a function of bond length comes about through the swapping of target state potential curves as the bond length changes. The input to INTERF requires the matching up of the target states as they are ordered in CONGEN.
with the energy ordered target states from the target properties file. Clearly, if the target states cross in energy, the matching must change with bond length.

A UNIX routine, GETORD, was written which examines the target properties file to ascertain the order of the target states. This information is then automatically included in the input to INTERF. The routine is given in appendix B.

### 3.7 Vibrationally resolved resonances

Once a series of calculations across a range of bond lengths has been completed, resonances are parameterized using the time delay and/or eigenphase sum method (see chapter 4). From these positions it is possible to build up potential curves of these $\text{H}_2^-$ resonances.

![Figure 3.6: Error in the energy gap between ground and each of the target states](image)

The program ‘LEVEL’ (Le Roy 1996) is used to find vibrational wavefunctions from the potential curves by solving the one dimensional Schrödinger equation using the Numerov algorithm (see, for example, Smith (1971)). The eigenvalues found give the resonance vibrational levels.
Despite the optimization of the STOs, there are still small errors in the target state energy levels, due to the compact size of the basis. Figure 3.6 shows these energy gap errors derived from the 'exact' energies of the target states described in section 3.2. The error in the energy gap between the ground and excited states is particularly pertinent when comparison is to be made with the experimental results of the vibrational series.

To obtain the best \textit{ab initio} estimate, a correction to the resonance vibrational positions is made for this error. Since it was found that a resonance can be associated at different bond lengths with different, often multiple parents, at many bond lengths it is often difficult to make more than a rough estimate of the correction required. Because of this, and since in tests it was found that including a correction at all bond lengths made little difference to the vibrational spacings, it was decided to include a correction only in the absolute position as determined at the lowest point of the potential curve for each resonance.

Another method previously used to mitigate the target state energy errors (Branchett et al. 1991) involves adding a correction to the diagonal matrix elements of the (N+1) Hamiltonian. However, as the off-diagonal elements cannot be corrected, the effects of doing this are somewhat unpredictable and so this method has not been followed here.
In this chapter, different types of resonances, pseudostates of the molecule plus scattering electron system, are discussed. A new method of fitting these resonances, the time-delay method, is introduced. The method is tested for two systems: $e-H_2^+$ and $e-H_2$ and compared with the eigenphase sum method which has commonly been used in the past. Using the time-delay method, it is also possible to find the 'branching ratios', the probabilities of decay of the resonance to the continuum of each target state and it is shown how these can sometimes be useful in helping to determine the parentage of a resonance.

4.1 Resonances

When an electron collides with an atom or molecule, it is possible under certain conditions for it to be captured for a short time close to the target and form a temporary pseudostate or resonance. For this to happen, the scattering electron must find a suitable quasistationary orbit in the field of the target. This will only occur at very specific energies. Resonances can have a great effect on elastic collision, vibrational, electronic excitation, dissociation and dissociative attachment processes. These collision processes can normally proceed without the involvement of a resonance but it is possible for cross sections to be enhanced by an order of magnitude or more if there is one present.

Resonances are parameterized by an energy position and width. The more stable the resonance, the longer it lasts and, by the uncertainty principle, the narrower the width.
Chapter 4: Resonances and resonance fitting

Sec. 4.1

4.1.1 Ground state shape resonances

Resonances associated with the ground state of a molecule are due to an appreciable barrier in the effective potential caused by a combination of a centrifugal repulsive potential \( (l(l + 1)/r^2) \) and an attractive polarisation potential. On entering the region inside the barrier the electron will be trapped there for a time forming a molecule plus electron resonance until it can eventually tunnel out. They are known as shape resonances as they are caused by a particular shape in the effective potential.

Shape resonances appear a few eV above the ground state threshold and normally have short lifetimes as they can decay easily back into the ground state. They do not occur for s-waves as, in this case, \( l = 0 \).

There are well known shape resonances found in e–H\(_2\), e–N\(_2\) and e–CO collisions (Schultz 1973). The resonance in e–H\(_2\) is of \( ^2\Sigma^+_u \) symmetry and is at low energy (< 4 eV). It is very wide (up to 9 eV depending on bond length) and short-lived and hence has very little effect on the elastic cross section. However, both vibrational and rotational excitations can proceed via the resonant state and their respective cross sections are much enhanced. The resonance also plays a role in dissociative attachment of the molecule, enhancing the cross section at an energy in the region of 3.75 eV (Schultz 1973). The resonance is discussed fully in section 5.2.1.

4.1.2 Core-excited resonances

Resonances associated with excited states are known as core-excited resonances and consist of a hole in a normally occupied orbital and two electrons in normally unoccupied orbitals i.e. an excited target state with an electron in an orbit of the field produced by the excited target state. They can be of two types. The first, Feshbach (or closed-channel or Type I) resonances (Feshbach 1958, 1962) are associated with parents that exhibit a positive electron affinity and lie below their parent. They are thus prevented from decaying into their parent by energy restrictions and must decay into lower target states.

The second type, core-excited shape or Type II resonances are associated with parents of negative electron affinity and lie above their parent. These resonances share some similarities with the ground state shape resonances. They can feasibly decay into all lower target states but are normally likely to decay preferentially into their parent excited state.

In the case of scattering by positively charged molecular ions, there will be a positive electron affinity and so Feshbach type resonances are to be expected, with an infinite Rydberg
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Figure 4.1: Diagrammatic representation of a shape resonance

Figure 4.2: Diagrammatic representation of a core-excited resonance
series of resonances below the parent. For neutral molecules, Weiss & Krauss (1970) showed
that any Rydberg excited states are also likely to have positive electron affinity and, again,
Feshbach resonances would be expected. Valence excited states may have either positive or
negative electron affinity and can result in either type of core-excited resonance.

In fact, the distinction between the two types of core-excited resonance is a little over
simplified and for a molecule it is possible for a resonance to move between the two types as
the internuclear separation changes.

4.2 Fitting resonances

Resonances can often appear near or on top of a threshold which can have the effect of distorting
the resonance or of cutting off most of the characteristic form of the resonance. This
clearly makes the resonance difficult to fit. Many stable molecules, including H₂, have a forest
of excited states in the 10 eV region and this yields complicated, and often poorly understood,
resonance structures (Schultz 1973) due to the proliferation of thresholds and multiple reso-
nances.

In recent years there have been several attempts to improve on traditional methods of res-
onance fitting. Quigley & Berrington (1996) used the properties of the R-matrix method in
a procedure to fit automatically single or multiple resonance using the 'QB' method. Busby,
Scott, Burke & Noble (1996) have written a graphical user interface to interactively zoom in
on possible resonances which are then fitted using traditional methods. Spence & Scott (1996)
borrowed the 'Hough transformation' from image processing to help detect resonances. Noble,
Dör & Burke (1993) found resonance parameters by direct search of the complex S plane. The
two methods described here are the eigenphase method and the time-delay method which has
been specially developed over the course of this work.

4.2.1 Eigenphase sum method

The most common method of finding resonances is to look at the K-matrix or eigenphase
sum. Standard programs such as RESFIT (Bartschat & Burke 1986), and RESON (Tennyson
& Noble 1984) have been written for this purpose. A resonance will produce a characteristic
form in the eigenphase sum as a function of energy that can be fitted to find the position and
width of the resonance.
Hazi (1979) showed that near an isolated multichannel resonance, the eigenphase sum as a function of energy, $\Delta(E)$, satisfies the formula due to Breit & Wigner (1936):

$$\Delta(E) = \Delta_0(E) + \tan^{-1}\left(\frac{\Gamma}{2(E_0 - E)}\right)$$  \hspace{1cm} (4.1)

where $\Gamma$ is the (full) width of the resonance and $E_0$ is its position. $\Delta_0(E)$ is the sum of the background phases which is usually assumed to be a low-order polynomial.

The value of the arctan function will change approximately from zero to $\pi$ as $E$ increases through $E_0$. For example, as $E$ moves from, say, $(E_0 - 2\Gamma)$ to $(E_0 + 2\Gamma)$, the value of the function will increase by $\approx \frac{11\pi}{13}$. The position of the resonance lies at the point of inflection of the curve.

By fitting the eigenphase sum to this functional form, it should be possible to extract the resonance parameters. RESON (Tennyson & Noble 1984) is used here for this purpose.

There are three situations which can thwart this, however. The first is due to the sum of the background phases, $\Delta_0$. If the resonance is narrow, these will change little and can be set as a constant or modelled linearly. If on the other hand the resonance is a wide, short-lived resonance, then the background can vary by a large and unpredictable amount. Attempts to model this using high order polynomials often leads to unreliable solutions. Typically the position of the resonance remains reasonably stable since the background would have to vary quite wildly to affect the point of inflection greatly, but the width of the resonance is more sensitive.

Secondly, if two or more resonances overlap, the number of independent variables increases further and the results become very unreliable. Eigenphase fitting programs, such as RESON, work well for single, narrow resonances away from threshold. They tend to come unstuck, however, when trying to fit a double resonance. Under these circumstances, even the resonance positions are likely to be inaccurate.

Resonances can often appear near or on top of a threshold which can have the effect of distorting the resonance or of cutting off most of the characteristic form of the resonance. This clearly makes the resonance difficult to fit.

4.2.2 Time-delay method

The time-delay method, using the time-delay matrix originated by Smith (1960) and used by Sadeghpour, Greene & Cavagnero (1992) to study photodetachment of $H^-$, is based on the
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time-delay experienced by the electron as it interacts with the target. At resonance, the time-delay as a function of energy conforms to a characteristic shape which can be fitted to give the relevant parameters. This method affords considerable advantage and can remove or at least alleviate the problems associated with studying complicated resonance structures near thresholds.

The time-delay of a collision can be thought of classically as the difference between the total time the electron spends within a distance $R$ of a target in the limit of $R \to \infty$ and the time it would have taken without any interaction. The quantum mechanical equivalent for steady state wavefunctions is to take the particle density in the region around the target divided by the total flux, both with and without an interaction.

A method of finding these times was formulated by Smith (1960). The time-delay matrix $Q$ is formed from the scattering matrix $S$ (and its conjugate $S^*$) and the time operator $-i\hbar \frac{d}{dE}$ and is defined as

$$Q = -i\hbar S^* \frac{dS}{dE}$$  

(4.2)

The largest eigenvalue of the $Q$-matrix, $q_{\text{max}}$, represents the time-delay experienced by the channel with the largest time-delay and hence is sensitive to any resonances. Smith also showed that the probability of decay of the $(N+1)_\text{th}$ electron into a particular continuum, the branching ratio $\beta$, is given by the square of the corresponding component of the eigenvector associated with $q_{\text{max}}$.

At resonance, the maximum eigenvalue $q_{\text{max}}$ has a Lorentzian form given (in atomic units) by:

$$q_{\text{max}}(E) = \frac{\Gamma}{((E - E_0)^2 + (\Gamma/2)^2)}$$  

(4.3)

As discussed in chapter 2, a new module, TIMEDEL, was written to find the $Q$-matrix and hence the time-delay. The $Q$-matrix is found numerically by calculating the $S$-matrix just above and just below the energy $E$. We found this procedure was stable for energy separations in the range $0.1\Gamma$ to $0.01\Gamma$. This is performed over a range of energies from which $q_{\text{max}}$ is found as a function of energy. A plot of $q_{\text{max}}$ is examined for peaks that characterize a resonance. These are then fitted to find the resonance parameters. The method of fitting varies depending on whether the resonances are isolated or overlapping. If the resonances are isolated then each resonance is fitted independently to a Lorentzian form using a least-squares fitting routine. In these cases a small constant background is used to account for other far away resonances. If there are two resonances overlapping, there are two methods for fitting them depending on their
relative heights. If one is much narrower, then the narrower one is fitted first with a constant background and the wide one is then fitted to the eigenphase sum minus the fitted resonance. If the resonances are of similar height then they are fitted together as a double Lorentzian.

An important advantage of the Q-matrix method over eigenphase sum fits is that in the Q-matrix method only the channel with the longest time-delay is fitted. This means that strongly varying but non-resonant channels do not need to be considered. This is particularly important for molecular targets as these have many degenerate channels.

As mentioned previously, the branching ratios of decay of the (N+1) system into a particular target state plus continuum electron can be found as a function of the electron energy. Useful information on the character of the resonance can be gained from the branching fraction as the electron energy passes through the resonant energy. For molecular calculations, the branching fractions at resonance as a function of internuclear separation can give insight into how the character of the resonance changes with bond length.

### 4.3 Comparing and contrasting the two resonance fitting methods

#### 4.3.1 $e$–H$_2^+$ scattering

R-matrix calculations were performed for the $^1\Sigma_g^+$ total symmetry at a bond length of $R = 1.4$ a$_0$, the equilibrium separation of H$_2$. The calculations used the wavefunctions developed and tested by Branchett & Tennyson (1992) and explicitly included three H$_2^+$ target states, X $^2\Sigma_g^+$, A $^2\Sigma_u^+$ and B $^2\Pi_u$ in the close-coupled expansion. The continuum electron was treated using a partial wave expansion which included partial waves with $l \leq 6$ in the external region.

The calculations reported here were performed as part of a wider study of superexcited states of H$_2$ as a function of internuclear separation (Tennyson 1996b). An important issue in these calculations is the branching ratio for the so-called Q$_2$ resonance series which converges to the $^2\Pi_u$ state of H$_2^+$ and, usually, can autoionize to either the ground $^2\Sigma_g^+$ state or the excited $^2\Sigma_u^+$ state of H$_2^+$.

Figure 4.3 shows the eigenphase sum and the time-delay as a function of energy. In the eigenphase picture, the resolved resonances appear as a series of steps of $\pi$ as the energy moves through each resonance in turn. As the resonances approach a threshold, their widths become so narrow that they begin to appear as characteristically shaped discontinuities. This effect is due to the energy resolution at which the calculation is executed and how the plotting
Figure 4.3: Electron–$H_2^+$ scattering at $R = 1.4 \ a_0$, $^1\Sigma_g^+$ total symmetry: a) Eigenphase sum ($\Delta$) as a function of energy (E); b) time-delay ($q_{\text{max}}$) as a function of energy (E). The insert, at higher resolution, shows the 4f and 5f resonances more clearly.
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Sec. 4.3

<table>
<thead>
<tr>
<th>Qi series</th>
<th>Eigenphase method</th>
<th>Time-delay method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_0 ) (eV)</td>
<td>( \Gamma ) (eV)</td>
</tr>
<tr>
<td>2p</td>
<td>12.7575</td>
<td>0.7300</td>
</tr>
<tr>
<td>3p</td>
<td>16.4750</td>
<td>0.09520</td>
</tr>
<tr>
<td>4p</td>
<td>17.3110</td>
<td>0.03992</td>
</tr>
<tr>
<td>4f</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5p</td>
<td>17.6730</td>
<td>0.02020</td>
</tr>
<tr>
<td>5f</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

| Q2 series | 2p        | 18.3791 | 0.1744 | 18.3604 | 0.1995 |

Table 4.1: e-\( H_2^+ \) scattering at \( R = 1.4 \ a_0 \), \( ^1\Sigma_g^+ \) total symmetry: resonance positions and widths of the eigenphase sum is performed. At the resonance position, arbitrary jumps by \( \pi \) in the eigenphase sum cause a discontinuity.

The resolved resonances in figure 4.3 are all dominantly p-wave in character; there are also f-wave and h-wave resonances but these are too narrow to be picked up at the resolution at which this calculation is performed. They can be seen more easily using the time-delay method.

In the time-delay picture, each resonance shows up as a Lorentzian with essentially no background and two distinct sets of Feshbach resonances can be seen. The \( Q_1 \) series converges to the \(^2\Sigma_u^+ \) first excited state of \( H_2^+ \) and the \( Q_2 \) converges to the \(^2\Pi_u \) state. Note that in the present calculations, the resonances can have up to three peaks, which can be assigned to their dominant partial waves, p, f and h, for each principal quantum number. The resonances associated with the f and h-waves are sharp. The insert, which enlarges the 4p and 5p resonance regions, clearly shows the full Lorentzians of the 4f and 5f resonances.

Table 4.1 gives the resonance parameters found using both methods for the first four resonances in the \( Q_1 \) series and the first resonance of the \( Q_2 \) series. The eigenphase sum is fitted using the program RESON (Tennyson & Noble 1984) and a linear background. The f-wave resonances were not fitted by the eigenphase sum method. This method requires a closely spaced grid of eigenphases and thus becomes sensitive to any numerical noise in the eigenphases when the resonances are very narrow.

For the first series, the p-wave resonances are sharp enough such that even though they do begin to overlap as the thresholds are approached, both methods can fit them to a high degree of accuracy and give the same result to within 0.1%.
At $R = 1.4\ a_0$, the lowest resonance of the $Q_2$ series is cut off by the $^2\Sigma_g^+$ threshold at 18.27 eV. In this case, the shape of the resonance is not distorted by the cut-off when the time-delay is viewed as a function of energy. This suggests there is very little interaction between the resonance and the $^2\Sigma_g^+$ target state. Nevertheless, the two methods give different results: $(E_0, \Gamma)$ are found to be (18.379 eV, 0.1744 eV) with the eigenphase sum method and (18.360 eV, 0.1995 eV) with the time-delay method. Examining the fits in detail shows that the eigenphase sum method is having to contend with a large background, which is common close to threshold, so that its fit is subject to error. In contrast, the fit to the Lorentzian using the time-delay method is almost perfect and the result found is thus extremely reliable.

Figure 4.4: Electron-$H_2^+$ scattering at $R = 1.4\ a_0$, $^1\Sigma_g^+$ total symmetry: Branching fraction ($\beta$) of decay into the ground state as a function of energy. The insert, at higher resolution, shows the effect of the f- and h-wave resonances more clearly.

Figure 4.4 shows the branching fraction for decay of the (N+1) system into the ground state for the $Q_2$ series; the $Q_1$ series is below threshold and so all decay is into the ground state. When the energy passes through a p-wave resonance there is almost no change in the branching
fraction which stays at around 92%. On passing through an f-wave or h-wave resonance there is a sharp drop for the duration of the resonance. For the 4f resonance, the branching fraction is 77% and for higher \( nf \) resonances it goes down almost to zero (the calculation is not at high enough resolution to find exact values) which means it decays almost purely into the first excited A \( ^2\Sigma_u^+ \) state. The insert is a blow up of one the spikes and shows that the \( n = 6 \) region does indeed contain two sharp resonances, one for the f-wave and one for the h-wave.

Analysis of a number of resonances and geometries show that in general the branching ratio given by the dominantly p-wave resonances is close to the background value, but that the f and h-wave resonances give branching ratios which differ significantly from this.

4.3.2 \( ^2\Sigma_g^+ \) e–H\(_2\) scattering

Figure 4.5 shows the eigenphase sum and the time-delay \( q_{\text{max}} \) with fitted Lorentzians at the equilibrium separation of \( R = 1.4 \) \( a_0 \). From the eigenphase sums, there appear to be two resonances between the first \( (b \ ^3\Sigma_u^+) \) and the second \( (a \ ^3\Sigma_u^+) \) thresholds. The first resonance (res1) lies just above the \( b \ ^3\Sigma_u^+ \) threshold and the eigenphase sum rises by less than \( \pi/2 \) rather than the expected \( \pi \). This is partly because it is cut off by the threshold and partly because the background of the eigenphase sum tends to change rapidly at the thresholds. The second, narrower resonance (res2), although also cut off by a threshold to higher energy, is accompanied by a rise of almost \( \pi \) in its eigenphase and is hence a much more pure resonance which should be easier to fit. Above the threshold at 12.3 eV there is a fair amount of structure but nothing that can clearly be called a resonance.

The existence of two \( ^2\Sigma_g^+ \) resonances below 12.3 eV is confirmed by the two clear peaks in figure 4.5b, the time-delay experienced by the electron. Res1 is a broad and thus short-lived resonance. As predicted from the eigenphase sum, it is cut off at low energy by the threshold. It is also seen that the shape of the left limb is distorted from a pure Lorentzian suggesting a strong interaction between the resonance and the target state. Res2 on the other hand is a narrow, long-lived resonance that is far enough away from any threshold to be undistorted close to its maximum, although it is distorted close to the \( a \ ^3\Sigma_u^+ \) threshold. In the region near its maximum it is a near-perfect Lorentzian that can be fitted very well. As was seen in the eigenphase picture, above the 12.3 eV threshold there is much structure some of which could be due to resonances but the bunching of thresholds makes it impossible to resolve. This region will not be considered further.

For both resonances the eigenphase sums were fitted using RESON and a linear back-
Figure 4.5: Electron–$\mathrm{H}_2$ scattering at $R = 1.4 \ a_0$, $^2\Sigma_g^+$ total symmetry: a) Eigenphase sum ($\Delta$) as a function of energy (E); b) time-delay ($q_{\text{max}}$) as a function of energy (E) with Lorentzian fit (dashed line)
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### Table 4.2: e–H$_2$ scattering at $R = 1.4$ a$_0$, $^2\Sigma_g^+$ total symmetry: resonance positions and widths

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eigenphase method</td>
<td>10.677</td>
<td>1.555</td>
</tr>
<tr>
<td>Time-delay method</td>
<td>10.673</td>
<td>1.035</td>
</tr>
<tr>
<td>res2</td>
<td>12.048</td>
<td>0.0973</td>
</tr>
<tr>
<td>Time-delay method</td>
<td>12.049</td>
<td>0.0971</td>
</tr>
</tbody>
</table>

The time-delay was fitted using a double Lorentzian, least squares fitting routine. For res1, the latter fitting was set to ignore the region near threshold where the Lorentzian is distorted. The parameters fitted with the two procedures are given in table 4.2. The positions found by both methods for res1, which is a distorted resonance, are close (within 0.04%) but the fitted widths differ significantly, by $\sim 50\%$. This exemplifies the point mentioned previously, that the width fitted by the eigenphase sum method is always more sensitive to distortion than the position. The fit by the time-delay method is a much better one (in terms of residues to the expected form) and the result are thus more reliable.

In the case of res2 which suffers little distortion, both methods give almost the same position and widths.

The branching ratios are shown in figure 4.6. In this case, unlike for $e–H_2^+$ scattering, the ratios vary smoothly and there are no sudden changes as the resonance positions are scanned across. From the figure it can be seen that res1 has more than a 90% chance of decaying into the continuum of the first excited state ($b^3\Sigma_u^+$) and res2 has an 85% chance of decay into this state. Since the resonance lies below its parent states, the branching ratios are not helpful in determining the parentage of res2 and other methods such as reduced state calculations are required (see chapter 6).

### 4.4 Conclusions

The time-delay method can be used in any calculations in which it is possible to find the S-matrix as a function of energy. It provides a way of fitting resonances in difficult situations where the standard eigenphase sum fitting methods fail. These situations tend to occur at energies near to thresholds, when multiple resonances overlap, or when the resonance is very wide.

In the case of $e–H_2^+$ scattering, the time-delay method and the eigenphase sum method gave the same results for the first Rydberg series, in which the resonances are all quite narrow.
Figure 4.6: Electron–H₂ scattering at $R = 1.4 \ a₀$. $^2\Sigma^+_g$ total symmetry: Branching ratios ($\beta$) as a function of energy (E). $\beta_0$ decays into the $X\ ^1\Sigma^+_g$ state, $\beta_1$ into the $b\ ^3\Sigma^+_u$ and $\beta_2$ into the $a\ ^3\Sigma^+_g$. 
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Sec. 4.4

and away from threshold. The time-delay method proved essential, however, in fitting the first resonance (2p) of the second Rydberg series. The eigenphase method was thrown both by the large, varying background near the threshold and the fact that the resonance is cut off by the threshold. Neither of these problems affected the time-delay method.

For $e^{-}H_2$ scattering, the eigenphase method was found to be inadequate in fitting a resonance close to threshold. The time-delay method succeeded in fitting the resonance. Both methods successfully fitted a narrow, isolated resonance.

The branching ratios that come out of using the time-delay, and other (Bartschat & Burke (1986), Quigley & Berrington (1996)) methods can prove extremely useful. In particular, finding the greatest branching ratios should identify immediately core-excited shape (i.e. above threshold) resonances. They cannot be used to identify Feshbach (below threshold) resonances without other evidence as they cannot decay into their parent.

Further details of finding the parent states of resonances can be found in chapter 6.
Chapter 5

e–H$_2$ resonances as a function of bond length

The results of calculations performed for bond lengths from 0.8 a$_0$ to 4.0 a$_0$ for eight total symmetries of the H$_2^-$ complex, $^2\Sigma_g^+$, $^2\Pi_u$, $^2\Delta_u$, $^2\Phi_u$, $^2\Phi_g$ are presented here. Resonances have been tracked over as wide a range of bond lengths as possible and parameterized. The energy positions allow a series of H$_2^-$ potential curves to be built up from which it is possible to compute vibrational levels of the resonances. Comparison of these with experiment has allowed a complete theoretical description of the low energy (< 13 eV) resonances and cleared up much of the confusion that has reigned in the past over symmetry and parental assignments of these resonances.

5.1 $^2\Sigma_g^+$ total symmetry

Three resonances are found for this symmetry and are shown in figure 5.1. The widths and positions of these resonances are parameterized (energy position given relative to the ground state) and the branching ratios of decay of each of the resonances found.

5.1.1 $^2\Sigma_g^+$ resonance 1 - parent state: b $^3\Sigma_u^+$

Resonance 1 follows the b $^3\Sigma_u^+$ repulsive target state across the full range of bond lengths. It lies above the threshold for nearly all of this range (and is thus a core-excited shape resonance) but appears to be pushed below it for $R < 1.1$ a$_0$ by an avoided crossing with resonance 2 which would reassign the resonance as Feshbach for this region. The resonance parameters are
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Sec. 5.1

Figure 5.1: \( ^2\Sigma^+ \) symmetry: resonance positions \( E_0 \) and target state energies as function of bond length \( R \).
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Sec. 5.1

given in table 5.1.

Figure 5.2 shows how the width and branching ratios of resonance 1 change as a function of geometry. For \( R \leq 1.00 \ a_0 \), the resonance is long-lived and narrow at around 0.02 eV. As it is below threshold, it can only decay to the ground state. As the separation increases, the resonance moves above threshold and the predominant decay is now to the \( b \ 3 \Sigma_u^+ \) state (around 83%). The width also increases with separation up to a maximum of about 2.25 eV at \( R \sim 2.0 \ a_0 \). In this region the resonance is very broad which makes it difficult and inaccurate to fit. The lack of smoothness in the curves of width and position in this region is a manifestation of this. On increasing the separation further, the width narrows and the branching fraction to the excited state drops until at \( R = 4.0 \ a_0 \), the width is around 0.45 eV and the branching ratios are only 56:44 in favour of the first excited state.

This '10 eV' \( \Sigma_g^+ \) H₂− resonance is well recorded in the scientific literature as the \( B \ 2 \Sigma_g^+ \) H₂− state and is associated particularly with dissociative attachment. On the theory side, Eliezer et al. (1967) calculated the state and found that at short bond length it lay above the \( b \ 3 \Sigma_u^+ \) H₂ state and then crossed below it as the bond length increases, the reverse behaviour of the resonance found in this work. Later calculations by Buckley & Bottcher (1977) and Bardsley & Cohen (1978) locate the H₂− state about 1 eV above its \( b \ 3 \Sigma_u^+ \) parent state compared to between 0.2 and 0.6 eV in this work. Bardsley & Wadehra (1979), by fitting to experimental dissociative attachment cross sections near 10 eV, found the \( B \ 2 \Sigma_g^+ \) potential curve to lie only a few meV above the \( b \ 3 \Sigma_u^+ \) state. They also found resonance widths which, although in the same ball park as those found in this work (around 1.7 eV compared with 1.04 eV in this work for \( R = 1.4 \ a_0 \)), differ both quantitatively and qualitatively as function of bond length to the results presented here.

Experimentally, the resonance has perhaps best been studied indirectly by Esaulov (1980) who looked at electron detachment and charge exchange in collisions between H⁻ and D. Esaulov concluded that the \( B \ 2 \Sigma_g^+ \) resonant state should lie around 0.8 ± 0.3 eV above the \( H_2 \ b \ 3 \Sigma_u^+ \) parent state which is a little, but not significantly, higher than that found in this calculation. The experiment found evidence that the resonance decays into the \( b \ 3 \Sigma_u^+ \) state, a result corroborated in this work and also in several of the previous calculations (Bardsley & Wadehra 1979, Buckley & Bottcher 1977, Bardsley & Cohen 1978).
### Table 5.1: $^2\Sigma^+_g$ Resonance 1: Energy Positions $E_0$ Above Ground State, Widths $\Gamma$ and Branching Fractions $\beta_0$ and $\beta_1$ as a Function of Bond Length $R$. $\beta_0$ Decays into the $X^1\Sigma_g^+$ State and $\beta_1$ into the $b^3\Sigma_u^+$ State.

<table>
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<th>$R (\text{a}_0)$</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma$ (eV)</th>
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<th>$\beta_1$</th>
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Figure 5.2: $2\Sigma_g^+$ symmetry resonance 1: a) resonance width ($\Gamma$) and b) branching fractions ($\beta$) for resonance 1 as a function of bond length ($R$). $\beta_0$ decays into the $X\Sigma_g^+$ state and $\beta_1$ into the $b\Sigma_u^+$. 
5.1.2 $^2\Sigma_g^+$ resonance 2 - joint parent states: a $^3\Sigma_g^+$, E $^1\Sigma_g^+$, c $^3\Pi_u$ and C $^1\Pi_u$

Resonance 2 lies in the 12 eV region where there is a forest of target states. From figure 5.1 it can be seen that the resonance is cut off at short bond length by the a $^3\Sigma_g^+$ threshold for $R < 1.1$ a₀. At around $R = 3.6$ a₀, it crosses the E,F $^1\Sigma_g^+$ threshold which makes it difficult to fit due to other, non-resonant interactions with the threshold. It is not readily obvious which (if any) target state curve the resonance is following. The resonance parameters, including branching ratios, are given in table 5.2.

Figure 5.3 shows the width and branching ratios of resonance 2 as a function of bond length. The resonance starts off at its broadest (around 0.42 eV) with the majority of decay into the b $^5\Sigma_u^+$ state (95%). As the bond length increases, the width narrows and decay into the ground state X 1$\Sigma_g^+$ begins to predominate up to a maximum of 96% at around $R = 2.0$ a₀. At $R = 2.1$ a₀, resonance 2 crosses the B $^1\Sigma_u^+$ threshold but is not greatly affected by this – its width does not change significantly and the branching ratios remain reasonably continuous. As $R$ increases, the width begins to increase and the branching fraction to the B $^1\Sigma_u^+$ state increases at the expense of decay into the other two states. Beyond $R = 3.5$ a₀, the E,F $^1\Sigma_g^+$ threshold causes a jump in the resonance width to around 0.30 eV which drops again as the bond length continues to increase. The branching fraction also shows a discontinuity due to the extra available decay state although decay into the B $^1\Sigma_u^+$ state still dominates (around 60%) with the newly available E,F $^1\Sigma_g^+$ taking around 30%.

This resonance is well known experimentally as the ‘series a’ resonance. Its potential curve closely follows the series a $H_2^+$ potential curves determined experimentally by Comer & Read (1971) and Joyez et al. (1973). The minima of these potentials were found at 1.83 ± 0.02 a₀ and 1.85 ± 0.04 a₀ respectively, in very good agreement with the minimum of the absolute resonance energy found in this work of 1.87 a₀.

The parentage of this resonance, however, has been a matter of much debate as it lies below four possible parent states: c $^3\Pi_u$, C $^1\Pi_u$, a $^3\Sigma_g^+$ and E,F $^1\Sigma_g^+$. In their stabilization calculations, Eliezer et al. (1967) found resonances associated with three of these. Similarly, Buckley & Bottcher (1977) found multiple resonances associated with different target states. A resonance also appeared in the five target state Schwinger multichannel calculation of da Silva et al. (1990). The calculation did not include the Π target states and represented the E,F $^1\Sigma_g$ state by only the E $^1\Sigma_g$ inner section and so their identification of the parent as the a $^3\Sigma_g^+$ target state is by no means positive. In their experiment, Comer & Read (1971), by comparing their observed resonant state with potential curves presented by Sharp (1969), concluded that only the a $^3\Sigma_g^+$ and the c $^3\Pi_u$ were possible candidates and chose the c $^3\Pi_u$ as it was found by
### Table 5.2: $^2\Sigma_g^+$ resonance 2: energy positions $E_0$ above ground state, widths $\Gamma$ and branching fractions $\beta_0, \beta_1, \beta_2$ and $\beta_3$ as a function of bond length $R(\text{a}_0)$. $\beta_0$ decays into the $X\ ^1\Sigma_g^+$ state, $\beta_1$ into the $b\ ^3\Sigma_u^+$, $\beta_2$ into the $B\ ^1\Sigma_u^+$ and $\beta_3$ into the $E,F\ ^1\Sigma_g^+$. 

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<th>$\Gamma$ (eV)</th>
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Figure 5.3: $^2\Sigma_g^+$ resonance 2: a) resonance width ($\Gamma$) and b) branching fractions ($\beta$) as a function of bond length ($R$). $\beta_0$ decays into the $X^1\Sigma_g^+$ state, $\beta_1$ into the $b^2\Sigma_u^+$, $\beta_2$ into the $B^1\Sigma_u^+$ and $\beta_3$ into the $E,F^1\Sigma_g^+$. 
Eliezer et al. (1967) to be the lowest of the resonant states. Later, however, Joyez et al. (1973) concluded that the parent state could be either $e^3\Pi_u$ or $C^1\Pi_u$.

When two-state calculations (ground plus possible parent) were performed here, resonances were found associated with each of the possible parent states. However, when all the states are included, only a single resonance is seen (see section 6.3). It is therefore suggested that in fact this resonance has multiple parent states, i.e. all the possible parent states contribute in some way to the temporary trapping of the scattering electron, and it is the coupling between the states that results in the formation of only a single resonance. It is thus likely that the multiple resonances found by Eliezer et al. (1967) and Buckley & Bottcher (1977) are due to a lack of coupling between the different target states and are in fact phantom resonances. It is also now clear that the da Silva et al. (1990) resonance seen with only five states is not the complete picture as it misses out contributions from other target states. Multiple parent states are discussed in detail in chapter 6.

As described in section 3.7, it is possible to find the vibrational levels and wavefunctions of the resonance from the resonance potential curve. These have been calculated for $H_2$, HD and $D_2$ and are given in table 5.3 along with experimental results. At the equilibrium separation of the resonance (approximately $R = 1.90 \ \text{a}_0$) the dominant parents are the $b^3\Sigma_u^+$ and the $c^3\Pi_u$ target states. Coincidentally (and felicitously), it can be seen from figure 3.6 that both these states have an error correction of 0.08 eV and, following the procedure also described in section 3.7, this correction has been added to our results.

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The results for $H_2$ are in superb agreement with all the previous experimental results. For HD, the spacings are in good agreement with both comparison experiments although the ab-
solute values are around 0.1 eV lower than those of Furlong & Newell (1995). Other experimental results for the series c HD$^-$ resonance (seen in the same run as series a) are around 0.1 eV lower than those of Furlong and Newell which suggests their calibration for HD could be out by this amount. HD is known to dissociate to form H$_2$ and D$_2$ and so can be difficult to work with experimentally. The series a results for D$_2$ are again in excellent agreement with both comparison experiments, particularly those of Comer & Read (1971).

The fixed-nuclei resonance widths determined here are clearly dependent on the bond length. Since different vibrational levels of the resonance sample different regions of internuclear separation, one would expect the resonance widths seen experimentally to be dependent on vibrational level. Similarly, since the nuclear motion is dependent on the mass of the nuclei, isotopic effects would also be expected. Figure 5.4 is a superposition of H$_2^-$ and D$_2^-$ vibrational wavefunctions on the resonance width as a function of bond length and demonstrates the different regions sampled by the vibrations.

An adiabatic estimate of this effect can be gained by simply averaging the resonance width over the resonance vibrational wavefunction and this has been done for the first five vibrational levels of H$_2$ and D$_2$. The results are shown in table 5.4.

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Table 5.4: $^2\Sigma_g^+$ resonance 2: vibrationally averaged widths for H$_2^-$ and D$_2^-$.  

As expected, the resonance width increases with increasing vibrational level as the more extreme bond lengths, at which the resonance has large width, are sampled to a greater degree. As a heavier molecule, the nuclear vibration of D$_2^-$ does not sample as wide a range of bond lengths as H$_2^-$ and so in this case its resonance width is narrower than that for H$_2^-$. It is clear from these results that any calculation fixed at the H$_2$ equilibrium bond length will overestimate the resonance width. In this calculation the width at $R = 1.4\ a_0$ was found to be 0.1 eV, a factor of five times greater than that found for the H$_2^-$ v = 0 vibrationally averaged width of 0.019 eV.

The determination of these widths experimentally has proven difficult due to resolution limitations. For instance, the e–H$_2$ experiment of Comer & Read (1971) estimated a constant...
Chapter 5: $e^-$-$H_2$ resonances as a function of bond length

Sec. 5.1

Figure 5.4: $^3\Sigma^+_u$ resonance 2: superposition of $H_2^-$ (red) and $D_2^-$ (blue) vibrational wavefunctions on the resonance width as a function of bond length.
Chapter 5: e–H₂ resonances as a function of bond length

Sec. 5.2

resonance width of around 0.045 eV which was very close to the resolution of the experiment. For D₂ they found a steadily increasing width of around 0.03 eV for the \( v = 0 \) rising to 0.06 eV for the \( v = 6 \), qualitative behaviour in agreement with our results. In a later experiment which looked at rotational excitation of H₂, Joyez et al. (1973) had difficulty estimating the width but suggested that it might be narrower than the resolution of their apparatus, giving an upper limit of 0.016 eV, and implied it would probably be much less. However, given that the narrowest width they measured was 0.020 eV, this is rather uncertain. The estimation of widths close to the resolution limit of the experiment is tricky and experiments at much higher resolution are required for accurate determination.

5.1.3 \( ^2\Sigma_g^+ \) resonance 3 - parent state: B \( ^1\Sigma_u^+ \)

A third resonance, resonance 3, is only apparent at bond lengths \( R \geq 3.0 \) a₀. For \( R < 3.7a₀ \) it is cut off by the B \( ^1\Sigma_u^+ \) threshold at low energy before \( q_{\text{max}} \) reaches the maximum of the Lorentzian and table 5.5 shows the fitted parameters for \( 3.7 < R \leq 4.0 \) a₀.

<table>
<thead>
<tr>
<th>( R( a₀) )</th>
<th>( E₀ (eV) )</th>
<th>( Γ (eV) )</th>
<th>( β₀ )</th>
<th>( β₁ )</th>
<th>( β₂ )</th>
</tr>
</thead>
<tbody>
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<td>3.70</td>
<td>8.0485</td>
<td>0.2391</td>
<td>0.056</td>
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<td>0.815</td>
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<td>4.00</td>
<td>8.0371</td>
<td>0.0156</td>
<td>0.265</td>
<td>0.303</td>
<td>0.432</td>
</tr>
</tbody>
</table>

Table 5.5: \( ^2\Sigma_g^+ \) total symmetry: resonance positions, widths and branching fractions as a function of bond length for resonance 3

At \( R = 4.0 \) a₀, the resonance is very sharp at \( Γ = 0.016 \) eV. As the bond length decreases, the width rapidly increases and by \( R = 3.7 \) a₀ it is already up to 0.24 eV. The branching ratios for \( R = 3.7, \, 3.8 \) and \( 3.9 \) a₀ give about an 85% decay into the B \( ^1\Sigma_u^+ \) state. For \( R = 4.0 \) a₀, the fraction is only \( β = 43% \) but this is still the dominant decay.

When this resonance was first detected in this work, it was initially suggested that it might be responsible for the resonance series \( b \) seen experimentally (Comer & Read 1971) which was originally classified as having \( ^2\Sigma_g^+ \) symmetry. It has become clear, however, that this is not the case and in fact series \( b \) is of \( ^2\Sigma_u^+ \) symmetry (see section 5.2.3). As resonance 3 is not seen near the H₂ equilibrium separation, it is not seen experimentally.
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5.2  $^2\Sigma_u^+$ total symmetry

Three resonances are seen of $^2\Sigma_u^+$ symmetry: the well-known, broad $1\sigma_g^21\sigma_u$ ground state shape resonance which was found untestable at short bond lengths; a resonance which is testable for $R < 1.4$ a$_0$ (and is weakly apparent at longer bond lengths) which closely tracks its parent, the $3\Sigma_u^+$ state and a higher resonance which we detect for all $R$. These resonances can be seen in figure 5.5.

5.2.1  X $^2\Sigma_u^+$ resonance 1 - ground state shape resonance

At bond lengths less than $R = 1.4$ a$_0$, there is some evidence for a wide (over 10 eV) low energy resonance. The eigenphase sum shows a steady increase over a very wide range of energy, and the time-delay shows some Lorentzian-like structure. Any such resonance, however, is too wide to be fitted using the eigenphase sum method and, because the time-delay is so small (less than 7 a.u.), slight perturbations possibly due to polarization effects at very low energy, make it impossible to fit accurately to a Lorentzian. From $R = 1.4$ a$_0$ to about $R = 1.9$ a$_0$, the resonance, although still very wide, can be fitted using the cruder eigenphase sum method although the fits are very approximate. For instance, at $R = 1.4$ a$_0$ the resonance appears to have a width of around 9.5 eV at an energy only 0.8 eV above the ground state. As the separation increases, the width decreases exponentially. At $R = 1.7$ a$_0$ the resonance is at its highest energy relative to the ground state of around 1.42 eV and has a width of 5.2 eV. As the bond length increases with the width decreasing further, the resonance can be fitted more and more accurately using both the eigenphase sum and time-delay methods. Its energy gets closer to zero until, just slightly over $R = 2.9$ a$_0$(where it has a width of 0.034 eV), it crosses the H$_2$ ground state, becomes bound and can no longer be seen. The parameters of the resonance are shown in table 5.6.

This resonance is well known experimentally as the $(1s\sigma_g)^22p\sigma_u$ (X $^2\Sigma_u^+$) ground state shape resonance. Since the resonance is wide there is little or no evidence of it in the experimental elastic cross section (Schultz 1973) but it can be seen in vibrational and rotational excitation channels. It also plays a particularly important role in low energy dissociative attachment in which H and H$^-$ (Ésaulov 1980) are produced.

There has been a significant number of calculations (Eliezer et al. 1967, Chen & Peacher 1968, Bardsley et al. 1966, DeRose et al. 1988) which have attempted to determine this resonance. Our results for bond lengths where the resonance can be fitted more confidently ($R > 1.9$ a$_0$) are qualitively and, with some of these results, quantitatively in good agreement.
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Figure 5.5: $^2\Sigma_u^+$ symmetry: resonance positions $E_0$ and target state energies as function of bond length $R$. 

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with many of these. In particular the exponential decay in resonance width in this region is well
reproduced by the relatively simple calculation of Bardsley et al. (1966). The position where
our resonance becomes bound (just over $R = 2.9 \, \text{a}_0$) is close to that found by DeRose et al.
(1988) and Chen & Peacher (1968) at around $R = 3.0 \, \text{a}_0$. Below $R = 1.9 \, \text{a}_0$, where the fit is
uncertain, so is the agreement with previous results.

<table>
<thead>
<tr>
<th></th>
<th>Resonance 1</th>
<th></th>
<th>Resonance 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R(\text{a}_0)$</td>
<td>$E_0$ (eV)</td>
<td>$\Gamma$ (eV)</td>
<td>$R(\text{a}_0)$</td>
</tr>
<tr>
<td>1.4*</td>
<td>0.83</td>
<td>9.5</td>
<td>0.8</td>
</tr>
<tr>
<td>1.5*</td>
<td>1.23</td>
<td>7.8</td>
<td>0.9</td>
</tr>
<tr>
<td>1.6*</td>
<td>1.38</td>
<td>6.4</td>
<td>1.0</td>
</tr>
<tr>
<td>1.7*</td>
<td>1.43</td>
<td>5.2</td>
<td>1.1</td>
</tr>
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<td>1.8</td>
<td>1.385</td>
<td>4.187</td>
<td>1.2</td>
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<td>2.081</td>
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<td>0.922</td>
<td>1.591</td>
<td></td>
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<td>0.790</td>
<td>1.119</td>
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<td>0.534</td>
<td>0.593</td>
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<td>2.9</td>
<td>0.0088</td>
<td>0.0340</td>
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</table>

Table 5.6: $^2\Sigma_u^+$ symmetry resonances 1 and 2 energy positions $E_0$ above the ground state
energy and widths as a function of bond length. Results for bond lengths marked * are
very approximate. Resonance 1 becomes bound after $R = 2.9 \, \text{a}_0$.

5.2.2 $^2\Sigma_u^+$ resonance 2 - parent state $b \, ^3\Sigma_u^+$

At $R = 0.8 \, \text{a}_0$ there is a narrow ($\Gamma < 0.004 \, \text{eV}$) resonance, clearly visible in both the
eigenphase sum and time-delay picture, about 0.1 eV below the first excited $b \, ^3\Sigma_u^+$ state. It is still
apparent at $R = 0.9 \, \text{a}_0$ although here it is just above the $b \, ^3\Sigma_u^+$ state. By $R = 1.0 \, \text{a}_0$, the resonance
width has increased to around 0.20 eV and continues increasing with $R$. The eigenphase
sum shows a Breit-Wigner rise against a sharply falling background which flattens out the rise
to a greater and greater extent as the bond length is increased. The time-delay Lorentzian is
also distorted by the nearby thresholds and the resonances can only be fitted approximately.

For $R > 1.2 \, \text{a}_0$, the resonance can no longer be fitted. Indeed, in the earlier, single bond
length calculation of Branchett & Tennyson (1990) at $R = 1.4 \, \text{a}_0$, the change in eigenphase
sum was noted only as a 'feature'. An avoided crossing with resonance 3 would account for the
dipping of resonance 2 below its parent \( b^3\Sigma_u^+ \) state at short bond length. Since the resonance is so weak and is in approximately the same position as the \( ^2\Sigma_g^+ \) repulsive resonance, it would be difficult to observe experimentally. The parameters of the resonance are given in table 5.6.

5.2.3 \( ^2\Sigma_u^+ \) resonance 3 - joint parent states: \( a^3\Sigma_g^+ \) and \( B^1\Sigma_u^+ \)

Tracking resonance 3 as a function of bond length produces an attractive \( H_2^- \) potential curve with a minimum at around \( R = 2.33 \) \( \text{a}_0 \). The resonance can be seen to swap between parent target states.

At \( R = 0.8 \) \( \text{a}_0 \), the resonance lies just below the \( a^3\Sigma_g^+ \) state and has a width of 0.02 eV. As the bond length increases, the resonance rises just above the threshold and, as it does so, its width jumps to 0.16 eV at \( R = 0.9 \) \( \text{a}_0 \). It then proceeds to follow the \( a^3\Sigma_g^+ \) state as a core-excited shape resonance with the width rising to a maximum of 0.27 eV at \( R = 1.10 \) \( \text{a}_0 \), from which point the resonance width begins to fall slowly. At around \( R = 1.4 \) \( \text{a}_0 \), the resonance drops below the \( a^3\Sigma_g^+ \) threshold and continues to move further below it and eventually, at around \( R = 2.3 \) \( \text{a}_0 \), it joins up with the \( B^1\Sigma_u^+ \) threshold and proceeds to follow this target state. From \( R = 2.4 \) to 3.4 \( \text{a}_0 \), the resonance sits almost exactly on the threshold and so no width can be fitted. When the resonance begins to fall below threshold at \( R = 3.5 \) \( \text{a}_0 \) the width has dropped to 0.007 eV but slowly increases as it falls further away from threshold to 0.02 eV at \( R = 4.0 \) \( \text{a}_0 \).

Since the equilibrium position of the resonance at around \( R = 2.33 \) \( \text{a}_0 \) is so much greater than that of the ground state \( R = 1.4 \) \( \text{a}_0 \), the Franck-Condon overlap between the resonance and the ground state would only be significant for high vibrational levels of the ground state. Comer & Read (1971) when looking at decay of \( H_2^- \) resonances into the ground state \( v = 8 \) and above levels saw a resonance which they called 'series \( b \)'. Huetz & Mazeau (1981) appeared to see evidence of the series \( b \) resonance but they did not mention it when reporting a later experiment (Huetz & Mazeau 1983). No other experiment has seen this resonance as the necessary decay channels have not been monitored.

Comer and Read roughly estimated the width of their resonance at 30 meV. As the width of the resonance in our calculations was unobtainable for many bond lengths close to the equilibrium position, it is impossible to perform the averaging procedure used for the \( ^2\Sigma_g^+ \) resonance 2. However, by looking at the known widths near the equilibrium it is clear that this value is at least consistent with our results. Comer and Read in attempting to fit their data to a Morse potential produced only a poor fit. For this they assumed there were two missing levels as dif-
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Table 5.7: $^2\Sigma^+_u$ symmetry: resonance 3 energy positions $E_0$ above the ground state and widths $\Gamma$ as a function of bond length

<table>
<thead>
<tr>
<th>$R(a_0)$</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma$ (eV)</th>
<th>$R(a_0)$</th>
<th>$E_0$ (eV)</th>
<th>$\Gamma$ (eV)</th>
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<td>0.2716</td>
<td>2.7</td>
<td>8.902</td>
<td>-</td>
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<td>0.1855</td>
<td>2.8</td>
<td>8.743</td>
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<td>0.1365</td>
<td>2.9</td>
<td>8.601</td>
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<tr>
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<tr>
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<td>0.0807</td>
<td>3.2</td>
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</table>

Different assumptions resulted in even worse fits. Given that the resonance swaps from one parent state to another, it is not surprising that a Morse potential would not be a particularly good approximation in this case. They found an equilibrium bond length of $R = 2.22$ $a_0$ compared with that found here of 2.33 $a_0$. If only one missing level was assumed, they noted that the equilibrium bond length would be larger.

The symmetry of the resonance considered most likely by Comer and Read was $^2\Sigma^+_u$ due to an apparent isotropy of the angular distribution. However, determination of this distribution is difficult to perform definitively, particularly with interference due to other series in the same area (Mason 1997b), and it is not believed that the assignment is reliable in this case. No differential cross section data for this resonance has been published.

Theoretically, a $^2\Sigma^+_u$ resonance in this region was seen in calculations by Buckley & Bottcher (1977). However, their resonance was only in qualitative agreement with the results presented here for short bond length and diverged away completely at longer bond lengths.

Vibrational levels of the resonance can be estimated from the potential curve. At the equilibrium position of the resonance ($R = 2.33$ $a_0$), the $^1\Sigma^+_u$ state is the dominant parent. At this bond length, this state can be seen from figure 3.6 to require an energy correction of $-0.08$ eV and this has been added to the results of our vibrational calculations. These are
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shown in table 5.8 for H\textsubscript{2}\textsuperscript{-}, HD\textsuperscript{-} and D\textsubscript{2}\textsuperscript{-}.

<table>
<thead>
<tr>
<th>Vib. level</th>
<th>H\textsubscript{2}\textsuperscript{-}</th>
<th>HD\textsuperscript{-}</th>
<th>D\textsubscript{2}\textsuperscript{-}</th>
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<td></td>
<td>This work</td>
<td>Expt.</td>
<td>This work</td>
</tr>
<tr>
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<tr>
<td>7</td>
<td></td>
<td>11.96</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.8:** Resonance series b vibrational energy level positions compared with experiment (Comer & Read 1971). The vibrational numbering of the experimental levels follows the assumption of Comer and Read that the first two levels were unobserved. This is by no means certain.

Our results fit remarkably well with those of the experiment if it is assumed that in fact there is only one missing level in the experiment. In this case the experiment series b has spacings from \( v = 1 \) of 0.20, 0.16, 0.12, and 0.10 eV compared with our results of 0.18, 0.16, 0.14 and 0.09 eV.

The close matching of these results allows the definitive assignment of resonance series b as \(^{2}\Sigma^+_u\) with joint parent states \(^{5}\Sigma^+_g\) and \(^1\Sigma^+_u\).

5.3 \(^2\Pi_u\) total symmetry

Figure 5.6 shows a resonance that can be tracked across the whole range of bond lengths and exhibits swapping between parent states. Also shown is a weak resonant ‘feature’ which can also be tracked.

5.3.1 \(^2\Pi_u\) resonance 1 - joint parent states \(^{3}\Sigma^+_g\), \(^{3}\Pi_u\), \(^{3}\Pi_u\), \(^1\Sigma^+_g\)

At \( R = 0.8 \) a\textsubscript{0} resonance 1 sits just above the \(^{3}\Sigma^+_g\) state. The resonance is distorted by a wider resonance feature a little above it and its width is fitted only approximately at 0.03 eV.

The resonance continues above the threshold with similar widths and gets closer and closer to the threshold until just after 1.5 a\textsubscript{0} (where its width has dropped to 0.005 eV) it cuts through it. It then proceeds to move further below the \(^{3}\Sigma^+_g\) state before approaching from below its new adopted parent, the \(^{3}\Pi_u\) state. It lies just below this state for a while, its width increasing
Figure 5.6: $^3\Sigma_u^-$ symmetry: resonance and 'feature' positions $E_0$ and target state energies as function of bond length $R$. See text for details.
slowly. At around $R = 3.3 \ a_0$ this rather fickle resonance again begins to diverge from its parent, this time to join up with the $E_F \ 1^1\Sigma_g^+$ at $R = 3.5 \ a_0$. It then seems content to sit on this threshold for the remainder of the region considered. The resonance parameters are given in table 5.9.

Experimentally, this resonance was observed by Comer & Read (1971) (series $c$) in a $D_2$ experiment looking at vibrational structure. They were unable to decide between the $a \ 3^3\Sigma_g^+$ and the $c \ 3^3\Pi_u$ states as possible parent states for the resonance. In subsequent work, looking at the rotational structure of $H_2$, Joyez et al. (1973) assigned it to the $c \ 3^3\Pi_u$ state and gave it a maximum width of 16 meV, the limit of their resolution. The resonance width found here does not change a great deal close to the equilibrium position and is of the order of 4 meV. Note that again, a single fixed-nuclei calculation at the $H_2$ equilibrium bond length of 1.4 $a_0$ would overestimate the width at around 30 meV. Much higher experimental resolution is required to determine accurately the resonance width.

The difficulty in assigning the resonance can be explained, similarly to the $^E+ \ 3$ (series $b$), by the fact that Comer and Read attempted to fit a Morse potential to their series data to compare the equilibrium separation of the resonance with that of the excited target states. With the resonance swapping over dominant parent, the Morse potential is a poor approximation and indeed the fit they found was poor even when trying different numbers of missing levels. They found an equilibrium bond length of 1.83 $a_0$ assuming one missing level and 1.95 $a_0$ assuming two missing levels in comparison with our result of 1.94 $a_0$.

Vibrational levels can again be found from the potential curve. From figure 3.6 it can be seen that 0.08 eV needs to be added to our results to take into account the error in energy gap between the ground and the $a \ 3^3\Sigma_g^+$ and $c \ 3^3\Pi_u$ dominant parent states at the equilibrium separation of $R = 1.94 \ a_0$. The results are shown in table 5.10 along with several experimental results. It has been common (and misguided) practice to compare series $c$ experimental results with a calculation by Eliezer et al. (1967) and obtain ‘good agreement’ (Mason & Newell 1986, Furlong & Newell 1995). However, the calculation of Eliezer et al. (1967) is for a resonance of $2^2\Sigma_u^+$ symmetry and not the $2^2\Pi_u$ considered here. As was mentioned in section 5.1, Eliezer et al. (1967) obtained multiple phantom resonances associated with all the target states in the region and it is not too surprising that there is superficial agreement between this $2^2\Pi_u$ series $c$ resonance and one of these $2^2\Sigma_u^+$ phantoms.

The vibrational labelling used in table 5.10 for the energy levels of series $c$ is determined by the existence of the 11.19 eV level from Joyez et al. (1973) in $H_2^-$ and the 11.25 eV level from Weingartshofer & Eyb (1975) in $D_2^-$. Under the assumption that these are correct, our
### Table 5.9: \(^2\Pi_\alpha\) symmetry resonance 1 energy position \(E_0\) above ground state and width \(\Gamma\) and ‘feature’ position as a function of bond length. Widths marked * are approximate due to the proximity of the target thresholds.
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### Table 5.10: Resonance series $c$ vibrational energy level positions.

<table>
<thead>
<tr>
<th>Vib. Level</th>
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<th>HD$^-$</th>
<th>D$_2^-$</th>
</tr>
</thead>
<tbody>
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<td>11.64</td>
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result appear to be just over 0.4 eV above the experimental results with excellent matching between the vibrational spacings for all the molecules, particularly for the lower levels. If on the other hand those two levels are not correct or are actually due to another resonance, then all the experimental results would be shifted down by one level and our results would then be too high by around 0.14 eV for the H$_2^-$, between 0.08 and 0.20 eV for the HD$^-$ depending on which experimental result is used and 0.21 eV too high for the D$_2^-$.

This overestimate of the absolute energy positions comes about for two reasons. Firstly, the fixed-nuclei series $c$ resonance positions are difficult for us to pinpoint with a high degree of accuracy. This is due to the proliferation of target thresholds and associated resonance activity very close by. This is particularly true at around $R = 1.9 \ a_0$ where three target thresholds (including the two dominant parents of the resonance) intersect and it is unfortunate that this is also exactly where the resonance has its equilibrium position. The difficulty in finding the resonance positions is manifested in the potential curve which is not smooth in this region and its minimum point cannot be found with a high degree of confidence. The end result is an uncertainty in the absolute positions of the vibrational series of around 0.05 eV and in the low-lying vibrational levels. As they have different nuclear wavefunctions, the results for different molecules will be affected to different extents.

The second source of error is due to poor representation of the polarization for this symmetry and this is discussed in section 5.8.

It is interesting to note how the spacings of the highest vibrational levels observed by Furlong & Newell (1995) for D$_2$ suddenly drop between $v = 6$ and $v = 8$. This would be expected if the potential curve were to level out at higher energy, which is the behaviour seen.
in our potential curve, at around $R = 3.5 \ a_0$ when the resonance swaps to the $F^{1\Sigma_g^+}$ state.

### 5.3.2 Other features of $^2\Pi_u$ symmetry

At low energy, between 1.3 and 1.4 eV, there is some structure in the time-delay that appears to be a very distorted, wide resonance. It can also be seen as a gentle undulation in the eigenphase sum. This feature changes very little both in position and shape over the range of bond lengths considered. Although it is impossible to fit, the width can be estimated at around 5 eV. Given the width, even if this feature were a resonance, it would be likely to have only a small effect on experimental observables.

There are much clearer signs of a resonance higher up in energy. In the eigenphase sum between $R = 0.8$ and $R = 3.1 \ a_0$, there is what appears to be a characteristic resonance shape deformed by a quickly falling background. It also shows up in the time-delay but the characteristic Lorentzian shape is greatly deformed and it is impossible to fit. It is however possible to approximate a position and that is what is given in table 5.9. It is difficult to know exactly the parentage of the feature without a number of further calculations which, since it is not clearly a true resonance, are not performed here. The feature has a minimum at approximately 11.7 eV above the $v = 0$ ground state at a bond length of $R = 1.94 \ a_0$.

### 5.4 $^2\Pi_g$ total symmetry

The eigenphase sum for the $^2\Pi_g$ is characterized by a very complicated structure in which there are several rises between thresholds which give the appearance of cut-off resonances. The time-delay paints a similar picture with Lorentzian type rises suddenly blowing up at threshold. It is therefore often very difficult to track resonances with a great degree of certainty. Figure 5.7 shows the resonances as far as they could be fitted or approximated as a function of bond length.

#### 5.4.1 $^2\Pi_g$ resonance 1 - parent state $b^{3\Sigma_u^+}$

At short internuclear separation there is evidence of a resonance tracking the $b^{3\Sigma_u^+}$ target state. At $R = 0.8 \ a_0$, the resonance is overwhelmingly likely to decay into the $b^{3\Sigma_u^+}$ state despite the availability of a higher state, the $a^{3\Sigma_g^+}$, into which it could decay. Between $R = 0.9 \ a_0$ and $R = 1.0 \ a_0$, the resonance crosses the $a^{3\Sigma_g^+}$ state and so from $R = 1.0 \ a_0$ onwards can only
Figure 5.7: $^2\Pi_g$ symmetry: resonance positions as a function of bond length
Chapter 5: \( e^{-}H_{2} \) resonances as a function of bond length  

Sec. 5.4

Resonance 1

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Table 5.11: \( ^2\Pi_g \) symmetry: resonances 1 and 2 energy positions \( E_0 \) above ground state and widths \( \Gamma \) as a function of bond length.

decay into the ground or \( b \, ^3\Sigma_u^{+} \) state and again the latter is strongly favoured. At \( R = 0.8 \, \text{a}_0 \) the resonance has width 0.13 eV. As the bond length is increased, the resonance becomes wider and its definition deteriorates. The drop in the background to the eigenphase sum becomes more pronounced so that the Breit-Wigner form becomes flattened and the increase in eigenphase sum at resonance becomes far less than the characteristic \( \pi \). The time-delay also becomes distorted from the perfect Lorentzian shape and the fit becomes more and more approximate. For \( R > 1.5 \, \text{a}_0 \) (at which the width is 3.2 eV) it is no longer possible to fit a resonance. However, the eigenphase sum continues to show a weak undulation just above the \( b \, ^3\Sigma_u^{+} \) target state over the entire range of bond lengths. The resonance parameters are given in table 5.11.

This resonance appears in exactly the same position as the \( ^2\Sigma_g^{+} \) repulsive resonance. Because of this, and because it is only a weak feature, particularly in the region near the equilibrium geometry, it would be difficult to observe experimentally and indeed does not appear to have been.
5.4.2 $^2\Pi_g$ resonance 2 - parent state $c^3\Pi_u$

There is a resonance which follows the $c^3\Pi_u$ target state. For the majority of bond lengths, the resonance sits at threshold and so is not possible to fit. However, there is clear evidence in both the eigenphase sum and the time-delay to show its existence. In the case of the eigenphase sum, it appears as the upper half of the characteristic shape and the time-delay rises, if not in perfect Lorentzian form, at the threshold. At $R = 1.0 \ a_0$, the resonance moves away from threshold and can be fitted (although only approximately) with a width of around 0.2 eV. At $R = 1.1 \ a_0$ and $R = 1.3 \ a_0$, the resonance returns to the threshold and again cannot be fitted. Where it can be fitted at longer bond length, the width stays between 0.1 and 0.2 eV, although, possibly because of the effect of a number of nearby thresholds in this region, there seems to be no clear trend in width. $R = 1.8 \ a_0$ is the last point at which the resonance can be fitted and has a width of around 0.1 eV. Beyond this point the resonance sits on the threshold over the rest of the internuclear separations. The resonance parameters can be seen in table 5.11.

A resonance series in this region was observed experimentally, most notably by Weingartshofer et al. (1970) (who called it series I) and Kuyatt et al. (1966). It had been suggested that this resonance was the same as the series $^2\Sigma^+_g$ resonance due to the closeness in energy of their vibrational series (Schultz 1973). Comer & Read (1971), did not observe this resonance but reanalysed the data of Weingartshofer et al. (1970) and using angular distribution arguments assigned it as $^2\Pi_g$ symmetry and called it series $d$. They assigned the resonance to the $c^3\Pi_u$ target state and found the minimum point of the resonance potential at $R = 1.83 \ a_0$ (compared with the value found here of $R = 1.97 \ a_0$) but warned that this was rather uncertain due to a possibly invalid approximation.

Vibrational calculations have been performed on the resultant resonance potential curve. The parent state $c^3\Pi_u$ has an energy gap error of 0.07 eV at the resonance potential minimum point of $R = 1.97 \ a_0$ (from figure 3.6). This has been corrected for in our results which are shown in table 5.12.

The series $d$ results of Weingartshofer et al. (1970) and of Kuyatt et al. (1966) are shown with our $^2\Pi_g$ resonance vibrational results in table 5.12. The results of Kuyatt et al. disagree with those of Weingartshofer et al. and must be considered unreliable as their results for all other series have disagreed to a greater or lesser extent with other experiments.

Our vibrational spacings are consistently smaller by 0.02 eV than those of Weingartshofer et al. and are at an absolute energy around 0.4 eV higher. However, it may be possible that their first level is not of this series and has been confused with, for instance, one of the levels of
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5.5 total symmetry

The time-delay and eigenphase sum again show a very complicated structure which is difficult to follow. There is a mess of interactions between various resonances including a pair (resonances 1 and 2) that lie very close together and another which appears to swap between parent states before then dropping down and interfering with the pair. The resonances are shown in figure 5.8 and their parameters given in table 5.13.

5.5.1 $^2\Delta_g$ resonances 1 and 2 - avoided crossing with parents $a^3\Sigma_g^+$ and $c^3\Pi_u$

Between the $a^3\Sigma_g^+$ and the $c^3\Pi_u$ thresholds across the full range of bond length there is a complicated structure in the time-delay and eigenphase sum. At short bond length the structure suggests a combination of two resonances. Resonance 1, with a width of order 0.5 eV, sits on the $a^3\Sigma_g^+$ threshold and only shows up in the time-delay or eigenphase sum at energies greater than the threshold suggesting this is a core-excited shape resonance. Resonance 2 with a width around 0.1 eV, lies just below the $c^3\Pi_u$ and is apparent on both sides of the threshold although the eigenphase sum above threshold is heavily modified by a strongly varying background. As with most cut-off resonances such as resonance 1, it is largely a question of luck whether

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Table 5.12: $^2\Pi_g$ resonance vibrational energy level positions compared with experimental series $d$ (series I) positions. [1] Weingartshofer et al. (1970), [2] Kuyatt et al. (1966)

series $a$ for which this series has previously been mistaken. If this were the case, our vibrational levels would fit in well with those of the relabelled experimental results with an absolute energy higher by 0.07 eV. Unfortunately, Weingartshofer et al. did not give an estimate of the width of their resonance and further experimental determination would be useful. However, it is likely that our $^2\Pi_g$ resonance is indeed the series $d$ resonance.
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Figure 5.8: $^2\Delta_g$ symmetry: resonance positions as a function of bond length with target state thresholds. The dots are resonance 1, the crosses resonance 2 and the dashed line resonance 3. The diamonds give the approximate position of resonance that is seen but is not identified. Note that for reasons of clarity the energy scale is relative to the ground state potential.
the resonance position (the turning point of the eigenphase sum or the maximum of the time-delay) is sufficiently far from the threshold so that it can be fitted. If it cannot be fitted, but there is clearly a resonance, then an estimated position (normally the threshold) is used. If, as is the case with resonance 1 at some longer bond lengths, the resonance position is significantly below threshold and is only visible as a tail above threshold, no resonance position is given.

As the bond length increases, resonance 1 moves slightly above its threshold and resonance 2 rises to join its threshold. At $R = 1.5 \, \text{a}_0$ with resonance 1 approaching from below and the B $^1\Sigma_u^+$ threshold bearing down from above, resonance 2 can no longer be seen. At $R = 1.7 \, \text{a}_0$, after the B $^1\Sigma_u^+$ threshold has moved below the c $^3\Pi_u$, and the a $^3\Sigma_g^+$ is closely below the c $^3\Pi_u$, resonance 2 reappears, this time well above its parent c $^3\Pi_u$ threshold. It is likely to have been pushed up by the presence of resonance 1 so closely below it. This is consistent with an avoided crossing of the resonances around $R = 1.9 \, \text{a}_0$ where their two parent thresholds cross. After this point, the two resonances take on the character of the other. When resonance 1 is again visible after $R = 2.0 \, \text{a}_0$, it is now following the c $^3\Pi_u$, almost directly on top of it with resonance 2 now following the a $^3\Sigma_g^+$. From $R = 2.30$ to $R = 2.80 \, \text{a}_0$, resonance 1 falls below its new parent state threshold, possibly pushed by resonance 2 dropping below its new parent a $^3\Sigma_g^+$ threshold which in turn could be due to the presence of resonance 3 above it. From this point on, the presence of all three resonances and accompanying target states makes the calculation very sensitive to variation in bond length, the resonances difficult to fit and interpretation extremely difficult. As the three resonances are so close in energy, they take on the character of each other and it is impossible to follow each of them individually. In this region, the figure shows the estimated positions of the resonances where possible.

Vibrational calculations have been performed for resonance 2 although due to interactions with the other resonances, the potential curve of the resonance is not very smooth and has missing points. Resonance 1 has too many missing points for vibrational calculations to be meaningful but as it is so close to resonance 2 would have very similar resonance vibrational positions.

The parents of resonance 2 at the position of equilibrium (approximately $R = 1.98 \, \text{a}_0$) have an energy gap error of around 0.07 eV and this has been added to our results. These are shown in table 5.14 along with the series $e$ results of Weingartshofer et al. (1970). The results of Kuyatt et al. (1966) are also shown although, as mentioned previously, they are unreliable and no attempt has been made to compare them with our results.

A $^2\Delta_g$ resonance was seen in calculations by Bardsley & Cohen (1978) who described a single resonance from $R = 1.70$ to $R = 2.50 \, \text{a}_0$ which starts very close to and just above the
### Table 5.13: $^2\Delta_g$ symmetry resonances 1, 2 and 3 energy positions $E_0$ above ground state and widths $\Gamma$ as a function of bond length.
Chapter 5: $e$-$H_2$ resonances as a function of bond length

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$^2\Delta_g$ resonances as a function of bond length

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Table 5.14: $^2\Delta_g$ resonance 2 vibrational energy level positions compared with experimental series $e$ (series II) positions [1] Weingartshofer et al. (1970) and [2] Kuyatt et al. (1966)

As the bond length increases it stays above the $c^3\Pi_u$ which crosses the $a^3\Sigma_g^+$ at around $R = 1.9$ $a_0$. The resonance then crosses the $a^3\Sigma_g^+$ at about $R = 2.2$ $a_0$ before falling slightly away from it. This fits in exactly with our resonance 2.

A resonance with anisotropic angular distribution was seen in this region by Kuyatt et al. (1966) with a width of around 0.3 eV (similar to the widths of resonance 1 and resonance 2 at equilibrium) and by Weingartshofer et al. (1970) who labelled it series II. It was later renamed series $e$ (Comer & Read 1971). As its vibrational energy splittings are close to those of series $c$ it had been suggested that series $c$ and $e$ are in fact the same resonance. Comer & Read (1971), however, analysing the results of Kuyatt et al. (1966) found this resonance potential curve to have a minimum of 11.36 ± 0.1 eV (relative to the $v = 0$ ground state), around 0.2 eV higher than series $c$ and suggested $^2\Delta_g$ as the resonance symmetry.

Our vibrational spacing results for resonance 2 are in excellent agreement with the series $e$ results of Weingartshofer et al. although our absolute energies are around 0.3 eV higher. Experimentally it would be difficult to differentiate between resonances 1 and 2 since they are so close in energy and it is even possible that the appearance of two resonance is due to an incomplete calculation. It is therefore suggested that our $^2\Delta_g$ resonances 1 and 2 might be manifestations of the experimental series $e$ resonance, confirming the symmetry assignment of Comer & Read (1971) for that resonance.

5.5.2 $^2\Delta_g$ resonance 3 - joint parents $C^1\Pi_u$ and $E,F^1\Sigma_g^+$

In both the eigenphase sum and time-delay pictures, there is evidence for a further weak resonance at higher energy although it is distorted and cut-off by thresholds. It starts off following
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the \( E,F \, ^1\Sigma_g^+ \) state at low energy, swaps to the \( C \, ^1\Pi_u \) state when those states cross at around \( R = 1.78 \ a_0 \) and then swaps back to the \( E,F \, ^1\Sigma_g^+ \) when the two target states swap again at around \( R = 3.0 \ a_0 \). At \( R = 0.8 \ a_0 \) it has a width of approximately 1.8 eV which has reduced to 0.08 eV by \( R = 1.0 \) after which it sits on threshold and its width cannot be determined.

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*Table 5.15:* \( ^2\Delta_g \) resonance 3 vibrational energy level positions. This resonance is only weak and has not been seen experimentally.

This resonance has not as yet been sighted experimentally and may only be a very weak feature. Nonetheless calculations have been performed on the potential curve to find the vibrational level positions. The equilibrium position of the resonance \( (R = 1.98 \ a_0) \) coincides with the crossing of its parent states, \( E,F \, ^1\Sigma_g^+ \) and \( C \, ^1\Pi_u \). The error in energy gap for these states at this point are -0.04 and -0.005 eV respectively. In all cases of parent swapping, the resonance has been found to follow the lower parent and so the error correction used here is the energy gap error of the \( E,F \, ^1\Sigma_g^+ \) which is the lower of the two states after correction to their positions. This has been added to our results which are displayed in table 5.15.

5.6 \( ^2\Delta_u \) total symmetry

The time-delay shows evidence of resonance-type activity for this symmetry with resonances associated with several excited target states. However, there is so much distortion caused by the bunching of all these resonances with the thresholds that there is a very complicated structure with no clear characteristic Lorentzian shapes in the time-delay. The eigenphase sum shows a series of rises which are all cut off by the next threshold before they have completed even a third of the required jump of \( \tau \), suggesting they are not true resonances. Indeed, at no bond length are any of these resonance features reliably fittable.
5.7 $^2\Phi_u$ and $^2\Phi_g$ total symmetries

For both of these symmetries there were no pronounced resonances at any bond length. The time-delay did fluctuate a fair amount, particularly near to thresholds but there were no characteristic Lorentzians to suggest the formation of a real resonance. The eigenphase sum varied only very slightly and never came close to jumping by the $\pi$ required for a resonance.

These results fit in with all previous studies, none of which, to the best of our knowledge, have ever attributed a resonance to a $\Phi$ state.

5.8 Underrepresentation of polarisation effects

It is notable that, once we have corrected for minor errors in our representation of the target states, our absolute positions of the $^2\Sigma_u^+$ and $^2\Sigma_u^+$ resonances are in near perfect agreement with experiment. Conversely, we find that our calculations for resonances of higher symmetry are up to 0.4 eV too high in absolute energy even though the vibrational spacings fit extremely well.

As the major source of binding for these resonances is the polarization of the nearby ('parent') electronically excited states of $H_2$, there seems to be a likely explanation for this problem. Our calculations included no $\delta$ or higher orbitals located on the target, nor any target states of $\Delta$ or higher symmetry in the close-coupling expansion. Inclusion of these would not significantly add to the polarization potential of $\Sigma$ symmetry resonances but would be expected to for resonances of higher symmetries. This would have the effect of pushing the resonance position down in energy and closer to the experimental values.
<table>
<thead>
<tr>
<th>Symm.</th>
<th>Series</th>
<th>Parent state(s)</th>
<th>$R$ (a₀)</th>
<th>$E_0$(eV)$^1$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Sigma_g^+$</td>
<td>b $^3\Sigma_u^+$</td>
<td>-</td>
<td>-</td>
<td>Well known B $^2\Sigma_g^+$ repulsive state of H$_2^-$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a $^3\Sigma_g^+$, c $^3\Pi_u$, C $^1\Pi_u$, E $^1\Sigma_g^+$</td>
<td>1.90</td>
<td>11.05</td>
<td>Multiple parent states (no swapping)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B $^1\Sigma_u^+$</td>
<td></td>
<td></td>
<td>Seen only for $R &gt; 3.0$ a₀, not noted experimentally</td>
<td></td>
</tr>
<tr>
<td>$^2\Sigma_u^+$</td>
<td>X $^1\Sigma_g^+$</td>
<td></td>
<td></td>
<td>Ground state shape resonance X $^2\Sigma_u^+$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b $^3\Sigma_u^+$</td>
<td></td>
<td></td>
<td>Weak feature only seen for $R &lt; 1.3$ a₀</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a $^3\Sigma_g^+$, B $^1\Sigma_u^+$</td>
<td>2.33</td>
<td>11.05</td>
<td>Swaps between parent states</td>
<td></td>
</tr>
<tr>
<td>$^2\Pi_u$</td>
<td>c $^3\Sigma_g^+$, c $^3\Pi_u$, F $^1\Sigma_g^+$</td>
<td>1.94</td>
<td>11.39</td>
<td>Swaps between parent states</td>
<td></td>
</tr>
<tr>
<td>$^2\Pi_g$</td>
<td>b $^3\Sigma_u^+$</td>
<td></td>
<td></td>
<td>Seen only for $R \leq 1.5$ a₀</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c $^3\Pi_u$</td>
<td>1.97</td>
<td>11.46</td>
<td>Possibly series d (series I)</td>
<td></td>
</tr>
<tr>
<td>$^2\Delta_g$</td>
<td>e? $^3\Sigma_g^+$, c $^3\Pi_u$</td>
<td>1.94$^2$</td>
<td>11.51$^2$</td>
<td>Avoided crossing between two close lying resonances - possibly accounts for series e (series II)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E, F $^1\Sigma_g^+$, C $^1\Pi_u$</td>
<td>1.97</td>
<td>12.06</td>
<td>Swaps back and forth between parents</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.16: Summary of all resonances found. $^1$Relative to the $v = 0$ ground state energy. $^2$These figures are an estimation of the shared potential minimum of the two resonances.
Multiple parent states and parent state swapping

In this chapter it is shown how, contrary to the normal assumption, a resonance can have more than one excited target state as a parent. This explains the result seen in chapter 5 that certain resonances swap parent states as the bond length is changed. It also explains many of the difficulties encountered in the assignment of these resonances and in the difficulty of fitting resonance potential curves to experimental data.

6.1 The multiple parent model

It has in the past been standard practice to assign a single parent state to a resonance in the belief that every resonance was associated with one particular target state (Schultz 1973). However, it was seen in chapter 5 that certain resonances swap between target states as the bond length is increased suggesting that the situation is more complicated than the single parent model.

It is suggested here that resonances can actually be associated with multiple target states i.e. that the potential in which the electron is temporarily trapped is made up of contributions from a number of target states. At a particular bond length, it is possible that one parent dominates and the resonance is largely associated with that state (the dominant parent would have custody with the other parents allowed limited visiting rights). However, as the bond length is varied, and particularly if target states cross, the relative importance of each of the parent target states changes and this can result in a change in the dominant parent. This will be seen as an apparent
swapping between states as the bond length is varied.

Previous multi-state electron-\(\text{H}_2\) scattering calculations performed at a single bond length would simply assign any resonance seen to what would appear to be a single parent target state, the dominant parent at that particular bond length.

In this chapter the parentage of two resonances: the series \(a\) resonance of \(^2\Sigma^+_g\) symmetry and the series \(b\) resonance of \(^2\Sigma^+_u\) are investigated in detail. The series \(a\) resonance lies under a group of four target states and there is no obvious swapping of parents as a function of bond length. The series \(b\) resonance, on the other hand, is seen to swap parents.

### 6.2 Methods for investigating parentage

In the inner region it may be possible to correlate a resonance with one particular R-matrix pole (inner region (N+1) system eigenvalue). This can be attempted by plotting the resonance along with all the R-matrix poles as a function of bond length. In some cases the resonance may be seen to follow one pole thus allowing it to be identified with the target plus continuum configuration represented by that pole. This is unlikely to be possible whenever there is a high density of R-matrix poles in the region.

An alternative approach to help identify a parent, this time in the outer region, is to try to identify the resonance structure with a particular exit channel. This is normally done by looking at the eigenphase of each separate channel or at the branching ratios found from the time-delay eigenvectors. A resonance lying above its parent would be expected to decay overwhelmingly into that parent, as indicated by the branching ratios. The majority of the rise in the eigenphase sum would also be expected to appear in the eigenphase of the exit channels associated with the parent target state. However, this method clearly relies on the resonance being above its parent and will not work for Feshbach resonances which lie below their parent.

In chapter 2 it was shown how configuration state functions (CSFs) are used in the expansion of the inner region wavefunctions. A resonance purely associated with one excited target state parent would be expected to have eigenfunctions overwhelmingly made up of the CSFs of only that target state. By performing a series of calculations with only the ground and each candidate target parent state in turn, it should be possible in the single parent model, to tell which is the parent as the resonance would be apparent only in the calculation that included the real parent.
6.3 **Parentage of the $^2\Sigma_g^+$ series $a$ resonance**

The series $a$ resonance lies just below a bunch of four target states ($c \, ^3\Pi_u$, $C \, ^1\Pi_u$, $a \, ^3\Sigma_g^+$ and the inner E region of the $E, F \, ^1\Sigma_g^+$) and it is impossible to tell from the shape of the curve which state it is following.

Figure 6.1 shows the series $a$ resonance plotted along with the R-matrix poles of $^2\Sigma_g^+$ symmetry. It is clear that due to the high density of interacting poles, avoided crossings make the situation too complicated to allow a correlation of the resonance with one particular pole and this method cannot be used. The complicated interaction of the R-matrix poles, incidentally, makes a non-adiabatic treatment of the resonance very difficult.

Since the resonance lies below its candidate parents, it is also impossible to identify the resonance with a particular exit channel and no information can be gleaned from the separate channel eigenphases or the branching ratios. It is therefore necessary to perform a series of 2-state (ground + candidate parent) calculations to help find the parent in this case.

Figure 6.2 shows the eigenphase sum for both the full 7-state and four 2-state calculations with the ground plus $c \, ^3\Pi_u$, $C \, ^1\Pi_u$, $E, F \, ^1\Sigma_g^+$ and a $^3\Sigma_g^+$ respectively. A resonance can be seen in all of the 2-state calculations. This suggests that contrary to the single parent model, the resonance in fact has multiple parent states.

As discussed in section 5.1, Eliezer et al. (1967) used a quasi-vibrational method to calculate the potential energy functions of the $^2\Sigma_g^+$ states of H$_2^-$ and found H$_2^-$ states associated with three of these target states ($c \, ^3\Pi_u$, $C \, ^1\Pi_u$, $a \, ^3\Sigma_g^+$). From our results it would seem likely that this is due to a lack of coupling between the different target states in their calculations. The resonance seen in our 7-state calculation is trapped by a potential which has contributions from all four target states. The calculation of Eliezer et al. (1967) gives multiple phantom resonances because it fails to combine together these different contributions to the potential.

Comer & Read (1971) saw the series $a$ resonance experimentally and following the lead of Eliezer et al. (1967) assigned it to the $c \, ^3\Pi_u$ parent state. da Silva et al. (1990) performed a 5-state calculation which despite not including any $\Pi$ states still saw the resonance and assigned it to the $a \, ^3\Sigma_g^+$ parent. These apparent inconsistencies are entirely explained by the idea that this resonance in actual fact has multiple parent states. It is clear that calculations using different methods and including different states and experiments which measure different aspects of the same interaction could easily assign resonances differently if forced to choose a single parent.
Figure 6.1: Series a resonance (thick line, red) plotted with the R-matrix poles of $^3\Sigma^+_g$ symmetry
Figure 6.2: Eigenphase sums for $^2\Sigma_g^+$ symmetry: i) 7-state (black), ii) Ground + a $^3\Sigma_g^+$ (blue), iii) Ground + c $^3\Pi_u$ (red), iv) Ground + C $^1\Pi_u$ (green), v) Ground + E,F $^1\Sigma_g^+$ (dark purple) along with the target thresholds (black dashed lines).
6.4 Parentage of the $2\Sigma_u^+$ series $b$ resonance

The series $b$ resonance is closely associated with, and lies just above, the $a\, ^3\Sigma_g^+$ target state for bond lengths up to the region of $R = 1.7 \, a_0$ where it falls below the state, swapping to the $B\, ^1\Sigma_u^+$ state. It then continues to follow this state for the remainder of the bond lengths considered. There is no second resonance in the vicinity that would explain this phenomenon through an avoided crossing.

Figure 6.3 shows the resonance plotted along with the $2\Sigma_u^+$ R-matrix poles. As in the case of the series $a$ resonance, the density of the poles is too great to try and correlate the resonance with a particular pole.

To investigate the parentage, a set of reduced state calculations are performed, concentrating on the $a\, ^3\Sigma_g^+$ and $B\, ^1\Sigma_u^+$ states between which the resonance appears to swap. It should be noted, however, that other target states might also be involved.

When performing these reduced-state calculations, it was found necessary also to include the $b\, ^3\Sigma_u^+$ state as its omission results in the disappearance of the lower $2\Sigma_u^+$ resonance and consequently produces spurious resonance-like features in the time-delay.

The following reduced state calculations were performed at several bond lengths: i) $X\, ^1\Sigma_g^+$, $b\, ^3\Sigma_u^+$ and $a\, ^3\Sigma_g^+$ ($3\text{-state}/a\, ^3\Sigma_g^+$); ii) $X\, ^1\Sigma_g^+$, $b\, ^3\Sigma_u^+$ and $B\, ^1\Sigma_u^+$ ($3\text{-state}/B\, ^1\Sigma_u^+$); and iii) $X\, ^1\Sigma_g^+$, $b\, ^3\Sigma_u^+$, $a\, ^3\Sigma_g^+$ and $B\, ^1\Sigma_u^+$ (the ‘4-state’).

Figure 6.4 shows the results of the reduced and 7-state calculations at $R = 1.2 \, a_0$ (when the resonance is associated with the $a\, ^3\Sigma_g^+$ state), $R = 1.7 \, a_0$ (when the resonance is in the process of crossing between states) and $R = 3.5 \, a_0$ (when the resonance is associated with the $B\, ^1\Sigma_u^+$ state). The figures show plots of the time-delay experienced by the scattering electron. The thresholds of the two key target states, $a\, ^3\Sigma_g^+$ and $B\, ^1\Sigma_u^+$, are labelled and other thresholds from the 7-state calculation are marked. As described in chapter 4, in the time-delay picture, an undistorted resonance will appear as a perfect Lorentzian although a nearby threshold can distort the shape of, or cut off, a resonance. It should be remembered that the time-delay at threshold itself should become infinite although this point can be missed due to the coarseness of the grid$^1$.

At $R = 1.2 \, a_0$, the resonance in the 7-state calculation appears approximately at the $a\, ^3\Sigma_g^+$ threshold. The 3-state/ $a\, ^3\Sigma_g^+$ calculation shows little or no sign of resonance. The 3-state/B $^1\Sigma_u^+$ calculation shows a resonance just above its threshold. With the 4-state cal-

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$^1$Thresholds are necessarily avoided in all the outer region codes
Figure 6.3: Series $b$ resonance (thick line, black) plotted with the R-matrix poles of $^2\Sigma_u^+$ symmetry relative to the ground state energy
Figure 6.4: Time-delay as a function of electron energy for i) Full 7-state (black) ii) 3-state/ $a^3\Sigma_g^+$ (green); iii) 3-state/ $B^1\Sigma_u^+$ (blue); and iv) 4-state (red) at bond lengths of a) $R = 1.20a_0$, b) $R = 1.70a_0$ and c) $R = 3.50a_0$. 
Chapter 6: Multiple parent states and parent state swapping

Sec. 6.4

culation, this resonance forms a part of a resonance of about double the width of the 7-state resonance at approximately 0.3 eV above it. The decay fractions of the 4-state and 7-state resonance to the $\text{a} \ 3\Sigma_g^+$ state are very similar (0.33 for the 7-state calculation and 0.31 for the 4-state) and they are almost certainly the same resonance. The differences in shape and position are due to the additional target states in the 7-state calculation. It is well known that increasing the number of states in a close-coupling calculation pushes down the position of a resonance Branchett et al. (1990); usually it also leads to a corresponding narrowing.

At $R = 1.7 \ \text{a}_0$, the thresholds of the $\text{a} \ 3\Sigma_g^+$ and $\text{B} \ 1\Sigma_u^+$ cross and the 7-state calculation has a well-resolved resonance at around 11.35 eV, approximately 0.2 eV below the crossing energy. The 3-state/$\text{a} \ 3\Sigma_g^+$ calculation is affected by the threshold but shows no sign of resonance. The 3-state/$\text{B} \ 1\Sigma_u^+$ calculation shows slight traces of a resonance around the target threshold. When both these states are included in the 4-state calculation, a clear resonance is seen at around 11.55 eV, with almost exactly the same shape as the full 7-state resonance but at an energy about 0.2 eV higher. This energy shift can again be explained by the greater number of states in the 7-state calculation.

At $R = 3.5 \ \text{a}_0$, the $\text{a} \ 3\Sigma_g^+$ threshold is now well above the $\text{B} \ 1\Sigma_u^+$ threshold and in the 7-state, a sharp resonance appears just below the $\text{B} \ 1\Sigma_u^+$ threshold and cut off at higher energies by it. In the 3-state/$\text{a} \ 3\Sigma_g^+$ calculation, there is a very clear resonance that appears a little above the $\text{a} \ 3\Sigma_g^+$ threshold. In the 3-state/$\text{B} \ 1\Sigma_u^+$ calculation, there is a feature just above threshold that appears to be the tail end of a resonance cut-off by the threshold. In the 4-state calculation, including both of these states, the 3-state/$\text{a} \ 3\Sigma_g^+$ resonance can no longer be seen at its original position. Just above the $\text{B} \ 1\Sigma_u^+$ threshold, the tail-end of a resonance much sharper than the 3-state/$\text{B} \ 1\Sigma_u^+$ feature and closer to the one with the 7-state calculation is seen, cut-off at lower energy by the threshold.

At all the bond lengths, the resonance seen in the full calculation only appears when both the $\text{a} \ 3\Sigma_g^+$ and $\text{B} \ 1\Sigma_u^+$ states are included. When resonances do appear in the 3-state calculations such as in the 3-state/$\text{a} \ 3\Sigma_g^+$ at $R = 3.5 \ \text{a}_0$ or the 3-state/$\text{B} \ 1\Sigma_u^+$ at $R = 1.2 \ \text{a}_0$, then in the 4-state calculation they become part of the new resonance. These facts strongly suggest that this new resonance has both those target states as joint parents.

At short bond length, the $\text{a} \ 3\Sigma_g^+$ parent state is almost fully dominant. At $R = 1.2 \ \text{a}_0$ the resonance in the 7-state calculation lies just above its apparent parent, the $\text{a} \ 3\Sigma_g^+$. Assuming the single parent model, the decay fraction to this parent would be expected to be almost unity but in fact is only 0.33 suggesting that this state is no longer totally dominant. At the equilibrium distance, $R = 1.4 \ \text{a}_0$, the $\text{a} \ 3\Sigma_g^+$ is still dominant but only just. A previous calculation.
performed at the fixed equilibrium geometry saw a resonance at this energy but could not fit a resonance using the eigenphase sum method due to a falling background (Branchett et al. 1990). At the point where the two parents meet in energy (around \( R = 1.7 \text{ a}_0 \)), they have approximately joint custody of the resonance. At greater bond length, the \( B \, ^1\Sigma_u^+ \) state becomes the dominant parent.

### 6.5 Other resonances

Parent swapping was encountered for the \( ^2\Pi_u \) series \( c \) resonance. In chapter 5 it was seen how this resonance follows the \( a \, ^3\Sigma_u^+ \) state for \( R < 1.7 \text{ a}_0 \), swaps to the \( c \, ^3\Pi_u \) state before swapping again and settling on the \( E,F \, ^1\Sigma_u^+ \) for \( R \geq 3.5 \text{ a}_0 \). These results are very interesting when compared with experimental results for this series \( c \) (Schultz 1973) resonance. Comer & Read (1971) could not decide between the \( c \, ^3\Pi_u \) and the \( a \, ^3\Sigma_u^+ \) as parents when looking at \( D_2 \). Mason & Newell (1986) when looking at this resonance in \( H_2 \) took the parent to be the \( c \, ^3\Pi_u \) state in agreement with what they called the accepted designation.

The problems of assignment are explained by the multiple parents/parent swapping model. The first swapping between states occurs in the region close to equilibrium bond length which is the region mostly sampled by the experiments. It is not surprising if forced artificially to choose one or the other that different target states will be chosen as parent.

A further resonance that exhibits parent swapping is one of symmetry \( ^2\Delta_g \) ('resonance 3') that swaps from the \( E,F \, ^1\Sigma_g^+ \) to the \( C \, ^1\Pi_u \) and then back again (see section 5.5.2).

### 6.6 Conclusion

The observation that the parentage of particular resonances can be more complicated than the single parent model has been made before (Buckley & Bottcher 1977) but has seemingly been ignored. The idea of multiple parents and the possibility of swapping between parents with bond length provides an explanation for the difficulties previously encountered when trying to assign resonances under the assumption of a single parent target state.

For example, one method of finding the parent state from experimental vibrational series data is to deduce a potential curve of the resonance and then compare this curve with those of the target states. This requires the assumptions that the resonance width is independent of the internuclear separation and that the resonance potential follows a Morse function (Comer &
Read 1971). In the case of a resonance that swaps parent, both of these assumptions can fail. This would lead to poor fits to experimental data which was a problem encountered by Comer and Read for the series $b$ and $c$ resonances which both swap parent.

Given this, a re-examination of previously found or calculated raw data might well prove fruitful. Also, since parent swapping appears in electron collisions with the most basic, fundamental neutral molecule, $H_2$, it is likely to be important in electron collisions with larger, more complicated molecules where there can easily be a bunching of target states (although it will not affect the low-energy shape resonances often seen in large molecules) and indeed inconsistencies and difficulties in the assignment of resonances in $N_2$ and CO electron scattering have been noted previously (Mason 1987).

The dropping of the single parent assumption has major consequences, both for any future electron molecule scattering calculations in which the motion of the nuclei is considered and in the interpretation of experimental data. Multiple parents of Feshbach resonances might also be important in other areas of physics where resonances are prominent.
Chapter 7

Conclusion

7.1 Summary of results

The low energy (< 15 eV) region in electron-H\textsubscript{2} scattering has been studied using a series of fixed-nuclei R-matrix calculations over a range of bond lengths. The time-delay method for finding and parameterizing resonances, developed in this work, has proven extremely successful in tracking resonances where previous methods have failed. The complicated structure revealed shows even more resonance activity than has previously been suspected.

A major result of this work has been to prove that the standard, single parent model of a Feshbach resonance does not work under all circumstances. It has been shown that resonances can have multiple parent states and can even swap parent states as a function of bond length. This might prove to be important in other areas of physics where resonance activity is significant.

The series \textit{a} resonance has been confirmed as \textit{a} \textit{\Sigma} \textsubscript{g} \textsuperscript{+} symmetry. It has been found to have joint parent states of \textit{a} \textit{3} \textit{\Sigma} \textsubscript{g} \textsuperscript{+}, \textit{C} \textit{1} \textit{\Pi} \textsubscript{u}, \textit{c} \textit{3} \textit{\Pi} \textsubscript{u} and the inner 'E' region of the \textit{E},\textit{F} \textit{1} \textit{\Sigma} \textsubscript{g} \textsuperscript{+} state through a series of 2-state calculations. This joint parentage explains why previous determinations of parentage, both theoretical and experimental, have been inconclusive or contradictory. Calculations of vibrational levels fit perfectly with experiment for \textit{e}–\textit{H}_2, and \textit{e}–\textit{D}_2. There is insufficient reliable experimental data for comparison of results for \textit{e}–\textit{HD}. Simple calculations of resonance width suggest that the width should increase with resonance vibrational level and decrease isotopically from \textit{H}_2 through \text{HD} to \text{D}_2. This is as yet to be tested experimentally.

The series \textit{b} has been seen experimentally twice before and never modelled theoretically.
Its existence has been the subject of much debate over the years. The difficulty in seeing it experimentally has been explained by the fact that its potential minimum is at long bond length in comparison with the ground state. Because of Franck-Condon factors, it will decay preferentially into high vibrational levels of the ground state and so will only be seen in experiments which monitor these exit channels. The resonance was originally assigned as $^{2}\Sigma_g^+$ but the results seen here definitively reassign it as $^{2}\Sigma_u^+$ symmetry. The resonance has been found to swap between its parent states, the $^3\Sigma_g^+$ and the $^1\Sigma_u^+$ as the bond length is increased. Calculations of vibrational energy levels fit well with experiment for the vibrational spacings and are close in absolute energy assuming one level was not seen experimentally.

The series $c$ resonance was found to be of $^2\Pi_u$ symmetry in agreement with some of the experimental determinations. It has joint parents and is seen to swap from the $^3\Sigma_g^+$ to the $^1\Pi_u$ close to its potential minimum and then over to the $E,F^1\Sigma_g^+$ at high bond length. Vibrational spacings fit well with experiment although absolute the excitation energy appears to be too high. This is likely to be due to an underrepresentation of polarization effects for this symmetry, an underestimate shared by all the non-$\Sigma$ symmetries due to limitations in the size of the basis set and close-coupling expansion.

A resonance of $^2\Pi_g$ symmetry has been found which is likely to be the series $d$ resonance. It follows its parent, the $^3\Pi_u$ across almost the full range of bond lengths. Vibrational energy levels would agree well with experiment assuming that the first experimental level in fact belongs to a separate series, possibly series $a$ with which the resonance series has been confused in the past. The absolute energy level is again too high, suffering from the same underrepresentation of polarization as the series $c$.

$^2\Delta_g$ symmetry calculations reveal two resonances very close together. They start off following the $a^3\Sigma_g^+$ and $^3\Pi_u$ target state respectively before taking on each other’s character after an avoided crossing near the potential minimum. Vibrational spacings for one of the resonances (the other resonance would have very similar spacings) fit well with a resonance seen experimentally. This resonance has been assigned as $^2\Delta_g$ although others have argued that it is actually just series $c$. It seems likely that the resonances revealed in this work are responsible for the series $e$ resonance. A further weak resonance of $^2\Delta_g$ symmetry has been found at higher energy and vibrational levels found although it has not as yet, been seen experimentally.

In addition to these bound resonances, the $^2\Sigma_g^+$ repulsive state of $H_2^-$ ($B^2\Sigma_g^+$) and the $^2\Sigma_u^+$ ground state shape resonance ($X^2\Sigma_u^+$) have been successfully modelled. Several other weak resonant features or resonances only trackable over limited ranges of bond lengths have also been seen.
This analysis clears up the problems and difficulties encountered by experimentalists in their analysis of resonances in the complex 10–12 eV region and explains many of the contradictions found among theoretical studies.

### 7.2 Improvements to the calculation

The target in this calculation is represented by a very small basis set of Slater type orbitals. Such a compact basis set was required at the start of this calculation due to computational limitations in the number of configurations that could be considered in the expansion of the \((N+1)\) wavefunction. Since that time, considerable improvements to the codes have been made (Tennyson 1996b) which allow a far greater number of configurations to be considered. Although it was shown in chapter 3 that increasing the basis set might cause problems of linear dependence, it could be advantageous to utilize a more extensive basis set in order to model the target states better. More accurate target state energies would allow direct comparison of resonance positions with experimental results.

The underrepresentation of the polarization for non-\(\Sigma\) resonances discussed in section 5.8 is probably the greatest source of error in the resonance positions. It is, however, not a simple problem to alleviate in the R-matrix method. To improve the polarization, it is necessary to include basis functions of higher angular momentum (\(\delta, \phi\) etc...) and higher target states. These basis functions and target state wavefunctions are necessarily diffuse and so cannot be contained within a standard sized R-matrix boundary. The boundary used in this work at a radius of \(20\) \(a_0\) is already the largest used for any molecular target and increasing it any further could remove many of the efficiencies gained through the use of the R-matrix method. It would therefore be useful to examine the effect of including the extra basis functions and target states to determine the size of the inner region necessary to accommodate the functions and hence to determine the feasibility of such a calculation.

### 7.3 Future work

The calculation of the \(K_-,\) and hence the \(S-\) and \(T-\) matrices over a range of bond lengths has opened up a wide range of possibilities for future calculations. Data has already been supplied to collaborators looking at collisions of electrons with molecules physisorbed onto a metal surface and charge transfer in molecule-surface collisions. Other possible future calculations include the following:
7.3.1 Adiabatic vibrational calculations

In the adiabatic-nuclei model, cross sections for excitation from an initial state $i$ to a final state $f$ can be approximated by vibrationally averaging the fixed-nuclei T-matrices over the nuclear wave functions of the two states (Morrison 1993):

$$T_{vi\rightarrow vf} = \langle \Xi_{vf} | T | \Xi_{vi} \rangle. \quad (7.1)$$

with the nuclear wavefunctions $\Xi$ found by solving the Schrödinger equation for the potential curves.

Using this approximation, the following can, for example, be calculated:

- Electronically elastic, vibrational excitation cross sections $\nu = 0 \rightarrow 1, 2, 3$ etc.
- Electronic and vibrational excitation cross sections
- Dissociation cross sections through excitation to the $b^3\Sigma_u^+$ dissociative state
- Dissociative attachment cross sections through excitation to the $B^2\Sigma_g^+$ $\text{H}_2^-$ resonance

7.3.2 Non-adiabatic calculations

In non-adiabatic R-matrix theory, configuration space is split by a hypersphere defined by $0 < r < a$, where $r$ is the electron-centre of mass distance, and $A_{in} \leq R \leq A_{out}$ (see figure 7.1). $A_{in}$ is chosen so as just to exclude the singularity in the potential at the nuclei and $A_{out}$ such that the target vibrational states have negligible amplitude for $R > A_{out}$.

In this model, configuration space can be split into three distinct regions depending on the outcome of the collision. $r > a$, with the bond length $R$ remaining within the boundary, is equivalent to the electron simply scattering from the molecule. $r$ remaining within the boundary but $R > A_{out}$ is characterized by dissociative attachment. With both $r > a$ and $R > A_{out}$, the molecule dissociates.

The non-adiabatic model includes vibrational functions in the close-coupling expansion. The functions are derived from the potential curves of the R-matrix poles which are tracked as a function of bond length in a series of adiabatic fixed-nuclei calculations. However, in order to calculate the vibrational functions, the diabatic potential of each R-matrix pole (i.e. the potential without avoided crossings) is required. Therefore, if there are avoided crossings between poles, the pole energies need to be reordered, a process which is currently performed by hand.
Figure 7.1: Splitting of configuration space in the non-adiabatic model. \( R \) is the bond length and \( r \) the electron-molecular centre of mass distance.
As shown in figures 6.1 and 6.3, there can be a bunching of R-matrix poles around target states and the high bond length area is riddled with avoided crossings which makes it virtually impossible to reorder the pole energies in this region. Until a better reordering procedure is introduced, this limits the adiabatic calculations in this case to areas where there are few avoided crossings, such as vibrational excitation of the ground state.
Appendix A

Documentation of the **TIMEDEL** module

**TIMEDEL**

TIMEDEL is an adaptation of the module RSOLVE and is used to calculate the time-delay of the electron as it interacts with the molecule. It can also calculate branching ratios. It takes its input from INTERF.

The input is very similar to that of RSOLVE although, unlike RSOLVE, it is currently limited to a single energy range and a single geometry. As with RSOLVE, the asymptotic codes RPROP and CFASYM are called. Although these have their own namelist inputs (see OUTER documentation), the default values will often prove sufficient.

The output time-delay on unit LUTD will be read into the FITLOR module and a Lorentzian fitted to the data.

**Input files:**
- Target and channel data (on unit LUCHAN)
- Fixed nuclei R-matrix data (on unit LURMT)

**Output files:**
- Time-delay (on unit LUTD)
- Branching ratios (on unit LUBR)
Appendix A: Documentation of the TIMEDEL module

The following PARAMETERS are used to define array dimensions

MAXFCH = 100  maximum number of fixed nuclei scattering channels
MAXTGT = 20  maximum number of target electronic states

Namelist input /TIMEDEL/

The format of the following is (Name, Type, Dimension, Default, Limits, ! description) Unless specified otherwise, the default value applies to all elements of array variables.

BBLOCH R 1  0. [:]  
! Coefficient in electronic Bloch operator

BIGB R 1  0. [:]  
! Coefficient in nuclear Bloch operator

EINC R 2  0. [:]  
! Scattering energies relative to lowest level of target
  EINC(1) = initial energy
  EINC(2) = energy increment
  units are as specified by IEUNIT

GUTOT I 1  0 [-1:1]  
! G/U symmetry of total system

ICFORM C 1  'U' ['U'|'F']  
! format flag for channel dataset, 'F' for formatted, 'U' for unformatted

IEUNIT I 1  1 [1,2]  
! units in which input scattering energies are input
  1= Ryd, 2= eV

INRFRM C 1  'U' ['U'|'F']  
! Formatted/unformatted switch for unit LUNRMT

IPRINT I 6  0 [0|1]  
! Debug print switches:
  In each case -1 gives less than the default output and +1 more than the default
Appendix A: Documentation of the TIMEDEL module

(1) =1 Print all input data
(5) =1 Print R-matrices

IRFORM C 1 'U' ('U'|'F')
! format flag for R-matrix dataset, 'F' for formatted, 'U' for unformatted

ISMAX I 1 0 [0:]
! maximum multipole to be used in the expansion of the long range potentials (note that if either ALPHAO or ALPHA2 is non-zero then ISMAX must be at least 3)

IWRITE I 1 6 [1:]
! logical unit for printed output

LUBR I 1 40 [1:]
! Logical unit for branching ratio output

LUCHAN I 1 10 [1:]
! logical unit for input channel and target datasets

LURMT I 1 21 [1:]
! logical unit holding input R-matrix poles and amplitudes together with multipole expansion of asymptotic potentials, and parameterized Butt correction

LUTD I 1 42 [1:]
! logical unit for time-delay output

MDMAX I 1 0 [0:]
! maximum multipole to be retained in expansion of asymptotic internuclear (dissociation) potential

MGVN I 1 [0:]
! total symmetry of system

NAME C 60
! title for any output

NCHSET I 1 1 [0:]
! set numbers of required channel dataset(s)

NRMSET I 1 1 [0:]
! set number of required R-matrix dataset(s)
Appendix A: Documentation of the TIMEDEL module

NRQUAD I 1 201 [1:]
! number of quadrature points for integrals in adiabatic approximation (if =0 then code decides)

NVCSET I 1 1 [1:]
! set number for input vibrational/dissociating channel data

R R 1 [0.:]
! internuclear separation

SEPR R 1 0.001 [0.:]
! energy separation at which the two S-matrices are found in order to calculate the energy derivative of the S-matrix

STOT I 1 [1:]
! spin multiplicity of total system
Appendix B

GETORD routine for automatically ordering target states

As described in section 3.6, it is necessary to match the energy order of the target states with the order in which the states are outputted from CONGEN. As the bond length is varied, target state potentials can swap so that the energy ordering changes. The following routine examines the target properties file and puts the numbering positions of the target states $X\,^{1}\Sigma_{g}^{+},\, E,\, F\,^{1}\Sigma_{g}^{+},\, B\,^{1}\Sigma_{u}^{+},\, b\,^{3}\Sigma_{u}^{+},\, a\,^{3}\Sigma_{g}^{+},\, C\,^{1}\Pi_{u}$ and $c\,^{3}\Pi_{u}$ into the UNIX variables: ssg0, ssg1, ssu0, tsu0, tsg0, spu0, tpu0. It is run in the current shell before the input file to INTERF is created. The variables are then used in the namelist input to INTERF, as follows:

```
IMCSF=$ssg0,0 , $ssg1,0 , $tsu0,0 , $ssu0,0 ,
       $tpu0,1, $spu0,1, $tsg0,0 ,
```

where the data couplets are placed in the order in which the configurations involving each target state are outputted by CONGEN (the second digit is the scattering electron symmetry).

Routine: GETORD

Extract the position and symmetry details of the target states from the target property file:
```
grep '5 $comdatadir/targprop | awk {'print $2,$5,$6,$8'} > ordtarg
```

The information in the file ordtarg is now as follows:
Position, Symmetry ($\Sigma = 0, \Pi = 1$, etc...), Spin (1 or 3), gerade (1) or ungerade (-1)

Extract the positions of both states of $^{1}\Sigma_{g}^{+}$ symmetry:
```
ssg='`grep "0 1 1" ordtarg | awk '{print $1}'`
ssg0='`echo $osg | awk '{print $1}'`
ssg1='`echo $osg | awk '{print $2}'`
```
Appendix B: GETORD routine for automatically ordering target states

Extract the position of the $^1\Sigma^+_u$ state

\[
\text{ssu} = \text{grep "0 1 -1" ordtarg | awk \{ print $1\}}' \\
\text{ssu0} = \text{echo $osu | awk \{ print $1\}}'
\]

Extract the position of the $^3\Sigma^+_u$ state

\[
\text{tsu} = \text{grep "0 3 -1" ordtarg | awk \{ print $1\}}' \\
\text{tsu0} = \text{echo $tsu | awk \{ print $1\}}'
\]

Extract the position of the $^3\Sigma^+_g$ state

\[
\text{tsg} = \text{grep "0 3 1" ordtarg | awk \{ print $1\}}' \\
\text{tsg0} = \text{echo $tsg | awk \{ print $1\}}'
\]

Extract the position of the $^1\Pi_u$ state:

\[
\text{spu} = \text{grep "1 1 -1" ordtarg | awk \{ print $1\}}' \\
\text{spu0} = \text{echo $spu | awk \{ print $1\}}'
\]

Extract the position of the $^3\Pi_u$ state

\[
\text{tpu} = \text{grep "1 3 -1" ordtarg | awk \{ print $1\}}' \\
\text{tpu0} = \text{echo $tpu | awk \{ print $1\}}'
\]
References


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