Application of $R$-Matrix Theory
To Low-Energy $e$-$H_2$ Scattering

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Derek John Daniel

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The work contained in this thesis is my own original research, produced in collaboration with my supervisor Dr. Brian Robson, and Drs Kailash Kumar and Bill Woolcock. Any material taken from other references is explicitly acknowledged as such.

Derek Daniel
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This thesis is dedicated to my parents.
ABSTRACT

In this thesis a theoretical framework for low-energy e-H₂ is developed using
the R-matrix method and applied in the context of avoiding (i) the use
of fixed-nuclei assumptions and (ii) the characterisation of exchange and
polarisation effects via local model potentials.

In Chapter 1 the present research is motivated in relation to the large
effort being made towards resolving the discrepancy between various experi­
ments and theories for the $v = 0 \rightarrow v = 1$ vibrational excitation cross section
of H₂ near threshold. The state of the theory of e-H₂ scattering is therefore
briefly examined and the method for the present R-matrix approach outlined,
as it has so far been developed. The latter discussion is based on showinf
how objectives (i) and (ii) above fit into the present R-matrix framework.

In Chapter 2 the structure theory of the H₂ molecule is developed and the
wave functions formulated with the intention of avoiding those assumptions
related to objectives (i) and (ii) above in the context of low-energy e- H₂
scattering. The wave functions are therefore constructed in a manner which
retain the coupling between the electronic, vibrational and rotational degrees
of freedom of molecule. For the purpose of the scattering problem, variational
calculations are carried out for the ground $^1\Sigma_g^+$ state as well as the excited
odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ states of H₂. The latter form the closed electronic
channels needed for a rigorous treatment of polarisation effects in e-H₂ scat­
tering. The matrix elements for the quadrupole moment and polarisabilities
of H₂ are also computed, and, in particular, characterised in relation to their
importance in determining the behaviour of the cross sections near threshold.

In Chapter 3 the R-matrix theory is applied to low-energy e-H₂ scatter­
ing with the configuration space partitioned into internal, intermediate and
external regions. The formal aspects concerning the treatment of exchange and
polarisation effects and the numerical techniques needed for the char­
acterisation of the different regions of configuration space within a complete
R-matrix framework are developed in this chapter. Calculations, in which
only the ground state wave functions of H₂ are used, are also performed with
the resulting cross sections the presented and discussed. The emphasis is on
the behaviour of the cross sections near threshold.

In Chapter 4 the calculations are extended to include the excited elec­
tronic closed channels and the cross sections compared with those in Chap­
ter 3. An unexpected result is found when polarisation is included and shown
to contradict previous scattering predictions. An explanation is found to be due to the sensitive nature of the cross sections on the coupling between the elastic and inelastic cross sections. This is discussed further.
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Chapter 1

Introduction

1.1 BACKGROUND AND MOTIVATION

The desire to formulate a rigorous theoretical framework for low-energy $e$-$H_2$ is prompted by the discrepancy between experiment and theory for the $v = 0 \rightarrow v = 1$ vibrational excitation cross section of $H_2$ (Morrison et al., 1987) and the shortcoming of the current state of the theory (Buckman et al., 1990; Crompton and Morrison, 1993) to clarify the theoretical issues surrounding the latter.

The implications leading up to this discrepancy have been addressed at length in Morrison et al. (1987). The study of Morrison et al. represents a combined theoretical and experimental effort that was instigated initially towards refining transport data from swarm analysis at energies above the first vibrational threshold of $H_2$ by using as input the theoretical results supplied in that study. The difficulty in determining accurate vibrational cross sections using swarm analysis has also been described in detail by Morrison et al.. Essentially, the circumstances when swarm analysis becomes unfavourable is if a significant fraction of electrons in the swarm have energies that enable them to excite more than one inelastic process. In the case of $H_2$ the transport data due to the effect or rotation is never negligible above the vibrational excitation threshold, so that swarm derived data for the vibrational cross section near threshold can never be determined uniquely, without knowing the rotational cross section reasonably accurately.

Whereas the theoretical results in the study of Morrison et al. were found to be in good agreement with the swarm results for the rotational cross section, there was a significant difference between the theory and the swarm derived results for the vibrational excitation cross section in the near threshold regime. The latter situation which, as remarked by Morrison et al., is made "more puzzling by the excellent agreement between theoretical cross section and data obtained in low-energy beam measurements". Notwithstanding the implications of this, Morrison et al. expressed doubts on these early beam data on the basis that these measurements were not intended for the study of absolute cross sections in the near threshold region. This and the difficulties inherent with beam experiments in measuring the distributions
of electrons scattered in both forward and backward directions, led Morrison et al. to suggest that further experimental as well as theoretical studies be undertaken with the view of resolving the situation.

It is therefore not surprising that everything associated with the discrepancy described above, from experiments (Buckman et al., 1990; England et al., 1988; Brunger et al., 1991) and procedures for fitting data to the kinetic theory of swarm process and ab initio theories (Morrison and Trail, 1993; Rescigno et al., 1993) of e-H$_2$ scattering is being reexamined (see Crompton and Morrison, 1993) . However, despite this large effort so far, the situation remains unresolved.

The present research on the theory of e-H$_2$ scattering, is motivated as part of this large effort towards "underpinning" the nature of the situation described above. In Section 1.2 the theory of e-H$_2$ scattering is briefly reviewed, and then in Section 1.3, the method used in the present research, as it has so far been developed and applied, is outlined.

1.2 THE STATE OF THE THEORY

The literature on the theory of e-H$_2$ scattering is enormous. The development of the theory from a historical perspective (up to 1980) may be found in the review article by Lane (1980). A recent review, concerned more with the status of the theory in the context of near-threshold electron-molecule scattering, is that of Morrison (1988). The difficult nature of the problem arises from the combination of the need to treat the rotational and vibrational degrees of the molecule, the requirement of antisymmetrisation of the three electrons or the exchange effects, and the need to take account of the polarisability of the molecule or the polarisation effects (i.e., virtual dipole transitions to states with negative electronic parity).

The usual starting point for theories of e-H$_2$ scattering is the (laboratory-frame) "close-coupling" (LFCC) or "eigenfunction" expansion of the electron-molecule wave function in terms of a complete set of unperturbed states of the isolated molecule. The resistance to this type of approach can be understood from the large number of scattering equations that are coupled as a result of the nonspherical nature of the molecule and also because of the large number of vibrational and rotational states that are energetically accessible even at energies as low as 1 eV. At this point one uses the fixed- or adiabatic-nuclei approximation to reduce the number of equations to a more practical level. The approximation in this situation parallels the Born-Oppenheimer approximation treatment of the molecular dynamics, in which the potential description of the molecule is obtained with the nuclear vibrational and rotational degrees of freedom held fixed.

While the latter assumption has a well defined basis at the level of a structure theory, the same assumption in scattering theory can only be applied in certain
circumstances, and, in particular, when the collision time, i.e., the time spent by
the scattering electron in the vicinity of the molecule, does not exceed the periods
for molecular rotations or vibrations (cf Lane, 1980). The expected breakdown of
the adiabatic-nuclei approximation when the latter conditions are not met is well
documented in the literature (Morrison, 1988; Lane, 1980; Morrison et al., 1991).

In view of the computational demands of the LFCC scheme mentioned above, it
comes as no surprise that by the time the further requirements due to exchange and
polarisation effects are implemented in this approach a large number of assumptions
and approximations are imported into the theory.

For example, the proper treatment of antisymmetrisation in an LFCC scheme
leads to nonlocal terms, with the result that the scattering equations are now a set
of coupled-integro differential equations. The scattering equations are thus more
difficult to solve when exchange is included. Because of this, a number of model
potentials have been developed to simplify the treatment of exchange (see Morrison
and Collins, 1978). One type of exchange potential, is the free electron gas exchange
model, based on the picture of a Fermi gas of noninteracting electrons. Apart from
the rather crude approximations which are used to obtain such a potential (cf.
e.g., Lane, 1980), there is also the introduction of an adjustable parameter into the
theory, which must be tuned or calibrated with another calculation. The extent to
which these types of model potentials are effective can then really only be judged as
to whether the latter calculation has treated the problem of exchange as a proper
nonlocal effect.

The use of an effective model potential for the treatment of polarisation effects
is also difficult to justify. In a strict sense, these effects are manifested through
the energetically closed (channel) excited electronic states of the molecule in close­
coupling expansion of the wave function. To represent such effects rigorously by
a potential, one must construct an optical potential that is properly nonlocal and
energy dependent. This can be accomplished in a variety of ways. The novel ap­
proach is based on the paper of Bell and Squires (1959), whereby the self-energy
one-particle Green's function propagator in Dyson's equation is identified as the
term needed to characterise the many-body polarisation effects in the scattering.
The formal implementation of this many-body term in e-H$_2$ scattering is difficult
and may be formulated either perturbatively or non-perturbatively, as, for exam­
ple, in the random phase approximation used by Ficoceli Varrachio et al., (1986).
Another, though equally problematic method for constructing the optical potential
is the Feshbach projection technique (Schneider and Collins, 1983). The main dif­
ficulty with this approach, as also in the previous ones, is that the implementation
of optical potentials generally require a large basis set in order to obtain accurate
results. It is for this reason that all such methods have been applied only within
the fixed-nuclei approximation, thus precluding them from the study of vibrational excitation. As remarked by Morrison and Trail (1993), if the vibrational dynamics are to be explicitly included in the scattering, "it is infeasible to treat correlation and polarisation effects via an optical potential".

The more commonly employed procedure that extends the potential treatment of polarisation to studies other than elastic scattering, is the cutoff, asymptotic polarisation potential (cf. Lane, 1980). Here the asymptotic limit of the potential exhibits an inverse quartic dependence \( r^{-4} \) on the radial coordinate of the scattered electron and involves only the polarisabilities of the molecule. While the dynamic or nonadiabatic effects of this potential can be approximated by the use of a single parameter or cutoff radius, the \textit{ad hoc} procedure of reproducing some physical property of the scattering with that determined by experiment, to which the choice of the cutoff radius is based on, does not provide a flexible enough form for the potential to sufficiently describe the polarisation.

A better procedure is to calculate the effective adiabatic polarisation potential (Lane, 1980; Gibson and Morrison, 1984) in which the distortion of the molecule is accounted for by the field of the electron at a given fixed position. The dynamic effects in this potential, which account for the situation when the scattered electron penetrates the molecular charge cloud, is often reproduced by a short range cut off, based on the polarised-orbital method of Temkin and Vasavada (1967). Whereas this technique is effectively designed to cut off the interaction between the bound and scattered electrons once the scattered electron is inside the charge cloud, and has been described in detail by Gibson and Morrison (1984), the problem with all these nonpenetrating type of approximations, as noted by Schneider and Collins (1983), "is the difficulty in systematically assessing the accuracy of this representation of the nonadiabatic terms".

The most elaborate theory so far developed with the intention of resolving the situation described in the previous section is that in Buckman \textit{et al.} (1990) (see also Morrison and Trail, 1993). The theory in that study treats exchange exactly by solving the vibrational close coupling equations with the nonlocal terms included. While this calculation gave vibrational excitation cross sections in better agreement with the cross beam measurements than those derived from swarm measurements, it should be reminded that there were two approximations made in the theory of that study. The first, is the adiabatic treatment of the rotations, so that the coupling between rotational and vibrational motions of the molecule is neglected. The second approximation, which is considered to be more significant by Morrison and Trail (1993), is the treatment of polarisation effects using the adiabatic polarisation potential of Gibson and Morrison (1984) mentioned above.

The state of the theory of \textit{e-H}_2 scattering is thus fraught with approximations. A
combination of fixed-nuclei approximations and the use of effective model potentials for the characterisation of exchange and polarisation effects, based on semiclassical arguments, are widely used to calculate low-energy cross sections, and often without ample considerations as to whether they are suitable for modelling the scattering process. As mentioned in the previous section, when one is making comparison between swarm experiment and theory, it should be remembered that the theory from which the swarm experiment derives its cross section, is itself filled with a body of assumptions and approximations.

1.3 OUTLINE OF THE METHOD, AIMS AND OBJECTIVES

So far, the gaps yet to be filled by previous scattering theories, and which form the objectives of the present $R$-matrix framework for low-energy $e$-$H_2$ scattering, are: (i) the construction of the molecular wavefunctions without the fixed-nuclei approximation and (ii) the characterisation of exchange and polarisation effects without model potentials. The primary aim of the present research is to provide a theoretical basis that enables calculations to be carried out for the elastic scattering and rotational and vibrational excitation cross sections of $H_2$, with the intention of providing accurate results for comparisons with experiment. A long term objective of this research is to therefore point to a resolution of the discrepancy between theory and experiment described in the introduction of this chapter. While this objective is not achieved in the present research, the formal aspects of the present $R$-matrix framework for low-energy $e$-$H_2$ scattering and the subsequent application for the calculation of the cross sections have been accomplished in this thesis. The formulation of the present $R$-matrix framework, and how objectives (i) and (ii) above fit into it, is outlined below.

In constructing the wave functions of the $H_2$ molecule, the view is taken that the molecule is to be looked upon as a four-body system with its wave functions represented by linear combinations of products of nuclear and electronic wave functions. In Chapter 2, this is developed further to show how one can characterise the electronic, vibrational and rotational dynamics of the molecule even though there is a certain degree of independence between their respective basis functions. To achieve this, the single centre method is used. Although such wave functions are necessarily approximate, because of the slow convergence inherent in single centre expansions, and while it may be more desirable and in fact natural to use two-centre methods for the wave functions, it is argued in Chapter 2 that two center methods are technically more difficult to construct in the context of avoiding the adiabatic-nuclei approximation.

Thus, it is the ability to factorise the basis functions in the above sense and subsequent characterisation of the molecular wave functions in terms of them that
allows the present approach to avoid the assumptions of the fixed-nuclei kind that have so far been used in previous methods for low-energy e-H₂ scattering.

The formulation of the wave functions in a form simple and practicable for use in the scattering problem is the principal aim of Chapter 2. The variational calculations carried out in this chapter, therefore give precedence to obtaining those properties of the molecule that have an important role to play in the scattering process through the energy differences produced by the wave functions and their matrix elements for the quadrupole moment and static dipole polarisabilities. Hence, calculations are carried out for the ground $^1\Sigma^+_g$ and excited odd parity $^1\Sigma^+_u$ and $^1\Pi_u$ states of H₂.

In Chapter 3, the theory of low-energy e-H₂ scattering is developed within the framework of the R-matrix method, with the configuration space partitioned into internal, intermediate and external regions.

In the internal region the R-matrix is calculated in a basis of fully antisymmetrised wave functions formed from products of molecular wave functions and single electron wave functions whose logarithmic derivative is fixed at the boundary of the internal region. A major advantage of the R-matrix method is that it permits antisymmetrisation to be taken into account in a completely transparent manner in the internal region.

In the intermediate region, the criterion that exchange effects can be neglected is applied and the coupled differential equations obtained, to propagate the R-matrix. In this region the scattering wave function is thus not antisymmetrised with the rest, in the expectation that the rapid decay of the electronic wave functions of the molecule will make the effects of antisymmetrisation unimportant in the intermediate region. The collision matrix, and hence the cross sections, are obtained by matching to free electron wave functions at the boundary of the intermediate and external regions.

The important features to note in the present R-matrix approach is that (i) the method avoids the use of potentials and three-body pseudo-states; (ii) full antisymmetrisation of the three electrons is taken into account; (iii) The polarisability of the molecule is treated directly by means of its physical origin in virtual excitations to states with odd electronic parity; and (iv) the molecular wave functions used in the scattering wave function expansion do not rely on the fixed-nuclei approximation, so that the R-matrix and thus the collision matrix are not parametrised in terms of the (internuclear) distance of the two protons of the H₂ molecule.

In the heirarchy of the investigations carried out, questions concerning a judicious choice of the radius of internal region and the number of single-particle basis states in it are discussed in Chapter 3. Calculations are also performed by using only the ground state channels in the scattering wave function expansion. Results for the cross section are then presented and interpreted in relation to understanding
the main mechanisms driving the different transition cross sections through those properties of the molecule (mentioned above) that are important to the scattering and which are characterised by the wave functions used in the calculations. The emphasis is on the near threshold behaviour of the cross sections.

In Chapter 4, the $R$-matrix scheme of calculation is extended to include polarisation. The closed excited electronic states are therefore retained in the scattering wave function. The characterisation of the long range potential when such states are included is shown to lead to the form of polarisation potential which in theory is expected to be the principal factor enhancing the cross sections, especially the vibrational ones. The results for the cross sections are therefore compared with those produced in Chapter 3. The departure of the present results form those predicted by previous theories are analysed and interpreted as being due to the sensitive nature of the cross sections on the coupling between the elastic and inelastic channels retained in the present calculations. the latter is discussed in more detail in Chapter 4.
Chapter 2

Wave Functions for $\text{H}_2$

2.1 INTRODUCTION

In the previous chapter the objectives of a structure programme were delineated in the context of avoiding certain assumptions that have so far been used in low-energy $e\text{-H}_2$ scattering. As stated there the present framework for $e\text{-H}_2$ scattering, breaks sharply away from tacit assumptions of the fixed-nuclei kind and also the treatment of polarisation effects via local model potentials. The structure programme developed here therefore allows for sufficient modelling of the required molecular states in the scattering problem, and moreover, in relation to the former assumption, constructs the wave functions in a manner whereby the electronic, vibrational and rotational degrees of freedom of the molecule are treated on par with one another. The formulation of nonadiabatic wave functions in the latter sense thus abandons the notion of computing the molecular energies by way of a potential energy curve that is parametrised in terms of the (inter-nuclear) separation variable, $R$, of the two protons. In other words, the fixed- or adiabatic-nuclei method, a mainstay of previous structure studies, is not used.

In Section 2.2, the position coordinates of the two electrons of the hydrogen molecule are taken relative to the molecular midpoint (along the line joining the two protons), and the general method for separating the rotations for an arbitrary diatomic system then applied, to obtain a set of equations governing the internal motions. This provides the key equations necessary for a single-center representation of the molecular wave functions.

The further aim of retaining the nonadiabatic coupling between the electronic and vibrational motions in the description of the wave functions of the $\text{H}_2$ molecule is made in Section 2.3 via the internal functions. In particular, the internal functions are defined as superpositions of an appropriately chosen set of basis functions and then solved using the linear variational method. The choice of basis functions, and the subsequent formulation of the matrix elements, subject to analytical methods, are therefore stressed in this section.

In Section 2.4, the single-center method of expansion adopted for the wave func-
tions is properly justified with respect to those properties of the hydrogen molecule, other than the molecular energies, that are important to the e-H\(_2\) scattering problem. Both the matrix elements for quadrupole moment and static-dipole polarisabilities of the H\(_2\) molecule are thus formulated in this section as additional criteria for assessing the quality of the wave functions used in the scattering calculations.

In Section 2.5, variational calculations of the vibrational and rotational energy levels for the ground \(^1\Sigma^+_g\) state and the lowest odd-parity \(^1\Sigma^+_u\) and \(^1\Pi_u\) bands of the hydrogen molecule are described, with the wave functions then used for the evaluation of the quadrupole and polarisability matrix elements. The procedures used in the calculations are systematic enough to produce wave functions with highly accurate absolute energies, though in conjunction with criteria imposed (Section 2.4), the importance of such energies is relegated in favour of reproducing those features of the molecular wave functions that are likely to be of more value to the e-H\(_2\) scattering problem.

As an illustration of what can be expected to be achieved from the present structure scheme, results for the energy levels and the quadrupole and polarisability matrix elements are tabulated in Section 2.6, and examined and contrasted with other structure studies which produce accurate values for such quantities using the fixed-nuclei approximation.

Finally, the main achievements and possible extensions of the structure scheme in relation to clarifying the goals for the larger framework of low-energy e-H\(_2\) scattering are summarised in Section 2.7.

### 2.2 THE HAMILTONIAN AND THE WAVE FUNCTIONS

In this section, the hamiltonian and the wave functions of the hydrogen molecule are formulated relative to a coordinate system that is attached and rotating with the molecule. This approach is essentially based on the general exposition given by Kolos and Wolniewicz (1963) (in this section referred to as KW), which exploits the invariance property of an arbitrary diatomic system under rotations of the coordinate system, and will be applied below using center of mass of the nuclei coordinates (CMN), i.e., the position vectors of the electrons are taken relative to the centre of mass of the two protons. Subtle differences of the present approach to that of KW are then briefly stated.

#### 2.2.1 Transformation of the Hamiltonian

In a coordinate system \(O_{x'y'z'}\) with space-fixed axes \((x'y'z')\), denote the position vectors in CMN coordinates by \(\mathbf{R}\), for the two protons and by \(\mathbf{r}_i (i = 1, 2)\), respectively for the two electrons. The separation of the center of mass motion from the total hamiltonian is straightforward in CMN coordinates. The spin-independent
The Hamiltonian of the hydrogen molecule in the center of mass system is then

$$H_{mol} = T + V_{mol}$$  \hspace{1cm} (2.1)

where

$$T = -\frac{1}{2\mu} \nabla^2_R - \frac{1}{2} \left( \nabla^2_{r_1} + \nabla^2_{r_2} \right),$$  \hspace{1cm} (2.2)

$$V_{mol} = \frac{1}{R} + \frac{1}{|r_1' - r_2'|} + \sum_{i=1}^{2} \left( \frac{1}{|r_i' - \frac{1}{2} R|} + \frac{1}{|r_i' + \frac{1}{2} R|} \right).$$  \hspace{1cm} (2.3)

Here $\mu$ is the reduced mass for the two protons and the term involving cross derivatives with respect to the two electrons,

$$-\frac{1}{8\mu} \left( \nabla_{r_1} + \nabla_{r_2} \right)^2,$$

has been omitted on account of the fact that the relative magnitude of this term, i.e., $O(\mu^{-1}) \leq O(10^{-3})$, is negligible by comparison with the total electron kinetic energy $-\frac{1}{2} \sum_{i=1}^{2} \nabla_i^2$.

Another consequence of the large ratio of proton mass to electron mass is that the average electronic velocity is typically very much greater than that associated with the protons. This makes it more appropriate to refer the motion of the electrons relative to a frame $O_{xyz}$ that has its body-fixed axes $(xyz)$ anchored along the internuclear axis (i.e., the line joining the two protons) and also rotating with the molecule, rather than to the spaced-fixed system $O_{x'y'z'}$.

In particular, the set of body-fixed axes is chosen so that the spaced-fixed axes are rotated to bring $R$ along the $z$-axis and $O_x$ is in the direction of the unit vectors $e_{x'} \times e_z$ in the rotating frame. If $R$, $\theta$, and $\phi$ are now taken as the spherical polar coordinates for $R$, then the new body-fixed axes, $e_i (i = x, y, z)$, just mentioned, are simply the unit vectors of $R$ in spherical polar coordinates:

$$e_x = e_{\theta}, \quad e_y = e_{\phi}, \quad e_z = e_R.$$

Clearly, this particular choice of body-fixed axes serves to define the operator of rotations with Euler angles $\theta$, $\phi$ and $0$. The matrix representation of this operator is well known and is given by

$$D(\theta, \phi) = \begin{pmatrix} \cos \theta \cos \phi & \cos \theta \sin \phi & -\sin \theta \\ -\sin \phi & \cos \phi & 0 \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \end{pmatrix}.$$  \hspace{1cm} (2.4)

The transformation of the electronic coordinates from the spaced-fixed (primed) system $O_{x'y'z'}$ to the body-fixed (unprimed) system $O_{xyz}$ is then specified through (2.4):

$$\mathbf{r}_i = D(\theta, \phi) \mathbf{r}'_i.$$  \hspace{1cm} (2.5)
Owing to the unitarity of this transformation, it is straightforward to verify that
the replacement of the electronic variables prescribed by (2.5), leaves the hamilto-

nian $H_{\text{mol}}$, defined by Eqs. (2.1)--(2.3), unaltered, and that the differentiations with
respect to the spherical polar coordinates of $R$ (reproduced in Section A.1 of the
Appendix) lead to additional terms, because of the implicit dependence of the elec­
tronic coordinates on $\theta$ and $\phi$. The additional terms are displayed in Eq. (A.7) of
the Appendix. Introducing the operators $A^{\pm}$,

$$ A^{\pm} = \mp \frac{\partial}{\partial \theta} + L_{\text{ez}} \cot \theta \mp \frac{i}{\sin \theta} \frac{\partial}{\partial \phi}, \tag{2.6} $$

the hamiltonian (2.1)--(2.3) in the rotating reference system $O_{xyz}$ may then be writ­
ten in terms of the independent variables $(R, r_1, r_2)$,

$$ H'_{\text{mol}} = H^{(0)}_{\text{mol}} + H^{(1)}_{\text{mol}}, \tag{2.7} $$
$$ H^{(0)}_{\text{mol}} = T(0) + V'_{\text{mol}}, \tag{2.8} $$

$$ T^{(0)} = T_R - \frac{1}{2} \left( \nabla^2_{r_1} + \nabla^2_{r_2} \right), \tag{2.9} $$

$$ T_R = -\frac{1}{2\mu R^2} \left\{ \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\
+ L_{\text{ez}}^2 (\cot^2 \theta - 1) + 2i \frac{\cot \theta}{\sin \theta} L_{\text{ez}} \frac{\partial}{\partial \phi} \right] \right\} + L_e^2, \tag{2.10} $$

$$ V'_{\text{mol}} = \frac{1}{R} + \frac{1}{|r_1 - r_2|} - \sum_{i=1}^2 \left( \frac{1}{|r_i - \frac{1}{2} Re_z|} + \frac{1}{|r_i + \frac{1}{2} Re_z|} \right), \tag{2.11} $$

$$ H^{(1)}_{\text{mol}} = -(1/2\mu R^2) \left( L_e^+ A^+ + L_e^- A^- \right), \tag{2.12} $$

where

$$ L_e^\pm = L_{ex} \pm L_{ey}, \quad L_e = -i \sum_{i=1}^2 r_i \times \nabla r_i, $$

and $L_{ei}(i = x, y, z)$ are the components of the electronic angular momentum $L_e$ in
the rotating frame $O_{xyz}$.

Equations (2.7)--(2.12) correspond to a special case of Eqs. (7), (12) and (13)
of KW, since their third term in $H'$ vanishes for a homonuclear diatomic molecule.
Nevertheless, these equations are invariant under the group of three-dimensional
rotations (e.g., see Curtiss, 1953), which follows as a consequence of the conservation
of the total angular momentum of the system. It is natural, then, to seek a set of
(angular momentum) operators which commute with each other and also with the
hamiltonian $H'_{\text{mol}}$, so that the wave functions can be appropriately labelled by the
eigenvalues of a set of commuting operators. This is the content of the discussion
below.
2.2.2 Separation of the Rotational Coordinates

In the spaced-fixed frame $O_{x'y'z'}$, the total angular momentum $K'$ is the sum of the proton $L_p$ and electron $L'_e$ angular momenta:

$$K' = L_p + L'_e, \quad (2.13)$$

$$L_p = -i R e_R \times \nabla_R, \quad L'_e = -i \sum_{i=1}^2 r'_i \times \nabla r'_i. \quad (2.14)$$

The $z'$-component of $K'$ is

$$K' \cdot e_{z'} \equiv K_{z'} = -i \frac{\partial}{\partial \phi}, \quad (2.15)$$

while the component of $K'$ along the direction of the unit vector $e_R (= R/R)$ is the $z$-component in the rotating or body-fixed frame $O_{xyz}$:

$$K' \cdot e_R = L'_e \cdot e_R \equiv L_{ez}. \quad (2.16)$$

This shows that the only angular momentum along the internuclear axis is electronic angular momentum, and as such, allows for a third Euler angle (say, $\psi$) degree of freedom to be specified; so that (2.16) is explicitly

$$L_{ez} = -i \frac{\partial}{\partial \psi}. \quad (2.17)$$

Thus in addition to $\theta$ and $\phi$, the hamiltonian (2.7) also depends on $\psi$.

The simultaneous eigenfunctions of the set of commuting operators $K'^2$, $K_{z'}$ and $L_{ez}$ are the wave functions of a rigid-rotator, which following the notation of Rose (1957), will be denoted by

$$D_{MK, \Lambda}^{K_e}(\phi, \theta, \psi) = e^{iMK\phi} d_{MK, \Lambda}(\theta) e^{i\Lambda \psi}, \quad (2.18)$$

where $K(K+1)$, $M_K$ and $\Lambda$ are the eigenvalues of the operators $K'^2$, $K_{z'}$ and $L_{ez}$, respectively. The orthogonality properties of these functions and the differential equations satisfied by $d_{MK, \Lambda}^{K}(\theta)$ are well known and may be applied to also show that the operators $A^\pm$, defined in Eq. (2.6), are in fact the raising and lowering operators for the rigid-rotator functions (2.18) via the relations:

$$A^\pm d_{MK, \Lambda}^{K}(\theta) = [(K \mp \Lambda)(K \pm \Lambda + 1)]^{1/2} d_{MK, \Lambda \pm 1}(\theta). \quad (2.19)$$

Such relations were in fact used by KW to separate the rotations. For example, if $|K, M_K, \Lambda\rangle$ is the ket for the normalised rigid-rotator functions in (2.18) and corresponding matrix elements of the hamiltonian $H_mol'$, defined in Eqs. (2.7)–(2.12), are denoted by

$$\langle K, M_K, \Lambda'| H_mol'| K, M_K, \Lambda \rangle \equiv \langle \Lambda'| H_mol| \Lambda \rangle = H_{\Lambda', \Lambda}' \quad (2.20)$$
where the indices \( K \) and \( M_K \) are omitted, since \( H_m' = H_{\text{mol}}' \) is diagonal in these quantum numbers; then, from the relations in (2.19), together with the orthogonality properties of the rigid-rotator functions, one obtains the result that the only non-vanishing matrix elements of \( H_m'_{\Lambda',\Lambda} \), are those connected by \( \Lambda' = \Lambda \) and \( \Lambda' = \Lambda \pm 1 \). This shows that the transformation of the hamiltonian \( H_m' = H_{\text{mol}}' \) to a representation in which the operators \( K^2 \), \( K_x \) and \( L_{zz} \) are diagonal, will in general have a non-diagonal form, since \( L_{zz} \) does not commute with \( H_{\text{mol}}' \), or more precisely, with \( H_{\text{mol}}^{(1)} \).

Indeed, as noted by KW, any solution of the Schrödinger equation

\[
H_m' \Psi = E \Psi, \tag{2.21}
\]

with definite quantum numbers \( K \) and \( M_K \) can be represented (up to a given normalisation) in the form

\[
\Psi = \sum_{\Lambda} D_{M_K,\Lambda}^{K*} (\theta, \phi, \psi) u_{\Lambda}, \tag{2.22}
\]

where the labels, \( K, M_K \) and \( \Lambda \), satisfy \(-K \leq M_K \leq K, K \geq |\Lambda|\), and \( u_{\Lambda} \) are functions of the internal coordinates of the hydrogen molecule, which depend only on the proton distance \( R = |R| \), the electronic coordinates \( r_i \) \((i = 1, 2)\) and also the spin functions for the protons and electrons, respectively.

On substitution of (2.22) in (2.21) and taking matrix elements according to (2.20), it follows from the selection rule established above with respect to \( \Lambda \), that one can eliminate from the Schrödinger equation (2.21) the dependence on the angles \((\theta, \phi, \psi)\), to obtain a set of coupled equations for the \( u_{\Lambda} \) functions describing the internal motions of the hydrogen molecule. The exact solution of the Schrödinger equation (2.21) with definite \( K \) is therefore determined by a set of \( 2K + 1 \) equations for the \( 2K + 1 \) components \( u_{\Lambda} \) of the wave function (2.22):

\[
H_{\Lambda,\Lambda+1}^{(1)} u_{\Lambda+1} + H_{\Lambda,\Lambda}^{(0)} u_{\Lambda} + H_{\Lambda,\Lambda-1}^{(1)} u_{\Lambda-1} = E u_{\Lambda}, \tag{2.23}
\]

where

\[
H_{\Lambda,\Lambda}^{(0)} = -\frac{1}{2\mu} \left\{ \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} + \frac{2\Lambda^2 - K(K + 1) - \langle \Lambda | L_z^2 | \Lambda \rangle}{R^2} \right\} + \langle \Lambda | -\frac{1}{2} (\nabla_{r_1}^2 + \nabla_{r_2}^2) | \Lambda \rangle + V_{\text{mol}}', \tag{2.24}
\]

with \( V_{\text{mol}}' \) given by (2.11) and

\[
H_{\Lambda_{\pm 1}, \Lambda}^{(1)} = -\frac{[(K \mp \Lambda)(K \pm \Lambda + 1)]^{1/2}}{2\mu R^2} \langle \Lambda \pm 1 | L_{zz}^\pm | \Lambda \rangle. \tag{2.25}
\]

Here the matrix elements of the electronic operators, e.g., \( \langle \Lambda | L_z^2 | \Lambda \rangle \), are operators acting on the internal coordinates and their form depends on the choice of the internal coordinates. The specific choice of the internal coordinates and hence the matrix elements for the case of the two electrons will be specified later in Section 2.3.
However, independent of the form the electronic operators, Eqs. (2.21)–(2.25) may be regarded as a formal application of the concept of rigid-body rotations generalised to diatomic molecules, in that the wave functions (2.22) of the molecule can be represented as functions of the rotational coordinates (i.e., degenerate representations of the rotation group) that are separate to those used for its internal motion. Further, the wave function must be expressed as linear combinations of products of these functions, rather than simple products of them. This is due to the presence of the off-diagonal matrix elements \( H_{\Lambda\pm 1,\Lambda}^{(1)} \) in Eqs. (2.23)–(2.25), the latter of which are responsible for the coupling between the electronic and rotational motion. This shows that the electronic and the rotational motions of the molecule cannot be rigorously separated from the body-fixed hamiltonian (2.7), nor can the coupling between them be strictly neglected.

On the other hand, the relative size of the operators \( H_{\Lambda\pm 1,\Lambda}^{(1)} \) in (2.23) are smaller, in comparison with \( H_{\Lambda\Lambda}^{(0)} \), by a factor of \((1/\mu)\), where \( \mu \) is the reduced mass, which implies that for the the comparatively low-lying states of the molecule, the coupling between the different \( \Lambda \) components of the wave functions occurs only “weakly”. This in turn suggests postponing the analysis of the operators \( H_{\Lambda\pm 1,\Lambda}^{(1)} \) until the end of the calculations, as minor corrections to the energies and the wave functions. This is in fact the usual procedure, where in actual calculations, \( H_{\Lambda\pm 1,\Lambda}^{(1)} \) is treated as a perturbation, after classification as one of Hund's cases.1

Without going into the details of the cases, the off-diagonal matrix elements \( H_{\Lambda\pm 1,\Lambda}^{(1)} \) are now put to one side and omitted altogether from (2.23), to define the wave functions of the hydrogen molecule as eigenfunctions of the major contribution to the hamiltonian, given by \( H_{\text{mol}}^{(0)} \) in (2.8). The further symmetry property associated with the “hamiltonian” \( H_{\text{mol}}^{(0)} \) and the wave functions is next identified below with respect to the inversion operation, \( P \), that inverts all (proton and electron) coordinates through the origin of the molecule. Energy corrections due to the operators \( H_{\Lambda\pm 1,\Lambda}^{(1)} \) are then estimated, with an interpretation of their significance to the structure scheme discussed briefly in the last part of this section.

### 2.2.3 The Molecular Wave Functions

From the preceding analysis, eigenfunctions \( \Psi \) of \( H_{\text{mol}}^{(0)} \) are labelled by the eigenvalues, \( K(K + 1) \), \( M_K \) and \( \Lambda \), of the operators, \( K^2 \), \( K_z \) and \( L_{zz} \), defined by Eqs. (2.13)–(2.16) respectively, that commute with it. Thus, \( \Psi \) has the relatively

---

1Note, that in some of the cases the electron spin angular momentum should be included with that of the electronic angular momentum defined previously by (2.14). As the present treatment deals only with the electrons in their singlet spin state, no attempt has been made here (or in the work of KW) to quantise the electron spin along the molecular axis, though this generalisation is possible (cf. for details see Chapter 6 of Judd, 1975).
simple form:
\[ \Psi = D_{MK,A}^{K^*}(\theta, \phi, \psi)u_A \]  
(2.26)

where \( D_{MK,A}^{K^*}(\theta, \phi, \psi) \) are the rigid-rotator functions given by (2.18), and \( u_A \) are the internal functions of the hydrogen molecule given in (2.22), with the exception that these functions are now eigenfunctions solely of the operator \( H_{A,A}^{(0)} \), defined in Eq. (2.24).

The wave functions (2.26) are further classified according to parity, since the inversion operator, \( P \), commutes with \( H_{mol}^{(0)} \), or, more generally, with the hamiltonian \( H_{mol}^{(0)} \) in (2.7).

In the spaced-fixed frame \( O_{x'y'z'} \), \( P \) inverts both the proton and electron coordinates through the orgin or midpoint of the internuclear axis of the hydrogen molecule as follows:
\[ P : \mathbf{R} \rightarrow -\mathbf{R} \quad \mathbf{r}_i \rightarrow -\mathbf{r}_i \]  
(2.27)

In the body-fixed frame \( O_{xyz} \) this inversion corresponds to a reflection in the \( yz \)-plane, and reads as
\[ P : \mathbf{R} \rightarrow -\mathbf{R} \quad (x_i, y_i, z_i) \rightarrow (-x_i, y_i, z_i), \]  
(2.28)

or, in polar coordinates,
\[ P : \theta \rightarrow \pi - \theta \quad \phi \rightarrow \pi + \phi \quad \vartheta_i \rightarrow \vartheta_i \quad \varphi_i \rightarrow \pi - \varphi_i. \]  
(2.29)

The conditions to be fulfilled by \( u_A \), in order to assure a definite parity \( \pi \) of the state \( \Psi \) with respect to the inversion \( P \), are conveniently analysed by assuming that \( u_A \) will in practice be determined, self-consistently or otherwise, from superpositions of electronic atomic orbitals that are eigenfunctions of \( L_{ez} \) (as is done in Section 2.3). The electronic orbitals in \( u_A \), then have an azimuthal dependence of the type \( e^{im\varphi} \), so that the independent variable \( \psi \) introduced into the definition of \( L_{ez} \), Eq. (2.16), serves to identify the simultaneous rotations of all electrons about the molecular axis, thereby also allowing for the azimuthal angles of the electrons contained in \( u_A \) to be fixed. For the case of the two electrons, the choice for \( \psi \) and for the relative azimuthal angle, say \( \chi \), may be specified as
\[ \psi = \frac{1}{2}(\varphi_1 + \varphi_2), \quad \chi = \varphi_1 - \varphi_2. \]  
(2.30)

It can then be seen from (2.29) that \( \psi \) becomes \( \pi - \psi \), and, subsequently, \( L_{ez} \) in (2.17) changes sign: \( L_{ez} \rightarrow -L_{ez} \). In other words, the reflection in a plane containing the internuclear axis (Eq. (2.29)) is equivalent to reversing the sign of \( \Lambda \) in \( u_A \), and thus, since \( H_{A,A}^{(0)} \) in (2.24) is invariant under the replacement \( \Lambda \rightarrow -\Lambda \), it follows that the functions \( u_A \) in (2.26) with opposite signs of \( \Lambda (\Lambda \neq 0) \) are degenerate; only appropriate linear combinations of \( u_A \) and \( u_{-\Lambda} \) will therefore have
a well-defined symmetry. This makes it convenient to use $|\Lambda|$ as a label for the various electron terms of the molecule (i.e., the states $\Sigma, \Pi, \Delta, \ldots$ correspond to the labels $|\Lambda| = 0, 1, 2, \ldots$), which is the accepted convention (cf. Herzberg, 1950).

Hence, a state of definite parity $\pi$ and definite $|\Lambda| > 0$ will be a superposition of states $\Lambda = \pm|\Lambda|$. Accordingly, using standard properties for the rigid-rotator functions with respect to the inversion (2.29), the eigenfunctions (2.26) of $H_{mol}^{(0)}$ may now be expressed in the form

$$
\Psi_{\alpha K M K}^\pi(R; r_1, r_2) = N_\alpha(K/4\pi)e^{iMK\phi}\left\{d_{MK\Lambda_\alpha}^K(\theta)u_{\alpha K}(R; r_1, r_2) + \pi(-1)^{K}d_{MK,-\Lambda_\alpha}^K(\theta)u_{\alpha K}(R; Pr_1, Pr_2)\right\},
$$

(2.31)

where $\Lambda_\alpha$ has the meaning of $|\Lambda| > 0$ in (2.26), $\alpha$ is an index which denotes the electronic and vibrational character of the state, and $Pr_i$ corresponds to the transformation prescribed by (2.28). $u_{\alpha K}(R; r_1, r_2)$ thus has the $\psi$ dependence $e^{i\phi\Lambda_\alpha}$, whereas $u_{\alpha K}(R; Pr_1, Pr_2)$ has the $\psi$ dependence $e^{-i\phi\Lambda_\alpha}$. Further, it is noted that for a $\Sigma^n$ electronic state with $\Lambda_\alpha = 0$,

$$
u_{\alpha K}(R; Pr_1, Pr_2) = \eta u_{\alpha K}(R; r_1, r_2),
$$

(2.32)

so that a state with total angular momentum $K$ has parity $\eta(-1)^K$. This is consistent with the usage of the labels $\pm$ (as superscripts) respectively for those electron terms that are positive or negative under the reflection transformation (2.29). Equation (2.31), then, holds for $\Lambda_\alpha = 0$ as well as for $\Lambda_\alpha > 0$.

For the case of the hydrogen molecule, the $u_{\Lambda_\alpha}$ components of the wave function (2.31) also have a definite (intrinsic) parity with respect to the interchange of the two protons. This is true for any diatomic molecule possessing identical nuclei, i.e., homonuclear diatomic molecules, since in this case, the hamiltonian is additionally invariant with respect to the interchange of the nuclei alone (cf. Judd, 1975, Chapter 6). In the body frame $Oxyz$, this corresponds purely to electronic inversions in the midpoint of the internuclear axis. A state with definite electronic parity $\pi_\varepsilon$ may then be classified by its intrinsic parity labels $u$ or $g$ (as subscripts) according to whether the orbital parts of the electronic functions contained in $u_{\Lambda_\alpha}$ are odd or even with respect to the interchange of the nuclei. Thus, since the total wave function $\Psi$ (which includes the spin state of the two protons) changes sign under the interchange of the protons, it follows that the parity $\pi$ is

$$
\pi = \pi_\varepsilon(-1)^{S_p},
$$

(2.33)

where $S_p$ is the total spin of the two protons.

Here, it is possible to go further and formulate explicit relations for $\pi_\varepsilon$ in terms of the quantum numbers $K$ and $\Lambda_\alpha$ with respect to the interchange of the two
protons and the inversion $P$, and thereby cover quite generally the symmetric and antisymmetric spin cases of the $u_{\alpha K}$ components of the wave function; as is done, for example, in Judd (1975, Chapter 6; see also KW). Such details, however, need not be reproduced here, as only a few electron terms of the hydrogen molecule are required in the present work. Namely, the electronic $^{1}\Sigma_{g}^{+}$, $^{1}\Sigma_{u}^{+}$ and $^{1}\Pi_{u}$ bands in which the two electrons of the $\text{H}_2$ molecule are in their singlet spin state (indicated by the prefixed superscript). The values of $\pi_{c}$ corresponding to these electronic bands are displayed in Table 2.1 of the next section (cf. Section 2.3), together with the acceptable values of $K$, which as shown, depend on whether para-$\text{H}_2$ ($S_{p} = 0$) or ortho-$\text{H}_2$ ($S_{p} = 1$) is considered.

Finally, from the normalisation conditions
\begin{align*}
\int dR \int d\mathbf{r}_1 d\mathbf{r}_2 |\Psi_{\alpha KM_{K}}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_1)|^2 &= 1, \\
\int R^2 dR \int d\mathbf{r}_1 d\mathbf{r}_2 |u_{\alpha KM_{K}}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_1)|^2 &= 1,
\end{align*}
and noting also that $K/4\pi$ with $\hat{K} = \sqrt{2K + 1}$ corresponds to the normalisation factor for the rotational $(\theta, \phi)$ degrees of freedom in (2.31), one obtains
\begin{equation}
N_{\alpha} = \begin{cases} 
\frac{1}{2} & \text{for } \Lambda_{\alpha} = 0 \\
\frac{1}{\sqrt{2}} & \text{for } \Lambda_{\alpha} > 0
\end{cases},
\end{equation}
for the normalisation constant in (2.31).

### 2.2.4 Significance of the Off-Diagonal Matrix Elements

It was already noted in Section 2.2.2 that the residual or nondiagonal $H_{\text{mol}}^{(1)}$ part of the hamiltonian (2.7) commutes with the angular momentum operators $K'^{2}$ and $K_{\nu}'$, given by Eqs. (2.13) and (2.15) respectively, but not with $L_{cz}$ (Eq. (2.16)). Since it also commutes with the inversion operator $P$, Eq. (2.28), and the wave functions (2.31) have been chosen as a representation in which the operators, $K'^{2}$, $K_{\nu}'$, $L_{cz}$ and $P$ are diagonal, it follows that the matrix elements of $H_{\text{mol}}^{(1)}$ with respect to the wave functions are diagonal in the quantum numbers, $K$, $M_K$, and the parity $\pi$, but not in $\Lambda_{\alpha}$. The effect of including $H_{\text{mol}}^{(1)}$, is then seen to cause a mixing between the different electronic $\Lambda_{\alpha}$ states of the $\text{H}_2$ molecule, and consequently, the two-fold degeneracy mentioned above in connection with the internal functions $u_{\alpha K}$ (for $\Lambda_{\alpha} \neq 0$) is removed — as a result, electron terms with $\Lambda_{\alpha} \neq 0$ are split into two levels close together. This doubling of the energy levels, to which attention is now turned, is the origin of $\Lambda$-doubling.

The formal demonstration of the $\Lambda$-doubling effect relies on the application of second-order perturbation theory (see e.g., Lefebvre-Brion and Field, 1986). For example, if (2.31) are taken as the zeroth-order wave functions, and keeping in mind
the remarks of the previous paragraph, it is a simple matter to show that the second-order corrections to the energy levels for the $^1\Sigma^+$ and $^1\Pi$ states are essentially the square of the off-diagonal matrix elements given by $H_{\Lambda^1\Lambda}^{(1)}$ in (2.25); provided that the label $\Lambda$ in the latter terms is replaced by $\Lambda_\alpha$, in accordance with that used in the definition of the wave functions (2.31), and that the integration is carried over the proton distance $R$ as well as the electronic variables. Subsequently, without going into parity questions, one finds that the $^1\Sigma^+$ and $^1\Pi$ states are the only two terms mixed in by the perturbation, so that the $\Lambda$-doubling, the splitting of the $^1\Pi$ term, may be obtained in the form

$$\Delta E = \text{constant} \times K(K + 1),$$

where the constant is of the order of magnitude $B^2/\epsilon$, $B$ being proportional to $(1/\mu)$ and $\epsilon$ is the energy difference between neighbouring electronic $^1\Sigma^+$ and $^1\Pi$ states. A modest estimate for the lowest energy levels of the hydrogen molecule in these neighbouring states, is typically $\Delta E \approx 10^{-5} K(K + 1)$. A similar expression to this, if not slightly smaller in magnitude, is also found for the corrections to the energies in the rotational band of the $^1\Sigma^+$ ground state (see also Kolos and Wolniewicz, 1963). In any case, for the small values of $K$ which shall be considered, all these type of corrections are sufficiently small for $H_{\text{mol}}^{(1)}$ to be safely omitted.

2.2.5 Interpretation

It is, of course, expected that in situations when the electrons are no longer able to follow the molecular rotations or when one can no longer specify the component of electron angular momentum about the internuclear axis, as in the Rydberg states of the molecule, the energy corrections obtained above from perturbation theory will no longer be valid. Nevertheless, these corrections provide a reasonable way to estimate the extent to which $H_{\text{mol}}^{(1)}$ will become significant to the structure problem. In the present study, in which only the comparatively low-lying $K$ rotational states of the H$_2$ molecule are considered, the energy contributions from $H_{\text{mol}}^{(1)}$ are considered insignificant.

To summarise, the main difference in the present structure scheme to that of KW is the omission of the small perturbative term $H_{\text{mol}}^{(1)}$ and the use of states of definite parity as eigenfunctions of the major $H_{\text{mol}}^{(0)}$ part of the hamiltonian (2.8), based on the premise that the wave functions $\Psi$ in (2.31), formulated as such, are physically well represented for the purposes of modelling the low-lying molecular states of the hydrogen molecule in the $e$-H$_2$ scattering problem. In retrospect, KW contend instead with forming states of definite parity according to the wave functions given by (2.22), which expresses the formal solution of the Schrödinger equation (2.21) as linear combinations of products of the rigid-rotator functions and the internal functions. The status of $\Lambda$ in their wave functions is thus ill-defined, which is not
the case in the present approach, as the assignment of $\Lambda_\alpha$ in (2.31) labels the various electron terms of the hydrogen molecule, and, as remarked earlier (Section 3.1) is consistent with the accepted convention.

While this shows that the identification of the quantum numbers $(\pi KM_K \Lambda_\alpha)$ in the present formulation of the wave functions $\Psi$ (Eq. (2.31)) is clearer than that of KW, it also serves to remind that $\Lambda_\alpha$ is in principle not a true symmetry label. The consequence of this was already noted in Section 2.2.2, and was shown there to lead to a set of coupled differential equations (2.23) for the internal motions of the molecule. The direct solution of these equations must inevitably start with a convenient basis set of functions. The wave functions formulated in the present structure scheme are, in this sense, designed to take into account the effect of the operators $H^{(1)}_{\Lambda_\alpha Aa}$ in the coupled equations (2.23) on the wave functions of the molecules. The motivation here being different to that in KW, where the concern is more with energy eigenvalues. Consequently, for a given $(\pi KM_K)$, there will be a separate matrix which connects the unperturbed state $\alpha$, with definite $\Lambda_\alpha$, to all other possible states with $\alpha'$, with $0 \leq \Lambda_{\alpha'} \leq K$ (i.e., there will be $(K+1)$ values of $\Lambda_\alpha$). Such schemes in fact form much of the subject matter in the manuscript by Lefebvre-Brion and Field (1986), where the calculation of second or higher-order effects (e.g., $\Lambda$-doubling or hyperfine interactions) may be examined and categorised in molecular spectroscopy as “perturbations in the spectra of diatomic molecules”.

Even apart from the effect of the perturbative term $H_{\text{mol}}^{(1)}$, the computation of the wave functions (2.31) is still a difficult task, as there is yet the issue of how to treat the coupling between the electronic and vibrational motions of the molecule. This problem rests on the definition and determination of the internal functions $u_{\alpha K}$, which will be examined in the next section by way of the variational method.

### 2.3 METHOD OF CALCULATION

The basic statement of the structure problem requires solving (in principle rather than in practice) the eigenvalue equation:

$$H_{\text{mol}}^{(0)} \Psi_{\alpha K M_K} = E_{\alpha K} \Psi_{\alpha K M_K},$$  \hspace{1cm} (2.37)

where $H_{\text{mol}}^{(0)}$ is defined by Eq. (2.8), $\Psi$ are the molecular wave functions defined in Eq. (2.31), and $E_{\alpha K}$ are the corresponding molecular energies. The main result to be noted from the formalism of the preceding section, is that the separation of the rotational motion from (2.37), permits an eigenvalue equation to be obtained for the $u_{\alpha K}$ functions describing the internal motions of the H$_2$ molecule, so that determination of the wave functions $\Psi$ proceeds via its internal functions, $u_{\alpha K}$. In the present section, the internal functions will be defined as superpositions of an appropriately chosen set of basis functions and the linear variational method
applied, with the aim of retaining the nonadiabatic effects in the description of
the wave functions, i.e., the effects due to the coupling between the electronic and
vibrational motions of the hydrogen molecule. As mentioned in the introduction to
this chapter, this is needed in order to meet the requirements of the e-H₂ scattering
problem.

As a prelude to notation, and, in what follows, the operator, $H_{\Lambda_a}^{(0)}$ (Eq. (2.24)),
governing the internal motions of the H₂ molecule will now be denoted as $H_{\Lambda_a}^{(0)}$, where the label, $\Lambda_a$, coincides with that used in the definition of the wave functions $\Psi$.

2.3.1 The Variational Method

A more suggestive form of the eigenvalue equation (2.37), then, requires (in
practice) diagonalising the operator $H_{\Lambda_a}^{(0)}$ in the basis set of the internal functions $u_{aK}$:

$$\langle u_{\beta K} | H_{\Lambda_a}^{(0)} | u_{aK} \rangle = E_{aK} \delta_{a\beta}. \quad (2.38)$$

There is no doubt that the most favoured approach to solving this problem is
the fixed- or adiabtic-nuclei method, which proceeds by computing (2.38) as two
separate Schrödinger equations, i.e., the equation for the electronic motion with the
internuclear distance $R$ fixed, is solved first and then used to solve the equation
for the nuclear (vibrational and rotational) motion (for details see e.g., Goodisman,
1973). This is partly, because the method is well understood and there are well-
tested techniques that have been developed over the years for the calculation of
electronic and nuclear wave functions. However, if one is to avoid tacit assump­
tions of the fixed-nuclei kind within the context of low-energy e-H₂ scattering, then,
Eq. (2.38) must be solved with the vibrational $R$ degree of freedom treated on par
with the electronic $r_i (i = 1, 2)$ degrees of freedom.

Hence, no further division of the operator $H_{\Lambda_a}^{(0)}$ in (2.38) is made in the present
approach. The trial functions $u_{aK}$ are thus taken as a linear combination of products
of functions of $R$ and those of $r_1$ and $r_2$. In particular, the electronic basis functions
are taken to be independent of any scaling involving the proton distance, $R$. This
allows the electronic and vibrational motions of the hydrogen molecule to be mod­
elled simultaneously, even though there is a certain degree of independence between
the electronic and vibrational basis functions. This is entirely consistent with the
programme pursued in the previous section, where the effects of rotation were au­
tomatically incorporated in the wave functions via the rigid-rotator functions. Thus,
since $H_{\Lambda_a}^{(0)}$ is diagonal in the total $K$ rotational angular momentum quantum num­
ber, diagonalisation of (2.38), for each $K$, automatically produces vibrational and
rotational levels within a given electronic species.

It is the factorisation of the basis functions, in the manner described above, that
permits the nonadiabatic coupling between the electronic and vibrational motions to be obtained in a form that is practicable for the treatment of such wave functions in the scattering calculations. This derives from the convenience offered by the single-center or central-orbital method used for the representation of the wave functions when evaluating the necessary matrix elements. The single-center method was in fact introduced into molecular structure calculations primarily for this reason.

In contrast, it is technically more difficult (if at all possible) to obtain the same convenience in the scattering calculations, using, say, two-center (confocal elliptical) coordinates for the representation of the wave functions, because of the implicit dependence of the electronic coordinates on the internuclear separation variable, $R$. The complication with two-center coordinates is most directly seen when the asymptotic boundary conditions in scattering theory must be satisfied. Here the wave function for the scattered electron depends explicitly on the internuclear variable, $R$. This makes the task of modelling the vibrational motion in the scattering problem difficult, at least from the perspective of avoiding the fixed-nuclei approximation.

The important point to note in the present approach, is that the channel scheme described in Chapter 3 for the scattering problem, makes reference to those quantum numbers appropriate to describe the electronic, vibrational and rotational motions of the system, rather than in terms of a scheme which involves the proton distance, $R$, as part of its overall channel description. Thus, the use of nonadiabatic wave functions in the present context is not so much due to an expectation of large physical effects of a nonadiabatic nature, as to the fact that having the electronic-vibrational wave functions available avoids some intermediate steps in the scattering calculations. This advantage was already noted by Kolos and Wolniewicz (1963), in connection with the calculation of certain matrix elements in structure problems, such as those of the dipole and quadrupole moments.

Here, the application of the linear variational method, invites the opportunity to incorporate greater flexibility in the trial functions $u_{\alpha K}$ through the introduction of adjustable (nonlinear) parameters, which will be characterised below.

### 2.3.2 The Nonadiabatic Trial Functions and the Basis States

The label $\alpha$ in (2.38) will now be taken as $(\alpha v)$, with the new $\alpha$ denoting the electronic band and $v$ the molecular vibrational state in it. In this notation, the nonadiabatic trial functions $u$, when expanded in a linear combination of products of vibrational and electronic basis functions, take the form

$$u_{\alpha v K}(R; r_1, r_2) = \sum_{n \leq L_e} C_{n\alpha L_e}^\alpha \chi_{n}(R)/R)\psi_{n\alpha L_e\Lambda}(r_1, r_2)$$

(2.39)
where \( n \) is the quantum number which labels the vibrational basis states \( \chi \) and \( \psi \) are the two-electron basis functions with total electron orbital angular momentum \( L_e \), which are labelled by the index \( n_e \).

The coefficients, \( C \), and hence the trial functions, \( u \), in (2.39) are obtained when the matrix of \( H^{(0)}_{\Lambda \alpha} \) is diagonalised in the basis set. The diagonalisation of the matrix \( H^{(0)}_{\Lambda \alpha} \) proceeds independently for each electronic band considered due to the fact that each electronic band \( \alpha \) will have a definite electronic parity \( \pi^\epsilon_\alpha \) and a definite \( \Lambda_\alpha \), already introduced in Section 3.1 (see also Table 2.1 below), and that there is no mixing (by choice) between the different \( \alpha \) bands. Although, it is possible to choose a different basis set for each of the different electronic bands \( \alpha \), or, for that matter, also for each \( K \), the basis functions will, however, for convenience be taken to have the same general form in each subspace, but the parameters occurring in them will be optimised for each electronic band \( \alpha \) considered.

### Table 2.1. Values of quantities appearing in the wave functions \( \Psi \) (Eq. (2.31)) and also the electronic basis \( \psi \) defined below.

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( \Lambda_\alpha )</th>
<th>( N_\alpha )</th>
<th>( \pi^\epsilon_\alpha )</th>
<th>((-1)^L_e)</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1\Sigma^+_g )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>1</td>
<td>1</td>
<td>even (para), odd (ortho)</td>
</tr>
<tr>
<td>( ^1\Sigma^+_u )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>-1</td>
<td>-1</td>
<td>odd (para), even (ortho)</td>
</tr>
<tr>
<td>( ^1\Pi_u )</td>
<td>1</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>-1</td>
<td>( \pm 1 )</td>
<td>( \geq 1 ) (para or ortho)</td>
</tr>
</tbody>
</table>

The two-electron basis functions \( \psi \) in (2.39), are constructed from single particle three-dimensional oscillator wavefunctions and have the symmetry appropriate to the electronic bands \( \alpha \) listed in Table 2.1. Thus, for the singlet spin states shown in the table, the electronic functions are symmetric under the exchange of the electronic coordinates (1 \( \leftrightarrow \) 2):

\[
\psi^\alpha_{n_eL_e\Lambda_\alpha}(r_1, r_2) = N_{ab} \sum_m (l_a m, l_b (\Lambda_\alpha - m)|L_e\Lambda_\alpha) \\
\times \left\{ R^\alpha_{n_a l_a}(r_1)Y_{l_a m}(\hat{r}_1)R^\alpha_{n_b l_b}(r_2)Y_{l_b \Lambda - m}(\hat{r}_2) + (1 \leftrightarrow 2) \right\},
\]

(2.40)

where the the Clebsch-Gordan coefficients, \( (Aa, Bb|Cc) \), and the spherical harmonics, \( Y_{lm} \), are in the convention of Rose (1957), and \( n_e \) denotes collectively the labels, \( n_a, l_a, n_b, \) and \( l_b \). The radial functions, \( R^\alpha_{nl} \), are defined in terms of the associated
Laguerre polynomials, \( L_n^{l+\frac{1}{2}} \) (e.g., see Eq. (A.8) of the Appendix):

\[
R_{nl}^{\alpha}(r) = \left[ \frac{\Gamma(n + 1)}{a^3 \Gamma(n + l + \frac{3}{2})} \right]^{1/2} \left( \sqrt{\omega_\alpha^2 r} \right)^l \exp(-\omega_\alpha^2 r^2/2) L_n^{l+\frac{1}{2}}(\omega_\alpha^2 r^2), \quad (2.41)
\]

and admit a single adjustable parameter \( \omega_\alpha^2 \), which is optimised for each \( \alpha \).

The orthornormality condition,

\[
\int_0^{\infty} r^2 dr R_{nl}^{\alpha}(r) R_{n'l'}^{\alpha}(r) = \delta_{n'n},
\]

leads to

\[
\int \int dr_1 dr_2 \Psi^*_{n_xL_x\Lambda_x}(r_1, r_2) \Psi_{n'_xL'_x\Lambda_x}(r_1, r_2) = \delta_{n_n'} \delta_{L_L'} \delta_{\Lambda_{\Lambda'}} \quad (2.43)
\]

where \( \delta_{n_n'} \) is used as a shorthand for \( \delta_{n_a n_a'} \delta_{l_a l_a'} \delta_{\Lambda_a \Lambda_a'} \) and the constant \( N_{ab} \) in (2.40) is

\[
N_{ab} = \begin{cases} 
\frac{1}{2} & \text{if } l_a = l_b \text{ and } n_a = n_b \\
\frac{1}{\sqrt{2}} & \text{otherwise}
\end{cases} \quad (2.44)
\]

Furthermore, since the electronic basis functions (2.40) are classified by their intrinsic parity labels, \( g \) or \( u \), according to whether they are odd or even with respect to electronic inversions (as discussed in Section 3.1), the electronic basis orbitals of \( \psi \) in (2.40) are restricted by the relation

\[
\pi_e^{\alpha} = (-1)^{(l_a + l_b)}. \quad (2.45)
\]

Hence, from Table 2.1, electronic states with \( g(u) \) symmetry have even(odd) values of \( l_a + l_b \).

For the vibrational part of the problem, the one-dimensional harmonic oscillator functions are used as the basis:

\[
\chi_n^{\alpha}(R) = (\beta^{\alpha})^{1/4} N_n \exp(-\xi^2/2) H_n(\xi), \quad n = 0, 1, 2 \ldots, \quad (2.46)
\]

\[
N_n^2 = \sqrt{\pi} 2^n n!, \quad \xi = \sqrt{\beta^{\alpha}(R - R_0^{\alpha})}. \quad (2.47)
\]

where \( H_n(\xi) \) are the Hermite polynomials (e.g., see Eq. (A.20) of the Appendix), and \( \beta^{\alpha} \) and \( R_0^{\alpha} \) are variational parameters optimised accordingly for the different bands \( \alpha \). The oscillator frequency \( \omega_0^{\alpha} \) is given by \( \omega_0^{\alpha} = \beta^{\alpha}/\mu \).

The same vibrational basis functions (2.46) were also used by Kolos and Wolniewicz (1963). It is noted here, that these functions are not orthogonal over the interval \( R \geq 0 \) and that the matrix elements of \( 1/R \) and \( 1/R^2 \) in this basis, do not strictly exist. However, for the actual choices of the parameters and for the values of \( n \) which are used, they are actually very close to orthornormal and the divergence of integrals which arises from the behaviour of the integrand as \( R \to 0 \) may be avoided.
by the use of an appropriate cutoff (however, see also the remarks in Section 2.3.3).
Effectively, then, the orthornormality condition for (2.46) is
\[ \int_0^\infty dR \chi_n^\alpha(R) \chi_n^\beta(R) = \delta_{n,n'}. \]  
(2.48)

It can be shown from the orthornormality relations, (2.43) and (2.48), that the linear variational coefficients, \( C \), of Eq. (2.39) satisfy the relation
\[ \sum_{nn'LL} |C_{nn'LL}|^2 = 1. \]  
(2.49)

These coefficients are useful for assessing the relative importance of the basis configurations, since the number produced for them give an indication of the amount of mixing between the electronic and vibrational basis functions used in the calculations. This is described in Section 2.5, when selecting the most dominant configurations.

It is worth mentioning, that other options for a vibrational basis set, which do not lead to the divergent integrals mentioned above, are possible; such as the Fues-type or Morse type functions discussed by Moss and Sadler (1989). However, the integrals encountered with these functions are more difficult to obtain analytically than (2.46). Moreover, both the bound states for the Fues-type and Morse type functions do not comprise a complete set. Nonetheless, their use for low-vibrational studies of molecules is not without promise (Moss and Sadler, 1989).

Similarly, other choices in the basis functions for the electronic distribution of the structure problem could have been made (e.g., see the bibliography section in McLean et al., 1960). For example, it is known that the Gaussian dependence in (2.40) for the three-dimensional oscillator functions tend to require a larger set of orbitals in the expansion (2.39) for the trial functions \( u_{\alpha v K} \) than say a basis set involving Slater-type orbitals (Reeves, 1963). However, as noted by Reeves (1963), the main obstacle to progress with Slater functions is that some of the many-centred integrals (for example, the electron-electron interaction terms) that may be encountered with them in molecular structure calculations can only be obtained numerically.

In contrast, Gaussian functions have the advantage that all the necessary integrals can be evaluated exactly by closed analytical formulas (Boys, 1950). The matrix elements of \( H_{A,A}^{(0)} \) with respect to the basis, Eqs. (2.40) and (2.46), are thus amenable to analytical methods, which is the content of the discussion pursued below.
2.3.3 The Matrix Elements and the Integrals

The matrix elements of $H^{(0)}_{\Lambda\alpha}$, with respect to the vibrational $\chi_n$ and the electronic $\psi$ basis, are defined as,

$$H_{ij} = \int R^2 dR \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_n'(R) \psi_{n'\ell'\Lambda}^*(\mathbf{r}_1, \mathbf{r}_2) \left( H^{(0)}_{\Lambda} \right) \chi_n(R) \psi_{n\ell\Lambda}(\mathbf{r}_1, \mathbf{r}_2), \quad (2.50)$$

where the labels $i$ and $j$ are an obvious shorthand respectively for $(n'n_1'L_1')$ and $(nn_1 L_1)$, and the index $\alpha$ is omitted for clarity, since it is evident that the matrix elements (2.50) are only well-defined when both the electronic and vibrational basis states belong to the same $\alpha$ band given above in Table 2.1.

The evaluation of $H_{ij}$ in (2.50) proceeds by a further regrouping of $H^{(0)}_{\Lambda}$:

$$H^{(0)}_{\Lambda} = H^{(0)} + H^{(1)} + H^{(2)} + H^{(3)} + H^{(4)} + H^{(5)} + H^{(6)} \quad (2.51)$$

where

$$H^{(0)} = -\frac{1}{2\mu} \left[ \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right] + V(R) + \sum_{j=1}^{2} \left( -\frac{1}{2} \nabla_{\mathbf{r}_j}^2 + V(\mathbf{r}_j) \right) \quad (2.52)$$

$$H^{(1)} = -V(R) \quad V(R) = \frac{1}{2} \mu \omega_0 (R - R_0)^2 \quad (2.53)$$

$$H^{(2)} = -\sum_{j=1}^{2} V(\mathbf{r}_j) \quad V(r) = \frac{1}{2} \omega_e r^2 \quad (2.54)$$

$$H^{(3)} = \frac{[K(K+1)+L_z^2-2\Lambda^2]}{2\mu R^2}, \quad (2.55)$$

$$H^{(4)} = \frac{1}{R} \quad (2.56)$$

$$H^{(5)} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2.57)$$

$$H^{(6)} = -2\sum_{i=1}^{2} \left( \frac{1}{|\mathbf{r}_i - \frac{1}{2} R \hat{e}_z|} + \frac{1}{|\mathbf{r}_i + \frac{1}{2} R \hat{e}_z|} \right). \quad (2.58)$$

Here the first term gives the differential equations satisfied by the vibrational and electronic basis functions; the second and third terms are the oscillator potentials subtracted accordingly from the first term; the former potential with $\omega_0 = \beta/\mu$ is the oscillator frequency for the vibrational functions. The remaining terms then correspond to a further partitioning of $V'_{mol}$ given by Eq. (2.11), so that the third and fourth terms are respectively the rotational and repulsion potentials for the protons, and the last two terms, the potential energies of the electron-electron repulsion and the electron-proton attraction respectively.

Some simplification occurs in (2.50) by first performing the angular integrations for the spherical harmonics contained in the two-electron basis functions $\psi$. Routine procedures for angular momenta recoupling are applied in the usual manner for the summations involving double and triple products of the Clebsch-Gordan coefficients.
These sums lead at most to products of the Racah 3-j and 6-j symbols, which occur only in the matrix elements for the electron-electron repulsion and electron-proton attraction potentials, due to the fact that such interactions require a multipole expansion of the type:

$$\frac{1}{|r - r'|} = 4\pi \sum_{L} \sum_{r' > r}^{r_L} Y_{LM}(\hat{r})Y_{LM}(\hat{r'})$$

where \(r_<(r_>)\) is the lesser(greater) of \(r\) and \(r'\).

Attention is now drawn to the evaluation of the \(\mathcal{H}^{(p)}\) (\(p = 0\) to \(6\)) terms, displayed in Eqs. (2.52)—(2.58), with respect to the radial functions for the basis, i.e., \(R_{nl}\) and \(\chi_n\), given respectively in Eqs. (2.41) and (2.46).

Since \(\mathcal{H}^{(0)}\) gives the differential equations satisfied by \(R_{nl}\) and \(\chi_n\), the evaluation of \(\mathcal{H}^{(0)}\) with respect to the basis functions, follows easily from their orthogonality relations (2.43) and (2.48). The same applies for the evaluation oscillator potentials, \(\mathcal{H}^{(1)}\) and \(\mathcal{H}^{(2)}\), after using also the standard recursion relations for the Hermite polynomials \(H_n\) and associated Laguerre functions \(L_n^p\):

$$\xi H_n(\xi) = \frac{1}{2} H_{n+1}(\xi) + H_{n-1}(\xi), \quad (2.60)$$

$$xL_n^p(x) = -(n + 1)L_{n+1}^p(x) + (2n + p + 1)L_n^p(x) - (n + p)L_{n-1}^p(x). \quad (2.61)$$

A slightly different approach is needed for the \(\mathcal{H}^{(3)}\) and \(\mathcal{H}^{(4)}\) potentials, as both potentials depend on inverse powers of the variable \(R\) (only) of the two protons, and, as remarked earlier (in Section 2.3.2), are in fact divergent in the vibrational basis (2.46). The cutoff procedure mentioned there, is one way to avoid the singularity as \(R \to 0\), though, an alternative method, is to represent both \((1/R)\) and \((1/R^2)\) as an ascending series in the variable \(\xi = \sqrt{\beta}(R - R_0)\) and then carry out the required integrations term by term. It has been checked numerically, that the latter method is as accurate as using the cutoff procedure, provided that a sufficient number of terms are retained in the series. Thus, it is easy to see from the expansions

$$\frac{1}{R} = \sqrt{\beta} \sum_{r=0}^{\infty} (-1)^r \frac{\xi^r}{\xi_0^{r+1}}, \quad (2.62)$$

$$\frac{1}{R^2} = \beta \sum_{r=0}^{\infty} (-1)^r (r + 1) \frac{\xi^r}{\xi_0^{r+2}}, \quad (2.63)$$

where \(\xi_0 = \sqrt{\beta}R_0\), that the matrix elements of \((1/R)\) and \((1/R^2)\) in the vibrational basis lead to integrals involving powers of \(\xi^r\) and products of the Hermite polynomials \(H_n\), which can be obtained by elementary means (Gradshteyn and Ryzhik, 1965, 7.375.2), viz.:

$$I_{n'n}^{r} = \int_{-\infty}^{\infty} d\xi e^{-\xi^2} \xi^r H_{n'}(\xi)H_n(\xi)$$

$$= \sqrt{\pi} \sum_k \frac{2^s k!n'!n!}{(s - k)!((s - n')!(s - n)!)}$$

where \(2s = k + n' + n\) and \(k + n' + n\) is even.
Both the radial integrals for the electron-electron repulsion potential \( \mathcal{H}^{(5)} \) and electron-proton attraction potential \( \mathcal{H}^{(6)} \) have been evaluated in closed-form in the Appendix (see Section A.2), and, in what follows, only a brief description of the procedures outlined there will be recalled. It is worth noting that Fourier transform techniques could have also been applied for the evaluation of these integrals (see e.g. Ruedenberg, 1951), though no practical advantage is gained in doing so, apart from a possibly more compact analysis of the integrals than that carried out in Section A.2 of the Appendix.

For the electron-electron repulsion potential (2.57), the integrals consist of products of the electronic radial basis functions \( R_{n_i i} \) (Eq. (2.41)), which from the multipole expansion (2.59), requires splitting the integration limits for one of the radial variables of the two electrons (choosing \( r_1 \), say):

\[
E(\mathcal{H}^{(5)}) = \int_{0}^{\infty} \int_{0}^{\infty} r_1^2 dr_1 r_2^2 dr_2 R_{n_{a\alpha}a}(r_1) R_{n_{b\beta}b}(r_2) W(r_1) W(r_2) + \int_{0}^{\infty} r_2^2 dr_2 R_{n_{\beta}b}(r_2) \left[ \frac{1}{r_2^{L+1}} \int_{0}^{r_2} r_1^2 dr_1 r_1 R_{n_{\alpha}a}(r_1) R_{n_{b\beta}b}(r_1) \right] R_{n_{\alpha}a}(r_1) R_{n_{\beta}b}(r_2).
\]

(2.65)

Since each of the radial functions \( R_{nl} \) displayed above is specified in terms of associated Laguerre functions, the latter have a finite series representation (e.g., see Eq. (A.8) of the Appendix), which when inserted in (2.65) lead to integrals consisting of products of exponentials and powers in the variables \( r_1 \) and \( r_2 \). In particular, the integrations inside the square paranthesis of (2.65), when performed, lead to the incomplete gamma functions \( \gamma(\alpha, x) \) and \( \Gamma(\alpha, x) \), where \( x \) depends on the variable \( r_2 \), so that the final integration over of the variable \( r_2 \) in (2.65), then requires evaluating integrals whose integrands consist of powers of \( x \), \( \exp(-x) \) and the incomplete gamma functions, which, from (A.13), may be evaluated as:

\[
\int_{0}^{\infty} dx e^{-x} \left\{ x^q \gamma(p + \frac{3}{2}, x) \right\} = \left\{ \frac{\Gamma(p + q + \frac{3}{2})}{(p + \frac{3}{2})^{p+q+\frac{3}{2}}} F(1, p + q + \frac{5}{2}, p + \frac{5}{2}, \frac{1}{2}) \left( p' + q' + \frac{3}{2}, \frac{1}{2} \right) \right\},
\]

(2.66)

where \( F(a, b; c; x) \) is the hypergeometric series and the indices \( p, q, p' \) and \( q' \), as defined in Eqs. (A.10) and (A.12), are related to the assignment of quantum numbers appearing in (2.65). A further transformation of the hypergeometric functions displayed on the right hand side of (2.66), shows that they are in fact a terminating series in the arguments \( p, q, p' \) and \( q' \), so that the final result for (2.65), is then seen in (A.14), as an analytical expression involving four finite summations (one for
each expansion of the Laguerre functions contained in $R_{nl}$ over the hypergeometric functions.

Finally, the radial integrals for the electron-proton attraction potential $\mathcal{H}^{(6)}$ involve combinations of the radial functions $R_{nl}$ and the vibrational basis functions $\chi_n$:

$$J_L(n', n; n'_a, n_a) = \int dR \int r_1^2 dr_1 \chi_{n'}(R) R_{n'_a}^{\mu}(r_1) \left( \frac{R_L}{R} \right) R_{n_a}(r_1) \chi_n(R)$$  \hspace{1cm} (2.67)

where $R_{<}(R_{>)}$ is the lesser(greater) of $r_1$ and $R/2$. It is convenient to consider the integration in the variable $r_1$ first, in which case, the splitting of the integration limits coincides with the treatment given above for electron-electron repulsion integrals and leads to the same result involving integrals with the incomplete gamma functions. Some further manipulation of the incomplete gamma functions is then carried out in Eqs. (A.15)-(A.17) of the Appendix, to obtain the final integration over $R$ in terms of two types of integrals involving the vibrational basis $\chi_n$:

$$F^L_{n'n} = \int_0^\infty R^2 dR \chi_{n'}(R) \left( \frac{\gamma(\alpha, x^2)}{x^{L+1}} \right) \chi_n(R), \quad G^m_{n'n} = \int_0^\infty R^2 dR \chi_{n'}(R)x^m e^{-x^2} \chi_n(R)$$  \hspace{1cm} (2.68)

where $\alpha = (L + 1)/2$, $x = \sqrt{\omega_e} R/2$, and $\gamma(\alpha, x^2)$ is the incomplete gamma function.

To evaluate the integrals shown in (2.68), the incomplete gamma function in the first integral is expanded as a rapidly convergent power series in $x$, while the usual series expansion for the Hermite polynomials (e.g., see Eq. (A.20) of the Appendix) contained in each of the $\chi_n$'s is used for the second integral. Consequently, the expression for $F^L_{n'n}$ (Eq. (A.18)) resembles sums over integrals of the type given by $I^{n'}_{n'n}$ in (2.64), while the evaluation of an exponential integral, (A.22), follows easily to obtain a simple result for $G^m_{n'n}$ (Eq. A.24). The final formula for $J_L$ is then displayed in Eq. (A.26), as sums over the analytical expressions derived there for $F^L_{n'n}$ and $G^m_{n'n}$.

For easier reading, the matrix elements $\mathcal{H}_{ij}$ (Eq. (2.50)), in the order given by Eqs. (2.51)-(2.58), are listed in Section A.3 of the Appendix. While these matrix elements have so far been elucidated in terms of several kinds of basic integrals, there is an obvious need to truncate the infinite sums which occur in some of the expressions for them, especially if they are to be of any practical use to the structure problem.

For example, the matrix elements for the centrifugal potential, (A.30), and the proton repulsion potential, (A.31), both contain infinite sums. Some caution is advised here, however, since as remarked above, the matrix elements of $1/R$ and $1/R^2$ in the vibrational basis (2.46) do not strictly exist, and so the resulting series expansions (2.63) used for them are of an asymptotically divergent nature. However, provided that the sums in these expansions are truncated with appropriate limits,
it is possible to obtain realistic values for the matrix elements of $1/R$ and $1/R^2$. In practice, the search for the appropriate limits is largely a trial and error process.

Such considerations do not apply to the electron-electron repulsion matrix elements (A.32), as the sums occurring in them are all finite, including the partial sums over $L$ in the multipole expansion (2.59), which is restricted according to the assignment of orbital electron angular momenta values appearing in the Racah symbols. While this latter restriction applies also to the electron-proton attraction matrix elements (A.32), these matrix elements, on the other hand, do contain an infinite sum, due to the series expansion of the incomplete gamma function used for the evaluation of $F_{n'n}^L$ in (2.68). However, the series for the incomplete gamma function is rapidly convergent, so that (for reasonably low values of $n$ and $n'$ in the vibrational basis) the first ten to twenty terms in the series is usually sufficient for the numerical evaluation of $F_{n'n}^L$ (defined in Eq. (A.18)).

In general, the convergence of $F_{n'n}^L$ and thus also the convergence (in the asymptotic sense) of the infinite sums for the matrix elements of the centrifugal and proton repulsion potentials, depend on the size of the parameters $\omega$, $\alpha$, and $R_0$, used in the calculations. These parameters were introduced in Section 2.3.2 as nonlinear variational parameters for the basis functions and the strategy used for the optimisation of the nonlinear parameters in the problem will be made more specific in Section 2.5.

### 2.4 OTHER PROPERTIES OF THE H₂ MOLECULE

In the previous section, a single-center expansion for the internal trial functions $u$ (Eq. (2.39)) was adopted in view of modelling the electronic and vibrational motions of the H₂ molecule simultaneously in a form that is practicable for the e-H₂ scattering problem. As noted there (Section 2.3.1), it is technically more difficult to achieve this using a two-center expansion of the wave functions in confocal elliptical coordinates, because the evaluation of the matrix elements become necessarily complicated with respect to such coordinates. Thus, in rejecting two-center coordinates, one must now expect the slow convergence inherent in a single-centre expansion of the wave functions. This in fact led one set of authors (Hagstrom and Shull, 1959) to remark that they could see no further use for the single-center method in diatomic problems. Indeed, the most accurate wave functions for the ground and first few excited electronic states of the H₂ molecule use correlated orbitals, i.e., orbitals expressed in a basis of two-center coordinates and also including the interelectronic distance explicitly.

While the statement by Hagstrom and Shull (1959) is certainly true, if the only aim here was to produce wave functions with highly accurate absolute energies, such energies, on the other hand, may not have the same precedence in scattering
problems. In fact, the mechanisms responsible for the different low-energy transition cross sections in electron-molecule scattering are more directly related to the quadrupole and induced electric-dipole moments of the molecule (cf. Lane, 1980), rather than the molecular energies themselves. Further, it is well established that highly accurate wave functions which yield "good" values for the energies, do not necessarily yield "good" values for other properties, such as the quadrupole and electric-dipole moments (Kolos and Roothaan, 1960). It is this observation, coupled with that in the former remark, that makes it conceivable to expect reliable values for the quadrupole and electric-dipole moments of the H₂ molecule, and thus also the e-H₂ scattering cross sections, even though orbitals "inferior" in quality to correlated orbitals are used for the representation of the molecular wave functions.

It is this point of view which underlies the present approach concerning the use of single-center wave functions in low-energy e-H₂ scattering. This section therefore provides definitions for the quadrupole and polarisability matrix elements of the hydrogen molecule, in which the calculated values of these quantities serve as additional criteria for assessing the quality of such wave functions in the context of the scattering problem.

2.4.1 The Quadrupole Moment

Judging the quality of an approximate wave function by how well the calculated energy values compare with experiment, is not the only criterion that can be used. More importantly, whereas this type of comparison is judged according to the energy values produced when evaluating the expectation value of the "hamiltonian" $H_{mol}^{(0)}$ (Eq. (2.8)) with the approximate wave function $\Psi$ (Eq. (2.31)), it does not necessarily follow that expectation values of operators other than $H_{mol}^{(0)}$ will approach the correct values on improvement of the wave function $\Psi$. An example of this situation is typified in the calculations of Kolos and Roothan (1960) for the quadrupole moment of H₂, and it would therefore be interesting to investigate whether such a behaviour will also be reproduced within the present formulation of the wave functions $\Psi$.

In the present study, the vibrational and rotational transition matrix elements of the quadrupole moment, as defined by Karl and Poll (1967), has the following expression:

$$
\langle g'v'K'|Q|gvK \rangle = \int_0^\infty R^2 dR \int \int d\mathbf{r}_1 d\mathbf{r}_2 u_{gvK} \left[ \frac{1}{2} R^2 - 2 r_1^2 P_2(\hat{r}_1 \cdot \mathbf{e}_z) \right] u_{g'v'K'}. \quad (2.69)
$$

where the label $g$ denotes the electronic $^1\Sigma_g^+$ ground state of H₂ and $u$ are the internal trial functions, defined in (2.39). Since $u$ by definition can be expressed in terms of the basis functions (given by Eqs. (2.40) and (2.46)), Eq. (2.69) yields,

$$
\langle g'v'K'|Q|gvK \rangle =
$$
\[
\sum_{n_n E_e} \sum_{n_n L_n} C^{n_n L_n}_n C^{n_n L_n}_e \left\{ \frac{1}{2} \delta_{n_n n_n} \delta_{L_n L_e} Q_1(n'n) - 2 \delta_{n'n} \hat{L}_e \hat{L}_e \right\} Q_2(n'a', n'a)
\]

\[
\times N_{a'b'} N_{a'b} (-1)^{l_a} \left[ \delta_{n_n n_n} \delta_{l'_a l_a} \hat{p}_{a'b'} \left( \begin{array}{ccc}
I_a & I'_a & 2 \\
0 & 0 & 0 \\
L_e & L'_e & 2
\end{array} \right) \right] \left\{ \begin{array}{ccc}
I_b & I'_b & 2 \\
L_a & L'_a & 2 \\
l_b & l_a & l_b
\end{array} \right\} Q_2(n'_a, n'_a, n_a, l_a)
\]

\[
+ \delta_{n'_a n_a} \delta_{l'_a l_a} \hat{p}_{a'b'} \left( \begin{array}{ccc}
I_a & I'_a & 2 \\
0 & 0 & 0 \\
L_e & L'_e & 2
\end{array} \right) \left\{ \begin{array}{ccc}
I_b & I'_b & 2 \\
L_a & L'_a & 2 \\
l_b & l_a & l_b
\end{array} \right\} Q_2(n'_a, n'_b, n_a, l_a)
\]

\[
+ \delta_{n'_a n_a} \delta_{l'_a l_a} \hat{p}_{a'b'} \left( \begin{array}{ccc}
I_a & I'_a & 2 \\
0 & 0 & 0 \\
L_e & L'_e & 2
\end{array} \right) \left\{ \begin{array}{ccc}
I_b & I'_b & 2 \\
L_a & L'_a & 2 \\
l_b & l_a & l_b
\end{array} \right\} Q_2(n'_a, n'_b, n_b, l_b)
\]

where \( Q_1 \) and \( Q_2 \) are the integrals:

\[
Q_1(n'n) = \int_0^\infty dR R^2 \chi_{n'}(R) \chi_n(R),
\]

\[
Q_2(n'_a n'_a, n_a l_a) = \int_0^\infty dr_1 r_1^4 R^2_{n'_a l'_a}(r_1) R_{n_a l_a}(r_1).
\]

The computation of the quadrupole matrix elements (2.70) also serve another purpose: the quadrupole interaction between the electron and the \( H_2 \) molecule is known to have a strong influence on the rotational excitation cross section (Lane and Henry, 1968) and thus determines the quadrupole potential used, later, in propagating the \( R \)-matrix in the intermediate region (cf. Chapters 1 and 3). It is therefore expected that accurate rotational cross sections will depend on whether the ground state wave functions computed in this work are able to reproduce reasonably well the matrix elements (2.70) of the quadrupole moment of \( H_2 \).

### 2.4.2 Polarisation of the \( H_2 \) Molecule

If one accepts the viewpoint that polarisation effects, in the context of electron-molecule scattering, arise from distortions of the molecule due to the presence of the scattered electron, and that the extent of such distortions, can be ascertained (in the region when the electron is far from the molecule) through the static polarisabilities of the molecule, then, the significance (to the structure programme) of the wave functions of the type, \( ^1 \Sigma_u^+ \) and \( ^1 \Pi_u \), with odd electronic parity, is that such wave functions yield numbers for the matrix elements of the static polarisabilities of the \( H_2 \) molecule between selected rotational and vibrational levels in the electronic \( ^1 \Sigma_g^+ \) ground state, the latter of which, can furthermore be compared with the highly accurate values obtained in the clamped-nuclei or fixed-nuclei approximation by Kolos and Wolniewicz (1967).

Even at the level of the structure problem there is a large difference between obtaining the polarisabilities of \( H_2 \) using the fixed-nuclei method to that of the
present approach, without the fixed-nuclei approximation. The comparison between
the two methods is therefore only effective at the level of the matrix elements.
For instance, the fixed-nuclei method takes into account electronic excitations at
fixed values of $R$ and delivers the polarisability tensor of $H_2$ as a function of $R$,
whose matrix elements are then taken with respect to rotational-vibrational wave
functions. In contrast, the present method, without fixed-nuclei assumptions, is
based on forming the matrix elements for the electric-dipole transitions between
ground state levels and levels in the odd electronic $1\Sigma_u^+$ and $1\Pi_u$ parity bands. A
perturbation theory argument is then used to obtain the polarisabilities as sums
over these intermediate levels with odd electronic parity. They include rotational,
vibrational and electronic states, and considerations involving the Franck-Condon
principle enter in a significant way, the details of which will be omitted here (however,
see Section 2.5.3) and only the final formulas will be given below for comparison.

The calculation of the electric-dipole matrix elements ignores the rotational spacings
for the odd-parity bands. This corresponds to neglecting the rotational contribution
(given by Eq. (A.30) of the Appendix) in the structure calculations, for
$\alpha = 1\Sigma_u^+, 1\Pi_u$. It is anticipated that the main contributions to the polarisabilities
will arise from those vibrational levels residing in the odd-parity bands. Consequently,
the electronic states in the $1\Sigma_u^+$ and $1\Pi_u$ bands are characterised only by an
energy $E_{ov}$, so that the trial functions $u$ (Eq. (2.39)) for them omit any dependence
on the $K$ rotational quantum number. Obviously, this applies also to the expansion
coefficients, $C$, in (2.39). Hence, it is not hard to show that the electric-dipole
matrix elements $M_{\alpha'\nu',gu K}$, for $\alpha' = 1\Sigma_u^+, 1\Pi_u$, take the form

$$M_{\alpha'\nu',gu K} =$$

$$2 \sum_{n'n''L'} \sum_{L''L'''} N_{ab} N_{c'd'} C_{n'n''L'} C_{n''L''}$$

$$\times \left[ (-1)^{L_e} \delta_{l' a} \hat{\rho}_{l'a} \right] \left( \begin{array}{ccc} l_a & l' a & 1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L_e & L'_e & 1 \\ 0 & -\Lambda_{\alpha'} & \Lambda_{\alpha'} \end{array} \right) \hat{L}_e \hat{L}_e (-1)^{l a} O_1(\alpha'n', gn)$$

$$+ \delta_{l' a} \hat{\rho}_{l'a} \left( \begin{array}{ccc} l_a & l' a & 1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L_e & L'_e & 1 \\ l_a & l_b \end{array} \right) O(\alpha' a', gb) I_1(\alpha' a', ga)$$

$$+ (-1)^{L_e} \delta_{l' a} \hat{\rho}_{l'a} \left( \begin{array}{ccc} l_b & l' b & 1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L_e & L'_e & 1 \\ l_b & l_a \end{array} \right) O(\alpha' b', ga) I_1(\alpha' a, gb)$$

$$+ \delta_{l' a} \hat{\rho}_{l'a} \left( \begin{array}{ccc} l_b & l' b & 1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L_e & L'_e & 1 \\ l_b & l_a \end{array} \right) O(\alpha' a', ga) I_1(\alpha' b', gb) \right].$$

(2.73)

where

$$O_1(\alpha'n', gn) = \int_0^\infty dR \psi_{\alpha' n'}^*(R) \psi_{\alpha' n}^2(R), \quad O(\alpha' a', ga) = \int_0^\infty drr^2 R_{\alpha' n}^2(r) R_{\alpha' n}^2(r),$$
The matrix elements of the static polarisabilities are then given by

$$
\langle g'v'K' | \alpha_{||} | gvK \rangle = 2 \sum_{\beta} \frac{M_{\Sigma \beta,gv'K'} M_{\Sigma \beta,gvK}}{(E_{\Sigma \beta} - E_{gvK})},
$$

$$
\langle g'v'K' | \alpha_{\perp} | gvK \rangle = 2 \sum_{\beta} \frac{M_{\Pi \beta,gv'K'} M_{\Pi \beta,gvK}}{(E_{\Pi \beta} - E_{gvK})},
$$

where $\Sigma, \Pi_u$ is used as a shorthand for $1\Sigma_u^+, 1\Pi_u$, and the label $\beta$ characterises the quantum numbers appropriate to a given electronic type, e.g., electronic and vibrational.

The sums occurring above have their counterparts in scattering theory as excitations of the corresponding closed channels. The number of such channels grows very rapidly and is probably the reason why previous works mentioned in Chapter 1 have been reluctant to include such channels directly in the scattering.

In the scattering problem, it will be shown that only specific combinations of the polarisabilities in (2.75) enter through the asymptotic form of the polarisation potential (cf. Chapter 4). These combinations are defined by the spherical $\alpha_0$ and non-spherical $\alpha_2$ parts of the polarisability of $H_2$; and, subsequently, the matrix elements for them can be expressed in terms of those given for $\alpha_{||}$ and $\alpha_{\perp}$ in (2.75):

$$
\langle g'v'K' | \alpha_0 | gvK \rangle = \langle g'v'K' | \frac{1}{3}(\alpha_{||} + 2\alpha_{\perp}) | gvK \rangle
$$

$$
\langle g'v'K' | \alpha_2 | gvK \rangle = \langle g'v'K' | \frac{2}{3}(\alpha_{||} - \alpha_{\perp}) | gvK \rangle.
$$

It should be noted, however, that no such approximations in the form of a local potential are actually used in representing the long-ranged induced polarisation effects in the scattering problem. Rather, the relations in (2.76) for $\alpha_0$ and $\alpha_2$, facilitate an alternate and more direct way of gauging the importance of the excited odd-parity states of the $H_2$ molecule used in the scattering calculations, since these polarisabilities, together with the quadrupole matrix elements, are expected to dominate the long-ranged interactions in the propagation procedure developed for the $R$-matrix in Chapter 3 (see also Chapter 4).

It is also worth mentioning that irrespective of whether polarisation effects in $e-H_2$ scattering are represented by a local potential, or whether the excited electronic states of the $H_2$ molecule are included from first principles, both approaches, in the context of scattering theory, are characterised by the appearance of the static-dipole polarisabilities of $H_2$ molecule in the asymptotic region of scattered electron. Thus having the values of the polarisibility matrix elements (2.75) available in the
scattering calculations provide an important point of comparison with those calculations which rely on local potentials to model polarisation effects in low-energy e-H$_2$ scattering.

2.5 THE CALCULATIONS

In this section, the process of optimisation of the nonlinear parameters (introduced into the definitions of the basis functions in Section 2.3) for producing the best possible rotational and vibrational energy spacings for the wave functions of the hydrogen molecule in the electronic $^1\Sigma_g^+$ ground state, as well as for those in the odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ bands will be described. The energy level spacings together with the quadrupole and polarisability matrix elements formulated in the previous section, are the properties of the molecular wave functions most likely to be of importance in the scattering problem. The computation of the quadrupole and polarisability matrix elements with respect to the calculated wave functions are therefore also briefly described.

2.5.1 Diagonalisation of the Matrix

For a given rotational quantum number $K$ and a given electronic band $\alpha$, a program, involving a code written for the matrix elements listed in the Appendix (Section A.3), solved the linear variational problem:

$$\sum_i (H_{ij} - E_{\alpha K} \delta_{ij}) C_{\alpha K}^i = 0,$$

(2.77)

for each $j$, where $H_{ij}$ is the matrix defined in (2.50) with respect to the electronic $\psi$ and vibrational $\chi_n$ basis. The system (2.77) involves a denumerable basis set, which in practice must be truncated, so that the eigenvalues, $E$, and corresponding coefficients, $C$, of a real symmetric matrix need to be determined. More specifically, since $H_{ij}$ affords three adjustable nonlinear parameters, $\omega_\alpha$, $\beta_\alpha$ and $R_\beta$, numerical minimisation of the energies $E_{\alpha K}$, proceeds by solving the secular equation, $|H_{ij} - E_{\alpha K} \delta_{ij}| = 0$, as a function of the three nonlinear parameters. For this part of the calculations, a Jacobi-rotation technique (a subroutine from Numerical Recipes, 1992) was incorporated into the program. This technique is very efficient for the diagonalisation of large matrices, which is especially useful, particularly since relatively large expansions for the trial functions $u$ in (2.39) and systematic variations in the nonlinear parameters were explored, for each $K$, in the calculations.

In general, $\omega_\alpha$ was used to “tune” the energy levels in the electronic subspace of the system (2.77), whereas, the vibrational and rotational energy levels were found to be sensitive to variations in $\beta_\alpha$ and $R_\beta$, respectively. Further, since a monotonic decrease in the electronic energy levels arises as a consequence of increasing the number of configurations in the subspace of the electronic basis $\psi$, Eq. (2.40),
and that such levels set a lower bound for a given vibrational band, it naturally followed that the energy values produced for the electronic levels were not, to any appreciable extent, affected by the size of the vibrational basis (2.46) used. Rather, expansion of the latter basis leads to an accumulation of vibrational levels, so that diagonalisation of $H_{ij}$ in (2.77), yields electronic levels embedded with vibrational ones. Obviously, these levels are enumerated further in sequence by the rotational quantum number, which arises when $H_{ij}$ is diagonalised for successive values of $K$. This portion of the calculations was fully automated to investigate more carefully the variations with respect to the nonlinear parameters, $\beta\beta$ and $R_0$, and, as will be illustrated below, also ensured that the best possible vibrational and rotational levels were produced when computing the wave functions.

2.5.2 Energy Levels and Optimisation of the Parameters

The advantage of having adjustable nonlinear parameters built into the basis functions (Section 2.3), is that such parameters may be optimised to give accurate energy level spacings, even though relatively crude trial functions $u$ (Eq. (2.39)) are used for the representations of the wave functions, i.e., wave functions whose absolute energies are not so well reproduced.

In particular, as this part of the calculations aims at producing accurate rotational and vibrational energy spacings, especially for the ground $^1\Sigma^+_g$ state wave functions of the H$_2$ molecule in the scattering problem, the electronic basis orbitals, $\psi$ (Eq. (2.40)), may be selected according to the relative weights of the expansion coefficients, $C$, that are produced concurrently with the corresponding energies, $E$, on diagonalisation of $H_{ij}$ in (2.77). Thus upon examination of the expansion coefficients, one can "sift" out the relatively insignificant basis configurations from the dominant ones, to obtain, in a completely systematic manner, quite large and sophisticated models for the wave functions.

This was the procedure used to produce the 35-electronic basis configuration model shown in the next section for the ground $^1\Sigma^+_g$ state of H$_2$. The numerical minimisation of the energies for such a model, first begins by systematically varying $\omega^g$ until the best value possible for the lowest electronic energy level, $E_{g00}$ (usually with the vibrational basis size held at its minimum value of $n_{max} = 0$) is attained. Adjustments to the size of the vibrational basis were then explored to the extent that was found sufficient to obtain convergence in the spacings for the first few vibrational levels. Once this was established, a more careful tuning of the vibrational and rotational spacings, $\epsilon_{0K} = E_{g00K} - E_{g00}$, with respect to the nonlinear parameters, $\beta\beta$ and $R_0$, was also carried out, by diagonalising $H_{ij}$ successively for several values of the $K$ rotational quantum number, and at the same time varying the nonlinear parameters systematically.
The latter step is summarised in Table 2.2, using, as an example, a 7-state electronic configuration model with a vibrational basis size of \( n_{\text{max}} = 6 \) and with the rotational quantum number restricted to \( K = 0 \) and \( K = 2 \). As can be seen from the values of the parameters shown in the table, the rotational spacing is rather insensitive to any further variations with respect to them, while the vibrational spacings do, however, show subtle changes with respect to \( \beta \) and also appear to have a shallow minimum at \( R_0 = 1.42 \) a.u. This behaviour in the energy level

<table>
<thead>
<tr>
<th>( \beta ) (a.u.)</th>
<th>( R_0 ) (a.u.)</th>
<th>( \varepsilon_{\beta 02} \times 10^3 )</th>
<th>( \varepsilon_{\beta 10} \times 10^2 )</th>
<th>( \varepsilon_{\beta 12} \times 10^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.4</td>
<td>1.32</td>
<td>1.56</td>
<td>1.922</td>
<td>2.071</td>
</tr>
<tr>
<td>16.4</td>
<td>1.42</td>
<td>1.56</td>
<td>1.918</td>
<td>2.067</td>
</tr>
<tr>
<td>16.4</td>
<td>1.52</td>
<td>1.56</td>
<td>1.919</td>
<td>2.068</td>
</tr>
<tr>
<td>17.4</td>
<td>1.32</td>
<td>1.56</td>
<td>1.923</td>
<td>2.073</td>
</tr>
<tr>
<td>17.4</td>
<td>1.42</td>
<td>1.56</td>
<td>1.919</td>
<td>2.067</td>
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<tr>
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<td>1.52</td>
<td>1.56</td>
<td>1.919</td>
<td>2.067</td>
</tr>
<tr>
<td>Experiment</td>
<td>1.615</td>
<td>1.8595</td>
<td>2.0490</td>
<td></td>
</tr>
</tbody>
</table>

spacings with respect to variations in the nonlinear parameters, is typical of that observed in other configuration models leading up to the 35-state model mentioned above for the ground electronic \( ^1\Sigma_g^+ \) state of \( \text{H}_2 \).

In contrast, no attempt was made to particularise any of the electronic basis configurations used in constructing the states of the type, \( ^1\Sigma_u^+ \) and \( ^1\Pi_u \), with odd electronic parity. Rather, the main aim in the calculations was to produce a sufficient number of these states to enable trends to be identified when assessing the importance of the intermediate states occurring in the static-dipole polarisability matrix elements (2.75).

Up to 21(27) electronic configurations for the \( ^1\Sigma_u^+ \) \((^1\Pi_u)\) bands were used in the calculations. Recall, that these states are configured from odd \((\ell_a + \ell_b)\) values of the electronic basis orbitals, due to the parity restriction given in (2.45), and also, as remarked in Section 2.4.2, neglect the rotational contribution (Eq. (A.30) of the Appendix) when diagonalising the matrix \( \mathcal{H}_{ij} \) in (2.77). Consequently, \( R_0^\alpha \) was taken to correspond to the equilibrium bond length values that are typically found for the lowest lying electronic levels residing in the \( \alpha = ^1\Sigma_u^+, ^1\Pi_u \), bands respectively, with the remaining parameters, \( \omega^\alpha \) and \( \beta^\alpha \), optimised accordingly to produce the lowest
value for the electronic energy levels and the best possible vibrational spacings.

As far as the size of the vibrational basis in the odd-parity bands is concerned, this was dictated according to whether or not convergence in the electric-dipole matrix elements (2.73) was sought after. As will be addressed below, this is related to the considerations mentioned in Section 2.4.2 involving the Franck-Condon principle.

2.5.3 Other Properties

As noted in Section 2.4.1, the function of the quadrupole matrix elements (2.70) serves as an indication as to whether the $K = 0 \rightarrow K = 2$ rotational excitation cross sections will be reasonably well reproduced. This is especially important near the excitation threshold for such a process. As will be discussed further in the next section, the fluctuations observed in the values of the quadrupole matrix elements computed with several of the ground state models produced from the calculations described above are indicative of the behaviour also observed in other structure calculations.

Another kind of sensitivity observed, is that associated with the electric-dipole matrix elements (2.73). The part most sensitive in these matrix elements is due to the overlap integrals $O_1$ (Eq. (2.74)) between the harmonic oscillator basis functions in the ground state band and those used for the odd-parity states, so that rather high orders of $n$ must be used in the latter basis, before one can be assured of no significant changes in the results produced for the overlap integrals, and thus also the electric-dipole matrix elements. For example, to ensure convergence in the electric-dipole matrix elements, when, say, $n_{\text{max}} = 6$ was used for the vibrational functions in the ground state, required using (at least) $n_{\text{max}} = 15$ for the vibrational functions for the odd-parity states.

Such behaviour in the electric-dipole matrix elements, may of course be anticipated on physical grounds as a consequence of the Franck-Condon principle, which in the simplest approximation (e.g., see Wolniewicz, 1969), can be characterised roughly through the static-dipole polarisability matrix elements (2.75) as sums over the square of the overlap integrals $O_1$, i.e., the Franck-Condon factors for the band transitions, $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+, ^1\Pi_u$, between harmonic oscillator functions. As a result, one must expect, irrespective of the size of the vibrational basis used, that not all the intermediate transitions to the odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ states (i.e., electric-dipole matrix elements) will contribute significantly to the polarisabilities (2.75) — rather, only those which have the greatest overlap with the ground state wave functions.

This is illustrated in Table 2.3. To calculate the polarisability matrix elements shown in the table, the 7-state configuration model presented earlier in Table 2.2 for the ground $^1\Sigma_g^+$ state was used, whereas a single electronic basis configuration with $n_{\text{max}} = 3$ for the vibrational basis size was used for both the $^1\Sigma_u^+$ and $^1\Pi_u$
Table 2.3. Cummulative sums $\sum_{\nu'}$ for the polarisability matrix elements of the H$_2$ molecule (a.u.).

| $\nu'$ | $\langle 00|\alpha_{\|}|00 \rangle$ | $\langle 02|\alpha_{\|}|00 \rangle$ | $\langle 00|\alpha_{\perp}|00 \rangle$ | $\langle 02|\alpha_{\perp}|00 \rangle$ |
|------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1    | 6.370[-4]                     | 6.080[-4]                     | 0.115                         | 0.119                         |
| 2    | 1.254[-2]                     | 1.414[-2]                     | 0.897                         | 0.919                         |
| 3    | 3.272                         | 3.302                         | 2.732                         | 2.741                         |

bands. Diagonalisation of the matrix $\mathcal{H}_{ij}$ in (2.77) therefore produced for each of the $^1\Sigma_u^+$ and $^1\Pi_u$ bands, a single electronic energy level supporting four vibrational levels, $\nu' = 0, 1, 2$ and 3. Table 2.2 thus shows the contributions to the polarisability matrix elements as cummulative sums due to these vibrational states. As can be seen, the greatest overlap with the ground state model occurs only with the last vibrational level shown in Table 2.2, while those with the lower vibrational levels are considerably smaller by comparison.

This is actually an exception, since in the more realistic calculations for the odd-parity bands, supporting considerably more vibrational levels than the example cited above, it was generally observed that the greatest overlap with the 7-state configuration model occurred between an intermediate range of values for the odd-parity vibrational levels, while the corresponding lower and higher vibrational levels were found to be less significant in their overall contribution to the static polarisabilities.

2.6 RESULTS AND DISCUSSION

In this section, a sample of results relating to the structure of the hydrogen molecule will be given, as an illustration of what can be expected to be achieved from the structure scheme formulated in Sections 2.2–2.4 and the procedures used in Section 2.5 for its implementation. Comparisons are also made in this section with those structure studies which use the fixed-nuclei method. In the following, numbers will be quoted to an accuracy necessary for the purposes of comparison.

Also in what follows, single electron orbitals will be denoted as $((n_a + 1)l_a)$ in the usual spectroscopic notation, with the two-electron basis configurations $\psi$ in Eq. (2.40) thus represented as $((n_a + 1)l_a, (n_b + 1)l_b)$. In the case when both electron orbitals occupy the same configuration, the latter will be abbreviated as $((n_a + 1)l_a)^2$.
2.6.1 Wave Functions and Quadrupole Matrix Elements for the $^1\Sigma^+_g$ State of $\text{H}_2$

In accord with the procedures described in Section 2.5.2, three types of single-center expansion models consisting of 7, 24 and 35 electronic basis configurations were obtained systematically for the wave functions of the hydrogen molecule in its electronic $^1\Sigma^+_g$ ground state. For each of the configuration models, a vibrational basis size of $n_{\text{max}} = 6$ was used to calculate the energies for the lowest level, $E_{g00}$, and the vibrational-rotational spacings, $\epsilon_{gvK} = E_{gvK} - E_{g00}$. The results are tabulated in Table 2.4, with the particular type of electronic basis orbitals used for each of the configuration models given in the footnote of the table. Also displayed in the table are the corresponding energy results obtained from the fixed-nuclei studies of Kolos and Wolniewicz (1965, 1968a) [KW], Morrison, Feldt and Austin (1988) [MFA], and Hagstrom and Shull (1959) [HS]. With the exception of KW, the values shown in Table 2.4 for MFA and HS, have been adjusted to allow for the zero-point energy of the molecule, since both MFA and HS calculate $E_{g00}$ when the internuclear distance of the hydrogen molecule is held fixed at its equilibrium bond length value of $R = 1.4$ a.u.. This adjustment is not needed for the calculations of KW, since in addition to solving for the electronic wave functions at fixed values of $R$, KW also solve for the vibrational-rotational functions to produce the corresponding energies. Note, also, that KW use correlated orbitals in two-center confocal elliptic coordinates for solving the electronic problem, so that their wave functions contain the interelectronic distance explicitly.

On comparison between the 7-, 24- and 35-configuration models obtained in the present study, it can be seen from Table 2.4 that improvement in the lowest state, $E_{g00}$, is not accompanied by a comparable improvement in the level spacings, $\epsilon_{gvK}$; increasing the number of electronic basis states has an adverse effect on them in the third significant figure. This is most likely due to the fact that $\omega_e$ (the nonlinear parameter for the electronic basis functions) has already reached its optimum value with as many as 7 electronic configurations, while the tuning of the vibrational and rotational levels, with respect to the vibrational basis parameters, $\beta$ and $R_0$, are sensitive to the particular type of electronic basis orbitals used in the calculations. Further work which extend the procedures outlined in Section 2.5.2 is required in order to clarify this point. Nevertheless, the numbers obtained in for the nonlinear parameters are the optimum ones for the 7-, 24- and 35-configuration models presented in Table 2.4, and moreover, enable energy level spacings to be calculated within an accuracy that is no worst than 5 percent of the experimental values quoted in the table.

It is also possible to gain some insight into the convergence behaviour associated with single-center expansions. For instance, the single-center expansions of HS use a
Table 2.4. Comparison of the calculated vibrational and rotational spacings \( \epsilon_{vK} \) and energy of the lowest level \( E_{g00} \) in Hartree a.u. for the \( ^1\Sigma_g^+ \) ground state of \( \text{H}_2 \) with those obtained from other studies (see the text). The 7-, 24- and 35-configuration models shown below are of this research with \( \omega_c = 0.35 \) a.u., \( \beta = 17.404 \) a.u., \( R_0 = 1.42 \) a.u., \( n_{\text{max}} = 6 \).

<table>
<thead>
<tr>
<th>Approximate Wave Functions</th>
<th>( E_{g00} )</th>
<th>( \epsilon_{g02}(\times10^3) )</th>
<th>( \epsilon_{g10}(\times10^2) )</th>
<th>( \epsilon_{g12}(\times10^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7(^a)</td>
<td>(-1.060)</td>
<td>1.56</td>
<td>1.918</td>
<td>2.067</td>
</tr>
<tr>
<td>24(^b)</td>
<td>(-1.108)</td>
<td>1.54</td>
<td>1.938</td>
<td>2.087</td>
</tr>
<tr>
<td>35(^c)</td>
<td>(-1.121)</td>
<td>1.55</td>
<td>1.972</td>
<td>2.124</td>
</tr>
<tr>
<td>KW</td>
<td>(-1.165)</td>
<td>1.615</td>
<td>1.896</td>
<td>2.0498</td>
</tr>
<tr>
<td>MFA</td>
<td>(-1.123)</td>
<td>(-)</td>
<td>1.990</td>
<td>(-)</td>
</tr>
<tr>
<td>HS</td>
<td>(-1.139)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>Experiment(^d)</td>
<td>(-1.16456)</td>
<td>1.615</td>
<td>1.8959</td>
<td>2.0490</td>
</tr>
</tbody>
</table>

\( ^a(1s)^2, (1s, 2s), (1s, 3s), (1s, 4s), (1s, 1d), \) and \((1p)^2 \).
\( ^b\)Terms in footnote a plus: \((1s, 5s), (2s)^2, (2s, 3s), 2s, 4s), (3s)^2, (1s, 2d), (1s, 3d), \( (1s, 4d), (2s, 1d), (2s, 2d), (2s, 3d), (3s, 1d), (3s, 2d), (1p, 2p), \) and \((1p, 3p) \).
\( ^c\)Terms in footnote b plus: \((1s, 6s), (1s, 7s), (2s, 5s), (2s, 6s), (3s, 4s), (3s, 5s), (1s, 5d), (1s, 6d), (2s, 4d), (2s, 5d) \) and \((3s, 4d) \).
\( ^d\)Experimental values taken from Kolos and Wolniewicz (1965, 1968a)

basis comprising a complete and discrete set of hydrogen-like orbitals. Their energy results shown in Table 2.4 are for a 35-configuration set \((-1.139 \) a.u.) and for a 44-configuration set \((-1.152 \) a.u.). Comparison of the \( E_{g00} \) ground level energies shown in the table between HS and that obtained by KW, and the close agreement of the latter with experiment, only affirms the doubts (mentioned also in Section 2.4) by HS for the use of single-center expansions in diatomic problems; HS indicate that even with their 44-configuration set, many more basis orbitals would need to be added in order to achieve the binding energies comparable with those obtained from the correlated type wave functions, such as those used by KW.

There is no doubt that many more configurations than the 35-configuration model obtained in this study would also be required in order to achieve a value comparable to that of KW for the lowest energy level, \( E_{g00} \). To carry out such an
investigation, it would seem more profitable, however, to use the same choice of orbitals adopted by HS, since, on comparison, their energy value for a 35-configuration set (−1.139 a.u.) is considerably better than that possible with the present 35-configuration model (−1.121 a.u.). This observation also confirms the closing remarks made in Section 2.3.2, concerning the fact that expansions with Gaussian-type functions tend to require larger sets of orbitals than, say, Slater-type functions, or, for that matter, exponential-type functions, like those used by HS.

On the other hand, the 7-, 24- and 35-configuration models of the present study, have been constructed for use in low-energy e-H₂ scattering, so a more instructive comparison is with the Hartree-Fock wave functions of MFA (see Table 2.4). In particular, MFA demonstrate that their Hartree-Fock wave functions, which consist essentially of Gaussians contracted in terms of Cartesian coordinates centered on the nuclei (two protons) of the H₂ molecule, are capable of producing cross sections for low-energy e-H₂ scattering that are in excellent agreement with those obtained using the correlated wave functions of KW. This result is striking in view of the substantial difference in energy seen in Table 2.4 between the MFA wave function and the KW wave function for the $E_{g00}$ ground level. It would appear, here, that there are definite grounds for placing precedence towards obtaining accurate vibrational-rotational spacings for the ground state wave functions of H₂, rather than on their absolute energies. Moreover, the fact that the MFA result for the ground level, $E_{g00}$, is only displaced slightly lower than that of the 35-configuration model, encourages the prospect of attempting a scattering calculation with the 35-configuration model. Whether reliable cross sections may also be achieved with the 7- and 24-configuration models obtained in the present study, would be an interesting investigation to carry out.

While the latter remark, suggests one possibility for assessing cross sections according to improvements of the wave functions with respect to the energies, such wave functions do not automatically guarantee accurate values for those quantities that are important to the scattering problem. This was already ascertained in Section 2.4.1, in connection with the quadrupole moment of the H₂ molecule (see Eq. (2.69)). Selected matrix elements for the quadrupole moment have therefore been calculated with the 7-, 24-, and 35-configuration models obtained in Table 2.4, and are displayed in Table 2.5 alongside those obtained from the highly accurate calculations of Poll and Wolniewicz (1978) [PW] in the clamped-nuclei approximation.

The main feature to note in Table 2.5, is that the matrix elements produced with the 24-configuration model are not intermediate between those of the 7- and 35-configuration models. This corresponds to the fluctuations observed by Kolos and Roothan (1960), in which these authors express further concern:
Table 2.5. Quadrupole moment matrix elements \( \langle v'K'|Q|vK \rangle \) (a.u.). Also shown are the results obtained by Poll and Wolniewicz (1978) [PW].

<table>
<thead>
<tr>
<th>( v'K' )</th>
<th>( vK )</th>
<th>PW configurations</th>
<th>7 configurations</th>
<th>24 configurations</th>
<th>35 configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>02 00</td>
<td>0.48516</td>
<td>0.480</td>
<td>0.619</td>
<td>0.588</td>
<td></td>
</tr>
<tr>
<td>12 00</td>
<td>0.07833</td>
<td>0.099</td>
<td>0.110</td>
<td>0.106</td>
<td></td>
</tr>
<tr>
<td>02 02</td>
<td>0.48689</td>
<td>0.482</td>
<td>0.621</td>
<td>0.591</td>
<td></td>
</tr>
<tr>
<td>10 02</td>
<td>0.09770</td>
<td>0.117</td>
<td>0.132</td>
<td>0.127</td>
<td></td>
</tr>
<tr>
<td>12 02</td>
<td>0.08811</td>
<td>0.109</td>
<td>0.121</td>
<td>0.117</td>
<td></td>
</tr>
<tr>
<td>12 10</td>
<td>0.53660</td>
<td>0.564</td>
<td>0.693</td>
<td>0.653</td>
<td></td>
</tr>
<tr>
<td>12 12</td>
<td>0.53865</td>
<td>0.567</td>
<td>0.695</td>
<td>0.655</td>
<td></td>
</tr>
</tbody>
</table>

To judge the quality of an approximate wave function, the criterion of how close the calculated energy agrees with the experimental one is often only a crude measure. ... it is therefore quite possible that wave functions which yield good energies yield poor values for the expectation values of other operators.

Indeed, the data obtained in Tables 2.4 and 2.5 for the ground state configuration models of the present study, shows this to be the case; although the 7-configuration model has the worst ground state energy, \( E_{g00} \), in comparison to the 24- and 35-configuration models, its quadrupole matrix elements are closer to the accurate values of PW than those produced using the latter two models. This result is thus consistent with that uncovered by Kolos and Roothan (1960), and as they claim is “almost always true in practice”, due to the fact that the errors in the energy are generally smaller than errors in other properties, which may be proved quite generally as a natural consequence of applying the variational principle.

2.6.2 Excited \( ^1\Sigma_u^+ \) and \( ^1\Pi_u \) States and the Polarisability of the Hydrogen Molecule

Satisfactory modelling of the excited \( ^1\Sigma_u^+ \) and \( ^1\Pi_u \) states with odd electronic parity is a much more difficult task. Fortunately, this is not a serious defect, as modelling of the excited odd-parity states has been characterised in Section 2.4.2 strictly in view of a first principle treatment of polarisation effects in the e-H\(_2\) scattering problem, so the fact that the energies shown in Table 2.6 are poorly
reproduced with respect to the models used, should not matter as much in the scattering calculations as those for the electronic $^1\Sigma_u^+$ ground state band. This is further evident in the preliminary calculations discussed in Section 2.5.3, since, as noted there (e.g., see Table 2.3), not all of the intermediate transitions from the odd-parity states contribute significantly to the polarisabilities.

As outlined in Section 2.5.2, the wave functions for the excited $^1\Sigma_u^+$ and $^1\Pi_u$ states are constructed from electronic basis orbitals with odd $(l_a + l_b)$ values. Therefore starting from the $(1s, 1p)$ configuration it was possible to construct two models (hereafter referred to as Model 1 and Model 2) for each of the $^1\Sigma_u^+$ and $^1\Pi_u$ bands. In particular, Model 1 corresponds to the single $(1s, 1p)$ configuration with $n_{max} = 3$ for the vibrational basis size, whereas Model 2 consists of all configurations with $(2n_a + 2n_b + l_a + l_b)$ equal to 1, 3, and 5 with $n_{max} = 15$ for the vibrational basis. Model 2 therefore amounts to $21(27)$ electronic basis configurations for the $\Sigma_u(\Pi_u)$ bands. The first few energies for the odd-parity states produced with these models are displayed in Table 2.6.

It is clear from Table 2.6, that Model 2 has considerably better vibrational spacings than those produced with Model 1. This is due to the larger vibrational basis size used for Model 2 than that used for Model 1, which for the reasons outlined in Section 2.5.3 is needed in order to ensure convergence in the electric-dipole matrix elements. However, it is also seen that for both models, the energies of the first excited levels and the vibrational spacings in each band are too large by spectroscopic standards, implying that many more electronic configurations than those used here are needed, if the calculated energies are to be comparable to those determined by experiment.

Turning now to the polarisability matrix elements, Table 2.7 is representative of the results that can be attained for them using the 7-configuration model in Table 2.4 for the ground state band, and the two models (Model 1 and Model 2) in Table 2.6, for the odd-parity states. Also shown in the table is a selection of results from the polarisability studies of Kolos and Wolniewicz (1967) [KW], which were calculated using the fixed-nuclei method, in the manner described in Section 2.4.2.

In the context of scattering theory, the relevant parts of the polarisability matrix elements are those defined via the spherical and non-spherical components, $\alpha_0$ and $\alpha_2$, of the polarisability tensor of the H$_2$ molecule, as given in Eq. (2.76). In particular, it will be shown in Chapter 4, that in the region when the scattered electron is far from the molecule, the combinations of the matrix elements, $\langle 00|\alpha_0|00 \rangle$, $\langle 02|\alpha_2|00 \rangle$, and $\langle 10|\alpha_0|00 \rangle$, represent those terms respectively in the scattering channels that are relevant for the determination of the elastic, rotational and vibrational transitions cross sections. Accordingly, the matrix elements $\langle 00|\alpha_0|00 \rangle$ and $\langle 02|\alpha_2|00 \rangle$ shown at the bottom of Table 2.7 allow for some significance to be attached to the induced
Table 2.6. Energy levels for states in the ^1Σ⁺_u and ^1Π_u bands of H₂. The calculated results are for Model 1 and Model 2 discussed in the text. The results for Model 2 (n_{max} = 15) is shown first and that of Model 1 (n_{max} = 3) directly below. For both cases the parameters used for the ^1Σ⁺_u (^1Π_u) bands were ω_e = 0.35 a.u. and β = 4.80 a.u. (9.18 a.u.), R_0 = 2.5 a.u. (2.0 a.u.)

<table>
<thead>
<tr>
<th></th>
<th>Calculated (a.u.)</th>
<th>Experiment^a (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{D0} (lowest level)</td>
<td>-0.656</td>
<td>-0.754</td>
</tr>
<tr>
<td></td>
<td>-0.558</td>
<td></td>
</tr>
<tr>
<td>E_{D1} (vibrational spacing)</td>
<td>0.0077</td>
<td>0.00599</td>
</tr>
<tr>
<td></td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>E_{D0} (first excited level)</td>
<td>-0.324</td>
<td>-0.661</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{Π0} (lowest level)</td>
<td>-0.566</td>
<td>-0.713</td>
</tr>
<tr>
<td></td>
<td>-0.355</td>
<td></td>
</tr>
<tr>
<td>E_{Π1} (vibrational spacing)</td>
<td>0.0109</td>
<td>0.01025</td>
</tr>
<tr>
<td></td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>E_{Π0} (first excited level)</td>
<td>-0.310</td>
<td>-0.656</td>
</tr>
</tbody>
</table>

^aExperimental values taken from Kolos and Wolniewicz (1968b)

effects of polarisation in the elastic and rotational channels. The numbers for these matrix elements must therefore be reproduced reasonably well if the corresponding cross sections are to be accurately determined.

To achieve this carries with it a serious implication. The first and obvious fact is that accurate results for the polarisabilities require the inclusion of many more odd-parity states than that achieved with Model 2. Secondly, Model 2 alone contemplates a considerable number of channels for the odd-parity states, which must be included on top of those already present for the ground state band. To take into account all of the channels which arise from these states would thus render an impractical proposition for the e-H₂ scattering problem. Some form of a compromise is therefore needed.

In this respect, the considerations involving the Franck-Condon principle in Section 2.5.3, are somewhat of a blessing in disguise. For example, the preliminary results for the polarisabilities shown there in Table 2.3, revealed that only the last one or two vibrational levels with odd electronic parity contribute appreciably. This
Table 2.7. Comparisons of calculated matrix elements of the polarisabilities for the hydrogen molecule with those obtained by Kolos and Wolniewicz (1967) [KW].

<table>
<thead>
<tr>
<th></th>
<th>KW</th>
<th>Model 1</th>
<th>Model 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>\langle 00</td>
<td>a</td>
<td></td>
<td>00\rangle</td>
</tr>
<tr>
<td>\langle 02</td>
<td>a</td>
<td></td>
<td>00\rangle</td>
</tr>
<tr>
<td>\langle 10</td>
<td>a</td>
<td></td>
<td>00\rangle</td>
</tr>
<tr>
<td>\langle 00</td>
<td>a\perp</td>
<td></td>
<td>00\rangle</td>
</tr>
<tr>
<td>\langle 02</td>
<td>a\perp</td>
<td></td>
<td>00\rangle</td>
</tr>
<tr>
<td>\langle 10</td>
<td>a\perp</td>
<td></td>
<td>00\rangle</td>
</tr>
</tbody>
</table>

suggests a way of reducing the computational effort in the scattering calculations, since one may select only those odd-parity states which make significant contributions to the polarisabilities.

Carrying out such an exercise, also has some conceptual advantages. Firstly, polarisation effects in scattering theory are maintained at an \textit{ab initio} level, and, secondly, cross sections can be monitored systematically through refinements of the polarisabilities with respect to the odd-parity states, and, subsequently, also the scattering channels which arise from them. Whether such advantages are possible within the existing methods reviewed in Chapter 1, which choose to model polarisation effects using local potentials, based on a known asymptotic form of the polarisabilities in the fixed-nuclei approximation, seems doubtful.

### 2.7 FURTHER REMARKS AND SUMMARY

In this chapter a structure scheme for the calculation of the wave functions of H$_2$ has been developed, with the intention of avoiding the fixed-nuclei approximation and a model potential treatment of polarisation effects in low-energy e-H$_2$ scatter-
ing. This relied in Sections 2.2 and 2.3 on the ability to factorise the wave functions as products of rotational functions and electronic-vibrational functions and the further characterisation of the latter in terms of a simultaneous set of electronic and vibrational basis functions.

While this was made possible by adopting a single centre expansion for the wave functions and involved rejecting the more accurate expansions, such as the two-center method used in the calculations of Kolos and Wolniewicz (1965, 1968a, b), it has however been argued elsewhere (Section 2.4) that the present structure scheme aims more towards understanding the main mechanisms driving the different transitions cross sections in the scattering problem, and that the single centre method adopted for the wave functions for such purposes is in no way prevented from being any inferior in quality to other types of wave functions used in e-H$_2$ scattering, such as the Hatree-Fock wave functions used by Morrison et al. (1984)

The premise for this was based in Section 2.4 on accepting the view that (i) the matrix elements responsible for driving the different transition cross sections are related to different matrix elements such as those of the quadrupole moment and polarisabilities of H$_2$ and (ii) that such matrix elements can be determined reliably even though the wave functions they are calculated with do not reproduce the energies observed by experiment.

The procedures used in the calculations (Section 2.5) were therefore aimed at substantiating the latter point for the principal purpose of the present research which is contained in the first point. Indeed, the results of the previous section illustrate the content of the first point exclusively, through the insensitive nature observed for the quadrupole and polarisability matrix elements with respect to the accuracy of the absolute energies produced by the wave functions.

For example, the quadrupole matrix elements (see Table 2.5) produced with the 7-configuration model in the present study were found to be in excellent agreement with the highly accurate values of Poll and Wolniewicz (1978), whereas those for the larger 24- and 35-configuration models, whose absolute values for the ground state energy are much better than that for the latter, are considerably worse.

The computation of the polarisability matrix elements (see Table 2.7) is also of a similar nature, but with the observation that the polarisability matrix elements depend more critically on the number of odd-parity states used in the calculations, rather than their individual energy levels; the number of such states being large, if accuracy in the matrix elements is required.

Although the latter requirement implies a considerably number of closed channels would be required in the scattering calculations inorder to take into account polarisation effects, it is somewhat fortitious that not all odd-parity states were observed to contribute significantly to the polarisability matrix elements. This was
noted in Section 2.6.2, and suggests a way of reducing the numerical workload in the scattering problem. Here, the use of different types of basis functions, than those employed in the present study, provides another option for alleviating the computational demands implied in the latter statement.

For example, Table 2.4 shows that the electronic basis orbitals used by Hagstrom and Shull (1959) are more economical for calculating energy levels than the ones employed in the present structure scheme. In this respect, replacing the associated Laguerre functions $R_{nl}$ used for the electronic basis in the present study in Eq. (2.40) by those of Hagstrom and Shull, would be ideal, since as well as being orthonormal, their basis functions are also associated Laguerre polynomials. This suggests that many of the matrix elements already formulated for the structure problem (Appendix B) would require only very minor modifications; the changes being mainly made with respect to the radial integrals, $I_L$ and $J_L$ obtained for the electron-electron repulsion and electron-proton attraction contributions to the matrix elements (cf. Eqs. (A.33) and (A.32)). For the vibrational part of the problem, the use of the Fues-type of functions is also tempting, which, as mentioned in Section 2.3.2, do not lead to any of the divergent type of integrals found with the one-dimensional oscillator basis functions $\chi_n$ (Eq. (2.46)) used in the present work.

While there is some merit in pursing these suggestions at some future stage of the work, the present study on the structure of $H_2$ already provides a sufficient foundation for the modelling of the wave functions in the $e-H_2$ scattering problem, especially since the wave functions have been formulated without using the fixed-nuclei approximation and that there are many candidates for the ground $^1\Sigma_g^+$ state wave functions as well as those for the excited odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ states that can be inferred through the results obtained so far for the quadrupole and polarisability matrix elements. This is the start, as will be demonstrated in subsequent chapters, to developing a framework for low-energy $e-H_2$ scattering that is not based on assumptions related to the fixed-nuclei kind or the treatment of polarisation effects via local model potentials.
Chapter 3

*R*-Matrix Formalism and Calculation of the Cross Sections: I

In Chapter 1, a theoretical framework for low-energy $e$-$H\textsubscript{2}$ scattering was proposed with the intention of avoiding two frequently made approximations in the context of electron-molecule scattering: (i) the fixed-nuclei approximation and (ii) the use of an effective local model potential for the treatment of polarisation effects. The formulation of the wave functions, based on the molecular structure theory of Kolos and Wolniewicz (1960), for the ground $^1\Sigma\textsubscript{g}^+$ and excited $^1\Sigma\textsubscript{u}^+$ and $^1\Pi\textsubscript{u}$ states of the hydrogen molecule, were therefore prepared in Chapter 2 in a form suitable for use in the present context of low-energy $e$-$H\textsubscript{2}$ scattering. In this chapter, the wave functions formulated in Chapter 2 are incorporated within the framework of the *R*-matrix formalism, with the intention of producing accurate low-energy electron scattering cross sections by the $^1\Sigma\textsubscript{g}^+$ ground state of the $H\textsubscript{2}$ molecule. The emphasis is on elastic scattering and rotational and vibrational excitations in the energy regime ($\leq$1eV) near threshold for such processes.

The *R*-matrix method employed in the present work is well suited for an explicit treatment of exchange effects as well as for the treatment of polarisation effects which are included in the scattering wave function expansion via the closed channels that are formed from the excited $^1\Sigma\textsubscript{u}^+$ and $^1\Pi\textsubscript{u}$ electronic states. Because of the well known difficulties associated with the integration of the scattering equations in both inward and outward directions when closed channels are included, a technique for the propagation of the *R*-matrix in the region when the scattered electron is far from the molecule has been adopted. This approach is similar to that used by Burke and others in the study of atomic and molecular processes. An extensive review of this work has recently been given by Burke and Berrington (1993).

In analogy to the other *R*-matrix methods, configuration space is therefore divided into internal, intermediate and external regions. The basic mathematical framework and techniques needed to characterise these different regions of configuration space for the scattering problem are thus expounded upon in Sections 3.1–3.3
of the present chapter. Some differences between the present approach and other related R-matrix programmes are then briefly examined in Section 3.4.

An important and nontrivial result of the present approach is the reproduction of the threshold laws for various inelastic processes. For this purpose, the scattering calculations described in Section 3.5 includes only the ground $^1\Sigma_g^+$ state wave functions of the hydrogen molecule generated in Chapter 2. The results for the calculated cross sections are then discussed in Section 3.6, with emphasis on the behaviour of the inelastic cross sections in the near-threshold energy regime.

Section 3.7 is a summary and general discussion of the main elements covered in the R-matrix programme of the present chapter.

3.1 R-MATRIX FORMALISM

In this section, a brief exposition of the basic mathematical framework of R-matrix theory, essentially following Barrett et al. (1983) (see also Lane and Thomas, 1958), will be outlined below as a series of definitions and conventions involving the concept of channel, needed to characterise the asymptotic boundary conditions and in turn formalise the link between the R matrix and the collision matrix $U$.

3.1.1 Definitions, Wave Functions and Channel States

Briefly, a scattering state $\psi_k$ is defined to be a solution of the Schrödinger equation,

$$(H - E)\psi_k = 0,$$  \hspace{1cm} (3.1)

subject to certain asymptotic boundary conditions, formulated in terms of the concepts of partition and channel. Following Barrett et al. (1983), a partition $\alpha$ is defined to be a division of the many-body system (3.1) into $n$ groups or clusters; each partition containing an infinite set of channels $c, c', c'', \ldots$

For purposes of definiteness, it will be assumed that initially one particle is in the continuum and the remaining particles are in a bound state forming a single composite system (T). The Hamiltonian $H$ for the complete system is then composed of a one particle Hamiltonian $H_{\text{inc}}$, the composite Hamiltonian of the target system $H_T$, and the residual or potential energy interaction $V_\alpha$:

$$H = H_{\text{inc}} + H_T + V_\alpha = H_\alpha + V_\alpha. \hspace{1cm} (3.2)$$

Let $u^{(k)}_{\alpha c}(r_\alpha)$ denote the single particle eigenstates of $H_{\text{inc}}$. The asymptotic boundary conditions are then specified through the introduction of channel states $\hat{X}_c$, formed by by coupling the spherical harmonics $Y_{l_m c}(\hat{r}_\alpha)$ of $u^{(k)}_{\alpha c}(r_\alpha)$ to the eigenstates of $H_T$. Here it is customary and conventional to couple the spherical harmonic to the spin states of the two partition components, $H_{\text{inc}}$ and $H_T$, to form an angular
momentum eigenstate. Thus, if $\Psi_{ac}$ are eigenstates of $H_T$:

$$(H_T - \epsilon_{ac}) \Psi_{ac} = 0, \quad (3.3)$$

where $c$ is a channel index, then, a channel state is defined by the quantity

$$\hat{X}_c = \Psi_{ac} \times Y_{\ell mc}(\hat{r}_a). \quad (3.4)$$

where $\times$ denotes spin-angular momenta coupling.

Hence, when $r_\alpha$ becomes large, $\Psi_k$ can be expanded in terms of the channel states,

$$\Psi = \sum_c \hat{X}_c u_{ac}^{(k)}(r_\alpha) \quad \text{(large } r_\alpha), \quad (3.5)$$

where the radial functions $u_{ac}^{(k)}(r_\alpha)$ are necessarily solutions to

$$\left\{ -\frac{1}{2m_\alpha} \frac{d}{dr_\alpha} - \frac{\ell_c(\ell_c + 1)}{r_\alpha^2} + V(r_\alpha) - E_{ac} \right\} u_{ac}^{(k)}(r_\alpha) = 0. \quad (3.6)$$

Here,

$$E_{ac} = E - \epsilon_{ac}, \quad (3.7)$$

$$V(r_\alpha) = \frac{Z_a^1 Z_a^2}{r_\alpha}, \quad (3.8)$$

$m_\alpha$ is the reduced mass of the partitions, $H_T$ and $H_{inc}$, and $Z_a^1$ and $Z_a^2$ are their respective electric charges. (Note: In the asymptotic region, $u_{ac}^{(k)}(r_\alpha)$ is assumed to be affected only by the Coulomb interaction $V(r_\alpha)$.)

The form of $u_{ac}^{(k)}(r_\alpha)$, and hence the asymptotic boundary conditions for the scattering wave function $\Psi_k$, now follow from the positive and negative energy solutions of (3.6) (for large $r_\alpha$). For the former case, the solutions consists of the two linearly independent Coulomb wave functions, which are regular ($F_{lc}$) and irregular ($G_{lc}$) at the origin. For the latter, only the regular solution, given by the Whittaker function $W$ has physical meaning.

It follows by taking linear combinations of these solutions, via the incoming ($\zeta^+$) and outgoing ($\zeta^-$) current waves, that $u_{ac}^{(k)}(r_\alpha)$ for large values of $r_\alpha$ must necessarily have the form

$$u_{ac}^{(k)}(r_\alpha) = \zeta_{c}^{(-)}(r_\alpha) \delta_{ck} - \zeta_{c}^{(+)}(r_\alpha) U_{ck}, \quad \text{for large } r_\alpha, \quad (3.9)$$

where, for open channels ($E_{ac} > 0$),

$$\zeta_{c}^{(\pm)}(r_\alpha) = \left( \frac{m_\alpha}{k_c} \right)^{1/2} e^{\mp i \sigma_c} \left[ (G_{lc}(k_c r_\alpha) \pm i F_{lc}(k_c r_\alpha)) r_\alpha^{-1} \right]$$

$$\sim \left( \frac{m_\alpha}{k_c} \right)^{1/2} \frac{i}{r_\alpha} \exp[\pm i (k_c r_\alpha - \eta_c \ln 2k_c r_\alpha - \frac{1}{2} l_c \pi)]. \quad (3.10)$$
while for closed channels \((E_{ac} < 0)\),

\[
\zeta_{c}^{(+)}(r_{a}) = W(-\eta_{c}, l_{c} + \frac{1}{2}; 2k_{c}r_{a}) \\
\sim \frac{1}{r_{a}} \exp(-k_{c}r_{a} - \eta_{c}\ln 2k_{c}r_{a}).
\]  

(3.11)

In Eqs. (3.10) and (3.11), additional channel characterisations have been introduced;

\[
k_{c} = (2m_{a}|E_{ac}|), \quad \text{the channel wave number}; \quad (3.12)
\]

\[
\eta_{c} = Z_{a}^{2}Z_{c}^{2}m_{a}/k_{c}, \quad \text{the coulomb field parameter}; \quad (3.13)
\]

\[
\sigma_{c} = \text{arg}\Gamma(l_{c} + 1 + \eta_{c}), \quad \text{the coulomb phase shift}; \quad (3.14)
\]

and \(U\), the collision or scattering matrix.

It therefore clear from (3.9) that the scattering state \(\Psi_{k}\) has unit flux incident in channel \(k\) and purely outgoing flux in all other channels. It is convenient to denote such a state by \(\Psi_{k}^{+}\). It then follows, with the aid of Eqs. (3.9) and (3.5), that the asymptotic states of the scattered wave function may be written, finally as,

\[
\Psi^{+} = \sum_{c} \hat{X}_{c}\zeta_{c}^{(-)}(r_{a})\delta_{ck} - \zeta_{c}^{(+)}(r_{a})U_{ck}, \quad \text{for large } r_{a}.
\]  

(3.15)

3.1.2 Derivation of the R-Matrix

As in the standard R-Matrix theory, the external and internal regions of configuration space are separated by boundaries defined by the channel radii \(r_{a} = a_{a}\). In the internal region, the continuum radial functions \(u^{(k)}_{ac}(r_{a})\) in (3.5) may be expanded in terms of a complete set of orthonormal functions, say \(f_{\lambda c}(r_{a})\),

\[
u^{(k)}_{ac}(r_{a}) = \sum_{\lambda} a^{(k)}_{\lambda c} f_{\lambda c}(r_{a}), \quad 0 \leq r_{a} \leq a_{a},
\]  

(3.16)

satisfying

\[
\left\{-\frac{1}{2m_{a}r_{a}} \frac{d}{dr_{a}} \frac{d}{dr_{a}} r_{a} - \frac{l_{c}(l_{c} + 1)}{r_{a}^{2}} + V(r_{a}) - \epsilon_{ac}\right\}f_{\lambda c}(r_{a}) = 0,
\]  

(3.17)

with boundary conditions (at \(r_{a} = a_{a}\)) given by

\[
\left(\frac{d}{dr_{a}} r_{a} - B_{c}\right) f_{\lambda c}(r_{a}) = 0, \quad r_{a} = a_{a}.
\]  

(3.18)

Here, \(V(r_{a})\) is given by (3.8), and \(B_{c}\) is a real parameter independent of \(\lambda\). In addition, \(f_{\lambda c}(r_{a})\) is assumed to be normalised according to

\[
\int_{0}^{a_{a}} dr_{a} f_{\lambda c}f_{\lambda'c} = \delta_{\lambda\lambda'}.
\]  

(3.19)
The scattering state wave function (3.5), then has the following form in the internal region,

\[ \Psi_k = \sum_{\lambda c} a_{\lambda c}^{(k)} X_{\lambda c}, \tag{3.20} \]

with the basis states \( X_{\lambda c} \), given by

\[ X_{\lambda c} = f_{\lambda c}(r_\alpha) \hat{X}_c. \tag{3.21} \]

The coefficients \( a_{\lambda c}^{(k)} \) in (3.20) are determined by solving the Schrödinger equation (3.1) with respect to the basis states (3.21). However, since the integrations are carried over the finite interaction region, the matrix elements involving the kinetic energy operators require the addition of a surface operator \( L \) – the Bloch operator (Bloch, 1957) – to enable Green’s theorem to be used when carrying out the required integrations. This reflects the nonhermitian character of the kinetic energy operators when confined to a finite region. The effect of introducing the Bloch operator is then to restore hermiticity to such terms. It also provides, very concisely, the link between the internal and external wave functions, as the Green’s-function relationship which expresses the value of the scattering wave function at any point in the inside region in terms of its value and derivative at the channel surface \( r_\alpha = a_\alpha \).

In the notation of Bloch (1957) (see also Barrett et al, 1983), the Bloch operator has the multi-channel form

\[ L(b_c) = \sum_{\alpha} \sum_{c} |\hat{X}_c \rangle \delta(r_\alpha - a_\alpha) \left( \frac{d}{dr_\alpha} r_\alpha - b_c \right) |\hat{X}_c \rangle, \tag{3.22} \]

where \( |\hat{X}_c \rangle \) are the channel states defined in (3.4) and \( b_c \) are arbitrary channel constants.

The quantity \( | \rangle \) is in accord with the convention introduced by Bloch (1957), and serves to denote functions of all coordinates except \( r_\alpha \). This meaning carries over when performing the integrations with respect to the channel quantities \( |\hat{X}_c \rangle \). For instance, the “projection” of the channel \( \hat{X}_c \) state onto the basis \( X_{\lambda c} \) state is

\[ (X_{\lambda c}|\hat{X}_c \rangle = f_{\lambda c}(r_\alpha) \delta_{c c'}, \tag{3.23} \]

\[ (\hat{X}_{c'}|\hat{X}_c \rangle = \delta_{c c'}. \tag{3.24} \]

where it is implicitly assumed that the channel states \( |\hat{X}_c \rangle \) are orthogonal to one another, so that the first result above serves to denote integration over all coordinates except \( r_\alpha \), which in the formalism of Barrett et al. (1983) is conventionally set equal \( a_\alpha \).

With this understanding, the Bloch operator (3.22) may be added to both sides of the Schrödinger equation (3.1), to yield

\[ [H + L(b_c) - E] \Psi_k = L(b_c) \Psi_k, \tag{3.25} \]
where, after projecting both sides of this equation onto the channel states \( \langle \hat{X}_c | \), the coefficients in Eq. (3.20) are obtained explicitly as

\[
a^{(k)}_{\lambda c} = \frac{a_\alpha}{2m_\alpha} \sum_{\lambda' c'} (G^{-1})_{\lambda c, \lambda' c'} f_{\lambda' c'}(a_\alpha) \left( \frac{d}{da_\alpha} a_\alpha - b_{c'} \right) u^{(k)}_{\alpha c'}(a_\alpha),
\]

(3.26)

where \( G^{-1} \) is the inverse of the matrix \( G \) whose elements for a given total energy \( E \) are

\[
(G)_{\lambda c, \lambda' c'} = \langle X_{\lambda c} | (H + L - E) | X_{\lambda' c'} \rangle.
\]

(3.27)

If (3.26) is now substituted back into (3.16), one arrives at the fundamental \( R \)-matrix relation,

\[
u^{(k)}_{\alpha c}(r_\alpha) = \sum_{c'} R_{cc'}(r_\alpha) \left( \frac{d}{da_\alpha} a_\alpha - b_{c'} \right) u^{(k)}_{\alpha c'}(a_\alpha),
\]

(3.28)

with the \( R \) matrix given by

\[
R_{cc'}(r_\alpha) = \frac{a_\alpha}{2m_\alpha} \sum_{\lambda \lambda'} f_{\lambda c'}(r_\alpha) G^{-1}_{\lambda c, \lambda' c'} f_{\lambda' c'}(a_\alpha).
\]

(3.29)

This relates the internal scattering wave function \( \Psi_k \), (3.20), to its value and derivative at the channel boundary \( r_\alpha = a_\alpha \) via the radial functions \( u^{(k)}_{\alpha c}(r_\alpha) \).

### 3.1.3 The Collision Matrix \( U \)

By matching the internal (Eq. (3.20)) and external (Eq. (3.15)) solutions for \( \Psi_k \equiv \Psi^+_k \) at the boundary \( r_\alpha = a_\alpha \), and projecting onto the channel state \( \langle \hat{X}_c | \), one obtains the set of coupled equations

\[
\zeta_{c'}(a_\alpha) \delta_{c' c} - \zeta_{c'}^+(a_\alpha) U_{c' k} = \sum_c R_{c c'}(a_\alpha) \left( \frac{d}{da_\alpha} a_\alpha - b_{c'} \right) \left[ \zeta_{c'}^-(a_\alpha) \delta_{c k} - \zeta_{c'}^+(a_\alpha) U_{c k} \right].
\]

(3.30)

To extract the collision matrix \( U \) explicitly from these equations, the differentiation on the right hand side of (3.31) must be carried out. Here, the appearance of delta functions makes it convenient to introduce diagonal matrix elements, defined as follows.

For the open channels, let \( L^\pm \) denote the matrix whose elements are

\[
L^\pm_{cc'} = (S_{c'} \pm iP_{c'} - b_{c'}) \delta_{cc'},
\]

(3.31)

where \( S_{c'} \) and \( P_{c'} \) are related to the Coulomb wave functions (given in Eq. (3.10));

\[
S_{c'}(k_{c'} a_\alpha) = \left[ G_{c'}(k_{c'} a_\alpha) \frac{d}{da_\alpha} G_{c'}(k_{c'} a_\alpha) + F_{c'}(k_{c'} a_\alpha) \frac{d}{da_\alpha} F_{c'}(k_{c'} a_\alpha) \right] P_{c'}(k_{c'} a_\alpha) k_{c'}^{-1},
\]

(3.32)

\[
P_{c'}(k_{c'} a_\alpha) = (k_{c'} a_\alpha) \left[ G_{c'}^2(k_{c'} a_\alpha) + F_{c'}^2(k_{c'} a_\alpha) \right]^{-1}.
\]

(3.33)
Similarly, for the closed channels,

\[ L_{cc'}^+ = (S_c - b_c) \delta_{cc'}, \]  

(3.34)

\( S_c \) is related to the Whittaker function \( W \) (given in Eq (3.11));

\[ S_c(k_c a_\alpha) = (k_c a_\alpha) W'(\eta_c, l_c + \frac{1}{2}, 2k_c r) / W'(\eta_c, l_c + \frac{1}{2}, 2k_c r)(k_c a_\alpha). \]  

(3.35)

where the prime denotes differentiation with respect to the argument.

In addition, let \( \zeta^\pm \) denote the matrix whose elements are

\[ \zeta^\pm = \zeta_{cc'}^\pm \delta_{cc'}. \]  

(3.36)

Eqs. (3.31)–(3.36) then correspond to Eqs. (4.5), (4.6), (4.30) and (4.31) of Barrett et al. (1983), where \( S_c \) and \( P_c \) can be identified there as the shift and penetration factors, respectively.

The link between the \( R \) matrix in (3.29) and the collision matrix, can now be established in terms of the matrices introduced above. This is done by substituting

\[ Z^\pm = [1 - RL^\pm] \zeta^\pm, \]  

(3.37)

into the coupled equations (3.31), to obtain the collision matrix \( U \) in the form:

\[ U = (Z^+)^{-1}Z^- . \]  

(3.38)

### 3.1.4 Unitarity of \( U \)

The essence of the \( R \) matrix introduced above, is that it specifies the form of the wave function at the boundary \( r_\alpha = a_\alpha \), whereas the collision matrix \( U \) specifies the form of the latter at infinity (i.e., at large \( r_\alpha \)). The connection between the two is thus the content of Eq. (3.31), and formalises the link between the collision matrix in terms of the \( R \)-matrix. Since the \( R \)-matrix (Eq. 3.29)) is a real and symmetric matrix, this in turn implies that similar properties are also inherent in the collision matrix.

To show this, it is convenient to partition the channels \( c \) in the coupled equations (3.31) into groups of (o) open and (c) closed channels. The collision matrix in the subspace of the open-open channels, i.e., \( U_{oo} \), can then be extracted according to this division of the channels in (3.31), which in the matrix notation introduced above, reads as,

\[ \zeta^-_{oo} L_oo - \zeta^+_{oo} U_{oo} = R_{oo} \left( L^-_{oo} \zeta^-_{oo} - L^+_{oo} \zeta^+_{oo} U_{oo} \right) - R_{oo} \left( L^+_{cc} \zeta^+_{cc} U_{co} \right), \]

(3.39)

\[-\zeta^+_{cc} U_{co} = R_{co} \left( L^-_{oo} \zeta^-_{oo} - L^+_{oo} \zeta^+_{oo} U_{oo} \right) - R_{cc} \left( L^+_{cc} \zeta^+_{cc} U_{co} \right). \]
The second equation in (3.39) immediately gives
\[
(1_{cc} - R_{cc}L_{cc}) \zeta_{cc}^+ U_{cc} = R_{cc} \left( L_{cc}^+ \zeta_{cc}^+ U_{cc} - L_{cc}^- \zeta_{cc}^- \right),
\]
(3.40)
which when substituted back and rearranged into the first equation of (3.39), leads to
\[
\left(1_{oo} - \tilde{R}_{oo} L_{oo}^+ \right) \zeta_{oo}^+ U_{oo} = \left(1_{oo} - \tilde{R}_{oo} L_{oo}^- \right),
\]
(3.41)
where
\[
\tilde{R}_{oo} = R_{oo} + R_{cc} L_{cc}^+ \left(1_{cc} - R_{cc} L_{cc}^+ \right) R_{cc}.
\]
(3.42)
This is analogous to the reduced \( R \)-matrix defined in Eq. (1.4) of Lane and Thomas (1958). It is useful for many practical applications since it retains only those channels that are physically meaningful to the problem. It is also symmetric, since the \( R \) matrix (Eq. (3.29)) is symmetric and \( L^\pm \) and \( \zeta^\pm \) (Eqs. (3.31) and (3.36)) are diagonal matrices. Hence, defining the matrices
\[
W^\pm = \left(1_{oo} - \tilde{R}_{oo} L_{oo}^\pm \right) \zeta_{oo}^\pm,
\]
(3.43)
on par with those defined in (3.37), it follows that the collision matrix in subspace of the open-open channels,
\[
U_{oo} = (W^+)^{-1} W^-,
\]
(3.44)
is a symmetric and unitary matrix, i.e.,
\[
U_{oo}^T = U_{oo}, \quad U_{oo}^+ U_{oo} = 1_{oo}.
\]
(3.45)

3.2 APPLICATION TO LOW-ENERGY ELECTRON-\( H_2 \) SCATTERING

Because the scattering wave function inherits the same fixed boundary conditions (Eq. (3.18)) imposed on the basis states in the internal region, it will in general have a discontinuity of slope at the channel radii \( a_\alpha \). This is a major flaw of the standard \( R \)-matrix theory discussed in the previous section, which is repaired when natural boundary conditions methods or related techniques are employed (for details see Sections. IV and V of Barrett et al., 1983). Another approach within the framework of the standard \( R \)-matrix theory, is to employ the “Buttle correction”, though even this is found to be small in the context of low-energy electron-molecule scattering (cf. Lane, 1980; Burke et al., 1977). In the present context, these technical remarks are put aside, and left as reminder of the options that are open when the need for adequate convergence in the basis set arises. Rather, the only real issue of physical concern here is to provide a suitable criterion for specifying the partition radii of the internal region. For simplicity, it will be assumed from now on that all the channel radii have the same value, i.e., \( a_\alpha = a \).
In the context of electron-molecule scattering, a rough qualitative guide is to choose the partition radius for the internal region just large enough to envelope the charge distribution of the target states of interest. In this way, the short range correlation and exchange effects can be confined to the internal region where they are likely to be of most importance. However, in contrast to the standard $R$-matrix theory, as discussed and applied by Lane and Thomas (1958) in the context of nuclear physics, the interactions between the scattered electron and the molecule still persist outside the finite size of the internal region. Such long range interactions are crucial to the behaviour of the cross section at low energy, and consequently, must be taken into account.

The purpose of the present section is to make the conditions for defining the radius of the internal region more precise and to extend the $R$-matrix formalism of the previous section in two ways. The first way, is to define antisymmetrised channel basis functions for the explicit treatment of exchange effects in the internal region, and the second, is to divide configuration space further into an intermediate region, for the treatment of the long range electron-molecule interactions.

This approach to the e-H$_2$ scattering problem, is in analogy with that of Burke and others (see e.g., the review by Burke and Berrington, 1993) applied in the context of atomic and molecular processes. It prepares the ground for a similar technique involving the propagation of $R$-matrix in the intermediate region, which in turn is based on the solution of a set of coupled equations. Thus the main content of the discussion below is the characterisation of the equations needed to demonstrate the suitability of the present standard $R$-matrix formalism approach to the scattering problem. The channels and related quantities, which were left arbitrary in the previous section, are therefore made more explicit in relation to antisymmetrisation, and then applied to verify fundamental $R$-matrix relationship in Eq. (3.28). The relationship between the observable cross sections and the collision $U$-matrix elements is also derived.

### 3.2.1 The Schrödinger Equation and Channel Wave Functions

The hamiltonian of the e-H$_2$ system is described in the centre of mass of the nuclei (CMN) coordinate frame (see Chapter 2), whereby the electronic position coordinates are referred relative to the midpoint of the internuclear axis with the relative position vector of the two protons of the hydrogen molecule denoted by $R$.

In accordance with the basic definitions given in Section 3.1.1, the e-H$_2$ scattering state $\Psi_k$ is governed by the Schrödinger equation,

$$ (H - E)\Psi_k = 0, $$

with the hamiltonian of the system being composed of the target hamiltonian $H_T$ for the hydrogen molecule, the single particle hamiltonian $H_{inc}$ for the scattering
electron, and the residual interaction $V$, which read as follows:

$$
H = H_{\text{inc}} + H_T + V,
$$

(3.47)

$$
H_{\text{inc}} = -\frac{1}{2}\nabla^2_{\tilde{r}_0},
$$

(3.48)

$$
H_T = -\frac{1}{2\mu}\nabla^2_R + -\frac{1}{2}\left(\nabla^2_{r_1} + \nabla^2_{r_2}\right) + V_T,
$$

(3.49)

$$
V_T = \frac{1}{|r_1 - r_2|} + \frac{1}{|r_1 - \frac{1}{2}R|} + \frac{1}{|r_2 - \frac{1}{2}R|} + \frac{1}{R},
$$

(3.50)

$$
V = \frac{1}{|r_0 - \frac{1}{2}R|} + \frac{1}{|r_0 - \frac{1}{2}R|} + \sum_{i=1}^{2} \frac{1}{|r_i - |r_0 - r_i|}.
$$

(3.51)

Here $\mu$ is the reduced mass of the two protons and the cross terms between the electronic momentum operators, i.e., $-(1/8\mu)(\nabla_{r_0} + \nabla_{r_0} + \nabla_{r_0})^2$, has been neglected in the course of separating the center-of-mass motion of the system.

As in Eq. (3.4), the channel states are formed by vector coupling the spin and spherical harmonic $Y_{lm}(\hat{r}_0)$ components of the scattered electron’s continuum wave function $u(r_0)$ to those of the target states, to form an angular momentum eigenstate, viz:

$$
\chi_c(R; r_0, r_1, r_2) = \sum_{mm_s, m_l, M_K} \left(\frac{1}{2} m_s, l m_l | m_m\right) \left(K M_K, j m_j | I M_I\right) \chi_m^{(0)}(\hat{r}_0) Y_{lm}(\hat{r}_0) \Psi_\beta(R; r_1, r_2).
$$

(3.52)

Here, the Clebsch-Gordan coefficients $(Aa, Bb|Cc)$ and the spherical harmonics $Y_{lm}(\hat{r}_0)$ are in the convention of Rose (1965), $\chi_m^{(0)}$ is the spin function of the scattered electron, and $c$ is the channel index, specified by

$$
c = (\alpha \nu K; l j; I M_I)
$$

(3.53)

where $(\alpha \nu K)$ denote respectively the electronic, vibrational and rotational quantum numbers of the hydrogen molecule, $M_K$ is the rotational projection quantum number, $l$ and $j (= l \pm \frac{1}{2})$ are the orbital and total angular momentum of the scattering electron, and $I$ and $M_I$, the total angular momentum quantum numbers of the electron-molecule system.

In Eq.(3.52), and in what follows, the molecular states $\Psi_\beta$ will be assumed to be diagonal with respect to the hamiltonian $H_T$ in (3.49);

$$
\langle \Psi_\beta | H_T | \Psi_\beta \rangle = E_{\alpha \nu K} \delta_{\beta \beta}.
$$

(3.54)

subject to the normalisation or orthogonality condition given by

$$
\int \int \int dRdr_1dr_2 \Psi_\beta^* (R; r_1, r_2) \Psi_\beta (R; r_1, r_2) = \delta_{\beta \beta},
$$

(3.55)

where $\beta$ is a shorthand for the labels $\beta = (\alpha \nu KM_K)$, and $E_{\alpha \nu K}$ are the corresponding molecular energies.
3.2.2 The Internal Region

Since all the distances are measured from the midpoint of the line joining the two protons, the channel radius \( a \) of the internal region is chosen so that

\[
|\Psi_\beta(R; r_1, r_2)| \approx 0, \quad |\nabla_R \Psi_\beta(R; r_1, r_2)| \approx 0, \quad |\nabla_{r_i} \Psi_\beta(R; r_1, r_2)| \approx 0. \tag{3.56}
\]

whenever any of the distances \((\frac{1}{2}R, r_1, r_2)\) is equal to \( a \). This condition ensures that the effects of antisymmetrisation and molecular structure are confined to the internal region. It also ensures that the relations (3.54) and (3.55) are effectively true when the integrations over the molecular states are restricted to the finite interval \([0, a]\).

The antisymmetrised form of the scattering wave function in the internal region is given by

\[
\Psi_k(R; r_0, r_1, r_2) = \mathcal{A} \sum_{c} u_c^{(k)}(r_0) X_c(\hat{r}_0, r_1, r_2)
\]

where \( \mathcal{A} \) antisymmetrises the scattered electron coordinate \( r_0 \) with the molecular electronic coordinates in the channel states \( X_c \).

The second line in (3.57) makes use of (3.16), to expand the continuum radial wave function \( u_c^{(k)}(r) \) in terms of a complete orthonormal set of basis functions \( f_{\lambda i}(r_0) \) for \( 0 \leq r \leq a \) which are determined by the differential equation given by (3.17), subject to the boundary conditions given in (3.18) at \( r = a \). They are orthogonal in the sense of the normalisation condition given in (3.19), where \( l \) now specifies the channel index \( c \) given there. Note, also that the Coulomb potential in (3.17) vanishes on account of the overall charge neutrality of the hydrogen molecule, so that the basis functions \( f_{\lambda i}(r_0) \) correspond to those of a free particle Schrödinger equation.

The antisymmetrised form of channel basis set in (3.57), now follow as

\[
X_{\lambda c}(R; r_0, r_1, r_2) = \frac{1}{\sqrt{3}} \left\{ f_{\lambda i}(r_0) \hat{X}_c(R; \hat{r}_0, r_1, r_2) + f_{\lambda i}(r_1) \hat{X}_c(R; \hat{r}_1, r_0, r_2) + f_{\lambda i}(r_2) \hat{X}_c(R; \hat{r}_2, r_1, r_0) \right\}. \tag{3.58}
\]

It is also expedient to define antisymmetrised channel states as

\[
|\hat{X}_c\rangle = \mathcal{A} \hat{X}_c(R; \hat{r}_0, r_1, r_2) \tag{3.59}
\]

where the notation \( |\rangle \) follows the convention of Bloch adopted in (3.22).

As stated in Section (3.1.2), this notation serves to denote all coordinates except the radial coordinate of the scattered electron. To carry this meaning over, with
respect to the antisymmetrised states (3.58) and (3.59), it only remains to permute the electronic distances \( r_i (i = 0, 1, 2) \) accordingly. The same is true when applying the channel projections, as in Eqs. (3.24), where it is understood here that the radial coordinate not integrated over there is not only set equal to the channel radius \( a \), but this is to be now permuted accordingly over all of the electronic coordinates. The example below serves to illustrate this point.

Thus, following Barrett and Robson (1979),

\[
\langle \hat{X}_c | X_{\lambda c} \rangle = \frac{1}{\sqrt{3}} \left\{ \int d\hat{r}_0 d\hat{r}_1 d\hat{r}_2 dR \hat{X}_c(R; \hat{r}_0, \hat{r}_1, \hat{r}_2) X_{\lambda c}(R; r_0 = a, r_1, r_2) \\
+ \int d\hat{r}_1 d\hat{r}_0 d\hat{r}_2 dR \hat{X}_c(R; \hat{r}_1, \hat{r}_0, \hat{r}_2) X_{\lambda c}(R; r_0, r_1 = a, r_2) \\
+ \int d\hat{r}_2 d\hat{r}_0 d\hat{r}_1 dR \hat{X}_c(R; \hat{r}_2, \hat{r}_1, \hat{r}_0) X_{\lambda c}(R; r_0, r_1, r_2 = a) \right\}
\]

(3.60)

Here, \( r_i = a (i = 0, 1, 2) \) means that the electronic radial coordinates \( r_i \) not integrated over have been set to the value \( a \). By virtue of the conditions (3.56), one then obtains the result

\[
\langle \hat{X}_c | X_{\lambda c} \rangle = \sqrt{3} \int d\hat{r}_1 d\hat{r}_0 d\hat{r}_2 dR \hat{X}_c(R; \hat{r}_0, \hat{r}_1, \hat{r}_2) X_{\lambda c}(R; r_0 = a, r_1, r_2) = f_{\lambda}(a) \delta_{\lambda c}.
\]

(3.61)

which is in agreement with the first of Eq. (3.24).

Similarly, it can be shown that

\[
\langle \hat{X}_c | \hat{X}_c \rangle = \delta_{\lambda c},
\]

(3.62)

provided of course that conditions (3.56) hold.

The Bloch operator defined previously in (3.22) can also be expressed in terms of the antisymmetrised channel states \( |\hat{X}_c \rangle \) (Eq. (3.59)),

\[
L(b) = \sum_c |\hat{X}_c \rangle L(b_c)(\hat{X}_c|
\]

(3.63)

where \( b \) denotes the set of \( b_c \) and

\[
L(b_c) = \frac{1}{2} \sum_{i=0}^{2} \delta(r_i - a) \left[ \frac{d}{dr_i} r_i - \frac{b_c}{a} \right].
\]

(3.64)

is the sum of one-body Bloch operators. Here the omission of any reference to the proton distance \( R \), makes explicit the fact that no dissociation of the molecule is allowed for within the present approach, which is consistent with the remarks below (3.56).

As stated (Section. 3.1.2), the role of the Bloch operator, is to provide a link between the scattering radial wave function \( u_c^{(k)}(r_0) \) in the internal region to those in
the external region, by effectively selecting the first derivative of the wave functions \(u^{(k)}(r_0)\) at the radius \(r_0 = a\). Since this result depends on the relations contained in (3.24) involving the projection onto the channel states \(\hat{X}_c\), which were also verified above with respect to antisymmetrisation, it follows that upon adding the Bloch operator \(L(b)\) (Eq. (3.64)) to both sides of the Schrödinger equation (3.46) for the \(e\)-H\(_2\) system and projecting onto the antisymmetrised channel states (3.59), one obtains the desired \(R\)-matrix relationship in (3.28), as the \(R\)-matrix in Eq. (3.29) that relates the scattering radial wave function \(u^{(k)}(r_0)\) to its value and derivative at the radius \(a\) of the internal region; which is thus needed to link up with those characterised below in the intermediate region.

3.2.3 The Intermediate Region

In this region, \(r_0 > a\) and since only the bound states of the hydrogen molecule are considered, \((\frac{1}{2}R, r_1, r_2) \leq a\), so that the distances of the protons and the resident electrons of the molecule are effectively confined to the internal region. Consequently, the effects of antisymmetrisation can be neglected and the \(e\)-H\(_2\) scattering wave function then taken in the form

\[
\Psi_k(R; r_0, r_1, r_2) = \sum_c u_c^{(k)}(r_0) \hat{X}_c(R; r_1, r_2),
\]

(3.65)

where \(\hat{X}_c\) are the channel states defined in Eq. (3.52).

Since the target states \(\Psi_\beta\) diagonalise \(H_T\) (given by Eq. (3.54)), i.e., \(\langle \Psi_\beta | H_T | \Psi_\beta \rangle = E_\alpha \delta_{\alpha \beta}\), and are orthogonal (Eq. (3.55)), it can be verified that the channel projections over the target molecular hamiltonian also satisfy

\[
(\hat{X}_c | H_T | \hat{X}_c) = E_\beta \delta_{\alpha \beta}.
\]

(3.66)

Thus, projecting out the channel dependence in the Schrödinger equation (3.46) for \(r_0 \geq a\),

\[
(\hat{X}_c | (-\frac{1}{2} \nabla^2 + H_T + V - E) | \Psi_k) = 0,
\]

(3.67)

leads to a set of coupled equations for \(u_c^{(k)}(r_0)\):

\[
\left\{ \frac{1}{r_0^2} \frac{d^2}{dr_0^2} r_0^2 - \frac{l(l' + 1)}{r_0^2} + 2(E - E_\nu) \right\} u_c^{(k)}(r_0) = 2 \sum_c V_{cc'}(r_0) u_c^{(k)}(r_0).
\]

(3.68)

Here, \(E_\nu\) are the molecular energies, with \(\nu = (\alpha \nu K)\) an abbreviation for the electronic, vibrational and rotational quantum numbers, and \(V_{cc'}(r_0)\) are the matrix elements of the direct or residual potential \(V\), given by

\[
V_{cc'}(r_0) = (\hat{X}_{c'} | \sum_{i=1}^2 |r_0 - r_i|^{-1} |\hat{X}_c) + (\hat{X}_{c'} | (|r_0 - \frac{1}{2} R|^{-1} + |r_0 - \frac{1}{2} R|^{-1}) |\hat{X}_c.
\]

(3.69)

where the integrations, as mentioned previously, are carried out over all coordinates except the radial coordinate \(r_0\) for the scattered electron.
Because of the relationship between the distances in this region, the interactions in (3.69) have the form
\[
\frac{1}{|r_0 - r_i|} = 4\pi \sum_L \frac{r_i^L}{r_0^{L+1}} \sum_M Y_{LM}^*(\hat{r}_0)Y_{LM}(\hat{r}_i),
\]
which allows Eq (3.69) to be written as a multipole series,
\[
V_{c'c}(r_0) = \sum_L \left( \frac{V_{ee}^L}{r_0^{L+1}} \right)_{c'tc} + \sum_L \left( \frac{V_{ep}^L}{r_0^{L+1}} \right)_{c'tc}.
\]
where
\[
(V_{ee}^L)_{c'tc} = (8\pi/\hat{L}^2) \int d\hat{r}_0 \sum_M Y_{LM}^*(\hat{r}_0) \left[ \int dR dr_1 dr_2 \hat{X}_{c'} \left( r_1^L Y_{LM}(\hat{r}_1) \right) \hat{X}_c \right],
\]
\[
(V_{ep}^L)_{c'tc} = -\left(8\pi/\hat{L}^2\right) \int d\hat{r}_0 \sum_M Y_{LM}^*(\hat{r}_0) \left[ \int dR dr_1 dr_2 \hat{X}_{c'} \left( R^L Y_{LM}(\hat{r}_1) \right) \hat{X}_c \right].
\]

These equations, as will be shown and discussed further in the next section, are related to various static moments of the hydrogen molecule and play a crucial role in determining the behaviour of the cross sections near-threshold. In practice, the number of channels \(c\) in the coupled equations (3.68) are truncated, so that the multipole sums over \(L\) in (3.72) and (3.73), are restricted accordingly through the recoupling of angular momenta coefficients, i.e., Racah algebra.

The asymptotic form of the solutions \(u_c^{(k)}(r_0)\) to the coupled equations Eq. (3.68) determine the collision matrix. This form of \(u_c^{(k)}(r_0)\) was discussed in Section 3.1.1. There the requirement in (3.9) is such that for large values of \(r_0\), \(u_c^{(k)}(r_0)\) be constrained in terms of the incoming \(\zeta_c^{-}(r)\) and outgoing \(\zeta_c^{(+)}(r)\) current waves. As given in Eqs. (3.10) and (3.11), the form of these current waves correspond to the Coulomb wave solutions of Eq.(3.6). However, because \(H_2\) is a neutral molecule, the latter solutions can be further simplified to those of a free particle: the electron.

The appropriate identification follows after noting that with the exception of the channel wave number \(k_c\), the remaining channel characterisations in Eqs. (3.12)–(3.14), for the coulomb field parameter and its phase shift, are identically zero. The positive energy \((E_c > 0)\) solutions to (3.6), i.e., the regular \((F_{ic})\) and irregular \((G_{ic})\) Coulomb wave functions, then reduce to those of the spherical-type Bessel functions (e.g., see Eqs. (2.15a) and (2.15b), Lane and Thomas, 1960). The \(\zeta_c^{(+)}(r)\) and \(\zeta_c^{(-)}(r)\) current waves are thus related to the Hankel functions:
\[
\zeta_c^{(-)}(r) = (\pi k_c r/2)^{1/2} H_{i+\frac{1}{2}}^{(2)}(k_c r),
\]
\[
\zeta_c^{(+)}(r) = (\pi k_c r/2)^{1/2} H_{i+\frac{1}{2}}^{(1)}(k_c r),
\]
as defined, for example in Appendix B of Messiah (1961). Similarly, the negative energy \((E_c < 0)\) solutions to (3.6), given by the Whittaker function \(W\) in (3.11), reduce, in the absence of a Coulomb field, to those of the modified Bessel functions of the second kind:

\[
\zeta^{(+)}(r) = (2k_r r / \pi)^{1/2} K_{1+\frac{1}{2}}(k_r r).
\]  

Subject to these modifications, the collision matrix \(U_{kc}\) is determined by integrating the solutions \(u_c^{(k)}(r_0)\) of Eq. (3.68) numerically outwards to a distance \(b\), such that they satisfy the asymptotic boundary conditions,

\[
u_c^{(k)} \sim (1/k_c)^{1/2} \frac{i}{r} [e^{-ik_c r} \delta_{kc} - e^{ik_c r} U_{kc}] \quad (E_c > 0),
\]

\[
u_c^{(k)} \sim -(1/k_c)^{1/2} \frac{1}{r} [e^{-ik_c r} U_{kc}] \quad (E_c < 0),
\]

where \(E_c = \frac{1}{2} k_c^2\) are the channel energies.

As will be shown below, once the collision matrix \(U\) is obtained, the various reaction cross sections can be calculated straightforwardly from the matrix elements of \(U\).

### 3.2.4 Derivation of the Cross Sections

Since the total angular quantum numbers \(I\) and \(M_I\) of the e-H\(_2\) scattering system are conserved in the collision process, and the collision matrix will be independent of \(M_I\), the matrix elements that are required may be labelled by the initial and final channel labels \(i\) and \(f\) (see Eq. (3.53),

\[
i = (\alpha_0 \nu_0 K_0; l_0 j_0; I), \quad f = (\alpha \nu K; l_0 j_0; I).
\]

Furthermore, the scattering is described in a frame fixed in space, with the initial momentum of the scattered electron chosen to be coincident with the space-fixed \(O_z\) axis, so that its initial and final momentum will be denoted by \(k_i\) and \(k_f\), respectively. The final channel energies are then given by

\[
\frac{1}{2} k_f^2 = \frac{1}{2} k_i^2 - \epsilon_{\nu, \nu_0}
\]

where \(E_{\nu}\) are the molecular energies in the notation used in (3.68) and \(\epsilon_{\nu, \nu_0} = E_{\nu} - E_{\nu_0}\), the corresponding energy level spacings.

In analogy with Eq.(3.15), the scattered part of the e-H\(_2\) wave function in the external region \((r_0 \geq b)\) can be taken in the form

\[
\Psi_+^e(R; r_0, r_1, r_2) = \sum \hat{X}_c(R; \hat{r}_0, r_1, r_2) [\zeta^{(-)}(r_0) \delta_{ck} - \zeta^{(+)}(r_0) U_{ck}] - \sum \hat{X}_c(R; \hat{r}_0, r_1, r_2) \zeta^{(+)}(r_0) U_{ck}.
\]
where, in the notation of Barret et al. (1983), $c$ and $\bar{c}$ denotes respectively the split between open and closed channel subspaces.

The asymptotic part of the scattered wave function (3.81), for a given projection $m_s$ of the spin of the outgoing electron and a final molecular state $\beta = (\alpha \nu KM_K)$, may be written as

$$\Psi_f^+(R; r_0, r_1, r_2) r_0 \sim \frac{e^{i k_f r_0}}{r_0} \chi(0) m_s \tilde{f}_\nu M_K m_s, \nu_0 M_K \nu_0 m_0 (k_0, k_f) \Psi_\beta (R; r_1, r_2).$$

(3.82)

where it can be shown from Eqs. (3.81), (3.78), and (3.52), (e.g., see Chapter 2 of Smith, 1971) that the scattering amplitude is

$$\tilde{f}_\nu M_K m_s, \nu_0 M_K \nu_0 m_0 (k_i, k_f) =$$

$$\sqrt{\pi} (k_v k_0)^{-1/2} \sum_{l_0 l_a l_j} i^{l_0 - l_a - 1} C(1, m_{s_0}, l_0 | j_0 m_{s_0}) C(1, m_s, l \mu | (\mu + m_s))$$

$$\times C(KM_K, j(\mu + m_s) | I(M_K \nu + m_s)) Y_{l_\mu} (r_0) (U_{f_i} - \delta_{f_i}).$$

$$\mu = M_K \nu + m_s - M_K - m_s$$

(3.83)

Here, $\delta_{f_i}$ is shorthand for $\delta_{\alpha \alpha_0} \delta_{\nu \nu_0} \delta_{K K_0} \delta_{l_0 l_j} \delta_{j_0 j_0}$ and $U_{f_i}$ is the the collision matrix elements.

The differential cross sections for the transition $\nu_0 = (\alpha \nu_0 K) \rightarrow \nu = (\alpha \nu K)$, averaged over initial and summed over final magnetic substates, $M_K, m_s$ and $m_s$, is

$$\left( \frac{d \sigma}{d \Omega} \right)_{\nu_0, \nu} = \left( \frac{k_f}{k_i} \right) \frac{1}{2(2K + 1)} \sum_{M_K m_s, M_K \nu_0 m_0} \left| \tilde{f}_\nu M_K m_s, \nu_0 M_K \nu_0 m_0 (k_i, k_f) \right|^2$$

(3.84)

The summations in (3.84) permit considerable simplification of the final expressions (cf. Chapter 2, Smith, 1971). The integral cross sections for an inelastic transition, when the integration over the angle and the magnetic sums are performed, is then

$$\sigma_{\nu_0, \nu} = \frac{\pi k_i^2}{2(2K + 1)} \sum_{l_0 j_0} (2I + 1) \left| U(\nu l j, \nu_0 l_0 j_0; I) \right|^2,$$

(3.85)

while for elastic scattering, the cross section is

$$\sigma_{\nu_0, \nu} = \frac{\pi k_i^2}{2(2K + 1)} \sum_{l_0 j_0} (2I + 1) \left| 1 - U(\nu l j, \nu_0 l_0 j_0; I) \right|^2,$$

(3.86)

where for clarity all quantum numbers needed to define the elements of the collision matrix $U$ are shown.

### 3.3 METHOD OF CALCULATION

In the previous section, the framework for the application of the $R$-matrix formalism (Section. 3.1) to low-energy $e$-$\text{H}_2$ scattering relies on the assumption that the
molecular states $\Psi_\beta$ used in the expansion (3.57) for the scattering wave function $\Psi_k$ diagonalise the hamiltonian $H_T$ (Eq. (3.49)). Since $H_T$ includes the motion of the two protons as well as that of the two electrons of the hydrogen molecule, it is clear that the present implementation of $R$-matrix theory does not import assumptions from previous structure theories that have their basis built around the framework of the Born-Oppenheimer approximation, i.e., the fixed- or adiabatic-nuclei approximation.

The structure theory and formulation of molecular wave functions that diagonalise $H_T$ have already been dealt with in Chapter 2, where they were formulated and generated in a body-fixed frame rotating with the molecule. However, since the scattering problem is described in the spaced-fixed (laboratory) frame, the body-frame wave functions of the $H_2$ molecule must be transformed back to the space-fixed lab-frame.

Hence, in this section, the form of the molecular wave functions in the space-fixed frame is given, and applied to define the matrix elements of $G$ (Eq. (3.27)), the inverse of which is needed to obtain the $R$ matrix at the boundary of the internal region. Since the long-range electron-molecule interactions play a crucial role in determining the behaviour of the cross sections near-threshold, the leading terms in the potential matrix $V_{cc}(r_0)$ (Eq. (3.71)) are examined, and shown to be related to various static moments of the $H_2$ molecule. Further, as such terms are expected to dominate the interactions when propagating the $R$-matrix in the intermediate region, the basic scheme for the propagation technique is briefly described, and in particular, illustrated by setting up the solutions to the coupled equations (3.68) as an initial-boundary value problem. This is then applied to derive the connection between the $R$-matrices at the internal and external boundaries. The last result of the present section follows from this connection and related connections made in earlier sections, to state the final link between the $R$ matrix and the observable cross sections derived in Section 3.2.4.

### 3.3.1 The Molecular States

Following the work in Chapter 2, the molecular wave functions in the rotating reference system $O_{xyz}$, are given by Eq. (2.31), as

$$\Psi^\pi_{\alpha vKM}(R; r_1, r_2) = N_\alpha \left( K / \sqrt{4\pi} \right) \left\{ d^K_{M_K\Lambda_\alpha}(\theta) u_{\alpha vK}(R; r_1, r_2) + \pi(-1)^K d^K_{M_K,-\Lambda_\alpha}(\theta) u_{\alpha vK}(R; P r_1, P r_2) \right\}. \quad (3.87)$$

where the notation is that used in Sections 2.2 and 2.3, so that $N_\alpha$ is the normalisation constant (2.36); $P$ is the parity operator (2.29) whose eigenvalue is given by the parity label $\pi$; $\Lambda_\alpha$ is the component of the electronic $L_e$ angular momentum along the body-fixed $z$-axis which labels the electronic states indexed by the label $\alpha$; and
\( v \) and \( K \) are respectively the vibrational and rotational quantum numbers.

The eigenfunctions \( u \) in (3.87) describe the internal motions of the \( \text{H}_2 \) molecule and are symmetric in the electronic coordinates. As described in Section 2.3, they are constructed in terms of a linear combination of vibrational \( \chi_n \) and two-electron \( \psi \) basis functions:

\[
u_{avK}(R; r_1, r_2) = \sum_{nn_{LE}} C_{nn_{LE}}^{avK} (\chi_n(R)/R) \psi_{\alpha_{LE}\Lambda_\alpha}^{a}(r_1, r_2).	ag{3.88}\]

The coefficients \( C \) in (3.88), and hence the eigenfunctions \( u \), were determined by diagonalising the equations of motion of \( u \) (given by Eq. (2.24)) in this basis. In particular, the basis used comprised of the one-dimensional harmonic oscillator functions (Eq. (2.46)) for the vibrational basis \( \chi_n \), and the three-dimensional harmonic oscillator (associated Laguerre) functions \( R_{nl} \) (Eq. (2.40)) for the two-electron basis set \( \psi \).

The molecular wave functions \( \Psi' \) in the laboratory spaced-fixed frame can be obtained from the body-frame wave functions \( \Psi \),

\[
\Psi'(R; r_1', r_2') = \Psi(R; r_1, r_2),	ag{3.89}\]

by using Eq. (2.5) in Section 2.2.1 to recall that the electronic body-fixed coordinates (unprimed) are related to the electronic spaced-fixed coordinates (primed) by the rotation matrix \( D \) (Eq. (2.4)). Thus, using the transformation property,

\[
\Psi_{\alpha\Lambda_\alpha}^{a}(D r_1', D r_2') = \sum_{M_e} D_{M_e\Lambda_\alpha}^{LM_\alpha} (\phi, \theta, 0) \Psi_{\alpha\Lambda_\alpha}^{a}(r_1', r_2')	ag{3.90}\]

in (3.88) and (3.87), one obtains the result

\[
\Psi_{avKM_K}(R; r_1', r_2') = N_{\alpha}(1/\hat{\mathcal{K}}) \sum_{LM_\alpha M_{L\alpha} M_e} \hat{L}_{P} \left(1 + (-1)^{(S_e+L_p)}\right) (L_e\Lambda_\alpha, L_P 0|K\Lambda_\alpha)(L_e M_e, L_P M_P|K M_K) \times \frac{1}{2} \left[ \chi_{1/2}^{(1)} \chi_{-1/2}^{(2)} - \chi_{-1/2}^{(1)} \chi_{1/2}^{(2)} \right] \sum_{nn_{LE}} C_{nn_{LE}}^{avK} (\chi_n(R)/R) Y_{LM_{P}}^{M_{P}}(\theta, \phi) \psi_{\alpha_{LE}\Lambda_\alpha}^{a}(r_1', r_2')(i = 1, 2) \tag{3.91}\]

where the spin functions \( \chi_{\pm 1/2}^{(i)}(i = 1, 2) \) are now explicitly introduced.

The additional labels in (3.91) arise from the fact that the total rotational angular momentum \( K \) in the spaced-fixed frame consists of a sum of the electronic \( L_e \) and proton \( L_P \) angular momenta, so that \( M_e \) is the projection of the total electronic angular momentum in the direction \( O_{z'} \).

Further, since only the singlet electronic states of \( \text{H}_2 \) are considered, and the wave functions (3.91), which consist of the total spin \( S_p \) of the two protons, changes sign under the interchange of the two protons, it is evident that \( L_P \) in (3.91) is even for para-hydrogen (\( S_P = 0 \)) and odd for ortho-hydrogen (\( S_P = 0 \)). For the purposes of the scattering calculations carried out in this chapter and in Chapter 4, the molecular wave functions that will be used will be those defined in Eq. (3.91).
3.3.2 The Basis States and Matrix Elements

At the radius $a$ of the internal region, the calculation of the $R$ matrix in (3.29) at a given energy $E$, relies on the inversion of the matrix $G$ whose elements are defined by

$$G_{\lambda\varepsilon',\lambda\varepsilon} = \langle \hat{X}_{\lambda\varepsilon'} | (H + L - E) | \hat{X}_{\lambda\varepsilon} \rangle,$$

where $H$ is the hamiltonian (3.47) of the e-H$_2$ system, $L$ is the Bloch operator (3.64), and $\hat{X}_{\lambda\varepsilon}$ are the antisymmetrised channel basis states $\hat{X}_{\lambda\varepsilon}$ defined in (3.58). Here, and in what follows, in the inner product $\langle | \rangle$ between the channel basis states the integrations are over the finite region $0 < \rho_0, r_1, r_2 < a$.

By definition, the channel basis states are formed by coupling the wave functions of the scattered electron to those of the hydrogen molecule described above. In particular, the radial wave functions $u^{(k)}_{\varepsilon}(\rho_0)$ (Eq. (3.16)) of the scattered electron in the internal region are expanded in terms of a complete orthonormal set of basis functions $f_{\lambda i}(r)$, which, as mentioned in Section 3.2.2, correspond to those of a free particle Schrödinger equation. The basis functions $f_{\lambda i}(r)$ are thus (up to a normalisation constant $A_{\lambda i}$) spherical Bessel functions of argument $l$:

$$f_{\lambda i}(r) = A_{\lambda i} j_l(k_{\lambda i} r),$$

with eigenvalues $\epsilon_{\lambda i} = \frac{1}{2} k_{\lambda i}^2$, determined by the boundary condition (3.18) at $r = a$.

The boundary condition,

$$\left( \frac{d}{dr} - \frac{B}{r} \right) f_{\lambda i}(r) = 0 \quad \text{at} \quad r = a,$$

is specified in the present case through a single dimensionless real-valued parameter $B$, which is independent of $\lambda$ and in principle can be chosen arbitrarily to optimise the convergence of the expansion of $u^{(k)}_{\varepsilon}(\rho_0)$ (Eq. (3.16)) in the internal region.

The formulation of the matrix elements in (3.92) is a large task, and it is useful to take advantage of symmetry and related properties associated with the problem. The reduction in the workload that can be achieved by this is worthwhile.

For instance, since $\hat{X}_{\lambda\varepsilon}$ is symmetric with respect to the interchange of any two electrons and the hamiltonian $H$ of the e-H$_2$ system is symmetric in the coordinates of the three electrons, the matrix elements (3.92) may be written as a sum of contributions involving a direct term and an exchange term. Thus, on writing the channel basis states as

$$\hat{X}_{\lambda\varepsilon} = \frac{1}{\sqrt{3}} [0(12) + 1(02) + 2(10)]_{\lambda\varepsilon},$$

where $[i(jk)](i, j, k = 0, 1, 2)$ are obvious labels for the electronic coordinates, it is not hard to show that the matrix elements of $G$ in Eq. (3.92) may be evaluated as
a sum of two terms,

\[ G_{\lambda'\lambda, \lambda c} = \langle (0)(12) | (H + L - E) | (0)(12) \rangle_{\lambda c} + 2 \langle [1(02)] (H + L - E) | (0)(12) \rangle_{\lambda c}; \]  

(3.96)

the first of which represents the direct contribution, while the second is the exchange contribution.

It is clear from (3.96) that since the energy \( E \) is constant, there will be an inner product between the channel basis. The states \( \hat{X}_{\lambda c} \) are not orthogonal. They have an hermitian overlap matrix \( O \) whose elements, in the notation of (3.96), are

\[ O_{\lambda'\lambda, \lambda c} = \langle \hat{X}_{\lambda'\lambda} | \hat{X}_{\lambda c} \rangle = \delta_{\lambda \lambda} \delta_{\lambda' \lambda c} + 2 \langle [1(02)] | (0)(12) \rangle_{\lambda c}. \]  

(3.97)

If one now makes use of the fact the molecular states diagonalise the \( H_T \) (see Eq. (3.54)) component of the total hamiltonian \( H \), and that the basis functions \( f_i(r) \), as remarked above, are eigenfunctions of a free particle Schrödinger equation with eigenvalues \( \epsilon_i \), then it can be shown that the direct contribution to (3.96) will have a form

\[ \langle (0)(12) | (H + L) | (0)(12) \rangle_{\lambda'\lambda, \lambda c} = (E_v + \epsilon_i) \delta_{\lambda' \lambda} \delta_{\lambda' \lambda c} + L_{\lambda'\lambda, \lambda c} + \left( V_{ee}^{(1)} \right)_{\lambda'\lambda, \lambda c} + \left( V_{ee}^{(1)} \right)_{\lambda'\lambda, \lambda c}. \]  

(3.98)

where, for convenience, the energy constant \( E \) has been omitted. Here, the matrix elements for last two terms arise form the residual interactions between the scattered electron and the \( \text{H}_2 \) molecule (given by \( V \) in Eq. (3.51)), which will be defined later below.

\( L_{\lambda'\lambda, \lambda c} \) in (3.98), are the matrix elements of the Bloch operator (3.64). For convenience, and as in the other applications of \( R \)-matrix theory; for example, Burke et al. (1977), the zero derivative condition at the radius \( a \) is applied, so that all channel constants \( b_c \) for the Bloch operator are taken to be zero. Thus, from the condition in (3.56), the matrix elements \( L_{\lambda'\lambda, \lambda c} \) are essentially given by the first derivative of the basis functions \( f_{\lambda}(r) \):

\[ L_{\lambda'\lambda, \lambda c} = \frac{1}{2} a B f_{\lambda'}(a) f_{\lambda}(a) \delta_{\lambda' \lambda c}, \]  

(3.99)

where the boundary condition (3.94) imposed on \( f_{\lambda}(r) \) has also been used. In principle, there will be corrections to (3.99), arising from the exchange part in (3.96). In practice, however, these corrections can be made negligible by a suitable choice of \( a \), and were therefore omitted.

The residual interaction matrix elements in (3.98) as well as those for the exchange contribution in (3.96), are rather involved to discuss here explicitly. They
involve recoupling of angular momenta in the usual way to arrive at their specific form. In particular, the considerable amount of Racah algebra that must be carried out is due to a further division of the $H_T$ (Eq. (3.49)) into its molecular constituents, which arises from the fact that molecular states used in the scattering calculations are not true eigenfunctions of $H_T$, i.e., $H_T \Psi_\beta = E_\beta \Psi_\beta$ does not hold, though $(\Psi_\beta | H_T | \Psi_\beta) = E_\beta \delta_\beta \gamma$ does. This is illustrated here according to the division of of the system hamiltonian $H$ given below, but with the formal expressions for their corresponding matrix elements, together with the integrals used in computations, reproduced in an appendix to this thesis (see Appendix B).

In matrix notation, Eq. (3.92) is written as

$$G = H + L - EO$$

(3.100)

where it is understood that the matrix elements of $L$ correspond to those given in (3.99). $O$ is the overlap matrix whose elements were defined in(3.97). $H$ in the sense of (3.96), is then given by,

$$H = E_L \mathbf{1} + \epsilon_M O + T_R + T_e + V^{(1)}_{ee} + V^{(1)}_{ep} + V^{(2)}_{ee} + V^{(2)}_{ep} + V^{(3)}_{ee} + V^{(3)}_{ep} + V_{R}.$$  

(3.101)

where, using the ket notation $|\lambda c\rangle = |[i(jk)]\lambda c\rangle$ for a given electronic configuration $i(jk)$ in (3.95),

$$V^{(1)}_{ee} = \langle \lambda' c' | \sum_{i=1}^{2} |r_0 - r_i|^{-1} |\lambda c\rangle,$$

(3.102)

$$V^{(1)}_{ep} = \langle \lambda' c' | |r_0 - \frac{1}{2} R|^{-1} + |r_0 + \frac{1}{2} R|^{-1} |\lambda c\rangle,$$

(3.103)

$$T_R = \langle \lambda' c' | - \frac{1}{2} \nabla^2 |\lambda c\rangle,$$

(3.104)

$$T_e = \langle \lambda' c' | - \frac{1}{2} \left( \nabla^2_{r_1} + \nabla^2_{r_2} \right) |\lambda c\rangle,$$

(3.105)

$$V^{(2)}_{ee} = \langle \lambda' c' | |r_0 - r_1|^{-1} |\lambda c\rangle,$$

(3.106)

$$V^{(3)}_{ee} = \langle \lambda' c' | |r_0 - r_2|^{-1} |\lambda c\rangle,$$

(3.107)

$$V^{(3)}_{ee}^T = \langle \lambda' c' | |r_1 - r_2|^{-1} |\lambda c\rangle,$$

(3.108)

$$V^{(2)}_{ep} = -2 \langle \lambda' c' | |r_0 - \frac{1}{2} R|^{-1} + |r_0 + \frac{1}{2} R|^{-1} |\lambda c\rangle,$$

(3.109)

$$V^{(2)}_{ep}^T = -2 \langle \lambda' c' | |r_1 - \frac{1}{2} R|^{-1} + |r_1 + \frac{1}{2} R|^{-1} |\lambda c\rangle,$$

(3.110)

$$V^{(3)}_{ep} = -2 \langle \lambda' c' | |r_2 - \frac{1}{2} R|^{-1} + |r_2 + \frac{1}{2} R|^{-1} |\lambda c\rangle,$$

(3.111)

$$V_{R} = 2 \langle \lambda' c' | (1/R) |\lambda c\rangle.$$  

(3.112)

Upon inspection of the matrix elements listed in Appendix B, it is at once seen that $G$ is diagonal in the total angular quantum numbers $I$ and $M_I$ (i.e., $\delta_{II} \delta_{MI} M_I$).
and in fact independent of the latter, which shows that in a single collision event $I$ and $M_I$ are conserved. Therefore $G$ can be separated into submatrices with definite values $I$.

In the actual calculations $G$ is decomposed further. This is possible because the total electronic parity of the $e$-H$_2$ wave function for the channel $c$ is, using Eqs. (3.57) and (3.87),

$$\pi_c = \pi_c^o (-1)^{I+L_P}. \quad (3.113)$$

Since the Coulomb interactions (3.103) in the system hamiltonian $H$, conserves total parity, and being spin-independent, also preserves the ortho- or para- nature of the molecule, i.e., the latter via the Pauli principle implies conservation of $(-1)^{L_P}$, it follows that the total electronic parity of the channel, $P = \pi_c^o (-1)^I$, is also conserved in a single collision event. The matrix $G$ may therefore be decomposed into submatrices labelled by $I^P$, where $P = \pm$.

The calculation of $G$ is a major part of the computations. It is important to note that the size of this matrix is determined by the number of channels and the number of values of $\lambda$ used for the basis functions $f_{\lambda}(r)$. It is also worth noting that the matrix elements of $G$ listed in Appendix B have been formulated to include all channels that arise from the ground $^1\Sigma_u^+$ state as well as those from the excited odd-parity, $^1\Sigma_u^+$ and $^1\Pi_u$, states of the H$_2$ molecule. The latter represent the closed electronic channels in the problem, and account for the effects due to polarisation, i.e., virtual transitions to the energetically closed excited electronic states. For the case when a large number of such states may be required, it does not take very long for the matrix of $G$ to boost somewhat considerably in size. Here, one can make explicit use of the fact that the channel basis states $\hat{X}_{\lambda}$ are energy $E$ independent, so that the matrix elements of $G$ need only be computed once, and perhaps stored according to the pattern suggested above, for all subsequent scattering energies $E$ investigated in the problem. This advantage is also inherent in the work of Burke and others (as reviewed by Burke and Berrington, 1993), the difference being that in their work they rely on a diagonalisation scheme to obtain the $R$-matrix at $a$, whereas in the present study the latter is obtained by calculating the inverse matrix of $G$. Some details concerning this portion of the calculations will be discussed further in Section 3.5.

### 3.3.3 The Long-Range Interactions

In the context of low-energy electron-molecule scattering the rotational and vibrational excitation cross sections near threshold are dominated by the long-ranged electron-molecule interactions (cf. Lane, 1980). Briefly, one can argue that rotational transitions arise as the result of a torque acting on the molecule produced by the electric field of the scattered electron. This field is also responsible for vi-
brational transitions, but unlike rotational excitation, it is the component along the internuclear axis, rather than the one perpendicular to it, that is the most important for this process. This suggests that certain components of the electric field exerted by the scattered electron will be related to certain static moments of the molecule. This, and the fact that the field of the scattered electron can still have a considerable influence even when the electron is still rather far from the molecule, can be seen by examining the terms, $V_{ee}^{(L)}$ and $V_{ep}^{(L)}$, Eqs. (3.72) and (3.73), that occur in the potential matrix $V_{cc}(r_0)$ (given by Eq. (3.71)) as coefficients of various inverse powers of the scattered electron distance $r_0$.

For example, when $L = 0$, $V_{ee}^{(L)}$ and $V_{ep}^{(L)}$ give equal and opposite contributions because of the overall charge neutrality of the $H_2$ molecule. This shows the absence of monopoles, as one would expect in the case of non-polar molecules. The sums in Eq. (3.71) therefore run over values of $L > 0$. In general, the index $L$ is associated with the change in the orbital angular momentum of the scattering electron, which is balanced by an equal and opposite change in the angular momentum of the molecule. It can then be deduced from symmetry considerations, involving parity arguments and the Pauli principle, that the interactions between the scattered electron and the molecular electrons, carried by $V_{ee}^{(L)}$, will vanish between channels of the same electronic parity for odd $L$, and those between channels of opposite electronic parity for even $L$. Similarly, the interaction of the scattered electron with the two protons of the molecule, represented by $V_{ep}^{(L)}$, is always zero for odd $L$ and also between channels of opposite electronic parity.

It follows that for $L = 1$, only $V_{ee}^{(L)}$ contributes and this is related to the electric-dipole part of the potential matrix $V_{cc}(r_0)$ in (3.71). Transitions between rotational and vibrational levels in the ground $^1\Sigma_g^+$ state to those residing in the excited odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ bands of the the $H_2$ molecule, are thus induced via the electric-dipole matrix elements $M_{\alpha'_\sigma'\sigma'\nu'K}$, which were defined in Chapter 2 (cf. Eq. (2.73) in Section 2.4.2):

\[
(V_{ee}^{(1)})_{cc} = 2N_{\alpha'}\delta_{I' I'}\delta_{M'_I M_I}(-1)^{\frac{1}{2}+I'+K'} j_{j^*}j_{K^*} K\hat{n}\begin{pmatrix} l & l & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & K & 1 \\ 0 & \Lambda & -\Lambda_\alpha \end{pmatrix} \times \left\{ \begin{pmatrix} j & j & 1 \\ l & l & \frac{1}{2} \end{pmatrix} \right\} \left\{ \begin{pmatrix} j & j & 1 \\ K' & K & I \end{pmatrix} \right\} M_{\alpha'_\sigma'\sigma'\nu'K},
\]

where $\alpha' = ^1\Sigma_u^+$, $^1\Pi_u$.

As the primary aim of this research is to calculate near-threshold cross sections for rotational and vibrational transitions in the ground $^1\Sigma_g^+$ state of the $H_2$ molecule, it is clear that intermediate or virtual transitions to excited $^1\Sigma_u^+$ and $^1\Pi_u$ states will manifest themselves in the closed channel subspace portion of the scattering calculations, at least in the energy range of interest. It will be shown in Chapter 4, that
polarisability enters the scattering problem as part of the second order perturbation contribution from the $V_{ee}^{(1)}$ matrix elements. This will then further clarify the purpose of computing the polarisability matrix elements in Chapter 2 (cf. Eq. (2.75) in Section 2.4.2).

In a similar way, when $L = 2$, the coefficients $V_{ee}^{(L)}$ and $V_{ep}^{(L)}$ are related to the quadrupole part of the potential matrix $V_{c/c}(r_0)$ by

$$
(V_{ee}^{(2)} + V_{ep}^{(2)})_{\gamma'\gamma} = \delta_{l'I}\delta_{M_l'M_i}(-1)^{\frac{1}{2}+l'}j^2K_p^2K_p^2l^2(0 0 0 0 0 0 0 0 0) \\
\times \left\{ \begin{array}{c}
\begin{array}{cc}
  j & j' \\
  l' & l \\
\end{array}
\end{array} \right\}
\left\{ \begin{array}{c}
\begin{array}{cc}
  j & j' \\
  K' & K \\
\end{array}
\end{array} \right\}
\langle gv'K'|Q|gvK \rangle,
$$

where $\langle gv'K'|Q|gvK \rangle$ are the ground $^{1}\Sigma_g^+$ state rotational ($K$) and vibrational ($\nu$) transition matrix elements for the quadrupole moment of the $H_2$ molecule, which were defined in Chapter 2 (cf. Eq. (2.70) in Section 2.4.1).

While higher values of $L$ in the multipole series of the potential matrix $V_{c/c}(r_0)$ are retained in accordance with the triangular restrictions placed on the quantum numbers that enter through $3-j$ and $6-j$ symbols of the Racah algebra, it is, however, worthwhile to note that the leading $L = 1$ and $L = 2$ contributions in $V_{c/c}(r_0)$ given above demonstrate the importance, and the point stressed in Chapter 2, of having wave functions which produce accurate value for other properties of the molecule, such as those of the quadrupole and polarisability matrix elements.

### 3.3.4 Propagation of the $R$-Matrix

A major problem associated with including closed channels in the coupled equations (3.68) is that direct numerical integration of the equations in both inward and outward directions accumulates round off errors in the closed channel solutions of $u_c^{(k)}(r_0)$ that grow exponentially. Not only does this destroy the linear independence associated with such solutions, but it also completely degrades the symmetry of the collision matrix $U$.

In contrast, since the $R$ matrix (Eq. (3.29)) is essentially the linear factor relating the wave functions to their derivatives, one might expect that dealing directly with the $R$ matrix (Eq. (3.29)) rather than the solutions $u_c^{(k)}(r_0)$, might give better results. Furthermore, the fact that a real and symmetric $R$ matrix guarantees unitarity in the collision matrix $U$, as was shown in Section 3.1.4, in turn suggests that the propagation of the $R$ matrix may be better placed for carrying the desired physical information in an inherently more stable manner. In this way one never really computes the values of the wave functions $u_c^{(k)}(r_0)$ or its derivatives.

Such traits are in essence the main motivation underlying the $R$-matrix propagation technique of Light and Walker (1976), the method of which, has also been
applied by Burke and others in the context of atomic and molecular physics (e.g., see the review by Burke and Berrington, 1993).

To show how one can link the \( R \)-matrices between the internal and external boundaries, let \( f_x^{(k)}(r) = ru_x^{(k)} \) denote the solutions to the coupled equations in (3.68). Eq. (3.68) then reads

\[
\frac{d^2}{dr^2} f_x'(r) = \sum_c B(r)_{cc} f_x(r),
\]

(3.116)

where the channel wave number \( k_c \) and the potential matrix \( V_{cc} \) are now absorbed into

\[
B_{cc}(r) = l'(l' + 1) r^{-2} \delta_{cc} - k_c^2 \delta_{cc} + 2V_{cc}(r).
\]

(3.117)

Further, let \( f(r) \) and \( f'(r) \) each denote the \( m \)-dimensional vectors of the radial functions \( f_x^{(k)}(r) \) and their derivatives respectively, with \( m \) being the number of total channels considered. Then, using

\[
z(r) = \begin{pmatrix} f(r) \\ f'(r) \end{pmatrix},
\]

(3.118)

Eq. (3.116) can be cast into the form of a first-order linear homogeneous differential equation:

\[
z'(r) = \begin{pmatrix} 0 & 1 \\ B(r) & 0 \end{pmatrix} z(r),
\]

(3.119)

where \( B \) is the matrix whose elements are given by (3.117).

It follows from the general theory of ordinary differential equations (e.g., see Section 2.4 of Smith, 1971), that there exist matrices \( M_{ij}(r_2, r_1)(i, j = 1, 2) \) which solve Eq. (3.119) as

\[
z(r_2) = \begin{pmatrix} M_{11}(r_2, r_1) & M_{12}(r_2, r_1) \\ M_{21}(r_2, r_1) & M_{22}(r_2, r_1) \end{pmatrix} z(r_1).
\]

(3.120)

Hence, given the \( R \)-matrix condition (3.28) at \( r_1 \), i.e., \( f(r_1) = R(r_1)f'(r_1) \), that at \( r_2 \), can be obtained from Eq. (3.120) via:

\[
r_2 R(r_2) = (r_1 M_{11} R(r_1) + M_{12}) (r_1 M_{21} R(r_1) + M_{22})^{-1}.
\]

(3.121)

Eq. (3.121) thus permits the \( R \) matrix calculated at \( r = a \), to be propagated outwards to the asymptotic region, \( r \geq b \), by a series of integration steps, each of which requires the solution (3.120) of the coupled differential equations (3.68); this procedure being applied recursively until it is reasonably certain that the scattered electron wave functions \( u_x^{(k)}(r_0) \) correspond essentially to those of a free particle specified by the asymptotic boundary conditions in (3.78). Further details concerning the numerical procedures used in the propagation scheme will be given in Section 3.5.
In summary, the propagation scheme, as characterised by the above equations, provides the physical link between the \( R \)-matrices at the two boundaries, and in turn the final link between the \( R \) matrix and the cross sections, the latter of which follows from the relationship between the \( R \)-matrix and the collision matrix formalised in Section 3.1.3 and that between the observable cross sections and collision matrix derived in Section 3.2.4.

### 3.4 COMPARISONS WITH OTHER R-MATRIX AND RELATED METHODS

The characterisation of \( R \)-matrix theory for low-energy e-H\(_2\) scattering outlined in the preceding section demonstrates similarities to other such methods applied in the context of atomic and molecular processes (see, Burke and Berrington, 1993; see also, Barrett\ et al., 1983). There are however also technical and conceptual differences. These will be stated below, following a brief review of other related \( R \)-matrix programmes applied in the context of low-energy electron-molecule scattering (e.g., see the references cited above).

The \( R \)-matrix approach, for example, of Burke\ et al.\ (1977), makes use of the frame transformation theory of Chang and Fano (1972) to take advantage of the partial adiabaticity of the rotational and vibrational motitions of the molecule with respect to the different ranges of the incident electron's trajectory. As pointed out by Jerjian and Henry (1985), "in its simple elegance, the frame transformation theory incorporates the best features of the body-frame and the Laboratory (Lab)-frame representations" of the scattering equations. To make the connection between the different partitions of configuration space, and thus bring the molecular dynamics back into the picture, a unitarity transformation to the Lab-frame is performed, by averaging over the vibrational and rotational wave functions of the molecule.

The main deficiency with this approach, however, lies in the fact that the body-frame channel energies are ill-defined with respect to the Lab-frame channel energies. This introduces ambiguities into the transformation procedure, when attempting to make the connection between the different partition boundaries of configuration space. This mismatch at the transformation point is the root cause of the problem in applying the frame-transformation theory, and as illustrated in the low-energy e-H\(_2\) scattering work of Jerjian and Henry (1985), results in anomalous structures in the near-threshold rovibrational cross sections.

While the energy modification version of the theory attempts to restore the correct threshold behaviour, by effectively multiplying the cross sections by a kinematic energy factor, the uncertainty of this \textit{ad hoc} procedure, coupled with the failure to deliver a strict criterion for the selection of the transformation radius, has limited the applications of frame transformation theory, at least in the context of low-energy
electron molecule near the threshold energy regime. (For applications of energy modified approximations in electron-molecule scattering theory, see the recent review by Morrison, 1988)

In the $R$-matrix approach of Schneider et al. (1979), the problem mentioned above with the frame transformation is circumvented by taking into account the nuclear dynamics of the molecule, through the use of diabatic basis states. Schneider's approach is thus an attempt to include nonadiabatic corrections within the framework of $R$-matrix theory. While applications of this approach is successful for calculating elastic and vibrational cross sections based on a resonance mechanism (e.g., see the low-energy $e$-$N_2$ scattering work of Gillan et al., 1987), it is difficult to say whether or not Schneider's approach will be applicable to those scattering problems whose near threshold rotational and vibrational cross sections are not driven by a resonance mechanism, as in the present context of low-energy $e$-$H_2$ scattering.

The underlying premise in Schneider's approach and in the $R$-matrix calculations mentioned so far, is the factorisability of the scattering wave function as products of fixed-nuclei electronic wave functions and vibrational wave functions. Not only does this approach incorporate assumptions based on the Born-Oppenheimer approximation, but it also makes a clear division of the scattering problem into one based on a fixed-nuclei type of calculation. The $R$ matrix and thus the collision matrix are therefore calculated as functions of the internuclear distance before an average over the vibrational functions is taken.

This is both conceptually and technically different to the present $R$-matrix treatment of $e$-$H_2$ scattering. The present approach does not rely or import assumptions based or related to the Born-Oppenheimer approximation. Moreover, the channel scheme introduced in Section 3.2, has been completely characterised in terms of quantum numbers necessary to fully account for the dynamics of the $H_2$ molecule in the scattering problem. Consequently, the present approach does not involve a parametrisation of the $R$ matrix and hence the collision matrix $U$ in terms of a fixed internuclear variable. This point was stressed in the structure programme developed in Chapter 2, in view of the fact that having available the electronic-vibrational wave functions eliminates the need to carry out intermediate steps in the scattering calculations.

The synthesis of $R$-matrix methods with optical potentials, also represents some recent developments in the treatment of polarisation effects in electron-molecule scattering, with that of the linear algebraic method of Schneider and Collins (1983), based on a Feshbach projection-operator formalism, being the most notable. As in other nonadiabatic polarisation potentials (cf. Chapter 1), this approach is designed to correct the approximate nature of previously used effective adiabatic polarisation potentials that adhere to a "cutoff" procedure to mock the dynamic response of the
incident electron with respect to the molecule. However, this method seems to have only been applied only within the framework of the adiabtic-nuclei approximation (e.g., see the total cross section results obtained by Schneider and Collins (1983) for low-energy e-H\textsubscript{2} and e-N\textsubscript{2} scattering).

As mentioned in the Chapter 1, the use of optical potentials require a large number of basis states inorder to obtain accurate results. For this reason optical potential approaches to electron-molecule scattering have been only limited to studies concerning elastic scattering (Morrison and Trail, 1993).

In contrast, the present adaptation of \textit{R}-matrix theory to low-energy e-H\textsubscript{2} scattering does not preclude the study of inelastic scattering cross sections, such as those for rotational and vibrational excitations. It would appear that the present \textit{R}-matrix framework for e-H\textsubscript{2} scattering has been somewhat more ambitious than the previous \textit{R}-matrix methods discussed so far, with the major conceptual shifts within the present programme—being the complete rejection of the fixed-nuclei approximation and that of an effective model potential to represent polarisation effects. Furthermore, the present approach does not inherit any of the uncertainties associated with the frame-transformation theory approach mentioned above. This is clear when one realises that the entire e-H\textsubscript{2} scattering problem has been formulated in Sections 3.2 and 3.3 exclusively in the Lab-frame—the channel energies are therefore never ill-defined.

### 3.5 THE CALCULATIONS

The practical implementation of the \textit{R}-matrix formalism and the method for its application to low-energy e-H\textsubscript{2} scattering outlined in Sections 3.1–3.3 requires essentially three major steps: (i) the computation of the matrix elements of \textit{G} (Eq. (3.100) in the internal region \(r < a\) and the calculation of the \textit{R} matrix at \(r = a\); (ii) the propagation of the \textit{R} matrix (Eq. (3.29)) in the intermediate region \(a < r < b\); and (iii) the matching of the wave functions with the asymptotic boundary conditions (3.78) at the external region \(r = b\) to obtain the collision matrix \textit{U}. In this section, one of the variational wave functions generated in Chapter 2 to model the \(1\Sigma^{+}\) state of the H\textsubscript{2} molecule will be used to described the numerical procedures employed for these steps in some detail. Thus throughout all of configuration space, the scattering wave function expansion (3.57) will be assumed to retain only the ground \(1\Sigma^{+}\) state wave functions of H\textsubscript{2}. Polarisation effects arising from the virtual excitations to the closed channel \(1\Sigma^{+}\) and \(1\Pi\) electronic states are therefore not considered in the present calculations, though exchange effects are fully accounted for. The cross sections produced from these calculations will then be presented and discussed in the next section.
3.5.1 The Internal Region

The channel radius of the internal region was set at \( a = 10 \) a.u. In this region, the eigenvalues \( \epsilon_{\lambda l} \) of the regular Bessel functions of argument \( l \) in Eq. (3.93) for the basis functions \( f_{\lambda l} \) were determined subject to the boundary conditions (3.94) with \( B = -1 \). When \( B \) is set to zero, the eigenvalues \( \epsilon_{\lambda l} \) are essentially the zeros of the derivative of the Bessel function. This was a useful check to ensure that the code produces quite accurately the eigenvalues for the value of \( B \) chosen. At this stage, no attempt was made to investigate whether other values of \( B \) would lead to a more rapid convergence (in the cross sections) with respect to the basis set \( f_{\lambda l} \). In the present work, it was found necessary to include (for each value of \( l \)) as many as up to twelve values of \( \lambda, 1 \leq \lambda \leq 12 \).

The ground \(^1\Sigma^+_g\) state wave functions used in the scattering calculations for the \( \text{H}_2 \) molecule, implement the 7-configurational variational model generated in Chapter 2. The corresponding molecular states produced with this model, and which were included in the present scattering work are recalled in Table 3.1. As can be seen from the table, the molecular states employed in the calculations, consisted of three vibrational levels \( v = 0,1, \) and \( 2 \), with the rotational states in each vibrational band restricted to \( K = 0 \) and \( K = 2 \). For comparison, the corresponding energy spacings obtained from experiment are also quoted in the table. This serves to illustrate the importance of having the correct energy differences built into the wave functions if the rotational \( \sigma(K = 0 \rightarrow K = 2) \) and vibrational \( \sigma(v = 0 \rightarrow v = 1) \) transition cross sections are to be accurately determined in the near-threshold energy regime for such excitations.

<table>
<thead>
<tr>
<th>( v )</th>
<th>( K )</th>
<th>( \epsilon_{vK} \times 10^3 )</th>
<th>( E_{g00} = -1.060 ) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>1.92</td>
<td>1.972</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1.56</td>
<td>1.615</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2.07</td>
<td>2.124</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3.82</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3.96</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 3.1. The vibrational and rotational spacings \( \epsilon_{vK} = E_{vK} - E_{00} \) (a.u.) for the 7-state variational model of the \(^1\Sigma^+_g\) state of \( \text{H}_2 \). The lowest level is \( E_{00} = -1.060 \) a.u.
In the present work only the cross sections for the rotational \((K = 0 \rightarrow K' = 2)\), vibrational \((\nu = 0 \rightarrow \nu' = 1)\) and rovibrational \((\nu K = 00 \rightarrow \nu' K' = 12)\) transitions were calculated. The cross section for the transition to the \(\nu = 2\) vibrational level was therefore not calculated. In fact for most part of the energy range of interest \((\leq 1.2 \text{ eV})\), the channels associated with the vibrational \(\nu = 2\) level are closed, i.e., energetically inaccessible. This may be regarded as an attempt to avoid problems that may arise from an improper truncation of vibrational levels in the ground state channels of the scattering wave function (Henry and Chang, 1972). This point in the present context of the scattering problem is still at an exploratory stage of development, though increasing the number of vibrational levels in the calculations is intended in future, at least up to an additional two more vibrational states, especially since the inclusion of such states do not in effect increase the overall number of radial integrals (see Appendix B) needed in the computation of the matrix elements of \(G\) in the internal region.

As discussed in Section 3.3.2, the matrix \(G\) is decomposed into submatrices that are classified according to definite values of the total angular momentum number \(I^P\), where \(P = \pm\) denotes the total electronic parity of the channel. For each \(I^P\), there will be a set of permitted values of \((K, l, j)\) that determine the channels, the number of which in turn depends on the restrictions placed on the rotational \(K\) and \(l\) orbital angular momentum values. In the present calculations, \(l\) is restricted to \(l = 0, 1, 2\), since the most dominant contributions to the cross sections are expected to arise from the corresponding partial \(s-, p-,\) and \(d-\)waves of the scattered electron. Table 3.2 summarises the structure associated with this channel scheme. The number of channels indicated in the table depend also on the number of vibrational states used in the calculations, which in the present study correspond to those shown in Table 3.1. The size of \(G\) follows after also counting the number of values of \(\lambda (12)\) used for the basis set \(f_\lambda\).

In the code written for the computation of \(G\), the matrix elements (listed in Appendix B) were assembled and organised as essentially comprising of a sum of components of the system hamiltonian \(H\), the Bloch operator \(L\), and the overlap matrix \(O\) (as suggested in Eq. (3.100)):

\[
G = H + L - EO. \tag{3.122}
\]

It is always assumed that the \(\text{H}_2\) molecule is initially in its lowest ground \(E_{\text{g}00}\) level, so that the total energy is \(E = \frac{1}{2} k_0^2 + E_{\text{g}00}\), where \(\frac{1}{2} k_0^2\) is the incident energy of the scattered electron.

As listed in Appendix B, the radial integrals needed for the computation of the \(G\)-matrix elements, involve combinations between the basis set and basis functions used in constructing the molecular wave functions. In particular, the integrals were evaluated numerically over the finite range \([0, a]\) using Weddle's rule. To ensure
Table 3.2. Channel structure associated with the ground $^1\Sigma_g^+$ state the H$_2$ molecule. The number of vibrational and rotational states correspond to the 7-state variational wave function used in the scattering calculations. See Table 3.1

<table>
<thead>
<tr>
<th>$I^\pi$</th>
<th>$K$</th>
<th>$l$</th>
<th>$j$</th>
<th>Number of channels</th>
<th>Size of G</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}^-$</td>
<td>0</td>
<td>1</td>
<td>1/2</td>
<td>= 6</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{3}{2}^-$</td>
<td>2</td>
<td>1</td>
<td>1/2</td>
<td>= 9</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{2}^+$</td>
<td>2</td>
<td>2</td>
<td>3/2</td>
<td>= 9</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>5/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{3}{2}^+$</td>
<td>2</td>
<td>0</td>
<td>1/2</td>
<td>= 12</td>
<td>144</td>
</tr>
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<td></td>
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<td>2</td>
<td>3/2</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>5/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{5}{2}^+$</td>
<td>2</td>
<td>0</td>
<td>1/2</td>
<td>= 12</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>5/2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

reasonable accuracy for the double radial integrals, the splitting of the integration limits were evaluated over a mesh size of 180 x 180 steps with each step equal to 0.056 units.

Even with just the ground state, the number of such integrals calculated were estimated at several orders of $10^5$. To avoid excessive computations, the radial integrals were therefore precalculated and stored in multi-dimensional arrays. The arrays then serve as input to the main program, so that for each definite value of $I^\pi$, G was assembled and stored in terms of the matrix components indicated in (3.122). In this way, the inversion of G could be carried out and the R matrix calculated at all subsequent values of the scattering energies $E$ used in the present investigation.

Since a real and symmetric R matrix preserves the unitary nature of the collision matrix (see Section 3.1.4), it was crucial to make certain the matrix elements
calculated for $\mathbf{G}$ produced a real-symmetric matrix. For this purpose, two separate programs were coded and all matrix elements of $\mathbf{G}$ calculated independently, and then inspected and double-checked numerically until consistency between the two calculations was obtained.

### 3.5.2 The Intermediate Region

The propagation of the $\mathbf{R}$ matrix between the boundaries of the internal region at $r = a$ and external region at $r = b$ described in Section 3.3.4, relies on having obtained a complete set of $2m$ linearly independent solutions $\mathbf{z}(r)$ of the coupled equations (3.116). As stated there, the solutions are generated via the matrices $\mathbf{M}_{ij}(r_2, r_1)$ given in Eq. (3.120). The numerical method which accomplished this, is based on the Runge-Kutta method for forward interpolation of the solutions. The latter are initiated by a set of linearly independent vectors having zeros and ones as their components according to the pattern suggested below.

Since the components of the vector $\mathbf{z}(r)$ are composed of the radial functions $f_j^{(i)}(r)$ and their first derivatives, let $\mathbf{f}^{(i)} = (f_1^{(i)}, f_2^{(i)}, \ldots, f_m^{(i)})$ ($i = 1, 2, \ldots, m$) denote the $m$-dimensional vector of the radial solutions $f_j^{(i)}(r)$, where $m$ is the number of channels retained in the coupled equations. The initial values are then defined by the equations (at $r = a$)

$$
\begin{align*}
    f_j^{(i)}(a) &= \delta_{ij}, \\
    f_j^{(i)}(a)' &= 0, & j &= 1, 2, \ldots, m, \\
    f_j^{(i)}(a) &= 0, & f_j^{(i)}(a)' &= \delta_{ij}, & j &= m + 1, m + 2, \ldots, 2m.
\end{align*}
$$

(3.123)

It follows from Eq. (3.121), that the matrices $\mathbf{M}_{ij}$ linking the $\mathbf{R}$ matrices between the two boundaries

$$
\mathbf{R}(r_2) = r_2^{-1}(a\mathbf{M}_{11}(r_2)\mathbf{R}(a) + \mathbf{M}_{12}(r_2))(a\mathbf{M}_{21}(r_2)\mathbf{R}(a) + \mathbf{M}_{22}(r_2))^{-1}. 
$$

(3.124)

may be generated row by row:

$$
\begin{align*}
\mathbf{M}_{11}(r_2) &= \begin{pmatrix} f^{(1)}(r_2) \\ \vdots \\ f^{(m)}(r_2) \end{pmatrix}, & \mathbf{M}_{21}(r_2) &= \begin{pmatrix} f^{(1)}(r_2) \\ \vdots \\ f^{(m)}(r_2) \end{pmatrix}, \\
\mathbf{M}_{12}(r_2) &= \begin{pmatrix} f^{(m+1)}(r_2) \\ \vdots \\ f^{(2m)}(r_2) \end{pmatrix}, & \mathbf{M}_{22}(r_2) &= \begin{pmatrix} f^{(m+1)}(r_2) \\ \vdots \\ f^{(2m)}(r_2) \end{pmatrix},
\end{align*}
$$

(3.125)

(3.126)

where the second argument of the matrices $\mathbf{M}_{ij}(i, j = 1, 2)$ has been suppressed.
To avoid the problem mentioned in Section 3.3.4, associated with errors accumulating exponentially in the solutions when closed channels are retained in the coupled equations, the $R(r_2)$ matrix in (3.124) was calculated recursively over intervals of 5.0 a.u. Thus for each such interval the coupled equations were solved, in the above sense, by forward interpolation of the solutions using a series of integration steps of $\Delta r_2 = 0.1$ units.

Hence, once the $R$ matrix was calculated at $r = a$, it was then propagated step by step over intervals of 5.0 a.u., to obtain the $R$ matrix at the external region $r = b$ where matching to the asymptotic boundary conditions, as given by Eq. (3.78) (see also Eqs. (3.37) and (3.38)), was then performed to obtain the matrix elements of the collision matrix $U$. The actual choice of $b$ was determined by inspecting the calculated cross sections over several values of $b$ until the cross sections obtained from the last few steps of the propagation procedure did not differ significantly form each other. In practice, $b = 100$ a.u. was found to be sufficient.

<table>
<thead>
<tr>
<th>$v'K'$</th>
<th>$vK$</th>
<th>PW</th>
<th>model</th>
</tr>
</thead>
<tbody>
<tr>
<td>02</td>
<td>00</td>
<td>0.48516</td>
<td>0.480</td>
</tr>
<tr>
<td>12</td>
<td>00</td>
<td>0.07833</td>
<td>0.099</td>
</tr>
<tr>
<td>02</td>
<td>02</td>
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<td>0.482</td>
</tr>
<tr>
<td>10</td>
<td>02</td>
<td>0.09770</td>
<td>0.117</td>
</tr>
<tr>
<td>12</td>
<td>02</td>
<td>0.08811</td>
<td>0.109</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>0.53660</td>
<td>0.564</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>0.53865</td>
<td>0.567</td>
</tr>
</tbody>
</table>

As stressed in Section 3.3.3, the long range electron-molecule interactions determine the behaviour of the cross sections near threshold. Since these interactions were also shown there to be characterised by various static moments of the molecule, it is important that the molecular wave functions used in the calculations reproduce as reliably as possible values for such properties.

In the calculations performed here, the most important part of the potential
matrix \( V_{c}(r_0) \) (Eq. (3.71)) that enter into the coupled equations (3.68) was found to be the quadrupole potential, as given by (3.115). This is the case because only ground \( ^1\Sigma_g^+ \) state wave functions were used in the present calculations (see also the remarks in Section 3.3.3). The multipole series for \( V_{c}(r_0) \) therefore run over values of \( L \geq 2 \). In fact one of the criteria for using the 7-state variational wave function (Table. 3.1) as a model for the \( ^1\Sigma_g^+ \) state of the \( \text{H}_2 \) molecule in the calculations, is the excellent values it produces (see Chapter 2) for the various matrix elements of the quadrupole moment, which is surprising in view of the simplicity of the wave function. For convenience, Table. 3.3, displays the values of the selected quadrupole matrix elements that were produced with the 7-state variational model, as well as those calculated highly accurately by Poll and Wolniewicz (1978) [PW].

As shown in Table 3.2, the largest number of channels retained in the coupled equations was 12 channels, which occurs when \( I^P = \frac{1}{2}^+ \) and \( \frac{5}{2}^+ \). As these channels will increase considerably in number by the time the excited \( ^1\Sigma_u^+ \) and \( \Pi_u \) odd-parity states are also included, some steps were taken to increase the overall efficiency in the propagation subroutine of the main program.

The first step makes use of the fact that for a given \( I^P \) all multipole coefficients of \( V_{c}(r_0) \) that enter into the coupled equations can be fully predetermined at the outset and stored, so that each call to the propagation subroutine, accesses the coefficients directly, thus eliminating unnecessary additional computer time. In the second step, the coupled equations were integrated directly to the external region without stripping the intermediate region into finite intervals. This is possible in the present case because the closed channel solutions arise only from the ground state wave functions, and consequently, the errors in them do not accumulate as exponentially fast as they would when the excited odd-parity states are retained. This more or less illustrates the inherent stability of the propagation subroutine. Therefore, by comparing the cross section produced this way with that produced by propagating the \( \text{R} \) matrix over finite intervals (as described above), it was possible to verify that all step sizes used in the propagation subroutine are sufficiently accurate for the calculation of the cross sections.

The last part of the main program calculates the collision matrix \( \text{U} \), as defined by Eq. (3.38). This occupies only a fraction of the total computer time, and essentially involved the inversion of matrices carried out by standard subroutines based on a triangualar decompositon of a matrix. This technique was found to be extremely efficient for the size of the matrices encountered in the present work (the largest being 54 for the calculations carried out in Chapter 4). Thus it was found unnecessary to truncate the \( \text{R} \) matrix to obtain the collision matrix in the subspace of the open-open channels, as suggested in Eq. (3.42). Consequently, no elimination of the closed channels were made in the present approach, so that for each definite value of \( I^P \)
indicated in Table 3.2, all elements (channels) of the collision matrix were calculated.

In brief, once the \( \mathbf{R} \) matrix was calculated at \( r = a \), the coupled equations (3.68) were then solved by series of integration steps, to propagate the \( \mathbf{R}(r_2) \) matrix in (3.124) over intervals of 5.0 a.u. step by step up to the radius of the external region at \( r = b \) (\( b = 100 \) a.u.) in such a way that the cross sections obtained from \( \mathbf{R}(r_2) \) for the last few steps did not differ significantly from each other.

### 3.6 DISCUSSION OF THE CROSS SECTIONS

In this section, integrated cross sections for the collision of low-energy electrons (\( \leq 1.2 \text{eV} \)) by the ground \( ^1\Sigma_g^+ \) state of \( \text{H}_2 \) are presented. The cross sections are for elastic scattering and rotational and vibrational excitation processes. These were calculated in terms of the partial wave contributions, which may be obtained from Eqs. (3.85) and (3.86) as follows:

\[
\sigma(00 \rightarrow vK') = \sum_{l_0} \sigma_{l_0 l}(00 \rightarrow vK') = \sum_{l_0} \sigma_{l_0 l}(00 \rightarrow vK')
\]  

(3.127)

where \( \sigma_{l_0 l} \) are the partial wave contributions given by

\[
\sigma_{l_0 l}(00 \rightarrow vK') = \frac{\pi k_f^{-2}}{2(2K + 1)} \sum_{I} (2I + 1) \sum_{j \text{to}} |\delta_{if} - U(00j_0; v'K'j; I)|^2
\]  

(3.128)

Here \( l_0 \) and \( l \) are the orbital angular momentum quantum numbers of the scattered electron respectively in the initial (entrance) \( i \) and final (exit) \( f \) channels, where it is understood that the transition cross sections of primary interest to the present study are those excited from the lowest energy level of the molecule (\( vK = 00 \)) to corresponding rotational and vibrational energy levels (\( v'K' \)) in the ground \( ^1\Sigma_g^+ \) state. The electronic labels \( \alpha_0, \alpha \) given originally in the cross section formulas (3.85) and (3.86) have therefore been omitted in writing (3.127).

For the elastic cross section \( \sigma(vK = 00 \rightarrow vK = 00) \) the orbital angular momentum values of the scattered electron are the same in both the entrance (\( i \)) and exit (\( f \)) channels, i.e., \( l_0 = l \). Since the channel scheme described in Section. 3.5.1, restrict these values to \( \leq 2 \), the partial wave transitions (3.128) to the elastic cross section arise from the corresponding partial \( s- \), \( p- \) and \( d- \)wave components of the scattered electron. The results for these transitions are displayed accordingly in Fig. 3.1.

As can be seen from the plots shown, the elastic cross section is predominantly caused by \( s- \)wave electron scattering. This is consistent with many of the earlier calculations reviewed by Lane (1980). As stressed there, one of the important requirements in calculating elastic cross sections is the inclusion of exchange effects. The omission of exchange effects are known, for example, to over estimate the behaviour of the cross section at energies near zero due to the fact that the resulting \( s- \)wave phase shifts are too small at such energies.
Figure 3.1. Partial wave contributions to the elastic cross section 
\[ \sigma(vK = 00 \rightarrow v'K' = 00) \] in units of \((\text{Å}^2)\). Results plotted are for: (a) 
\[ s \rightarrow s (---); \text{ and (b) } d \rightarrow d (--), p \rightarrow p (- -). \]

This is in many ways similar to the behaviour found in electron-helium scattering studies (see for example the discussion in Section IV of Tully and Berry, 1969). As in the electron-He case, one can understand that the effect of incorporating exchange effects in the scattering problem is to increase the overall "attractiveness" of the short range static (electron-molecule) interactions. Consequently, there will be a general increase in the phase shifts. The result of this, is then a lowering of the elastic cross section at very low energies, accompanied by a corresponding increase at higher energies.

Since the present calculations neglect polarisation effects, but account for exchange effects fully, one might expect similarities with those calculations carried out at the level of a static-exchange treatment of the problem.

To illustrate this the present result for the total elastic cross section, obtained by adding all the partial contributions from Fig. 3.1, is compared in Fig. 3.2 with that of Morrison and Collins (1978). While these authors include exchange effects exactly, by solving the resulting set of coupled integro-differential equations directly, it is important to note that Morrison and Collins use the rigid-rotor approximation, so that in their scattering calculations the molecule is held "frozen" at its equilibrium value of \( r = 1.402 \) a.u. throughout the collision.

It is reasonable to suppose that the rigid-rotor approximation used by Morrison and Collins does not introduce serious errors into the scattering calculations, at least for elastic scattering, so that difference seen in Fig. 3.2 between the two plots
at the low energy end must lie in the different methods for calculating the short range static electron-molecule interactions. Since such interactions are essentially an average over the distribution of the molecular charge cloud, the latter difference must in turn be the result of using different ground state wave functions for the H$_2$ molecule. For instance, Morrison and Collins use the Hartree-Fock wave function of Fraga and Ransil (1961) whose ground state energy at $R = 1.402$ a.u. is $-1.1335$ a.u., as compared with the ground state energy of $-1.060$ a.u. produced by using the 7-configuration model in the present treatment of the problem (see Table. 3.1). While this serves to emphasize the comments above concerning the importance of the short-range forces in the scattering problem, especially at energies lower than 0.5eV, it can also be seen from Fig. 3.2 that at higher energies both plots for the elastic cross section begin to merge closer. The explanation for this can be attributed to the fact that short range forces, such as exchange effects, diminish in importance at higher energies.

An important and nontrivial test as to whether a theory for low-energy electron-molecule scattering is reliable or not, is the reproducibility of the threshold laws in the cross sections. Turning now to the inelastic cross sections, one can expect the behaviour of the cross sections near the channel threshold energy regime to be roughly in accord with the Wigner threshold laws:

$$\sigma(i \rightarrow f) \sim (\sqrt{E - E_f})^{2l+1}$$

(3.129)
where \( l \) is the lowest orbital angular momentum observed in the exit channel.

To see if this is the case in the present study, the partial wave contributions to the pure rotational \( \sigma(K = 0 \rightarrow K = 2) \) cross section have been plotted in Fig. 3.3. It can be seen, that the different partial wave components contribute differently to the rotational cross section near threshold. Further, the rotational cross sections near threshold is dominated by a \( d \)-electron wave in the initial channel with an \( s \)-wave produced in the exit channel, i.e., \( d \rightarrow s \), while at energies well above threshold (\( \geq 0.1 \text{eV} \)) the cross section is essentially dominated by the \( p \rightarrow p \) contribution. The explanation of this has been discussed in detail by Lane and Geltman (1967) (see also Gerjuoy and Stein, 1955).

Briefly, the way in which the different partial wave components contribute differently to the rotational cross section can be understood on the grounds that the total angular momentum must be conserved during the collision process, i.e., an \( s \)-wave electron cannot go in and come out as an \( s \)-wave, and the fact that at low energies (i.e., large wavelengths) only the \( s \)-wave electrons have an appreciable probability of being detected near the vicinity of the molecule. Thus at low energies near the threshold for rotational excitation (\( \approx 0.05 \text{eV} \)), there is only sufficient energy to allow \( s \)-wave electrons to escape into the exit channel. At such energies the \( p \)-waves cannot penetrate the effective barrier of the centrifugal potential. Rather, the \( p \)-wave component becomes more important at energies well above the threshold for rotational excitation.
Similar trends in the partial wave contributions $\sigma_{\text{rot}}$ to the rotational $\sigma(0 \rightarrow K = 2)$ cross section were also obtained in the off-shell T-Matrix approach of Ficocelli Varracchio and Lamanna (1983). As in the energy modification frame transformation theory (discussed in Section 3.4), the off-shell T-matrix approach aims (in a less ad hoc way) at curing the breakdown of the fixed-nuclei approximation near-threshold by building into the theory the compensating kinematical factor required to restore the correct threshold behaviour in the cross sections. Thus these authors find, as in the present results shown in Fig 3.3, that partial wave contributions to the rotational cross section from the $s \rightarrow d$ process is not the same as the $d \rightarrow d$ process; which is not predicted by those scattering methods based on the adiabatic-nuclei approximation.

Another important factor determining the behaviour of the cross sections near-threshold is the influence of the long-range electron-molecule interactions. This was discussed in Section 3.3.3, where it was mentioned that the behaviour of rotational cross near threshold will be largely determined by the quadrupole moment. This is made clear in the first Born approximation (FBA) studies of Gerjuoy and Stein (1955). The applicability of the FBA to this situation is discussed at length by these authors, based essentially on the general criteria that the kinetic energy of the scattered electron be smaller than the interaction energy. Since the latter interaction in the case of nonpolar molecules is primarily dominated by the quadrupole part of the interaction potential (e.g., see Eq. (3.115)) and varies as $r^{-3}$, Gerjuoy and Stein demonstrate further that the FBA result for rotational excitation is increasingly valid as the incident energy approaches the threshold for such a process. This serves to stress the remark made in Section 3.3.3, of using wave functions which are able to reproduce as reliable as possible values for the quadrupole moment. The latter point is illustrated further in Fig 3.4, where it can be seen that the FBA result of Gerjuoy and Stein (1955) for the rotational cross section near threshold is in excellent agreement with that obtained in the present study. Of course, as remarked in Section 3.5.1, the variational wave functions used in the present calculations is based on the values they produce for the quadrupole matrix elements (see Table 3.3).

Of course, at energies well above the rotational threshold, the FBA no longer applies, and consequently the difference seen between the two plots in Fig. 3.4 at such energies is as to expected. Another reason for this difference is that exchange effects are fully accounted for in the present study whereas such effects are entirely omitted in the FBA studies of Gerjuoy and Stein. The importance of exchange effects to the rotational excitation cross section is emphasised in the close-coupling calculations of Ardill and Davison (1968). In particular, these authors show that the result of including exchange effects is to increase the $p$-wave phase shifts. As found also in the earlier case studies on the elastic cross section (mentioned above), this
will in turn lead to a corresponding increase in the rotational cross section at higher energies. Thus since the rotational cross section calculated in the present study is dominated by the $p$-wave contributions above threshold (Figure. 3.3), the consequence of including exchange effects, yields a much larger rotational cross section than the FBA result of Gerjuoy and Stein (1955).

![Figure 3.4](image)

**Figure 3.4.** A comparison between the FBA result (---) of Gerjuoy and Stein (1955) and the present study (——) for the pure rotational $\sigma(K = 0 \rightarrow K = 2)$ cross section in units of ($\text{Å}^2$).

Finally, for completeness, plots of the main partial wave contributions to the pure vibrational $\sigma(vK = 00 \rightarrow v'K' = 10)$ and ro-vibrational $\sigma(vK = 00 \rightarrow v'K' = 12)$ cross sections are displayed in Fig. 3.5. At this stage very little can be said about the vibrational cross sections as the proposed mechanism responsible for such excitations arise from the inclusion of polarisation effects, which have not been included in the scattering calculations carried out in the present chapter. Nevertheless, the plots in Fig 3.5 serve to illustrate the behaviour of the vibrational cross sections near threshold. It is worth noting that the threshold behaviour of these cross sections are very similar to those obtained by Takayanagi (1965), which are based on the application of the FBA in direct analogy with that of Gerjuoy and Stein (1955) for the rotational cross section. In this respect, the vibrational cross sections obtained by Takayanagi are effectively proportional to the square of vibrational transition matrix elements of the quadrupole moment.
3.7 SUMMARY

In this chapter, an $R$-matrix approach to low-energy $e$-$H_2$ scattering has been developed with the intention of avoiding two frequently made approximations in the context of low-energy electron-molecule scattering theory: (i) the fixed-nuclei approximation; and (ii) the use of an effective local model potential for the treatment of polarisation effects.

The reasons for such an approach were outlined in Chapter 1, in relation to the uncertainties, and in particular, the theoretical issues surrounding the discrepancy between experiment and theory for the $\sigma(\nu = 0 \rightarrow \nu' = 1)$ vibrational excitation cross section of the hydrogen molecule by low energy electron impact. The resolution of this discrepancy is therefore a long-term objective of the present research.

The important stages of development of the $R$-matrix programme of the present chapter have been the extension of the standard $R$-matrix formalism in Section 3.1 to allow for an explicit treatment of exchange effects (Section 3.2) and the merging of the structure theory of Chapter 2 into a form practicable and suitable for the present $R$-matrix framework (Section 3.3).

It is the nonadiabatic formulation of the wave functions in the latter work, for the modelling of the ground $^1\Sigma_g^+$ and excited $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states of $H_2$ and the subsequent composition of the channel states, and hence the matrix elements (Appendix B), in terms of them, that permits the present framework for $e$-$H_2$ scattering to avoid assumptions of the fixed-nuclei approximation kind as well as those

Figure 3.5. Contributions in ($\AA^2$) of various partial-wave transitions to: (a) pure vibrational $\sigma(\nu' = 0 \rightarrow \nu = 1)$ cross section; (—) $s \rightarrow s$, (...) $p \rightarrow p$; and (b) ro-vibrational $\sigma(\nu K = 00 \rightarrow \nu'K' = 12)$ cross section; (—) $d \rightarrow s$, (...) $p \rightarrow p$. 

3.7 SUMMARY

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on a model potential treatment of polarisation effects. These points were discussed in Section 3.4, and show that the only real link between the present $R$-matrix approach and previous $R$-matrix methods, is the partitioning of configuration space into internal, intermediate and external regions, based on the criteria that certain electron-molecule interactions (e.g., exchange effects) are more significant in one region than in another.

The techniques and the numerical procedures required to mesh these different regions of configuration space within a complete $R$-matrix description of the scattering problem, as described in Section 3.5, represent one of the main purposes in the present chapter. Another purpose has been to investigate the behaviour of the cross sections near threshold for rotational and vibrational excitations. This provides a test as to whether the theory can reproduce the threshold laws for the cross sections without having to rely on the *ad hoc* procedure, employed in other scattering methods (cf. Morrison, 1988), which rely upon restoring the correct threshold behaviour by multiplying the cross sections with a kinematical energy factor. The latter procedure, as mentioned in Section 3.4, reflects the breakdown of the fixed-nuclei approximation in scattering theory. The fact that no such *ad hoc* procedure was required in the present work demonstrates the purpose of having used wave functions which do not treat the rotational and vibrational degrees of freedom of the molecule as being fixed during the collision.

The present $R$-matrix theory framework for low-energy $e$-H$_2$ scattering provides all the main ingredients needed to produce highly accurate low-energy cross sections for elastic scattering and rotational and vibrational excitations. Such calculations are clearly needed if the discrepancy between theory and experiment for the $\sigma(v = 0 \rightarrow v = 1)$ vibrational excitation cross section near-threshold is to be resolved. The final demonstration that is needed to bring this research a step closer towards any hope of resolving this discrepancy, is the inclusion of polarisation effects; which of course relies on extending the present calculations to include the excited $^1\Sigma^+_u$ and $^1\Pi_u$ states of H$_2$. This is the purpose of Chapter 4.
Chapter 4

R-Matrix Formalism and Calculation of the Cross Sections: II

4.1 INTRODUCTION

In this chapter the $R$-matrix theory and scheme of calculation described in the previous chapter will be applied in the context of incorporating polarisation effects by extending the previous calculations to include the closed electronic $1\Sigma^+_u$ and $\Pi_u$ channels. Section 4.2 reviews the $R$-matrix theory, as developed in chapter 3, but with attention drawn to the characterisation of polarisation effects in the scattering. In Section 4.3 the numerical procedures are described with the results for the cross sections then presented in Section 4.3.2. Comparisons are made with the cross sections results of the previous chapter. Finally, Section 4.4, concludes the thesis.

4.2 THEORY AND METHOD

As in Chapter 3, the scattering of low-energy electrons by the ground $1\Sigma^+_g$ of the $H_2$ molecule is described in a frame $O_{xyz}$ fixed in space, with the initial momentum $k_i$ of the incident electron chosen to be coincident with the $O_z$ direction. The total energy in the overall centre of mass frame is

$$E = \frac{1}{2}k_i^2 + E_{g\nu K}$$

(4.1)

where $\frac{1}{2}k_i^2$ is the energy of the incident electron and $E_{g\nu K}$ are the ground $g = 1\Sigma^+_g$ state vibrational ($\nu$) and rotational ($K$) energy levels of the molecule, which, in what follows, will be assumed to be in the lowest energy state, i.e., $E_{g00}$. The incident channel, say $k$, is therefore always open (e.g., see Eqs. (3.80) and (3.12)).

The scattering wave function $\Psi_k$ is governed by the Schrödinger equation,

$$(H - E)\Psi_k = 0,$$

(4.2)

where $H$ is the Hamiltonian given by Eqs. (3.47)-(3.51) for the $e-H_2$ system. The Hamiltonian $H$ is essentially a sum of the single particle Hamiltonian $H_{\text{inc}}$ for the
incident electron, the molecular hamiltonian $H_T$ for $H_2$ and the Coulomb interactions $V$ between the scattering electron and the molecule:

$$H = H_{\text{inc}} + H_T + V.$$  \hfill (4.3)

In analogy with the $R$-matrix scheme described in Chapter 3, configuration space is divided into internal, intermediate and external regions, with the scattering wave function (throughout all of configuration space) expanded in terms of the channel states $\hat{X}_c$, defined in Eq. (3.52), where $c$ follows the notation used in (3.53) for the channel index:

$$c = (\alpha \nu K; l j; I M_I);$$  \hfill (4.4)

($\alpha \nu K$) being the electronic, vibrational and rotational quantum number of the molecular state, $l$ and $j(j = l \pm \frac{1}{2})$ the orbital and total angular momenta of the scattering electron, and $I$ and $M_I$ the total angular momentum quantum numbers of the electron-molecule system.

We recall that the channel states $\hat{X}_c$ are formed by coupling the spin-angular momentum of the scattered electron wave function $u_c^{(k)}(r_0)$ to those of the molecular states $\Psi_\beta$, where the latter are obtained from the variational calculations performed in Chapter 2. The molecular wave functions used in the scattering calculations (for a summary see Section. 3.3.1) are thus orthogonal to one another ($\beta = (\alpha \nu KM_K)$)

$$\int \Psi_\beta^* \Psi_\beta = \delta_\beta^\beta$$  \hfill (4.5)

and also diagonalise the molecular hamiltonian $H_T$:

$$\langle \Psi_\beta | H_T | \Psi_\beta \rangle = E_{\alpha \nu K} \delta_\beta^\beta.$$  \hfill (4.6)

For the radial wave functions $u_c^{(k)}(r_0)$ of the scattering electron, these were taken in Chapter 3 in different forms for the different regions of configuration space. The form for these functions are recalled below for convenience, as this will also provide the opportunity to highlight the essentially new element of incorporating polarisation effects into the present $R$-matrix scattering work, which is accomplished below by explicitly including into the scattering wave function expansion the closed channels that are formed from the excited odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ states of $H_2$.

4.2.1 The Internal Region

Remembering that all distances are measured from the midpoint of the line joining the two protons of the $H_2$ molecule (see Section. 3.2.2), the partition radius $a$ for the internal region is, as before, chosen just large enough to confine the molecular bound states of interest, i.e., $(\frac{1}{2}R, r_0, r_1, r_2) \leq a$ (see also the condition given in (3.56)). This is to ensure that the effects of antisymmetrisation are also effectively
confined to the internal region. Thus the scattering wave function in the internal region is taken in the form

\[ \Psi_k(R; r_0, r_1, r_2) = A \sum_{\lambda c} u^{(k)}_c(r_0) a^{(k)}_{\lambda c} X_c(R; r_0, r_1, r_2), \]  

(4.7)

where \( A \) antisymmetrises the scattered electron coordinate with all electron coordinates of the molecule. It is important to note, in contrast to work in Chapter 3, the channel index in (4.7) includes the (closed) channels arising from the coupling to the excited odd-parity \( ^1\Sigma^+_u \) and \( ^1\Pi_u \) states of \( H_2 \) as well as those for the ground \( ^1\Sigma^+_g \) state.

Following Section 3.3.2, \( u^{(k)}_c(r_0) \) in (4.7) is expanded in a complete orthonormal set of basis functions \( u_{\lambda l}(r_0) \) for \( 0 \leq r_0 \leq a \) (where \( l \) belongs to the channel index \( c \)). The latter are solutions of

\[ \left( \frac{1}{r_0^2} \frac{d^2}{dr_0^2} r_0^2 \frac{d}{dr_0} - \frac{l(l+1)}{r_0^2} - \epsilon_{\lambda l} \right) f_{\lambda l} = 0, \]  

(4.8)

which were obtained in (3.93) (up to a given normalisation constant \( A_{\lambda l} \)) as spherical Bessel functions of argument \( l \):

\[ f_{\lambda l}(r_0) = A_{\lambda l} r_0 j_l(k_{\lambda l} r_0) \]  

(4.9)

with the normalisation condition for them given by (3.19). The eigenvalues \( \epsilon_{\lambda l} = \frac{1}{2} k_{\lambda l}^2 \) in (4.8) are determined by the boundary condition (3.94) imposed at \( r_0 = a \):

\[ \left( \frac{d}{dr_0} - B \right) f_{\lambda l}(r_0) = 0 \quad \text{at } r_0 = a. \]  

(4.10)

where, as before, \( B \) is a real parameter independent of \( \lambda \).

As mentioned in Section 3.1.2, the Bloch operator \( L(b_c) \) (Eq. (3.22)) provides the link between the scattering wave function (4.7) in the internal region to that in the external region. This is the content of Eq. (3.28), which essentially establishes the Green's function relationship for the scattering wave function, as the \( R \)-matrix (Eq. (3.29)), which relates the scattering wave function to its value and derivative at the radius \( a \) of the internal region.

As given by Eq. (3.63), the Bloch operator is taken as

\[ L = \sum_c \langle \hat{X}_c \rangle L(b_c)(\hat{X}_c) \]  

(4.11)

where \( \langle \hat{X}_c \rangle \) are the antisymmetrised channels states \((\hat{X}_c)\) defined in (3.59), and \( L(b_c) \) is the sum of the one body Bloch operators (one for each electron), as defined by (3.64):

\[ L(b_c) = \frac{1}{2} \sum_{i=0}^2 \left[ \frac{d}{dr_i} - \frac{b_c}{a} \right], \]  

(4.12)
where \( b_c \) are arbitrary channel constants. In the present case, as also in previous \( R \)-matrix methods (e.g., see Lane, 1980), the channel constants are taken to be zero, i.e., zero derivative condition.

As previously outlined (see Section 3.2.2), the \( R \)-matrix at \( a \),

\[
R_{cc'}(a) = \sum_{\lambda \lambda'} f_{\lambda 
(4.13)
\]
can be obtained after adding the Bloch operator (4.12) to both sides of the Schrödinger equation (4.2), and projecting onto the channel states \( \hat{X}_c \), where the matrix elements of \( G \) in (4.13) follows from (3.92), as those determined by integrating over the antisymmetrised channel basis functions \( \hat{X}_{\lambda c} \) (defined in Eq. (3.58)):

\[
G_{\lambda c, \lambda' c'} = \langle X_{\lambda c} | H + L - E | X_{\lambda' c'} \rangle. \quad (4.14)
\]

These matrix elements were discussed in some detail in Section 3.3.2, where the necessary Racah algebra, which includes the recoupling of angular momenta for the channels arising form the excited odd-parity \( ^1\Sigma_u^+ \) and \( ^1\Pi_u \) states as well as those for ground \( ^1\Sigma_g^+ \) state of the molecule, has already been carried out to obtain complete expressions for all the matrix elements required in the present work, as listed in Appendix B.

### 4.2.2 The Intermediate Region

As mentioned above the radius \( a \) of the internal region is chosen so that for \( r_0 > a \), the effect due to antisymmetrisation in the wave function (4.7), i.e., exchange effects can be neglected. The scattered electron wave function \( u_{\lambda'}^{(k)}(r_0) \) is then determined by solving the set of coupled differential equations (3.68), which in the notation used in Section 3.2.3, are given by:

\[
\left\{ \frac{1}{r_0^2} \frac{d^2}{dr_0^2} r_0^2 - \frac{l'(l' + 1)}{r_0^2} + 2(E - E_{\lambda'}) \right\} u_x^{(k)}(r_0) = 2 \sum_c V_{x' c}(r_0) u_x^{(k)}(r_0). \quad (4.15)
\]

where the potential matrix \( V_{x' c}(r_0) \) on the right hand side of (3.68) (as defined by Eq. (3.71)) consists of sums over inverse powers of \( r_0 \).

As was discussed in Section 3.2.3, the coefficients for the various inverse powers of \( r_0 \) are related to various multipole moments of the molecule (see Eqs. (3.72) and (3.73)), where the absence of monopoles follows naturally from the parity arguments considered there. It was also stressed there, that the different static moments determine the near-threshold behaviour of the different transition cross sections in low-energy \( e - H_2 \) scattering.

For example, the main mechanism responsible for vibrational excitations of the molecule is due to the component of the electric field of the scattered electron exerting a force along the internuclear axis. As discussed in Section 3.3.3, the latter
is related to the electric-dipole part of $V_{ee}(r_0)$ (i.e., the $L = 1$ term), which is represented by $\left( V_{ee}^{(1)} \right)_{ee}$ (see Eq. (3.114));

$$\left( V_{ee}^{(1)} \right)_{ee} = \sum_{M_0^e M_0^i} 2N_{\ell \ell'} \delta_{M_0^i M_0^e} (-1)^{\frac{3}{2} + I + K' + K} \hat{J} \hat{J} \hat{K} \hat{K} \hat{l} \hat{l}' \left( \begin{array}{ccc} \ell & l' & 1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} K & K' & 1 \\ 0 & \Lambda' & -\Lambda_\sigma' \end{array} \right) \right) \times \left\{ \begin{array}{ccc} j & j' & 1 \\ \ell' & l & 1/2 \end{array} \right\} \left\{ \begin{array}{ccc} j & j' & 1 \\ K' & K & I \end{array} \right\} M_{\sigma' \nu', \sigma \nu K}^{(1)} \right.$$  

(4.16)

where $M_{\sigma' \nu', \sigma \nu K}^{(1)}$ are the electric-dipole matrix elements.

Whereas the electric-dipole potential (4.16) was absent in the scattering calculations carried out in the preceding chapter, this will not be the case in the present calculations, because of the induced transitions caused by this potential between rotational and vibrational levels in the ground $^1\Sigma_g^+$ state to those residing in the excited odd-parity $^1\Sigma_u^+$ and $^1\Pi_u$ bands of $H_2$.

Furthermore, it can be shown in scattering theory that polarisability enters the calculations indirectly as part of a second-order contribution from the matrix elements of (4.16). The analysis required to show this is based on a perturbative treatment of the coupled differential equations (4.15) in analogy with that carried out by Castillejo et al. (1960) in the context of electron-atom scattering theory. However, unlike the latter, the polarisation potential obtained in the context of electron-molecule scattering theory, involves the parallel ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) components of the polarisability tensor of the molecule, viz:

$$\left( V_{pol}(r) \right)_{\gamma' \gamma} = \frac{-\frac{1}{3}}{r^4} \delta_{\ell \ell'} \delta_{M_0^i M_0^e} \left[ \delta_{j'j} \delta_{K'K} \delta_{\nu'\nu} (gv'K'|(\alpha_\parallel + 2\alpha_\perp)|gvK) \right]$$

$$+ 2(-1)^{\frac{3}{2} + I + K' + K} \hat{J} \hat{J} \hat{K} \hat{K} \hat{l} \hat{l}' \left( \begin{array}{ccc} \ell' & l & 2 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} K' & K & 2 \\ 0 & 0 & 0 \end{array} \right) \right) \times \left\{ \begin{array}{ccc} j & j' & 2 \\ \ell' & l & 1/2 \end{array} \right\} \left\{ \begin{array}{ccc} j & j' & 2 \\ K' & K & I \end{array} \right\} \langle gv'K'|(\alpha_\parallel - \alpha_\perp)|gvK \rangle \right.$$  

(4.17)

It should noted that this approximation is not made in the present work. Eq. (4.17) above is used only to provide a framework for assessing the relative importance of the odd-parity states used in present context of the $e-H_2$ scattering problem. This is in fact the main reason why the matrix elements of the polarisabilities, $\alpha_\parallel$ and $\alpha_\perp$, were calculated in Chapter 2.

One may expect that the spherical component, $\alpha_0 = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$, of the polarisability tensor or, in other words, the isotropic contribution in (4.17), will have a considerable effect on those channels that are not associated with a change in the rotational quantum states of the molecule (e.g., elastic scattering and vibrational excitation). The nonspherical component, $\alpha_0 = \frac{2}{3}(\alpha_\parallel - \alpha_\perp)$, or the anisotropic
contribution in (4.17) will, on the other hand, influence those channels that are associated with a change in the rotational quantum states of the molecule (e.g., rotational and ro-vibrational excitations).

These considerations in turn suggest that there will be corresponding changes in the behaviour of the elastic scattering, rotational and vibrational excitations cross sections. This is in fact the situation found in the literature (e.g., see Lane, 1980), where if one also now takes into consideration the quadrupole, \( L = 2 \), part of the potential \( V_{cc}(r_0) \), given by Eq. (3.115):

\[
\left( V_{ee}^{(2)} + V_{cp}^{(2)} \right)_{\gamma'\gamma} = \delta_{P'l'}\delta_{M'l'}(-1)^{\frac{1}{2}+l'J'}\hat{K'}\hat{K}l'l' \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & K' & 2 \\ 0 & 0 & 0 \end{pmatrix} 
\times \left\{ j, j', 2 \right\} \left\{ j, j', 1 \right\} \left( g_{v'K'}|Q|g_{vK} \right),
\]

(4.18)

the effect of retaining the closed electronic \( ^1\Sigma^+ \) and \( ^1\Pi_u \) channels in the coupled differential equations (4.15), is such that the long range part of \( V_{cc}(r_0) \) will be dominated by the quadrupole (Eq. 4.18) and polarisation (Eq. (4.17)) potentials.

With the understanding that the coupled equations (4.15) include both odd and even parity channels, these equations are then numerically integrated, as outlined in Section. 3.3.4, to propagate the \( R \)-matrix calculated at \( a \) outwards to the external region, which is accomplished via the relation given in (3.121):

\[
r_2R(r_2) = (r_1M_{11}R(r_1) + M_{12})(r_1M_{21}R(r_1) + M_{22})^{-1}.
\]

(4.19)

where the matrices \( M_{ij} \) are generated by obtaining the \( 2m \)-dimensional linearly independent solutions of the coupled equations, with \( m \) being the total number of channels considered (see Eq. (3.120)).

### 4.2.3 The Collision Matrix and the Cross Sections

Following Section. 3.2.3, the collision matrix \( U_{kc} \) is determined by integrating the solutions \( u^{(k)}_c(r_0) \) of Eq. (4.15) numerically outwards to a distance \( b \), such that they satisfy the asymptotic boundary conditions,

\[
u^{(k)}_c \sim \left( 1/k_c \right)^{1/2} \frac{i}{r} \left[ e^{-ik_c r} \delta_{kc} - e^{ik_c r} U_{kc} \right] \quad (E_c > 0),
\]

(4.20)

\[
u^{(k)}_c \sim -\left( 1/k_c \right)^{1/2} \frac{1}{r} \left[ e^{-k_c r} U_{kc} \right] \quad (E_c < 0),
\]

(4.21)

where \( E_c = \frac{1}{2}k_c^2 \) are the channel energies.

As in the method adopted in Section. 3.5.2, the \( R \)-matrix is propagated outwards by a series of integration steps, in such a way that it is reasonably certain that the scattered electron wave functions \( u^{(k)}_c(r_0) \) correspond essentially to those of a free particle, as specified above by the asymptotic boundary conditions.
At this point \((r_0 = b)\), the equations obtained from matching the intermediate and external solutions \(u^{(h)}(r_0)\) at \(r_0 = b\) (see Eq. (3.31)), are then solved to determine the collision matrix in terms of the \(R\)-matrix calculated at \(b\):

\[
U = (Z^+)^{-1}Z^-.
\]  

(4.22)

where

\[
Z^\pm = [1 - RL^\pm] \zeta^\pm,
\]

(4.23)

and \(L^\pm\) and \(\zeta^\pm\) are the diagonal matrices defined in Eqs. (3.31), (3.34) and (3.36).

The cross sections are then calculated in terms of collision \(U\)-matrix elements. In the present work which is concerned only with integrated cross sections for a transition from the ground vibrational and rotational level \((vK = 00)\) to corresponding vibrational and rotational levels \((v'K')\) of the \(^1\Sigma_g^+\) state of \(H_2\), the integrated cross sections can be obtained from Section 3.2.4, using Eqs. (3.85) and (3.86). In particular, the cross section for a given transition, \(00 \rightarrow v'K'\), is

\[
sigma(00 \rightarrow v'K') = \frac{\pi k_i^{-2}}{2(2K + 1)} \sum_{l_j l_0 j_0} (2I + 1) |\delta_{f_i} - U(v'K'l_j; 00l_0 j_0; I)|^2,
\]

(4.24)

where \(i\) and \(f\) are the initial and final channels respectively (e.g., see Eq. (3.79)), and \(U\) the collision matrix.

4.3 CALCULATION OF THE CROSS SECTIONS

In this section the procedure used for the scattering calculations are described and the results for the cross sections presented and discussed. The details for the calculations of the matrix elements of \(G\) to evaluate the \(R\)-matrix at the internal radius region and the subsequent technique for the propagation of the \(R\)-matrix have already been described in detail in Chapter 3 and only a brief description of the procedures used in the present calculations will be given below to emphasise the differences between these calculations and the previous ones in Chapter 3 when the closed electronic channels are included. Since all the matrix elements of \(G\) (listed in Appendix B) were already coded previously for the work in Chapter 3, there was no need to make any extensive modifications to the main program.

4.3.1 Numerical Procedures

As in the \(R\)-matrix calculations of the previous chapter, the radius of the internal region was set at \(a = 10\) a.u. However, in contrast to the latter calculations the number of radial integrals (listed in Appendix B) that are now required to compute the matrix elements of \(G\) (also listed in Appendix B) for the internal region, increase considerably in size, because of the different basis functions that were used when
constructing the wave functions for the different electronic $1\Sigma_g^+, 1\Sigma_u^+$, and $1\Pi_u$ states of H$_2$. Even with the relatively small basis set size used for the molecular wave functions (described below), the number of radial integrals is several million.

This increase in the number of integrals is also due to the fact that there are also integrals which overlap between the basis set $f_M$ used for the scattering wave function expansion in the internal region with those used for the different molecular wave functions (cf. Appendix B). In the present work, $f_M$ are taken as regular spherical functions of argument $l$ (Eq. (4.9)), whose eigenvalues $\epsilon_M$ are determined by the boundary condition given in (4.10), with $B = -1$. In particular, for each $l$, 12 values of $\lambda$ were taken, i.e., $1 \leq \lambda \leq 12$. As in Chapter 3, this was found necessary, in order to obtain sufficient convergence in the calculated cross sections.

Table 4.1. Selected quadrupole ($Q$) and polarisability ($\alpha_{||}, \alpha_{\perp}$) matrix elements (in a.u.) produced by the variational wave functions used in the scattering calculations and comparisons with those calculated by Poll and Wolniewicz (1978)[PW] and Kolos and Wolniewicz (1967)[KW].

| $v'K'$ | PW $\langle v'K'|Q|00\rangle$ | PW $\langle v'K'|\alpha_{||}|00\rangle$ | PW $\langle v'K'|\alpha_{\perp}|00\rangle$ | KW $\langle v'K'|Q|00\rangle$ | KW $\langle v'K'|\alpha_{||}|00\rangle$ | KW $\langle v'K'|\alpha_{\perp}|00\rangle$ | Present results $\langle v'K'|Q|00\rangle$ | Present results $\langle v'K'|\alpha_{||}|00\rangle$ | Present results $\langle v'K'|\alpha_{\perp}|00\rangle$ |
|-------|-------------------------------|---------------------------------------------|---------------------------------------------|-----------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| 00    | 0.48354                       | 6.7632                                      | 4.7493                                      | 0.480                       | 3.272                                       | 2.732                                       | 0.480                                       | 3.272                                       | 2.732                                       |
| 02    | 0.07833                       | 6.7814                                      | 4.7476                                      | 0.099                       | 3.302                                       | 2.741                                       | 0.099                                       | 3.302                                       | 2.741                                       |
| 10    | 0.08789                       | 1.1454                                      | 0.5357                                      | 0.1076                      | 1.844                                       | 0.535                                       | 0.1076                                      | 1.844                                       | 0.535                                       |

For the molecular wave functions used in the calculations, these are implemented from those generated in Chapter 2 (see Section 2.5). The ground $1\Sigma_g^+$ state wave functions, as used for example in Chapter 3, correspond to the 7-state configuration variational model described in Section 2.5, which was obtained there using 7 configurations for the electronic basis functions $\psi_{\alpha}$ and $n_{\text{max}} = 6$ for the vibrational basis functions $\chi_{\alpha}^2$. The molecular states produced with this model, and which are used in the present scattering calculations, have already been listed in Table 3.1. The states employed therefore consist of three vibrational levels $v = 0, 1, \text{and } 2$, with the rotational states in each vibrational band restricted to $K = 0$ and $K = 2$.

For the excited $1\Sigma_g^+$, and $1\Pi_u$ states, the Model 1 wave functions that were generated for them in Chapter 2 (see Section 2.5) are used. As described there, these wave functions consist of a single electronic basis configuration $\psi_{\alpha}$ with odd
electronic parity, and are obtained with a basis set size of $n_{\text{max}} = 3$ for the vibrational functions $\chi_n^\alpha$. The corresponding molecular states that are retained in the present calculations are two vibrational levels $v = 1$, and 2, for $1\Sigma_+^+$, and three vibrationla ones $v = 1, 2, \text{and } 3$, for $1\Pi_u$.

It is worth remembering that the molecular states for the odd-parity $1\Sigma_+^+$, and $1\Pi_u$ bands are taken to be degenerate with respect to their rotational levels and that the vibrational energy levels produced by them are poor by comparison with spectroscopic standards (see Table 2.6). There were essentially two reasons given in Chapter 2 (see Sections 2.4 and 2.6), why this should not be be a serious defect. The first is that the rotational and vibrational transition cross sections calculated in the present study are associated with those in the $1\Sigma_+^+$ state of $\text{H}_2$, so the fact that the energy levels for the odd-parity states are poorly reproduced, should not be important in the scattering problem. Secondly, the significance of polarisation effects in the scattering problem, is expected to be reflected through the numbers that are produced for the polarisability matrix elements (see also the remarks below Eq. (2.76)). Indeed, the calculations carried out in Chapter 2, gave precedence to obtaining wave functions that are able to reproduce those properties of the molecule that are expected to be important for the scattering problem.

It is for these reasons that the present scattering work aims more at an understanding of the main quantities controlling the scattering, by using relatively simple molecular wave functions that have been selected according to the values they produce for the quadrupole and polarisability matrix elements. For the wave functions employed in the present calculations the values for the latter matrix elements that were produced by them in Chapter 2, are recalled in Table 4.1. The accurate values for the matrix elements, as calculated by Poll and Wolniewicz (1978) and Kolos and Wolniewicz (1967), are also listed in the table for comparisons.

As previously explained (see Section 3.5), the matrix $G$ is decomposed into submatrices that are classified according to definite values of the total angular quantum number $P$, where $P = \pm$ denotes the total electronic parity of the channel. The permitted values of $(K, l, j)$ and the channels that arise when the restrictions on $l$ is $l = 0, 1, 2$ for the ground $1\Sigma_+^+$ state, and when $1 \leq l \leq 3$ for the odd-parity $1\Sigma_+^+$ and $1\Pi_u$ states are listed in Table 4.2. The restriction on $l$ for the ground state is justified to the extent that the main contributions to the cross sections are expected to come from the first few partial waves of the scattered electron as was discovered in the cross section results of the preceding chapter. For the odd-parity channels, the values of $l$ are retained in so far as they are required to ensure that the full effects of polarisation which arise from these closed channels are taken into account. The total number of channels when all these considerations are taken into account lead to the numbers quoted in Table 4.2. The reluctance of previous scattering studies
Table 4.2. The channels and permitted values of \( (k, l, j) \) used in the scattering calculations when the ground \( 1\Sigma_g^+ \), and excited \( 1\Sigma_u^+ \) and \( 1\Pi_u^+ \) states were retained in the scattering wave function expansion.

<table>
<thead>
<tr>
<th>( I^* )</th>
<th>( 1\Sigma_g^+ )</th>
<th>( 1\Sigma_u^+ )</th>
<th>( 1\Pi_u^+ )</th>
<th>Total Number of channels</th>
<th>Size of ( G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2}^- )</td>
<td>( (0,1,1/2) )</td>
<td>( (0,1,1/2) )</td>
<td>( (1,0,1/2) )</td>
<td>27</td>
<td>324</td>
</tr>
<tr>
<td>( \frac{1}{2}^- )</td>
<td>( (2,1,3/2) )</td>
<td>( (1,2,3/2) )</td>
<td>( (2,2,3/2) )</td>
<td>( (3,2,5/2) )</td>
<td></td>
</tr>
<tr>
<td>( \frac{3}{2}^- )</td>
<td>( (0,1,3/2) )</td>
<td>( (1,0,1/2) )</td>
<td>( (1,2,3/2) )</td>
<td>( (3,2,5/2) )</td>
<td>43</td>
</tr>
<tr>
<td>( \frac{3}{2}^- )</td>
<td>( (2,1,1/2) )</td>
<td>( (1,2,5/2) )</td>
<td>( (2,2,5/2) )</td>
<td>( (3,2,5/2) )</td>
<td>35</td>
</tr>
<tr>
<td>( \frac{1}{2}^+ )</td>
<td>( (0,0,1/2) )</td>
<td>( (1,1,1/2) )</td>
<td>( (1,1,1/2) )</td>
<td>54</td>
<td>648</td>
</tr>
<tr>
<td>( \frac{3}{2}^+ )</td>
<td>( (0,2,3/2) )</td>
<td>( (1,1,1/2) )</td>
<td>( (1,1,1/2) )</td>
<td>( (3,3,7/2) )</td>
<td>59</td>
</tr>
<tr>
<td>( \frac{5}{2}^+ )</td>
<td>( (0,2,5/2) )</td>
<td>( (1,1,1/2) )</td>
<td>( (1,1,1/2) )</td>
<td>70</td>
<td>848</td>
</tr>
</tbody>
</table>
to represent polarisation effects in collision theory as manifestations arising from the virtual transitions to the closed electronic $^1\Sigma_u^+$ and $^1\Pi_u$ channels, can be appreciated from the overall number of channels that increases substantially in number (as can be seen from Table. 4.2) when excited electronic states are included.

Once the matrix elements of $G$ were evaluated and the inverse of $G$, and hence the $R$-matrix, calculated at $r = a$, the coupled equations were then solved by a series of integrations steps to propagate the $R$-matrix in the intermediate region outwards to the external region radius at $r = b$. The details of the propagation has already been described in detail in Section. 3.5, where the matrices $M_{ij}$ (in Eq. 4.19) which link the $R$-matrices between the internal and external boundaries, are most simply determined by numerically integrating the coupled equations using $2m$ linearly independent vectors having zeros and ones as their components according to the pattern suggested by Eq. (3.123). In this way the well known difficulty with the exponentially increasing solutions corresponding to the closed electronic $^1\Sigma_u^+$ and $^1\Pi_u$ channels may be circumvented by carrying out the integrations in steps of 5.0 a.u. Thus the strategy employed in Section. 3.5.2 makes use of this option to propagate the $R$-matrix calculated at $r = a$ in such steps to a radius $r = b$ such that the collision matrix, and hence the cross sections, obtained from $R(r)$ for the last few steps did not differ significantly from each other. As in the calculations of the previous chapter, the value of $\theta = 100$ a.u. was in practice found to be sufficient.

As before (Section. 3.5), checks were made to ensure that the matrix elements of $G$ produced a real and symmetric matrix, since this ensures that the $R$-matrix is also real and symmetric, which in turn is needed to preserve the unitarity and symmetric nature of the collision matrix. Because of the size of the matrices considered for $G$ (see Table. 4.2), these checks were carried out over randomly selected matrix elements for each value of $I^P$.

### 4.3.2 The Cross Sections

In this section, integrated cross sections for the collision of low-energy electrons ($\leq 1.2$ eV) by the $^1\Sigma_u^+$ state of $\text{H}_2$ are presented. The cross sections are for elastic scattering and rotational and vibrational excitation processes. These were calculated in terms of the partial wave contributions, which may be obtained from Eq. (4.24) as follows:

\[
\sigma(00 \rightarrow v'K') = \sum_{I\ell_0} \sigma_{I\ell_0}(00 \rightarrow vK')
\]

where $\sigma_{I\ell_0}$ are the partial wave contributions given by

\[
\sigma_{I\ell_0}(00 \rightarrow v'K') = \frac{\pi k_i^{-2}}{2(2K + 1)} \sum_I (2I + 1) \sum_{j\ell_0} |\delta_{ij} - U(00;0;v'K';j;I)|^2
\]
Here $l_0$ and $l$ are the orbital angular momentum quantum numbers of the scattered electron respectively in the initial (entrance) $i$ and final (exit) $f$ channels.

To make comparisons with the results produced in the previous chapter, the present calculations, in which all the channels listed in Table 3.2 were used in the scattering calculations (i.e., when polarisation effects from the closed electronic $^1\Sigma_u^+$ and $^1\Pi_u$ channels are included) will be referred to as the CEPOL model calculation. Likewise the results of the previous chapter in which only $^1\Sigma_g^+$ channels were used in the scattering calculations, will be referred to as the GS model calculation.

**Table 4.3.** Partial $l_0 \rightarrow l$ wave transitions for elastic $\sigma_{l_0l}(00 \rightarrow 00)$ scattering and rotational $\sigma_{l_0l}(00 \rightarrow 02)$ excitation cross sections (in units Å$^2$) at selected energies.

(1.0$[-1]$ = 10$^{-1}$)

<table>
<thead>
<tr>
<th>E(eV)</th>
<th>$s \rightarrow s$</th>
<th>$p \rightarrow p$</th>
<th>$d \rightarrow s$</th>
<th>$p \rightarrow p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>19.121 0.478$[-1]$</td>
<td>0.140$[-1]$</td>
<td>0.103$[-2]$</td>
<td></td>
</tr>
<tr>
<td>0.08</td>
<td>18.689 0.145</td>
<td>0.135$[-1]$</td>
<td>0.113$[-2]$</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>18.209 0.284</td>
<td>0.144$[-1]$</td>
<td>0.217$[-1]$</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>16.689 0.917</td>
<td>0.779$[-2]$</td>
<td>0.260$[-1]$</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>13.939 2.918</td>
<td>0.719$[-2]$</td>
<td>0.509$[-1]$</td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>13.517 3.544</td>
<td>0.563$[-2]$</td>
<td>0.175$[-1]$</td>
<td></td>
</tr>
<tr>
<td>0.70</td>
<td>13.256 3.932</td>
<td>0.494$[-2]$</td>
<td>0.929$[-1]$</td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td>13.114 4.372</td>
<td>0.529$[-2]$</td>
<td>0.153$[-1]$</td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>13.057 4.790</td>
<td>0.457$[-2]$</td>
<td>0.109</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>13.057 4.544</td>
<td>0.429$[-2]$</td>
<td>0.126</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.961 0.979$[-1]$</td>
<td>0.356$[-2]$</td>
<td>0.178</td>
<td></td>
</tr>
</tbody>
</table>
Also in Tables 4.3 and 4.4, only the dominant partial wave transitions to the cross sections are listed. The first number shown in these tables at a given energy are the CEPOL results and those directly below are the GS ones.

By comparing the results for the CEPOL and GS calculations, it can be seen from Table 4.3, that the effects of polarisation is to decrease the partial wave \( s \rightarrow s \) contribution to the elastic cross section as the energy approaches zero and increase its \( p \rightarrow p \) component as the energy increases. These results have also been plotted in Figure 4.1.

**Table 4.4.** Partial \( l_0 \rightarrow l \) wave transitions for pure vibrational \( \sigma_{l_0l}(00 \rightarrow 10) \) and ro-vibrational \( \sigma_{l_0l}(00 \rightarrow 12) \) excitation cross sections (in units \( \text{Å}^2 \)) at selected energies. 

\[ (1.0 \times 10^{-1}) \]

<table>
<thead>
<tr>
<th>E(eV)</th>
<th>( \sigma_{l_0l}(00 \rightarrow 10) )</th>
<th>( \sigma_{l_0l}(00 \rightarrow 12) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( s \rightarrow s )</td>
<td>( p \rightarrow p )</td>
</tr>
<tr>
<td>0.52</td>
<td>0.143[-3]</td>
<td>-</td>
</tr>
<tr>
<td>0.60</td>
<td>0.141[-2]</td>
<td>-</td>
</tr>
<tr>
<td>0.70</td>
<td>0.943[-3]</td>
<td>-</td>
</tr>
<tr>
<td>0.727[-3]</td>
<td>0.106[-3]</td>
<td>0.340[-3]</td>
</tr>
<tr>
<td>0.70</td>
<td>0.164[-2]</td>
<td>0.396[-4]</td>
</tr>
<tr>
<td>0.70</td>
<td>0.100[-1]</td>
<td>0.378[-3]</td>
</tr>
<tr>
<td>0.80</td>
<td>0.225[-2]</td>
<td>0.189[-3]</td>
</tr>
<tr>
<td>0.80</td>
<td>0.117[-1]</td>
<td>0.788[-3]</td>
</tr>
<tr>
<td>0.90</td>
<td>0.278[-2]</td>
<td>0.501[-3]</td>
</tr>
<tr>
<td>0.90</td>
<td>0.126[-1]</td>
<td>0.133[-2]</td>
</tr>
<tr>
<td>1.00</td>
<td>0.324[-2]</td>
<td>0.101[-2]</td>
</tr>
</tbody>
</table>

The explanation of the behaviour observed in the the partial \( s \)- and \( p \)-wave transitions to the elastic cross section can be understood along a similar line of reasoning given in Chapter 3 (see Section 3.6), where the consequence of including exchange effects in the scattering was noted to increase the overall attractiveness of the static electron-molecule interactions, and thus produce a general increase in the phase shifts. By incorporating polarisation effects one has also effectively increased the attractiveness of the long range part of the potential, so that the \( s \)- wave phase shifts now become closer to \( \pi \) with the \( p \)-wave phase shifts increasing as well. As
pointed out by Schneider (1975) this causes the elastic cross section to turn over and decrease towards zero as the energy approaches zero. Similarly, the consequence of an increase in the $p$-wave phase shifts is to increase the elastic cross section as the energy becomes higher. As can be seen by comparing the numbers between the CEPOL and GS models in Table 4.3 (see also Figure 4.1), the present results seem to follow this trend. It is worth mentioning that similar trends are also observed in the elastic cross section for $e$-He when polarisation effects are included (e.g., see Barrett and Robson, 1979b).

In Figure 4.2, the present results produced with the CEPOL and GS models for the total elastic cross section (with all the partial $s$, $p$, and $d$-wave components included) are plotted and compared with the elastic cross section results of Nesbet et al. (1986), Morrison and Saha (1986) and Morrison and Collins (1978). In contrast to Morrison and Collins, both Nesbet et al. and Morrison and Saha include polarisation effects in their calculations. For example, the $R$-matrix variational calculations of Nesbet et al. incorporate polarisation effects by using $^{1}\Sigma_u^+$ and $^{1}\Pi_u$ pseudo states to represent the closed channels. Their calculations are based on the fixed-nuclei approximation in which the internuclear distance of the $H_2$ molecule is held fixed at its equilibrium value of $R = 1.4$ a.u. The calculations of Morrison and Saha include polarisation effects by using a model potential that was developed by Gibson and Morrison (1984). The latter authors refer to this model potential as the “better than adiabatic dipole potential” (BTAD), because it retains only the electric-
Figure 4.2. Comparison of the total elastic $\sigma(00 \rightarrow 00)$ scattering cross sections (in Å²) from the present study using the CEPOL (——) and GC (-----) models with Nesbet et al. (1986) (○), Morrison and Saha (1986) (●) and Morrison and Collins (1978) (△).

dipole term in the potential. Their calculations are also based on the fixed-nuclei approximation whereby exchange effects are treated exactly, with the elastic cross section calculated by averaging over the ground state vibrational wave functions. On the other hand, the calculations of Morrison and Collins neglect polarisation effects, and as mentioned in Section 3.6, use the rigid-rotor approximation with exchange effects treated exactly.

As can be seen in Figure 4.2, when polarisation effects are neglected the calculations of Morrison and Collins do not reproduce the expected trend mentioned above in relation to the elastic cross section approaching zero as the energy goes to zero, such as that seen in the calculations of Nesbet et al. and Morrison and Saha. It can also be seen that the elastic cross section result for all these other calculations lie below those produced in the present study with the GS and CEPOL models. This is probably due to the fact that long range part of the polarisation potential is not well represented in the present study (i.e., the polarisability matrix elements that enter the polarisation potential in Eq. (4.17); see also the remarks below it). For example, the polarisabilities used by Nesbet et al. are (at $R$=1.4 a.u)

$$\alpha_{||} = 6.29298 \text{ a.u.}, \quad \alpha_{\perp} = 4.4573 \text{ a.u.},$$

(4.27)

whereas those for Morrison and Saha are (at $R$=1.4 a.u)

$$\alpha_{||} = 6.499 \text{ a.u.}, \quad \alpha_{\perp} = 4.542 \text{ a.u.}$$

(4.28)
Figure 4.3. Present results for the (a) rotational $\sigma(00 \rightarrow 02)$ and the (b) total vibrational $\sigma(00 \rightarrow 02)$ excitation cross sections (in Å²). Plots in each figure are for the CEPOL (—) and GS (- - -) models.

In the present study, the polarisability matrix elements relevant to the elastic scattering are those taken between the ground state wave functions given in Table 4.1 as

$$\langle 00|\alpha_\parallel|00 \rangle = 3.272 \text{ a.u.}, \quad \langle u'K'\alpha_\perp|00 \rangle = 2.732 \text{ a.u}$$

These values are clearly smaller than those used above by Nesbet et al. and Morrison and Saha, which are closer to the accurate values calculated by Kolos and Wolniewicz (1967) (see Table 4.1).

As was discussed in Section 3.6, another reason why the present results for the elastic cross section are higher than those of Morrison and Collins in Figure 4.2, and which may also be the reason why it is so in the present case when polarisation effects have been included, is probably because the ground state wave functions used in the present calculations do not produce a strong enough attractive static potential. This is of course due to the fact that the ground state energy for the wave functions used in this study for the $^1\Sigma_g^+$ of H$_2$ is $-1.060$ a.u (see Table 3.1) as compared with the corresponding values of $-1.16989$ a.u., $-1.13295$ a.u. and $-1.1335$ a.u., used by Nesbet et al., Morrison and Saha, and Morrison and Collins, respectively. Nevertheless, the present results for the elastic cross section, as mentioned above, appear to reproduce the correct trends in the elastic cross section, in so far as there is a lowering in the elastic s-wave component as the energy approaches zero and an increase in the p-wave component as the energy becomes higher.

In Figure 4.3, the present results for the pure rotational $\sigma(00 \rightarrow 02)$ and total $\sigma(00 \rightarrow 10)$ vibrational excitation cross sections are displayed. The total vibrational
cross section is obtained by summing the vibrational cross sections over the final rotational states or in other words by adding the pure vibrational $\sigma(00 \rightarrow 10)$ and ro-vibrational $\sigma(00 \rightarrow 12)$ excitations cross sections together.

As can be seen, the CEPOL results for both the rotational and vibrational cross sections, are smaller than the corresponding ones for the GC model (see also Tables. 4.3 and 4.4).

This is in contradiction with that observed in previous scattering studies. Indeed, polarisation effects are supposed to be the main factor enhancing both the rotational and vibrational cross sections. In the case of the rotational excitations, and in the language of Lane and Geltman (1967), the effects due to polarisation or distortion, are to draw the wave functions of the scattered electron closer to the molecule where it can overlap strongly with the anisotropic part of the interaction potential thereby giving a larger rotational cross section. This means that the anisotropic part of the polarisation potential (see Eq.-(4.17)) will affect the $p$-wave component of the scattered electron. This is in fact the case, where the $p$-wave contribution to the rotational cross section is found to enhance the rotational cross section at energies well above threshold. This is in contradiction with that observed in the present results, which can be seen by comparing the numbers in Table. 4.3 between the CEPOL and GC models. The CEPOL results show, instead, that the effect of including polarisation effects reduces the $p$-wave component when compared with those produced with the GC model, which does not include polarisation effects.

For the case of the vibrational cross sections shown in Figure. 4.3, the situation is even more serious, since polarisation effects are in fact the main mechanism enhancing vibrational excitations. The study by Takayanagi (1965), for example, is based on the idea that the vibrational cross sections become large in magnitude because the $p$-wave electron becomes temporarily trapped near the vicinity of the molecule at low energies. Thus, in his distorted wave treatment of the problem, Takayanagi finds that both the anisotropic and isotropic parts of the long range polarisation potential are extremely important for enhancing the magnitude of the vibrational cross sections.

Though polarisation effects in the present study are found not to enhance the vibrational cross section to a great extent there are indications that the present results for the vibrational cross sections are sensitive to $p$-waves. For example, by comparing the numbers between the CEPOL and GC results in Table. 4.4, it can be seen that the effect of polarisation effects is to increase the partial $p$-wave contributions for both the pure vibrational and ro-vibrational cross sections, with the latter being affected only slightly.

Despite these sensitivities, the discrepancies mentioned above between this study and those observed in other studies for the rotational and vibrational cross sections
still lacks explanation. At this stage several checks for numerical and programming errors were carried out. Firstly, the subroutine for the propagation of the $R$-matrix was interrupted at several intermediate values of $b$ to check that the symmetry of the $R$-matrix was preserved throughout its propagation in the intermediate region. When this was satisfied, instructions were also included into the propagation subroutine to output numbers for the matrix elements for the quadrupole and electric-dipole parts of the potential in Eqs. (4.16) and (4.18). This was to check that the wave functions that entered into the scattering calculations were in fact the correct ones within the values they specified on input into the main program for the quadruple and polarisability matrix elements. The code for the calculation of the matrix $G$ was also checked to make certain that the matrix elements as listed in Appendix B and the Racah algebra for them were coded correctly. So far no programming errors have been detected in this part of the calculations though more detailed checks are intended at a later date.

Some insight into understanding the present results was also gained by analysing the work of Lane and Geltman (1967). These authors, for instance, stress that the coupling of the different partial wave components between the elastic and inelastic cross sections must be taken into account. In particular they demonstrate that using polarisation potentials to fit elastic cross sections to experiment, which require adjusting the $s$-wave phase shifts, in no way guarantees the correctness in the $p$-wave scattering. As a result, Lane and Geltman find that a change in the rotational cross section can produce changes in the elastic scattering by a factor of 3.

This result is important to the present work, because it suggests that perhaps what is being reproduced in the present calculations is a consequence of the coupling between the elastic, rotational and vibrational channels. Thus, since the present results for the elastic cross sections have yet to converge, in the sense observed for the other calculations shown in Figure. 4.2, the corresponding changes (i.e., the amount of outgoing flux in the inelastic channels) in the rotational and vibrational cross sections are underestimated. This in turn suggests that the effect due to coupling between the elastic and inelastic channels are important and that having polarisation effects in the scattering calculations in no way automatically ensures an increase in the magnitude of the rotational and vibrational cross sections.

At the present stage, this is still on exploratory grounds, and further calculations are definitely needed in order to underpin the precise nature of the effects due to coupling between the elastic, rotational and vibrational channels. Such calculations are intended in the near future, especially since the ultimate aim of the present $R$-matrix framework developed for low-energy $e$-$\text{H}_2$ scattering is to provide reliable cross sections for comparison with experiment.
4.4 OUTLOOK

In this chapter, the $R$-matrix framework developed in Chapter 3 has been applied to incorporate the effects of polarisation by including the closed odd-parity electronic channels in the calculations. The results of this chapter show that the cross section for elastic rotational and vibrational excitation are sensitive to the polarisation effects. Further, the cross sections appear to be sensitive to the coupling between the elastic and inelastic channels. If conservation of flux in these channels is to be conserved, the intimate nature of the coupling between the elastic and inelastic channels may explain why the present results for the inelastic cross sections are underestimated. This stresses the importance of obtaining reliable elastic cross sections in order to derive meaningful inelastic cross sections.

At this stage, this is rather speculative and further calculations are needed to clarify the present results. The obvious directions for future work are (i) more accurate wave functions for ground state of $H_2$ and (ii) the inclusion of more odd-parity states to give a better representation of the polarisation effects in the scattering.

Despite the unexpected nature of the cross sections calculated in this chapter, the present research has completed all the necessary formal aspects of a theory of low-energy $e$-$H_2$ scattering within the framework of the $R$-matrix method. Further, the present approach does not rely on the use of either the fixed-nuclei approximation or an effective potential for the treatment of polarisation effects. This provides a solid theoretical basis for further calculations to be carried out within the present $R$-matrix approach. The calculations performed in Chapter 3 and the present chapter have therefore been useful in demonstrating the techniques and numerical procedures required for more sophisticated calculations. This is important if the long term objective of their research is to be attained: the resolution of the discrepancy between the various experiments and theories for the vibrational excitation cross section of $H_2$.

Perhaps the best way to summarise this research is to appeal to authority (Lane, 1980):

If one judges a careful *ab initio* calculation... by how well the cross section agrees with experiment, the value of the work will be totally missed.
Appendix A

A.1 TRANSFORMATION TO BODY-FIXED COORDINATES

To carry out the transformation of the Laplacian $\nabla_R^2$ from the spaced fixed system $O_{x'y'z'}$ to the rotating reference system $O_{xyz}$, introduced in Section 2.2.1, requires first evaluating the partial derivatives with respect to the $R$ in the two systems. This may be characterised in the following way (written in vector operator form):

$$\frac{\partial}{\partial R} \to \frac{\partial}{\partial R} + \sum_{i=1}^{2} \frac{\partial r_i}{\partial R} \frac{\partial}{\partial r_i}. \quad (A.1)$$

where the differentiations carried out on the right hand side of (A.1) acquire additional terms in the body-frame $O_{xyz}$, because of the implicit dependence of the electronic $r_i$ coordinates on the $\theta$ and $\phi$ coordinates of $R$. This was specified in the main text via the rotation matrix $D(\theta, \phi)$ in Eq. (2.5):

$$r_i = D(\theta, \phi)r_i'. \quad (A.2)$$

It is then straightforward to show from this transformation that the partial derivatives of (A.1) with respect to the spherical polar coordinates of $R$ lead to the following replacements in the body-frame $O_{xyz}$:

$$\frac{\partial}{\partial \theta} \to \frac{\partial}{\partial \theta} - i L_{ey} \quad (A.3)$$

$$\frac{\partial}{\partial \phi} \to \frac{\partial}{\partial \phi} - i \cos \theta L_{ey} + i \sin \theta L_{ex} \quad (A.4)$$

where the transformation to body-fixed coordinates is seen to involve the components $L_{ei}(i = x, y, z)$ of the total electronic angular momenta in $O_{xyz}$:

$$L_e = -i \sum_{i}^{2} r_i \times \nabla r_i. \quad (A.5)$$

Subsequently, the transformation of $\nabla_R$ to the rotating frame $O_{xyz}$ takes the form

$$\nabla_R \to \nabla_R - i(1/R)[e_\theta L_{ey} + e_\phi (\cot \theta L_{ex} - L_{ex})], \quad (A.6)$$
so that, after some lengthy vector calculus, one obtains for the transformation of \( \nabla^2_R \) to body-fixed coordinates, the result:

\[
\nabla^2_R \rightarrow \nabla^2_R + \frac{1}{R^2} \left( L_{ex} - L^+_e L^-_e - \cot \theta^2 L^2_{ez} - 2i \frac{\cot \theta}{\sin \theta} L_{ez} \frac{\partial}{\partial \phi} \right) + \frac{L^+_e}{R^2} \left( -\frac{\partial}{\partial \theta} + \cot \theta L_{ez} + \frac{i}{\sin \theta} \frac{\partial}{\partial \phi} \right) + \frac{L^-_e}{R^2} \left( -\frac{\partial}{\partial \theta} + \cot \theta L_{ez} + \frac{i}{\sin \theta} \frac{\partial}{\partial \phi} \right)
\]

(A.7)

where \( L^\pm_e = L_{ez} \pm i L_{ex} \) are the raising and lowering operators of the electronic angular momentum in the rotating frame \( O_{xyz} \).

### A.2 EVALUATION OF THE RADIAL INTEGRALS

The radial integrals for the electron-electron repulsion contribution to the matrix elements, as given by Eq. (2.65), contain products over the electronic radial basis functions \( R_{nl} \). Each of these radial functions were related in terms of the associate Laguerre polynomials \( L_n^{\alpha} \) (given in Eq. (2.41)), which in turn have a finite series representation of the form (cf. 8.971.1, Gradshteyn and Ryzhik, 1965):

\[
L_n^\alpha(x) = \sum_k A_k^\alpha x^k,
\]

(A.8)

where \( A_k^\alpha \) have binomial coefficients given by

\[
A_k^\alpha = (-1)^k \binom{n + \alpha}{k} \frac{1}{m!}.
\]

(A.9)

If one uses (A.8) for each of the Laguerre polynomials occurring in (2.65), one can obtain the first integration inside in the square paranthesis of (2.65) as integrals over powers and exponentials of the variable \( x = \omega_e r^2 \):

\[
\frac{N_{n_a l_a} N_{n_b l_b}}{2 \omega_e} \sum_{k_a k'_a} A_{k_a}^n A_{k'_a}^n \left\{ \frac{1}{(\sqrt{\omega_e r^2})^{L+1}} \int_0^{\omega_e r^2} dx e^{-\frac{x}{2}} \left( \frac{2}{L+1} \right)^{L+1} \Gamma \right\}
\]

(A.10)

These integrals (as defined, e.g., in 8.350.1 and 8.350.2 of Gradshteyn and Ryzhik, 1965) are respectively the incomplete gamma functions, \( \gamma(\alpha, x) \) and \( \Gamma(\alpha, x) \). Thus, (A.10) gives

\[
\frac{N_{n_a l_a} N_{n_b l_b}}{2 \omega_e} \sum_{k_a k'_a} A_{k_a}^n A_{k'_a}^n \left[ \frac{1}{(\sqrt{\omega_e r^2})^{L+1}} \Gamma(p + \frac{3}{2}, \omega_e r^2) + (\sqrt{\omega_e r^2}) L \Gamma(p' + 1, \omega_e r^2) \right]
\]

(A.11)
The final integration over the variable \( r_2 \) in (2.65) then, involve integrals over products of the incomplete gamma functions, and powers and exponentials of the variable \( x = \omega_c r_2^2 \):

\[
\frac{N_{n_a l_a} N_{n_b l_b}}{4\omega_c^2} \sum_{k_a k_b' k_b} A_{n_a l_a} A_{n_b l_b} A_{n_b l_b'} A_{n_b l_b} \times \left[ \int_{0}^{\infty} dx e^{-x} x^q \Gamma(p, 1, x) + \int_{0}^{\infty} dx e^{-x} x^{q'} \Gamma(p', 1, x) \right],
\]

\( q = k_b + k_b' + \frac{l_b + l_b' - L}{2}, \quad q' = k_b + k_b' + \frac{l_b + l_b' + L}{2} \) \hspace{1cm} (A.12)

which can be obtained by elementary means (cf. 6.455.1, 6.455.2, Gradshteyn and Ryzhik, 1965):

\[
\int_{0}^{\infty} dx e^{-x} \left\{ x^{q'} \Gamma(p, 1, x) \right\} = \frac{\Gamma(p + q + \frac{5}{2})}{(p + \frac{3}{2})^{q' + \frac{3}{2}}} F(1, p + q + \frac{1}{2}; p + \frac{5}{2}; \frac{1}{2}) \hspace{1cm} (A.13)
\]

where \( F(a, b; c; x) \) are the hypergeometric functions (9.100, Gradshteyn and Ryzhik, 1965).

That the final result for \( I_L \) (Eq. (2.65)) may be written as finite sums over the terminating series of the hypergeometric functions:

\[
I_L(n_{a l_a} N_{n_b l_b}, n_{a l_a} N_{n_b l_b}) = (\omega^{-5/2}/4) N_{n_b l_b} N_{n_b l_b} \sum_{k_a k_b' k_b} A_{n_a l_a} A_{n_b l_b} A_{n_b l_b} A_{n_b l_b} \times \left[ \Gamma(p + q + \frac{5}{2}) \right] (p + \frac{3}{2})^{2p + \frac{5}{2}} F(1, p, q + \frac{3}{2}; q + \frac{5}{2}, \frac{1}{2}) \]

\( \hspace{1cm} (A.14) \)

follows from substituting the transformation (cf. 9.131.1, Gradshteyn and Ryzhik, 1965), \( F(a, b; c; x) \rightarrow (1 - x)^{-a-b} F(c-a, c-b; c; x) \), for the hypergeometric functions contained on the right hand side of (A.13), and using the fact that the arguments \( p', q', p, \) and \( q \), in Eqs. (A.10) and (A.12), all take on integral values.

The radial integrals \( J_L \) (Eq. (2.67)) for the electron-proton attraction terms, consist of products involving the electronic radial basis functions \( R_{nl} \) and the vibrational basis \( \chi_n \) (Eq. (2.46)). It is convenient to first carry out the integration over the radial functions \( R_{nl} \). This then leads to the same result given by (A.10) above. Thus \( J_L \), so far, is given by

\[
\frac{N_{n_a l_a} N_{n_b l_b}}{2\omega_c} \sum_{k_a k_b} A_{n_a l_a} A_{n_b l_b} \int_{0}^{\infty} dR \chi_n(R) \left[ \frac{1}{(\sqrt{\omega_c r_2})^{L+1}} \gamma(p + \frac{3}{2}, \omega_c R^2/4) \right. \left. + (\sqrt{\omega_c r_2})^{L} \Gamma(p' + 1, \omega_c R^2/4) \right] \chi_n(R) \]

\( \hspace{1cm} (A.15) \)
where the arguments $p$ and $p'$ appearing in the incomplete gamma functions shown above are those defined in (A.10). Some further manipulation of the incomplete gamma functions are made as follows. This requires using the relations (cf. 8.356.3, 8.356.5, Gradshteyn and Ryzhik, 1965):

$$
\Gamma(N + \alpha + 1, x) = \Gamma(N + \alpha + 1) \left[ \frac{\Gamma(\alpha, x)}{\Gamma(\alpha)} + e^{-x} \sum_{s=0}^{N} \frac{x^{s+\alpha}}{\Gamma(s + \alpha + 1)} \right],
$$

$$
\gamma(\alpha, x) + \Gamma(\alpha, x) = \Gamma(\alpha),
$$

(A.16)
to rewrite the first incomplete gamma function appearing inside the square paranthesis of (A.15) as

$$
\gamma(N + \alpha + 1, x) = \frac{\Gamma(N + \alpha + 1)}{\Gamma(\alpha)} \gamma(\alpha, x) - \Gamma(N + \alpha + 1)e^{-x} \sum_{s=0}^{N} \frac{x^{s+\alpha}}{\Gamma(s + \alpha + 1)},
$$

$$
N = k_a + k'_a + \frac{l_a + l'_a}{2}, \text{ and } \alpha = \frac{l_a + 1}{2}
$$

(A.17)

where $x = \omega_x R^2 / 4$. It follows from the Racah algebra for the electron-proton matrix elements (see Eq. A.33 in Section A.3 of this Appendix) that since $L$ is even, the only nonvanishing values occurs when $l_a + l'_a$ is also even. Thus $N$ in (A.17) take on integral values, so that there are now essentially two types of integrals required to complete the evaluation of (A.15) above.

The first involves the incomplete gamma functions $\gamma(\alpha, x)$ and products of the vibrational basis functions $\chi_n$. This may be evaluated by expressing $\gamma(\alpha, x)$ as a convergent series expansion in the variable $x$ and then performing the integration term by term as products over the basis $\chi_n$ and powers of the variable $\xi = \sqrt{\beta}(R - R_0)$. The integrals of the latter type are defined by Eq. (2.64) in the main text and were denoted there as $I_{n'n}^L$, so that the result for the first integral follows as,

$$
F_{n'n}^{L} = \frac{N_{n'}N_n}{\sqrt{\beta}} \int_0^\infty dR \chi_n'(R) \left( \frac{\gamma(\alpha, x)}{x^{L+1/2}} \right) \chi_n(R)
$$

$$
= \sum_{m=0}^{\infty} \frac{(-1)^m (\omega_x / \sqrt{\beta})^{2m}}{m!2^m[m + L + 1]} \sum_{l=0}^{2m} \left( \begin{array}{c} 2m \\ l \end{array} \right) \left( \sqrt{\beta} R_0 \right)^{2m-l} I_{n'n}^l
$$

(A.18)

The second type of integral has a simple form:

$$
G_{n'n}^m = \int_0^\infty dR \chi_n'(R) x^m e^{-x} \chi_n(R).
$$

(A.19)

This can be obtained rather easily by expanding the Hermite polynomials contained in $\chi_n$ according to their primitive series form (8.950, Gradshteyn and Ryzhik, 1965):

$$
H_n(x) = \sum_k B_{nk}(2x)^{n-2k},
$$

(A.20)
where the $B_{nk}$ are the binomial coefficients

$$B_{nk} = (-1)^k \frac{1}{k!(n-2k)!}.$$  

(A.21)

In terms of the variable $\xi = \sqrt{\beta} (R - R_0)$, $G_{n'n}^m$ is now expressed as

$$G_{n'n}^m = \frac{N_{n'}N_n}{\sqrt{\beta}} \sum_{kk'} B_{n'k'} B_{nk} \sum_{l=0}^{m} \binom{m}{l} (\sqrt{\beta} R_0)^{m-l} \exp[\beta^2/a - c] \times \int_{-\infty}^{\infty} d\xi \exp[-(\sqrt{a}\xi + b/\sqrt{a})\xi^M],$$  

(A.22)

where $a = (9\omega_e + 4\beta)/4\beta$, $b = \omega_e R_0/4\sqrt{\beta}$, $c = \omega R_0^2/4$, and $M = l + n' - 2k' + n - 2k$.

The exponential integral in (A.22) has a simple result (3.462.4, Gradshteyn and Ryzhik, 1965):

$$\int_{-\infty}^{\infty} dx e^{-(x-y)^2} x^M = \sqrt{\pi} (2i)^{-M} H_M(\text{i}y),$$  

(A.23)

which on substitution in (A.22), with $y = -b/\sqrt{a}$, yields

$$G_{n'n}^m = \frac{N_{n'}N_n}{\sqrt{\beta}} \sum_{kk'} B_{n'k'} B_{nk} \sum_{l=0}^{m} \binom{m}{l} (\sqrt{\beta} R_0)^{m-l} \sqrt{\pi} (2i)^{-M} \frac{1}{(x_0/R_0)^{M+1}} \times e^{-\omega_e x_0^2} H_M[-(\omega_e x_0/2\sqrt{\beta})],$$  

(A.24)

where

$$x_0 = \sqrt{\frac{\beta}{4\beta + \omega_e}} R_0.$$  

(A.25)

Combining this result with that obtained above for $F_{n'n}^L$ in (A.18), it follows that the final result for $J_L$ can be expressed as sums over the analytic expressions derived for $F_{n'n}^L$ and $G_{n'n}^m$, viz.

$$J_L(n', n; n_a l_a', n_a l_a) = \frac{N_{n_a l_a} N_{n' l_a'}}{2\omega_e} \sum_{k_a k_a'} A_{k_a}^{n_a l_a} A_{k_a'}^{n' l_a'} \frac{1}{2\omega_e} \left[ \frac{\Gamma(N + \alpha + 1)}{\Gamma(\alpha)} F_{n'n}^L - \Gamma(N + \alpha + 1) \sum_{s=0}^{N} \frac{G_{n'n}^{2s}}{\Gamma(s + \alpha + 1)} + p'! \sum_{s=0}^{p'} \frac{G_{n'n}^{2s + L}}{s!} \right].$$  

(A.26)

A.3 THE MATRIX ELEMENTS FOR $(\mathcal{H})_{ij}$

In this section of the appendix, the matrix elements discussed in Section 2.3.3 of the main text are listed, where in, what follows, $I_{n'n}$, $I_L$, and $J_L$ are the radial integrals defined in Eqs. (2.64), (2.65) and (2.67), respectively. For the analytical forms of $I_L$ and $J_L$, refer to Eqs. (A.14) and (A.26) respectively.

$$\mathcal{H}_{ij}^{(0)} = \delta_{n'n} \delta_{n_a l_a} \delta_{L L_a} \left[ (n + \frac{1}{2}) \omega_e + (2n_a + l_a + 2n_b + l_b + 3) \omega_e \right].$$  

(A.27)
\( \mathcal{H}_{ij}^{(1)} = -\frac{1}{2} \omega_0 \delta_{n'_i, n'_j} \delta_{L'_i, L'_j} \left[ (n + \frac{1}{2}) \delta_{n'_i, n'_j} + \frac{1}{2} ((n + 1)(n + 2))^{1/2} \delta_{n'_i, n'_j+2} \right. \\
+ \left. \frac{1}{2} ((n' + 1)(n' + 2))^{1/2} \delta_{n'_i, n'_j+2, n} \right] \\
(A.28)

\( \mathcal{H}_{ij}^{(2)} = -\omega_e N_a^\dagger \mathcal{N}_{ab} \delta_{n'_i, n'_j} \delta_{L'_i, L'_j} \left\{ \delta_{l'_i, l'_j} (\delta_{n'_i, n'_j+1} \delta_{n'_i, n'_j+1} - \delta_{n'_i, n'_j+1, n} \delta_{n'_i, n'_j+1, n}) \\
+ (2n_a + l_a + 2n_b + l_b + 3) \delta_{n'_i, n'_j} - \delta_{n'_i, n'_j+1, n} \delta_{n'_i, n'_j+1, n} - \delta_{n'_i, n'_j+1, n} \delta_{n'_i, n'_j+1, n} \right\} \\
(A.29)

\( \mathcal{H}_{ij}^{(3)} = -\frac{1}{2} \omega_0 \left[ 3(K + 1) + L_e (L_e + 1) - 2 \Lambda^2 \right] \delta_{n'_i, n'_j} \delta_{L'_i, L'_j} \\
\times \mathcal{N}_{n'_i, n'_j} \sum_{r} (-1)^{r} \frac{L^r_{n'_i, n'_j}}{(\sqrt{\beta R})^{r+1}} \\
(A.30)

\( \mathcal{H}_{ij}^{(4)} = (\mu \omega_0)^{1/2} \delta_{n'_i, n'_j} \delta_{L'_i, L'_j} \mathcal{N}_{n'_i, n'_j} \sum_{r} (-1)^{r} \frac{L^r_{n'_i, n'_j}}{(\sqrt{\beta R})^{r+1}} \\
(A.31)

\( \mathcal{H}_{ij}^{(5)} = 2 N_a^\dagger \mathcal{N}_{ab} \delta_{n'_i, n'_j} \delta_{L'_i, L'_j} \tilde{I}_{ab} \tilde{I}_{ab} \sum_{L} (-1)^{L} \\
\times \left\{ (-1)^{L_e} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \left\{ (-1)^{L_e} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \\
\times \left[ I_{L}(n_a l_a n_b l_b; n'_a l'_a n'_b l'_b) + I_{L}(n_b l_b n_a l_a; n'_b l'_b n'_a l'_a) \right] \\
+ (-1)^{l_a + l_b} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \left\{ (-1)^{L_e} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \\
\times \left[ I_{L}(n_a l_a n_b l_b; n'_a l'_a n'_b l'_b) + I_{L}(n_b l_b n_a l_a; n'_b l'_b n'_a l'_a) \right] \right\} \\
(A.32)

\( \mathcal{H}_{ij}^{(6)} = \\
-4 N_a^\dagger \mathcal{N}_{ab} \tilde{I}_{ab} \tilde{I}_{ab} (-1)^{\Lambda} \sum_{L_{even}} \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \\
\times \left\{ (-1)^{L_e + l_a + l_b} \delta_{n'_i, n'_j} \delta_{l'_i, l'_j} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \\
+ (-1)^{L_e + l_a + l_b} \delta_{n'_i, n'_j} \delta_{l'_i, l'_j} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \\
+ (-1)^{L_e + l_a + l_b} \delta_{n'_i, n'_j} \delta_{l'_i, l'_j} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \\
+ (-1)^{l_a + l_b} \delta_{n'_i, n'_j} \delta_{l'_i, l'_j} \left( \begin{array}{c} l_a \cr l'_a \cr L \end{array} \right) \left( \begin{array}{c} l_b \cr l'_b \cr L \end{array} \right) \right\} \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \left( \begin{array}{c} L_e \cr L'_e \cr L \end{array} \right) \right\} \\
(A.33)
Appendix B

B.1 THE MATRIX ELEMENTS AND THE INTEGRALS

In this appendix a full listing of the matrix elements of \( G \), as used in the scattering calculations described in Chapters 3 and 4 of the thesis, is given. The notation is explained in Section 3.3. The single and double radial integrals are defined below as a series of integrations between the basis states \( f_{ji}(r) \) used for the scattered electron in the internal region and the electronic and vibrational basis functions, \( R_{ni}^\alpha(r) \) and \( \chi_{n}^\alpha(r) \), used for the expansion of the molecular wave functions (cf. Section 3.3.1; see also Chapter 2).

B.1.1 The Radial Integrals

In the following, all integrations over the radial coordinates are restricted to the finite interval \([0, a]\), i.e., \( 0 \leq (\frac{1}{2} R, r, r_1) \leq a \).

\[
I(\alpha'n', \alpha n) = \int dR \chi_n^\alpha(R) \chi_n^\alpha(R), \tag{B.1}
\]

\[
I(\alpha'n'l', \alpha n l) = \int drr^2 R_{ni'l'}^\alpha(r) R_{ni}^\alpha(r), \tag{B.2}
\]

\[
I(\lambda l, \alpha n l) = \int drr^2 f_{\lambda l}(r) R_{ni}^\alpha(r), \tag{B.3}
\]

\[
I(\lambda'l', \lambda; \alpha'n'a, \alpha n b; L) = \int dr_1 r_1^2 f_{\lambda'l'}(r_1) \left[ \int drr^2 R_{naa}^\alpha(r) \frac{r_L}{r_{L+1}} R_{nbb}^\alpha(r) \right] f_{\lambda l}(r_1), \tag{B.4}
\]

\[
I(\lambda'l', \alpha n a; \lambda, \alpha'n'a'L; L) = \int dr_1 r_1^2 f_{\lambda'l'}(r_1) \left[ \int drr^2 f_{\lambda'l'}(r) \frac{r_L}{r_{L+1}} R_{nbb}^\alpha(r) \right] R_{nla}^\alpha(r_1), \tag{B.5}
\]

\[
I(\lambda l, \alpha'n'b; \lambda, \alpha'n'a'L; L) = \int dr_1 r_1^2 f_{\lambda l}(r_1) \left[ \int drr^2 R_{nbb}^\alpha(r) \frac{r_L}{r_{L+1}} R_{nbb}^\alpha(r) \right] R_{nla}^\alpha(r_1), \tag{B.6}
\]

\[
I(\lambda'l', \lambda; \alpha'n', \alpha n; L) = \int dr_1 r_1^2 f_{\lambda'l'}(r_1) \left[ \int dr \chi_n^\alpha(R) \frac{r_L}{r_{L+1}} \chi_n^\alpha(R) \right] f_{\lambda l}(r_1), \tag{B.7}
\]

\[
I(\alpha'n'a'L, \lambda; \alpha'n', \alpha n; L) =
\]
\[
\int dr_1 r_1^2 R_n^{\alpha}(r_1) \left[ \int dR \chi_n^{\alpha}(R) \frac{r_L}{r_1} \chi_n^{\alpha}(R) \right] f_\lambda(r_1), \quad (\text{B.8})
\]

\[
I(\alpha^\prime \alpha, \alpha^\prime \alpha, \alpha^\prime \alpha; \alpha^\prime \alpha, \alpha; L) = \int dr_1 r_1^2 R_n^{\alpha}(r_1) \left[ \int dr \chi_n^{\alpha}(R) \frac{r_L}{r_1} \chi_n^{\alpha}(R) \right] R_n^{\alpha}(r_1). \quad (\text{B.9})
\]

where, \( r_<(r_>) \) has the usual meaning of lesser(greater) than the variables occurring in the double integrals.

**B.1.2 The Overlap Matrix and Kinetic Energy Operators**

The following abbreviations are used:

\[
\begin{align*}
&f_{\mu}^{(\lambda)(\mu)}(Kj,l, K'j', l', L_\alpha \Lambda_\alpha, L'_\alpha \Lambda'_\alpha) = \\
&\sum_{\gamma_1, \gamma_2} \left( \begin{array}{ccc}
\gamma_1 & j & j' \\
\gamma_2 & l' & l
\end{array} \right) \left( \begin{array}{ccc}
K \quad l
\end{array} \right) \left( \begin{array}{ccc}
K' \quad l'
\end{array} \right) \left( \begin{array}{ccc}
L_\alpha & L'_\alpha & Y \\\n\Lambda_\alpha & \Lambda'_\alpha & \Lambda_\alpha - \Lambda_\alpha
\end{array} \right) \left( \begin{array}{ccc}
K \quad K' \quad Y \\
\Lambda_\alpha & \Lambda'_\alpha & -\Lambda_\alpha - \Lambda_\alpha
\end{array} \right) + (-1)^{L'_\alpha + K'} \left( \begin{array}{ccc}
K \quad K' \quad Y \\
\Lambda_\alpha & \Lambda'_\alpha & -\Lambda_\alpha - \Lambda_\alpha
\end{array} \right) \right), (\text{B.10})
\end{align*}
\]

\[
X(\lambda', n_a^\prime, n_b^\prime, \lambda, n_a l_a; n_b l_b) =
\left\{ \begin{array}{l}
\frac{1}{2} [2(n_a + 1)(2n_a + 2l_a + 3)]^{1/2} I(\lambda', \alpha(n_a + 1)l') I(\alpha' n_b l_b, \alpha n_b l_b) \\
+ \frac{1}{2} [2(n_b + 1)(2n_b + 2l_b + 3)]^{1/2} I(\lambda', \alpha n_b l_b) I(\alpha' n_a l_a, \alpha (n_a + 1) l_a) \\
+ (2n_a + 2n_b + l_a + l_b + 3) I(\lambda', \alpha n_b l_b) I(\alpha' n_a l_a, \alpha (n_a + 1) l_a) \\
+ \frac{1}{2} [2n_a(2n_a + 2l_a + 1)]^{1/2} I(\lambda', \alpha(n_a - 1)l') I(\alpha' n_b l_b, \alpha n_b l_b) \\
+ \frac{1}{2} [2n_b(2n_b + 2l_b + 1)]^{1/2} I(\lambda', \alpha n_b l_b) I(\alpha' n_a l_a, \alpha (n_a - 1) l_a)
\end{array} \right\}. (\text{B.11})
\]

The overlap matrix \( O \) and the kinetic energy operators, \( T_e \) and \( T_R \), then have the form:

\[
O \equiv \langle X_{\lambda, \gamma'} | X_{\lambda \gamma} \rangle = \delta_{\lambda \lambda'} \delta_{\gamma' \gamma} + O_{\lambda, \lambda'}^{\gamma, \gamma}
\]

(\text{B.12})

where

\[
O_{\lambda, \lambda'}^{\gamma, \gamma} = 4(-1)^{1/2 + I} \delta_{\mu' I} \delta_{M' j'} K \bar{K} \delta_{\mu j} I(\lambda', \alpha n_b l_b, \alpha n_b l_b) I(\alpha' n_a l_a, \alpha (n_a + 1) l_a) \\
+ \delta_{\mu' j} \delta_{M j} I(\lambda', \alpha n_b l_b, \alpha n_b l_b) I(\alpha' n_a l_a, \alpha (n_a + 1) l_a)
\]

(\text{B.12})
\[ (T_e)_{\lambda', \lambda} = \sum_{n'=0}^{\infty} \sum_{L'=0}^{\infty} \sum_{n=0}^{\infty} \sum_{L=0}^{\infty} \frac{N_{n'\Lambda'} N_{n\Lambda}}{n'_e L'_e n_L L} C_{n'\Lambda' L'_e} C_{n\Lambda L} \]

\[ \times \{(-1)^{L'_e+L+K'+K} \delta_{M'_e M_L, J'_L J_L} \hat{K} \hat{K}' N_{n'\Lambda'} N_{n\Lambda} \sum_{n'_e L'_e} N_{n'_e L'_e} C_{n'\Lambda' L'_e} C_{n\Lambda L} \} \]

For these terms the following abbreviation is used:

\[ g_{n'_e L'_e, n_L L}^{\lambda'}(K', Y, L_e, L_e', L_e \Lambda_\alpha, L_e \Lambda_\sigma; l'_e, l_a) = \]

\[ \left\{ \begin{array}{l} j' j \ Y \ l' \ l \ \frac{1}{2} \\ \end{array} \right\} \left\{ \begin{array}{l} j j' \ Y \ l' \ l \ \frac{1}{2} \\ \end{array} \right\} \left\{ \begin{array}{l} L_e \ L'_e \ Y \\ \end{array} \right\} \left\{ \begin{array}{l} l'' \ l_a \ l_b \\ \end{array} \right\} \times \frac{1}{2} \left[ \begin{array}{ccc} L_e & L'_e & Y \\ \Lambda_\alpha & -\Lambda'_\alpha & -\Lambda_\alpha - \Lambda_\sigma \\ \end{array} \right] \left( \begin{array}{ccc} K & K' & Y \\ \Lambda_\alpha & -\Lambda'_\alpha & -\Lambda'_\alpha - \Lambda_\sigma \\ \end{array} \right) \]

\[ +(-1)^{L'_e+K'} \left[ \begin{array}{ccc} L_e & L'_e & Y \\ \Lambda_\alpha & -\Lambda'_\alpha & -\Lambda_\alpha - \Lambda_\sigma \\ \end{array} \right] \left( \begin{array}{ccc} K & K' & Y \\ \Lambda_\alpha & -\Lambda'_\alpha - \Lambda'_\alpha & -\Lambda_\sigma - \Lambda_\alpha \\ \end{array} \right). \]
\[ 8(-1)^{\frac{1}{2} + I + K' + K} \delta_{I' I} \delta_{M' 1 M_1} \bar{j} \bar{j}' \bar{K} \bar{K}' \bar{N} \alpha' N_\alpha \sum_{n_n' L_n} N_{a' b'} N_{a b} C_{\alpha' \omega' K'} C_{\alpha \omega K} L'_e L_e \]
\[ \times (-1)^{I_a} I(\alpha' n', \alpha_n) \sum_{L} \bar{L}^2 \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \left[ (-1)^{L'_e + L_e + I_a + I_b} \delta_{\bar{l}_{I_a} \bar{l}_{I_a}} \right] \]
\[ \times g_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{a}) \]
\[ \times \left( \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \right) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \lambda; \alpha' n'_b, \alpha_n b_b) \]
\[ + \bar{\delta}_{l_{I_a} l_{I_a}} \bar{I}_{a} \bar{I}_{a} \bar{g}_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{b}) \]
\[ \times \left( \begin{pmatrix} l & l' & l \\ 0 & 0 & 0 \end{pmatrix} \right) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \lambda; \alpha' n'_b, \alpha_n b_b) \]
\[ + \bar{\delta}_{l_{I_a} l_{I_a}} \bar{I}_{a} \bar{I}_{a} \bar{g}_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{b}) \]
\[ \times \left( \begin{pmatrix} l & l' & l \\ 0 & 0 & 0 \end{pmatrix} \right) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \lambda; \alpha' n'_b, \alpha_n b_b) \]
\[ \times (B.17) \]

\[ (V_{ee}^3)_{\lambda' \gamma', \lambda \gamma} = \]
\[ 4(-1)^{\frac{1}{2} + I + K' + K} \delta_{I' I} \delta_{M' 1 M_1} \bar{j} \bar{j}' \bar{K} \bar{K}' \bar{N} \alpha' N_\alpha \sum_{n_n' L_n} N_{a' b'} N_{a b} C_{\alpha' \omega' K'} C_{\alpha \omega K} L'_e L_e \]
\[ \times (-1)^{I_a} I(\alpha' n', \alpha_n) \]
\[ \times \sum_{L' Y} \bar{L}' \bar{Y}^2 \left[ (-1)^{L'_e + L_e + I_a + I_b} \delta_{\bar{l}_{I_a} \bar{l}_{I_a}} \bar{I}_{a} \bar{I}_{a} \right] \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \]
\[ \times g_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{a}) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \alpha_n l_a; \lambda, \alpha', \alpha'_n l'_a) \]
\[ + (-1)^{L'_e + L_e + I_a + I_b} \delta_{\bar{l}_{I_a} \bar{l}_{I_a}} \bar{I}_{a} \bar{I}_{a} \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \]
\[ \times g_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{b}) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \alpha_n l_b; \lambda, \alpha', \alpha'_n l'_a) \]
\[ + (-1)^{L'_e + L_e + I_a + I_b} \delta_{\bar{l}_{I_a} \bar{l}_{I_a}} \bar{I}_{a} \bar{I}_{a} \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \]
\[ \times g_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{b}) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \alpha_n l_b; \lambda, \alpha', \alpha'_n l'_a) \]
\[ + \bar{\delta}_{l_{I_a} l_{I_a}} \bar{I}_{a} \bar{I}_{a} \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \left( \begin{pmatrix} l & l' & \ell \ L \\ 0 & 0 & 0 \end{pmatrix} \right) \]
\[ \times g_{I_a}^{Y}(K' j', K j l, L' \Lambda' \alpha, L \Lambda \alpha; l_{a}, l_{b}) I(\alpha' n'_b, \alpha_n b_b) I(\lambda' \ell', \alpha_n l_b; \lambda, \alpha', \alpha'_n l'_a) \]
\[ \times (B.18) \]
B.1.4 The Electron-Proton Attraction Potentials

Finally, the matrix elements for the Coulomb attraction potentials between the electrons and the protons, read as follows:

\[
(V_{1\gamma}^1)_{\nu'\gamma', \gamma} = 4(-1)^{\frac{1}{2} + I + K' + K + \Lambda_\alpha} \delta_{II'} \delta_{M'_\gamma M_\gamma} \sum_{n'_\gamma L'_\gamma} N_{\alpha'} N_{\alpha} C_{n'_\gamma L'_\gamma} \psi_{n_\gamma L_\gamma} \psi_{n_{\nu'} L_{\nu'}} \sum_{n'_\gamma L'_\gamma} N_{\alpha'} N_{\alpha} C_{n'_\gamma L'_\gamma} \psi_{n_{\nu'} L_{\nu'}} \psi_{n_{\gamma} L_{\gamma}}
\]

\[
\times \left[ \left( \begin{array}{ccc} l'_b & l''_b & L''_b \\ l''_b & l''_b & L''_b \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_b & l'_b & L'_b \\ l'_b & l'_b & L'_b \\ 0 & 0 & 0 \end{array} \right) \right] \begin{array}{c} \{ j, j' \} \\ \{ l', l'' \} \end{array}
\]

\[
\times \left[ \left( \begin{array}{ccc} l''_a & l''_a & L''_a \\ l''_a & l''_a & L''_a \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_a & l'_a & L'_a \\ l'_a & l'_a & L'_a \\ 0 & 0 & 0 \end{array} \right) \right] \begin{array}{c} \{ j, j' \} \\ \{ l, l'' \} \end{array}
\]

\[
B.19
\]

\[
(V_{2\gamma}^2)_{\nu'\gamma', \gamma} = 8(-1)^{\frac{1}{2} + I + K' + K + \Lambda_\alpha} \delta_{II'} \delta_{M'_\gamma M_\gamma} \sum_{n'_\gamma L'_\gamma} N_{\alpha'} N_{\alpha} C_{n'_\gamma L'_\gamma} \psi_{n_{\nu'} L_{\nu'}} \psi_{n_{\gamma} L_{\gamma}}
\]

\[
\times \left[ \left( \begin{array}{ccc} l'_b & l''_b & L''_b \\ l''_b & l''_b & L''_b \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_b & l'_b & L'_b \\ l'_b & l'_b & L'_b \\ 0 & 0 & 0 \end{array} \right) \right] \begin{array}{c} \{ j, j' \} \\ \{ l', l'' \} \end{array}
\]

\[
\times \left[ \left( \begin{array}{ccc} l''_a & l''_a & L''_a \\ l''_a & l''_a & L''_a \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_a & l'_a & L'_a \\ l'_a & l'_a & L'_a \\ 0 & 0 & 0 \end{array} \right) \right] \begin{array}{c} \{ j, j' \} \\ \{ l, l'' \} \end{array}
\]

\[
B.20
\]
\[
\begin{align*}
&= \left\{ (1)^{L_e} \hat{p}_a \left( \begin{array}{ccc}
\bar{l} & \bar{l}' & L \\
\bar{l}_{a} & \bar{l}'_{a} & l_a \\
0 & 0 & 0
\end{array} \right) \left( \begin{array}{ccc}
X & Y & L \\
Y & L & X \\
L & X & L
\end{array} \right) I(\alpha'n'_{a}l_{a}, \lambda; \alpha'n', \alpha; L) \\
&= \left\{ (1)^{L_e+a+l_{b}} \delta_{\bar{l}_{a}l_{a}l_{a}l_{b}} I(\alpha'n'_{a}l_{a}, \alpha'n_{b}l_{b}) I(\lambda', \alpha_{a}l_{a}) \left( \begin{array}{ccc}
L_{e} & L'_{e} & X \\
L'_{e} & X & L_e \\
l_{a} & l'_{a} & l_{a}
\end{array} \right) \\
&= \left\{ (1)^{L_e+a+l_{b}} \delta_{\bar{l}_{a}l_{a}l_{a}l_{b}} I(\alpha'n'_{a}l_{a}, \alpha'n_{b}l_{b}) I(\lambda', \alpha_{a}l_{a}) \left( \begin{array}{ccc}
L_{e} & L'_{e} & X \\
L'_{e} & X & L_e \\
l_{b} & l'_{b} & l_{b}
\end{array} \right) \\
&= \left\{ (1)^{L_e+a+l_{b}} \delta_{\bar{l}_{b}l_{b}l_{b}l_{b}} I(\alpha'n'_{b}l_{b}, \lambda; \alpha'n', \alpha; L) \\
&= \left\{ (1)^{L_e+a+l_{b}} \delta_{\bar{l}_{b}l_{b}l_{b}l_{b}} I(\alpha'n'_{b}l_{b}, \alpha'n_{b}l_{b}) I(\lambda', \alpha_{b}l_{b}) \left( \begin{array}{ccc}
L_{e} & L'_{e} & X \\
L'_{e} & X & L_e \\
l_{b} & l'_{b} & l_{b}
\end{array} \right) \\
&= \left\{ (1)^{L_e+a+l_{b}} \delta_{\bar{l}_{b}l_{b}l_{b}l_{b}} I(\alpha'n'_{b}l_{b}, \alpha'n_{b}l_{b}) I(\lambda', \alpha_{b}l_{b}) \left( \begin{array}{ccc}
L_{e} & L'_{e} & X \\
L'_{e} & X & L_e \\
l_{a} & l'_{a} & l_{a}
\end{array} \right) \right\}, \tag{B.21}
\end{align*}
\]

\(\Lambda^\pm = \Lambda_{\alpha'} \pm \Lambda_{\alpha}\)

\[(V_{cp}^{3})_{\lambda \gamma', \lambda \gamma} =
8(1)^{L_e+a+l_{b}} \delta_{\bar{l}_{a}l_{a}l_{a}l_{b}} I(\alpha'n'_{a}l_{a}, \lambda; \alpha'n_{b}l_{b}) I(\lambda', \alpha_{a}l_{a}) \left( \begin{array}{ccc}
L_{e} & L'_{e} & X \\
L'_{e} & X & L_e \\
l_{a} & l'_{a} & l_{a}
\end{array} \right) \]

\(\times \left\{ (1)^{L_e+a+l_{b}} \delta_{\bar{l}_{b}l_{b}l_{b}l_{b}} I(\alpha'n'_{b}l_{b}, \lambda; \alpha'n_{b}l_{b}) I(\lambda', \alpha_{b}l_{b}) \left( \begin{array}{ccc}
L_{e} & L'_{e} & X \\
L'_{e} & X & L_e \\
l_{b} & l'_{b} & l_{b}
\end{array} \right) \right\}, \tag{B.22}
\]
Bibliography


