R-matrix Theory
for
Atomic and Molecular Systems

by

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to mother and father

Abstract

Calculations using the R-matrix theory involve solving the Schrödinger equation within two regions of space. The two solutions obtained are matched at the boundary to give the wave function for all space. The inner region can often be required to be quite large which means that a large basis set is needed to accurately represent the wave function. This can involve the diagonalisation of very large matrices which may require considerable amounts of computer time and memory.

In the present work, a propagation method is developed in which the radial basis functions spanning a given region, $a \leq r \leq b$ say, are expanded in terms of Legendre polynomials that are orthogonal on the range $[a, b]$. The method has the considerable advantage that the elements of the Hamiltonian matrix for this region can be generated exactly and extremely rapidly using recurrence relations and that also the use of Legendre polynomials leads to easy propagation of the physical solution from one region to the next. Thus the whole space can be subdivided into as many regions as required and the wave function can be generated for all space by matching at each range boundary. This greatly increases the flexibility of the R-matrix technique.

In order to assess the accuracy and the convergence properties of this method, test calculations for the electronic energy levels and oscillator strengths of the hydrogen atom, the hydrogen molecular ion and the HeH^{2+} ion have been carried out and some encouraging results obtained.

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Chapter 1

Introduction

Throughout the last decade considerable progress has been made in developing new methods for electron-atom and electron-molecule scattering. One approach which seems particularly useful is the R-matrix method. It was first introduced by Wigner (1946a,b) to treat problems of resonance in nuclear physics and was extended to include long-range interactions by Wigner and Eisenbud (1947). Subsequently, the method was introduced into the field of atomic and molecular physics by Burke *et al* (1971, 1977) as a tool for solving the close-coupling equations associated with electron-atom and electron-molecule collisions. This has proved to be a very fruitful approach and has been extensively used in calculations of a broad range of atomic and molecular processes including, as well as low energy electron-atom and electron-molecule scattering (Berrington *et al* 1974, 1978; Schneider 1975a,b; Gillan *et al* 1987), photoionisation of atoms (Burke and Taylor 1975; Le Dourneuf *et al* 1975; Hansen and Scott 1986; Aymar and Lecomte 1989), atomic polarisabilities and van der Waals coefficients (Allison *et al* 1972a,b; Robb 1973, 1974), inelastic and reactive heavy particle scattering (Light and Walker 1976; Light *et al* 1979; Maass *et al* 1986), spectral line shifts (Yamamota 1980), free-free transitions (Bell *et al* 1977), charge transfer collisions

(Gerrat 1984), photoabsorption (Aymar 1987; Tully 1988), attachment energies of negative atomic ions (Le Dourneuf *et al* 1977) and positron-molecule collisions (Tennyson 1986; Tennyson and Morgan 1987). Reviews of some of these developments have been given by Burke and Robb (1975), Burke (1982) and Burke and Noble (1986). More recently the R-matrix method has been used to study vibrational excitation (Schneider *et al* 1979; Burke *et al* 1985) and electron impact ionisation (Bartschat and Burke 1987; Furtado and O'Mahony 1988).

In applications of the R-matrix method to electron scattering, configuration space is usually divided into two regions and the boundary is chosen to just envelop the charge distribution of the target. In the inner region, the electron interaction with the target is strong since electron exchange and correlation effects are important and the interaction is difficult to calculate. In this region, a set of functions are selected and used to set up a matrix corresponding to the Hamiltonian operator for the atomic or molecular system. Diagonalisation of this matrix then gives a set of eigenenergies and eigenvectors that specify the basis set. As emphasised by Fano (1978), a key property of R-matrix theory is that the energy spectrum of particles confined within the limited volume of the inner region is discrete with a low density of states. Provided that the condition at the boundary is appropriately chosen, the Hamiltonian matrix is hermitian, and this is a convenient property for the matrix to have, although in principle is not the only possible choice. The great advantage of this approach is that, within the region, the physical solutions of the wave equation that are required can all be expanded in terms of the same basis set. Hence, once the basis set has been obtained, solutions at all energies can be generated directly. In the outer region, the electron interaction with the target is much simpler, as exchange and correlation effects can be neglected, and the problem has an analytical or relatively simple numerical solution. The wave functions generated within the two regions are linked on the boundary surface by a quantity called the R-matrix which gives, essentially, the logarithmic derivative of the wave function at the boundary and from this information the reactance matrix (K-matrix), scattering matrix (S-matrix) and cross sections can be calculated.

In the application to inelastic and reactive heavy particle scattering (Light and Walker 1976; reviewed by Light *et al* 1979), unlike the situation for electron scattering, the density of states in the scattering region is now often so high that it is no longer appropriate to use a single expansion in this region. Instead the scattering region is divided into a number of separate subregions by subdividing the range of the scattering coordinate, where each subregion is connected to its neighbours by an R-matrix. The R-matrix is propagated across each boundary for a finite region and the solution obtained is matched to asymptotic solutions in the outer region. This method is computationally fast, stable and allows different finite representations to be used in each subregion enabling the characteristics of a rapidly changing wave function to be described. A general R-matrix propagation program for solving second-order differential equations has been developed by Baluja *et al* (1982) and subsequently modified by Morgan (1984) to allow more general potentials to be used. Propagation methods become particularly useful when the radius at which electron exchange can be neglected is not large enough to allow asymptotic expansion methods or perturbation methods used for outer region solutions to converge to the required accuracy. In this intermediate region, an R-matrix propagation method may be used to give a solution.

A diagnostic study of the R-matrix method was carried out by Yu Yan and Seaton (1985) who studied the detailed properties of the expansions made in R-matrix theory by applying the technique to the solution of the Schrödinger equation for the hydrogen atom. That paper provided the initial inspiration for the present work. The work presented in this thesis is a propagator method similar to that of Baluja *et al* (1982) and Morgan (1984) but instead of propagating the R-matrix across a finite region outside the inner region, the wave function is generated for all space. For a restricted region, $a < r < b$ say, the R-matrix basis functions are expanded in terms of Legendre polynomials that are orthogonal on the range $[a, b]$. The method has the considerable advantage that the elements of the Hamiltonian matrix for this region can be generated exactly and extremely rapidly using recurrence relations and that also the use of Legendre polynomials leads to easy propagation of the physical solutions from one region to the next. Thus the whole space can be subdivided into as many regions as required and this greatly increases the flexibility of the R-matrix technique.

The theory required to implement this approach for two and three body systems is described in chapter 3. In order to assess the accuracy and the convergence properties of this method, test calculations have been carried out and the results are presented in chapters 4 and 5. Electronic energy levels, wave functions and oscillator strengths for the hydrogen atom, the hydrogen molecular ion and the HeH^{2+} ion have been calculated and some encouraging results obtained. The oscillator strengths depend on dipole matrix elements that can be generated rapidly in exactly the same way as the elements of the Hamiltonian matrix and provide a sensitive test of the theory.

Chapter 2

Basic concepts of the R-matrix method

2.1 Definition of the R-matrix

In applications of the R-matrix method to atomic processes, configuration space is divided into two regions, $0 \leq r \leq a$ and $r > a$, where a is chosen to just envelop the charge distribution of the target states of interest and r is the radial distance between the electron and the centre of mass of the target (see, for example, Burke 1978). In the inner region electron exchange and correlation effects are present and these make the interaction difficult to calculate *ab initio* but in the outer region, such effects can be neglected and the collision problem can be solved analytically or relatively easily by numerical methods.

Consider a system of N electrons moving in the field of a nucleus of charge Z. The Schrödinger equation for the system of interacting particles is

$$(H_N - E)\Psi_E = 0 \tag{2.1}$$

where the Hamiltonian for the system is (in Rydbergs)

$$H_N = \sum_{p=1}^{N} \left(-\nabla_p^2 - \frac{2Z}{r_p} \right) + \sum_{p>q=1}^{N} \frac{2}{r_{pq}} \ , \tag{2.2}$$

E is the energy and Ψ_E is the total wave function. Neglecting anti-symmetrisation and exchange (which will be discussed further in §2.3) one can use the expansion

$$\Psi_E = \sum_i \psi_i(\mathbf{R}) Y_{l_i m_i}(\hat{\mathbf{r}}) \frac{1}{r} F_i(r) \tag{2.3}$$

where r is the coordinate of an outer electron and $\mathbf{R}$ stands for all coordinates of inner electrons with wave functions ψ_i. The functions $Y_{l_i m_i}(\hat{\mathbf{r}})$ are known as spherical harmonics. The radial functions $F_i(r)$ satisfy coupled equations of the form

$$\sum_i (\mathcal{H}_{ji} - E\delta_{ji}) F_i(r) = 0 \tag{2.4}$$

where $\mathcal{H}_{ji}$ is the radial part of the Hamiltonian for the outer electron. Equation (2.4) is obtained by multiplying (2.1) on the left-hand side by $\psi_j^*(\mathbf{R}) Y_{l_j m_j}^*(\hat{\mathbf{r}})$ and then integrating over all electron coordinates $\mathbf{R}$ and the angular coordinates of the outer electron. For a one-channel problem, (2.4) reduces to

$$(\mathcal{H}_{ii} - E) F_i(r) = 0 \tag{2.5}$$

and it is this case that is considered in this section.

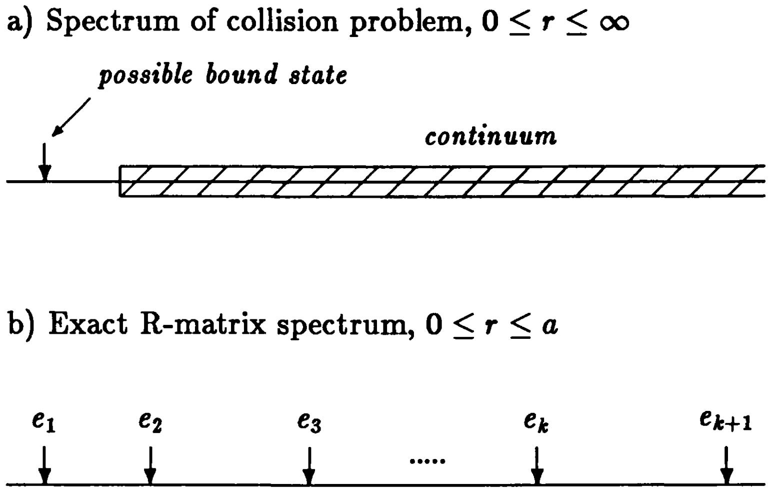
The solution $F_i(r)$ can be expanded in the inner region in terms of a complete discrete set of functions $f_{ik}(r)$, $k = 1, 2, ..., \infty$, defined by the equation

$$(\mathcal{H}_{ii} - e_k) f_{ik}(r) = 0 \tag{2.6}$$

and satisfying the logarithmic boundary condition

$$\left. \frac{a}{f_{ik}(a)} \frac{df_{ik}}{dr} \right|_{r=a} = \beta \tag{2.7}$$

where β is an arbitrary constant which may depend on the channel quantum numbers (see Burke 1978). The condition (2.7) is necessary to ensure that $\mathcal{H}_{ii}$ is


a) Spectrum of collision problem, $0 \leq r \leq \infty$

b) Exact R-matrix spectrum, $0 \leq r \leq a$

Figure 2.1: R-matrix energy spectra.

hermitian and hence that the eigenenergies e_k are real. A diagrammatic comparison of the energy spectrum of the Hamiltonian describing the electron-target system in the internal region with that of the wave function defined over all space is shown in figure 2.1. The usual continuum breaks up into a discrete set e_k, $k = 1, 2, \ldots, \infty$, and the corresponding eigenstates ψ_k form a complete set in the internal region which is used as a basis for the expansion of the total wave function Ψ_E in this region for any energy, i.e.

$$\Psi_E = \sum_k A_{Ek} \psi_k \tag{2.8}$$

or in terms of the radial parts only,

$$F_i(r) = \sum_k A_{Ek} f_{ik}(r) \quad . \tag{2.9}$$

Since the functions ψ_k are independent of E, the wave function Ψ_E can correspond either to a negative energy bound-state solution or to a positive energy scattering solution, the only distinction arising from the different boundary conditions satisfied in the external region. This result is of particular importance when applying the R-matrix method to processes such as photoionisation, where the initial bound state and the final continuum state are expanded in terms of the same basis. Use of the same basis for both states means that the Hamiltonian matrix only needs to be diagonalised once per symmetry to yield all the necessary eigenenergies and eigenvectors. Also, the use of the same basis avoids any systematic errors that may arise when using two separate calculations for the wave functions and this ensures that the representations of the relevant states are of consistent accuracy.

In order to calculate the collision cross section at some positive energy $E_s = E - E_0$, where E_0 is the energy of the ground state of the target, it is necessary to evaluate the logarithmic derivative of $F_i(r)$ on the boundary of the internal region. Substituting (2.9) into (2.5) and using the boundary condition (2.7) it can be shown that the logarithmic derivative of the radial wave function describing the scattered electron on the boundary is given by the expression

$$F_i(a) = \sum_j \Re_{ij}(a, E) \left[a \frac{dF_j}{dr} - \beta F_j \right]_{r=a} \tag{2.10}$$

where

$$\Re_{ij}(a, E) = \frac{1}{a} \sum_k \frac{f_{ik}(a) f_{jk}(a)}{e_k - E} \tag{2.11}$$

is the called the R-matrix. Once the surface amplitudes $f_{ik}(a)$ and the eigenenergies e_k are found, a complete description of the collision problem in the internal region can be obtained. The solution of the problem in the outer region then yields the phase shift of the radial wave functions and cross section.

One problem associated with the expression (2.11) for the R-matrix is that when the energy E is equal to the energies e_k, $\Re_{ij}$ and quantities expressed in terms of it become indeterminate. In this case, the R-matrix is written in a form such that F_i and f_{ik} are identical and only the k for which $e_k = E$ contributes to the sum. Alternatively, a diagonalisation procedure developed by Burke and Seaton (1984) can be used to obtain determinate expressions when E is near e_k.

2.2 Potential scattering

In order to get an initial idea of the assumptions and approximations used in the practical application of the R-matrix method it is of interest to look at a relatively simple collision problem – that of potential scattering.

Consider the case of s-wave scattering of a particle by a short-range central potential. The R-matrix boundary is chosen to just contain the range of the potential $V(r)$ so that

$$V(r) = 0 \qquad ; \qquad r \geq a \tag{2.12}$$

where a is known as the channel radius. The radial Schrödinger equation for the collision problem is

$$(H - E)F(r) = 0 \tag{2.13}$$

where

$$H = -\frac{d^2}{dr^2} + V(r) \quad . \tag{2.14}$$

The solution $F(r)$ can be expanded in the internal region $r < a$ in terms of the complete discrete set of real eigensolutions $f_k(r)$ which are solutions of

$$(H - e_k)f_k(r) = 0 \tag{2.15}$$

where the e_k are eigenenergies, and which satisfy the R-matrix boundary conditions

$$f_k(0) = 0 \qquad ; \qquad \frac{a}{f_k(a)} \frac{df_k}{dr}\bigg|_{r=a} = \beta \tag{2.16}$$

where β is an arbitrary constant. The functions are also required to satisfy the orthonormality condition

$$\int_0^a f_k(r) f_{k'}(r) dr = \delta_{kk'} \quad . \tag{2.17}$$

The solution of (2.13) in the inner region can then be expanded as

$$F(r) = \sum_{k=1}^{\infty} A_k f_k(r) \qquad 0 \leq r \leq a \tag{2.18}$$

where the coefficients A_k are obtained by multiplying (2.13) and (2.15) by $f_k(r)$ and $F(r)$ respectively and then integrating their difference to give

$$\int_0^a \left(f_k \frac{d^2F}{dr^2} - F \frac{d^2 f_k}{dr^2} \right) dr = (e_k - E) \int_0^a f_k F dr \quad . \tag{2.19}$$

The left-hand side of (2.19) can be evaluated using Green's theorem and the boundary condition satisfied by $f_k(r)$ and, after some algebra, one finally obtains the expression

$$A_k = \frac{1}{a} \frac{f_k(a)}{e_k - E} \left[a \frac{dF}{dr} - \beta F \right]_{r=a} \quad . \tag{2.20}$$

If the R-matrix is now defined, as in §2.1, as

$$\Re = \frac{1}{a} \sum_{k=1}^{\infty} \frac{[f_k(a)]^2}{e_k - E} \tag{2.21}$$

then, according to (2.18) and (2.20), $\Re$ relates the amplitude of $F(r)$ to its derivative on the boundary by

$$\Re = F(a) \left[a \frac{dF}{dr} - \beta F \right]_{r=a}^{-1} \quad . \tag{2.22}$$

The solution of (2.13) in the external region is

$$F(r) = \sin(\kappa r) + K \cos(\kappa r) \qquad r \geq a \tag{2.23}$$

where $\kappa^2 = E$, and the phase shift δ is related to the K-matrix by the relation $K = \tan\ \delta$ (see, for example, Bransden 1983). Substituting (2.23) into (2.22) gives

$$K = -\frac{\sin(\kappa a) - \Re[\kappa a \cos(\kappa a) - \beta \sin(\kappa a)]}{\cos(\kappa a) + \Re[\kappa a \sin(\kappa a) + \beta \cos(\kappa a)]} \tag{2.24}$$

which can be rewritten as

$$\tan(\delta + \kappa a) = \frac{\kappa a \Re}{1 + \Re \beta} \quad . \tag{2.25}$$

Equations (2.21) and (2.22) give two independent expressions for the R-matrix. The first expresses the R-matrix in terms of quantities determined solely from properties of the basis set in the internal region while the second expression gives the R-matrix in terms of the exact solution on the boundary. Therefore (2.21) can be used to obtain a value for $\Re$ on the boundary $r = a$ and this value can then be used in (2.24) to determine K and hence the phase shift.

The above theory can be extended quite easily to the case of non-zero angular momentum by including the $-l(l+1)/r^2$ term in the inner region as well as $V(r)$ in (2.15) when defining the complete set of eigenstates. In the outer region, where $V(r)$ is zero, the $\sin(\kappa r)$ and $\cos(\kappa r)$ terms appearing in (2.23) are replaced by the equivalent spherical Bessel functions, $j_l(\kappa r)$, where

$$\kappa r j_l(\kappa r) \underset{r \to \infty}{\sim} \sin(\kappa r - \frac{l\pi}{2}) \tag{2.26}$$

and the spherical Neumann functions, $n_l(\kappa r)$, where

$$- \kappa r n_l(\kappa r) \underset{r \to \infty}{\sim} \cos(\kappa r - \frac{l\pi}{2}) \tag{2.27}$$

(see Abramowitz and Stegun 1964). Similarly, if a long-range Coulomb potential, $-1/r$, is present in the external region then $\sin(\kappa r)$ and $\cos(\kappa r)$ must be replaced by the regular, s_l, and irregular, c_l, Coulomb wave functions which have asymptotic forms (see Abramowitz and Stegun 1964)

$$\left.\begin{array}{c} s_l(\kappa r) \\ c_l(\kappa r) \end{array}\right\} \underset{r \to \infty}{\sim} \left\{\begin{array}{c} \sin \\ \cos \end{array}\right. \left[\kappa r - \frac{l\pi}{2} + \frac{1}{\kappa}\ln(2\kappa r) + \arg\Gamma(l + 1 - \frac{i}{\kappa})\right] \quad . \tag{2.28}$$

The total wave function is given by

$$\Psi(\mathrm{r}) = \frac{1}{r} F(r) Y_{lm}(\theta, \phi) \tag{2.29}$$

and has the asymptotic form

$$\Psi(\mathbf{r}) \underset{r \to \infty}{\sim} e^{i\kappa . \mathbf{r}} + \frac{e^{i\kappa r}}{r} f(\theta, \phi) \tag{2.30}$$

where $f(\theta, \phi)$ is the scattering amplitude. For central scattering, which is the case being considered here, the scattering amplitude is independent of ϕ and this variable can be dropped from the notation. The S-matrix is defined by

$$F(r) \underset{r \to \infty}{\sim} e^{-i\kappa r} - S_l(-1)^l e^{i\kappa r} \tag{2.31}$$

for scattering of a particle with arbitrary angular momentum by a short-range potential and can be related to the K-matrix and to the phase shift δ_l by

$$S_l = \frac{1 + iK_l}{1 - iK_l} = e^{2i\delta_l} \ . \tag{2.32}$$

The total cross section is then given by the formula

$$\sigma(\kappa) = \int |f(\theta)|^2 d\omega \tag{2.33}$$

where $d\omega = \sin\theta d\theta d\phi$ and where the scattering amplitude $f(\theta)$ is given by

$$f(\theta) = \frac{1}{2i\kappa} \sum_{l=0}^{\infty} (2l+1)(e^{2i\delta_l} - 1) P_l(\cos\theta) \tag{2.34}$$

(see, for example, Geltman 1969).

2.2.1 Computation of the R-matrix

The theory outlined so far has shown that by solving the original differential equation (2.13) in the internal region, subject to the R-matrix boundary conditions (2.16), a complete set of amplitudes $f_k(a)$ and eigenvalues e_k can be obtained from which the R-matrix, and consequently the K-matrix, S-matrix, phase shift and cross section, can be derived. Up to this point, in principle, the theory has been exact. However, in practice, it is obviously impossible to deal with an infinite number of functions f_k so it is necessary to obtain a finite representation of this set. Also, in a practical problem, the original equation is difficult, if not impossible, to solve exactly so basis sets which satisfy some lower order, but physically significant, equation must be used. Burke and Robb (1975) (referred to as BR hereafter) have presented two approaches to the selection of basis functions and these are outlined here. The first employs an orthogonal basis set whose elements satisfy a fixed boundary condition while the second employs an analytic basis set whose elements satisfy arbitrary boundary conditions. A comparison between these two approaches has been made by Shimamura (1978) who uses them to solve a model scattering problem.

Expansion in an orthogonal basis

Consider the eigensolutions of the zero-order differential equation

$$(H_0 - e_{0k})v_k^0(r) = 0 \tag{2.35}$$

subject to the same boundary conditions (2.16), where

$$H_0 = -\frac{d^2}{dr^2} + V_0(r) \tag{2.36}$$

and $V_0(r)$ is some suitably solvable potential whose choice determines the convergence of the method. BR approximate the first N eigensolutions $f_k(r)$ in (2.15) by

$$f_k^{(N)}(r) = \sum_{k'=1}^{N} c_{kk'}^{(N)} v_{k'}^0(r) \quad ; \quad k = 1, N \tag{2.37}$$

where the expansion coefficients $c_{kk'}^{(N)}$ are obtained by diagonalising the symmetric matrix

$$H_{kk'}^{(N)} = \int_0^a v_k^0 \left(-\frac{d^2}{dr^2} + V(r)\right) v_{k'}^0 dr \quad ; \quad k, k' = 1, N \ . \tag{2.38}$$

In order to expand the solution at an arbitrary energy the basis $f_k^{(N)}$ is augmented by the zero-order basis functions v_k^0, $k = N+1, \infty$, to form a complete set. Thus the complete basis can be denoted by $f_k^{(N)}$ which is defined by (2.37) for $k = 1, N$ and by $f_k^{(N)} = v_k^0$ for $k = N+1, \infty$ and then the expansion in (2.18) can be written as

$$F^{(N)}(r) = \sum_{k=1}^{\infty} A_k^{(N)} f_k^{(N)}(r) \tag{2.39}$$

where $F^{(N)}$ is an approximation to the exact solution of (2.13) at the energy E. The analysis proceeds as before through equations (2.19) to (2.22) where now it is assumed that the operator $-d^2/dr^2 + V(r)$ is diagonal in the basis $f_k^{(N)}(r)$. This assumption introduces some error which, however, becomes small as N becomes large provided V_0 is chosen appropriately. The expression for the R-matrix becomes

$$\Re^{(N)} = \frac{1}{a} \sum_{k=1}^{\infty} \frac{[f_k^{(N)}(a)]^2}{e_k^{(N)} - E} \tag{2.40}$$

and for the coefficients $A_k^{(N)}$

$$A_k^{(N)} = \frac{1}{a} \frac{f_k^{(N)}(a)}{e_k^{(N)} - E} \left[a \frac{dF^{(N)}}{dr} - \beta F^{(N)} \right]_{r=a} \tag{2.41}$$

where $F^{(N)}$ and its derivative on the boundary are related by

$$\Re^{(N)} = F^{(N)}(a) \left[a \frac{dF^{(N)}}{dr} - \beta F^{(N)} \right]_{r=a}^{-1} . \tag{2.42}$$

In order to calculate $\Re^{(N)}$ it is necessary to approximate the infinite expansion (2.40) in some way. One could truncate the expansion to the first N terms but this leads to significant errors because the convergence of the R-matrix is quite slow when not in the vicinity of a pole (see Yu Yan and Seaton 1985). The reason for the slow convergence, as explained by Shimamura (1978), is that if all the basis functions have the same logarithmic derivative on the boundary then any linear combination of a finite number of these functions has the same logarithmic derivative. Therefore, as the number of terms is increased, the logarithmic derivative of the resultant wave function remains constant and does not converge uniformly to the exact value as $N \to \infty$ unless the value of β/a is chosen to be close to the logarithmic derivative of the true wave function at $r = a$. A useful procedure, first introduced by Buttle (1967) and later discussed by Heller (1973) and Seaton (1987), can be used whereby the contribution from the R-matrix poles $k = N+1, \infty$, defined by BR as

$$\Re_c^{(N)} = \frac{1}{a} \sum_{k=N+1}^{\infty} \frac{[v_k^0(a)]^2}{e_{0k} - E} \tag{2.43}$$

can be added to extrapolate the summation in (2.40) to completeness, where $v_k^0(a)$ and e_{0k} are the eigensolutions and eigenvalues of the zero-order equation (2.35). Expression (2.43) can be rewritten as

$$\Re_c^{(N)} = \left[\frac{a}{v^0}\frac{dv^0}{dr} - \beta\right]_{r=a}^{-1} - \frac{1}{a}\sum_{k=1}^{N} \frac{[v_k^0(a)]^2}{e_{0k} - E} \tag{2.44}$$

where the first term is the R-matrix of the zero-order problem and the second summation subtracts the first N poles which do not occur in (2.43). The first term in (2.44) can be obtained by solving (2.35) at the energy in question but, in practice, it does not have to be evaluated at each energy and can be approximated to a low order polynomial in E (see Yu Yan and Seaton 1985). The new result for the R-matrix is then

$$\Re^{(N)} = \frac{1}{a}\sum_{k=1}^{N} \frac{[f_k^{(N)}(a)]^2}{e_k^{(N)} - E} - \frac{1}{a}\sum_{k=1}^{N} \frac{[v_k^0(a)]^2}{e_{0k} - E} + \left[\frac{a}{v^0}\frac{dv^0}{dr} - \beta\right]_{r=a}^{-1} \tag{2.45}$$

where now all of the terms in this equation can be evaluated in a straightforward manner.

The advantage of this method is that, in most applications, the zero-order problem is very much easier to solve than the original equation describing the problem and the main calculation is the evaluation and diagonalisation of the Hamiltonian which only has to be done once to enable the R-matrix to be calculated at all energies.

The rate of convergence of the method with increasing N depends on the channel radius a, which should be as small as possible, and on the zero-order potential V_0 which should represent the actual potential $V(r)$ as closely as possible. Zvijac *et al* (1975) have shown how to allow variationally for convergence errors in the Buttle corrected R-matrix calculation.

Expansion in an arbitrary basis set

In the previous paragraphs, an expression for the R-matrix has been developed in terms of an orthogonal basis which satisfies a differential equation with R-matrix boundary conditions. An alternative approach suggested by BR is to use an arbitrary and, in general, nonorthogonal basis to give faster convergence.

The operator

$$H = -\frac{d^2}{dr^2} + V(r) \tag{2.46}$$

is not hermitian in the internal region $0 \leq r \leq a$ with respect to an arbitrary set of functions but Bloch (1957) and Lane and Robson (1966) have pointed out that by including an additional term in (2.46) of the form

$$L_\beta = \delta(r-a)\left(\frac{d}{dr} - \frac{\beta}{a}\right) \tag{2.47}$$

where β is arbitrary, an hermitian operator can be constructed. Then a complete set of functions $f_k(r)$ can be introduced which satisfy

$$(H + L_\beta - e_k)f_k(r) = 0 \tag{2.48}$$

where L_β is the Bloch operator given by (2.47). These functions $f_k(r)$ may be expanded in terms of arbitrary functions since the presence of the Bloch operator L_β guarantees that the $f_k(r)$ satisfy the boundary conditions (2.16) even though the expansion functions, from which the $f_k(r)$ are constructed, do not. The R-matrix and phase shift can then be evaluated by using the same procedure as outlined in §2.2.

The present approach may not require the inclusion of a contribution from the distant levels to obtain reasonable convergence since the basis functions are not restricted to a prescribed value on the boundary and can therefore converge more rapidly to the actual value of the logarithmic derivative of the wave function on the boundary. The convergence of methods using a nonorthogonal basis has been considered by Purcell (1969), Chatwin and Purcell (1971) and Oberoi and Nesbet (1973).

2.3 Scattering of electrons by complex atoms

The R-matrix theory was first introduced into the field of electron-atom collisions by Burke *et al* (1971) and it is this approach that is outlined in this section.

The most difficult and most important effects to be allowed for in the interaction of an electron with an N-electron atom are electron-electron exchange and correlation. In the R-matrix formulation, the total wave function Ψ_E for an electron interacting with an N-electron target can be expanded in the form

$$\Psi_E = \mathcal{A}\sum_{i=1}^{n} \tilde{\Phi}_i F_i + \sum_{j=1}^{m} d_j \phi_j \qquad (2.49)$$

(see Burke *et al* 1971), where

$$\begin{aligned}
\Psi_E &\equiv \Psi_E(\mathbf{x}_1, \ldots, \mathbf{x}_{N+1}) \, , \\
\tilde{\Phi}_i &\equiv \tilde{\Phi}_i(\mathbf{x}_1, \ldots, \mathbf{x}_N, \hat{\mathbf{r}}_{N+1}, \sigma_{N+1}) \, , \\
F_i &\equiv F_i(r_{N+1}) \, , \\
\phi_j &\equiv \phi_j(\mathbf{x}_1, \ldots, \mathbf{x}_{N+1}) \, ,
\end{aligned}$$

and where $\mathbf{x}_p = \mathbf{r}_p, \sigma_p$ are the space-spin coordinates of the p^{th} electron. The functions $\tilde{\Phi}_i$ are formed by coupling the N-electron target state wave functions Φ_i with the spin-angle functions for the scattered electron. The expansion coefficients F_i depend only on the radial coordinate of the scattered electron, r_{N+1}, and the ϕ_j are eigenstates of the $(N + 1)$-electron system. The operator $\mathcal{A}$

antisymmetrises the scattered electron coordinate with the N atomic electron coordinates. In principle the summations in (2.49) can retain an infinite number of terms but in practice they must be truncated to a finite number. Substituting equation (2.49) into the non-relativistic Schrödinger equation gives the equations

$$\begin{aligned} \langle \Phi_i | H_{N+1} - E | \Psi_E \rangle = 0 \quad &, \quad i = 1, n \\ \langle \phi_j | H_{N+1} - E | \Psi_E \rangle = 0 \quad &, \quad j = 1, m \end{aligned} \tag{2.50}$$

where the Hamiltonian for any system of N electrons moving in the field of a nucleus of charge Z is defined by (2.2) and where the integrals are taken over all electron coordinates except the radial coordinate of the scattered electron. These equations are known as the close-coupling equations and were originally introduced by Massey and Mohr (1932) and have subsequently been discussed in detail by many authors, for instance Burke and Smith (1962), Burke and Seaton (1971) and Smith (1971). In order to be able to evaluate the matrix elements in (2.50), using standard methods of atomic structure theory, it is necessary to impose the constraint that the channel functions F_i (with quantum number l_i) are orthogonal to the radial functions used to construct the functions ϕ_j. This does not imply a constraint on Ψ_E provided a suitable set of functions ϕ_j, usually called correlation functions, is included in (2.49) (see Burke 1978).

The expansion in (2.49) is fully anti-symmetrised. If the second sum in (2.49), the anti-symmetrisation and the orthogonality constraint are omitted, the equations (2.50) give for the functions F_i

$$(h - \kappa^2 + \mathbf{V})\mathbf{F} = 0 \tag{2.51}$$

c.f. (2.4), where

$$h = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2z}{r} , \tag{2.52}$$

$\mathbf{V}$ is a local potential operator, $\mathbf{F}$ is a column vector of the functions F_i and $z = Z - N$ (see Burke and Seaton 1971). The equations are of the form (2.51) if one considers a target not containing any electrons and it is this case that will be of main concern in the present thesis.

When the electron is close to the target, that is, within the effective radius a of the charge distribution of the N electrons, the interaction becomes quite complex since electron exchange and correlation effects are present and these effects make the close-coupling equations difficult to solve. Therefore, in this region the R-matrix method can be used to give a solution. In the outer region electron exchange effects can be neglected and the coupled equations simplify considerably enabling a solution to be evaluated directly.

A number of computer codes have been developed to solve the close-coupling equations in the inner region, of which IMPACT (Crees *et al* 1978) and RMATRX (Berrington 1974, 1978) are the most widely used. IMPACT uses finite difference formulae to reduce the integro-differential equations to linear algebraic equations which are then solved. RMATRX uses the R-matrix method to give a solution. Detailed checks have been made by Berrington *et al* (1987) between the two methods and they find that the results are in close agreement. However, of the two methods, RMATRX is considerably faster.

2.3.1 The R-matrix basis

As outlined by BR, the main problem in applying the R-matrix method to the scattering of electrons by complex atoms is to define a suitable zero-order basis in terms of which the total wave function can be expanded. The radius of the internal region a is chosen such that the charge distribution of the N-electron target is contained within the sphere $r = a$. The total wave function in the internal region can then be expanded for any energy in terms of the R-matrix basis functions ψ_k in the form

$$\Psi_E = \sum_k A_{Ek}\psi_k \tag{2.53}$$

(see Burke *et al* 1971) where

$$\psi_k = \mathcal{A}\sum_{ij} c_{ijk}\tilde{\Phi}_i u_{ij} + \sum_j d_{jk}\phi_j \tag{2.54}$$

and where the u_{ij} are the finite set of continuum orbitals describing the motion of the scattered electron.

The target functions Φ_i, used to construct the $\tilde{\Phi}_i$, are expanded in terms of orthonormal configurations in the form

$$\Phi_i = \sum_j a_{ij}\chi_j \tag{2.55}$$

where the index i includes the quantum numbers of the state and where the configurations $\chi_j \equiv \chi_j(\mathbf{x}_1, ..., \mathbf{x}_N)$ are formed from the atomic orbitals of the N-electron atom. Each orbital is a product of a radial function $P_{n_i l_i}(r)$, a spherical harmonic and a spin function. The radial functions $P_{n_i l_i}(r)$, which occur in the χ_j in (2.55), satisfy the orthogonality relations

$$\int_0^\infty P_{n_i l_i} P_{n_j l_j} dr = \delta_{n_i n_j} \tag{2.56}$$

when the orbital angular momenta satisfy $l_i = l_j$ and form the expansion basis for all configurations χ_j. The ϕ_j in (2.54) are analogous to the χ_j in (2.55) but contain all the electrons of the $(N+1)$-electron system.

Burke *et al* (1971) evaluate the $P_{n_i l_i}(r)$ by expanding them in terms of a linear combination of Slater orbitals and the coefficients a_{ij} can then be determined by diagonalising the matrix

$$\langle\Phi_i|H_N|\Phi_j\rangle = e_i^N\delta_{ij} \tag{2.57}$$

where H_N is defined in (2.2). The basis orbitals can be refined, if necessary, by using an iterative process and this procedure, together with the diagonalisation in

(2.57) has been programmed by Hibbert (1975). An alternative, but essentially equivalent, approach called the multiconfigurational Hartree-Fock scheme, has been programmed by Fischer (1969, 1972) and this involves solving a set of coupled nonlinear integro-differential equations for the orbitals, again by using an iterative process. BR point out that although this process yields exact numerical orbitals, it is often more difficult to obtain convergence than with the approach considered by Hibbert.

It may be necessary to add pseudo-states to the expansion in equation (2.55) in order to accurately reproduce the polarisability of the N-electron atom and the infinity of open channels (Burke *et al* 1969). While these pseudo-states cannot be written down exactly in the case of a complex atom they may be determined using a variational method (see Burke and Mitchell 1974).

The continuum basis orbitals u_{ij} are defined by Burke *et al* (1971) as eigen-solutions of the equation

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + V(r) + \kappa_j^2\right) u_{ij}(r) = \sum_{n=l_i+1}^{n_{max}(l_i)} \lambda_{ijn} P_{nl_i} \tag{2.58}$$

where the summation over n goes over all orbitals occurring in the expansion of the atomic states for each orbital angular momentum. The u_{ij} are required to satisfy the R-matrix boundary conditions

$$u_{ij}(0) = 0 \qquad ; \qquad \left.\frac{a}{u_{ij}(a)} \frac{du_{ij}}{dr}\right|_{r=a} = \beta \tag{2.59}$$

and the orthonormality condition

$$\int_0^a u_{ij} u_{ij'} dr = \delta_{jj'} \tag{2.60}$$

for each i. The λ_{ijn} are Lagrange multipliers and are chosen such that

$$\int_0^a u_{ij}(r) P_{nl_i}(r) dr = 0 \tag{2.61}$$

for all n and j. The conditions (2.60) and (2.61) are imposed mainly for numerical convenience (Burke 1978). The coefficients c_{ijk} and d_{jk} are determined by diagonalising H_{N+1} in the internal region to give

$$\langle \psi_k | H_{N+1} | \psi_{k'} \rangle = e_k^{N+1} \delta_{kk'} \quad . \tag{2.62}$$

The evaluation of the matrix elements in equation (2.62) proceeds in the same way as the diagonalisation of the atomic basis in equation (2.57) and therefore the same computer codes can be used.

An alternative approach to the evaluation of the basis orbitals u_{ij}, considered by Fano and Lee (1973) and Lee (1974), can be adopted whereby the parameter β in (2.59) is adjusted so that an eigenenergy e_k^{N+1} falls at the energy E of interest. In this approach, the R-matrix can be defined by a singular term and this avoids any convergence problems, and consequently the need for any Buttle corrections (discussed in the next section). The basis orbitals can, in this case, be expanded in terms of Slater-type-orbitals and the wave function obtained has a continuous derivative on the boundary. The main disadvantage of this approach, over that of Burke *et al* (1971), is that it requires a separate diagonalisation at each energy of interest and so is most efficient if only a small number of energy values are being considered. Fano and Lee have shown, however, that by suitable interpolation procedures the diagonalisations can be made fast over a limited energy range.

2.3.2 Calculation of the R-matrix

As before, the total wave function Ψ_E can be expanded in the internal region at any energy in terms of the basis ψ_k to give

$$\Psi_E = \sum_k A_{Ek} \psi_k \tag{2.63}$$

where

$$H_{N+1} \Psi_E = E \Psi_E \quad . \tag{2.64}$$

The coefficients A_{Ek} can be determined by considering the relation

$$\langle\psi_k|H_{N+1}|\Psi_E\rangle - \langle\Psi_E|H_{N+1}|\psi_k\rangle = (E - e_k^{N+1})\langle\psi_k|\Psi_E\rangle \qquad (2.65)$$

which follows from equations (2.62), (2.63) and (2.64), where the radial integrals in (2.65) are restricted to the internal region $r \leq a$. Writing

$$f_{ik}(r) = \sum_j c_{ijk} u_{ij}(r) \qquad (2.66)$$

and

$$F_i(r) = \sum_k A_{Ek} f_{ik}(r) \qquad (2.67)$$

which is the radial wave function of the scattered electron in channel i in Ψ_E, and using the boundary condition (2.59) at $r = a$ satisfied by the f_{ik}, one obtains the expression given by BR,

$$\sum_i f_{ik}(a)\left[a\frac{dF_i}{dr} - \beta F_i\right]_{r=a} = a(e_k^{N+1} - E)A_{Ek} \ . \qquad (2.68)$$

This can be rewritten in terms of the R-matrix, whose elements are defined by (see §2.1)

$$\Re_{ij} = \frac{1}{a}\sum_k \frac{f_{ik}(a)f_{jk}(a)}{e_k^{N+1} - E} \ , \qquad (2.69)$$

in the form

$$F_i(a) = \sum_j \Re_{ij}\left[a\frac{dF_j}{dr} - \beta F_j\right]_{r=a} \ . \qquad (2.70)$$

The amplitudes $f_{ik}(a)$ and the poles e_k^{N+1} of the R-matrix are obtained directly from the eigenvectors and eigenvalues of the Hamiltonian matrix defined by equation (2.62) and then, from equation (2.70), the logarithmic derivative of the scattered electron wave function on the boundary $r = a$ can be determined.

Of course, in practice, the expansion in (2.69) must be truncated to a finite number of terms and this can lead to significant error (see, for example, Yu Yan and Seaton 1985). However, the omitted levels can be included by adding the correction discussed by Buttle (1967), i.e.

$$\Re^c_{ii} = \left[\frac{a}{u_i^0} \frac{du_i^0}{dr} - \beta \right]^{-1}_{r=a} - \frac{1}{a} \sum_j \frac{[u^0_{ij}(a)]^2}{\kappa^2_{ij} - \kappa^2_i} \tag{2.71}$$

where $u^0_{ij}(r)$ is the j^{th} eigensolution of the differential equation

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + V^0_{ii}(r) + \kappa^2_i \right) u^0_i(r) = 0 \tag{2.72}$$

satisfying the boundary conditions (2.59) and $u^0_i(r)$ is the solution at an arbitrary energy. $V^0_{ii}(r)$ is the diagonal element of some zeroth-order potential in channel i. Again, as mentioned in §2.2.1, the first term in (2.71) does not have to be evaluated at each energy and can be approximated to a low order polynomial in E. The quantity κ^2_i in equation (2.71) is related to the total energy E by

$$\kappa^2_i = (E - e^N_i) \quad . \tag{2.73}$$

The summation in equation (2.71) subtracts those levels that have already been included in equation (2.69) so that $\Re^c_{ii}$ only contains the contribution from the distant neglected levels in the i^{th} channel. The differential equation (2.72) can easily be solved since exchange potentials are not included in V^0_{ii}.

2.3.3 Solution in the outer region

The R-matrix method can be used to provide a solution to the close-coupling equations in the internal region $r \leq a$ and now it is necessary to solve these equations in the external region $r > a$.

In the external region $r > a$ exchange effects between the scattered electron and the target can essentially be neglected, provided a is chosen appropriately, and the close-coupling equations (2.50) reduce to the set of coupled differential equations, c.f. (2.51) and (2.52),

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r} + \kappa^2_i \right) F_i(r) = \sum_{j=1}^{n} V_{ij}(r) F_j(r) \quad ; \quad i = 1, n \quad , \quad r \geq a \tag{2.74}$$

where the potential matrix $V_{ij}(r)$ is given by Burke *et al* (1971) as

$$V_{ij} = 2\langle\tilde{\Phi}_i|\sum_{k=1}^{N} r_{k,N+1}^{-1}|\tilde{\Phi}_j\rangle \tag{2.75}$$

and where the integrals are again taken over all electron coordinates except the radial coordinate of the scattered electron. Using the expansion

$$\sum_{k=1}^{N} r_{k,N+1}^{-1} = \sum_{\lambda=0}^{\infty} r_{N+1}^{-\lambda-1} \sum_{k=1}^{N} r_k^{\lambda} P_{\lambda}(\cos\theta_{k,N+1}) \tag{2.76}$$

where $\cos\theta_{k,N+1} = \hat{\mathbf{r}}_k \cdot \hat{\mathbf{r}}_{N+1}$, equation (2.74) becomes

$$\begin{aligned}\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2z}{r} + \kappa_i^2\right) F_i(r) &= \sum_{\lambda=1}^{M}\sum_{j=1}^{n} a_{ij}^{\lambda} r^{-\lambda-1} F_j(r) \\ &; \quad i = 1,n \quad , \quad r \geq a \end{aligned} \tag{2.77}$$

where

$$a_{ij}^{\lambda} = 2\langle\tilde{\Phi}_i|\sum_{k=1}^{N} r_k^{\lambda} P_{\lambda}(cos\theta_{k,N+1})|\tilde{\Phi}_j\rangle \tag{2.78}$$

$z = Z - N$ and M is the maximum value of λ allowed by the triangular relations imposed by the angular integrals in equation (2.78) (see Edmonds 1960).

Assuming that at the energy of interest

$$\begin{aligned} &\kappa_i^2 > 0, \quad i = 1, n_a, \qquad \textit{open channels} \\ &\kappa_i^2 < 0, \quad i = n_a + 1, n, \quad \textit{closed channels} \end{aligned} \tag{2.79}$$

the asymptotic form of the solution defining the K-matrix is then given by

$$\begin{aligned} F_{ij} &\underset{r\to\infty}{\sim} \kappa_i^{\frac{1}{2}}(\delta_{ij}\sin\theta_i + K_{ij}\cos\theta_i) \quad && i = 1, n_a \qquad j = 1, n_a \\ F_{ij} &\underset{r\to\infty}{\sim} O(r^{-2}) && i = n_a + 1, n \quad j = 1, n_a \end{aligned} \tag{2.80}$$

where the second index j has been introduced on the solution vector F_{ij} to label the n_a independent solutions and where

$$\begin{aligned} \theta_i &= \kappa_i r - \tfrac{1}{2} l_i \pi - \eta_i \ln(2\kappa_i r) + \sigma_{l_i} \\ \eta_i &= -z/\kappa_i \\ \sigma_{l_i} &= \arg\Gamma(l_i + 1 + i\eta_i) \qquad . \end{aligned} \tag{2.81}$$

To relate the $n \times n$ dimensional R-matrix given in equation (2.69) to the $n_a \times n_a$ dimensional K-matrix given in equation (2.80), a set of $n + n_a$ linearly independent solutions $v_{ij}(r)$ of equation (2.77) are introduced which satisfy the boundary conditions

$$\begin{array}{llll} v_{ij} \underset{r \to \infty}{\sim} \delta_{ij} \sin\theta_i + O(r^{-1}) & i = 1 \ldots n & j = 1 \ldots n_a & \\ v_{ij} \underset{r \to \infty}{\sim} \delta_{i(j-n_a)} \cos\theta_i + O(r^{-1}) & i = 1 \ldots n & j = n_a + 1 \ldots 2n_a & \\ v_{ij} \underset{r \to \infty}{\sim} \delta_{i(j-n_a)} e^{-|\kappa_i| r} + O(r^{-1}) & i = 1 \ldots n & j = 2n_a + 1 \ldots n + n_a & . \end{array} \tag{2.82}$$

These solutions can be calculated using any one of the codes ASYM (Norcross 1969), ASYPCK (Crees 1980, 1981) or CFASYM (Noble and Nesbet 1984). Alternatively, they may be represented by Bessel functions or evaluated using the perturbation method described by Seaton (1985).

Burke *et al* (1971) expand the radial wave function of the scattered electron in the form

$$F_{ij}(r) = \sum_{l=1}^{n+n_a} x_{lj} v_{il} \qquad i = 1 \ldots n \qquad j = 1 \ldots n_a \tag{2.83}$$

where the coefficients x_{lj} satisfy the $n + n_a$ equations

$$\begin{array}{ll} x_{lj} = \kappa_j^{-\frac{1}{2}} \delta_{lj} & l = 1 \ldots n_a \\ \displaystyle\sum_{l=1}^{n+n_a} x_{lj} \left(v_{il}(a) - \sum_{m=1}^{n} \mathfrak{R}_{im} \left[a \frac{dv_{ml}}{dr} - \beta v_{ml} \right]_{r=a} \right) = 0 & i = 1 \ldots n \end{array} \tag{2.84}$$

which must be solved for each $j = 1 \ldots n_a$. It follows from equation (2.80) that

$$K_{ij} = \kappa_i^{\frac{1}{2}} x_{(i+n_a)j} \qquad i,j = 1 \ldots n_a \tag{2.85}$$

and the S-matrix is now given by the matrix equation

$$\mathbf{S} = \frac{\mathbf{1} + i\mathbf{K}}{\mathbf{1} - i\mathbf{K}} \tag{2.86}$$

from which the cross section can be evaluated using standard methods (e.g. Blatt and Biedenharn 1952; Lane and Thomas 1958).

2.3.4 Calculation of bound states using the R-matrix

The close-coupling approximation of electron-atom collision theory can be used to make calculations for bound states of atomic systems and this application is usually referred to as the frozen-cores (FCS) approximation (see Seaton 1985). Extensive FCS calculations have been made, for many systems, using the computer program IMPACT (Crees *et al* 1978) to solve the integro-differential equations (see, for example Saraph and Seaton 1980; Giles *et al* 1979; Mendoza 1981, 1982) and using the computer program RMATRX to calculate bound states that are required for the determination of photoionisation cross sections (see, for example, Burke and Ohja 1983; Taylor and Burke 1976; Le Dourneuf *et al* 1975, 1976). Seaton (1985) has given a detailed account of the implementation of the FCS method with particular emphasis on its use in conjunction with the R-matrix method.

The idea of closed and open channels was introduced in §2.3.3. When all of the channels are closed the wave function corresponds to a bound state of the electron plus target atom and the problem reduces to finding a discrete eigenvalue and the corresponding eigenvector of H_{N+1}. In this case one can define a set of n linearly independent solutions of equations (2.77) spanning the outer region, $r > a$, which satisfy the boundary conditions

$$v_{ij} \underset{r\to\infty}{\sim} e^{-|\kappa_i|r}\delta_{ij} \quad , \quad i,j = 1,n \tag{2.87}$$

(see Seaton 1985) and which can be calculated using the computer codes and methods mentioned in the previous section. The required solution can then be expanded in terms of these solutions to give

$$F_i = \sum_{j=1}^{n} v_{ij}x_j \quad , \quad i = 1,n \quad a \le r \le \infty \tag{2.88}$$

and the coefficients x_j can then be determined by substituting equation (2.88) into equation (2.70) which leads to the n homogeneous equations

$$\sum_{j=1}^{n}\left(v_{ij}(a)-\sum_{k=1}^{n}\Re_{ik}\left[a\frac{dv_{kj}}{dr}-\beta v_{kj}\right]_{r=a}\right)x_j=0 \quad , \quad i=1,n \ . \tag{2.89}$$

These equations can be simplified by writing

$$\sum_{j=1}^{n}B_{ij}x_j=0 \quad , \quad i=1,n \tag{2.90}$$

where

$$B_{ij}=v_{ij}(a)-\sum_{k=1}^{n}\Re_{ik}\left[a\frac{dv_{kj}}{dr}-\beta v_{kj}\right]_{r=a} \quad . \tag{2.91}$$

Equations (2.91) only have non-trivial solutions at the negative energy eigenvalues corresponding to bound states of the electron-atom system and the condition for a solution is

$$\det \mathbf{B}=0 \ . \tag{2.92}$$

In order to find a solution BR suggest solving the equations

$$\sum_{j=2}^{n}B_{ij}x_j=-B_{i1} \quad , \quad i=2,n \tag{2.93}$$

obtained by setting $x_1=1$ in (2.90), and then looking for zeros of

$$g(E)=\sum_{j=1}^{n}B_{1j}x_j \tag{2.94}$$

as a function of energy. This can be achieved using Newton's iteration method which involves determining the asymptotic functions in equations (2.87) at a sequence of negative energies until convergence on the required root is obtained.

When $r>a$ the second expansion in (2.54) does not contribute and the first expansion when substituted into (2.53) can be summed to yield

$$\Psi_E=\mathcal{A}\sum_i\tilde{\Phi}_iF_i(r) \quad , \quad a\le r\le\infty \ . \tag{2.95}$$

If the state is sufficiently strongly bound this term will be very small due to the rapid exponential decay of the components v_{ij}. It can therefore usually be neglected in applications to photoionisation or electron-atom ionisation from the ground state. However, in the case of negative ions, where the electron affinity is small, a significant contribution to the integrals can be expected from this region.

In the previous sections, Buttle corrections have been considered only for positive energies. BR have considered the evaluation of a Buttle correction for negative energies and conclude that such a correction, given by equation (2.71), can be extended to negative energies without much difficulty.

2.4 Electron-molecule collisions

R-matrix theory has also been successfully introduced into the field of electron-molecule scattering by Schneider (1975a,b) and Schneider and Hay (1976) who show how the scattered electron can be represented by analytic rather than numerical orbitals. Subsequently, these ideas have been developed by Burke *et al* (1977) to formulate a general R-matrix theory of low-energy scattering of electrons by diatomic molecules based on the frame transformation of Chang and Fano (1972).

The R-matrix theory of electron-molecule scattering starts from the 'fixed-nuclei approximation' in which the motions of the scattered and target electrons are first calculated in the field of the nuclei which are assumed fixed in space. The fixed-nuclei approximation then provides the first stage in a calculation where the nuclear motion is explicitly included. The inclusion of the nuclear motion will not be covered here but a detailed account of this stage of the calculation can be found in the paper by Gillan *et al* (1987) who apply the R-matrix method to electron-nitrogen molecule scattering.

For each fixed internuclear separation, configuration space is partitioned into two regions separated by a sphere of radius $r = a$ where r is the relative coordinate of the scattered electron and the centre of gravity G of the N-electron target (see figure 2.2). The radius a is chosen large enough to just envelop the charge distribution of the target states of interest. Therefore, when the scattered electron is in the internal region, $r < a$, it lies within the molecular charge cloud and electron exchange and correlation effects must be included. In this region the target molecule plus scattered electron behave analogously to a bound state and a multi-centre configuration interaction expansion of the wave function can be used. On the other hand, when the scattered electron is in the external region, $r > a$, electron exchange between the scattered electron and the target is unimportant. The scattered electron then moves in the long-range multipole potential of the target and a single-centre expansion of the wave function can be adopted.

2.4.1 The inner region

The inner region is defined by $r_p \leq a$ for all p, where r_p is the distance between the p^{th} electron in the scattering system and the centre of gravity, G, of the molecule. Figure 2.2 shows the coordinate frame for the molecular expansion. Following the method of Burke *et al* (1977) (referred to as BMS hereafter) the trial wave function describing scattering of a low-energy electron by an N-electron diatomic molecule is expanded in terms of the multi-centre basis

$$\psi_k = \mathcal{A} \sum_{ij} \alpha_{ijk} \tilde{\phi}_i \eta_j + \sum_i \beta_{ik} \chi_i \tag{2.96}$$

where

$$\begin{aligned} \psi_k &\equiv \psi_k(\mathbf{x}_1, ..., \mathbf{x}_{N+1}) \,, \\ \tilde{\phi}_i &\equiv \tilde{\phi}_i(\mathbf{x}_1, ..., \mathbf{x}_N, \sigma_{N+1}) \,, \\ \eta_j &\equiv \eta_j(\mathbf{r}_{N+1}) \,, \end{aligned}$$

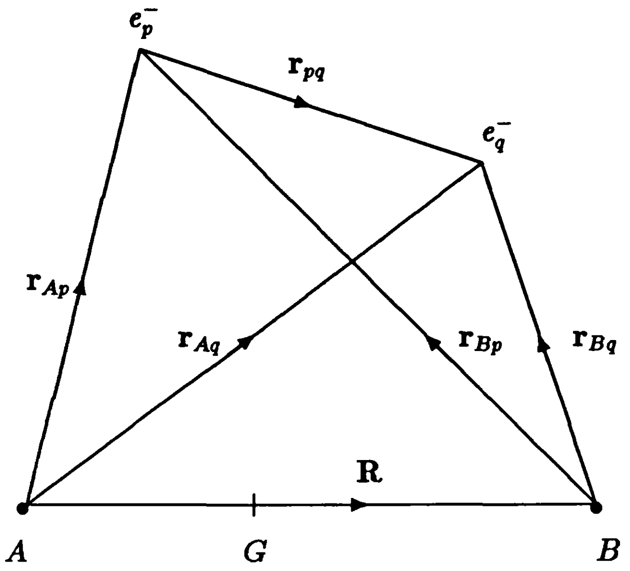


Figure 2.2: Coordinate frame for the molecular expansion.

$$\chi_i \equiv \chi_i(\mathbf{x}_1, ..., \mathbf{x}_{N+1}) ,$$

and where $\mathbf{x}_p = \mathbf{r}_p, \sigma_p$ are the space-spin coordinates of the electrons. The operator $\mathcal{A}$ antisymmetrises the scattered electron coordinate with the N target electron coordinates. All the quantities in (2.96) depend parametrically on R, the internuclear separation, and for any given situation R is considered to be fixed (making use of the Born-Oppenheimer approximation). The functions $\tilde{\phi}_i$ are formed by coupling two-centre target eigenstates ϕ_i to the spin function of the scattered electron to form eigenstates of the total spin operator and its z component. Some pseudo-states may also be included in the set ϕ_i (see Gillan *et al* 1988). The target eigenstates ϕ_i are expanded in the form

$$\phi_i = \sum_j d_{ij} \varphi_j \tag{2.97}$$

where φ_j are formed from bound molecular orbitals of the N-electron target. The molecular orbitals are constructed from atomic orbitals centred on the nuclei which become negligibly small on the boundary $r = a$. The coefficients d_{ij} are evaluated by diagonalising the Born-Oppenheimer Hamiltonian H_N for the N-electron system to give

$$\langle \phi_i | H_N | \phi_j \rangle = e_i^N \delta_{ij} \tag{2.98}$$

where

$$H_N = \sum_{p=1}^{N} \left(-\nabla_p^2 - \frac{2z_A}{r_{Ap}} - \frac{2z_B}{r_{Bp}} \right) + \sum_{p>q=1}^{N} \frac{2}{r_{pq}} + \frac{2z_A z_B}{R} \tag{2.99}$$

in Rydbergs.

The η_j are three-centre orbitals representing the scattered electron which are non-zero on the boundary of the internal region. BMS expand these functions in terms of linear combinations of Slater-type-orbitals (STO) centred on the two nuclei and on the centre of gravity of the target, G. An alternative expansion for the orbitals centred on G is given by Schneider (1975a) in terms of floating Gaussians which are evaluated in prolate spheroidal coordinates. Although this expansion is more flexible than that used by BMS for diatomic molecules, it leads to a more complicated matching procedure at the last stage of the calculation. The use of STO for the orbitals on the centre of gravity of the molecule has since been abandoned due to linear dependence effects (see Wilson 1987) and has been superseded by the use of numerical basis functions for these orbitals suggested by Burke *et al* (1983). Thus the η_j can be expanded in the form

$$\eta_j(\mathbf{r}) = \sum_i r^{-1} u_i(r) Y_{l_i m_{l_i}}(\hat{\mathbf{r}}) a_{ij} + \sum_i \chi_i^A(\mathbf{r}) b_{ij} + \sum_i \chi_i^B(\mathbf{r}) c_{ij} \tag{2.100}$$

where the u_i are the numerical basis functions, the $Y_{l_i m_{l_i}}$ are spherical harmonics and the χ_i^A and χ_i^B are STO centered on the nuclei. The coefficients a_{ij}, b_{ij} and c_{ij} are obtained by Schmidt orthogonalisation so that the η_j are normalised and orthogonal to the orbitals used to construct the ϕ_i and χ_i. The numerical basis functions satisfy the equation

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + V_0(r) + \kappa_i^2 \right) u_i(r) = \sum_j \lambda_{ij} P_j(r) \tag{2.101}$$

subject to the boundary conditions

$$u_i(0) = 0 \qquad ; \qquad \left.\frac{a}{u_i}\frac{du_i}{dr}\right|_{r=a} = b \ . \tag{2.102}$$

Some single-centre components $P_j(r)$ of the molecular orbitals can be included on the right hand side of (2.101). In this case the Lagrange multipliers λ_{ij} are chosen so that

$$\int_0^a u_i(r)P_j(r)dr = 0 \tag{2.103}$$

(see Tennyson *et al* 1987). $V_0(r)$ is a model potential and in the work of Gillan *et al* is chosen to be the spherically symmetric part of the static potential of the target.

2.4.2 The R-matrix

The development of the R-matrix for atomic processes, given in previous sections, requires a zeroth-order approximation to the true Hamiltonian to generate the basis functions. However, in the case of scattering by molecules there is no simple, solvable zeroth-order Hamiltonian so a theory, discussed in detail by Shimamura (1977) and Gillan *et al* (1987), has been developed which does not require such an approximation.

The Schrödinger equation for the total system in the Born-Oppenheimer approximation is

$$(H_{N+1} - E)\Psi = 0 \tag{2.104}$$

where H_{N+1} is defined analogously to H_N in (2.99) and Ψ is the total wave function. The restriction of the wave function to a finite region of configuration space leads to a non-hermitian Hamiltonian but by using the Bloch (1957) *L*-operator formalism, the operator

$$L_{N+1} = \sum_{i=1}^{N+1}\sum_j |\tilde{\phi}_j(\bar{\mathbf{r}}_i)Y_{l_j m_{l_j}}(\hat{\mathbf{r}}_i)\rangle\delta(r_i - a)\left(\frac{d}{dr_i} - \frac{b-1}{r_i}\right)\langle\tilde{\phi}_j(\bar{\mathbf{r}}_i)Y_{l_j m_{l_j}}(\hat{\mathbf{r}}_i)| \tag{2.105}$$

can be added to (2.99) to give an hermitian operator (see Gillan *et al* 1987), where

$$\tilde{\phi}_j(\bar{\mathbf{r}}_i) \equiv \tilde{\phi}_j(\mathbf{x}, ..., \mathbf{x}_{i-1}, \mathbf{x}_{i+1}, ..., \mathbf{x}_{N+1}, \sigma_i) \quad ,$$

and b is an arbitrary constant. The expansion coefficients α_{ijk} and β_{ik} in equation (2.96) are then determined by diagonalising the operator $H_{N+1} + L_{N+1}$ in the internal region to give

$$\langle \psi_k | H_{N+1} + L_{N+1} | \psi_{k'} \rangle = e_k \delta_{kk'} \tag{2.106}$$

where the eigenenergies e_k are real.

The Schrödinger equation in the internal region can be written for each fixed R as

$$(H_{N+1} + L_{N+1} - E)\Psi = L_{N+1}\Psi \tag{2.107}$$

and this can be formally solved to give

$$\Psi = (H_{N+1} + L_{N+1} - E)^{-1} L_{N+1}\Psi \quad . \tag{2.108}$$

The operator $(H_{N+1}+L_{N+1}-E)^{-1}$ can be expanded in terms of the eigenfunctions defined by (2.96) and (2.106) to give

$$|\Psi\rangle = \sum_k \frac{|\psi_k\rangle\langle\psi_k|L_{N+1}|\Psi\rangle}{e_k - E} \quad . \tag{2.109}$$

This equation is projected onto the channel functions $\tilde{\phi}_i Y_{l_i m_{l_i}}$ and evaluated on the boundary $r = a$. By defining the reduced radial functions F_i by

$$F_i(r) = \langle \tilde{\phi}_i Y_{l_i m_{l_i}} | \Psi \rangle \tag{2.110}$$

and the surface amplitudes f_{ik} by

$$f_{ik} = \langle \tilde{\phi}_i Y_{l_i m_{l_i}} | \psi_k \rangle_{r=a} \tag{2.111}$$

Gillan *et al* finally obtain the expression

$$F_i(a) = \sum_j \Re_{ij}(E) \left[a\frac{dF_j}{dr} - bF_j(a) \right]_{r=a} \tag{2.112}$$

where the R-matrix

$$\Re_{ij} = \frac{1}{a}\sum_k \frac{f_{ik}(a)f_{jk}(a)}{e_k - E} \tag{2.113}$$

has been introduced. The R-matrix is obtained at all energies by diagonalising $H_{N+1} + L_{N+1}$ once to determine the eigenvalues e_k and the corresponding eigenvectors ψ_k. The surface amplitudes f_{ik} can then be obtained directly. The calculations involved in setting up and diagonalising $H_{N+1} + L_{N+1}$ can be performed using the ALCHEMY molecular structure package programmed by McLean (1971) and modified by Noble (1982) to enable numerical orbitals to be included.

In practice, all the terms in (2.113) cannot be retained and in this case a Buttle (1967) correction (discussed in previous sections) may be included to allow for the effect of the higher lying poles not included explicitly.

2.4.3 The external region

In order to relate the R-matrix calculated on the boundary at $r = a$ to the solution of the problem in the outer regions it is necessary to derive the explicit form of the equations in these regions corresponding to expansion (2.96). These equations are assumed to be single-centre no-exchange close-coupling equations in the molecular frame.

Since exchange can be neglected in the outer regions the total wave function can be expanded in the form

$$\Psi = \sum_i \tilde{\phi}_i(\mathrm{x}_1, ..., \mathrm{x}_N, \sigma_{N+1}) r_{N+1}^{-1} F_i(r_{N+1}) Y_{l_i m_{l_i}}(\hat{\mathbf{r}}_{N+1}) \ . \tag{2.114}$$

Substituting (2.114) into the Schrödinger equation and projecting onto the channel functions $\tilde{\phi}_i Y_{l_i m_{l_i}}$ Gillan *et al* show that the reduced radial functions F_i satisfy, for each internuclear separation, the set of coupled differential equations

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \kappa_i^2\right) F_i(r) = \sum_j V_{ij}(r) F_j(r) \tag{2.115}$$

where

$$\kappa_i^2 = (E - e_i^N) \tag{2.116}$$

and e_i^N are the eigenenergies of the target states ϕ_i. In the outer region the radial coordinate of the scattered electron can be assumed to be greater than that of any of the target electrons. Therefore, as suggested by Burke and Schey (1962), Burke *et al* (1964) and Gailitis (1976), the potential V_{ij} can be written as a multipole expansion in inverse powers of r. The coupled equations must be solved for each energy E subject to the asymptotic boundary conditions

$$F_{ij} \underset{r \to \infty}{\sim} \kappa_i^{-\frac{1}{2}} (\sin\theta_i \delta_{ij} + \cos\theta_i K_{ij}) \tag{2.117}$$

where $\theta_i = \kappa_i r - l_i \pi/2$ in radians. This equation defines the K-matrix which couples the open channels. Substituting the solutions defined by (2.117) into (2.112) gives the K-matrix in terms of the R-matrix.

A number of codes have already been mentioned in earlier sections for calculating outer region solutions. Gillan *et al* use the R-matrix propagation code of Baluja *et al* (1982) and Morgan (1984) (which is described in detail in §2.5) together with the asymptotic code of Noble and Nesbet (1984) to solve (2.115) in the external region.

2.5 R-matrix propagation methods

R-matrix propagation methods were first introduced into scattering theory by Light and Walker (1976). They developed a new approach to the solution of close-coupled equations which essentially propagated information pertaining to a physical boundary value problem. This approach avoided all difficulties with exponential growth of closed channels and lead to algorithms which substantially reduced the computer time required for integrating close-coupled equations. The method is based upon a division of configuration space into smaller regions in each of which a local R-matrix may be determined analytically. These local R-matrices are then assembled recursively to give the R-matrix spanning the entire region. The scattering matrix (S-matrix) is then determined in a straightforward way from the final R-matrix.

This method has proved to be useful in a number of areas of physics. For example, it has recently been introduced into the field of semiconductor physics as a practical technique for estimating the electronic energy levels in multiquantum well structures (Schwartz 1987) and aperiodic semiconductor structures (Vasquez 1987). It has also proved useful in the study of chemical reactions where, for example, it has been used to develop a direct method for determining time delays for reactive scattering problems (Walker and Hayes 1989).

In electron scattering processes, propagation methods become particularly useful when the radius at which electron exchange can be neglected is not large enough to allow asymptotic expansion methods or perturbation methods, used for outer region solutions, to converge to the required accuracy. In this intermediate region, an R-matrix propagation method may be used to give a solution. Baluja *et al* (1982) have developed an R-matrix propagation program (RPROP) for solving coupled second-order differential equations over a given range of the independent variable. Given the R-matrix at one end of the range the program calculates the R-matrix at the other end of the range. This version of the program restricts the potential interaction to the long-range multipole potential between an electron and an atom ion or molecule. A modified version of the program (RPROP2) has been produced by Morgan (1984) in which more general potentials are treated.

The program of Baluja *et al* (1982) (referred to as BBM hereafter) propagates the solution of the set of n coupled differential equations

$$\left(\frac{d^2}{dr^2} + \kappa_i^2\right) F_i(r) = \sum_{j=1}^{n} V_{ij}(r) F_j(r) \ , \tag{2.118}$$

which are of the form (2.115), over a range from $r = a$ to $r = b$, where b may be greater or less than a. The R-matrix at $r = a$ is given by (see §2.1)

$$F_i(a) = \sum_{j=1}^{n} \Re_{ij}(a) \left[a\frac{dF_j}{dr} - \frac{\beta}{r} \right]_{r=a} \quad , \quad i = 1, ..., n \tag{2.119}$$

and the program calculates the corresponding R-matrix at $r = b$ for a specified set of energies, where $\Re_{ij}(b)$ is defined analogously to (2.119). In order to solve (2.118) it is rewritten in matrix form as

$$(\mathbf{H} - \mathbf{E})\mathbf{F} = 0 \tag{2.120}$$

where the matrix elements of $\mathbf{H}$ are

$$H_{ij} = -\left[\left(\frac{d^2}{dr^2} + \kappa_i^2 - \kappa^2 \right) \delta_{ij} - V_{ij}(r) \right] \tag{2.121}$$

and $\mathbf{E}$ is the diagonal matrix

$$E_{ij} = \kappa^2 \delta_{ij} \ . \tag{2.122}$$

BBM choose the value of κ such that $\kappa^2 = \kappa_1^2$ so that the total energy is measured relative to the first threshold.

In practice, the range a to b is divided up into a number of subranges, where $a_1, a_2, a_3, ...$ are the dividing points, and the R-matrix is propagated across each of these in turn. Consider the subrange $[a_1, a_2]$ where $a_2 > a_1$. BBM introduce the Bloch operator

$$L_{ij} = \left(\delta(r - a_2)\frac{d}{dr} - \frac{\beta_2}{a_2} - \delta(r - a_1)\frac{d}{dr} + \frac{\beta_1}{a_1} \right) \delta_{ij} \tag{2.123}$$

into (2.120), where β_1, β_2 are arbitrary constants, to give

$$(\mathbf{H} + \mathbf{L} - \mathbf{E})\mathbf{F} = \mathbf{L}\mathbf{F} \tag{2.124}$$

and this ensures that $\mathbf{H} + \mathbf{L}$ is hermitian over the interval $[a_1, a_2]$ for functions that satisfy arbitrary boundary conditions at a_1 and a_2. Equation (2.124) can be formally solved to give

$$\mathbf{F} = (\mathbf{H} + \mathbf{L} - \mathbf{E})^{-1}\mathbf{L}\mathbf{F} \ . \tag{2.125}$$

The Green's function $(\mathbf{H}+\mathbf{L}-\mathbf{E})^{-1}$ can be expanded in terms of an orthonormal basis $v_j(r)$ over the range $[a_1, a_2]$. If the functions $f_{ik}(r)$ are now defined as

$$f_{ik}(r) = \sum_{j=1}^{p} a_{ijk} v_j(r) \quad , \quad i = 1, n \quad k = 1, np \ , \tag{2.126}$$

where the coefficients a_{ijk} are obtained by diagonalising $\mathbf{H}+\mathbf{L}$ over the range $[a_1, a_2]$, i.e.

$$\langle \mathbf{f}_k | (\mathbf{H}+\mathbf{L}) | \mathbf{f}_{k'} \rangle = e_k \delta_{kk'} \quad , \quad k, k' = 1, np \ , \tag{2.127}$$

equation (2.125) can then be written as

$$|\mathbf{F}\rangle = \sum_k \frac{|\mathbf{f}_k\rangle\langle \mathbf{f}_k|\mathbf{L}|\mathbf{F}\rangle}{e_k - E} \ . \tag{2.128}$$

Substituting for the Bloch operator $\mathbf{L}$ from (2.123) and evaluating (2.128) at $r = a_1$ and $r = a_2$ gives the equations

$$F_i(a_1) = \sum_k \frac{f_{ik}(a_1)}{e_k - E} \sum_j \left[f_{jk}(a_2) \left(\frac{dF_j}{dr} - \frac{\beta_2}{a_2} F_j \right)_{r=a_2} - f_{jk}(a_1) \left(\frac{dF_j}{dr} - \frac{\beta_1}{a_1} F_j \right)_{r=a_1} \right] \tag{2.129}$$

and

$$F_i(a_2) = \sum_k \frac{f_{ik}(a_2)}{e_k - E} \sum_j \left[f_{jk}(a_2) \left(\frac{dF_j}{dr} - \frac{\beta_2}{a_2} F_j \right)_{r=a_2} - f_{jk}(a_1) \left(\frac{dF_j}{dr} - \frac{\beta_1}{a_1} F_j \right)_{r=a_1} \right] . \tag{2.130}$$

Using the definition in (2.119) and by defining the matrices

$$\begin{aligned} (\mathcal{R}_{11})_{ij} &= \sum_k \frac{f_{ik}(a_1) f_{jk}(a_1)}{e_k - E} & \qquad (\mathcal{R}_{12})_{ij} &= \sum_k \frac{f_{ik}(a_1) f_{jk}(a_2)}{e_k - E} \\ (\mathcal{R}_{21})_{ij} &= \sum_k \frac{f_{ik}(a_2) f_{jk}(a_1)}{e_k - E} & \qquad (\mathcal{R}_{22})_{ij} &= \sum_k \frac{f_{ik}(a_2) f_{jk}(a_2)}{e_k - E} \end{aligned} \tag{2.131}$$

equations (2.129) and (2.130) can be used to write the R-matrix at $r = a_2$ in terms of the R-matrix at $r = a_1$, i.e.

$$a_2 \Re(a_2) = \mathcal{R}_{22} - \mathcal{R}_{21}[\mathcal{R}_{11} + a_1 \Re(a_1)]^{-1} \mathcal{R}_{12} \ . \tag{2.132}$$

Equation (2.132) can be inverted to express $\Re(a_1)$ in terms of $\Re(a_2)$ to give

$$-\, a_1 \Re(a_1) = \mathcal{R}_{11} - \mathcal{R}_{12}[\mathcal{R}_{22} - a_2 \Re(a_2)]^{-1} \mathcal{R}_{21} \ . \tag{2.133}$$

BBM use equation (2.132) for outward propagation and (2.133) for inward propagation and demonstrate that, since $\mathcal{R}_{11}$ and $\mathcal{R}_{22}$ are symmetric and $\mathcal{R}_{12}^{\mathrm{T}} = \mathcal{R}_{21}$, both inward and outward propagation preserves the symmetry of the R-matrix.

Having chosen an orthogonal basis in each subrange in $[a, b]$, a single diagonalisation analogous to equation (2.127) is carried out for each subrange and the surface amplitudes f_{ik} and eigenenergies e_k are determined and stored. The R-matrix can then be propagated from a to b at each energy by just forming the $\mathcal{R}$-matrices defined by equation (2.131) and solving either equation (2.132) or (2.133) in each subrange.

BBM choose the basis functions $v_j(r)$ to be orthonormal shifted Legendre polynomials defined as

$$v_j(r) = \sqrt{\frac{2j-1}{a_2 - a_1}} P_{j-1}(x) \quad ; \quad j = 1, p \tag{2.134}$$

where

$$r = \frac{1}{2}(a_2 + a_1) + \frac{1}{2}(a_2 - a_1)x \tag{2.135}$$

and $P_n(x)$ is a Legendre polynomial of degree n. With this choice, BBM evaluate the matrix elements of the kinetic energy term in (2.121) analytically and the remaining terms using a ten-point Gauss-Legendre quadrature formula. The program also limits the number of basis functions in each range to ten which imposes a restriction on the maximum value of $|a_2 - a_1|$ in order to obtain results of sufficient accuracy. The most difficult radial function $F_i(r)$ to represent is the one with the largest wave number and, in practice, the criterion

$$\kappa_{max}|a_2 - a_1| = 6 \tag{2.136}$$

is imposed, where κ_{max} is the maximum wave number in any channel considered. If closed channels are included then κ_{max} is replaced by $|\kappa_{max}|$. The program uses this criterion to subdivide the total range into a number of subranges before carrying out the calculations.

Due to the imposition of (2.136) the program becomes less efficient if propagation is required for energies that span a large range. In such a case the energy range is subdivided into smaller ranges in each of which the program uses a different subdivision in the range of r. For each subrange in energy, the Hamiltonian matrices have to be set up and diagonalised, so a balance has to be achieved in the number of subranges in energy and subranges in r to achieve maximum efficiency.

In the modified version of RPROP (RPROP2, Morgan 1984), the restriction imposed on the form of the potential interaction is removed. Instead, the user must provide a subroutine which generates the potential matrix at the abscissae of the quadrature scheme.

Chapter 3

A modified propagation method

Chapter 2 provides a brief outline of the basic concepts of the R-matrix method in applications to atomic and molecular collisions. In such applications the basis functions are calculated numerically by diagonalising the Hamiltonian in the inner region. Although this needs to be done only once to obtain the R-matrix at all energies the Hamiltonian matrix can become very large and this limits the number of basis functions used to the amount of computer time and memory available for the diagonalisation.

In this chapter an R-matrix propagation approach, similar to that of Baluja *et al* (1982), is developed which involves the division of configuration space into many regions and in a given region, $a \leq r \leq b$ say, the radial basis functions spanning this interval are expanded in terms of an orthogonal set of Legendre polynomials. Unlike the work of Baluja *et al* who propagate the R-matrix across a finite range *outside* the inner region, the present method propagates the wave function for all space *including* the inner region and ensures that the conditions at the origin are obeyed exactly. Also, the elements of the Hamiltonian are generated exactly and extremely rapidly using recurrence relations that are satisfied by the Legendre polynomials and a stable and accurate method for doing this is presented. These, and other, differences between the present method and that of Baluja *et al* are covered in more detail in chapter 6.

The theory required to implement this approach for the hydrogen atom and one-electron diatomic systems is described below. Energies are in Rydbergs and all other quantities are in atomic units.

3.1 The hydrogen atom

3.1.1 The basis functions

The electronic wave function for the hydrogen atom in a bound or free state with energy E is

$$\Psi_E(r) = \frac{1}{r} F_E(r) Y_{lm}(\theta, \phi) \tag{3.1}$$

where l is the angular momentum quantum number, m is the magnetic quantum number and the $Y_{lm}(\theta, \phi)$ are spherical harmonics. The radial functions $F_E(r)$ satisfy the radial wave equation (see §2.1)

$$(H - E)F_E(r) = 0 \tag{3.2}$$

where

$$H = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2}{r} \tag{3.3}$$

and $E = -1/n^2$ for bound states and $E = \kappa^2$, say, for free states. The number n is an integer if (3.2) is solved exactly. The radial wave function is expanded in terms of the solutions $f_k(r)$ of

$$(H - e_k) f_k(r) = 0 \tag{3.4}$$

with r restricted to a finite range, $a \leq r \leq b$, say, such that H is an hermitian operator for the interval $[a, b]$, the real functions $f_k(r)$ being normalised according to

$$\int_a^b f_k(r) f_{k'}(r) dr = \delta_{kk'} \tag{3.5}$$

for any pair of k and k'. The condition that H should be hermitian means that

$$\int_a^b f_k(r) H f_{k'}(r) dr - \int_a^b f_{k'}(r) H f_k(r) dr = 0 \tag{3.6}$$

and this gives, on integration

$$\left[-f_k(r) f'_{k'}(r) + f_{k'}(r) f'_k(r) \right]_a^b = 0 \tag{3.7}$$

so that if one writes

$$\frac{f'_k(a)}{f_k(a)} = \alpha \quad ; \quad \frac{f'_k(b)}{f_k(b)} = \beta \tag{3.8}$$

for all values of k, where α and β are arbitrary constants, the operator H is hermitian.

The functions $f_k(r)$ are now expanded in the form

$$f_k(r) = \sum_\lambda c_{k\lambda} Y_\lambda(x) \tag{3.9}$$

where

$$r = \frac{1}{2}(b + a) + \frac{1}{2}(b - a)x \tag{3.10}$$

and $Y_\lambda(x)$ are the normalised Legendre polynomials defined by

$$Y_\lambda(x) = \sqrt{\frac{2\lambda + 1}{2}} P_\lambda(x) = \sqrt{2\pi} Y_{\lambda 0}(\hat{\mathbf{r}}) \tag{3.11}$$

and satisfying the normalisation condition

$$\int_{-1}^1 Y_\lambda(x) Y_{\lambda'}(x) dx = \delta_{\lambda\lambda'} \ . \tag{3.12}$$

The coefficients $c_{k\lambda}$ in (3.9) are therefore normalised according to

$$\sum_\lambda c_{k\lambda}^2 = \frac{2}{b - a} \ . \tag{3.13}$$

Substituting (3.9) and (3.11) into (3.8) and using $P_\lambda(1) = 1$, $P'_\lambda(1) = \lambda(\lambda+1)/2$ and $P_\lambda(-x) = (-1)^\lambda P_\lambda(x)$ gives the constraints

$$\sum_\lambda (-1)^\lambda \sqrt{\frac{2\lambda+1}{2}} \left[\frac{(b-a)}{2}\alpha + \frac{\lambda(\lambda+1)}{2}\right] c_{k\lambda} = 0 \qquad (3.14)$$

and

$$\sum_\lambda \sqrt{\frac{2\lambda+1}{2}} \left[\frac{(b-a)}{2}\beta - \frac{\lambda(\lambda+1)}{2}\right] c_{k\lambda} = 0 \qquad (3.15)$$

on the $c_{k\lambda}$ for the interval $[a,b]$ provided $a \neq 0$. For the interval with $a = 0$, some alternative conditions are required to ensure that the solutions $f_k(r)$ have the correct form as $r \to 0$, i.e.

$$f_k(r) \propto r^{l+1}(1 - \frac{r}{l+1}) \ . \qquad (3.16)$$

The $P_\lambda(x)$ in (3.11) can be expressed in terms of an hypergeometric function (see Lebedev 1972) denoted by ${}_2F_1$ as

$$P_\lambda(x) = (-1)^\lambda {}_2F_1(-\lambda, \lambda+1, 1; \frac{1+x}{2}) \ . \qquad (3.17)$$

For $a = 0$, r has the value $b(1+x)/2$. Therefore, (3.9), (3.11) and (3.17) together give

$$f_k(r) = \sum_\lambda \sum_{n=0}^{\lambda} \frac{\Gamma(n-\lambda)\Gamma(\lambda+n+1)}{\Gamma(-\lambda)\Gamma(\lambda+1)\Gamma(n+1)} (-1)^\lambda \frac{(1+x)^n}{2^n n!} \sqrt{\frac{2\lambda+1}{2}} c_{k\lambda} \ . \qquad (3.18)$$

In order to satisfy condition (3.16) the following conditions are imposed:

(a) all the coefficients in (3.18) for which $0 \leq n \leq l$ are zero, and

(b) the ratio of the coefficients with $n = l+2$ and $n = l+1$ is $-b/(l+1)$.

Condition (a) gives

$$\sum_{\lambda=n}^{N} \frac{\Gamma(n-\lambda)\Gamma(\lambda+n+1)}{\Gamma(-\lambda)\Gamma(\lambda+1)} \sqrt{\frac{2\lambda+1}{2}} (-1)^\lambda c_{k\lambda} = 0 \quad ; \quad 0 \leq n \leq l \qquad (3.19)$$

where in principle $N = \infty$ but in practice has some finite value. Condition (b) gives

$$\sum_{\lambda=l+1}^{N} \frac{\Gamma(l-\lambda+1)\Gamma(l+\lambda+2)}{\Gamma(-\lambda)\Gamma(\lambda+1)}\sqrt{\frac{2\lambda+1}{2}}$$

$$\times \qquad \left[\frac{(l+1)}{b(l+2)^2}(l-\lambda+1)(l+\lambda+2)+1\right](-1)^{\lambda}c_{k\lambda}=0 \ . \quad (3.20)$$

So for $a \neq 0$ there are two constraints, given by (3.14) and (3.15), and for $a = 0$ there are $l + 3$ constraints, $l + 1$ of them given by (3.19) and one each in (3.15) and (3.20). These constraints, $\mathbf{C}$, can be written in matrix form as

$$\mathbf{C}\mathbf{c}_k = 0 \qquad (3.21)$$

where $\mathbf{c}_k$ is a column vector of the coefficients $c_{k\lambda}$. Partitioning the matrices in (3.21), by writing

$$\mathbf{C} = (\mathbf{C}_1|\mathbf{C}_2) \qquad (3.22)$$

and

$$\mathbf{c}_k = \left(\frac{\mathbf{c}_k^1}{\mathbf{c}_k^2}\right) \qquad (3.23)$$

such that $\mathbf{C}_2$ is a square matrix, one obtains from (3.21) that

$$\mathbf{c}_k = \left(\frac{\mathbf{I}}{-\mathbf{C}_2^{-1}\mathbf{C}_1}\right)\mathbf{c}_k^1 \qquad (3.24)$$

where $\mathbf{I}$ denotes the unit matrix. Another column vector $\mathbf{d}_k$ is introduced given by

$$\mathbf{c}_k^1 = \mathbf{A}\mathbf{d}_k \qquad (3.25)$$

where the matrix $\mathbf{A}$ is determined so that

$$\mathbf{c}_k^{\dagger}\mathbf{c}_{k'} = \mathbf{d}_k^{\dagger}\mathbf{d}_{k'} = \delta_{kk'} \qquad (3.26)$$

for any pair of k and k' and then equations (3.24), (3.25) and (3.26) give

$$\mathbf{A} = \mathbf{S}^{-\frac{1}{2}} \qquad (3.27)$$

where

$$\mathbf{S} = (\mathbf{I}|(-\mathbf{C}_2^{-1}\mathbf{C}_1)^\dagger)\left(\frac{\mathbf{I}}{-\mathbf{C}_2^{-1}\mathbf{C}_1}\right) \ . \tag{3.28}$$

It is now necessary to set up the matrix **H** associated with the Hamiltonian operator H which has elements

$$\mathbf{H}(\lambda', \lambda) = \int_{-1}^{1} Y_{\lambda'}(x) H Y_\lambda(x) dx \tag{3.29}$$

where H is written in terms of the variable x as

$$H = -\left(\frac{2}{b-a}\right)^2 \left[\frac{d^2}{dx^2} - \frac{l(l+1)}{(y+x)^2} + \frac{(b-a)}{(y+x)}\right] \tag{3.30}$$

with $y = (b+a)/(b-a)$. The evaluation of the matrix elements in (3.29) is dealt with in detail in the next section.

Once the matrix elements for the Hamiltonian in (3.30) have been generated, the next step is to solve

$$\mathbf{H}\mathbf{c}_k = e_k \mathbf{c}_k \ . \tag{3.31}$$

Using the transformation

$$\mathbf{c}_k = \mathbf{R}\mathbf{d}_k \tag{3.32}$$

where **R** is the rectangular matrix

$$\mathbf{R} = \left(\frac{\mathbf{I}}{-\mathbf{C}_2^{-1}\mathbf{C}_1}\right) \mathbf{A} \tag{3.33}$$

(3.31) becomes

$$\mathbf{H}^{\mathbf{R}}\mathbf{d}_k = e_k \mathbf{d}_k \tag{3.34}$$

where $\mathbf{H}^{\mathbf{R}} = \mathbf{R}^\dagger \mathbf{H} \mathbf{R}$. This equation is solved for the e_k and $\mathbf{d}_k$, $k = 1, 2 \ldots$, by diagonalising $\mathbf{H}^{\mathbf{R}}$ using a NAG routine F02ABF. Hence, by using (3.32) and (3.9), the functions $f_k(r)$ can be calculated.

3.1.2 Matrix elements of the Hamiltonian

In order to evaluate the elements in (3.29) integrals $D(\lambda',\lambda)$ defined by

$$D(\lambda',\lambda) \equiv \int_{-1}^{1} P_{\lambda'}(x)\frac{d^2}{dx^2}P_\lambda(x)dx \tag{3.35}$$

and the integrals $I_n(\lambda',\lambda)$ defined by

$$I_n(\lambda',\lambda) \equiv \int_{-1}^{1} P_{\lambda'}(x)(y+x)^{-n}P_\lambda(x)dx \quad ; \quad n = 1,2... \tag{3.36}$$

need to be generated. The integrals (3.35) can be easily evaluated by writing

$$D(\lambda',\lambda) = \frac{1}{2^{\lambda+\lambda'}\lambda!\lambda'!}\int_{-1}^{1}\frac{d^{\lambda'}}{dx^{\lambda'}}(x^2-1)^{\lambda'}\frac{d^{\lambda+2}}{dx^{\lambda+2}}(x^2-1)^{\lambda}dx \tag{3.37}$$

and this equation can be integrated repeatedly by parts to give

$$\begin{aligned} D(\lambda',\lambda) &= 2\nu(2\lambda-2\nu+1) \quad &;& \quad \lambda-\lambda' = 2\nu \\ &= 0 &;& \quad \text{otherwise} \end{aligned} \tag{3.38}$$

where $\nu = 1,2,\ldots$. The integrals (3.36) are evaluated as follows. Although for hydrogen, only integrals $I_n(\lambda',\lambda)$ with values $n = 1,2$ are needed, a more generalised method for evaluating the $I_n(\lambda',\lambda)$ is described which can also be applied to the molecular case considered in §3.2. The Legendre polynomials $P_\lambda(x)$ satisfy the recurrence relation

$$(\lambda+1)P_{\lambda+1}(x) - (2\lambda+1)xP_\lambda(x) + \lambda P_{\lambda-1}(x) = 0 \tag{3.39}$$

and multiplying (3.39) through by $P_{\lambda'}(x)(y+x)^{-n}$ and integrating gives

$$(\lambda+1)I_n(\lambda',\lambda+1) - (2\lambda+1)I_{n-1}(\lambda',\lambda) + (2\lambda+1)yI_n(\lambda',\lambda) + \lambda I_n(\lambda',\lambda-1) = 0 \tag{3.40}$$

for the integrals (3.36). The first argument of I_n in (3.40), λ', remains unchanged throughout the recurrence relation. Clearly, the matrix $\mathbf{I}_n$ is symmetric and using the relation (derived from (3.39))

$$\begin{aligned} P_{\lambda'}(x)xP_\lambda(x) &= \frac{1}{(2\lambda+1)}[(\lambda+1)P_{\lambda'}(x)P_{\lambda+1}(x) + \lambda P_{\lambda'}(x)P_{\lambda-1}(x)] \\ &= \frac{1}{(2\lambda'+1)}[(\lambda'+1)P_\lambda(x)P_{\lambda'+1}(x) + \lambda' P_\lambda(x)P_{\lambda'-1}(x)] \end{aligned} \tag{3.41}$$

also gives, for each value of n,

$$
\begin{aligned}
&(2\lambda'+1)(\lambda+1)I_n(\lambda',\lambda+1)-(2\lambda+1)(\lambda'+1)I_n(\lambda'+1,\lambda)\\
&\quad + \quad (2\lambda'+1)\lambda I_n(\lambda',\lambda-1)-(2\lambda+1)\lambda' I_n(\lambda'-1,\lambda)=0 \ . \qquad (3.42)
\end{aligned}
$$

In principle, the recurrence procedure is extremely simple but in practice, some subtlety has to be employed when using relation (3.40) in order to avoid accumulation of numerical error when the matrix elements are rapidly varying with λ. Two cases need to be considered, $y=1$ and $y \neq 1$.

(a) $\underline{y=1}$

When $y=1$, the integrals (3.36) diverge. However, since functions that are finite combinations of the $Y_\lambda(x)$ are finally needed, the constraints that are applied remove the divergences. Therefore the singularities in the $I_n(\lambda',\lambda)$ can be subtracted out in a consistent way without affecting the final result. The recurrence process is started in this case by writing

$$
\left.\begin{aligned}
I_n(0,0) &= 0 \qquad \text{for } n \geq 1\\
I_n(0,1) &= I_n(1,0) \qquad \text{for } n \geq 3\\
I_n(1,1) &= 0 \qquad \text{for } n \geq 4\\
I_1(0,1) = I_1(1,0) &= 2\\
I_1(1,1) &= -2\\
I_2(1,1) &= 4\\
I_3(1,1) &= -\tfrac{3}{2}\\
I_2(0,1) = I_2(1,0) &= -1\\
I_0(\lambda',\lambda) &= \tfrac{2}{(2\lambda+1)}\delta_{\lambda'\lambda} \quad \text{for all } \lambda \text{ and } \lambda'.
\end{aligned}\right\} \qquad (3.43)
$$

Then (3.40) is used, for each value of $n=1,2,3,\ldots$, to generate the elements

$$
\begin{aligned}
&I_n(0,\lambda) \quad , \quad I_n(1,\lambda)\\
&I_n(0,\lambda) = I_n(\lambda,0) \qquad ; \qquad \lambda = 2,3,\ldots \qquad (3.44)\\
&I_n(1,\lambda) = I_n(\lambda,1)
\end{aligned}
$$

in the above order. Finally, the matrices $\mathbf{I}_n$ are completed by using (3.40) to generate the elements

$$I_n(\lambda', \lambda) \quad ; \quad \lambda = \lambda', \lambda' + 1, \ldots \tag{3.45}$$

together with

$$I_n(\lambda, \lambda') = I_n(\lambda', \lambda) \tag{3.46}$$

for each value of $\lambda' = 2, 3, \ldots$ in turn.

(b) $\underline{y \neq 1}$

The integrals $I_n(\lambda, \lambda')$ can be evaluated directly for $\lambda, \lambda' = 0, 1$ to give

$$\left.\begin{array}{lll} I_0(0,0) = 2 & I_1(0,0) = \ln\left(\frac{y+1}{y-1}\right) & I_{-1}(0,0) = 2 \\ I_n(0,0) = \frac{1}{n-1}\left[\frac{1}{(y-1)^{n-1}} - \frac{1}{(y+1)^{n-1}}\right] & ; & n \geq 2 \end{array}\right\} \tag{3.47}$$

and

$$\left.\begin{array}{l} I_n(0,1) = I_n(1,0) = I_{n-1}(0,0) - yI_n(0,0) \\ I_n(1,1) = I_{n-2}(0,0) - 2yI_{n-1}(0,0) + y^2 I_n(0,0) \end{array}\right\} \quad ; \quad n \geq 1 \tag{3.48}$$

The matrix $\mathbf{I}_0$ can be generated by using, firstly,

$$I_0(\lambda', \lambda) = \frac{2}{2\lambda + 1}\delta_{\lambda'\lambda} \tag{3.49}$$

and then using (3.42) repeatedly together with the symmetry relation $I_n(\lambda', \lambda) = I_n(\lambda, \lambda')$. Now $I_n(0, \lambda)$, $\lambda = 0, 1, 2\ldots$, can decrease very rapidly with increasing λ for each of the n values of interest. Thus it is better to use the recurrence relation (3.40) in the backwards direction i.e. starting at large values of λ and recurring in the direction of decreasing λ in order to avoid a build-up of numerical error. However, even this approach is not always adequate, as there can also be a build-up of numerical error by recurring in the backward direction. The following procedure has therefore been developed. Consider relation (3.40) in the form

$$(\lambda+1)I_n(0, \lambda+1) + (2\lambda+1)yI_n(0, \lambda) + \lambda I_n(0, \lambda-1) = (2\lambda+1)I_{n-1}(0, \lambda) \tag{3.50}$$

and it is desired to use this to recur in the direction of λ decreasing, to get the elements $I_n(0,\lambda)$. This clearly also requires the elements $I_{n-1}(0,\lambda)$ and so one must work in the direction of n increasing, given that $I_0(0,\lambda)$ is known from (3.49). The build-up of numerical error in this backwards recurrence can arise because a small multiple of the complementary quantities $Z_n(\lambda)$ satisfying the associated recurrence relation

$$(\lambda+1)Z_n(\lambda+1)+(2\lambda+1)yZ_n(\lambda)+\lambda Z_n(\lambda-1)=0 \tag{3.51}$$

can be added onto the actual solution and possibly totally dominate it. Therefore the $Z_n(\lambda)$ are generated first, by starting the backward recurrence of (3.51) with

$$Z_n(\lambda_T)=0 \qquad ; \qquad Z_n(\lambda_T-1)=10^{-30} \qquad ; \qquad \lambda_T \equiv 2\lambda_{max}+N \tag{3.52}$$

and then finally rescaling all the $Z_n(\lambda)$ generated by fixing $Z_n(0)=1$. In equation (3.52), λ_{max} is the maximum value of λ required finally in the matrix $\mathbf{I}_n$. The next step is to recur backwards to obtain $I_n(0,\lambda)$ from (3.50). The recurrence is started with

$$I_n(0,2\lambda_{max}+1)=0 \qquad ; \qquad I_n(0,2\lambda_{max})=0 \tag{3.53}$$

and then $I_n(0,2\lambda_{max}-1)$ is generated. Next, the term

$$[I_n(0,2\lambda_{max}-1)/Z_n(2\lambda_{max}-1)]Z_n(\lambda)$$

is subtracted from $I_n(0,\lambda)$, $\lambda=2\lambda_{max}-1, 2\lambda_{max}, 2\lambda_{max}+1$, and so for the next stage of the recurrence one uses

$$I'_n(\lambda)=I_n(\lambda)-[I_n(0,2\lambda_{max}-1)/Z_n(2\lambda_{max}-1)]Z_n(\lambda)=0 \quad ; \quad \lambda=2\lambda_{max}-1 \ . \tag{3.54}$$

This step-by-step subtraction out of the contribution from $Z_n(\lambda)$ is used for all values of λ, i.e. in general, having generated $I_n(0,\lambda)$ from $I_n(0,\lambda+1)$ and

$I_n(0, \lambda + 2)$ they are replaced by a new set $I'_n(0, \lambda)$ given by

$$I'_n(0, \lambda') = I_n(0, \lambda') - [I_n(0, \lambda)/Z_n(\lambda)]Z_n(\lambda') \quad ; \quad \lambda' = \lambda, \lambda + 1, \ldots 2\lambda_{max} + 1 \tag{3.55}$$

before going on to the next step of the recurrence. Finally, a set of $I_n(0, \lambda)$ for $\lambda = 0, 1, 2, \ldots$ is obtained but this set is not in general the set of integrals required. The actual set of $I_n(0, \lambda)$ that is required is then given by

$$I'_n(0, \lambda) = AZ_n(\lambda) + I_n(0, \lambda) \quad ; \quad \lambda = 0, 1, 2\ldots \tag{3.56}$$

where A is a constant chosen so that $I'_n(0, 0)$ has the value given in (3.47). This completes the generation of the required integrals $I_n(0, \lambda)$, $\lambda = 0, 1, \ldots(2\lambda_{max}+1)$, for each n in order of n increasing, and has been proved to be stable for all $y \neq 1$. The full matrix $\mathbf{I}_n$ is completed by using relation (3.42) repeatedly for each value of n. The elements are evaluated by using (3.42) for each $\lambda' = 1, \ldots\lambda_{max}$ and by taking $\lambda = \lambda', \lambda' + 1 \ldots (2\lambda_{max} - \lambda')$ with $I_n(\lambda, \lambda') = I_n(\lambda', \lambda)$.

3.1.3 Generation of the wave functions

The radial wave function $F_E(r)$ is expanded in terms of the set of functions $f_k(r)$, i.e.

$$F_E(r) = \sum_k A_k f_k(r) \tag{3.57}$$

where

$$A_k = \int_a^b f_k(r) F_E(r) dr \ , \tag{3.58}$$

and the coefficients A_k can be obtained from the relation

$$\int_a^b f_k(H - E) F_E dr - \int_a^b F_E(H - e_k) f_k dr = 0 \tag{3.59}$$

which gives

$$A_k = (e_k - E)^{-1} \left[F'_E(b) f_k(b) - F_E(b) f'_k(b) - F'_E(a) f_k(a) + F_E(a) f'_k(a)\right] \ . \tag{3.60}$$

The R-matrix $\Re_E$ is defined such that

$$F_E(a) = \Re_E(a) F'_E(a) \qquad ; \qquad F_E(b) = \Re_E(b) F'_E(b) \tag{3.61}$$

and using (3.8), (3.57) and (3.60) the expression for $F_E(r)$ becomes

$$F_E(r) = \sum_k \frac{f_k(r)}{(e_k - E)} \{F_E(b)[\Re_E^{-1}(b) - \beta] f_k(b) - F_E(a)[\Re_E^{-1}(a) - \alpha] f_k(a)\} \ . \tag{3.62}$$

At the point $r = a$,

$$F_E(a) = F_E(b)[\Re_E^{-1}(b) - \beta] S_{ab} - F_E(a)[\Re_E^{-1}(a) - \alpha] S_{aa} \tag{3.63}$$

and at $r = b$,

$$F_E(b) = F_E(b)[\Re_E^{-1}(b) - \beta] S_{bb} - F_E(a)[\Re_E^{-1}(a) - \alpha] S_{ab} \tag{3.64}$$

where

$$S_{aa} = \sum_k \frac{f_k(a) f_k(a)}{(e_k - E)} \qquad S_{ab} = \sum_k \frac{f_k(a) f_k(b)}{(e_k - E)} \qquad S_{bb} = \sum_k \frac{f_k(b) f_k(b)}{(e_k - E)} \ . \tag{3.65}$$

Writing

$$\begin{aligned} F_a &\equiv F_E(a) \ , \\ F_b &\equiv F_E(b) \ , \\ G_a &\equiv F_E(a)[\Re_E^{-1}(a) - \alpha] \ , \\ G_b &\equiv F_E(b)[\Re_E^{-1}(b) - \beta] \ , \end{aligned} \tag{3.66}$$

one obtains the relations

$$F_a = S_{ab} G_b - S_{aa} G_a \qquad\qquad F_b = S_{bb} G_b - S_{ab} G_a \tag{3.67}$$

from which the wave functions are generated.

The solution for $F_E(r)$ within the interval $[a, b]$ must be matched to the solutions generated within the intervals on either side of $[a, b]$. Taking $a_0, a_1, a_2, \ldots$ to be the points at which the range of r is divided the wave functions are generated for all space as follows:

(a) $\underline{E > 0}$

For positive energies the wave function of the electron oscillates out to infinity. In the first interval $[a_0, a_1]$, where $a_0 = 0$ and $F_{a_0} = 0$, (3.67) becomes

$$F_{a_1} = S_{a_1 a_1} G_{a_1} \ . \tag{3.68}$$

An arbitrary value is assigned to F_{a_1} and then the value of F_{a_2} in the next interval, $[a_1, a_2]$, is found by using the pre-determined values of F_{a_1} and G_{a_1}. Thus the wave function is propagated out to large values of r by matching at each range boundary and the scale is fixed at the end by overall normalisation of $F_E(r)$.

(b) $\underline{E < 0}$

For bound states the electronic wave function will decay to zero if r is large and the correct energy E is used. In the outermost range of r values, $a_{n-1} \leq r \leq a_n$ say, provided a_n is sufficiently large, then F_{a_n} and the $f_k(a_n)$ can be taken to be zero. Then (3.67) reduces to

$$F_{a_{n-1}} = -S_{a_{n-1} a_{n-1}} G_{a_{n-1}} \tag{3.69}$$

where $F_{a_{n-1}}$ is set to an arbitrary value and the wave function is then propagated inwards, again by matching at each range boundary. Eventually a solution F_{a_1} is obtained which will satisfy (3.68) and (3.69) simultaneously only if the energy E is correct for a bound state of the system.

3.2 One-electron diatomic systems

3.2.1 Coordinate frames for the molecular expansion

The wave equation that describes the electronic motion in the three-body diatomic system shown in figure 3.1 is

$$\nabla^2 \Psi_E + (\frac{2z_A}{r_A} + \frac{2z_B}{r_B} - \frac{2z_A z_B}{R} + E)\Psi_E = 0 \tag{3.70}$$

where z_A and z_B are the charges on nuclei A and B respectively and E is the total energy of the system. In this description of the electronic motion, which makes use of the Born-Oppenheimer approximation, the wave function Ψ_E depends parametrically on R, the internuclear separation, and for any given electronic state R is considered to be fixed.

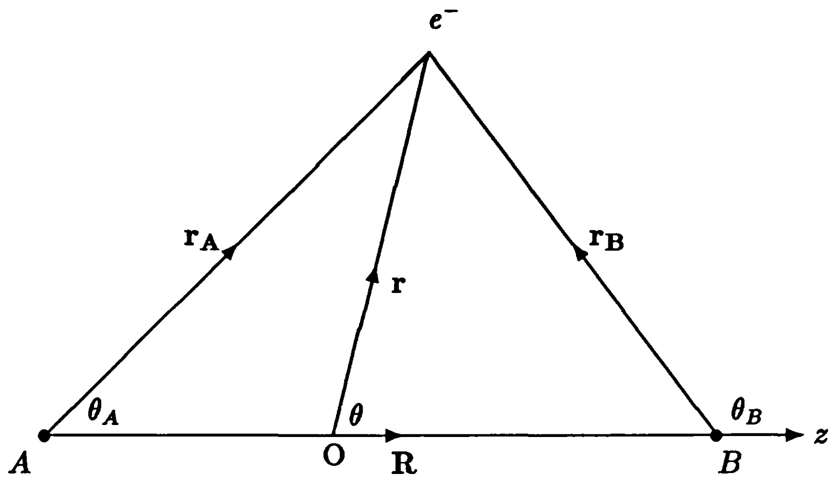


Figure 3.1: Coordinates of the three-body system.

If the two nuclei are close together, i.e. R is small, or the system is homonuclear, it is convenient to use a single-centre expansion of Ψ_E about the centre of mass, O. If m_A and m_B are the masses of nuclei A and B respectively, then

$$\mathbf{R}_A = \frac{m_B}{m_A + m_B}\mathbf{R} \qquad \mathbf{R}_B = \frac{m_A}{m_A + m_B}\mathbf{R} \tag{3.71}$$

so that $\vec{OA} = -\mathbf{R}_A$ and $\vec{OB} = \mathbf{R}_B$.

One looks for a solution, in terms of the centre of mass coordinates (r, θ, ϕ), of the form

$$\Psi_E = \psi(r, \theta)\Phi(\phi) \tag{3.72}$$

where ϕ is the azimuthal angle and

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \ , \tag{3.73}$$

and expands $\psi(r, \theta)$ in the form

$$\psi(r,\theta) = \sum_l \frac{1}{r} F_l(r,R) c_{lm} P_l^m(\eta) \quad ; \quad \eta = \cos\theta \tag{3.74}$$

where the $P_l^m(\eta)$ are associated Legendre polynomials and the c_{lm} are the corresponding normalisation coefficients (see Edmonds 1960). If the electron is in a bound state, ψ is normalised to unity and this means that

$$\sum_l \int_0^\infty [F_l(r,R)]^2 dr = 1 \tag{3.75}$$

for all R. Substituting (3.74) into (3.70) gives the expression

$$\sum_l c_{lm} P_l^m(\eta) \left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2z_A}{r_A} + \frac{2z_B}{r_B} - \frac{2z_A z_B}{R} + E \right] F_l = 0 \ . \tag{3.76}$$

The terms $1/r_A$ and $1/r_B$ are expanded using

$$\frac{1}{r_A} = \sum_{l''=0}^{\infty} \frac{r_{A<}^{l''}}{r_{A>}^{l''+1}} P_{l''}(-\eta) \quad ; \quad r_{A<} = \min(r, R_A) \quad , \quad r_{A>} = \max(r, R_A) \tag{3.77}$$

and

$$\frac{1}{r_B} = \sum_{l''=0}^{\infty} \frac{r_{B<}^{l''}}{r_{B>}^{l''+1}} P_{l''}(\eta) \quad ; \quad r_{B<} = \min(r, R_B) \quad , \quad r_{B>} = \max(r, R_B) \ . \tag{3.78}$$

Equation (3.76) is multiplied throughout by $c_{l'm} P_{l'}^m(\eta)$, integrated with respect to η, and then (3.77) and (3.78) are used to obtain

$$\sum_l \left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{2z_Az_B}{R} + E\right] F_l\delta_{l'l}$$

$$+ \quad 2\sum_l F_l \sum_{l''} A(l',l'',l)\left[z_A(-1)^{l''}\frac{r_{A<}^{l''}}{r_{A>}^{l''+1}} + z_B\frac{r_{B<}^{l''}}{r_{B>}^{l''+1}}\right] = 0 \qquad (3.79)$$

where

$$A(l',l'',l) = [(2l'+1)(2l+1)]^{\frac{1}{2}}(-1)^m \begin{pmatrix} l' & l'' & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & l'' & l \\ -m & 0 & m \end{pmatrix} \qquad (3.80)$$

for $|l'-l| \leq l'' \leq l'+l$, where the symbols $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ in (3.80) are 3-j symbols (see Edmonds 1960).

The energy E_U is now introduced, defined by

$$E_U = E - \frac{2z_Az_B}{R} \qquad (3.81)$$

and then equation (3.79) can be written as

$$\sum_l (H_{l'l} - E_U)F_l = 0 \qquad (3.82)$$

where

$$H_{l'l} = \delta_{l'l}\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r}\right)$$

$$-2\sum_{l''} A(l',l'',l)\left(z_A(-1)^{l''}\frac{r_{A<}^{l''}}{r_{A>}^{l''+1}} + z_B\frac{r_{B<}^{l''}}{r_{B>}^{l''+1}} - \frac{Z}{r}\delta_{l''0}\right) \qquad (3.83)$$

and $Z = z_A + z_B$.

For the homonuclear case, (3.83) simplifies to

$$H_{l'l} = \delta_{l'l}\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{4z_A}{r}\right) - 4\sum_{l''_{even}} A(l',l'',l)\left(z_A\frac{r_{A<}^{l''}}{r_{A>}^{l''+1}} - \frac{z_A}{r}\delta_{l''0}\right) . \qquad (3.84)$$

Since only even values of l'' occur in (3.84), the coefficients $A(l', l'', l)$ are only non-zero for $|l' - l| = 0, 2\ldots$ and thus the coupling term connects only even values of l' and l or odd values of l' and l. Therefore the gerade ($l + m$ even) and ungerade ($l + m$ odd) states can readily be identified by writing

$$\psi_g(r,\theta) = \sum_{l_{even}} \frac{1}{r} F_l^g(r,R) c_{lm} P_l^m(cos\theta) \tag{3.85}$$

and

$$\psi_u(r,\theta) = \sum_{l_{odd}} \frac{1}{r} F_l^u(r,R) c_{lm} P_l^m(cos\theta) \tag{3.86}$$

and the functions $F_l^g(r,R)$ and $F_l^u(r,R)$ are obtained from two separate solutions using the R-matrix method.

Alternatively, for large internuclear separations, a coordinate system that is appropriate to the separated atom limit $R \to \infty$ can be used. In this case it is supposed that the electron is localised on centre A and a set of spherical polar coordinates (r_A, θ_A, ϕ) is chosen. The analysis follows in the same way as before in terms of coordinates (r_A, θ_A, ϕ) where now, since $\mathbf{r_B} = \mathbf{r_A} - \mathbf{R}$, one uses the expansion

$$\frac{1}{r_B} = \sum_{l''=0}^{\infty} \frac{r_<^{l''}}{r_>^{l''+1}} P_{l''}(\eta) \quad ; \quad r_< = \min(r_A, R) \quad , \quad r_> = \max(r_A, R) \tag{3.87}$$

where $\eta = \cos\theta_A$. By introducing the energy E_S given by

$$E_S = E - \frac{2z_B(z_A - 1)}{R} \tag{3.88}$$

(3.70) can be written as

$$\sum_l (H_{l'l} - E_S) F_l = 0 \ , \tag{3.89}$$

where now

$$H_{l'l} = \delta_{l'l}\left(-\frac{d^2}{dr_A^2} + \frac{l(l+1)}{r_A^2} - \frac{2z_A}{r_A}\right) - 2z_B \sum_{l''}\left(\frac{r_<^{l''}}{r_>^{l''+1}} A(l', l'', l) - \frac{\delta_{l''0}}{R}\right) \ . \tag{3.90}$$

For the molecular work in this thesis, only the single-centre expansion about the centre of mass, O, is used.

3.2.2 The basis functions

For each value of R the radial functions $F_l(r,R)$ are expanded in terms of the solutions $f_k^l(r)$ of

$$\sum_l (H_{l'l} - e_k) f_k^l(r) = 0 \tag{3.91}$$

with r restricted to a finite range, $a \leq r \leq b$, where the expression for $H_{l'l}$ is that given in (3.83) or (3.90) depending on which set of coordinates is used. The real functions $f_k^l(r)$ depend parametrically on R, but for simplicity explicit reference to this is dropped in the analysis that follows. To ensure that the Hamiltonian is hermitian, the boundary conditions

$$\left.\frac{1}{f_k^l(a)}\frac{d}{dr}f_k^l(r)\right|_{r=a} = \alpha \quad ; \quad \left.\frac{1}{f_k^l(b)}\frac{d}{dr}f_k^l(r)\right|_{r=b} = \beta \tag{3.92}$$

are applied for all values of l, where α and β are arbitrary constants. The basis functions are normalised according to

$$\sum_l \int_a^b [f_k^l(r)]^2 dr = 1 \tag{3.93}$$

and are expanded in the form

$$f_k^l(r) = \sum_\lambda c_{k\lambda}^l Y_\lambda(x) \tag{3.94}$$

where r is related to x by (3.10). Then for each value of l the constraints $\mathbf{C}$, as defined in §3.1.1, are applied to the column vector of coefficients $\mathbf{c}_k^l$. To set up the Hamiltonian matrix $\mathbf{H}$, additional matrix elements are required to those given in (3.35) and (3.36) and these are defined by

$$J_n(\lambda',\lambda) = \int_{-1}^{X} P_{\lambda'}(x)(y+x)^n P_\lambda(x)dx \quad ; \quad n = 0,1,2\ldots \tag{3.95}$$

and

$$I_n(\lambda',\lambda) = \int_{X}^{1} P_{\lambda'}(x)(y+x)^{-n} P_\lambda(x)dx \quad ; \quad n = 1,2\ldots \tag{3.96}$$

which is a generalisation of the integral in (3.36). The evaluation of these elements is described in the following section.

If, for a given value of l, $\mathbf{R}_l$ denotes the rectangular matrix $\mathbf{R}$ as defined in (3.32) and (3.33), a reduced matrix $\mathbf{H}^{\mathbf{R}}$ is obtained which can be partitioned into blocks $\mathbf{H}^{\mathbf{R}}_{l'l}$ corresponding to a specified pair of l' and l where

$$\mathbf{H}^{\mathbf{R}}_{l'l} = \mathbf{R}^{\dagger}_{l'}\mathbf{H}_{l'l}\mathbf{R}_l \quad ; \quad l', l = |m|, |m|+1\ldots \tag{3.97}$$

The equation

$$\mathbf{H}^{\mathbf{R}}\mathbf{d}_k = e_k\mathbf{d}_k \tag{3.98}$$

is now solved for e_k and $\mathbf{d}_k$ where $\mathbf{d}_k$ contains the eigenvectors for all the l values under consideration. As for the case of the hydrogen atom, this is done by diagonalising $\mathbf{H}^{\mathbf{R}}$ using the NAG routine F02ABF. Partitioning $\mathbf{d}_k$ according to l value gives the relation

$$\mathbf{c}^l_k = \mathbf{R}_l\mathbf{d}^l_k \tag{3.99}$$

and once the $\mathbf{c}^l_k$ are found the set of functions $f^l_k(r)$ can be calculated.

3.2.3 Matrix elements of the Hamiltonian

For the particular cases $(y = 1, X = -1)$ and $(y \neq 1, \mathrm{all}\, X)$ the integrals (3.96) are evaluated by following the procedure as outlined in §3.1.2. It now remains to evaluate the integrals $I_n(\lambda', \lambda)$ for the case $(y = 1, X \neq -1)$. The procedure is similar to that described in §3.1.2 part (a), but conditions (3.43) have to be replaced by the more general expressions

$$\left.\begin{array}{l} I_0(0,0) = 1 - X \quad I_1(0,0) = \ln\left(\frac{y+1}{y+X}\right) \quad I_{-1}(0,0) = \frac{1}{2}(1-X)(3+X) \\ I_n(0,0) = \frac{1}{n-1}\left[\frac{1}{(y+X)^{n-1}} - \frac{1}{(y+1)^{n-1}}\right] \quad ; \quad n \geq 2 \end{array}\right\} \tag{3.100}$$

The matrix $\mathbf{I}_0$ can be generated by using, firstly,

$$\begin{aligned} I_0(0,\lambda) &= \int_X^1 P_\lambda(x)dx = \frac{1}{(2\lambda+1)}[P_{\lambda-1}(X) - P_{\lambda+1}(X)] \\ &= \frac{1}{\lambda(\lambda+1)}(1-X^2)^{\frac{1}{2}}\frac{dP_\lambda(X)}{dX} \quad ; \quad \lambda \geq 1 \\ &= I_0(\lambda, 0) \end{aligned} \tag{3.101}$$

and then using (3.42) repeatedly together with the symmetry relation $I_n(\lambda', \lambda) = I_n(\lambda, \lambda')$. Relations (3.100)-(3.101) replace relations (3.43) and then processes (3.44) and (3.45) proceed as before.

The integrals (3.95) satisfy relations similar to (3.40) and (3.42) for the integrals $I_n(\lambda', \lambda)$, i.e.

$$(\lambda+1)J_n(\lambda', \lambda+1) - (2\lambda+1)J_{n+1}(\lambda', \lambda) + (2\lambda+1)yJ_n(\lambda', \lambda) + \lambda J_n(\lambda', \lambda-1) = 0 \tag{3.102}$$

and

$$\begin{aligned}(2\lambda'+1)(\lambda+1)J_n(\lambda', \lambda+1) - (2\lambda+1)(\lambda'+1)J_n(\lambda'+1, \lambda)\\ + \quad (2\lambda'+1)\lambda J_n(\lambda', \lambda-1) - (2\lambda+1)\lambda' J_n(\lambda'-1, \lambda) = 0 \ .\end{aligned} \tag{3.103}$$

Firstly, the integrals $J_0(0, \lambda)$, $\lambda = 0, 1, 2, ...(2\lambda_{max} + N)$, given by

$$J_0(0,0) = 1+X \quad ; \quad J_0(0,\lambda) = \int_{-1}^{X} P_\lambda(x)dx = -I_0(0,\lambda) \quad ; \quad \lambda \geq 1 \tag{3.104}$$

are generated, where $I_0(0, \lambda)$ is given by (3.101). Then the integrals $J_n(0,0)$, $n = 0, 1, 2...$, which are given by

$$J_n(0,0) = \frac{1}{(n+1)}[(y+X)^{n+1} - (y-1)^{n+1}] \quad ; \quad n = 0, 1, 2...(2\lambda_{max} + N) \tag{3.105}$$

are generated. The integrals are now divided into two types:

a) <u>$(y + X) > 1$</u>

Each value of n is considered in turn in increasing order, $n = 0, 1, 2...N$. For each value of n the recurrence relation (3.102) is used to obtain $J_n(0, \lambda)$, $\lambda = 1, 2, ...(2\lambda_{max} + N - n)$.

b) <u>$(y + X) \leq 1$</u>

Each value of λ is considered in turn in increasing order, $\lambda = 1, 2, ...2\lambda_{max}$. For each value of λ the recurrence relation (3.102) is used to obtain $J_n(0, \lambda)$, $n = 1, 2, ...(2\lambda_{max} + N - \lambda)$.

The $J_n(0,\lambda)$ for $\lambda = 0,1,2...2\lambda_{max}$ and $n = 0,1,2,...N$ have now been generated by one or other of the above methods. The full matrices $\mathbf{J}_n$, $n = 0,1,2,...N$ can now be completed by using the recurrence relation (3.103). The elements are evaluated by using (3.103) for each $\lambda' = 1,2,...\lambda_{max}$ and by taking $\lambda = \lambda', \lambda'+1...(2\lambda_{max} - \lambda')$ with $J_n(\lambda,\lambda') = J_n(\lambda',\lambda)$.

3.2.4 Generation of the wave functions

The wave functions $F_l(r,R)$, are obtained exactly as before from (3.57), i.e.

$$F_l(r,R) = \sum_k A_k(R) f_k^l(r) \tag{3.106}$$

where

$$A_k(R) = \sum_l \int_a^b f_k^l(r) F_l(r,R) dr \ , \tag{3.107}$$

and the coefficients A_k are obtained from the relation

$$\sum_l \int_a^b f_k^l (H_{l'l} - E_i) F_l dr - \sum_l \int_a^b f_k^l (H_{l'l} - e_k) F_l dr = 0 \tag{3.108}$$

where $E_i = E_S$ or E_U. Using the boundary conditions (3.92) satisfied by the $f_k^l(r)$ for all values of l, equation (3.106) becomes

$$F_l(r,R) = \sum_k \sum_l \frac{f_k^{l'}(r)}{(e_k - E_i)} \{F_l(b,R)[\Re_l^{-1}(b) - \beta] f_k^l(b) - F_l(a,R)[\Re_l^{-1}(a) - \alpha] f_k^l(a)\} \tag{3.109}$$

where

$$F_l(a,R) = \Re_l(a) F_l'(a,R) \tag{3.110}$$

and

$$F_l(b,R) = \Re_l(b) F_l'(b,R) \tag{3.111}$$

and where $\Re_l(r)$ is the R-matrix which also depends on R parametrically. The matrices $\mathbf{S}_{aa}$, $\mathbf{S}_{ab}$ and $\mathbf{S}_{bb}$ are now defined as

$$\mathbf{S}_{aa}(l',l) = \sum_k \frac{f_k^{l'}(a) f_k^l(a)}{(e_k - E_i)} \quad \mathbf{S}_{ab}(l',l) = \sum_k \frac{f_k^{l'}(a) f_k^l(b)}{(e_k - E_i)} \quad \mathbf{S}_{bb}(l',l) = \sum_k \frac{f_k^{l'}(b) f_k^l(b)}{(e_k - E_i)} \tag{3.112}$$

and $\mathbf{S}_{ab} = \mathbf{S}_{ba}$. Then (3.109) gives relations similar to (3.67) for the hydrogen atom, i.e.

$$\mathbf{F}_a = \mathbf{S}_{ab}\mathbf{G}_b - \mathbf{S}_{aa}\mathbf{G}_a \qquad \mathbf{F}_b = \mathbf{S}_{bb}\mathbf{G}_b - \mathbf{S}_{ba}\mathbf{G}_a \tag{3.113}$$

where

$$\begin{aligned}
\mathbf{F}_a(l) &\equiv F_l(a,R)\,, \\
\mathbf{F}_b(l) &\equiv F_l(b,R)\,, \\
\mathbf{G}_a(l) &\equiv F_l(a,R)[\Re_l^{-1}(a) - \alpha]\,, \\
\mathbf{G}_b(l) &\equiv F_l(b,R)[\Re_l^{-1}(b) - \beta]\,.
\end{aligned}$$

The bound states of the three-body system occur for $E_U < 0$ and the energy E_S corresponding to the separated atom limit is related to E_U through equations (3.81) and (3.88) by

$$E_S = E_U + \frac{2z_B}{R}\ . \tag{3.114}$$

As for the case of the hydrogen atom, $a_0, a_1, a_2 \ldots$ are taken to be the dividing points defining the intervals in r.

(a) $E_U > 0$ or $E_S > 2z_B/R$

In the first interval $a_0 = 0$ and

$$\mathbf{F}_{a_1} = \mathbf{S}_{a_1 a_1}\mathbf{G}_{a_1} \tag{3.115}$$

since $\mathbf{F}_{a_0} = 0$. It is convenient to choose the vectors $\mathbf{G}_{a_1}$ such that

$$\mathbf{G}_{a_1} = \varepsilon_1 \mathbf{F}_{a_1} \tag{3.116}$$

where ε_1 is a scalar constant. By substituting (3.116) into (3.115), it can be seen that there are $L+1$ independent vectors $\mathbf{F}_{a_1}$ that are eigenvectors of $\mathbf{S}_{a_1 a_1}$ with eigenvalues $1/\varepsilon_1$, L being the maximum value of l taken in the expansion of ψ. By propagating these solutions out to large values of r, a complete set of functions is obtained from which the probability of all the different asymptotic states of the system occurring can be extracted.

(b) $\underline{E_U < 0 \text{ or } E_S < 2z_B/R}$

If the outermost range of r is considered, the wave function can be taken to be zero and in this interval expressions (3.113) reduce to

$$\mathbf{F}_{a_{n-1}} = -\mathbf{S}_{a_{n-1}a_{n-1}}\mathbf{G}_{a_{n-1}} \ . \tag{3.117}$$

If the vectors $\mathbf{G}_{a_{n-1}}$ are chosen such that

$$\mathbf{G}_{a_{n-1}} = \varepsilon_{n-1}\mathbf{F}_{a_{n-1}} \tag{3.118}$$

a set of $L+1$ linearly independent vectors is obtained that are eigenvectors of $-\mathbf{S}_{a_{n-1}a_{n-1}}$ with corresponding eigenvalues $1/\varepsilon_{n-1}$. These solutions are propagated inwards by matching at each of the range boundaries. Eventually a set of solutions, $\overline{\mathbf{F}}_{a_1}$ and $\overline{\mathbf{G}}_{a_1}$ is obtained such that $\mathbf{F}_{a_1} = \overline{\mathbf{F}}_{a_1}\mathbf{x}$ and $\mathbf{G}_{a_1} = \overline{\mathbf{G}}_{a_1}\mathbf{x}$ where $\mathbf{x}$ is the column vector of mixing coefficients that will determine the correct linear combination of the $L+1$ linearly independent vectors $\overline{\mathbf{F}}_{a_1}$. Then (3.115) is used to obtain

$$(\overline{\mathbf{F}}_{a_1} - \mathbf{S}_{a_1a_1}\overline{\mathbf{G}}_{a_1a_1})\mathbf{x} = 0 \tag{3.119}$$

which will only have a non-trivial solution for $\mathbf{x}$ if the value of the energy E_i corresponds to a bound state of the electron at the chosen internuclear separation.

Chapter 4

Atomic test calculations – the hydrogen atom

The propagation method developed in chapter 3 is tested on the simplest case of atomic hydrogen.

Calculations are made in one, or both, of two approximations which are described in more detail further on.

The first divides configuration space into two regions. In the inner region the wave function is expanded in terms of R-matrix basis functions while in the outer region exact analytic forms for the wave functions are used to give a solution. The two solutions obtained are matched on the boundary thus giving the wave function for all space. This approximation allows comparisons to be made with the work of Yu Yan and Seaton (1985) (referred to as YYS hereafter) who use numerically generated functions.

The second approximation divides configuration space into many regions and in each region the wave function is expanded in terms of an orthonormal R-matrix basis. The solution obtained in one region is matched to the ones obtained in adjacent regions and in this way the wave function is generated for all space.

This approach is more flexible as configuration space can be divided into smaller regions and fewer basis functions may be required in each region to represent the wave functions adequately.

Wave functions, quantum defects and radiative integrals are calculated for the hydrogen atom. The main purpose of performing these test calculations is to get an initial idea of the accuracy and convergence properties of the method. In all calculations the constants α and β in (3.8) are taken to be zero. Energies are in Rydbergs and all other quantities are in atomic units.

4.1 Two approximations

The bound-state energies E_n for hydrogen are calculated in two approximations:

Approximation I

Bound-state energies, E_n, are calculated using the methods described by Seaton (1985). Configuration space is divided into an inner region, $r < a$, and an outer region, $r > a$.

In the inner region the reduced Hamiltonian matrix $\mathbf{H}^{\mathrm{R}}$, of finite dimension $K \times K$, is set up and diagonalised to yield K eigenenergies e_k and K eigenvectors $\mathbf{d}_k$ from which the basis functions $f_k(r)$ are evaluated. These functions are used to evaluate S_{aa} given in equation (3.65) and then the value of the wave function on the boundary $r = a$ is given by (3.68). Using the definition of G_a given in (3.66), equation (3.68) can be written as

$$F_a = S_{aa}(F_a' - \beta F_a) \ . \tag{4.1}$$

The solution in the inner region is matched at the boundary to the exact wave function for the particular electronic state being searched for, the analytic form of which can be found using the equations given later in §4.2.

If the exact wave function for a state with quantum numbers n and l is denoted by $P_{nl}(r)$ then the matching conditions $F_E(a) \equiv P_{nl}(a)$, $F_E'(a) \equiv P_{nl}'(a)$ give, from (4.1),

$$P_{nl} - S_{aa}(P_{nl}' - \beta P_{nl}) = 0 \ . \tag{4.2}$$

The quantity $P_{nl} - S_{aa}(P_{nl}' - \beta P_{nl})$ is scanned for a range of energies and a bound state is located when (4.2) is satisfied.

In all calculations using this approximation the boundary is chosen to be $a = 5$a.u. so that comparisons can be made with the work of YYS.

Approximation II

Configuration space is divided into a finite number of regions, p say, of equal width with boundaries $a_0, a_1, ..., a_p$ and in each region the reduced $K \times K$ Hamiltonian matrix $\mathbf{H}^{\mathbf{R}}$ is diagonalised to yield the eigenenergies and eigenvectors, and hence, the basis functions $f_k(r)$ for the interval. These functions are then used to evaluate $S_{a_{q-1}a_{q-1}}$, $S_{a_{q-1}a_q}$ and $S_{a_q a_q}$, $q = 1, ..., p$, given in (3.65). For bound states the wave functions decay to zero for large r, so in the outermost range, $a_{p-1} \leq r \leq a_p$, F_{a_p} is set to zero and the wave function at a_{p-1} is given by (3.69) where, for convenience, $G_{a_{p-1}}$ is set to value 1. The wave function is then generated for all space for a range of energies using the relations (3.67) by matching solutions at each range boundary and then normalised. If the energy is correct for a bound state of the system, then (3.68) must be satisfied in the innermost region $a_0 \leq r \leq a_1$. To locate the bound state the quantity $F_{a_1} - S_{a_1 a_1} G_{a_1}$ is scanned for a change in sign with energy and the energy range is repeatedly refined to locate the bound state to the required accuracy.

In all calculations using this approximation the number of intervals is chosen to be 25 and the interval widths are chosen to be 2a.u.

4.2 Wave functions of the hydrogen atom

The radial wave functions for the states with associated quantum numbers $(n, l) = (1,0), (2,0), (2,1)$ are generated using the propagation method presented in chapter 3 using approximation II with $K = 15$. The solutions are plotted against the corresponding exact normalised radial wave functions, $P_{nl}(r)$, which are obtained from the equations (excluding normalisation constants)

$$p_{l+1,l} = y^l e^{-y} \tag{4.3}$$

and

$$p_{n\pm1,l} = \left(y\frac{d}{dy} \mp y \pm n + 1 \right) p_{nl} \tag{4.4}$$

where $P_{nl}(r) = rp_{nl}(r)$ and $y = r/n$ (see Johnson and Pederson 1986). The unnormalised functions given by the above equations are then normalised according to

$$\int_0^\infty [P_{nl}(r)]^2 dr = 1 \ . \tag{4.5}$$

For the states mentioned above, the exact normalised forms are

$$\begin{aligned} P_{10}(r) &= 2re^{-r} \ , \\ P_{20}(r) &= \frac{1}{2\sqrt{2}}(r^2 - 2r)e^{-\frac{r}{2}} \ , \\ P_{21}(r) &= \frac{1}{2\sqrt{6}} r^2 e^{-\frac{r}{2}} \ . \end{aligned}$$

The results are shown in figure 4.1 and it can be seen that there is close agreement between the propagated solutions and the exact solutions.

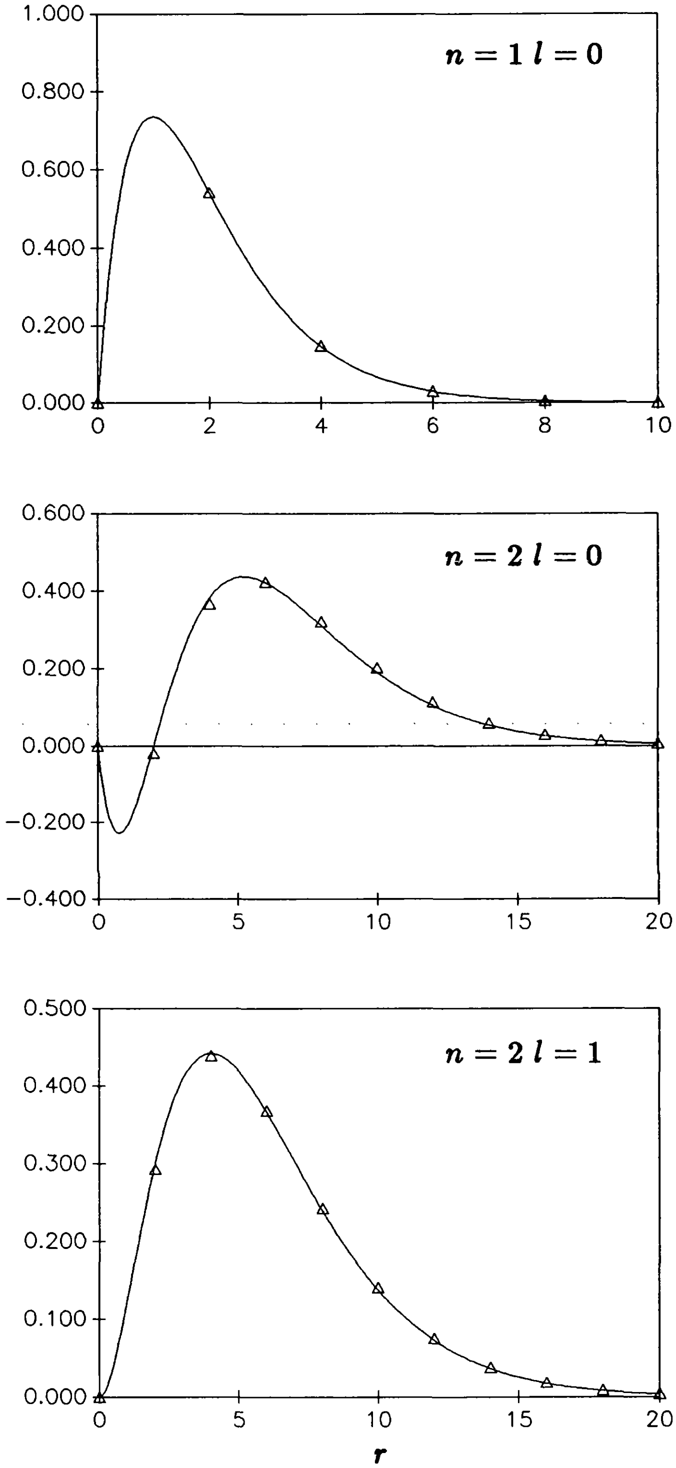


Figure 4.1: Graphs of the radial wave functions $F_E(r)$ generated using the propagation method ($\triangle$) plotted against the exact radial wave functions (—) for hydrogen.

4.3 Quantum defects

The bound-state energies for the hydrogen atom (ignoring finite mass effects), in Rydbergs, are given by

$$E_n = -\frac{1}{n^2} \ . \tag{4.6}$$

For outer electrons in non-hydrogenic atoms one may put

$$E_n = -\frac{1}{(n-\mu_n)^2} \tag{4.7}$$

and this defines the quantum defects μ_n. In making approximate calculations for hydrogen one can put

$$E_n(calc) = -\frac{1}{(n-\mu_n(calc))^2} \ . \tag{4.8}$$

An exact calculation gives $\mu_n(calc) = 0$ and a good approximate calculation gives $\mu_n(calc)$ to be small. Clearly then, quantum defects provide a measure of the errors in approximate calculations.

The quantum defect can be extended to positive energies $E \geq 0$ in which case the wave function $F_E(r)$ is fitted to

$$F_E(r) = s_E(r)\cos(\pi\mu) + c_E(r)\sin(\pi\mu) \quad ; \quad r > a \tag{4.9}$$

where $s_E(r)$ and $c_E(r)$ are regular and irregular Coulomb functions respectively and $\mu \equiv \mu(calc)$. The function $s_E(r)$ in (4.9) is the exact solution for the problem and so, again, $\mu(calc)$ is required to be small to give a good approximate calculation.

For $E > 0$ the functions $s_E(r)$ and $c_E(r)$ have asymptotic forms

$$\left.\begin{array}{c} s_E(r) \\ c_E(r) \end{array}\right\} \underset{r\to\infty}{\sim} \left\{\begin{array}{c} \sin \\ \cos \end{array}\right. \left[\kappa r - \frac{l\pi}{2} + \frac{1}{\kappa}\ln(2\kappa r) + \arg\Gamma(l+1-\frac{i}{\kappa})\right] \tag{4.10}$$

c.f. (2.28), where $E = \kappa^2$ and for $E = 0$ they have the forms

$$\begin{aligned} s_E(r) &= (4\pi r)^{\frac{1}{2}} J_{2l+1}(\sqrt{8r}) \\ &\underset{r\to\infty}{\sim} (8r)^{\frac{1}{4}} \sin(\sqrt{8r} - \tfrac{1}{2}(2l+1)\pi + \tfrac{\pi}{4}) \end{aligned} \tag{4.11}$$

and

$$\begin{aligned} c_E(r) &= -(4\pi r)^{\frac{1}{2}} \mathcal{Y}_{2l+1}(\sqrt{8r}) \\ &\underset{r\to\infty}{\sim} (8r)^{\frac{1}{4}} \cos(\sqrt{8r} - \tfrac{1}{2}(2l+1)\pi + \tfrac{\pi}{4}) \end{aligned} \tag{4.12}$$

where $\mathcal{J}_{2l+1}$ and $\mathcal{Y}_{2l+1}$ are Bessel functions. Using (4.9) together with

$$F_E'(r) = s_E'(r)\cos(\pi\mu) + c_E'(r)\sin(\pi\mu) \tag{4.13}$$

and

$$F_E(r) = \Re_E(r) F_E'(r) \tag{4.14}$$

evaluated at $r = a$ gives μ as

$$\tan\pi\mu = -\left[\frac{\Re_E(a)s_E'(a) - s_E(a)}{\Re_E(a)c_E'(a) - c_E(a)}\right] . \tag{4.15}$$

The Coulomb functions and their derivatives are generated for $E > 0$ using the program COULFG of Barnett (1982). For $E = 0$ the derivatives

$$s_E'(r) = \frac{(8\pi)^{\frac{1}{2}}}{z}\left[\mathcal{J}_{2l+1}(z) + z\mathcal{J}_{2l+1}'(z)\right] \tag{4.16}$$

and

$$c_E'(r) = -\frac{(8\pi)^{\frac{1}{2}}}{z}[\mathcal{Y}_{2l+1}(z) + z\mathcal{Y}_{2l+1}'(z)] \tag{4.17}$$

are needed, where $z = (8r)^{\frac{1}{2}}$. The recurrence relations for the Bessel functions give

$$\frac{1}{z}\left[\mathcal{J}_i(z) + z\mathcal{J}_i'(z)\right] = \frac{1}{2i}\left[(i+1)\mathcal{J}_{i-1}(z) + (i-1)\mathcal{J}_{i+1}(z)\right] \tag{4.18}$$

and similarly for the $\mathcal{Y}_i(z)$, and therefore (4.16) and (4.17) become

$$s_E'(r) = \frac{(8\pi)^{\frac{1}{2}}}{(2l+1)}\left[(l+1)\mathcal{J}_{2l}(z) + l\mathcal{J}_{2l+2}(z)\right] \tag{4.19}$$

and

$$c_E'(r) = -\frac{(8\pi)^{\frac{1}{2}}}{(2l+1)}\left[(l+1)\mathcal{Y}_{2l}(z) + l\mathcal{Y}_{2l+2}(z)\right] \tag{4.20}$$

respectively. Thus the Coulomb functions can be generated for all energies E.

Results

Quantum defects for bound states, given by (4.8), are calculated using approximations I and II for increasing values of K. For $E = 0$, the quantum defect, given by (4.15), is calculated using approximation I for increasing values of K.

Figure 4.2 shows quantum defects $\mu_n(calc)$ obtained for the lowest bound states of hydrogen with quantum numbers $(n, l) = (1,0); (2,0); (2,1)$. Figure 4.3 shows the quantum defects obtained when $E = 0$ and this figure can be compared with figure 2 of YYS. It is found that the use of the present Legendre basis functions, as opposed to the use of numerically generated basis functions, consistently gives smaller quantum defects for a given value of K.

From figure 4.2 it can be seen that $\mu_n(calc)$ provides a lower bound on the exact value μ_n. This, in principle, should be the case for $E = 0$ in figure 4.3 and the points at which this bound appears to be violated ($l = 0$, $l = 1$) most probably arise due to the principle value being taken for $\pi\mu$ in (4.15). These values for $\pi\mu$ should actually be $\pi\mu + p\pi$ where p is an integer (negative in this case).

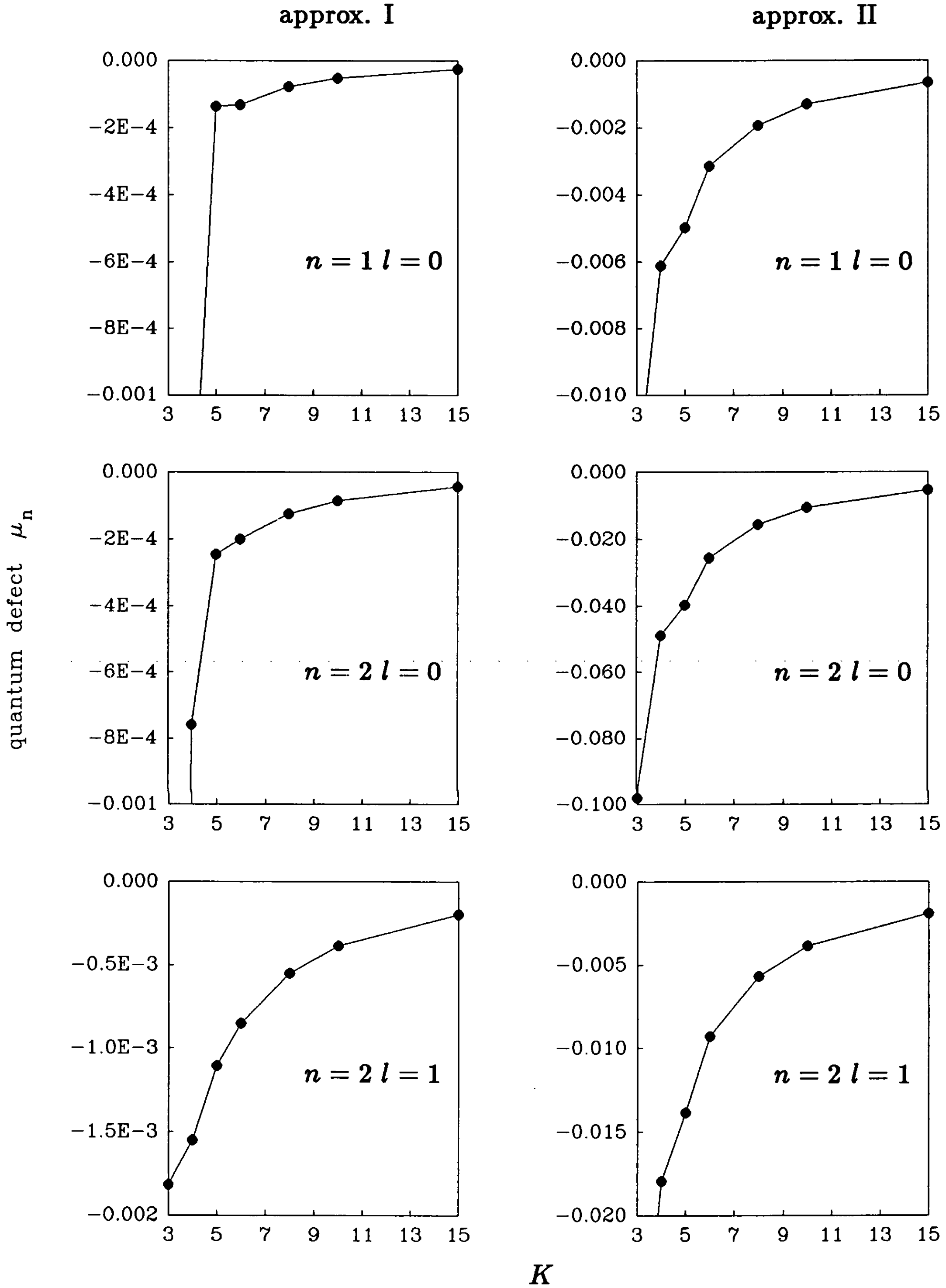


Figure 4.2: Quantum defects $\mu_n(calc)$ obtained for the lowest bound states of hydrogen with quantum numbers $(n,l) = (1,0);(2,0);(2,1)$ and with K terms in the expansion of $F_E(r)$.

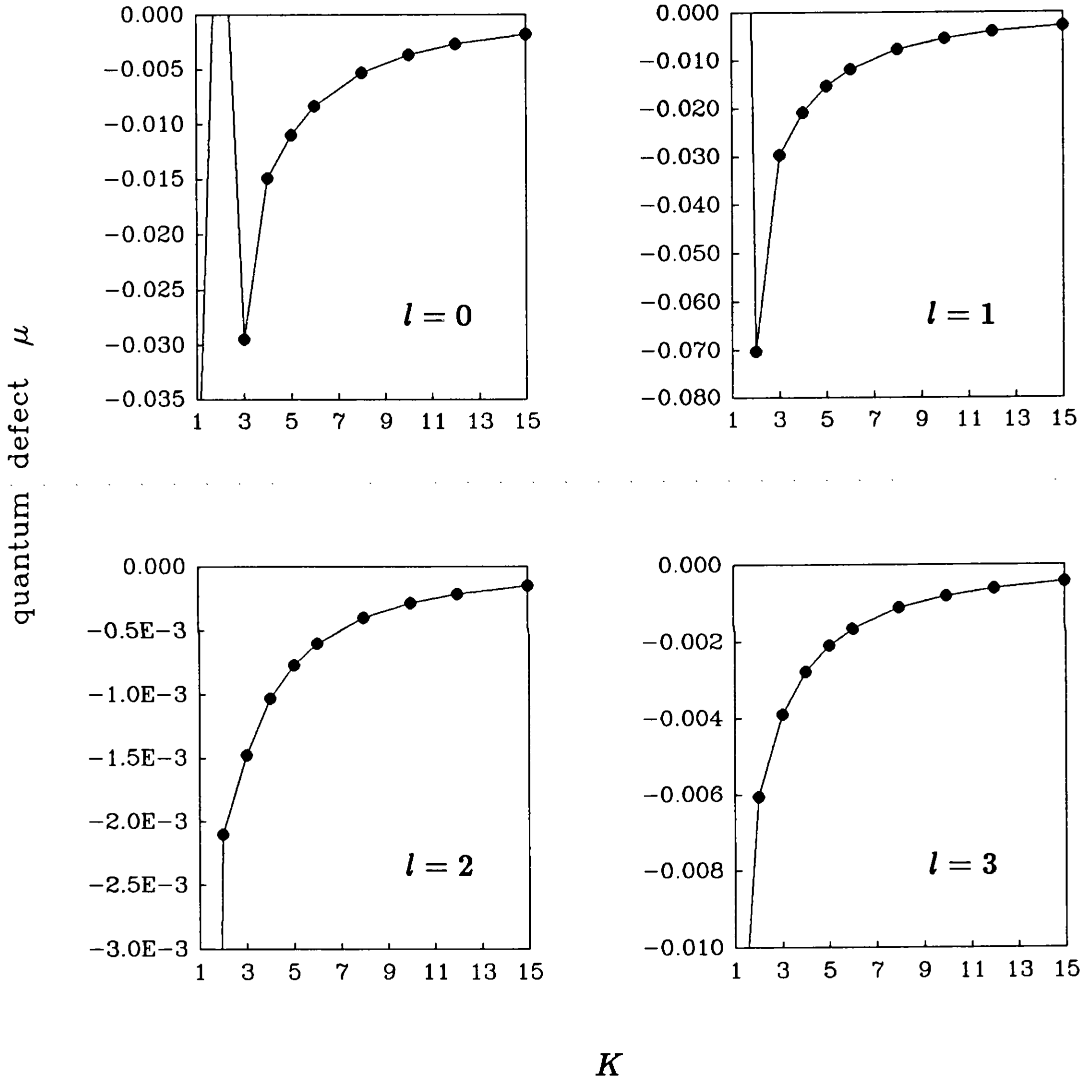


Figure 4.3: Quantum defects $\mu(calc)$ obtained for hydrogen with $E = 0$, $a = 5$a.u. and K terms in the expansion of $F_E(r)$.

4.4 Radiative integrals

For negative energies the bound-state functions are normalised according to

$$\int_0^\infty [F_E(r)]^2 dr = 1 \tag{4.21}$$

and for positive energies the functions $F_E(r)$ are taken to be normalised per unit energy with asymptotic forms

$$F_E(r) \underset{r \to \infty}{\sim} (\pi\kappa)^{-\frac{1}{2}} \sin(\xi + \pi\mu) \tag{4.22}$$

where $\kappa = E^{\frac{1}{2}}$ and

$$\xi = \kappa r - \frac{l\pi}{2} + \frac{1}{\kappa}\ln(2\kappa r) + \arg\Gamma(l + 1 - \frac{i}{\kappa}) \ . \tag{4.23}$$

The oscillator strength for the transition from an initial state i to a final state j depends on the quantity

$$\frac{1}{(2l_i + 1)} \sum_{m_i \nu m_j} |M_{ij}|^2 \tag{4.24}$$

where

$$M_{ij} = \int_\tau \Psi^*_{E_j}(\mathbf{r})\mathbf{r}\Psi_{E_i}(\mathbf{r})d\tau \ . \tag{4.25}$$

M_{ij} can be written in spherical polar coordinates as

$$M_{ij} = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \int F_j(r)Y^*_{l_j m_j}(\theta,\phi) r Y_{1\nu}(\theta,\phi) F_i(r) Y_{l_i m_i}(\theta,\phi) \sin\theta dr d\theta d\phi \tag{4.26}$$

where $F_{i(j)}$ has $E = E_{i(j)}$ and $l = l_{i(j)}$, $l_j = l_i \pm 1$ and where

$$\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} r Y_{1\nu}(\theta,\phi) \qquad ; \qquad \nu = -1, 0, 1 \tag{4.27}$$

are the spherical components of the vector $\mathbf{r}$. Using standard results for the angular integrals in (4.26) gives (see Edmonds 1960)

$$M_{ij} = \int_0^\infty F_j(r) r F_i(r) dr \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} (-1)^{m_j} \left[\frac{3(2l_j+1)(2l_i+1)}{4\pi}\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} l_j & 1 & l_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & 1 & l_i \\ -m_j & \nu & m_i \end{pmatrix} \tag{4.28}$$

and then (4.24) becomes

$$\begin{aligned} \frac{1}{(2l_i+1)} \sum_{m_i \nu m_j} |M_{ij}|^2 &= \left(\int_0^\infty F_j(r) r F_i(r) dr\right)^2 (2l_j+1) \begin{pmatrix} l_j & 1 & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 \\ &\times \sum_{m_i \nu m_j} \begin{pmatrix} l_j & 1 & l_i \\ -m_j & \nu & m_i \end{pmatrix}^2 \end{aligned} \tag{4.29}$$

which reduces to

$$\frac{1}{(2l_i+1)} \sum_{m_i \nu m_j} |M_{ij}|^2 = \frac{l_>}{2l_i+1} \left(\int_0^\infty F_j(r) r F_i(r) dr\right)^2 \tag{4.30}$$

(see Edmonds 1960, p47), where $l_> = \max(l_i, l_j)$. The radial integrals in (4.30) are defined as

$$\sigma_{ij} = \int_0^\infty F_j(r) r F_i(r) dr \tag{4.31}$$

and for bound-bound and bound-free transitions the integrand in (4.31) decays to zero for large r. Therefore, configuration space can be divided into a finite number of intervals, p say, with boundaries $a_0, a_1, ..., a_p$, and then (4.31) can be written as

$$\sigma_{ij} = \sum_{q=1}^{p} \int_{a_{q-1}}^{a_q} F_j(r) r F_i(r) dr \ . \tag{4.32}$$

Using the expansion in (3.57) gives

$$\sigma_{ij} = \sum_{q=1}^{p} \sum_{k_i k_j} A_{k_i} A_{k_j} \int_{a_{q-1}}^{a_q} f_{k_j}(r) r f_{k_i}(r) dr \tag{4.33}$$

and this can be further simplified using (3.9) to give

$$\sigma_{ij} = \sum_{q} \left(\frac{a_q - a_{q-1}}{2}\right)^2 \sum_{k_i k_j} A_{k_i} A_{k_j} \sum_{\lambda_i \lambda_j} c_{k_i \lambda_i} c_{k_j \lambda_j} \int_{-1}^{1} Y_{\lambda_j}(x)(y+x) Y_{\lambda_i}(x) dx \tag{4.34}$$

where $y = (a_q + a_{q-1})/(a_q - a_{q-1})$. The integrals in (4.34) are of the type (3.95) with $X = 1$ and $n = 1$ and can be generated using the same procedure as described for the matrix elements $J_n(\lambda', \lambda)$ in §3.2.3.

Results

The radiative integrals are calculated using the two approximations described in §4.1. In approximation I, expression (4.34) is evaluated for the interval $0 \leq r \leq 5$, i.e. $a_0 = 0$ and $a_1 = 5$. In the interval $r > 5$, the exact wave functions for hydrogen are used to evaluate the remaining integral

$$\int_5^\infty P_{n_j l_j}(r) r P_{n_i l_i}(r) dr \tag{4.35}$$

where $P_{n_i l_i}(r)$ and $P_{n_j l_j}(r)$ denote the wave functions for the initial and final states involved in the transition. The integral (4.35) is calculated numerically using the NAG routine D01AKF which employs Gauss-Laguerre quadrature.

The results are compared with those of exact calculations obtained by Green *et al* (1957) for bound-bound transitions and by Burgess (1964) for bound-free transitions. Table 4.1 gives fractional errors obtained in calculations for σ_{ij}^2 for the transitions $1s \rightarrow np$ and $1s \rightarrow \kappa p$ with $K = 15$ basis functions used in the expansion of the wave function in $F_E(r)$ in (3.57). The convergence in K is also considered for bound-free transitions $nl \rightarrow \kappa l'$ with $\kappa^2 = 0$ and results are tabulated in table 4.2.

(a) Bound-bound, 1s → np

n	approx. I	approx. II
2	-0.0157	0.0089
3	-0.0265	0.0041
4	-0.0288	0.0025
5	-0.0294	0.0016
6	-0.0296	0.0009

(b) Bound-free, 1s → κp

κ^2	approx. I	approx. II
0.00	-0.0156	0.0104
0.08	-0.0107	0.0110
0.16	-0.0059	0.0087
0.32	-0.0013	0.0055
0.64	-0.0150	0.0009
1.28	-0.0119	-0.0177

Table 4.1: Fractional errors obtained in the squares of radiative integrals, σ_{ij}^2, for (a) the bound-bound transitions 1s → np and (b) the bound-free transitions 1s → κp calculated with $K = 15$ terms in the expansion of $F_E(r)$.

	$1s \rightarrow p$		$2s \rightarrow p$	
K	approx. I	approx. II	approx. I	approx. II
3	1.396	0.176	0.061	0.469
4	-0.240	0.106	0.034	0.218
5	-0.084	0.073	0.026	0.172
6	-0.075	0.053	0.021	0.108
8	-0.046	0.033	0.014	0.065
10	-0.032	0.022	0.010	0.044
15	-0.016	0.010	0.005	0.022

	$2p \rightarrow s$		$2p \rightarrow d$	
K	approx. I	approx. II	approx. I	approx. II
3	0.054	-0.020	0.012	0.123
4	0.068	-0.044	0.007	0.042
5	0.050	-0.013	0.005	0.043
6	0.038	-0.022	0.004	0.021
8	0.025	-0.013	0.003	0.013
10	0.017	-0.008	0.002	0.009
15	0.009	-0.004	0.001	0.004

Table 4.2: Fractional errors obtained in the squares of radiative integrals, σ_{ij}^2, for transitions $nl \rightarrow \kappa l'$ with $\kappa^2 = 0$ and with K terms in the expansion of $F_E(r)$.

4.5 Conclusions

It is seen that the bound states and radiative integrals for the hydrogen atom converge towards exact calculations as K is increased. The convergence is fairly rapid for the first few terms and then becomes slower as more terms are taken into the expansion of $F_E(r)$. This behaviour is a well-known feature of R-matrix methods (see YYS). Nevertheless, the use of the Legendre polynomials in the construction of the basis functions leads to more accurate solutions of the wave equation for a specified number of basis states K than the use of the usual numerically generated basis set as described by YYS. Calculations made in approximation II give similar, and in some cases more accurate, results for the radiative integrals than approx I. The advantage of using approximation II is that the asymptotic forms of the exact wave functions are not needed as the method generates the wave function for all space. Also, a smaller interval length can be taken and this means that fewer basis functions are needed per interval thus leading to faster convergence.

The errors obtained in the radiative integrals cannot be compared directly with those of YYS as they use Buttle corrections. However, it is possible to reproduce their results without Buttle corrections by using the eigenvalues and surface amplitudes given in their paper to find the bound-state energies and then adapting the present method to calculate the radiative integrals. The procedure is described below.

The eigenvalues and surface amplitudes given by YYS, labelled here as e_{k_Y} and f_{k_Y}, are used to evaluate S_{aa} ($a = 5$) given in (3.65) and then the bound states are located following the procedure given in approximation I (see §4.1). A new parameter is introduced, k_{max}, to represent the total number of basis functions used in the evaluation of S_{aa} and bound-state energies are calculated for varying k_{max}. Table 4.3 gives the bound-state energies obtained for the states

$(n, l) = (1,0); (2,0)$ using the functions f_{k_Y}. These are the energies that YYS would have obtained had they omitted the Buttle correction. Also given in this table, for comparison, are the energies obtained using approximations I and II using the functions f_k.

The calculation of the radiative integrals is slightly more complicated as the f_{k_Y} are needed for the interval $0 \leq r \leq 5$ and not just on the boundary $r = 5$. From table 4.4, which gives the eigenvalues and surface amplitudes obtained using the Legendre basis, it is seen that the lower eigenvalues and surface amplitudes are almost identical to those obtained by YYS (apart from some differences in sign which do not affect the results) but the higher ones are more spread, thus spanning a greater energy range. If, in the interval $0 \leq r \leq 5$, the size of the basis is taken to be large enough, $K = 15$ terms say, then the lower 6 eigenvalues and surface amplitudes obtained upon diagonalisation of $\mathbf{H}^{\mathrm{R}}$ are identical to those of YYS (see table 4.4). These 6 eigenvalues and surface amplitudes, denoted by $e_{k'_Y}$ and $f_{k'_Y}$, are used in (4.34) to give the corresponding radiative integrals, σ^Y_{ij}. The fractional errors obtained in $(\sigma^Y_{ij})^2$ for different values of k_{max} are shown in table 4.5 together with the results obtained using the functions f_k.

To verify that the results for the σ^Y_{ij} actually do correspond exactly to the work of YYS, the Buttle correction, given by YYS for $l = 0$ as

$$0.178498 + 0.004669E + 0.000259E^2$$

was added to S_{aa} and the bound states were located again. The corresponding radiative integrals were then calculated. This was only done for $k_{max} = 6$ and it was found that exactly the same results as those of YYS were obtained (see table 4.5). Clearly then, the results for σ^Y_{ij} are what YYS would have obtained if they had not used a Buttle correction and comparisons can now be made with the present work.

Comparing the results given in table 4.6 it is seen that the results obtained using the Legendre basis are generally more accurate than the uncorrected ones of YYS for a given value of K. Use of the Buttle correction in the work of YYS reduces the fractional error by approximately 10^2 to 10^3. From the table, for the transition $2s \rightarrow p$, it can be seen that by using 15 basis functions in the internal region in approx. I, the fractional errors obtained are only an order of magnitude larger than those of YYS with Buttle corrections added. Clearly, the values of σ_{ij} are not fully converged at $K = 15$, and therefore an increase in K would reduce the errors even further to values comparable to the corrected results of YYS. Looking at the convergence in K in table 4.2 it is envisaged that, by using more basis functions in the expansion of the wave function, the need for a Buttle correction will be obviated.

$(n,l) = (1,0)$ - $E_n = -1.000$

k_{max}	A[a]	I[b]	II[c]
3	-0.998741	-0.946470	-0.975275
4	-0.999126	-0.997146	-0.987855
5	-0.999329	-0.999727	-0.990132
6	-0.999455	-0.999736	-0.993731

$(n,l) = (2,0)$ - $E_n = -0.250$

k_{max}	A[a]	I[b]	II[c]
3	-0.249760	-0.246974	-0.227160
4	-0.249832	-0.249810	-0.238215
5	-0.249870	-0.249939	-0.240405
6	-0.249894	-0.249950	-0.243767

[a] using data of YYS

[b] using Legendre basis – approx. I

[c] using Legendre basis – approx. II

Table 4.3: Bound-state energies obtained using the data of YYS compared with those obtained using the Legendre basis.

l	k	e_k	$e^a_{k_Y}$	$f_k(a)$	$f^a_{k_Y}(a)$
0	1	-1.007361	-1.007362	0.136305	0.136186
	2	-0.232335	-0.232335	0.719047	0.719054
	3	1.093785	1.093783	0.688819	0.688598
	4	3.342890	3.335493	-0.655957	-0.661618
	5	6.498145	6.400272	0.654206	0.650858
	6	13.105483	10.272967	-1.354787	-0.645343
1	1	-0.284606	-0.284605	0.617265	0.617265
	2	0.613128	0.613128	-0.677721	-0.677723
	3	2.436522	2.436493	0.656835	0.656099
	4	5.112969	5.092539	-0.641601	-0.647524
	5	8.671744	8.561348	0.640501	0.643094
	6	17.952773	12.834511	-1.522389	-0.640452
2	1	0.077579	0.077579	0.761349	0.761349
	2	1.461277	1.461277	-0.674975	-0.674974
	3	3.704096	3.703942	0.657274	0.655756
	4	6.795768	6.767297	-0.641736	-0.647673
	5	10.824075	10.638689	0.660962	0.643350
	6	23.530751	15.312001	-1.671249	-0.640718
3	1	0.494385	0.494385	0.847620	0.847620
	2	2.355728	2.355728	-0.689316	-0.689320
	3	5.018972	5.018493	0.665180	0.662793
	4	8.516367	8.489985	-0.646864	-0.652023
	5	13.183560	12.764539	0.702139	0.646353
	6	29.917027	17.838412	-1.804475	-0.642933
4	1	0.990220	0.990220	0.913494	0.913494
	2	3.329496	3.329495	-0.706337	-0.706365
	3	6.414503	6.413506	0.675087	0.672034
	4	10.311570	10.293937	-0.656827	-0.658013
	5	15.818770	14.972212	0.751550	0.650605
	6	37.115576	20.447048	-1.926487	-0.646129

^{a} data of YYS

Table 4.4: R-matrix energies e_k and surface amplitudes $f_k(a)$ obtained using the Legendre basis and approximation I compared with those of YYS with $a = 5$a.u.

	$l = 0$		$l = 1$	
k	e_k	$f_k(a)$	e_k	$f_k(a)$
1	-1.007362	0.136186	-0.284606	0.617265
2	-0.232335	0.719054	0.613128	-0.677723
3	1.093783	0.688598	2.436494	0.656099
4	3.335494	-0.661618	5.092540	-0.647524
5	6.400272	0.650858	8.561349	0.643094
6	10.272968	-0.645342	12.834512	-0.640446
7	14.947300	0.642216	17.907573	0.638879
8	20.420042	-0.639857	23.777953	-0.638105
9	26.706917	0.636443	30.471122	0.634619
10	33.884874	-0.639396	37.989151	-0.635491
11	43.002331	0.814702	48.080479	0.779914
12	55.056175	-0.638577	58.717002	0.768941
13	77.418910	-1.136613	88.403530	1.105561
14	120.828111	-0.666977	112.333303	-0.770124
15	213.154011	3.026429	254.560733	3.215629

Table 4.5: Eigenvalues e_k and surface amplitudes $f_k(a)$ obtained for hydrogen using approximation I with $K = 15$ and $a = 5$a.u.

$1s \rightarrow p$				
k_{max}	A[a]	B[b]	I[c]	II[d]
3	-0.326	–	1.396	0.176
4	-0.236	–	-0.240	0.106
5	-0.188	–	-0.084	0.073
6	-0.155	-0.0004	-0.078	0.053
10	–	–	-0.032	0.022
15	–	–	-0.016	0.010

$2s \rightarrow p$				
k_{max}	A[a]	B[b]	I[c]	II[d]
3	-0.070	–	0.061	0.469
4	-0.060	–	0.034	0.218
5	-0.052	–	0.026	0.172
6	-0.045	-0.0003	0.021	0.108
10	–	–	0.010	0.044
15	–	–	0.005	0.022

[a] using $f_{k'_Y}$

[b] using $f_{k'_Y}$ with Buttle correction

[c] using f_k – approx. I

[d] using f_k – approx. II

Table 4.6: Fractional errors obtained in the radiative integrals calculated with and without Buttle corrections from the reproduced data of YYS, compared with the results obtained using the Legendre basis.

Chapter 5

Molecular test calculations – H_2^+ and HeH^{2+}

The propagation method developed in chapter 3 is tested on the molecular systems H_2^+ and HeH^{2+}.

Bound-state energies and oscillator strengths are calculated for both systems and for H_2^+ the wave functions are presented. In all calculations centre of mass coordinates are used, the constants α and β in (3.92) are taken as zero and configuration space is divided into 25 intervals each of width 2a.u. Energies are in Rydbergs and all other quantities are in atomic units.

Two parameters, L and K, must be considered. L represents the maximum value of l retained in the expansion of $\psi(r)$ in (3.74) and K represents the number of basis functions $f_k^l(r)$ taken per interval in the expansion of $F_l(r)$ in (3.106). In calculations, either K is fixed and the convergence in L is considered, or L is fixed and the convergence in K considered.

5.1 Wave functions of H_2^+

In order to assess the stability and accuracy of the relations (3.113) it is of interest to compare the wave functions obtained from them with the exact forms.

The bound-state energies of the H_2^+ ion are located using the method described in §3.2.4 and for each state the wave functions $F_l(r)$ are generated. In each region $K = 15$ basis functions are used in the expansion of $F_l(r)$ and $L = 10$ angular functions are retained in the expansion of ψ.

The exact wave functions for H_2^+ can be obtained from the paper by Bates *et al* (1953) (referred to as BLS hereafter). They write the total wave function Ψ_E in confocal elliptic coordinates (λ, μ, ϕ) as

$$\Psi_E(\lambda, \mu, \phi) = \Lambda(\lambda) M(\mu) \Phi(\phi) \ . \tag{5.1}$$

The expansion used in this thesis is

$$\Psi_E(r, \theta, \phi) = \sum_l \frac{1}{r} F_l(r) c_{lm} P_l^m(\cos\theta) \times \Phi(\phi) \tag{5.2}$$

where (r, θ, ϕ) are centre of mass coordinates. Equating (5.1) and (5.2) gives

$$\Lambda(\lambda) M(\mu) = \sum_l \frac{1}{r} F_l(r) c_{lm} P_l^m(\cos\theta) \ . \tag{5.3}$$

Multiplying (5.3) by $c_{l'm} P_{l'}^m(\cos\theta)$ and integrating over $\cos\theta$ gives

$$\begin{aligned} &\int_{-1}^{1} \Lambda(\lambda) M(\mu) c_{l'm} P_{l'}^m(\cos\theta)\, d(\cos\theta) \\ &= \quad \int_{-1}^{1} c_{l'm} P_{l'}^m(\cos\theta) \sum_l \frac{1}{r} F_l(r) c_{lm} P_l^m(\cos\theta)\, d(\cos\theta) \ . \end{aligned} \tag{5.4}$$

It is known that the P_l^m satisfy the normalisation condition

$$\int_{-1}^{1} c_{l'm} c_{lm} P_{l'}^m(z) P_l^m(z)\, dz = \delta_{l'l} \tag{5.5}$$

so (5.4) becomes

$$\int_{-1}^{1} \Lambda(\lambda) M(\mu) c_{lm} P_l^m(\cos\theta)\, d(\cos\theta) = \frac{1}{r} F_l(r) \ . \tag{5.6}$$

Now λ and μ can be written as

$$\lambda = \frac{r_A + r_B}{R} \qquad ; \qquad \mu = \frac{r_A - r_B}{R} \tag{5.7}$$

and from figure 3.1

$$r_A^2 = \frac{R^2}{4} + r^2 + Rr\cos\theta \qquad ; \qquad r_B^2 = \frac{R^2}{4} + r^2 - Rr\cos\theta \ . \tag{5.8}$$

Using (5.8) in (5.7), λ and μ can be written in terms of the single radial coordinate r.

BLS use the expansions

$$M(l,m,p|\mu) = \sum_s f_s(l,m,p) P^m_{m+s}(\mu) \tag{5.9}$$

where the sum is over even values of s if $(l+m)$ is even and over odd values of s if $(l+m)$ is odd, and

$$\Lambda(\lambda) = (\lambda^2 - 1)^{\frac{m}{2}} (\lambda + 1)^\sigma \exp(-p\lambda) y(\xi) \tag{5.10}$$

with

$$\sigma = \frac{R}{p} - m - 1 \quad ; \quad \xi = \frac{\lambda - 1}{\lambda + 1} \quad ; \quad y = \sum_{t=0}^{\infty} g_t \xi^t \ . \tag{5.11}$$

They provide quantities

$$p, \quad \sigma, \quad f_s, \quad g_t,$$

for different values of R.

The wave functions $F_l(r)$ must be normalised to

$$\sum_l \int_0^\infty [F_l(r)]^2 dr = 1 \ . \tag{5.12}$$

Using expression (5.6) for $F_l(r)$, (5.12) becomes

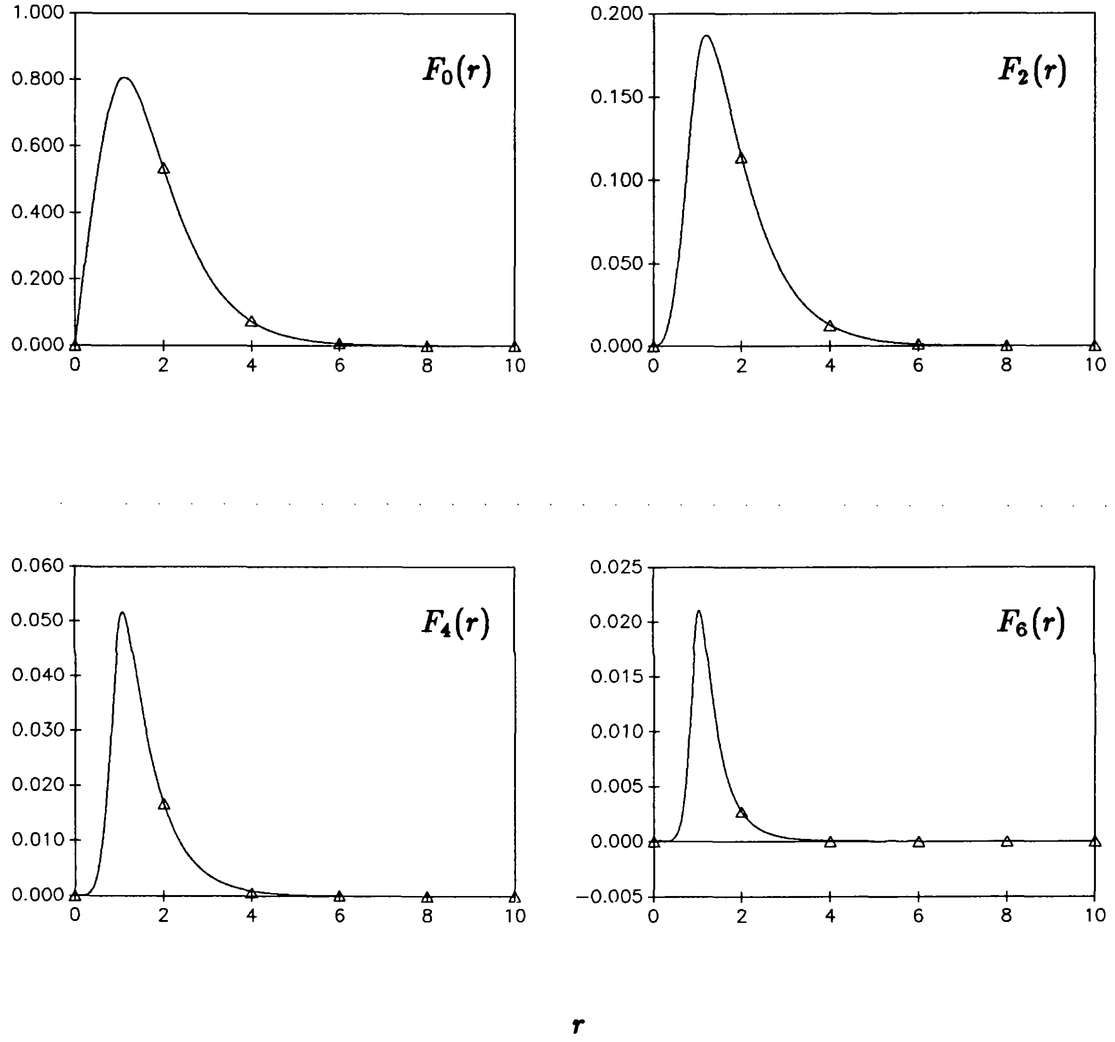
$$\sum_l \int_0^\infty c_{lm}^2 r^2 \left[\int_{-1}^{1} \Lambda(\lambda) M(\mu) P_l^m(\cos\theta)\, d(\cos\theta) \right]^2 dr = 1 \ . \tag{5.13}$$

In practice, since the bound-state wave functions decay to zero, the integral is truncated at $r = 50$a.u. and then evaluated using Gauss-Legendre quadrature using the NAG routine D01BBF. Also, the summation over l in (5.2) and (5.13) is truncated at $L = 10 = \max(l)$. Figure 5.1 shows plots of the first four radial wave functions $F_l(r)$ generated using the Legendre basis against the exact radial wave functions for H_2^+ for the states $1s\sigma_g$, $2s\sigma_g$, $2p\sigma_u$, $3p\sigma_u$, $3d\sigma_g$ at internuclear separations $R = 2$ and $R = 4$.

Some of the wave functions fit very well to the exact results but some give a poor fit. It is seen that the close fits occur for those functions that contribute most to the summation in (5.2), i.e. those that have the greatest magnitude. Since the other functions are of a smaller order of magnitude, the errors appear to be quite large, but in actual fact, if the functions were all plotted on the same scale the errors would not appear to be so great.

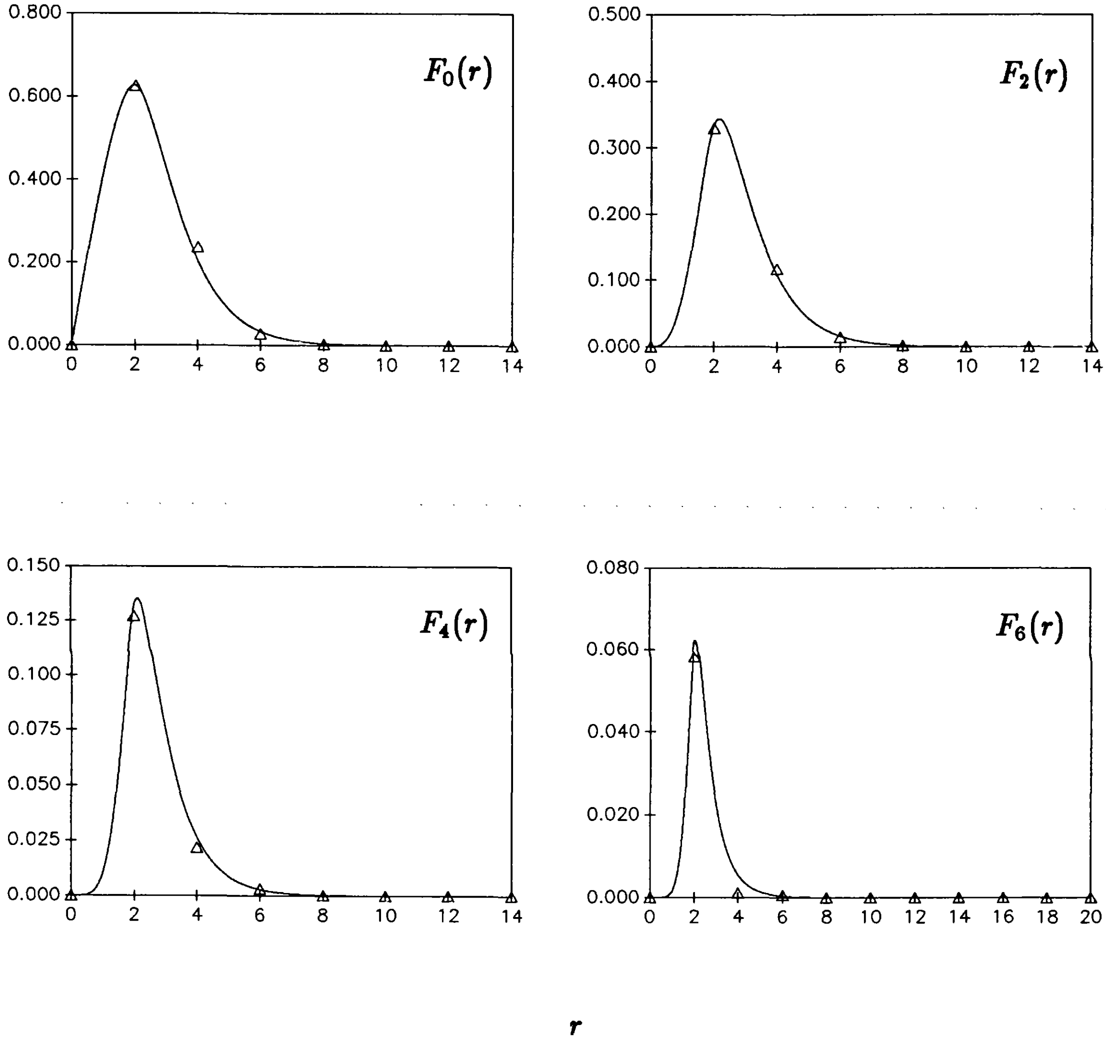
Figure 5.1: Graphs of the radial wave functions $F_l(r)$ generated using the propagation method (△) plotted against the exact radial wave functions (—) of the H_2^+ ion for two internuclear separations $R = 2$ and $R = 4$.

$1s\sigma_g$ $R = 2$



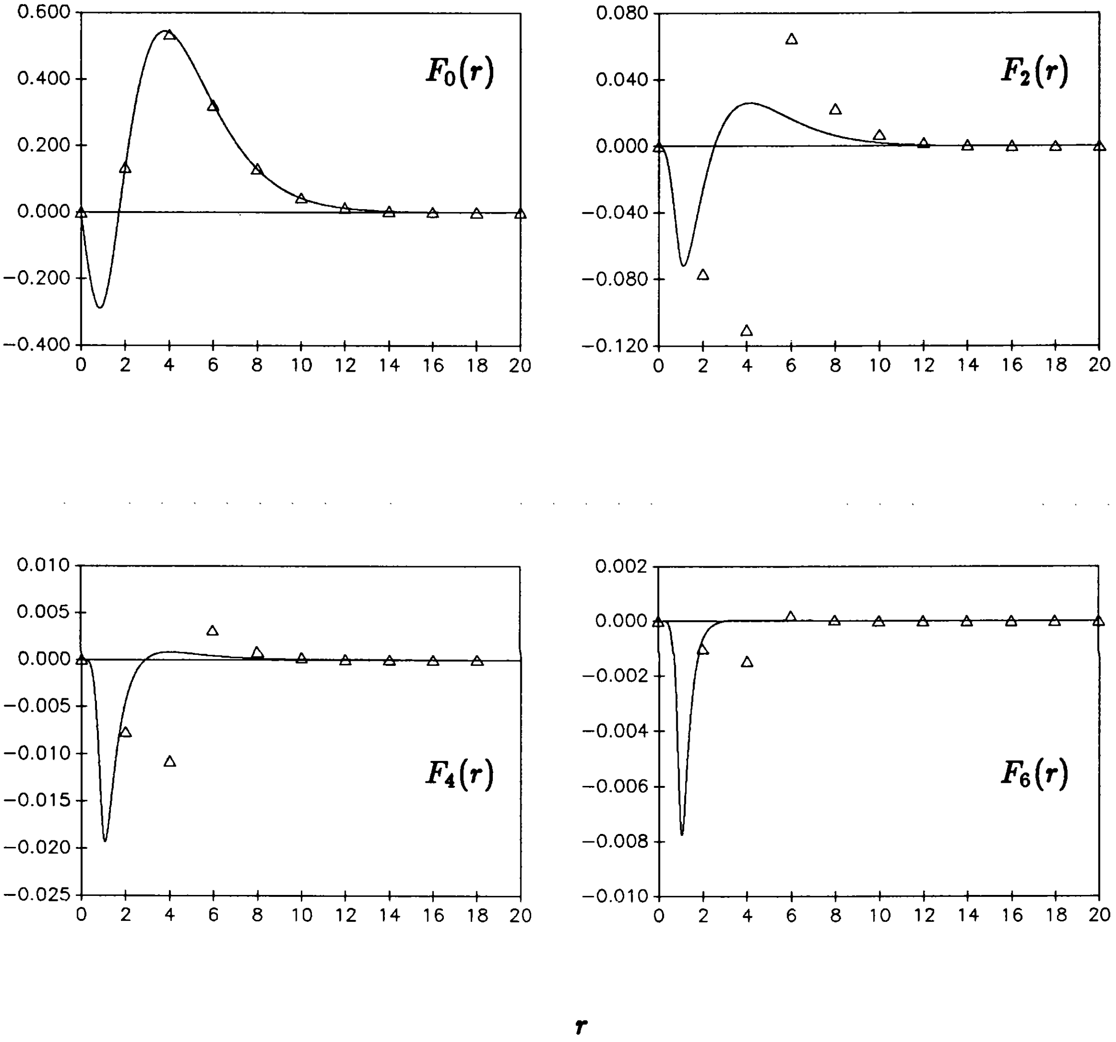
1.000
0.800
0.600
0.400
0.200
0.000
0
2
4
6
8
10
$F_0(r)$
0.200
0.150
0.100
0.050
0.000
0
2
4
6
8
10
$F_2(r)$
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0
2
4
6
8
10
$F_4(r)$
0.025
0.020
0.015
0.010
0.005
0.000
−0.005
0
2
4
6
8
10
$F_6(r)$
r

$1s\sigma_g$ $R = 4$

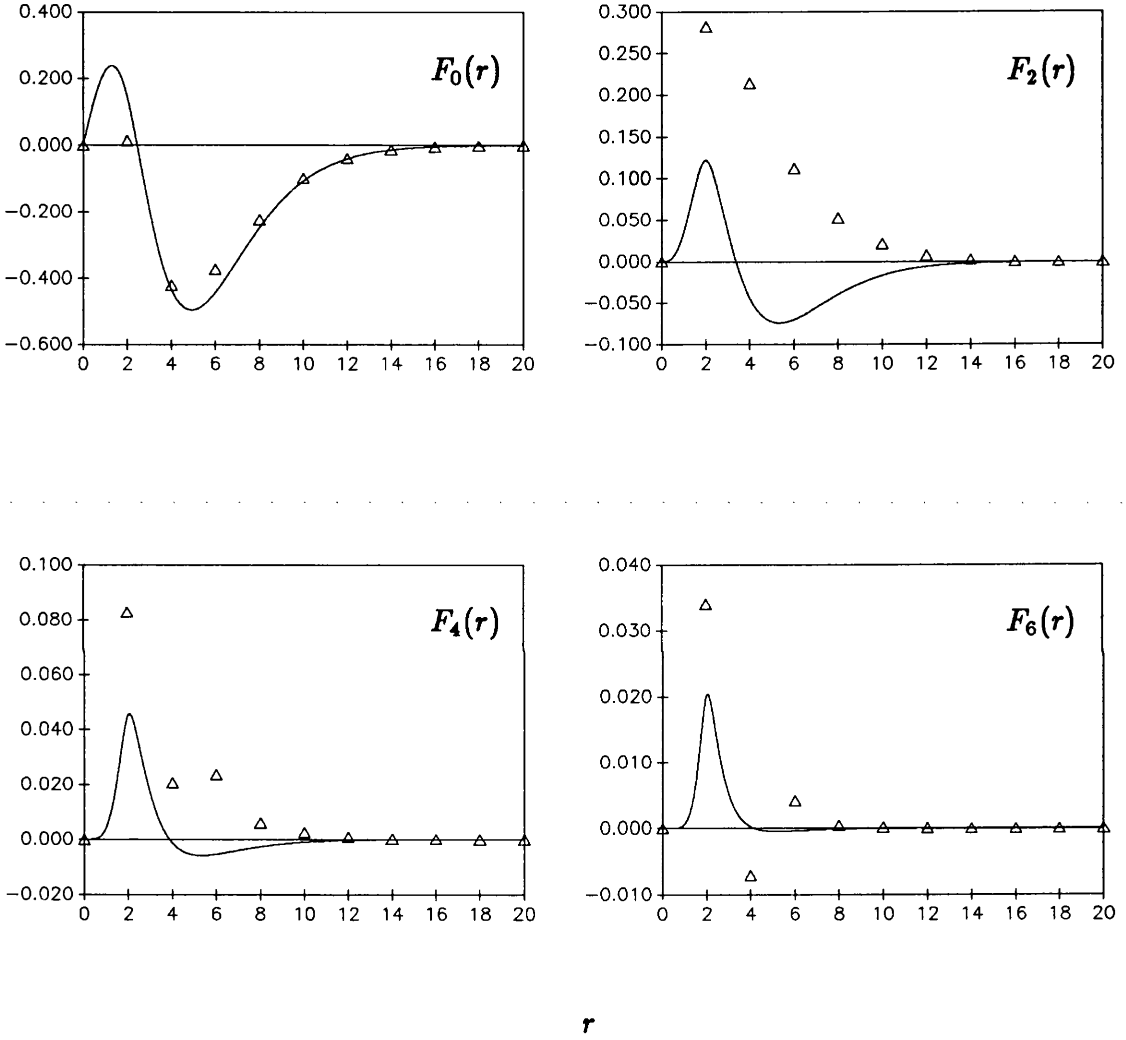


$F_0(r)$
0.800
0.600
0.400
0.200
0.000
0
2
4
6
8
10
12
14
$F_2(r)$
0.500
0.400
0.300
0.200
0.100
0.000
0
2
4
6
8
10
12
14
$F_4(r)$
0.150
0.125
0.100
0.075
0.050
0.025
0.000
0
2
4
6
8
10
12
14
$F_6(r)$
0.080
0.060
0.040
0.020
0.000
0
2
4
6
8
10
12
14
16
18
20
r

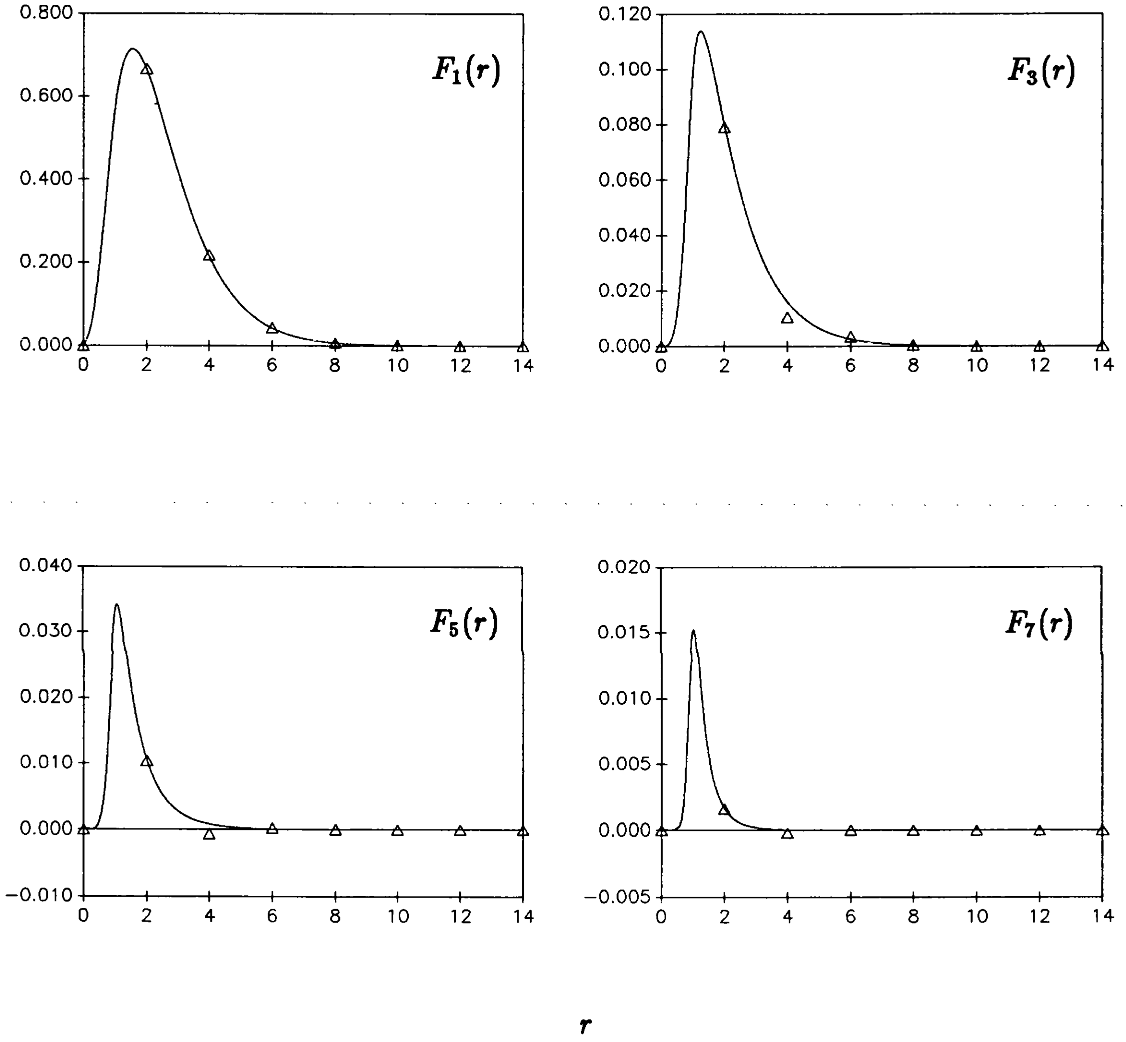
$2s\sigma_g \qquad R = 2$



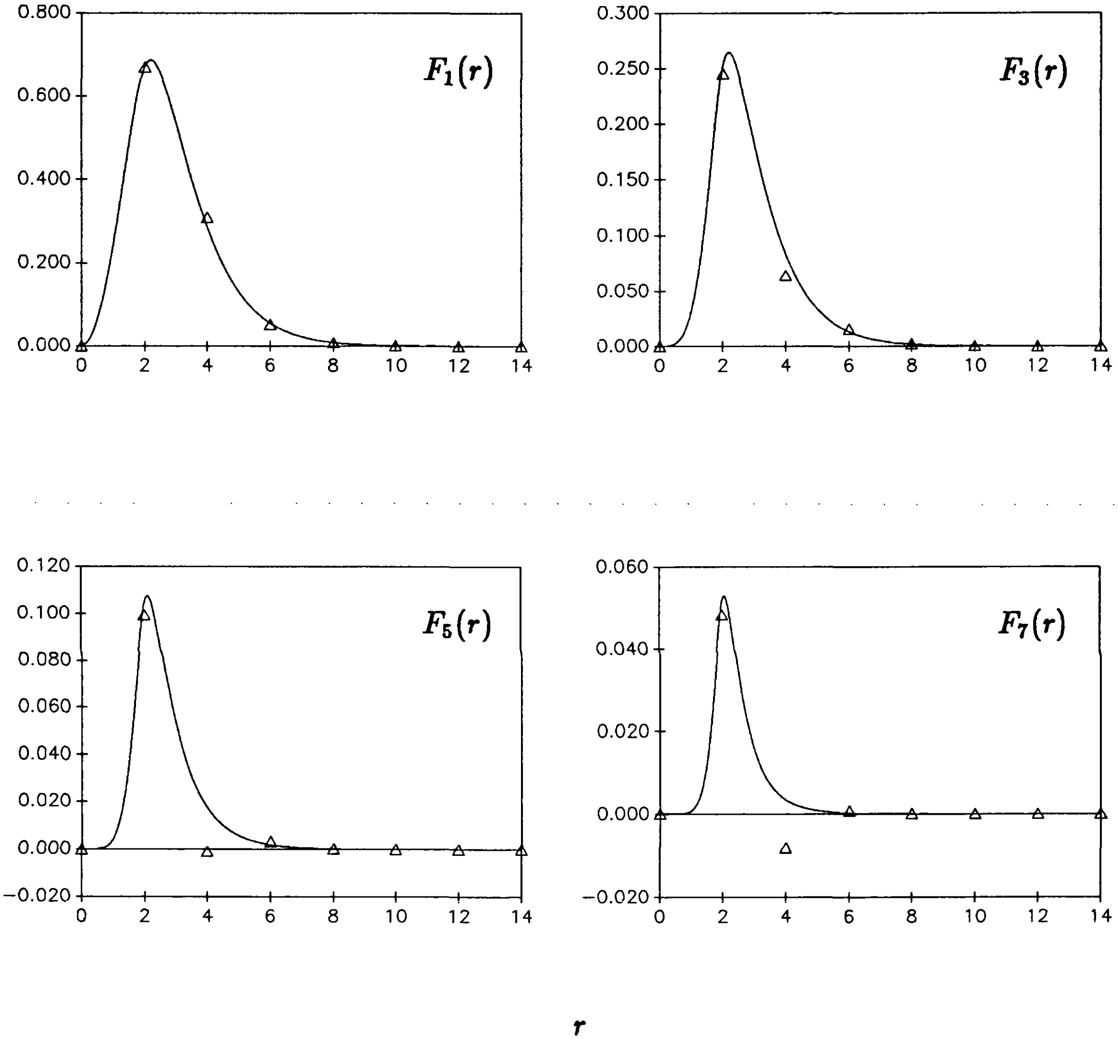
$2s\sigma_g$ $\qquad R = 4$



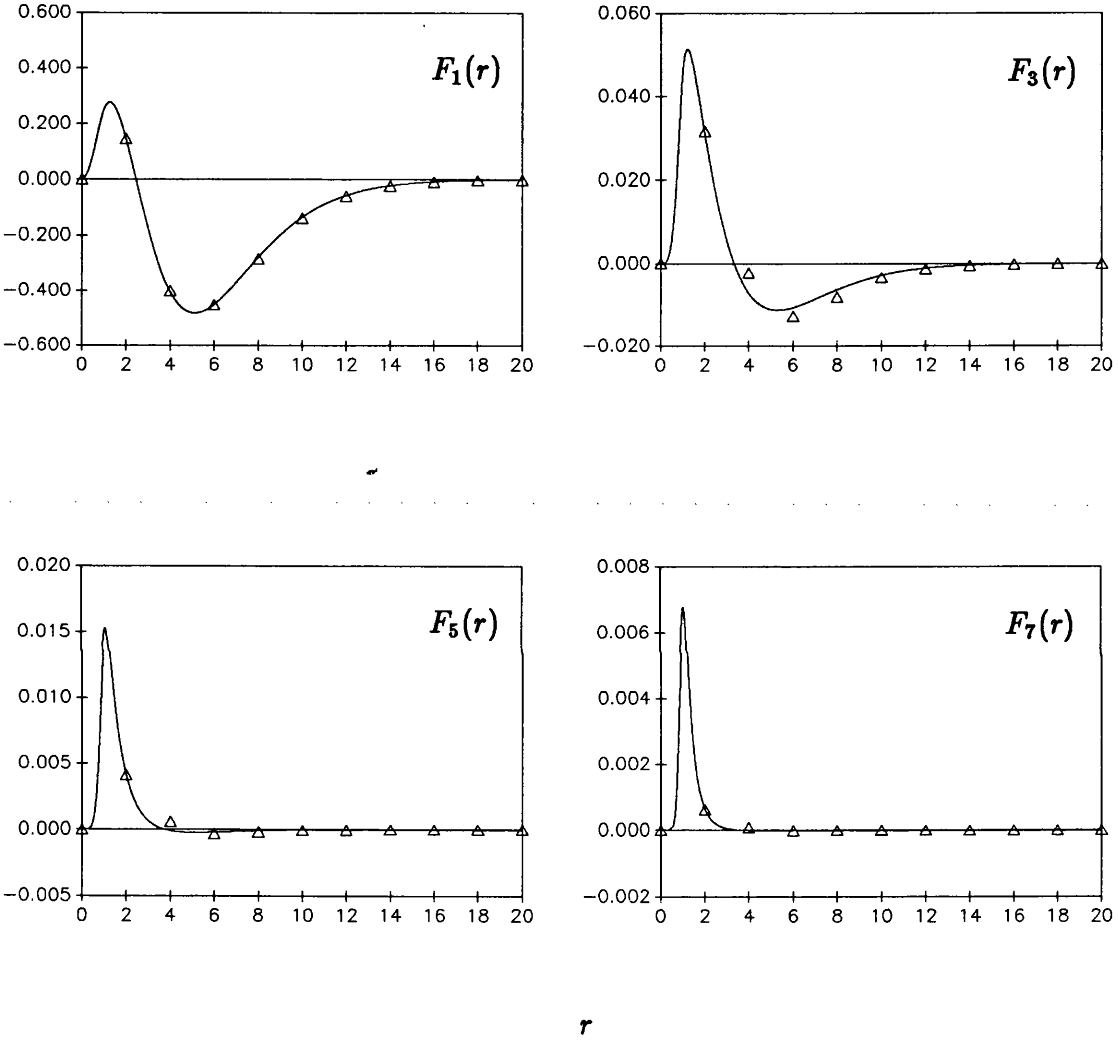
$2p\sigma_u \qquad R = 2$



$2p\sigma_u \qquad R = 4$

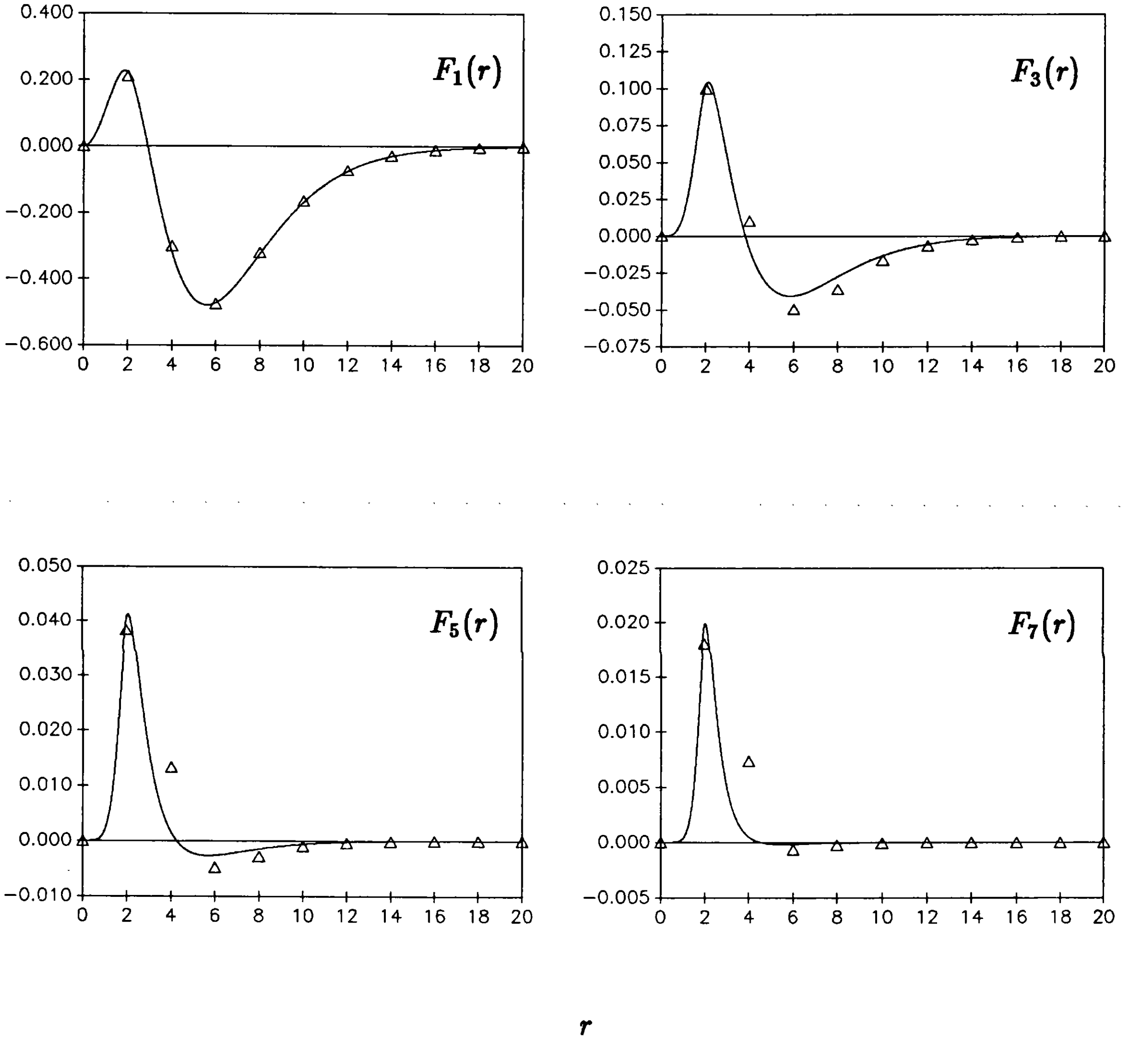


$3p\sigma_u$ $R = 2$

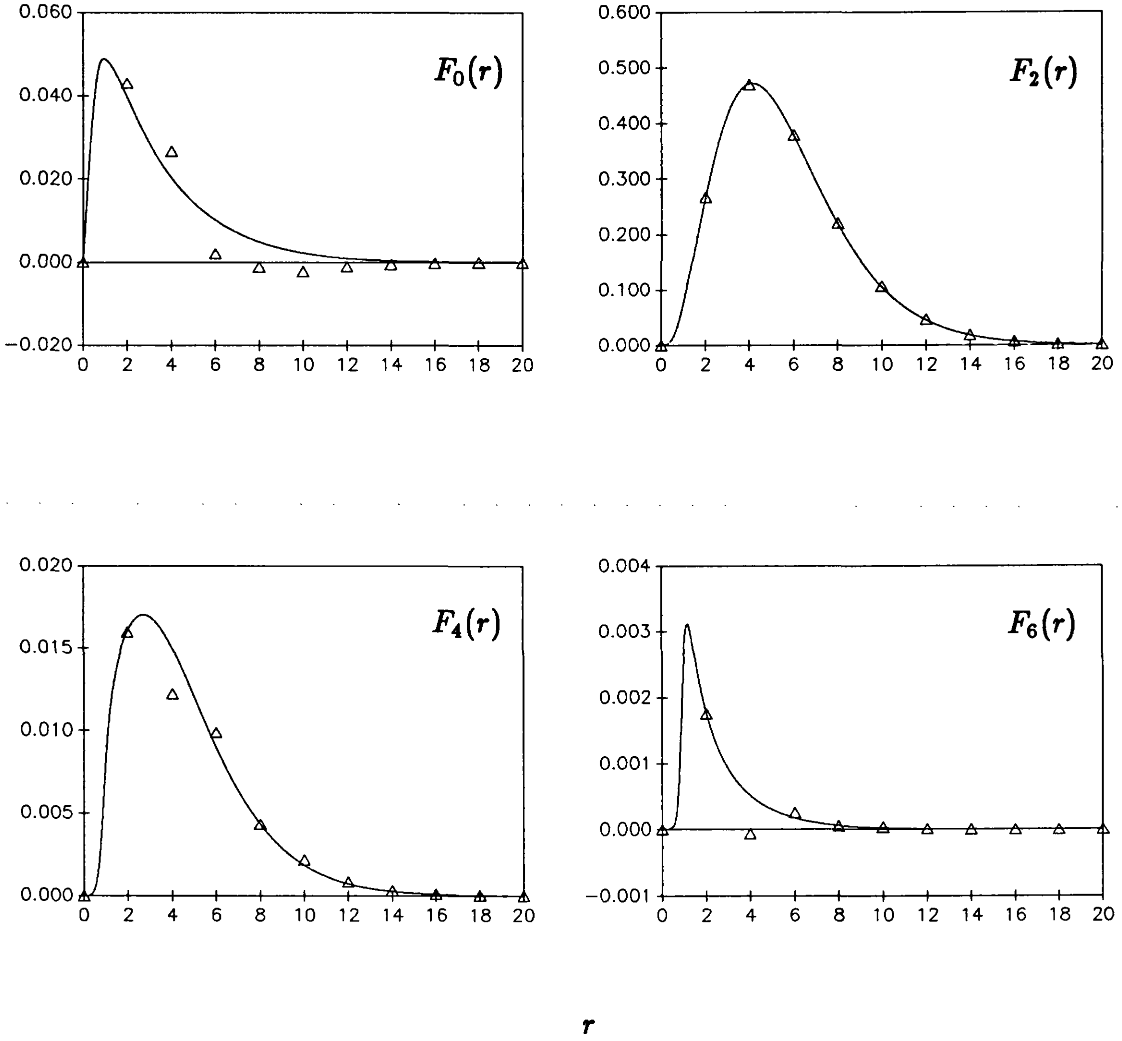


$F_1(r)$
0.600
0.400
0.200
0.000
−0.200
−0.400
−0.600
$F_3(r)$
0.060
0.040
0.020
0.000
−0.020
$F_5(r)$
0.020
0.015
0.010
0.005
0.000
−0.005
$F_7(r)$
0.008
0.006
0.004
0.002
0.000
−0.002
0 2 4 6 8 10 12 14 16 18 20
r

$3p\sigma_u$ $\qquad R = 4$

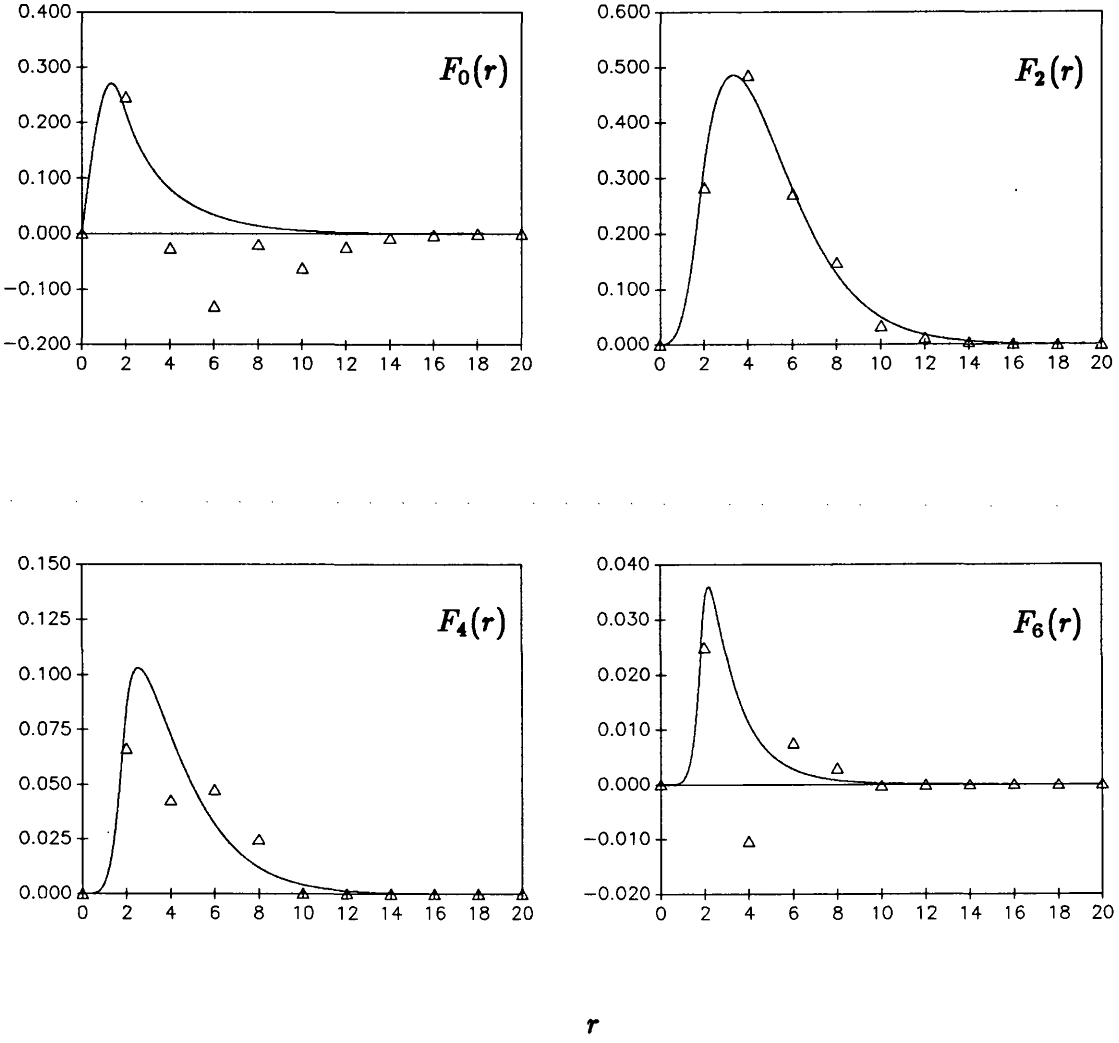


$3d\sigma_g$ $R = 2$



$F_0(r)$
0.060
0.040
0.020
0.000
−0.020
$F_2(r)$
0.600
0.500
0.400
0.300
0.200
0.100
0.000
$F_4(r)$
0.020
0.015
0.010
0.005
0.000
$F_6(r)$
0.004
0.003
0.002
0.001
0.000
−0.001
0
2
4
6
8
10
12
14
16
18
20
r

$3d\sigma_g$ $R = 4$


$F_0(r)$
0.400
0.300
0.200
0.100
0.000
−0.100
−0.200
$F_2(r)$
0.600
0.500
0.400
0.300
0.200
0.100
0.000
$F_4(r)$
0.150
0.125
0.100
0.075
0.050
0.025
0.000
$F_6(r)$
0.040
0.030
0.020
0.010
0.000
−0.010
−0.020
0 2 4 6 8 10 12 14 16 18 20
r

5.2 Errors in bound-state calculations

For a fixed internuclear separation, the errors in the bound-state energies can be defined as

$$\rho = n_U - n_U^* \qquad (5.14)$$

where n_U and n_U^* are the exact and calculated quantum defects given by

$$\left(\frac{Z}{n_U}\right)^2 = -E_U \qquad ; \qquad \left(\frac{Z}{n_U^*}\right)^2 = -E_U^* \qquad (5.15)$$

and $Z = z_A + z_B$. E_U is the exact energy and E_U^* is the calculated energy. The exact bound-state energies for one-electron diatomic systems are obtained from the program of Power (1973).

Figure 5.2 shows the variation of ρ with increasing L and with $K = 6$ for the states $1s\sigma_g$, $2s\sigma_g$, $2p\sigma_u$ and $3p\sigma_u$ of H_2^+. The variation of the errors with increasing K and $L = 10$ is also considered for the above states of H_2^+ and the results are shown in figure 5.3. Similar calculations are made for HeH^{2+} for the states $1s\sigma$, $2p\sigma$, $3d\sigma$ and $2s\sigma$ and the results are shown in figures 5.4 and 5.5.

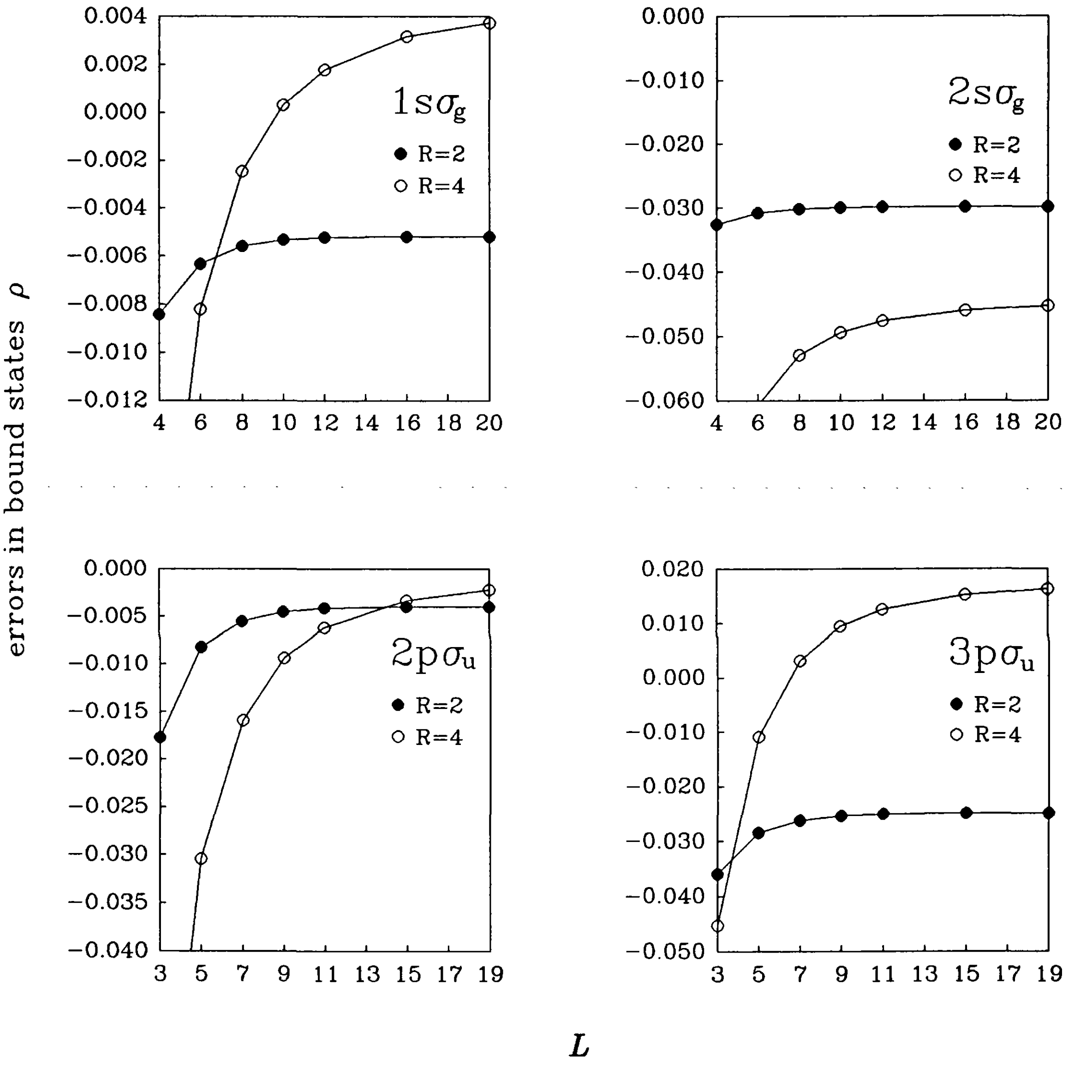


Figure 5.2: Errors, ρ, obtained in the bound states of H_2^+ calculated with $K = 6$ basis functions in the expansion of the functions $F_l(r)$ and L terms in the expansion of ψ.

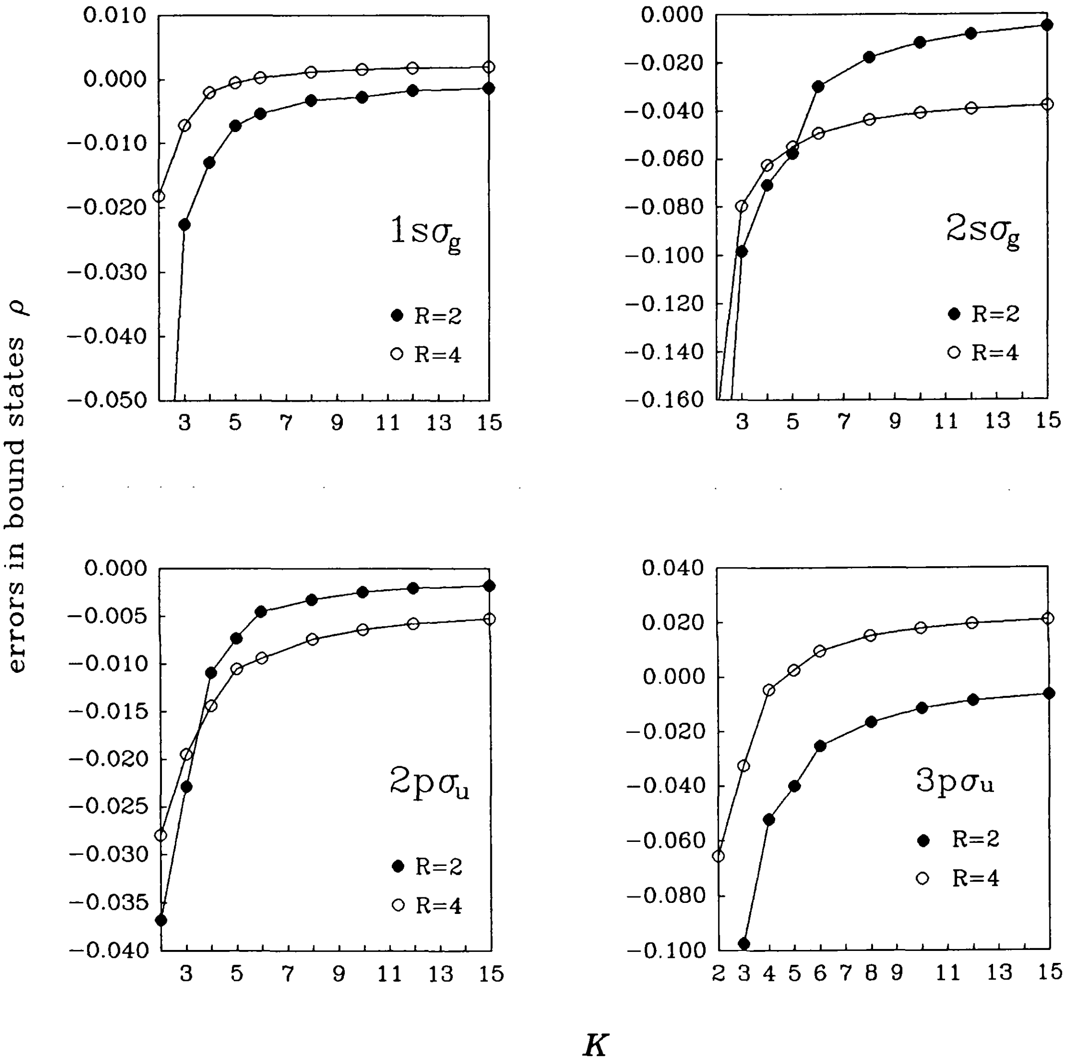


Figure 5.3: Errors, ρ, obtained in the bound states of H_2^+ calculated with K basis functions in the expansion of the functions $F_l(r)$ and $L = 10$ terms in the expansion of ψ.

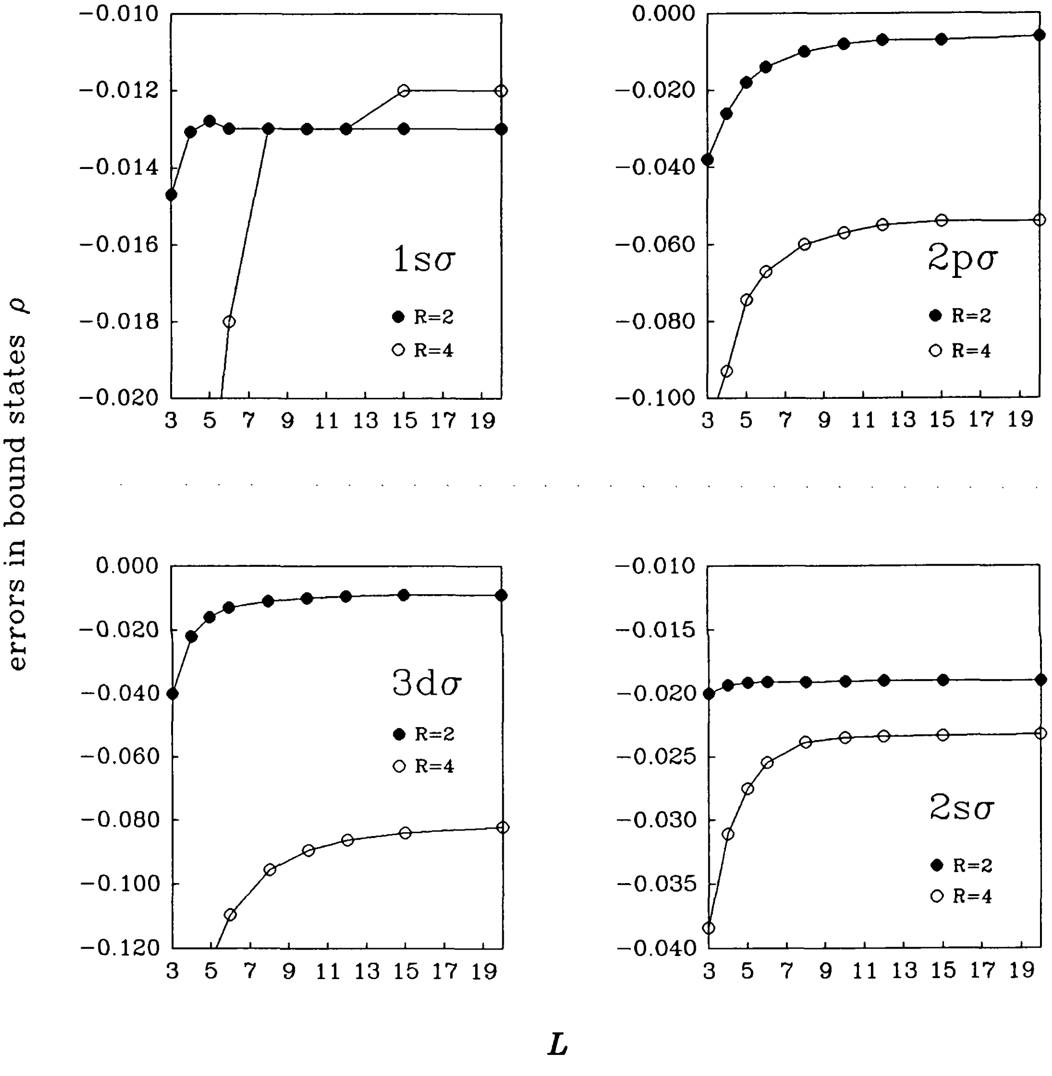


Figure 5.4: Errors, ρ, obtained in the bound states of HeH^{2+} calculated with $K = 6$ basis functions in the expansion of the functions $F_l(r)$ and L terms in the expansion of ψ.

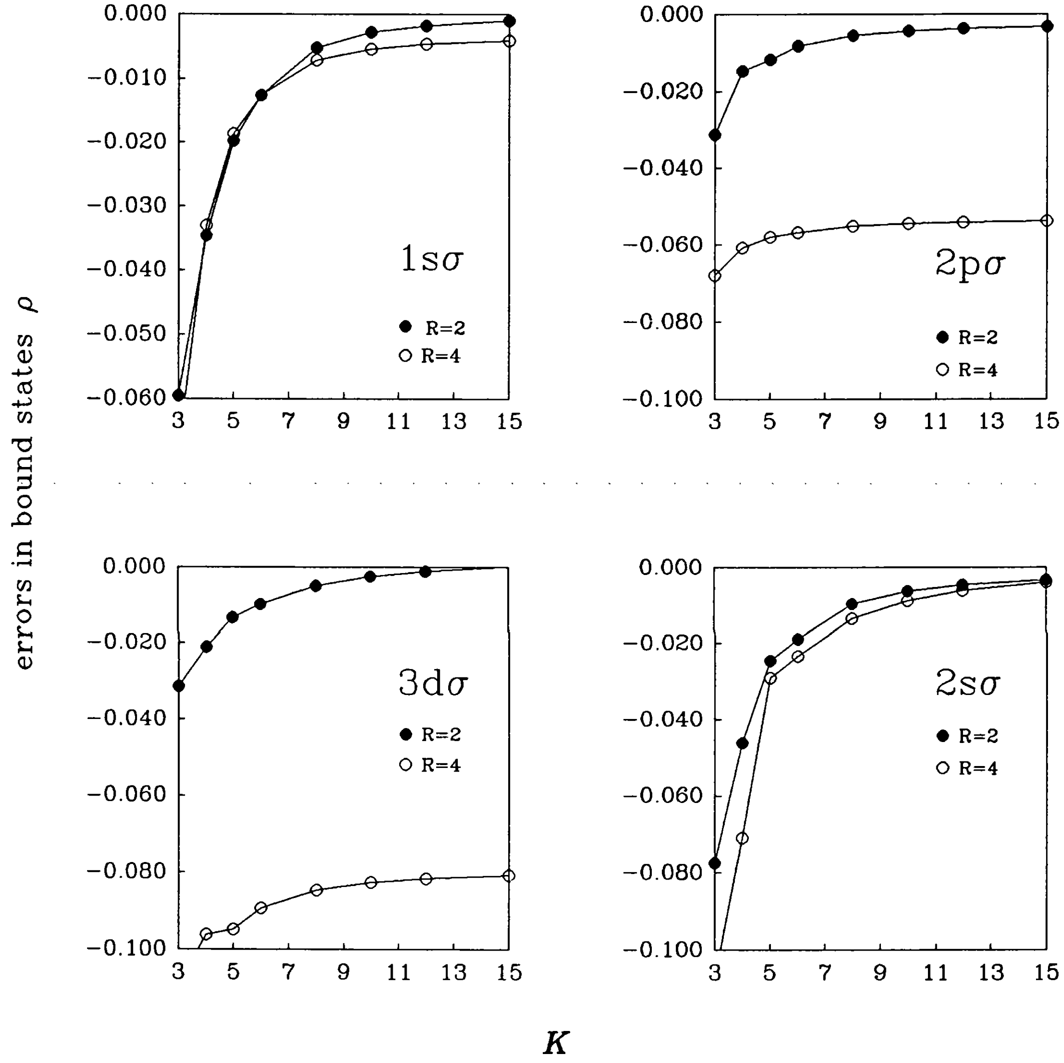


Figure 5.5: Errors, ρ, obtained in the bound states of HeH^{2+} calculated with K basis functions in the expansion of the functions $F_l(r)$ and $L = 10$ terms in the expansion of ψ.

5.3 Oscillator strengths

The oscillator strength f connecting a lower electronic state i to a higher electronic state j for R fixed is

$$f = \frac{1}{3} \triangle E_{ij}\ G_{ij}\ |M_{ij}|^2 \tag{5.16}$$

where

$$M_{ij} = \int_\tau \Psi^*_{E_j}(\mathbf{r})\mathbf{r}\Psi_{E_i}(\mathbf{r})d\tau \tag{5.17}$$

and $\triangle E_{ij}$ is the energy difference of the two states involved. G_{ij} is the orbital degeneracy factor.

Using the expansion in (3.74), the transition between states i and j has the associated matrix element

$$M_{ij} = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \int \Psi^*_{E_j}(\mathbf{r})rY_{1\nu}(\hat{\mathbf{r}})\Psi_{E_i}(\mathbf{r})d\mathbf{r} \tag{5.18}$$

which can be written in spherical polar coordinates as

$$M_{ij} = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \sum_{l_i l_j} \int F_{l_j}(r)rF_{l_i}(r)drY^*_{l_j m_j}(\theta,\phi)Y_{1\nu}(\theta,\phi)Y_{l_i m_i}(\theta,\phi)\sin\theta d\theta d\phi \tag{5.19}$$

where $\nu = m_j - m_i$. Using standard results for the angular integrals in (5.19) one obtains the expression

$$M_{ij} = \sum_{l_i l_j} \int_0^\infty F_{l_j}(r)rF_{l_i}(r)dr(-1)^{m_j}[(2l_j+1)(2l_i+1)]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} l_j & 1 & l_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & 1 & l_i \\ -m_j & \nu & m_i \end{pmatrix} \tag{5.20}$$

with $\nu = -1, 0, 1$. The radial integrals in (5.20) are evaluated in the same way as the σ_{ij} in §4.4.

The results are compared with exact calculations made by Bates (1951) and Bates *et al* (1954) for the transitions of H_2^+ and Arthurs *et al* (1957) for the transitions of HeH^{2+}. Tables 5.1 and 5.2 show the variation of the fractional errors obtained in the oscillator strengths for transitions between the lower σ states of the H_2^+ ion and tables 5.3 and 5.4 show the fractional errors obtained for transitions between the lower σ states of the HeH^{2+} ion.

	$1s\sigma_g \to 2p\sigma_u$		$1s\sigma_g \to 3p\sigma_u$	
L	$R=2$	$R=4$	$R=2$	$R=4$
4	0.026	0.251	0.158	-0.511
5	0.010	-0.020	-0.247	-0.094
6	0.017	0.122	-0.144	-0.336
8	0.015	0.072	-0.219	-0.268
10	0.014	0.050	-0.246	-0.242
12	0.014	0.040	-0.257	-0.227
16	0.014	0.032	-0.261	-0.216
20	0.014	0.028	-0.261	-0.212

	$2p\sigma_u \to 2s\sigma_g$			$2p\sigma_u \to 3d\sigma_g$	
L	$R=0.4$	$R=2$	$R=4$	$R=2$	$R=4$
4	-0.173	-0.437	-0.404	0.041	-0.030
5	-0.173	-0.462	-0.214	0.025	-0.085
6	-0.173	-0.429	-0.723	0.027	-0.001
8	-0.173	-0.425	-0.851	0.022	-0.009
10	-0.173	-0.423	-0.906	0.020	0.014
12	-0.173	-0.423	-0.928	0.019	0.018
16	-0.173	-0.423	-0.941	0.019	0.022
20	-0.173	-0.423	-0.956	0.019	0.023

Table 5.1: Fractional errors obtained in the calculation of oscillator strengths for H_2^+ with $K=6$ terms in the expansion of $F_l(r)$ and L terms in the expansion of ψ.

	$1s\sigma_g \rightarrow 2p\sigma_u$		$1s\sigma_g \rightarrow 3p\sigma_u$	
K	$R = 2$	$R = 4$	$R = 2$	$R = 4$
3	0.040	0.055	-0.707	-0.180
4	0.032	0.061	-0.432	0.037
5	0.018	0.050	-0.346	-0.205
6	0.014	0.050	-0.246	-0.242
8	0.010	0.044	-0.127	-0.261
10	0.007	0.043	-0.081	-0.267
15	0.005	0.040	-0.025	-0.273

	$2p\sigma_u \rightarrow 2s\sigma_g$			$2p\sigma_u \rightarrow 3d\sigma_g$	
K	$R = 0.4$	$R = 2$	$R = 4$	$R = 2$	$R = 4$
3	0.164	0.099	> 1	0.129	-0.182
4	0.293	0.105	-1.000	0.055	-0.124
5	0.200	-0.101	-0.988	0.042	-0.008
6	0.173	-0.423	-0.904	0.019	0.015
8	0.102	-0.268	-0.853	0.012	0.149
10	0.061	-0.222	-0.828	0.007	0.179
15	0.025	-0.186	-0.807	0.002	0.138

Table 5.2: Fractional errors obtained in the calculation of oscillator strengths of H_2^+ with K terms in the expansion of $F_l(r)$ and $L = 10$ terms in the expansion of ψ.

	$1s\sigma \rightarrow 2p\sigma$		$2p\sigma \rightarrow 2s\sigma$		$2p\sigma \rightarrow 3d\sigma$	
L	$R=2$	$R=4$	$R=2$	$R=4$	$R=2$	$R=4$
2	0.102	>1	0.221	>3	-0.235	-0.981
3	0.062	>1	0.138	>3	0.033	0.132
4	0.053	0.649	0.065	>3	0.015	0.177
5	0.048	0.368	0.043	>3	0.003	0.274
6	0.046	0.188	0.033	>3	-0.009	0.314
8	0.045	0.008	0.025	>3	-0.022	0.332
10	0.044	-0.067	0.022	>3	-0.029	0.306
12	0.044	-0.104	0.020	>3	-0.032	0.271
15	0.044	-0.132	0.019	>3	-0.034	0.226
20	0.044	-0.150	0.019	>3	-0.036	0.183

Table 5.3: Fractional errors obtained in the calculation of oscillator strengths for HeH^{2+} with $K = 6$ terms in the expansion of $F_l(r)$ and L terms in the expansion of ψ.

	$1s\sigma \to 2p\sigma$		$2p\sigma \to 2s\sigma$		$2p\sigma \to 3d\sigma$	
K	$R=2$	$R=4$	$R=2$	$R=4$	$R=2$	$R=4$
3	0.273	0.390	0.569	>1	-0.032	0.481
4	0.125	0.187	0.174	>1	-0.050	0.277
5	0.078	0.005	0.114	>1	-0.028	0.163
6	0.044	-0.067	0.022	>1	-0.029	0.306
8	0.017	-0.117	-0.039	0.305	-0.017	0.383
10	0.008	-0.139	-0.063	-0.209	0.010	0.389
12	0.004	-0.149	-0.073	-0.414	0.007	0.391
15	0.002	-0.156	-0.078	-0.526	0.004	0.390

Table 5.4: Fractional errors obtained in the calculation of oscillator strengths for HeH^{2+} with K terms in the expansion of $F_l(r)$ and $L = 10$ terms in the expansion of ψ.

5.4 Conclusions

For the H_2^+ ion the bound states for $R = 2$ converge towards their exact value but for $R = 4$, ρ tends to a finite value other than zero. The oscillator strengths for $R = 2$ converge towards exact values but the $2p\sigma_u \rightarrow 2s\sigma_g$ transition converges much more slowly than the other transitions. On further investigation of this transition it is found that the radial wave functions for the $2s\sigma_g$ state are quite sensitive to an increase in K in a region that contributes most to the radial integrals in (5.20). As the internuclear separation is increased to $R = 4$ the convergence deteriorates considerably.

The bound states of HeH^{2+} display similar behaviour to those of H_2^+. However, the oscillator strengths for $R = 4$ are not seen to converge. This may be because the centre of mass coordinate frame adopted in the calculations is no longer appropriate and it may be necessary to use the coordinates centred on one nucleus.

In the calculations for the oscillator strengths either K is set to 6 and L is varied or L is set to 10 and K is varied. It is clear that some of the oscillator strengths are not converged by $L = 10$. Choosing a higher number leads to numerical difficulties when imposing the constraints on the basis functions. If a large value of L is chosen it is found that only a small number of basis functions can be taken in the expansion of $F_l(r)$. Similarly, taking a large number of basis functions tends to restrict the value of L that can be taken. The calculations are performed in single precision on a Cray XMP28. Using double precision may overcome these numerical restrictions but it is not convenient to do so as the NAG routines that are employed in many stages of the calculations are designed to work only in single precision. Hence, for some transitions, it is not possible to tell whether the oscillator strengths converge or not. Clearly the method has to be improved to give accelerated convergence of the expansions used or to be able to cope with large values of L without restricting the number of basis functions, K, taken in the expansions.

The calculations are made using a single-centre expansion and a relevant question to ask is how appropriate this expansion is. The potential associated with a one-electron diatomic system has a singularity at the positions of the nuclei A and B. With the single-centre expansion it is difficult to obtain an appropriate wave function that will represent this irregular behaviour of the potential completely. Therefore, the lack of convergence of some of the oscillator strengths may be due to the inadequacy of the single-centre expansion of the wave function ψ in (3.74). As R is increased, the potential in the vicinity of the singularities becomes much sharper and for $R \rightarrow \infty$ one effectively has δ-functions at the positions of the nuclei. Clearly then, the single-centre expansion becomes much worse as R is increased and this deterioration is displayed by the results obtained. An alternative method is to use a multi-centre expansion where the wave functions are centred on each nuclei but with this method calculations become much more complex and cannot be extended asymptotically which prevents any application to scattering problems.

The results obtained are quite encouraging but much more work is required in order to overcome the restrictions of the method outlined above. In the calculations no corrections of the Buttle type have been invoked.

Chapter 6

Comparison with earlier work

The method presented in this thesis is a propagator method and is similar to that introduced by Baluja *et al* (1982) (referred to as BBM hereafter) in that it also uses expansions in terms of normalised Legendre polynomials. The present method propagates the wave function across a finite range *including* the inner region and ensures that the conditions at the origin are obeyed exactly. At any point in space the wave function can be used to give the R-matrix at that particular point. The method of BBM, however, has only been used to propagate the R-matrix across some finite region *outside* the inner region where, in a typical collision problem, exchange terms are not important. If the method of BBM is used, it is not clear how easily the wave function can be obtained or, indeed, how the conditions at $r = 0$ are imposed, particularly if the cusp condition is to be imposed rigorously.

In R-matrix calculations it is desired that the Hamiltonian matrix be hermitian. This can be attained by using fixed boundary conditions, as used by the present method, or by the use of a Bloch operator together with arbitrary boundary conditions, as used by BBM. Although both methods give the required results, the Bloch operator does have some small energy dependence which restricts the width of the energy range that can be considered.

The present method does not employ a quadrature approximation to evaluate the matrix elements of the Hamiltonian, as do BBM, but generates the elements directly and exactly using recurrence relations. Although use of these relations can lead to a build up of numerical error such difficulties have been overcome and a *stable* and *accurate* method has been found which is described in §3.1.2 and §3.2.3.

BBM have limited the number of basis functions in each subrange to 10 and this imposes a restriction on the maximum value of the interval length if results of sufficient accuracy are to be obtained. They impose the criterion that the maximum energy to be considered should relate to the interval length through (2.136). If the actual value of E is much less than E_{max} $(= \kappa^2_{max})$, then the method will become less efficient because the interval length is then shorter than it need be for a given number of terms retained in (2.128). Their solution to this problem is to suggest that the range of energies to be considered should be subdivided and a different set of divisions of the range of radial variable r be selected for each range. However, in the present work, such restrictions have been eliminated by fixing the interval length to a suitably small value and using as many basis functions as are necessary to give results of the required accuracy.

The method described in this thesis can be applied to any problem that has a potential that can be expressed as a polynomial e.g. a Lennard-Jones potential

$$ar^{-12} - br^{-6}$$

which is commonly used to represent heavy particle collisions. The matrix elements for such a potential can be obtained quickly and accurately using recurrence relations. If propagation is required from $r = 0$ then using the present method is advantageous as it is suitable for solving the problem in the inner region. If propagation is required outside the inner region then the two methods seem equally applicable. In this case, perhaps only numerical checks can sort out the relative merits of the two methods.

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