EU Socrates Intensive Programme

Introduction to R-matrix theory in atomic physics

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1 An introduction to R-matrix concepts: application to potential scattering

1.1 Potential scattering

Before launching in to tackling complex problems such as scattering electrons from a multi-electron atom or ion, we first consider a simple problem, that of S-wave scattering. Consider a particle scattered by a short-range central potential $V(r)$. The Schrödinger equation satisfied by the radial wavefunction $u(r)$ at energy k^2 is

$$\left(\frac{d^2}{dr^2} + k^2 + V(r)\right) u(r) = 0 \tag{1.1}$$

$$\begin{aligned} V(r) &= 0, \quad r \geq a \text{ for some radius } r = a \\ u(0) &= 0 \\ u(r) &= \sin kr + K \cos kr, \quad r \geq a \end{aligned}$$

The K-matrix is related to the phase shift δ by $K = \tan \delta$.
We can think of the problem in two parts:– $r \leq a$ and $r \geq a$.

1.1.1 The internal region, $r \leq a$

The R-matrix method is based upon expanding the solution $u(r)$ at any energy k^2 in the region $0 \leq r \leq a$ in terms of a complete set of eigensolutions defined by the equation

$$\left[\frac{d^2}{dr^2} + V(r) + k_\lambda^2\right] u_\lambda(r) = 0 \tag{1.2}$$

satisfying the R-matrix boundary conditions

$$\begin{aligned} u_\lambda(0) &= 0 \\ \frac{a}{u_\lambda(a)} \frac{du_\lambda}{dr}\bigg|_{r=a} &= b \end{aligned}$$

(where the logarithmic derivative b is an arbitrary constant normally chosen as zero) and the orthonormality condition

$$\int_0^a u_\lambda(r) u_{\lambda'}(r)\, dr = \delta_{\lambda\lambda'} \tag{1.3}$$

We now expand the "real" solution in terms of this basis

$$u(r) = \sum_{\lambda=1}^{\infty} a_\lambda u_\lambda(r) \qquad\qquad 0 \leq r \leq a \tag{1.4}$$

This expansion converges uniformly except on the boundary $r = a$ for all values of b.

How can we find a_λ?

1. premultiply (1.1) by $u_\lambda(r)$
2. premultiply (1.2) by $u(r)$
3. integrate both equations over the range $r = 0$ to $r = a$
4. subtract

This gives

$$\int_0^a \left[u_\lambda \frac{d^2u}{dr^2} - u \frac{d^2u_\lambda}{dr^2} \right] dr = \left(k_\lambda^2 - k^2 \right) \int_0^a u_\lambda u \, dr \tag{1.5}$$

Using Green's theorem and the boundary conditions we find that

$$a_\lambda = \frac{1}{a} \frac{u_\lambda(a)}{k_\lambda^2 - k^2} \left[a \frac{du}{dr} - bu \right]_{r=a} \tag{1.6}$$

Substituting into expression (1.4) for u :

$$u(r) = \sum_{\lambda=1}^{\infty} \frac{1}{a} \frac{u_\lambda(r) \, u_\lambda(a)}{k_\lambda^2 - k^2} \left[a \frac{du}{dr} - bu \right]_{r=a} \tag{1.7}$$

Evaluating this at $r = a$ and letting

$$R = \frac{1}{a} \sum_{\lambda=1}^{\infty} \frac{[u_\lambda(a)]^2}{k_\lambda^2 - k^2} \tag{1.8}$$

we find:

$$u(a) = R \left[a \frac{du}{dr} - bu \right]_{r=a} \tag{1.9}$$

Hence the R-matrix relates the amplitude of u to its derivative on the boundary.

1.1.2 The external region, $r \geq a$

Equations (1.8) and (1.9) define the inner region wavefunction on the boundary $r = a$. This must be related to the outer region wavefunction to solve the complete problem.
Since

$$u(r) = \sin kr + K \cos kr$$

then

$$\frac{du}{dr} = k \cos kr - Kk \sin kr$$

Substituting into (1.9) i.e. matching inner and outer solutions at $r = a$, and solving for K we find that

$$K = \frac{-\sin(ka) + R\left[ka \cos(ka) - b \sin(ka)\right]}{\cos(ka) + R\left[ka \sin(ka) + b \cos(ka)\right]} \tag{1.10}$$

Thus once R has been calculated, K can be easily determined.

The scattering matrix S can be found from K or the phase shift $\delta = \tan^{-1} K$:

$$\begin{aligned} S &= e^{2i\delta} \\ &= \cos 2\delta + i \sin 2\delta \\ &= \frac{1 - \tan^2 \delta}{1 + \tan^2 \delta} + \frac{2 \tan \delta}{1 + \tan^2 \delta} \\ &= \frac{(1 + iK)^2}{1 + K^2} \\ &= \frac{1 + iK}{1 - iK} \end{aligned}$$

We have seen that the R-matrix, and consequently the K-matrix, S-matrix, phase shift and the cross section can be expressed in terms of an expansion of a complete set of amplitudes $u_\lambda(a)$ and eigenvalues k_λ^2 . These quantities were determined by solving the original differential subject to the R-matrix boundary conditions. However, in a realistic problem, the potential may make the original equation very difficult to solve exactly and we approximate the actual potential by a suitable, easily-solvable, potential.
We note that the summation over λ in (1.8) is infinite. In practice this is truncated and a correction, called the Buttle correction, is added to R to account for any error.

2 Electron scattering by one-electron atoms and ions using the R-matrix approach

We move on now to consider the scattering of electrons by one-electron atoms and ions using the R-matrix method. However, the ideas presented are easily extended to multi-electron atoms and ions (see e.g. Berrington and Burke, 1993). While we will concentrate on atomic hydrogen, the theory and discussion also applies to hydrogen-like ions.

Consider the process

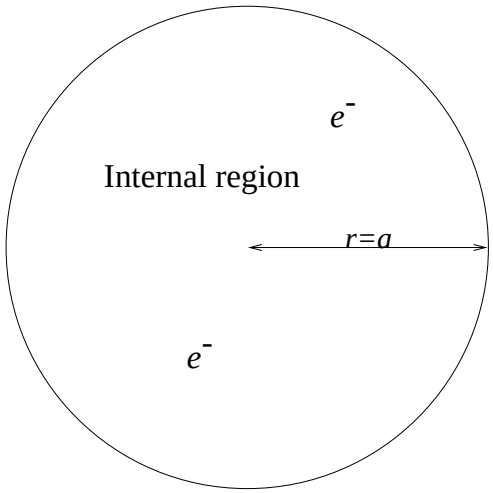
$$\mathrm{e}^- + \mathrm{H}_i \rightarrow \mathrm{e}^- + \mathrm{H}_j \tag{2.1}$$

where i represents the initial state of the H atom and j its state after the collision. This problem is more complicated than potential scattering from a static spherically symmetric potential which we discussed earlier because when the free electron comes close to the atom

1. the wavefunction of the atomic electron is distorted and modification to the interaction potential must be made to take this into account ;

2. electron exchange is possible since the two electrons are indistinguishable.

In the R-matrix method we partition the configuration space of the free or scattered electron into two regions using a sphere of radius $r = a$. r is the relative radial coordinate of the free electron.



External region

In the internal region the interaction between the scattered electron and the atomic electron is strong and the electron-atom complex behaves very much as a bound state. Consequently in this region a CI expansion of the total wavefunction similar to that used in atomic structure calculations is appropriate. The radius a is chosen so that the wavefunction of the atomic electron vanishes for $r \geq a$. Hence in the external region we can ignore exchange effects between the two electrons and the problem simplifies considerably.

We proceed by calculating the R-matrix at the boundary of the internal region at energy E for the internal region problem. By continuity this must

equal the R-matrix for the external region calculation. By 'matching' the R-matrices on the boundary it is possible to obtain the K-matrix and hence the S-matrix etc.

2.1 The internal region, $r \leq a$

In the internal region we expand the two-electron wavefunction at energy E , $\Psi_E(\mathbf{r}_1, \mathbf{r}_2)$ in terms of an energy independent basis set $\psi_k(\mathbf{r}_1, \mathbf{r}_2)$,

$$\Psi_E(\mathbf{r}_1, \mathbf{r}_2) = \sum_k A_{Ek} \psi_k(\mathbf{r}_1, \mathbf{r}_2) \tag{2.2}$$

The set $\psi_k(\mathbf{r}_1, \mathbf{r}_2)$ are constructed so that they diagonalize the two electron Hamiltonian matrix

$$< \psi_k | H | \psi_{k'} >= \delta_{kk'} E_k \tag{2.3}$$

where

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{2.4}$$

The basis set ψ_k is known as the R-matrix basis. In this case the ψ_k are expanded in terms of two electron functions $\chi_{n_1 l_1 n_2 l_2}(\mathbf{r}_1, \mathbf{r}_2)$,

$$\psi_k = \sum_{n_1 l_1} \sum_{n_2 l_2} \chi_{n_1 l_1 n_2 l_2}(\mathbf{r}_1, \mathbf{r}_2) \beta_{n_1 l_1 n_2 l_2 k} \tag{2.5}$$

The coefficients $\beta_{n_1 l_1 n_2 l_2 k}$ are obtained by diagonalizing the matrix $< \psi_k | H | \psi_{k'} >$.

The two-electron functions $\chi^{LS\pi}_{n_1 l_1 n_2 l_2}(\mathbf{r}_1, \mathbf{r}_2)$ we use are defined by

$$\begin{aligned} \chi^{LS\pi}_{n_1 l_1 n_2 l_2}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{2}} \Big[r_1^{-1} u_{n_1 l_1}(r_1) r_2^{-1} u_{n_2 l_2}(r_2) \mathcal{Y}_{l_1 l_2 L M_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\ &\quad + (-)^{L+S+l_1+l_2} r_1^{-1} u_{n_2 l_2}(r_1) r_2^{-1} u_{n_1 l_1}(r_2) \\ &\quad \times \mathcal{Y}_{l_2 l_1 L M_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \Big] \end{aligned} \tag{2.6}$$

for $n_1 l_1 \neq n_2 l_2$, and

$$\chi^{LS\pi}_{n_1 l_1 n_2 l_2}(\mathbf{r}_1, \mathbf{r}_2) = r_1^{-1} u_{n_1 l_1}(r_1) r_2^{-1} u_{n_2 l_2}(r_2) \mathcal{Y}_{l_1 l_2 L M_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$$

for $n_1 l_1 = n_2 l_2$

Here we have only considered the space part of the wavefunction which is symmetric when $S = 0$ and antisymmetric when $S = 1$ (where S is the total spin of the two electrons) in accordance with the Pauli exclusion principle. The angular functions

$$\mathcal{Y}_{l_1 l_2 L M_L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{m_1 m_2} (l_1 m_1 l_2 m_2 | L M_L)\, Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2) \tag{2.7}$$

where L is the total angular momentum amd M_L is its z component, $(l_1 m_1 l_2 m_2 | L M_L)$ are Clebsch-Gordan coefficients, $Y_{lm}\,(\hat{\mathbf{r}})$ are spherical harmonics and π is the parity defined by $(-)^{l_1+l_2}$. We note that L, S and Π are conserved in the collision.

We now consider the radial orbital basis functions $u_{nl}(r)$. The range of energies over which the method is accurate and the convergence properties of the method depend critically on the basis functions used. We divide the radial basis functions into two classes which we shall call bound and continuum. The bound orbitals denoted by $u^b_{nl}(r)$ correspond to 1s,2s,2p... states of atomic H. These orbitals are orthogonal over the internal region and the choice of boundary radius a ensures that they have decayed to be essentially zero by the boundary. The continuum orbitals denoted by $u^c_{nl}(r)$ are used to describe the radial motion of the scattered electron. They are chosen to satisfy the differential equation

$$\left(\frac{d^2}{dr^2} - \frac{l\,(l+1)}{r^2} + V\,(r) + k^2_{nl}\right) u^c_{nl}(r) = \sum_{n'} \lambda_{nn'} u^b_{n'l}(r) \tag{2.8}$$

subject to the boundary conditions

$$\begin{aligned} u^c_{nl}(0) &= 0 \\ \frac{a}{u^c_{nl}} \frac{du^c_{nl}}{dr}\bigg|_{r=a} &= b \end{aligned}$$

where the Lagrange multipliers $\lambda_{nn'}$ are chosen so that

$$\int_0^a u^c_{nl}\,(r)\, u^b_{n'l}\,(r) = 0 \qquad\qquad \forall\ \ n, n'$$

For any choice of potential $V(r)$, equation (2.8) defines a set of continuum orbitals which, when taken together with the bound orbitals, is complete over the internal region. However the choice of $V(r)$ is important for good convergence. It is essential that the continuum orbitals have the correct behaviour near the nucleus. This means that $V(r)$ must behave as $2Z/r$ near the origin (Z is the nuclear charge, which is one for atomic hydrogen). Normally we chose $V(r)$ to be the static potential of the H-atom. b is an arbitary constant which is usually chosen as zero for simplicity. We can now write equation (2.5) in more detail

$$\psi^{LS\pi}_k = \sum_{\substack{n_1 l_1 \\ [b,c]}} \sum_{\substack{n_2 l_2 \\ [b]}} \chi^{LS\pi}_{n_1 l_1 n_2 l_2}(\mathbf{r}_1, \mathbf{r}_2) \beta_{n_1 l_1 n_2 l_2 k} \tag{2.9}$$

Let us now return to consider the total wavefunction $\Psi_E(\mathbf{r}_1, \mathbf{r}_2)$ and we will omit the subscripts $L\ S$ and π. At this point we introduce the channel functions $\bar{\phi}_{n_2 l_1 l_2}$ which are obtained by coupling the wavefunction for the atomic electron with the angular functions of the free electron. We can expand Ψ_E in terms of these functions

$$\Psi_E\,(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{A} \sum_i \bar{\phi}_i r_1^{-1} F_i(r) \tag{2.10}$$

where F_i is known as the reduced radial function of the scattered electron, i is the channel index representing the channel labels $n_2 l_1 l_2$ and $\mathcal{A}$ is the operator which antisymmetrizes the expansion with respect to the exchange of all pairs of electrons in accordance with the Pauli exclusion principle. Projecting onto the channel functions ϕ_i we see that

$$F_i(r) = r < \bar{\phi}_i | \Psi_E > \tag{2.11}$$

where the integration is over all coordinates except the radial coordinate of the scattered electron. We now introduce the multichannel R-matrix R_{ij} defined by

$$R_{ij} = \frac{1}{2a} \sum_k \frac{\omega_{ik}(a)\,\omega_{jk}(a)}{E_k - E} \tag{2.12}$$

and the reduced width amplitudes $\omega_{ik}(a)$ given by

$$\omega_{ik}(a) = r < \bar{\phi}_i | \psi_k >|_{r=a} \tag{2.13}$$

It can be shown that $F_i(a)$ can be expressed in terms of the R-matrix as

$$F_i(a) = \sum_j R_{ij}(E) \left[a \frac{dF_j}{dr} - bF_j \right] \tag{2.14}$$

Substituting for $\bar{\phi}_{n_2 l_1 l_2}$ and ψ_k in (2.13) gives

$$\omega_{n_2 l_1 l_2 k}(a) = \sum_{n_1} \beta_{n_1 l_1 n_2 l_2 k} u_{n_1 l_1}(a) \tag{2.15}$$

Knowing the expansion coefficients $\beta_{n_1 l_1 n_2 l_2 k}$ and the value of the $u_{nl}(r)$ functions on the boundary, we are now in a position to calculate the R-matrix in the internal region.

2.2 The external region $r \geq a$

Our choice of boundary radius, $r = a$, is such that the bound orbitals describing the motion of the atomic electron have decayed to zero. This means that exchange effects between the atomic electron and the free electron vanish and the problem simplifies considerably. The set of differential equations describing the motion of the free electron become

$$\left[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r} + k_i^2 \right] F_i(r) = 2 \sum_{j=1}^{nchan} V_{ij} F_j(r) \quad i = 1, nchan \tag{2.16}$$

$nchan$ — the number of channels
i — the channel index $n_2 l_2 l_1$
k_i^2 — the energy of the scattered electron in channel i
Z — the nuclear charge which for H is 1
V_{ij} — a potential matrix coupling channel i and j

The potential matrix V_{ij} can be written as

$$V_{ij} = \sum_{\lambda=0}^{M} a_{ij}^{\lambda} r^{-\lambda-1} \tag{2.17}$$

where the coefficients a_{ij}^{λ} and the value M depend on the problem under consideration.

We now consider two simple cases as illustrations :

I. Consider the problem where the atomic electron is restricted to the 1s orbital and the total angular momentum of the two-electron system, L, is zero. In this case the angular momentum of the free electron must also be zero. Hence there is only one possible channel — $n_2 l_1 l_2 = 1\ 0\ 0$ where $n_2 l_2$ describes the state of the hydrogen atom and l_1 is the orbital angular momentum of the free electron. In this situation M has the value 0. We note that the $\lambda = 0$ contribution to (2.17) gives $a_{ii}^{\lambda} = N$, where N is the number of atomic electrons which for H is 1. Therefore (2.16) simplifies to

$$\left[\frac{d^2}{dr^2} + k^2\right] F(r) = 0 \tag{2.18}$$

This has two linearly independent normalised solutions —

$$k^{-\frac{1}{2}} \sin(kr) \text{ and } \quad k^{-\frac{1}{2}} \cos(kr) \tag{2.19}$$

The solution we require is of the form

$$F(r) \underset{r \to \infty}{\sim} k^{-\frac{1}{2}} \left(\sin(kr) + K \cos(kr)\right) \tag{2.20}$$

We can now express the R-matrix on the boundary in terms of the function $F(r)$ and its derivative. We now match this to the R-matrix obtained on the boundary from the internal region calculation and extract the value of K as in §1.

II. Now let us consider the case where the $2s$ and $2p$ orbitals of H for the atomic electron are included in the expansion of the two-electron wavefunction, but where the energy of the incoming free electron is not sufficient to excite the atomic electron into one of these orbitals. The set of differential equations (2.16) then becomes

$$\left[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + k_i^2\right] F_i(r) = 2 \sum_{j}^{nchan} \sum_{\lambda=1}^{M} a_{ij}^{\lambda} r^{-\lambda-1} F_j(r) \tag{2.21}$$

Let's consider the possible channels remembering that $L = 0$, $S = 0$, $\pi = 0$.

1. $n_2 l_2 = 1\ 0\ (1s)\ l_1 = 0$
2. $n_2 l_2 = 2\ 0\ (2s)\ l_1 = 0$
3. $n_2 l_2 = 2\ 1\ (2p)\ l_2 = 1$

At large r, (2.21) $\rightarrow$ (2.17) and we have

$$\left[\frac{d^2}{dr^2} + k_i^2\right] F_i(r) = 0$$

So far we have only considered $k_i^2 > 0$ where the solutions are of the form $k_i^{-\frac{1}{2}} \sin(kr)$ and $k_i^{-\frac{1}{2}} \cos(kr)$. When $k_i^2 < 0$ two linearly independent solutions

are $\exp(-|k_i|r)$ and $\exp(|k|r)$. However the second of these is not allowed since the physics tells us that $F_i(r)$ must be bound. Hence asymptotically we have 4 acceptable linearly independent solutions of (2.21) which can be written in vector form as

$$v_1 = \begin{bmatrix} k_1^{-\frac{1}{2}} \sin k_1 r \\ 0 \\ 0 \end{bmatrix} \qquad v_2 = \begin{bmatrix} k_1^{-\frac{1}{2}} \cos k_1 r \\ 0 \\ 0 \end{bmatrix}$$
$$v_3 = \begin{bmatrix} 0 \\ \exp -|k_2|r \\ 0 \end{bmatrix} \qquad v_4 = \begin{bmatrix} 0 \\ 0 \\ \exp -|k_3|r \end{bmatrix} \tag{2.22}$$

Equation (2.21) can then be integrated inwards from some large r, where solutions (2.22) are valid to the R-matrix boundary $r = a$. We can then expand the function $F_i(r)$ in each channel in terms of the solution vectors v_l as follows

$$F_i(r) = \sum_{l=1}^{4} v_{il}\alpha_l \qquad\qquad i = 1, 3 \tag{2.23}$$

If we consider the asymptotic form of the open channel solution we see that $\alpha_1 = 1$ and $\alpha_2 = K$ (which is what we are trying to find!). We can relate each function $F_i(r)$ and its derivative through the R-matrix on the boundary, remembering that the R-matrix will now be a 3x3 matrix relating the 3 channels rather than a single element as before. This gives the following equations in terms of the 4 coefficients α_l

$$\sum_{l=1}^{4} \left\{ v_{il}(a) - \sum_{m=1}^{3} R_{im} \left(a \frac{dv_{ml}}{dr} - b v_{ml} \right)_{r=a} \right\} \alpha_l = 0 \tag{2.24}$$

Remembering that $\alpha_1 = 1$, (2.24) can be solved using standard methods for the solution of simultaneous equations for the coefficients α_2, α_3 and α_4.

3 Computational solution of the electron hydrogen ion collision problem

3.1 The internal region

Remembering that

$$R_{ij} = \frac{1}{2a} \sum_k \frac{\omega_{ik}\omega_{jk}}{E_k - E} \tag{3.1}$$

and that

$$\omega_{ik} = \omega_{n_2 l_1 l_2 k} = \sum_{n_1} \beta_{n_1 l_1 n_2 l_2 k} u_{n_1 l_1}(a) \tag{3.2}$$

we need to set up and diagonalize the two-electron Hamiltonian matrix $\langle \chi_{n_1 l_1 n_2 l_2} | H \left| \chi_{n_1' l_1' n_2' l_2'} \right\rangle$ to obtain the $\beta_{n_1' l_1' n_2' l_2'}$ coefficients. The expression we obtain for $\langle \chi_{n_1 l_1 n_2 l_2} | H \left| \chi_{n_1' l_1' n_2' l_2'} \right\rangle$ is

$$\begin{aligned} &\delta_{l_1 l_1'} \delta_{l_2 l_2'} \left[I^{l_1}_{n_1 n_1'} \delta_{n_2 n_2'} + I^{l_2}_{n_2 n_2'} \delta_{n_1 n_1'} \right] \\ &+(-)^{L+S+l_1+l_2} \delta_{l_1 l_2'} \delta_{l_2 l_1'} \left[I^{l_1}_{n_1 n_2'} \delta_{n_2 n_1'} + I^{l_2}_{n_2 n_1'} \delta_{n_1 n_2'} \right] \\ &+ \textstyle\sum_\lambda f_\lambda \left(l_1 l_2 l_1' l_2'; L \right) R_\lambda \left(n_1 l_i n_2 l_2 n_1' l_1' n_2' l_2' \right) \\ &+ \textstyle\sum_\lambda f_\lambda \left(l_1 l_2 l_2' l_1'; L \right) R_\lambda \left(n_1 l_i n_2 l_2 n_2' l_2' n_1' l_1' \right) \end{aligned} \tag{3.3}$$

where

$$R_\lambda \left(n_1 l_i n_2 l_2 n_1' l_1' n_2' l_2' \right) = \int_0^a \int_0^a u_{n_1 l_1}(r_1)\, u_{n_2 l_2}(r_2)\, \frac{r_<^\lambda}{r_>^{\lambda+1}} u_{n_1' l_1'}(r_1)\, u_{n_2' l_2'}(r_2)\, dr_1 dr_2$$

and

$$f_\lambda \left(l_1 l_2 l_1' l_2'; L \right) = \left\langle \mathcal{Y}_{l_1 l_2 L M_L} \left(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2 \right) \left| P_\lambda \left(\cos\theta_{12} \right) \right| \mathcal{Y}_{l_1' l_2' L M_L} \left(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2 \right) \right\rangle$$

and

$$I^l_{n_1 n_2} = -\frac{1}{2} \int_0^a u_{n_1 l}(r) \left[\frac{d^2}{dr^2} - \frac{l\,(l+1)}{r^2} + \frac{2Z}{r} \right] u_{n_2 l}(r)\, dr$$

(a) Calculation of orbitals

   i. The bound orbitals used are the analytic H orbitals

   ii. The continuum orbitals are generated using the packages BASFUN to carry out the integration and FINDER to solve the eigenvalue problem.

(b) Angular factors

   It is possible to derive a simple analytic expression for the angular factors $f_\lambda \left(l_1 l_2 l_1' l_2'; L \right)$

(c) One electron integrals $I^l_{n_1 n_2}$

   The subroutine ONEELE is called to evaluate the $I^l_{n_1 n_2}$.

(d) Subroutine HMAT sets up the two electron Hamiltonian and outputs the upper right triangle to be diagonalized later.

(e) Subroutine DIAG diagonalizes the Hamiltonian matrix storing the eigenvalues and eigenvectors.

(f) The surface amplitudes are evaluated using the expression

$$\omega_{n_2 l_1 l_2 k} = \sum_{n_1} \beta_{n_1 l_1 n_2 l_2 k} u_{n_1 l_1}(a)$$

where $\beta_{n_1 l_1 n_2 l_2 k}$ and the components of the eigenvectors a_k of the diagonalized Hamiltonian and $u_{n_1 l_1}(a)$ are the values of the continuum orbitals $u_{n_1 l_1}$ on the R-matrix boundary a.

(g) The R-matrix on the boundary at energy E is now evaluated from the expression

$$R_{ij} = \frac{1}{2a} \sum_k \frac{\omega_{ik}\omega_{jk}}{E_k - E}$$

In practice, the summation over k has to be truncated. In order to account for this we add a correction to the diagonal elements of the R-matrix. This correction was first introduced by Buttle.

Note that up to step (f) is independent of the energy E of the total two-electron system. It therefore has to be carried out only once irrespective of the number of different energies we wish to consider. This is one of the big advantages of the R-matrix method. The energy dependence in the internal region occurs through the denominator of the simple expression used to evaluate the R-matrix in step (g).

3.2 External region problem

In the external region where exchange effects between the scattered electron and the residual atomic electron can be ignored, we are required to solve the set of radial equations

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r} + k_i^2\right) F_i(r) = 2\sum_{j=1}^{n}\sum_{\lambda=0}^{\lambda_{max}} a_{ij}^{\lambda} r^{-\lambda-1} F_j(r) \qquad (3.4)$$

for $i = 1, n;\ r > a$. A number of computer codes exist to solve (3.4) e.g. FARM.

The K-matrix is defined by the asymptotic form of the solution of these equations. To relate the $n \times n$ dimensional R-matrix with the $n_a \times n_a$ dimensional K-matrix we introduce $n + n_a$ linearly independent solutions s_{ij} and c_{ij} of equation (3.4) in a similar manner as we did in §2.2.

$$s_{ij} \underset{r\to\infty}{\sim} k_i^{-\frac{1}{2}} \sin\theta_i \delta_{ij} + O\left(r^{-1}\right) \qquad i = 1, n \;\; j = 1, n_a$$

$$c_{ij} \underset{r\to\infty}{\sim} k_i^{-\frac{1}{2}} \cos\theta_i \delta_{ij} + O\left(r^{-1}\right) \qquad i = 1, n \;\; j = 1, n_a$$

$$c_{ij} \underset{r\to\infty}{\sim} \exp(-\phi_i)\,\delta_{ij-n_a} + O\left(r^{-1}\exp(-\phi_{j-n_a})\right) \qquad i = 1, n \;\; j = n_a+1, n$$

where

$$\phi_i = |k_i|\, r - \frac{Z-N}{k_i} \ell n \left(2\,|k_i|\, r\right) \tag{3.5}$$

We can expand the reduced radial wavefunction of the scattered electron in the external region as a linear combination of these solutions. In matrix form this becomes

$$\mathbf{F} = \mathbf{s} + \mathbf{cK} \qquad (r \geq a)\ . \tag{3.6}$$

Differentiating this gives

$$\dot{\mathbf{F}} = \dot{\mathbf{s}} + \dot{\mathbf{c}}\dot{\mathbf{K}} \qquad (r \geq a). \tag{3.7}$$

From the internal region discussion, we know that the reduced radial function for the scattered electron $F_i(r)$ on the boundary $r = a$ satisfies

$$F_i(a) = \sum_j R_{ij}\,(E)\,\left(a\frac{dF_j}{dr} - bF_j\right)\Big|_{r=a} \tag{3.8}$$

which can be rewritten in matrix form as

$$\mathbf{F} = a\mathbf{R}.\dot{\mathbf{F}} - b\mathbf{R}.\mathbf{F}\ \ . \tag{3.9}$$

Substituting (3.6) and (3.7) into (3.9) to match the internal and external solutions on the boundary and so eliminate $\mathbf{F}$ and $\dot{\mathbf{F}}$ gives

$$\mathbf{s} + \mathbf{cK} = a\mathbf{R}(\dot{\mathbf{s}} + \dot{\mathbf{c}}\dot{\mathbf{K}}) - b\mathbf{R}(\mathbf{s} + \mathbf{cK})\ \ . \tag{3.10}$$

We define the matrices $\mathbf{A}$ and $\mathbf{B}$ as follows

$$\begin{aligned} \mathbf{A} &= -\mathbf{s} + a\mathbf{R}(\dot{\mathbf{s}} - \frac{b}{a}\mathbf{s}) \\ \mathbf{B} &= +\mathbf{c} - a\mathbf{R}(\dot{\mathbf{c}} - \frac{b}{a}\mathbf{c}) \end{aligned} \tag{3.11}$$

The K-matrix is then given by

$$\mathbf{K} = \mathbf{B}^{-1}\mathbf{A} \tag{3.12}$$

The T-matrix and the S-matrix are related to the K-matrix by

$$\mathbf{T} = \mathbf{S} - \mathbf{1} = \frac{2i\mathbf{K}}{\mathbf{1} - i\mathbf{K}} \tag{3.13}$$

The cross section for the transition from an atomic or ionic state with quantum numbers L_i, S_i to the atomic or ionic state with quantum numbers L_j, S_j after electron collision is given by

$$\sigma_{L_1 S_1 \to L_j S_j} = \frac{\pi}{2k_i^2} \sum_{l_i l_j} \frac{(2L+1)\,(2S+1)}{(2L_i+1)\,(2S_i+1)}\,|T_{ij}|^2$$

where L is the total orbital angular momentum of the atom/ion + electron system; S is the total spin angular momentum of the atom/ion + electron system; k_i^2 is the energy of the scattering electron in channel i. The summation over l_i and l_j is over all scattering electron angular momenta l_i and l_j which couple to the initial or final atomic/ionic states respectively to given states with orbital and spin angular momenta L and S and the required parity Π. The cross section is given in units of a_0^2.

4 Computer codes

4.1 Energy independent internal region

The code available to solve this part of the problem is **rmat**. This program will automatically prompt you for the required input data. **rmat** will calculate the surface amplitudes on the R-matrix boundary which are required as input into the outer region program .

4.2 External region code

The problem in the outer region, or asymptotic region, is solved by running the code **asym** . The code reads in the surface amplitudes evaluated by running **rmat** and evaluates the R-matrix at the R-matrix boundary for a given energy. It then proceeds to solve the scattering problem in the external region as outlined in §3.2 , matching the R-matrix on the boundary to give the K-matrix as discussed. Again, the code will prompt you for input data. However, you must remember to run **rmat** first and make sure that your data input for both codes are consistant!

Further Reading

1. P. G. Burke and K. A. Berrington *Atomic and Molecular Processes – An R-matrix Approach.* Bristol, Philadelphia:IOP Publishing, (1993).

2. K. Bartschat, Ed. *Computational Atomic Physics. Electron and Positron Collisions with Atoms and Ions* Berlin, Heidelberg, New York:Springer, (1996).

3. V. M. Burke and C. J. Noble, `FARM` – *a flexible asymptotic R-matrix package*, Comput. Phys. Commun. **85** (1995) 471.