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THE UK MOLECULAR R-MATRIX SCATTERING PACKAGE: A COMPUTATIONAL PERSPECTIVE

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1. INTRODUCTION

The R-matrix theory has been presented in the previous chapters of this book from a theoretical standpoint. Such is its complexity however that a separate chapter, that is this one, must be devoted to the implementation of the theory as a set of computer programs. Obviously if the R-matrix theory or any other method of solving the electron molecule scattering problem is to be viable it must be economic in the sense that it can be used routinely to produce numeric data for comparison with experimental measurements. Today, this means that the theory can be coded as a set of one or more computer codes which can be run in realistic time scales to produce data. This chapter attempts to show how the R-matrix method has been implemented, by a collaboration in the UK, in order to meet this objective. The reader should remember that the program suite reported here has been, and continues to be, developed and maintained by many people including overseas visitors and not just these authors.

Readers of R-matrix theory papers, of which there are now many in the literature, are used to seeing the R-matrix basis expansion of eq 18 as the starting point for any discussion of the theory. For the sake of completeness, however, the salient details of R-matrix theory and its approach to wavefunction expansion are given here. The reader should note that when using the R-matrix computer programs the wavefunction is in fact the last item to be built: a feature shared by the, closely related, configuration interaction method in atomic and molecular bound state studies.

We seek the quantum mechanical description of a scattering event where we know, or assume, that the system is described by the non-relativistic Schrödinger Hamiltonian which we denote by H_{N+1}; in this system there are N electrons which constitute the target and one other particle, the projectile, which will also be an electron in this article. The R-matrix codes can, it should be stated, handle the case of a positron incident on a molecule too. Basic quantum mechanics states that when the system has energy E

Computational Methods for Electron-Molecule Collisions
Edited by W.M. Huo and F.A. Gianturco, Plenum Press, New York, 1995

then it has a wavefunction, Ψ_E, given by

$$(H_{N+1} - E)\,\Psi_E = 0. \tag{35}$$

In fixed nuclei R-matrix theory we divide configuration space into two regions, the inner and outer, as shown in figure 1 and discussed by Gillan and co-workers,[1, 2] and apply

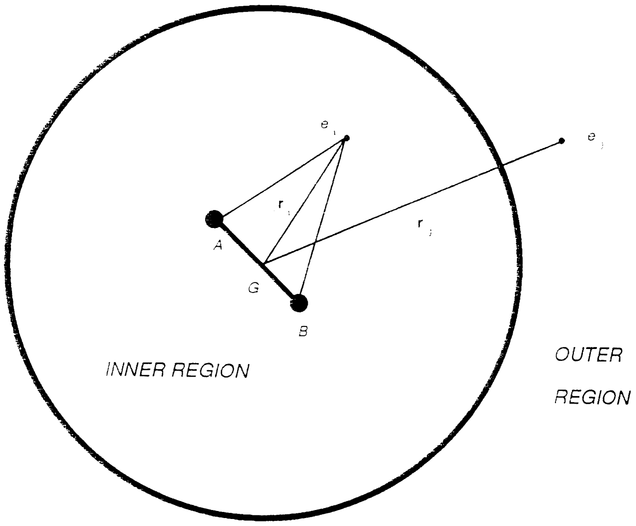

Figure 1. Division of configuration space in fixed nuclei R-matrix theory

the following expansion of the wavefunction in the inner region,

$$\Psi_E = \sum_k A_{Ek}\psi_k \tag{36}$$

where the ψ_k are energy independent basis functions and the A_{Ek} are coefficients whose value changes as we change the total energy E. The power of R-matrix theory lies in the fact that these ψ_k are independent of energy and need be constructed only once for all scattering energies.

The next section discusses the *morphology* of the ψ_k from the point of view of a fixed nuclei calculation leaving consideration of nuclear motion to chapters 2 and 5. A precis of the outer region part of a fixed nuclei calculation is then the subject matter of the subsequent section. Following these discussions there is a section outlining the steps that have to be performed when carrying out a full R-matrix study of any target and complimenting this is a section describing the algorithms used at various stages in the computer program implementation. The chapter closes with a prospective look at new developments taking place in the R-matrix code suite.

2. CHOOSING BASIS FUNCTIONS AND CONFIGURATIONS

The inner region R-matrix basis functions, ψ_k, are expansions over configuration state functions, CSFs, which in turn are composed of linear combinations of Slater determinants; these determinants involve spin orbitals with the spatial part of these, the orbitals ϕ_i, being linear combinations of functions defined on the nuclei and on the centre of gravity of the molecule. The strong connection with quantum chemistry, specifically configuration interaction studies of molecular bound states, should now be obvious. Thus in studying the fixed nuclei inner region problem one must consider two features:

1. The choice of the nuclear centred basis functions, the form of the functions defined on the scattering centre and their combination into a molecular orbital set.
2. The building of a vector space of CSFs by distribution of electrons, and their quantum number couplings, in the molecular orbital set.

Ultimately any fixed nuclei R-matrix calculation is judged by the specific form it employs for each of these.

2.1. Basis Functions and Orbitals

Clearly the expression of molecular orbitals, ϕ_i, as linear combinations of basis functions, U_j, may be best represented as a matrix, c_{ij}, where

$$\phi_i = \sum_j c_{ji}\, U_j. \tag{37}$$

The structure of the matrix, **C**, is illustrated in figure 2 where it is shown that the orbital set is composed of two distinct parts. In the present scheme Slater Type Functions

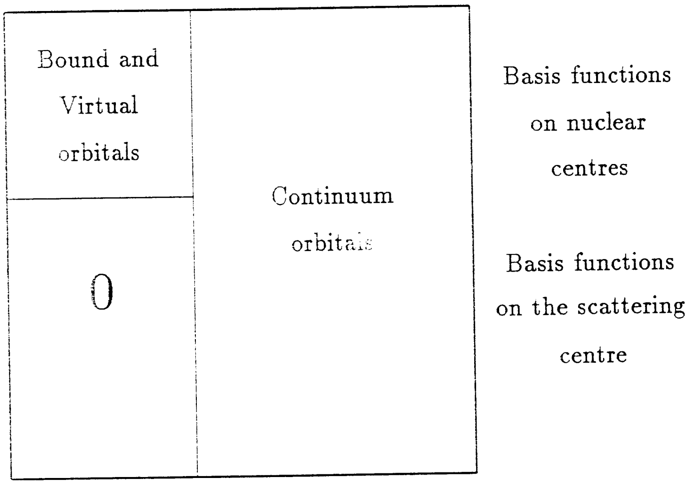

Figure 2. Structure of orbital set used in an R-matrix calculation showing that the one particle basis is composed of two distinct types of functions.

(STFs, also known as Slater Type Orbitals STOs) χ_i, centered on each of the atomic nuclei are used to span the bound space while numerical functions defined on the centre of gravity of the molecule comprise the continuum part. The STFs have the form,

$$\chi_i\,(n,l,m,k,\zeta) = \sqrt{\frac{(2\zeta_i)^{2n+1}}{(2n)!}}\; r_k^{n-1}\, e^{-\zeta_i r}\; Y_{lm}(\hat{\mathbf{r}}_k) \tag{38}$$

where k defines the nuclear centre and numerical functions have the form,

$$\frac{1}{r_G}\, u_{ij}\,(r_G)\; Y_{l_i m_i}(\hat{\mathbf{r}}_G) \tag{39}$$

the Y_{lm} being complex spherical harmonics.[3] The radial parts, u_{ij}, are obtained by solving the model, single channel scattering problem

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l_i(l_i+1)}{r^2} + 2V_0(r) + k_j^2\right] u_{ij}(r) = 0 \tag{40}$$

subject to the fixed boundary conditions

$$u_{ij}(0) = 0, \qquad \left[\frac{a}{u_{ij}(r)}\,\frac{\mathrm{d}u_{ij}(r)}{\mathrm{d}r}\right]_{r=a} = \mathrm{b} \tag{41}$$

Here a is the R-matrix boundary radius, b is an arbitrary constant frequently set at zero and V_0 is an arbitrary spherical potential which is often chosen to be the spherically symmetric part of the target ground state static potential. The numerical functions are therefore solutions of a Stürm-Liouville problem with homogeneous boundary conditions and the radial part of the scattering wave function is ultimately a generalized Fourier series expansion on these functions. Any finite expansion over these functions will exhibit the Gibbs phenomenon near the R-matrix boundary and so a correction term, proposed by Buttle[4] must be added to the R-matrix on the boundary to compensate for the finite expansion length. Note that only these numerical functions are non-zero on the R-matrix boundary and therefore they alone provide the link between the inner and outer regions.

It is important to note that the orbital set is chosen to be orthogonal; this is because such a choice simplifies greatly the evaluation of the Hamiltonian matrix elements (see later). The target occupied and virtual orbital part of the matrix **C** is computed first using standard quantum chemical techniques; numerical functions representing the continuum are then added to the basis set. Initially zero matrices are inserted on the target – continuum off-diagonal blocks and a unit matrix is placed in the lower right hand corner. At this stage an orthogonalization procedure is applied, typically the Schmidt process. This means that the continuum orbital space picks up a target orbital component a feature that can cause practical linear dependence problems at the four index transformation stage if the coefficients produced are too large.

The final structure of the orbital matrix **C** is illustrated in figure 2 where its morphology is clearly visible. It is, of course, imperative that the compound basis set, Slater functions and numerical functions, is linearly independence but it is necessary to distinguish between the mathematical and computational nature of this attribute. Computer arithmetic is performed using fixed size, floating point numbers a feature which imposes limits on the accuracy of the real numbers that can be represented. The numerical integration technique employed will add a further source of error. This means that it is possible to have basis sets which exhibit numerical linear independence on a thirty two or sixty four bit computer architecture but which would be linearly independent if more accuracy were available.

Having chosen the expansion basis for the molecular orbitals, the fundamental quantities on which the rest of the calculation depends are atomic integrals so called because they involve atomic centered functions (in scattering also the centre of gravity). In R-matrix theory integrals are required over a finite range of the radial co-ordinate not the infinite range needed in quantum chemistry and it is this feature which introduces a major distinction between bound state calculations and scattering evaluations. For a more detailed discussion of the classification of atomic integrals including a description of the breakdown of two electron integrals into Coulomb, hybrid and exchange types the reader should consult Shavitt.[5]

Bound state Slater integral codes perform their task using combinations of numerical quadrature over the different co-ordinates and hence they are easily modified to include functions which are defined numerically as in our scattering problem; it is for this reason that our integrals program has been developed from a Slater bound state package.[6] It should be noted however that Slater functions are only useful for linear molecules as noted in chapter 1.

2.2. Configurations for e-N_2 with an SCF Target Representation

Having defined a molecular orbital set we can now make the R-matrix basis functions ψ_k concrete thereby illustrating their relationship to the physics and chemistry of the problem. It will be shown, in particular, that the form chosen for the ψ_k is closely related to the close coupling expansion;[7] the R-matrix calculation reported by Gillan and co-workers[1] is an appropriate vehicle for this purpose.

The simplest possible representation of the ground state wavefunction is the Hartree Fock or single configuration model which is, following the aufbau principle,[8]

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4. \tag{42}$$

When an SCF evaluation of the $X^1\Sigma_g^+$ state of N_2 is performed, a basis of Slater type will be used which is much larger than just having one function for each atomic orbital. This leads to several extra orbitals being evaluated and these are known as virtual orbitals; chemically, they are approximately representing an extra electron outside an N_2 core. In the basis of Nesbet[9] there are seven σ type and three π type Slater functions on each atom yielding a molecular orbital space which may be classified as follows

- Occupied Space

$$1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 3\sigma_g, 1\pi_u \tag{43}$$

- Virtual Space

$$(4,\ldots,7)\sigma_g,\ (3,\ldots,7)\sigma_u,\ (2,3)\pi_u,\ (1,\ldots,3)\pi_g \tag{44}$$

Although the virtual orbitals are more diffuse than the occupied at a radius of 7 bohr from the center of gravity they have decayed to negligible amplitude whereas the continuum orbitals have not. Consider scattering in the $^2\Sigma_g^+$ symmetry, as reported by Gillan and collaborators,[1] where there are thirty continuum molecular orbitals of σ_g type; these can be numbered as orbitals $(8,\ldots,37)\sigma_g$ in our set. We may now make a convenient description of the R-matrix basis functions, ψ_k, in terms of orbital configurations. Thus,

1. The first part of each ψ_k corresponds to the configurations

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ (^1\Sigma_g^+)\ \{8\sigma_g,\ldots,37\sigma_g\}^1\ (^2\Sigma_g^+) \tag{45}$$

These are the configurations which account for one electron in a continuum orbital with the rest of the electrons in the target state.

2. The second part of each ψ_k consists of two types of configurations.
   - One particle terms with the form:

$$1\sigma_g^2\,1\sigma_u^2\,\left\{2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,1\pi_u^4\,({}^1\Sigma_g^+)\,\{4,5,6,7\sigma_g\}^1\right\}\,({}^2\Sigma_g^+) \tag{46}$$

     where the scattering electron drops down into the virtual orbitals of the same symmetry but the target electrons remain as before
   - Two particle - One hole terms with the form:

$$\begin{gathered}1\sigma_g^2\,1\sigma_u^2 \otimes \quad \left\{2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,1\pi_u^4\right\}^{-1} \otimes \\ \{4,\ldots,7\sigma_g,3,\ldots,7\sigma_u,2,3\pi_u 1,2,3\pi_g\}^2\,({}^2\Sigma_g^+)\end{gathered} \tag{47}$$

     in which there is one hole in the target and two particles in the virtual space.

   Both of these types are L^2 configurations because all the electrons are in short range orbitals but we distinguish the two types. We call the former type orthogonality configurations because they compensate for the fact we have imposed orthogonality of the continuum molecular orbitals to the virtual space, a restriction that simplifies the computer programs immensely but is in fact not required by the quantum theory. These configurations also allow the continuum electrons to occupy high angular momentum states in the region of the nuclear singularities. The latter configurations are correlation configurations, sometimes referred to as (short range) polarization configurations, which introduce correlation effects between target and projectile. Note that these are correlation effects within the radial range of the STFs and not long range effects such as dipole polarization, a feature which can be modelled by using dipole pseudo-states.[10]

In passing, we note that a calculation in which the correlation configurations are omitted is referred to as being at the static exchange level (SE) while the addition of correlation configurations is a static exchange plus polarization approximation (SEP).

2.3. Configurations for e-N_2 with a CI Target Representation

In multistate scattering studies it is almost always necessary to use a configuration interaction representation of the target states, usually in the valence orbital space,[11] in order to obtain good relative energy separations. Here e-N_2 elastic scattering is reconsidered, using the same basis as above, as a simple example to illustrate the general situation for a CI target. The N_2 ground state is now represented by a CSF expansion too. Thus its wavefunction Φ is given by

$$\Phi = \sum d_i\,\Delta_i \tag{48}$$

where the Δ_i are a set CSFs, the choice of which defines different types of target state approximation, and the d_i are coefficients which are obtained by diagonalizing the target state Hamiltonian in the basis Δ_i. Adopting the valence configuration interaction representation the CSF space is defined by the electron distribution,

$$1\sigma_g^2\,1\sigma_u^2\,\{2\sigma_g 2\sigma_u 3\sigma_g 1\pi_u 1\pi_g 3\sigma_u\}^{10}. \tag{49}$$

Thus we freeze the lowest two orbitals and distribute the remaining ten electrons in all possible ways over the rest of the orbital set; the dimension of this CSF space, for the ground state of N_2.

In the work of Gillan *et al* [1] there were twenty seven continuum molecular orbitals of symmetry π_g which we number $4, \ldots, 30$. Proceeding as before, but now looking at the resonant $^2\Pi_g$ scattering symmetry instead, the ψ_k can be analysed into parts as follows:

1. The first part of each R-matrix basis function

$$1\sigma_g^2\,1\sigma_u^2\,\{2\sigma_g 2\sigma_u 3\sigma_g 1\pi_u 1\pi_g 3\sigma_u\}^{10}\,(^1\Sigma_g^+)\,\{4\pi_g \ldots 30\pi_g\}^1\,(^2\Pi_g) \qquad (50)$$

   consists of the direct product of the Δ_i defining the target space with one electron in the continuum space. Note that the target eigenvector coefficients, d_i, associated with each CSF have not yet been accounted for. They are in fact introduced prior to diagonalization of the Hamiltonian matrix.
2. The L^2 part of each ψ_k may be further divided into three pieces:
   - Orthogonality CSFs

$$1\sigma_g^2\,1\sigma_u^2\,\{2\sigma_g 2\sigma_u 3\sigma_g 1\pi_u 1\pi_g 3\sigma_u\}^{10}\,(^1\Sigma_g^+)\,\{2, 3\pi_g\}^1\,(^2\Pi_g) \qquad (51)$$

     accounting for the fact that the continuum molecular orbitals are also orthogonal to the unoccupied virtual orbitals.
   - Correlation CSFs

$$1\sigma_g^2\,1\sigma_u^2\,\{2\sigma_g 2\sigma_u 3\sigma_g 1\pi_u 1\pi_g 3\sigma_u\}^{11}(^2\Pi_g). \qquad (52)$$

     where the scattering electron enters the charge cloud of the target state.
   - Two particle - One hole Additional Correlation CSFs

$$\begin{aligned} 1\sigma_g^2\,1\sigma_u^2 \otimes \quad & \{2\sigma_g 2\sigma_u 3\sigma_g 1\pi_u 1\pi_g 3\sigma_u\}^{9}\,(Z)\,\otimes \\ & \{4\ldots 7\sigma_g, 4\ldots 7\sigma_u, 2, 3\pi_u, 2, 3\pi_g\}^2\,(^2\Pi_g). \end{aligned} \qquad (53)$$

     These CSFs are analagous to the two particle one hole terms for the SCF target but are vastly increased in number with a CI target. The quantity Z indicates that the nine remaining target electrons must have their coupling restricted to represent a target *hole*. For the N_2 ground state Z takes the values $^2\Sigma_g^+$, $^2\Sigma_u^+$, $^2\Pi_u$, $^2\Pi_g$ etc.

In summary then, with a CI target it is not possible to delineate the role of specific configurations as clearly as in the case of an SCF target.

3. THE OUTER REGION

In the external region of configuration space, a single centre, no exchange, close coupling expansion of the scattering wavefunction is adopted, reflecting the fact that physical interactions, inherently different to those of the inner region, now dominate the scattering process.[12] A body fixed frame of reference is chosen and the expansion adopted is

$$\Psi_E = \sum_{i=1}^{n} \bar{\Phi}_i(x_1, \ldots x_N, \sigma_{N+1})\,\frac{1}{r_{N+1}}\,F_i(r_{N+1})\,Y_{l_i m_{l_i}}(\hat{\mathbf{r}}_{N+1}) \qquad (54)$$

where the $x_i = (\hat{\mathbf{r}}_i, \sigma_i)$ represent the angular and spin co-ordinates of electron i and the functions $\bar{\Phi}_i$ are formed by coupling the scattering electron spin with the target state spins to yield eigenfunctions of S^2 and S_z for the N+1 electron system. The channel functions for the problem, involving all but the radial co-ordinate of the scattering electron, are $\left[\bar{\Phi}_i Y_{l_i m_{l_i}}\right]_\Lambda$ and are eigenfunctions of the operator L_z with eigenvalue Λ as well as of the operators S^2 and S_z for the N+1 electron system.

On substituting this form of Ψ_E into equation (35) and projecting onto the channel functions one obtains

$$\left\{ \frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + k_i^2 \right\} F_i(r) = 2 \sum_j V_{ij}(r)\, F_j(r) \tag{55}$$

which is a set of n, coupled, homogeneous, differential equations for the reduced radial wavefunctions F_i. The quantity k_i^2 is defined as

$$k_i^2 = 2(E - \epsilon_i) \tag{56}$$

ϵ_i being the target state eigenenergies. The matrix V_{ij}, which is a function of the radial variable r_{N+1} is the potential matrix which describes the coupling between the channels of interest. It has the form

$$V_{ij} = < \bar{\Phi}_i Y_{l_i m_{l_i}} \mid \sum_{k=1}^{N} \frac{1}{\mid \mathbf{r}_{N+1} - \mathbf{r}_k \mid} - \frac{Z_A}{\mid \mathbf{r}_{N+1} - \mathbf{R}_A \mid} - \frac{Z_B}{\mid \mathbf{r}_{N+1} - \mathbf{R}_B \mid} \mid \bar{\Phi}_j Y_{l_j m_{l_j}} > \tag{57}$$

where $Z_A, \mathbf{R}_A$ and $Z_B, \mathbf{R}_B$ are the charges and position vectors of the two nuclei respectively and N is the number of electrons in the target. Since the radial co-ordinate of the scattered electron is greater than the radial co-ordinates of all of the target electrons, for this particular region of configuration space, it is possible to expand the matrix elements of the direct potential in inverse powers of r_{N+1}. Applying the spherical harmonic addition theorem yields the expression[2]

$$V_{ij} = \sum_{s=1}^{\infty} \frac{a^{(s)}_{il_i,jl_j}}{r^{s+1}_{N+1}} - \frac{Z_A + Z_B - N}{r_{N+1}}\ \delta_{ij}\, \delta_{l_i l_j}. \tag{58}$$

Evaluation of the asymptotic potential coefficients, $a^{(s)}_{il_i,jl_j}$ is straightforward and requires data on the properties and transition moments of the target states included in the R-matrix expansion.

From a mathematical perspective the set of equations (55) have $2n^2$ solutions at every scattering energy each of the n channels yielding n regular and n irregular solutions. Physically, we may distinguish between open and closed channels, using equation (56), because the channels may be ordered contiguously in the same fashion as their associated target eigenstates. The ground state energy defines the zero level for scattering so that at all positive scattering energies those channels associated with the ground state are open. At scattering energies above the highest target state threshold all channels will be open. Between these extremes there will be, in general, n_a open channels ($n_a < n$) and n_b closed channels ($n_b = n - n_a$).

In the limit that the electron-molecule distance tends to infinity we may define, within each open channel i, n_a different, linearly independent, standing wave solutions j, of the form

$$F_{ij} \sim \frac{1}{\sqrt{k_i}} \left(\sin(k_i r - \frac{1}{2} l_i \pi)\delta_{ij} + \cos(k_i r - \frac{1}{2} l_i \pi) K_{ij} \right). \tag{59}$$

The $n_a \times n_a$ coefficients K_{ij} define the K-matrix which embodies the information on the scattering process. From it, or more precisely the related T-matrix, we may calculate physical observables for the scattering process. In the n_b closed channels, the radial function decays exponentially,

$$F_{ij} \sim e^{-|k_{ij}|r} \tag{60}$$

indicating that there is no flux lost at infinity.

4. SCATTERING COMPUTATIONS: A TOP DOWN VIEW

The best way to present an overview of the computational steps that one carries out in applying the R-matrix method is to list those steps in a top down fashion. Thus we have:

1. Generation of target orbitals and target states.
   In fact this encompasses the entire field of molecular electronic structure theory and is not a trivial problem! In early work it was sufficient to use a simple single configuration representation of the lowest electronic state of the molecule. Therefore an SCF calculation in a chosen basis of STFs was sufficient to obtain the orbital expansion coefficients. In recent years coupled electronic state calculations have become more important thereby requiring more complicated evaluations. In R-matrix calculations all electronic states are expanded in one common set of target orbitals and since we are forced to use only moderate CI expansions for these states, it is often quite difficult to obtain an optimal common orbital set.
2. Evaluation of the numerical basis functions.
3. Evaluation of integrals between atomic and/or centre of mass functions.
4. Continuum orbital generation. Lagrange and/or Schmidt orthogonalization of the continuum orbitals to the bound state orbitals.
5. Four index transformation from atomic integrals to molecular orbital integrals using the results of the previous step.
6. Creation of the Hamiltonian matrix and its diagonalization to yield eigenvalues and eigenvectors at fixed geometry. This step, which has to be repeated for each scattering symmetry under study, actually may be divided into sequential substeps as follows:
   (a) Configuration state function generation
   (b) Hamiltonian matrix element evaluation in terms of coefficients and integral labels; otherwise known as the formula tape construction.
   (c) Formula tape reindexing and reordering for efficient Hamiltonian matrix construction
   (d) Unification of formula tape and actual integrals to construct the Hamiltonian matrix which is then diagonalized to yield eigenvalues and eigenvectors.
7. Data Management
   The previous steps are carried out for each scattering symmetry and with the nuclei held fixed in space. It is necessary then to collate all of the data from a range of internuclear geometries into an ordered set before proceeding to the nuclear motion stage.
8. Nuclear Motion
   When nuclear motion is being considered explicitly in the R-matrix calculations, it is necessary to set up and diagonalize a Hamiltonian incorporating the nuclear kinetic energy operator.

9. External Region

   This changes depending upon the problem in question. The possibilities in our present package are,
   - (a) Electron/Positron Scattering
   - (b) Dissociative Attachment/Recombination
   - (c) Photoionization
   - (d) Bound States

   Each of these possibilities must be considered separately. Of these, (a)-(c) produce a K-matrix, at each scattering energy, which is then used in the next step.
10. Once a K-matrix is obtained, several physical observables can be calculated from it, such as total and differential cross sections. It is these physical observables which are then compared with experiment.

This list, in itself, presents a coarse grain modularization of the computational task. In the next section we discuss the actual program modules which implement these steps and in so doing consider the fine grain modularization of the task. For each module we indicate where further information on the coded algorithms can be found.

5. DESCRIPTION OF INDIVIDUAL MODULES

Each step in the previous section is implemented by one or more programs in our package thus modularizing the task further. Much of the inner region code has been developed from the Alchemy I program suite written by scientists at the IBM Almaden Research Laboratory, San José California. The interested reader should consult an article by McLean[13] who has described the earliest versions of the Alchemy suite. Alchemy I and its modern counterpart Alchemy II[14] have been obtained by our group under license from IBM.

5.1. Atomic Integrals

This is the integral generator, for STFs, contained in the Alchemy suite adapted to generate all of the integrals for a scattering calculation. The algorithms used to evaluate the bound state integrals[3, 13] have been modified to restrict the range of the radial co-ordinate and to include functions defined numerically.[6, 15]

5.2. Hartree Fock Self Consistent Field

This is the self consistent field program from the Alchemy suite which solves the matrix Hartree Fock procedure.[16, 17]

5.3. Numerical Basis Function Generator

This program, described by Salvini,[18] solves the Stürm Liouville problem, equation (40), for the numerical continuum basis functions u_{ij} and evaluates the Buttle corrections[4] mentioned earlier.

5.4. Orthogonal Molecular Orbital Generator

This module reads a set of molecular orbital expansion coefficients and associated basis function overlap integrals and proceeds to generate an orthogonal orbital set. For bound state studies only the Schmidt option is used while for scattering situations an option exists to Lagrange orthogonalize the continuum molecular orbitals instead.[19]

Once the orthogonal continuum orbitals are available this code computes the magnitude of the continuum orbitals on the R-matrix boundary and then writes this data to disk; it is used by the external region codes to build the R-matrix elements at each scattering energy.

5.5. Four Index Transformation from Atomic to Molecular Integrals

This is essentially the unmodified Alchemy I four index transformation program which has been discussed by McLean;[13] it takes atomic integrals and multiplies them by combinations of molecular orbital coefficients to produce molecular integrals for Hamiltonian construction.

5.6. Configuration State Function Generator

This module generates CSFs with the appropriate spin and symmetry couplings for the system under study. In scattering work it is necessary to use a genealogical scheme to generate the configurations because of the form of the vector space of CSFs required; Nesbet has discussed a similar program for atomic scattering studies.[20] Specifically, it is imperative that one can specify exactly the coupling of the N electron target as well as the N+1 particle system. Orel *et al* [21] have given a detailed description of the method of pseudo-(N+1) electron CI calculation in order to circumvent the phase consistency problems inherent in CSF generation; this technique is also used in the R-matrix codes.

5.7. Formula Tape Evaluation and Symbolic Expansion

This code produces expressions for the Hamiltonian matrix elements in terms of coefficients and integrals labels. Assuming that molecular orbitals are orthonormal the Hamiltonian elements, H_{ij} may be written as linear combinations of one and two electron integrals[22] between these orbitals (transformed integrals),

$$\begin{aligned} < \Delta_i \mid H \mid \Delta_j > \quad &= \quad \sum_{kl} A^{ij}_{kl} < \phi_k(\mathbf{r}_1) \mid h_1 \mid \phi_l(\mathbf{r}_2) > \\ &+ \sum_{klmn} B^{ij}_{klmn} < \phi_k(\mathbf{r}_1)\,\phi_l(\mathbf{r}_1) \mid \frac{1}{r_{12}} \mid \phi_m(\mathbf{r}_2)\,\phi_n(\mathbf{r}_2) > \\ &+ \delta_{ij}\,\frac{Z_A Z_B}{\mid \mathbf{R}_A - \mathbf{R}_B \mid}. \end{aligned} \tag{61}$$

The structure of the CSF space for scattering readily lends itself to the use of a symbolic approach to formula tape evaluation. Morgan and Tennyson[23] have implemented a new section of code to embrace that symbolic technique first reported by Liu and Yoshimine[24] in a fashion appropriate for scattering calculations.

5.8. Formula Tape Reordering

Given the formula tape and the dataset containing the molecular integrals, the Hamiltonian matrix could be constructed straightforwardly by reading the formulae sequentially and then carrying out the summation in equation (61). This, however, would become a bottleneck in the calculation as it would require, for each matrix element, successive reading and re-reading of the sequentially organized, integrals dataset. Instead, Yoshimine,[25] has devised a three stage algorithm which leads to faster set up of the Hamiltonian. At the heart of the algorithm is the idea that the lengthy integrals tape should only be read once and a fundamental step in achieving this goal is the re-ordering of the energy (Hamiltonian) expressions.

5.9. Hamiltonian Matrix Construction and Diagonalization

The operations carried out by the CI program are:

1. Read the sorted energy expression tape
2. Read the transformed integrals tape
3. Build the lower half triangle of the real symmetric Hamiltonian matrix in core
4. Carry out a contraction with target eigenstate vectors, if needed.
5. Diagonalize the matrix to find *all* eigenvalues and eigenvectors using the Householder procedure and store these for use by the external region program.

The first three steps above are accomplished by use of stages two and three of the Yoshimine procedure.[25] The contraction process has been discussed by Orel *et al* [21] with regard to application of the Kohn method to electron molecule scattering; the same operation is carried out within the R-matrix codes.

5.10. Density Matrix and Property Analysis Code

Wavefunction properties provide, in general, a more stringent test of the charge density than the computed energy and so most molecular structure suites include a module to evaluate these quantities. Fortunately, most of the wavefunction properties that one needs to calculate are for one electron operators. The transition property, or transition moment, T_{IJ} between the pair of N-electron wavefunctions Ψ_I and Ψ_J is defined as

$$\mathrm{T}_{IJ} = < \Psi_I \mid \sum_{i=1}^{N} f(\mathbf{r}_i) \mid \Psi_J > \tag{62}$$

where $f(\mathbf{r})$ is a one electron property operator for example $z = r\cos\theta$. When $\Psi_I = \Psi_J$ then T_{II} is a wavefunction property or target state moment.

It is possible to write down expressions for T_{II} and T_{IJ} in terms of the density and transition density matrices respectively.[26, 27] Once a density matrix is available *any* one electron property may be evaluated by contracting that density matrix with a matrix of appropriate property integrals. The two most common types of expectation value required in R-matrix scattering studies are the target state properties needed for building the potential matrix in the asymptotic region[2] and transition dipoles needed to evaluate the contribution of dipole polarized pseudostates;[10] transition dipoles are also required to compute photoionization cross sections.

5.11. Nuclear Motion Inner Region

In essence this code sets up and diagonalizes the nuclear motion Hamiltonian matrix in the inner region[1] implementing the theory which is described in the previous chapter. The program is controlled by a driving routine which,

1. Reads all of the fixed nuclei eigenvectors, eigenvalues and primitive boundary amplitudes.
2. Generates or reads target vibrational wavefunctions.
3. Sets up the nuclear motion Hamiltonian which involves the nuclear kinetic energy operator.
4. For each scattering energy evaluates the generalized R-matrix.
5. Interfaces with external region programs.

Clearly, there is a very large amount of input scratch file data required, the exact amount depending on the number of internuclear separations used. Target vibrational wavefunctions, of the Morse variety, can be generated by the code if the required parameterization of the Morse potential energy curve is input. On the other hand, numerical vibrational wavefunctions can be read in. These are certainly required for when studying excitation to high vibrational levels where the Morse prescription is less accurate.

The bulk of the computation occurs in the third step where several integrals are evaluated. However, it should be stressed that, for diatomics, the elements of the nuclear motion Hamiltonian are much more straight forward to evaluate than those needed for the electronic part of the calculation. The input data is first fitted to a bicubic spline over the range of internuclear separations used. Then, the integrals are carried out using Simpson's rule although there is also an option to use Gauss Legendre quadrature. The Householder method is again used for the diagonalization. In summary the set up and diagonalization of the nuclear motion Hamiltonian is a microcausm of the electronic situation.

5.12. External Region Codes and Utility Programs

The end product of any scattering calculation is a set of calculated physical observables which allow comparison between different computational methods and with experiments. The solution of the external region equations produces initially a K-matrix at each energy as discussed previously. The eigenphases and eigenphase sum are easily obtained by diagonalizing the K-matrix and yield important information on resonances and on partial wave mixing; additionally multichannel quantum defects may be evaluated. The S and T-matrices are obtained from the definitions,

$$S = \frac{1 + \mathrm{i}K}{1 - \mathrm{i}K} \quad \text{and} \quad T = S - 1. \tag{63}$$

Given the T-matrix and the definition of the scattering channels in the problem, simple summation formulae yield the experimentally measurable values of the total and differential scattering cross sections.

Since the K-matrix serves as an intermediate to the evaluation of other data it is seldom necessary in practice to examine the actual matrix itself. Obviously, in any given situation one must always solve the coupled equations and obtain the K-matrices at each scattering energy of interest, but the user is free to choose the physical observables calculated by calling further subroutines from the library.

Library member INTERF reads a user defined input deck and combines the files of Buttle corrections, boundary amplitudes and CI vectors produced by the inner region codes. The information is passed to library member RSOLVE which solves the external region problem using a combination of R-matrix propagation[28] and Gailitis[29] asymptotic expansion techniques.[30] When wavefunctions are also required, they are propagated inwards using direct numerical integration.[31] The output of RSOLVE is a file of K-matrices from which eigenphase sums and other properties are calculated. The complete list of library members and their functions is as follows:

GETCOR	System dependent dynamic core allocation.
INTERF	Reads and formats the inner region and input data for use by the rest of the library members.
VIBRMT	Solves the nuclear motion R-matrix problem.
RSOLVE	Solves the external region coupled differential equations and obtains the K-matrix at each scattering energy.

EIGENP	Diagonalizes the K-matrices and calculates the eigenphases and eigenphase sum.
RESON	Locates resonances and fits the associated eigenphase sum to a Breit-Wigner form.[32]
MQDT	Calculates multichannel quantum defects.[33]
TMATRX	Computes the T-matrix from the K-matrix at each energy.
IXSECS	Evaluates integrated cross sections.
BOUND	Locates bound states using an adaptation[31] of the method of Seaton.[34]
TDIP	Transition dipoles among bound states obtained using BOUND.[31]
RATES	Integration of collision strengths over a Maxwellian temperature distribution.
DCS	The differential cross section evaluation from T-matrices using a previously published program.[35]

The use of the outer region code has been extensively adapted to study nuclear motion effects which go beyond the Born-Oppenheimer approximation. This is important for vibrational excitation near threshold or a resonance, dissociative recombination and dissociative attachment; these processes are discussed in chapter 2.

6. FUTURE DIRECTIONS

This article has described a large and complex software package which may be used to carry out state of the art, *ab initio* calculations on electron, positron and photon scattering by linear molecules. Inherent in all computer packages of this size is the need to develop and maintain it. Obviously this task may be divided into two sub-tasks as follows:

- more efficient algorithms must be found, where possible, and implemented as modules within the existing structure
- code must be kept up to date, transformed as needed, in order to exploit new and better FORTRAN compilers which in turn exploit new and better computer architectures.[36, 37]

The R-matrix method may be applied to areas of molecular physics beyond those discussed in this article and so the computer package is perpetually being expanded to encompass a larger problem domain. The refinements necessary to introduce Breit-Pauli type relativistic corrections into the theory have recently been discussed.[38] Until recently the R-matrix suite was restricted to linear systems, in practice only to diatomic molecules, because of the integral generator used. Working with the author of the Gaussian integrals code MOLECULE[39] new code is being added to the R-matrix suite to evaluate bound-continuum integrals for scattering from polyatomic targets. The R-matrix program suite has been radically enhanced from that which was used to study electron molecule scattering a decade ago and, clearly, the suite that has been discussed in this chapter is merely an outline of that which will hopefully exist at the end of the decade.

ACKNOWLEDGEMENTS

The authors wish to thank the International Business Machines Corporation who have provided copies of both the Alchemy I suite and their MOTECC-90 compilation of chemistry software under Joint Study agreements. Additional thanks are due to Prof. Jan Almlöf for providing a version of the program MOLECULE which has been optimized for vector processing on Cray architectures.

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