J. Phys. B: At. Mol. Opt. Phys. **29** (1996) 1817–1828. Printed in the UK

A new algorithm for Hamiltonian matrix construction in electron–molecule collision calculations

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Received 5 December 1995

Abstract. A method is presented for constructing configuration-interaction (CI) Hamiltonians for electron–molecule collision calculations based on close-coupling expansions. This method utilizes the structure of the wavefunction used in scattering calculations to greatly reduce the computational cost compared to conventional procedures. In particular, CI target configurations are treated only at the prototype configuration state function stage of the calculation. Only then are these prototype configurations expanded over all scattering functions using an improved version of a previous algorithm by Morgan and Tennyson. This new algorithm has been implemented as part of the UK R-matrix codes. Test calculations show that it leads to a large reduction in both the number of integrals and matrix elements which need to be explicitly constructed and evaluated. Use of this new program should allow significantly more sophisticated target wavefunctions to be employed in future scattering calculations.

1. Introduction

Electron–molecule impact data are required for a variety of applications including plasma, atmospheric and astrophysical studies. So far all calculations on electron–molecule collisions have used rather limited representations of the target wavefunctions with, in particular, correlation effects being severely restricted. Wavefunctions of this quality have been found to be satisfactory for some applications but are generally inadequate for accurate treatment of problems involving electron-impact electronic excitation of molecules.

The bottleneck in calculations with accurate target wavefunctions is not the computation of raw integrals. In procedures based on the use of standard quantum chemistry codes, these can be computed rapidly and in any case are essentially the same as those required for a calculation using an uncorrelated (SCF) target wavefunction. It is the construction of the Hamiltonian matrix which is computationally demanding.

The problem can be seen in terms of the R-matrix method by looking at (1) below. The number of configurations that have to be generated in a scattering calculation is the number of target configurations *multiplied by* the number of continuum orbitals summed over all target states. Even with rather modest target wavefunctions, this rapidly leads to calculations which require very large numbers of Hamiltonian matrix elements.

Calculations with all state-of-the-art scattering methods have so far struggled to use more than about a hundred configurations per target state (see Orel *et al* 1990, Rescigno 1994, Higgins *et al* 1995, Gillan *et al* 1996). This should be contrasted with quantum chemists

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0953-4075/96/091817+12$19.50

who routinely use more than a million configurations to represent wavefunctions of the same target (see, for example, Partridge *et al* 1990). Furthermore, in scattering calculations it is usually necessary to represent the wavefunctions of all target states used in the calculation with a single set of orbitals, which further degrades the quality of these wavefunctions. All the indications are that improved scattering calculations will not only require better target wavefunctions, but many more target states than have usually been included thus far (Gil *et al* 1994, Burke *et al* 1994).

Quantum chemists have designed a number of schemes based on the use of symmetry and 'direct' calculation of Hamiltonian matrices to increase the size of problems that can been tackled. These are generally inapplicable to scattering calculations which require models which give detailed control of the N- and $(N+1)$-electron description of the problem, including control over the coupling to the N-electron target states in the $(N+1)$-electron calculation. Furthermore, with accurate target wavefunctions, the Hamiltonian matrix elements are considerably more complicated than in the standard electronic structure problem and, at least in the R-matrix method, it is necessary to compute many, perhaps all, solutions of the Hamiltonian matrix.

In this paper an algorithm is developed which, instead of following previous quantum chemistry methods, employs the structure inherent in scattering calculations using CI target wavefunctions to reduce greatly the work required to construct the final Hamiltonian matrix. A new atomic R-matrix code, RMATRX II, has recently been developed (Burke *et al* 1994) which concentrates on reducing the time taken in Hamiltonian construction; however, the higher symmetry of the atomic problem means that totally different methods are employed to construct the matrix elements. Thus, although some of the ideas presented here are similar to those used in RMATRX II, the means used to implement them are completely different. Although the algorithm presented has been implemented as part of the R-matrix method (Burke and Berrington 1993), the problem with Hamiltonian construction is a general one and this procedure could be applied in other methods currently in use.

2. Theory

2.1. Constructing the Hamiltonian matrix

In methods employing a close-coupling expansion, the standard form of the electronic wavefunction for an electron collision with an N-electron target is (Huo and Gianturco 1995)

$$\psi_k = \sum_{ijn} A\phi_{in}(x_1 \ldots x_N)u_{ij}(x_{N+1})a_{injk} + \sum_{\ell} \chi_\ell(x_1 \ldots x_{N+1})b_{\ell k} \tag{1}$$

where A is the antisymmetrization operator, ϕ_{in} are target wavefunctions, see below, and the $u_{ij}(x)$ are continuum orbitals. There are J_i continuum orbitals associated with each target state. In the molecular R-matrix method J_i is typically between 20 and 60, depending on symmetry, R-matrix box size, the energy range of interest and the nature of the actual functions used to represent the continuum.

In equation (1), the χ_ℓ are two-centre quadratically integrable, or L^2, functions. In the R-matrix method these are constructed from the target occupied and virtual molecular orbitals; they are necessary to relax orthogonality constraints imposed on the u_{ij} continuum orbitals, as well as, in some calculations, to account for polarization effects not allowed for in the expansion over target states.

Electron-correlation effects in the target wavefunction in (1) are generally represented using configuration interaction (CI). This in turn leads to an expansion of the target wavefunction in terms of individual N-electron configurations

$$\phi_{in} = \sum_{m=1}^{M_i} c_{imn} \eta_{im}(x_1 \ldots x_{N_i}) \,. \tag{2}$$

In equations (1) and (2), the use of two indices on the target wavefunction is to allow for inclusion of target states of the same symmetry which are represented by a single set of configurations, η_{im}. The index n therefore runs over the N_i states of symmetry i included in (1). The coefficients c_{imn} are obtained as part of a standard electronic structure calculation, although for scattering calculations it is necessary to ensure phase consistency with the full $(N+1)$-electron scattering wavefunction (Orel *et al* 1991).

Put crudely, the size of expansion (2) determines the quality of the target wavefunction.

The variational coefficients a_{ijk} and $b_{\ell k}$ in (1) are obtained by diagonalizing a Hamiltonian matrix. However, matrix elements of this Hamiltonian are constructed initially in terms of the individual configurations making up the target states of interest:

$$\begin{aligned} H_{imj,i'm'j'} &= \langle \eta_{im} u_{ij} | \hat{H} | \eta_{i'm'} u_{i'j'} \rangle \\ &= \sum_{\alpha} C^{\alpha}_{imj,i'm'j'} X(I^{\alpha}_{imj,i'm'j'}) \,. \end{aligned} \tag{3}$$

In equation (3), the sum runs over the integrals required to construct the matrix elements; the C^{α} are the coefficients multiplying each integral; I^{α} are indices, constructed in terms of orbital numbers, which can be used to point to the required location in integral array X. Initially the matrix elements are constructed only at the symbolic level in terms of C^{α} and I^{α}. The algorithm developed here works with these symbolic matrix elements.

To illustrate what is meant by (3) a concrete example of electron scattering from molecular hydrogen will be used. Consider the configuration $1\sigma_g^2 5\sigma_g^1$, where the $5\sigma_g$ orbital is the first of two σ_g prototype continuum orbitals, see below. This configuration is designated $\Gamma_1, m = 1, j = 1$ below (see table 1); its diagonal matrix element comprises five integrals.

Table 1. Indices used to label the matrix elements of (i) the prototype Hamiltonian matrix, $\mathbf{H}$, and (ii) the contracted Hamiltonian matrix, $\tilde{\mathbf{H}}$.

		Range	
Index	Purpose	(i)	(ii)
j_i	Continuum orbital index	1, 2	$1, 2, \ldots, J_i$
γ_i	Continuum orbital symmetry	[a]	[a]
Γ_i	Target state symmetry	[a]	[a]
i	Index of target state symmetries	$1, 2, \ldots$	$1, 2, \ldots$
m_i	Index of target configurations	$1, 2, \ldots, M_i$	[b]
n_i	Index of target states of symmetry Γ_i	[b]	$1, 2, \ldots, N_i$
l	Index of 'L^2' configurations	$1, 2, \ldots, L$	$1, 2, \ldots, L$

[a] Symmetry of the continuum orbitals, γ_i, is given by the relationship $\Gamma_i \otimes \gamma_i = \Gamma$, where Γ is the total symmetry of the $N+1$ electron state. Note that target states which can couple to two continuum symmetries, for a given Γ, are treated as two independent states.

[b] Not applicable.

Two of these integrals, labelled 0 1 0 1 and 0 5 0 5, are identified by the leading zero as one-electron integrals. These integrals over a single electron coordinate run over the electron kinetic energy operator and electron–nuclear potential. The other integrals, labelled 1 1 1 1, 5 5 1 1 and 5 1 5 1, are two-electron integrals which involve the electron–electron repulsion potential.

In these labels, the non-zero integers correspond to orbital numbers in a scheme which numbers all orbitals sequentially. In practice it is computationally inefficient to store each integral label as four integers and these are packed into a single integer (Bauschlicher and Lengsfield 1981) giving the indices, I^{α}, 65 537, 327 685, 16 843 009, 24 214 017 and 83 952 897, respectively. The corresponding coefficients, C^{α}, are 2.0, 1.0, 1.0, 2.0 and -1.0. In general these coefficients are not integers.

The matrix elements constructed in (3) are not those required. It is necessary to transform these matrix elements to ones written in terms of the CI target wavefunctions given in (1).

$$\begin{aligned}\tilde{H}_{inj,i'n'j'} &= \langle\phi_{in}u_{ij}|\hat{H}|\phi_{i'n'}u_{i'j'}\rangle = \sum_{m,m'} c_{imn}c_{i'm'n'}H_{imj,i'm'j'}\\ &= \sum_{\beta} D^{\beta}_{inj,i'n'j'}X(I^{\beta}_{ij,i'j'})\end{aligned} \tag{4}$$

where D^{β} and I^{β} are the coefficients and indices of the contracted symbolic matrix elements. As the number of target states used is usually considerably less than the number of terms in the CI target expansion ($N_i \ll M_i$), this transformation leads to a substantially reduced Hamiltonian matrix, $\tilde{\mathbf{H}}$. For this reason, this step will be referred to as the CI contraction.

The matrix elements given in (3) and (4) only involve the first expansion in (1). Matrix elements involving the L^2 terms in (1) undergo at most only a partial CI contraction. This form will be given explicitly below.

In the present UK R-matrix codes (Gillan *et al* 1995), the CI contraction is performed on the actual full Hamiltonian matrix. As this matrix can get very large, this procedure is computationally undesirable. However, in the procedure outlined above it is the generation, storage and ordering of the symbolic matrix elements which is the computational bottleneck.

2.2. Prototype treatment of symbolic matrix elements

One method, originally proposed by Liu and Yoshimine (1981) and further developed by Liu and Lengsfield (1991), of speeding up the generation of symbolic matrix elements is by the use of prototype configurations. These workers noted that configuration lists generated in many calculations contain groups of similar configurations differing, for example, only by the occupancy of a single orbital. A feature of these configurations is that their matrix elements have similar symbolic lists for which the number of integrals and their coefficients are the same. Liu and co-workers showed that the matrix elements involving such configurations could be generated from only one or two prototype configurations by manipulating the integral indices I^{β}.

Morgan and Tennyson (1993) and Noble (1994) realized the importance of these prototype configurations in scattering calculations. Prototype configurations arise naturally in such calculations as there are typically $J_i \sim 20$–60 continuum functions multiplying each target state in expansion (1).

Thus, for example, the integrals arising from the $1\sigma_{\rm g}^2 5\sigma_{\rm g}^1$ diagonal element can be used to generate integrals for the diagonal element of configurations of the general type $1\sigma_{\rm g}^2 j\sigma_{\rm g}^1$ where $j = 5, 6, \ldots, 44$ in the actual calculations presented below. In this case the coefficient vector is independent of j and the unpacked integral labels are simply given by 0 1 0 1, 0 j 0 j, 1 1 1 1, j j 1 1 and j 1 j 1.

Morgan and Tennyson gave an algorithm based on symbolic matrix elements generated using the first two continuum functions in any expansion as prototypes. Their new procedure allowed them to increase significantly the size of CI target expansion to be used. The algorithm presented here uses many of the features of Morgan and Tennyson's, but it has been reworked to remove the redundancies implicit in always computing the symbolic matrix elements for two prototype configurations in each group.

2.3. CI contraction

To improve significantly on the prototype CI method of Morgan and Tennyson, it is necessary to address the problem of how best to perform the transformation of the full Hamiltonian into the CI contracted one.

Besides the method detailed above there are at least three other possible stages in the calculation at which the CI contraction can be performed. These are (i) on the initial configuration list, (ii) on the symbolic matrix elements and (iii) on the prototype symbolic matrix elements.

Contracting the initial configuration list is a superficially attractive option since, unlike any of the alternatives, the contraction can be performed in one dimension. However, the resulting 'super-configurations' no longer obey Slater's rules (Szabo and Ostlund 1982) and thus the evaluation of matrix elements becomes considerably more complicated. It may be possible to recover much of the simplicity given by Slater's rules by treating each determinant separately, but this would still lead to repeated integral evaluations whenever more than one target state of the same symmetry is included in the calculation.

Contraction of the symbolic matrix elements has some immediate advantages because it means that the full ($(\sum_i J_i \times M_i)$-dimensional) Hamiltonian need never be explicitly evaluated. However, the symbolic matrix elements often contain several integrals so this procedure may be slower than working with the matrix elements after evaluation.

However, there are $\sim J^2$ fewer prototype matrix elements than actual matrix elements. Contraction of the prototype symbolic matrix elements allows full advantage to be taken of both the contraction and expansion procedures. This is because the expansion of the prototype matrix elements leads to repeated integral labels, I^α, all with the same coefficients, whereas the presence of many target states of the same symmetry leads to repeated symbolic matrix element coefficients, C^α, which multiply the same integrals.

2.4. Contracted prototype matrix elements

In essence the algorithm used here starts with the minimal list of prototype symbolic matrix elements, as represented by the integral labels I^α and coefficients C^α. A set of contracted prototype symbolic matrix elements is constructed as a list of labels, stacked in I^β, and coefficients, generated using formulae of the general form

$$D^\beta_{inj,i'n'j'} = \sum_{m,m'} c_{imn} c_{i'm'n'} C^\alpha_{imj,i'm'j'} \, . \tag{5}$$

Specific formulae are given in the next section.

The list (D^β, I^β) is then expanded into the full set of symbolic matrix elements for the contracted Hamiltonian by analysing the labels list I^β and generating appropriate labels for all the continuum orbitals in the calculation. Although this algorithm sounds reasonably straightforward its actual application requires the symbolic matrix elements to be broken up into classes which are then analysed separately. The details of this are given in the next section.

3. Detailed algorithm

3.1. General considerations

The discussion of the previous section implies that all the prototype symbolic matrix elements are generated at once. For a large calculation such a procedure would place a strain on computer storage and is clearly undesirable. In practice the matrix construction is divided up into a series of classes. For each class the prototype symbolic matrix elements are generated in turn and their contribution to the contracted prototype symbolic matrix element is evaluated and stored using formulae like (5). Once all the contributions to a particular set of prototype symbolic matrix elements, grouped by (n, n'), have been processed, these are expanded to give the complete set of contracted symbolic matrix elements for that class from which the desired Hamiltonian can be computed.

In principle the final list of symbolic matrix elements can written to disk, sorted and combined with a 'tape' of integrals (Yoshimine 1973) in what can be regarded as the traditional CI method in quantum chemistry. In practice here it was decided to assume that the entire integral list, designated as X above, could be held in memory. This means that at this stage relevant Hamiltonian matrix elements can be explicitly evaluated and stored for later diagonalization.

3.2. Contraction and expansion of prototypes

As the Hamiltonian matrix is real symmetric, it is only necessary to consider a lower triangle of this matrix. In the most general case there are eight different classes of matrix elements

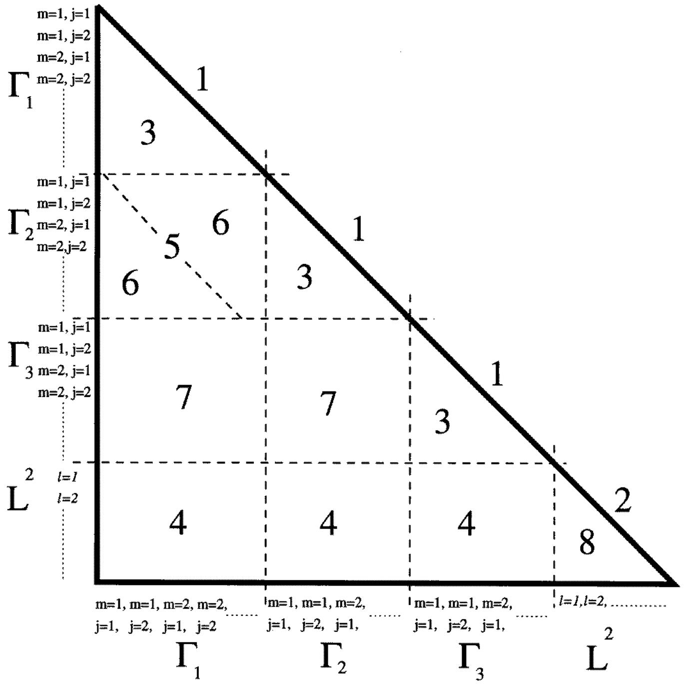

Figure 1. Structure of the uncontracted Hamiltonian matrix, **H**, for a calculation with target states of three symmetries (Γ_1, Γ_2, Γ_3) and L^2 functions. Target symmetries Γ_1 and Γ_2 couple to the same continuum functions. The numbers refer to classes of symbolic matrix elements as discussed in the text.

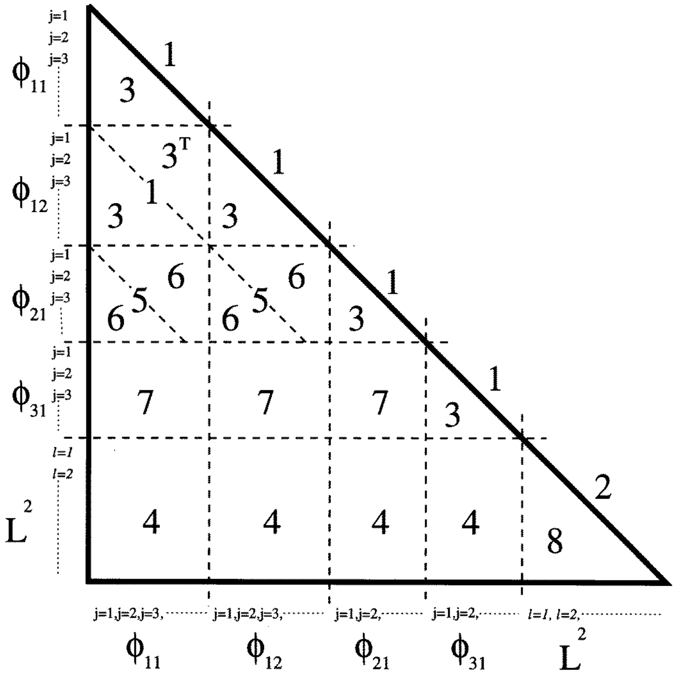

Figure 2. Structure of the contracted Hamiltonian matrix, $\tilde{\mathbf{H}}$, for a calculation with four target states, two of the same symmetry (ϕ_{11} and ϕ_{12}), and L^2 functions. Target states ϕ_{11}, ϕ_{12} and ϕ_{21} all couple to the same continuum functions. The numbers refer to classes of symbolic matrix elements as discussed in the text.

which need to be considered. These classes are illustrated schematically in figure 1 for the simplest case which gives rise to all eight classes: a calculation involving target states of three different symmetries but where two of the target symmetries, Γ_1 and Γ_2 in figure 1, couple to continuum orbitals with the same symmetry. An example of such a situation would be an electron–H_2 scattering calculation with ${}^2\Sigma_g^+$ overall symmetry and a close-coupled expansion with target states of symmetry ${}^1\Sigma_g^+$, ${}^3\Sigma_g^+$ and ${}^1\Pi_u$, which would couple to continuum orbitals of σ_g, σ_g and π_u symmetries, respectively.

As the classes of matrix elements map between the prototype uncontracted matrix and the final contracted matrix, this latter matrix also has eight classes of matrix elements. The simplest situation showing all possible structures is the three target symmetry case depicted in figure 1 where for one symmetry there are two target states included in the close-coupled expansion. Figure 2 depicts the schematic structure of the final matrix when two states of the first symmetry and one of the others are included in the close-coupling expansion.

The eight classes of matrix elements are considered in turn below. They are obtained by splitting up the intitial list of configurations into those depending on target states of different symmetry. In order to seed the prototype symbolic matrix element generation, configurations are generated based on an expansion with two prototypical continuum orbitals. Unlike the algorithm of Morgan and Tennyson (1993), only the minimal set of prototype symbolic matrix elements is actually evaluated.

Table 1 defines the various indices and parameters used in the contraction/expansion step presented below.

Class 1. 'Diagonal' elements involving continuum orbitals. For these elements $i = i'$ and

$j = j'$ in both $\mathbf{H}$ and $\tilde{\mathbf{H}}$; but as, in $\tilde{\mathbf{H}}$, n does not have to equal n' some of the resulting contracted elements do not lie upon the diagonal. Furthermore, these 'diagonal' elements of the contracted Hamiltonian contain contributions from matrix elements which are diagonal in the continuum orbitals but off-diagonal in configurations making up the target. It is therefore necessary to consider two contributions; this is done in two stages using the scheme

$$\tilde{H}_{inj,in'j'} = \sum_m c_{imn}c_{imn'}H_{imj,imj'} + \sum_{m>m'}(c_{imn}c_{im'n'} + c_{im'n}c_{imn'})H_{imj,im'j'} \tag{6}$$

with $j = j' = 1$. This prototype symbolic matrix element then gives all diagonal (and diagonal of the off-diagonal block) elements for the given target symmetry labelled $j = j' = 1, J_i;\ n = 1, N_i;\ n' = 1, n$.

Class 2. Diagonal elements not involving continuum orbitals. The L^2 diagonal elements do not undergo either contraction or expansion, although this point is discussed below. They are therefore evaluated directly using the standard algorithm.

Class 3. Off-diagonal elements within a given target symmetry. In this case $i = i'$ but $j = 2,\ j' = 1$ in $\mathbf{H}$; the contracted prototype symbolic matrix element is generated using (6). This prototype element is expanded to the entire lower triangle blocks for the given target states using $j = 2, J_i;\ j' = 1, j-1;\ n = 1, N_i;\ n' = 1, n$. For $n = n'$, these are all that is required. For $n > n'$, an upper-triangle of the off-diagonal block is also required; this is the transpose of the corresponding lower triangle and is marked 3^T in figure 2. The upper triangle elements are obtained simply by relabelling the lower triangle ones once they have been finally evaluated.

Class 4. Off-diagonal elements between a continuum and an L^2 configuration. For these elements the contraction is only one-dimensional

$$\tilde{H}_{inj,\ell} = \sum_m c_{imn}H_{imj,\ell} \tag{7}$$

where ℓ is used to denote an L^2 configuration. A single prototype with $j = 1$ is expanded to give all off-diagonal elements between target states of symmetry Γ_i and configuration ℓ using $j = 1, J_i;\ n = 1, N_i$.

Class 5. 'Diagonal' off-diagonal elements between continua of the same symmetry. The situation where two target states of different symmetry ($\Gamma_i \neq \Gamma_{i'}$) couple to continua of the same symmetry ($\gamma_i = \gamma_{i'}$) has to be treated as a special case. In particular extra integrals can arise for the diagonal ($j = j'$) case (class 5) which do not occur for the off-diagonal ($j \neq j'$) case (class 6). The contraction step is

$$\tilde{H}_{inj,i'n'j'} = \sum_{m,m'} c_{imn}c_{i'm'n'}H_{imj,i'm'j'} \tag{8}$$

with $j = j' = 1$. This prototype element is expanded along the diagonal of the block linking target states ϕ_{in} and $\phi_{i'n'}$. If the number of continuum orbitals associated with each of these target states differs, then this block is rectangular and the diagonal is defined by those elements for which $j = j'$. Thus the full set of elements is given by $j = j' = 1, \min(J_i, J_{i'});\ n = 1, N_i;\ n' = 1, N_{i'}$.

Class 6. 'Off-diagonal' off-diagonal elements between continua of the same symmetry. The remaining elements in the block discussed under class 5 are also formed from a prototype constructed using (8) but with $j = 2,\ j' = 1$. This prototype symbolic matrix element is then expanded into all off-diagonal locations in the block using $j = 1, J_i;\ j' = 1, J_{i'}$ with $j \neq j';\ n = 1, N_i;\ n' = 1, N_{i'}$.

Class 7. Off-diagonal elements between continua of different symmetry. Here $\gamma_i \neq \gamma_{i'}$, and thus j and j' label different orbitals by construction. Only a single contracted prototype symbolic matrix element is constructed from $j = 1, j' = 1$ using (8). This element is then expanded over the entire block using $j = 1, J_i;\ j' = 1, J_{i'};\ n = 1, N_i;\ n' = 1, N_{i'}$.

Class 8. Off-diagonal elements between L^2 configuration. There is no contraction or expansion for these matrix elements which are simply evaluated in the normal way.

3.3. Integrals

Even with the algorithm given above, the calculation involves the manipulation of, and table look-ups for, many integrals. Possible computational savings in this area should also be investigated. Two ways of reducing the integral lists have been identified and implemented.

During any of the CI contraction steps discussed above, lists of integrals, identified symbolically by a packed index I^α and coefficient C^α, are merged. In practice these lists are built up progressively as each target CI configuration which contributes to a particular prototype symbolic matrix element is processed.

When a new integral is added to the list, the list is inspected to see if the integral is already contained in the list. This is done by direct comparisons of the I^α coefficients, comprising the packed integer orbital labels, information about which is not required for this comparison. If the integral is already on the list then the weighted coefficients are simply summed; if not the new integral is added to the end of the list. This process will be referred to as integral compression.

Thus, for example, the $1\sigma_g^1 2\sigma_g^1 5\sigma_g^1$ configuration contributes to the same contracted diagonal elements as the $1\sigma_g^2 5\sigma_g^1$ configuration discussed previously. The new configuration gives four of the integrals discussed above, 0 1 0 1, 0 5 0 5, 5 5 1 1 and 5 1 5 1 with coefficients 1.0, 1.0, 1.0 and −0.5, respectively. A further five new integrals arise with labels 0 2 0 2, 2 2 1 1, 5 5 2 2, 2 1 2 1 and 5 2 5 2, and coefficients 1.0, 1.0, 1.0, 1.0 and −0.5, respectively. In the sample calculations detailed below, the lowest two ${}^1\Sigma_g^+$ target states of H_2, the coefficients of the CI expansion (2) of the $1\sigma_g^2$ and $1\sigma_g^1 2\sigma_g^1$ state are 0.9914 and −0.0007 for the ground electronic state, and 0.0017 and −0.9816 for the excited state. The merged coefficients are weighted by these CI coefficients.

As large target CIs may generate long integral lists, this search could, in principle, be slower than evaluating a few extra integrals. However, as these lists are constructed at the prototype stage of the calculation, prior to expansion, this procedure should always lead to savings.

The other reduction technique is more radical and is based directly on the structure of the wavefunction of the problem (1). Consider only the portion of the Hamiltonian matrix constructed from functions of the form target wavefunction times continuum function, i.e. the terms in the first sum in (1). The submatrix arising from the target wavefunctions, i.e. neglecting the extra terms from the continuum electron, is simply a diagonal matrix whose elements are the energy of the relevant target state.

It is possible to take advantage of this property, for matrix elements not involving L^2 configurations, by removing all integrals consisting of only target orbitals from the calculation. Thus half the integrals in the examples discussed above, those labelled 0 1 0 1, 0 2 0 2, 1 1 1 1, 2 2 1 1 and 2 1 2 1, need never be considered in the scattering calculation.

In return it is only necessary to adjust the corresponding diagonal elements by the energy of the CI target. This has already been calculated during the generation of the target wavefunction used for the contraction. In practice it is possible to adjust the symbolic matrix element generation step to skip all consideration of pure target integrals. The present version of the code has this as a user controlled option. The new atomic *R*-matrix code, RMATRX II, uses a similar procedure to skip target integrals (Burke *et al* 1994).

4. Sample applications and discussion

The algorithm described above has been implemented as a new module, SCATCI, in the UK molecular *R*-matrix program suite. Previously this suite used ALCHEMY I (McLean 1971, Yoshimine 1973) based programs to construct and diagonalize the Hamiltonian matrix.

Test calculations have been performed for electron scattering from molecular hydrogen, based on those presented by Branchett *et al* (1990). In particular, test results using different methods of calculation are presented in table 2 for a calculation involving five target states: X $^1\Sigma_g^+$ and E, F $^1\Sigma_g^+$ based on 28 configurations; c $^3\Pi_u$ and B $^1\Pi_u$ with 21 configurations each, and a $^3\Sigma_g^+$ with 15 configurations. Calculations were performed for both $^2\Sigma_g^+$ and $^2\Pi_u$ total symmetry. The σ_g and π_u continua were represented by 40 and 28 orbitals, respectively. All calculations gave the same eigenvalues of the CI matrix to all figures printed (10^{-10} Hartree).

Table 2 shows that the new procedure is much faster. The various steps discussed above lead to a very significant reduction in the number of matrix elements that need to be considered and the number of integral look ups that need to be performed.

The statistics in table 2 may well be typical but the nature of the calculation serves to mask somewhat the source of these savings. This is because over half, 182 for $^2\Sigma_g^+$ and 255 for $^2\Pi_u$, the configurations retained in the final, contracted Hamiltonian matrix are L^2. Of course, these represent less than 10% of all the configurations considered in generating the Hamiltonian, a proportion one would expect to drop further as the length of the target CI expansion is increased.

For this reason some test calculations were performed which neglected all L^2 configurations. These calculations are not physical in the sense that they cannot be used as the basis of reliable scattering calculations but, as sample results given in table 3 show, they do illustrate the strengths of the current procedure.

Table 2. Comparison of statistics for Hamiltonian construction and diagonalization for two typical electron–H_2 scattering calculations. A uses the standard ALCHEMY I programs (McLean 1971, Yoshimine 1973), method B uses SCATCI with all target integrals included and method C uses SCATCI with pure CI target integrals omitted.

	(*a*) $^2\Sigma_g^+$			(*b*) $^2\Pi_u$		
	A	B	C	A	B	C
Number of configurations generated	3 078	352	352	3 139	425	425
Contracted Hamiltonian dimension	358	358	358	418	419	419
Total number of matrix elements	473 851	64 261	64 261	4928 230	87 990	87 990
Non-zero prototype matrix elements		8 381	8 381		14 999	14 999
Non-zero matrix elements	1218 117	55 245	55 245	1325 949	87 990	87 990
Prototype integrals		32 547	30 391		48 496	46 340
Compressed prototype integrals		29 678	27 843		45 619	43 784
Number of integrals required	2300 692	953 427	891 139	2401 162	1050 164	987 672
CPU time (s)	1 399	70	71	1 188	84	82

Table 3. Comparison of statistics for Hamiltonian construction and diagonalization for a $^2\Sigma_g^+$ symmetry electron–H_2 scattering calculations with no L^2 configurations. A uses the standard ALCHEMY I programs (McLean 1971, Yoshimine 1973), method B uses SCATCI with all target integrals included and method C uses SCATCI with pure CI target integrals omitted.

	A	B	C
Number of configurations generated	2 896	170	170
Implied number of matrix elements	4194 856	14 535	14 535
Contracted Hamiltonian dimension	176	176	176
Non-zero prototype matrix elements		16	16
Non-zero matrix elements	1023 376	15 576	15 576
Prototype integrals		5 270	3 144
Compressed prototype integrals		2 784	949
Number of integrals required	1914 959	583 876	521 588
CPU time (s)	1 177	43	39

Table 3 shows that instead of considering the full lower triangle of a matrix of dimension 2896 × 2896, all the elements can be summarized using just 16 contracted matrix elements. Furthermore, even evaluation of the full matrix only requires about 30% of the integral look-ups required by the traditional procedure.

Table 2 suggested that integral compression and omission of pure target integrals led to little saving. However, table 3 shows that for the portions of the matrix not involving L^2 configurations this is not so. Using both these procedures reduces the initial prototype integral list to less than 20% of its original length. The effect on the total number of integral look-ups required is less marked. This is because the largest savings in both procedures is in the evaluation of the diagonal elements, but the final statistics are weighted heavily by the much more numerous but simpler off-diagonal elements. It should be remembered that the present tests are only for a two-electron target, H_2. For targets with more electrons, even greater savings are to be expected.

The above has implied that L^2 orbitals and continuum functions are somehow different and must always be treated as such. This is not strictly true. It is common practice in R-matrix calculations (Morgan and Tennyson 1993, Gillan *et al* 1996) to include extra (virtual) target orbitals to allow both for relaxation of the constraints which ensure that the continuum orbitals are orthogonal to the target orbital set (Tennyson *et al* 1987) and for high partial waves in the region of the nuclear singularities. These ‘correlation’ orbitals, if they are only singly occupied, can be treated as if they are continuum orbitals simply by altering how the prototype symbolic matrix elements are expanded. This procedure automatically contracts the correlation configurations with the CI target wavefunction ensuring that no artificial extra target correlation effects are introduced into the calculation.

5. Conclusions

A new algorithm has been developed for performing electron scattering calculations from molecules whose wavefunctions are represented using configuration-interaction (CI) expansions. This algorithm exploits both the implicit structure of the wavefunction expansions used in most techniques for treating electron–molecule collisions and the fact that the Hamiltonian matrix being constructed depends on target wavefunctions, not the individual configurations of this wavefunction.

This new algorithm re-orders the calculation so that Hamiltonian matrices of dimension length of continuum orbital expansion times number of target configurations need never be explicitly addressed. This means that calculations using both a greater number of target states and better representation of these target states will now be feasible. This should result in a concomitant improvement in the accuracy and range of problems that can be addressed by these calculations. The new code, SCATCI, is being used to study electron–NO^+ collisions where it has been found to be some 200 times faster than our old code (Rabadan and Tennyson 1996).

Acknowledgments

I thank the UK Collaborative Computational Project 2 (CCP2) for supporting discussions with several people in the course of this work. In particular I thank Cliff Noble for helpful discussions at the outset of the project and for pointing out the possibility of dropping the target integrals, and Charles Gillan for discussions on integral handling. I thank Darian Stibbe for help with the test runs and for many helpful comments on this manuscript. This work was supported by the UK Engineering and Physical Science Research Council, and the National Science Foundation through a grant for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory.

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