The partitioned R-matrix method

Jonathan Tennyson and Gabriela Halmova
Department of Physics and Astronomy,
University College London, London WC1E 6BT, UK

Introduction

The R-matrix method is a well established computational procedure for treating electron collisions with atoms and molecules [1]. The basis of the method is the division of space into two regions: an inner region, defined by a sphere of radius a, typically 10 to 15 a_0 for molecular problems, and an outer region. The inner region must contain the entire electron density of the target system which means that it is only in this region that complicated correlation and exchange processes need to be treated in detail. The R-matrix, defined below, provides the link between the two regions.

In order to solve the inner region problem, which does not depend on the precise scattering energy of the electron, it is necessary to find solutions of the inner region Hamiltonian. This is usually done by expressing the vavefunction as a linear combination of configuration spin functions (CSFs), see [2], and diagonalising the resulting secular matrix problem. The eigenvalues, E_k, and eigenvectors are used to construct the R-matrix on the boundary a:

$$R_{il,i'l'}(a,E) = \sum_{k=1}^{M} \frac{w_{ilk}(a)w_{i'l'k}(a)}{E_k - E} + \delta_{ii'}\delta_{ll'}R^B_{il} \tag{1}$$

where $w_{ilk}(a)$ is the amplitude of partial wave l associated with target state i in eigenvector k at a. E is the scattering energy and R^B_{il} is the Buttle correction which can be introduced to correct for the incompleteness of the continuum basis in the inner region [1].

A serious computational drawback of this procedure is that the construction of $R_{il,i'l'}(a,E)$ requires all M solutions of the M-dimensional secular matrix. Since computer time for diagonalising a matrix increase as M^3 and the memory requirement increases as M^2, this puts a significant constraint on problems that can be addressed.

In practice many of the inner region solutions lie at energies which are very significantly higher than the scattering energy of interest. This is particularly true for problems involving electron collisions with molecules where the region of interest is usually for electron collision energies below 20 eV.

Berrington and Ballance (BB) [3] derived a "partitioned R-matrix method" which only explicitly uses the lowest P inner region solutions and then approximated the higher solutions. Unfortunately the practical test given by BB required P to be about half M to give good results. This is too many solutions to provide any significant computational saving. This method was subsequently re-analysed and an alternative formulation of the partitioned R-matrix method was given by Tennyson [4]. These methods are discussed below.

Partitioned R-matrix theory

In BB's partitioned R-matrix method the R-matrix on the boundary is approximated as

$$R_{il_i,i'l_{i'}}(a,E) = \sum_{k=1}^{P} w_{ilk}(a)w_{i'lk}(a)\left(\frac{1}{E_k - E} - \frac{1}{E_0 - E}\right)$$

$$+\,\delta_{ii'}\delta_{ll'}\left(\frac{s_{il}}{E_0 - E} + R^B_{il} + R^C_{il}\right) \tag{2}$$

where R^C_{il} is an error correction term discussed below. E_0 is an average or effective energy for the poles omitted when only the lowest P solutions are explicitly considered; it is defined as:

$$E_0 = \frac{(\sum_{I=1}^{M} H_{I,I} - \sum_{k=1}^{P} E_k)}{M - P}, \tag{3}$$

where the first sum is simply the trace of the Hamiltonian matrix. In (2), s_{il} is the total probability distribution of a given channel on the R-matrix boundary

$$s_{il} = \sum_{j=1}^{n_{il}} (u_{ilj}(a))^2, \tag{4}$$

where $u_{ilj}(a)$ is the amplitude of the jth function used to represent the continuum electron inside the R-matrix box, see [5] for example. BB's error correction term was also expressed as a function of these quantities:

$$R^C_{il} = \sum_{j=J_i}^{n_{il}} (u_{ilj}(a))^2 \left(\frac{1}{E_{ilj} - E} - \frac{1}{E_0 - E}\right). \tag{5}$$

where BB defined E_{ilj} as the energy of the continuum function $u_{ilj}(x)$ and the sum runs over those states for which $E_{ilj} > E_P$, the energy of the highest pole explicitly considered.

Tennyson [4] identified two problems with this formulation. The first was that the definition of E_0 was such that it increases as more L^2 terms are added to the inner region wavefunction expansion as most of these tend to be high in energy. However such terms have zero amplitude at a and therefore do not contribute to the R-matrix. Secondly BB's error correction term over-corrected since s_{il} summed all the probability for a channel even if some of this probability had already been accounted for in the P terms explicitly considered in the sum. Finally for molecular problems he observed that the energy of a continuum basis function is not really well defined. This latter problem was solved by using the appropriate diagonal element of the Hamiltonian matrix instead.

Tennyson redefined the effective energy, E_0, as the average of those diagonal elements of the Hamiltonian matrix between continuum orbitals, $H_{ilj,ilj}$, which are not among the lowest P diagonal elements, ie for $H_{ilj,ilj} > E_P$. This definition leaves E_0 unaffected by increasing the number of purely L^2 functions used. Secondly, he estimated the contribution of the continuum orbitals to the states not explicitly included in the sum (2) as:

$$X_{ilj} = 1 - \sum_{k=1}^{P} c_{iljk}^2. \tag{6}$$

where c_{iljk} is the coefficient of continuum orbital u_{ilj} in the kth eigenvector. This factor is then used to define a new error correction formula:

$$R_{il}^C = \sum_{j=J_i}^{n_{il}} (u_{ilj}(a))^2 X_{ilj} \left(\frac{1}{H_{ilj,ilj} - E} - \frac{1}{E_0 - E} \right). \tag{7}$$

Test calculations

In the initial work [4] tests were performed against previous calculations on electron collisions with water [6] and CF_2 [7]. These showed that not only did the reformulated theory perform very significantly better than the original theory but also the goal of getting good results for the case where P is 10 % or less of M was indeed achievable for low-energy (below 20 eV) studies. However these initial studies by their nature were all performed on problems for which it was possible to obtain all M eigenvalues and eigenvectors.

Recently we have been considering calculations on electron collisions with the C_2^- anion for collision energies of about 10 eV. Given that the electron detachment energy for this anion is below 5 eV, such calculations can only performed using a method capable of treating the double continuum. Gorfinkiel and Tennyson [8, 9] introduced a molecular R-matrix with pseudo states (MRMPS) procedure for treating precisely this class of problem. However their

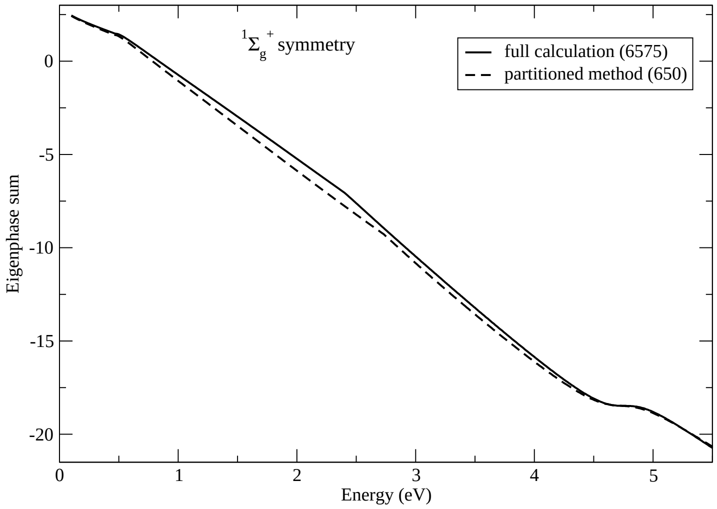

FIG. 1: Eigenphase sums for electron scattering from C_2^- for a full calculation (solid curve) and a partitioned R-matrix calculation (dashed curve).

applications of the MRMPS procedure were only to two electron targets (H_3^+ and H_2). Attempts to use the procedure for many electron targets have proved difficult because of the very large number of configurations that need to be treated as a result of trying to treat the double continuum even if it is discretised by being localised inside a box.

We have therefore combined the MRMPS method with the partitioned R-matrix method to treat the problem of electron collisions with C_2^-. Figure 1 shows some test results for one of the smaller wavefunctions that we considered. Eigenphases are shown calculated using the full, $M = 6575$, solutions and with less than 10 % of that number, $P = 650$. It can be seen that the results are very similar. Indeed the resonance feature just below 5 eV is essentially unmoved between the two calculations. This result is typical of the more extensive (in both energy range and number of states P) tests that we have performed.

Conclusions

The reformulation of the partitioned R-matrix method [4] provides a viable way of performing calculations on problems which are too large for full diagonalisation of the inner region Hamiltonian matrix to be computationally tractable. We are currently using this method to perform calculations on the electron impact detachment of C_2^- using molecular R-matrix with pseudo states models which give Hamiltonian matrices of dimension $M \sim 100,000$. For such calculations the partitioned R-matrix method represents a major saving. This is particularly true because the proportion of solutions required drops well below 10 %, indeed we anticipate obtaining good results with calculations which explicitly consider only about 1 % of the solutions of inner region Hamiltonian matrix.

P, the number of solutions explicitly obtained, is critical for the computational performance of the method but is perhaps the wrong parameter to focus on physically. Physically the important parameter is probably the energy span of the solutions which are explicitly calculated, as to get a good calculation it is clearly important to span the energy regime of the colliding electron. In this sense the key parameter should therefore be the eigen energy of solution P, E_P. Our calculations on the C_2^{2-} system show that to get stable results for collisions energies of 15 eV, E_P should be at least 40 eV.

Finally we note one computational issue with implementing the partitioned R-matrix method. The outer region of the UK R-matrix codes is written in a highly modular fashion [10]. Communication between the various modules, which perform tasks such as R-matrix propagation [11, 12] or resonance fitting [13], is achieved via a series of small input/output subroutines [10]. The partitioned R-matrix method requires significant extra information to be passed between these modules so that the error-corrected partitioned R-matrix can be constructed. The re-write of the communications routines makes it difficult for the new codes to be backwards compatible. There is no such problem with the only inner region code that needs amending, SCATCI [2].

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