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Partitioned *R*-matrix theory for molecules

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Abstract

R-matrix calculations usually require all the eigenvalues and eigenvectors of the inner region Hamiltonian matrix. For molecular problems, particularly when large configuration interaction expansions are used for the target, the Hamiltonian matrix is often too large to be completely diagonalized. Berrington and Ballance (2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 2275) proposed a partitioned *R*-matrix theory which only required a proportion of the solutions of the Hamiltonian matrix. This theory was implemented and tested in the atomic *R*-matrix code. The theory is adapted to the needs of *R*-matrix calculations on low-energy electron–molecule collisions. A number of alternative procedures are tested. The best is shown to give reliable results with explicit inclusion of only a fraction of the solutions. It is shown that with this revised theory the number of solutions required does not depend on the complexity of the target wavefunction even though this strongly influences the size of the final Hamiltonian matrix. This method will be implemented as part of the UK molecular *R*-matrix program suite.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electron–molecule collisions and the related process of molecular photoionization are important in all environments containing cold plasmas. The theory of low-energy electron–molecule collisions has made rapid advances and a number of methods are available to tackle problems of interest (Huo and Gianturco 1995). Prominent among these is the *R*-matrix method (Burke and Berrington 1993).

The *R*-matrix method relies on splitting configuration space into an inner and outer region. In the inner region the full electron–molecule problem is solved using basis sets. The resulting calculations are performed with adapted quantum chemistry codes but differ from standard quantum chemistry calculations both in the structure of the wavefunction and in the requirements of the *R*-matrix method. In particular, in standard *R*-matrix theory all solutions, i.e. eigenvalues and eigenvectors, of the Hamiltonian matrix must be explicitly computed.

This requirement acts as a strong constraint on the size of problem that can practically be tackled, see Tennyson (1996b) and Rozum *et al* (2003), for example.

Recently Berrington and Ballance (2002), henceforth BB, proposed a partitioned *R*-matrix theory. The major advantage of BB's theory is that it does not require all solutions of the Hamiltonian matrix to construct R-matrices which can be used to give reliable results up to a given electron collision energy. BB proposed not only a basic partitioning scheme but also considered a method for error correction. They also considered the energy derivative of the *R*-matrix and dipole matrix elements, topics that will not be addressed here. BB implemented their theory for the atomic *R*-matrix code and tested it for electron collisions on O^{7+}. Their tests consider rather high collision energies, over 1000 eV. Possibly as a consequence of this, BB retained between 40% and 60% of their solutions for their partitioned *R*-matrix.

Pfingst *et al* (1994) proposed an alternative molecular *R*-matrix procedure which only required the explicit calculation of selected low-lying roots for their full Hamiltonian matrix. Higher lying roots were approximated by simpler and smaller static exchange calculations. This method has been used for studying scattering off a single electronic state for a variety of molecules, but has yet to be applied successfully to the more general problem of coupled electronic states.

In this work BB's partitioning scheme and error correction are adapted to molecular systems. To achieve significant savings in the key Hamiltonian matrix diagonalization step this theory must require less than 20% of the solutions. When considering BB's atomic partitioned *R*-matrix procedure it is important to remember that there are a number of subtle differences between electron collisions with atoms and molecules. These will be discussed in the following section which develops possible theories for a molecular partitioned *R*-matrix method. In section 3, several variations of this theory are tested for electron collisions from water and the CF_2 and CF_3 radicals. Section 4 presents conclusions and discusses the physics which underlies the preferred theory.

2. Theory

2.1. Background

In *R*-matrix theory the internal region, discretized continuum wavefunction for the electron scattering problem can be written as

$$\Psi_k^{N+1} = \mathcal{A} \sum_{i=1}^{n_t} \psi_i^N(x_1, \ldots, x_N) \sum_{l_{\min}}^{l_{\max}} \sum_{j=1}^{n_{il}} u_{ilj}(x_{N+1}) a_{iljk} + \sum_{m=1}^{n_d} \chi_m^{(N+1)}(x_1, \ldots, x_N, x_{N+1}) b_{mk}, \tag{1}$$

where $\mathcal{A}$ is the anti-symmetrization operator and x_n represents the coordinates of the nth electron. ψ_i^N is the wavefunction of the ith N-electron target state, which itself is usually represented as a configuration interaction (CI) expansion. u_{ilj} is a continuum orbital for which the dependence on the partial wave expansion, given by l, has been made explicit. For molecules this expansion over l is, in principle, infinite but in practice is usually rapidly convergent for low-energy collisions and can therefore be truncated at some fairly low value of $l_{\max}$. $\chi_m^{(N+1)}$ represents terms where all $(N + 1)$ electrons have been placed in target orbitals. The exact choice of these 'L^2' configurations is quite subtle (see Tennyson (1996b) for example) but the number of such terms, n_d, is largely determined by the choice of target CI expansion. a_{iljk} and b_{mk} are variational coefficients determined by diagonalizing the internal region Hamiltonian. The energy, E_k, associated with Ψ_k^{N+1} is usually referred to as an

R-matrix pole. By convention the energy of an R-matrix pole is zero at the energy of the target ground state. This convention is followed for the values of E_0 quoted below.

The dimension of the Hamiltonian matrix, M, is given by

$$M = n_d + \sum_{i=1}^{n_t} \sum_{l=l_{\min}}^{l_{\max}} n_{il}, \tag{2}$$

where n_t is the number of target states included in the expansion and n_{il} is the number of continuum functions implied by a given value of l and target state symmetry. The number of terms in the sum over l may also depend on the symmetry of the target state. It must be emphasized that for calculations using sophisticated target functions, n_d makes the dominant contribution to M.

An important quantity in the R-matrix method is the boundary amplitude, which is the amplitude of the internal region wavefunction on the R-matrix sphere at $r = a$. In terms of wavefunction (1) these are given by

$$w_{ilk} = \sum_{j=1}^{n_{il}} u_{ilj}(a) a_{iljk}. \tag{3}$$

The R-matrix on the boundary can be constructed in terms of these boundary amplitudes

$$R_{il,i'l'}(a, E) = \sum_{k=1}^{M} \frac{w_{ilk}(a) w_{i'l'k}(a)}{E_k - E} + \delta_{ii'}\delta_{ll'} R^B_{il}, \tag{4}$$

where E is the electron collision energy and $\mathbf{R}^B$ is the Buttle correction which is included in some circumstances to account for the truncation at n_{il} of the continuum basis set expansion (Burke and Berrington 1993). For the molecular problems, equation (4) is often written with a factor $(2a)^{-1}$ in front of the first sum. The value of this factor depends on the precise definition of the radial continuum functions and boundary amplitude. Here I follow BB and set this factor to unity.

The aim of the partitioned R-matrix theory is to rewrite equation (4) so that only $P(< M)$ solutions of the Hamiltonian matrix are explicitly required. For this method to yield significant savings, particularly in the computationally expensive matrix diagonalization step of the calculation, it is desirable that $P \ll M$.

Berrington and Ballance (2002) start their partitioned R-matrix theory by defining two quantities. The first quantity is E_0, which is an average or effective energy for the poles omitted when only the lowest P solutions are explicitly considered. It is defined by BB as

$$E_0 = \frac{\left(\sum_{I=1}^{M} H_{I,I} - \sum_{k=1}^{P} E_k\right)}{N - P}, \tag{5}$$

where the first sum runs over all the diagonal elements of the Hamiltonian matrix giving its trace. The second quantity is the total probability distribution of a given channel on the R-matrix boundary

$$s_{il} = \sum_{j=1}^{n_{il}} (u_{ilj}(a))^2. \tag{6}$$

In terms of these quantities BB derive an expression for the partitioned R-matrix

$$R_{il_i,i'l_{i'}}(a, E) = \sum_{k=1}^{P} w_{ilk}(a) w_{i'lk}(a) \left(\frac{1}{E_k - E} - \frac{1}{E_0 - E}\right) + \delta_{ii'}\delta_{ll'} \left(\frac{s_{il}}{E_0 - E} + R^B_{il} + R^C_{il}\right), \tag{7}$$

where the final term gives the error correction for which BB derived the expression

$$R_{il}^{C} = \sum_{j=J_i}^{n_{il}} (u_{ilj}(a))^2 \left(\frac{1}{E_{ilj} - E} - \frac{1}{E_0 - E} \right) \tag{8}$$

where E_{ilj} is the energy of the continuum basis function u_{ilj}. The starting point for the sum in equation (8), J_i, is chosen such that $E_{ilj} > E_P$, where E_P is the highest R-matrix pole explicitly included in the sum in equation (7).

2.2. A molecular theory

There are a number of problems with the application of the above theory directly to the molecular case. The first problem to be addressed is the definition of the energy of individual continuum orbitals, E_{ilj}. The numerical procedure used to generate continuum orbitals (Salvini 1984) for the diatomic problem, and by analogy the one used to generate Gaussian-type orbitals (GTOs) to represent the continuum for scattering from polyatomic molecules (Faure *et al* 2002), give a well-defined energy for the raw continuum orbitals. However, the need for strong orthogonalization procedures between the continuum orbitals and the molecular orbitals used to represent the target (Tennyson *et al* 1987, Morgan *et al* 1998) means that the energy of the resulting continuum molecular orbital is not well defined. In practice this can be overcome by using the relevant diagonal element of the Hamiltonian matrix $H_{I,I}$. This gives a new expression for the error correction term

$$R_{il}^{C} = \sum_{j=J_i}^{n_{il}} (u_{ilj}(a))^2 \left(\frac{1}{H_{ilj,ilj} - E} - \frac{1}{E_0 - E} \right). \tag{9}$$

This theory, which is closest to that BB tested, is called theory A below. Within this theory there is some ambiguity over how the starting point for the sum in the error correction, J_i, is defined. Possible definitions are that J_i is chosen to include all diagonal elements of the relevant continuum orbitals such that $H_{ilj,ilj} > E_P$. Alternatively, J_i can be chosen such that the P lowest diagonal elements are omitted from the sum. In principle, these two methods could give different results but tests showed that in practice the answers obtained were very similar.

A more serious problem with the direct implementation of BB's theory for molecules occurs with the definition of E_0, equation (5). This definition averages over all diagonal elements of Hamiltonian regardless of whether the configuration involved makes any contribution to the boundary amplitude. This means that the many high-lying, L^2 configurations, which by construction make no contribution to the boundary amplitude, do contribute to the value E_0. As a result, systematic improvement of the CI representation of a target, and the consequent increase in the number of L^2 configurations, will lead to a steady rise in E_0 even if all the other parameters of the calculation remain the same. This is not desirable and it would seem to be preferable to define E_0 using only those configurations which contribute directly to the boundary amplitudes and hence to the R-matrix.

Assuming that the Hamiltonian matrix is diagonally dominant, which is generally the case, one can associate the lowest P diagonal elements with the lowest P R-matrix poles. In this case, one can obtain a value for E_0 simply by averaging those diagonal elements of the Hamiltonian matrix between continuum orbitals, $H_{ilj,ilj}$, which are not among the lowest P diagonal elements. This procedure is referred to as theory B below. Note that this procedure will be satisfactory even when the values of higher lying R-matrix poles are not dominated by the diagonal elements. Such a situation can arise with large CI expansions.

There is a final problem with the error correction procedure proposed by BB and adapted as theory A above. The use of the entire boundary amplitude of the higher lying continuum orbitals, $(u_{ilj}(a))^2$, in the error correction, equation (9), will lead to an over-correction if this orbital contributes to any significant extent to the lowest P states explicitly considered in the first sum in equation (7). It is straightforward to estimate the contribution of the continuum orbital to the states not explicitly included in the sum (7) as

$$X_{ilj} = 1 - \sum_{k=1}^{P} a_{iljk}^2. \tag{10}$$

Clearly orthonormality considerations show that $X_{ilj} \to 0$ as $P \to M$. BB's original procedure assumes X_{ilj} is unity for the higher orbitals. Tests performed below found values in the range 0.8–0.9 were more typical. It was therefore decided to allow for this in the error correction formula which then becomes

$$R_{il}^C = \sum_{j=J_i}^{n_{il}} (u_{ilj}(a))^2 X_{ilj} \left(\frac{1}{H_{ilj,ilj} - E} - \frac{1}{E_0 - E} \right). \tag{11}$$

Use of this expression with theory B will be referred to as theory C below.

3. Test calculations

To test various alternative molecular partitioned R-matrix theories, calculations were performed for electron collisions with a number of polyatomic molecules. These systems, all of which have been the subject of previous studies, were chosen because the Hamiltonian matrices were large but fully diagonalizable. However, it should be noted that Rozum *et al* (2003) abandoned some possible models for electron collisions with CF_3 because of the large number of L^2 configurations which would have made it impossible to diagonalize the full Hamiltonian. In all the calculations below the Buttle correction, $\mathbf{R}^B$, is zero since it is not required by our polyatomic R-matrix code (Morgan *et al* 1997). This means that the full calculations should behave variationally.

For the tests reported below the ARPACK diagonalizer (Lehoucq *et al* 1996) was implemented in the inner region module SCATCI (Tennyson 1996a). This diagonalizer obtains the P lowest solutions of an M-dimensional Hamiltonian. Options to store the Hamiltonian matrix elements in memory if possible, or on disk if necessary were implemented. Tests showed that if $\frac{P}{M} < 0.2$, then the ARPACK diagonalizer is much quicker than diagonalizing the full matrix. As many of the Hamiltonian matrix elements are zero, this procedure is also much cheaper on memory even for cases where the whole matrix is retained in memory.

A systematic series of test calculations were performed with each theory on the three systems mentioned. For brevity only the key features of these calculations are presented below.

3.1. Water

Tests for electron scattering from water were based on the seven-state calculations of $^2A_1$ symmetry reported by Gorfinkiel *et al* (2002). For this calculation $M = 5208$.

Figure 1 shows calculations performed using BB's theory with no error correction and error correction performed using theory A described above. In the absence of error correction the eigenphase sum is systematically too low, conversely the error corrected eigenphases are

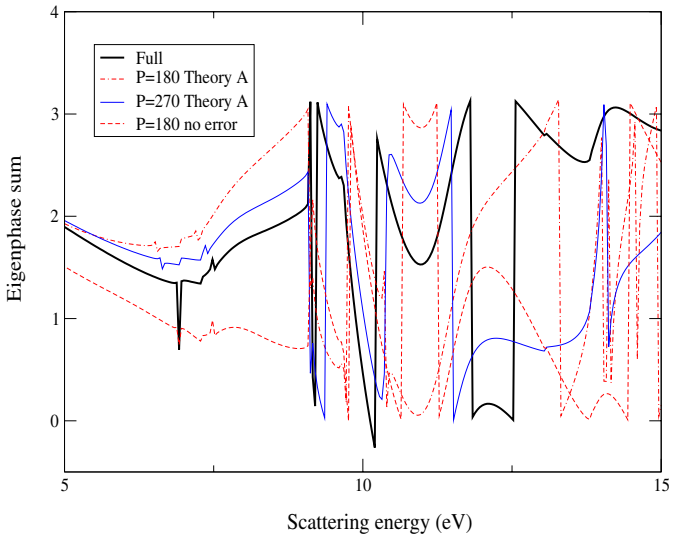

Figure 1. Eigenphase sums as a function of scattering energy for electron–water collisions with $^2A_1$ total symmetry. Details of the different models used are given in the text.

too high albeit somewhat closer to the correct answer denoted 'full' in the figure. For all cases displayed the eigenphase sums obtained using the partitioned R-matrix theory are a poor approximation to the correct results.

The partitioned R-matrix results displayed in figure 1 were all obtained using fairly small values of P. Using $P = 180$ and equation (5) gives $E_0 = 163.0$ eV, which rises to 165.1 eV for $P = 270$. As P is increased the results for theory A both with and without error correction move monotonically towards the correct eigenphase sums. However, this movement is fairly slow and it was found that even with error correction it was necessary to include explicitly about 50% of the poles to get acceptable results. This number is disappointingly high and suggests that theory A is not an adequate approximation.

By contrast figure 2 gives results obtained using theory C. This theory gives significantly lower values of E_0, 45.9 and 89.9 eV for $P = 200$ and 400, respectively. With $P = 200$, which is less than 4% of the poles, excellent agreement is obtained with the full eigenphases up to 12 eV and good agreement is obtained up to 17 eV. With $P = 400$, the excellent agreement extends above 15 eV. In this context, it should be noted that eigenphase sums are arbitrary to modulo π and the water eigenphases sums displayed are unusually complicated. In particular, the apparent disagreement between the $P = 400$ eigenphases sums and the other calculations in the 14 eV region can be eliminated by adding π to the $P = 400$ results in this region.

3.2. CF_2

Test calculations on low-energy electron collisions with the CF_2 radical were performed for $^2A_1$ symmetry using the seven-state model of Rozum *et al* (2002). For this model $M = 2397$.

Figure 3 reports a series of calculations performed using theory A for which values of E_0 span the range 131.3 eV for $P = 250$ to 173.5 eV for $P = 1500$. The results are somewhat unexpected. They show that as the number of poles explicitly considered, P, is increased from 250 to 1000 the eigenphase sum, which is already too high for $P = 250$, gets higher.

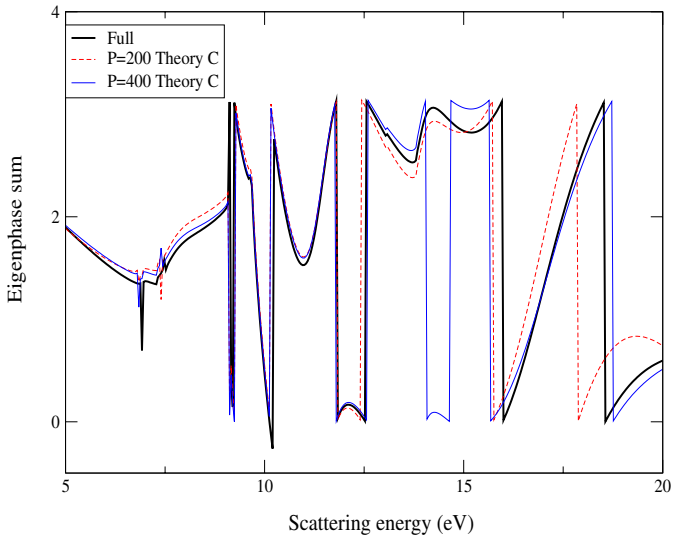

Figure 2. Eigenphase sums as a function of scattering energy for electron–water collisions with $^2A_1$ total symmetry. Details of the different models used are given in the text.

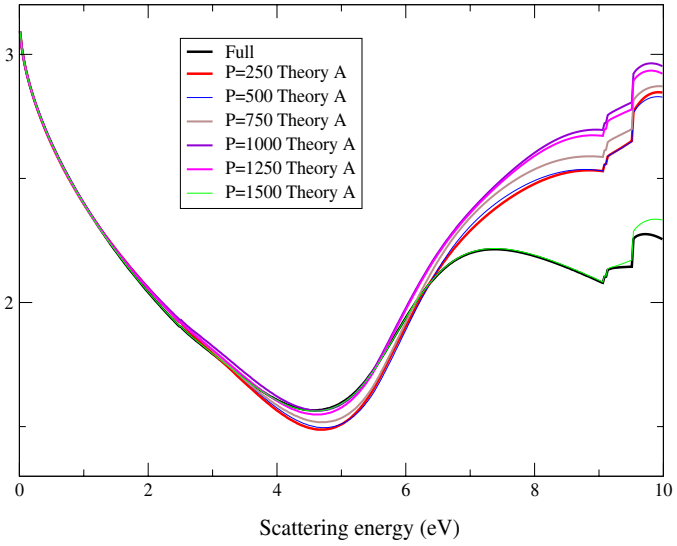

Figure 3. Eigenphase sums as a function of scattering energy for electron–CF_2 collisions with $^2A_1$ total symmetry. Details of the different models used are given in the text.

Only for $P > 1250$ do the eigenphase sums begin to move towards the correct value. As variational considerations show that theory A without the error correction must underestimate the eigenphase sum, this suggests that BB's error correcting method, as used in theory A, is over-correcting for the errors.

Figure 4 compares calculations with $P = 250$ for theories A, B and C. While theory A, equation (5) gives $E_0 = 131.3$ eV for $P = 250$, this is reduced to 75.5 eV for theories B and C, which use the same method for computing E_0. $P = 250$ is too small to get really converged

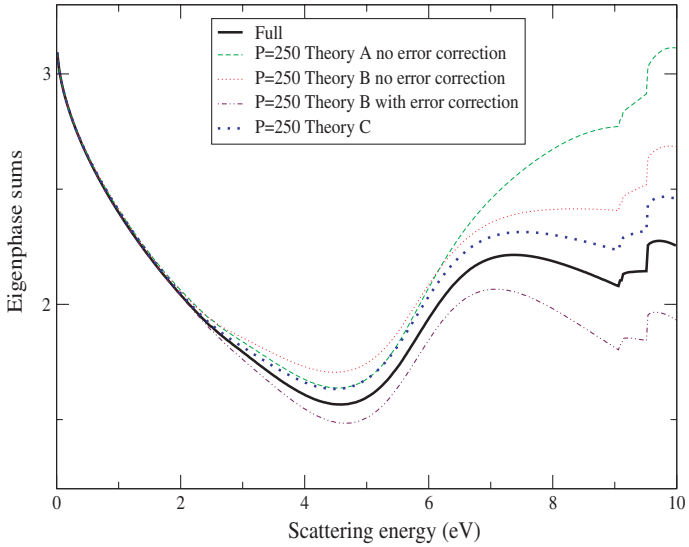

Figure 4. Eigenphase sums as a function of scattering energy for electron–CF_2 collisions with $^2A_1$ total symmetry. Details of the different models used are given in the text.

results for this system but is used for clarity. It is clear that the approximation improves as one moves from theory A to C, and that theory C gives a considerable improvement.

3.3. CF_3

One important further test is to study the behaviour as the size of the calculation is increased. Results for this test are only presented for theory C as the other theories do not perform well for this problem. These test calculations were performed for electron scattering from CF_3 which has been the subject of a recent study by Rozum *et al* (2003). Rozum *et al* discussed the use of a number of possible scattering models which differed in the target electrons which were correlated in the CI expansion and hence in the number L^2 terms included in the scattering wavefunction. Several of these models were deemed impractical because the number of L^2 configurations implied made it impossible to diagonalize the complete scattering Hamiltonian.

In BB's partitioned R-matrix theory and theory A discussed above, increasing the number of L^2 configurations tends to increase the number of R-matrix poles lying at higher energies. Test calculations were therefore performed using an expansion of six-target states and $^1A'$ symmetry within the C_s point group. Two different sets of L^2 configurations were tested; these were generated using the recipe $(1a'2a'3a'4a'5a'6a'7a'1a''2a''3a'')^{20}$ $(8a'9a'10a'11a'12a'13a'4a''5a''6a''7a'')^{14}$ which gives $n_d = 2798$ configurations and $(1a'2a'3a'4a'5a'6a'1a''2a''3a'')^{18}$ $(7a'8a'9a'10a'11a'12a'13a'4a''5a''6a''7a'')^{16}$ which gives $n_d = 4595$ configurations. The number of target states and the size of the continuum basis were kept the same in both calculations giving $M - n_d = 278$ configurations in both cases. These numbers illustrate the dominance of L^2 in determining the size of the Hamiltonian matrix, M, in molecular calculations.

Theory C performs very well for both the electron–CF_3 cases studied, see figure 5. The value of E_0 given by theory C is the same for both cases, 41.6 eV for $P = 200$ and 65.2 eV for $P = 400$. Partly as a consequence of this the results appear to be insensitive to n_d, the number

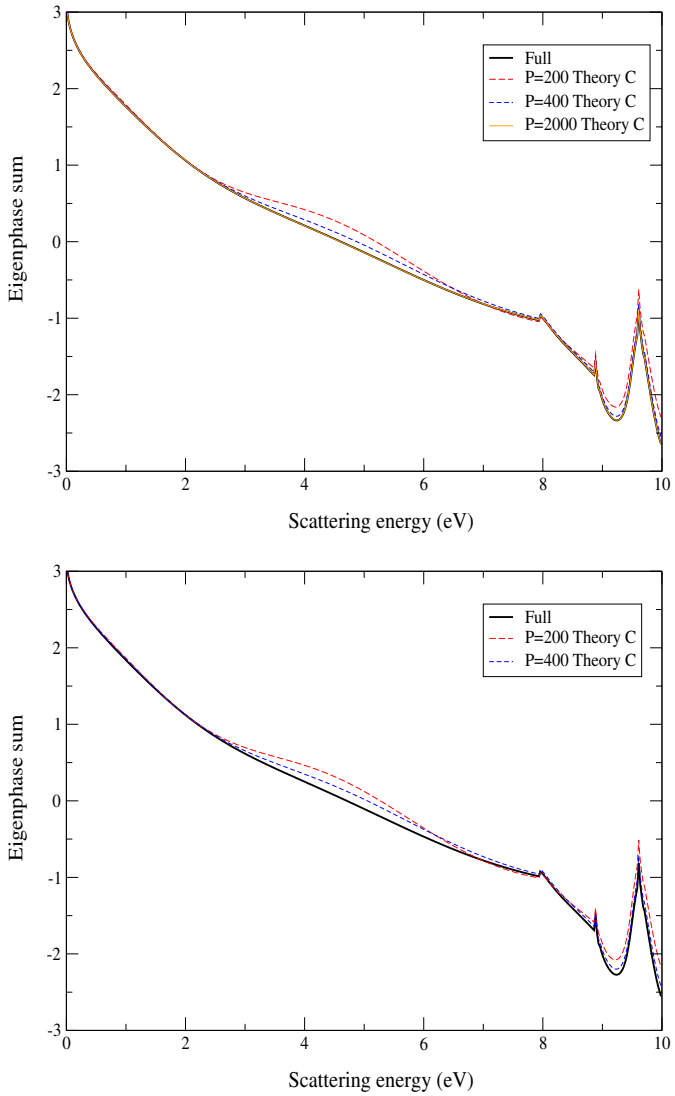

Figure 5. Eigenphase sums as a function of scattering energy for electron–CF_3 collisions with $^1A'$ total symmetry. Upper figure: $(1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''^2 3a''^2)^{20}(8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 13a'^2 4a''^2 5a''^2 6a''^2 7a''^2)^{14}$ target model; lower figure: $(1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 2a''^2 3a''^2)^{18}(7a'^2 8a'^2 9a'^2 10a'^2 11a'^2 12a'^2 13a'^2 4a''^2 5a''^2 6a''^2 7a''^2)^{16}$. Details of the different scattering models used are given in the text.

of L^2 terms included. This is a very encouraging result which suggests that this version of the partitioned R-matrix theory should still perform well even with very large numbers of L^2 functions.

4. Conclusions

The partitioned R-matrix theory of Berrington and Ballance (2002) has been adapted to electron–molecule calculations where only relatively low collision energies are important.

The equations of the recommended version of this theory can be summarized as

$$R_{il_i,i'l_{i'}}(a,E) = \sum_{k=1}^{P} w_{ilk}(a)w_{i'lk}(a)\left(\frac{1}{E_k - E} - \frac{1}{E_0 - E}\right) + \delta_{ii'}\delta_{ll'}\left(\frac{s_{il}}{E_0 - E} + R^B_{il} + R^C_{il}\right), \tag{12}$$

where E_0 is defined as the average of the diagonal Hamiltonian matrix elements involving continuum functions whose energy is greater than E_P. The error correcting term is given by

$$R^C_{il} = \sum_{j=J_i}^{n_{il}} (u_{ilj}(a))^2 X_{ilj}\left(\frac{1}{H_{ilj,ilj} - E} - \frac{1}{E_0 - E}\right). \tag{13}$$

This form of the theory will be implemented as a standard of option in the UK *R*-matrix codes (Morgan *et al* 1998).

Of course the usual observable parameter in an electron scattering experiment is the cross section not the eigenphase. Electron impact electronic excitation cross sections, particularly dipole forbidden ones, tend to be sensitive to the details of any calculation, so it is important to check the behaviour with the partitioning approximation. Tests showed that these cross sections are very stable with respect to P for calculations performed using theory C. Thus, for example, calculations which studied impact excitation to the lowest excited state of water, the X ^{1}A$'$–1^{3}A$''$ transition, for $P = 200$ and $P = 400$ were indistinguishable from those performed using a full calculation. The only exception was a small region about 7.5 eV where there were small changes in the energy dependence of the structure in the excitation cross section. This behaviour is also shown by the eigenphases, see figure 2.

It is anticipated that the use of partitioned *R*-matrix theory will significantly extend the complexity of target configuration interaction expansions and hence scattering wavefunctions that can be routinely used. One desirable feature of the chosen form of partitioned *R*-matrix theory is that it appears to be insensitive to the size of target expansion. The wavefunction information needed to construct the *R*-matrix on the boundary is carried by configurations of the form target wavefunction times continuum basis. Although the target wavefunction itself may be very complicated, there are relatively few configurations of this type, normally only a few hundred, even for a large multi-state calculation. This is because each target state is represented by a single wavefunction and the continuum functions are chosen to span the energy region of interest and not all energies, which limits their number. It should therefore be not altogether surprising that the number of *R*-matrix poles which need to be explicitly considered to get well-converged results corresponds approximately to the number of target times continuum configurations used in the calculation and that these solutions themselves span the energy range of interest. Other configurations, which give rise to higher poles, are important but largely contribute to the complicated and slowly convergent electron–electron correlation problem. By construction, these interactions are confined to the inner region which contains the entire target wavefunction. That they do not contribute significantly in the outer region should therefore not be a surprise.

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