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Electron collisions with polyatomic molecules using the R-matrix method

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R-matrix theory as applied by Burke and co-workers has been outstandingly successful at treating a range of electron collision problems. Recently, this work has been extended to the treatment of electron scattering from polyatomic molecules. The construction of a general electron–polyatomic–R-matrix code is discussed. Sample results are presented for electron collisions with atmospherically important species N_2O, O_3, H_2O and CO_2.

Keywords: nitrous oxide; ozone; water; carbon dioxide; elastic scattering; resonances

1. Introduction

Electron–molecule collisions are not only of fundamental interest but of immense importance for many applications. For example, a detailed knowledge of these processes is required for plasma physics, laser physics, atmospheric and interstellar models, stellar atmospheres, isotope separation, MHD power generation, electric discharges and radiation physics and chemistry. A number of these applications will be discussed below. The increased interest in the subject has been stimulated experimentally by the availability of electron beams with millivolt energy and the need for data for plasma modelling, particularly in relation to plasma etching.

Calculations of cross-sections and other parameters for electron collisions with polyatomic molecules are considerably more difficult than the analogous studies with atomic targets. This is due both to the loss of symmetry in molecular systems and the much greater difficulty in representing the target wavefunction. In addition molecules have vibrational and rotational degrees of freedom which can be excited by electron impacts. It is therefore not surprising that calculations of electron–polyatomic-molecule impacts are often much cruder than their electron–atom counterparts. However, many of the successes achieved in electron–molecule scattering have used ideas originally developed for atoms. A comprehensive survey of computational methods for electron–molecule collisions can be found in Huo & Gianturco (1995).

Until fairly recently the main theoretical method for treating electron collisions with nonlinear molecules relied on expanding the wavefunction for the problem around the molecular centre of gravity. Single-centre expansion methods are best for treating molecules with a single, central, heavy atom, such as methane (Gianturco *et al.* 1995). Work in this area by Gianturco and co-workers is continuing (see, for example, Gianturco & Lucchese 1998), most recently based on the use of wavefunctions computed using density functionals. However, the most serious problem with

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single-centre methods is their inability to treat electronic excited states of the target molecule.

Methods capable of treating the important electron-impact electronic-excitation process in molecules necessarily rely on using a multicentred representation of the target wavefunctions. Indeed reliable target wavefunctions for such calculations involve using many of the developments made by quantum chemists interested in electronic-structure calculations. The three major computational procedures employed for these electron–molecule impact studies are the complex Kohn variational method (Rescigno *et al*. 1995), the Schwinger variational method (Huo 1995) and the R-matrix method. The R-matrix method has been developed by Burke and co-workers and applied to a whole range of electron and photon collision processes in atomic and molecular processes (see Burke & Berrington 1993).

In this paper we are concerned with recent developments of the R-matrix method, particularly as it is applied to electron collisions with polyatomic molecules. In the next section we give an overview of some of the theoretical and computational developments that are needed in moving from atomic to polyatomic targets. In the following sections we present sample results, concentrating particularly on collisions with atmospheric molecules.

2. The R-matrix method

(*a*) *General comments*

The basic idea of the R-matrix method is the division of coordinate space into two regions, an inner region bounded by a sphere and an outer region. The outer region is so chosen that for scattering problems it is only necessary to consider the motions of the projectile governed by some simplified one-particle potential. The R-matrix is the mathematical construct designed to communicate the necessary information between the two regions. The R-matrix method was originally developed for treating nuclear reactions (see Wigner & Eisenbud 1947). In the original paper the 'R' in R-matrix stood for resonance, but this usage has now largely been lost. Part of the attraction of the method for nuclear physics was that it was not always necessary to have a complete model of the internal region provided an R-matrix could be constructed or parametrized on the boundary.

Some applications of R-matrix theory to atomic problems have also taken advantage of this feature of the theory; see, for example, the work of Meyerhof (Meyerhof 1963; Moxom *et al*. 1994). However, the real breakthrough for detailed numerical work in atomic physics came with a completely rigorous formulation of the electron–complex-atom scattering problem by Burke *et al*. (1971) and the consequent development of robust computational procedures for solving this problem (Berrington *et al*. 1974).

Stimulated by the work of Schneider (1975*a*, *b*), Burke *et al*. (1977) produced a rigorous formulation of the electron (diatomic) molecule scattering problem, which can be seen as the electron–molecule counterpart to the electron–atom work of Burke *et al*. (1971). However, the computational manifestation of the electron–molecule problem is significantly more difficult than the electron–atom case. The reasons for this are twofold: the need to compute multicentred integrals and the linear dependence/completeness problems, which are exacerbated by the use of wavefunction expansions located on more than one centre.

(*b*) *Representation of the continuum*

A basic difficulty in developing a robust electron–molecule scattering code is the choice of suitable functions with which to represent the continuum. The functions have to be complete for some energy range or, in the R-matrix method, within some region of configuration space. However, they must not be so complete that they cause problems of linear dependence on the functions chosen to represent the target wavefunctions. Since it has proved impossible in many cases to work without using over-complete sets, reliable methods for removing the linearly dependent functions must be found. Another consideration in the choice of functions is the fact that one must be able to evaluate rapidly and accurately a large number of multicentred and multidimensional integrals.

In atomic R-matrix calculations a complete set of functions can be generated by solving a model problem within an effective central potential. These numerically defined functions can be made rigorously orthogonal to the atomic wavefunctions by using Lagrange multipliers (see, for example, Burke & Taylor 1975). This approach necessarily leads to the numerical evaluation of integrals, but they are all confined to a single centre.

Molecular electronic-structure calculations usually use basis-function expansions to represent the target wavefunctions. Two types of functions have been extensively tested: the so-called Slater-type orbitals (STOs), which are based on solutions of the hydrogenic atom problem, and Gaussian-type orbitals (GTOs), which are the familiar Gaussian functions. Both approaches have advantages. STOs clearly give a much better starting point for the calculation as they correctly represent both the cusp in the wavefunction at the nucleus and the exponential fall-off of the wavefunction at long range. GTOs have the significant advantage that integrals involving them, even multicentred ones, can be evaluated in closed form. In general, ease and accuracy of integration has triumphed and nearly all quantum-chemical packages use GTOs.

There are reliable STO integrators for linear molecules since in this case the angular integrals can be performed analytically (see, for example, McLean 1971). The first attempts at electron–molecule scattering calculations using R-matrix theory concentrated on linear molecules and represented both target and continuum functions using STOs (Noble *et al*. 1982). However, the difficulty of representing continuum functions by STOs expanded about a single centre, combined with the limited accuracy of the integrals, meant that reliable results could only be obtained at low energies.

As an alternative to using STOs to represent the continuum, Burke *et al*. (1983) used numerical functions generated very much along the lines of the atomic method discussed above. This approach was successful in allowing calculations to be performed over an extended energy range. Of course, for molecules any isotropic or central field potential will be a fairly crude approximation; however, a more serious problem proved to be the orthogonalization procedure. Use of the Lagrangian multipliers led to unmanageably large continuum basis sets. Subsequent work (see, for example, Tennyson *et al*. 1984) therefore dropped the Lagrange multipliers in favour of a Schmidt orthogonalization procedure. This procedure imposes weaker orthogonality conditions as no (linearly dependent) functions are dropped from the basis. It is in principle possible to use the results of the Schmidt procedure to remove functions from the basis, but tests showed that this did not work well; similar tests using the alternative symmetric or Löwden orthogonalization also showed that functions could not safely be removed in this fashion (J. Tennyson and C. J. Noble, unpublished data).

Many R-matrix calculations have been performed on linear molecules using numerical functions and Schmidt orthogonalization (see Burke & Noble 1987). However, for some molecular targets, particularly molecular ions, linear dependence remains a major problem with this procedure. A new method, based on Lagrange orthogonalization to the actual target wavefunctions, rather than a spherical expansion of them, was implemented by Tennyson *et al*. (1987). This method has proved robust and has been used to treat a number of challenging problems involving electron impacts with both neutral and ionized molecules (Tennyson 1996*a*).

The use of numerical functions to represent the continuum has proved very successful for calculations involving electron collisions with both atoms and linear molecules. However, for nonlinear molecular targets, use of numerical functions would require multicentre multidimensional numerical integrals for which there are at present no adequate numerical procedures available.

An alternative approach, explored originally in the context of R-matrix calculations by the Bonn group (Nestmann & Peyerimhoff 1990; Nestmann *et al*. 1991), involves the use of GTOs to represent both the continuum and target electrons. Superficially this procedure would appear to suffer from the difficulties encountered by Noble *et al*. (1982) when they used STOs. However, the crucial difference is the accuracy to which integrals can be evaluated in a GTO rather than an STO basis, a difference of as many as five significant figures. Nestmann & Peyerimhoff (1990) and Beyer *et al*. (1997) developed GTO continuum basis sets that were optimized to mimic Bessel functions within the finite region of an R-matrix sphere of radius $10a_0$. Basis functions that give a good representation of the continuum up to intermediate energies were developed in this fashion, although problems with linear dependence remain.

The solution to the linear-dependence problems advocated by the Bonn group is to use symmetric or Löwden orthogonalization. Orthogonalized functions whose eigenvalue of the overlap matrix are lower than some critical value, typically about 10^{-7}, are then removed from the basis. This procedure appears to be reasonably robust and has been used successfully in a number of calculations. Indeed it is this procedure that we have adopted in our newly developed R-matrix suite for treating electron collisions with polyatomic targets (Morgan *et al*. 1997), which we discuss below. However, new GTO basis sets are required for each R-matrix radius and target ionization stage. So far this has restricted calculations using both the Bonn and our code to studies of electron scattering from neutral systems with an R-matrix radius of $10a_0$. Work is in progress developing further GTO basis sets for scattering calculations.

(*c*) *Electron–polyatomic collisions*

The UK R-matrix diatomic code (see Gillan *et al*. 1987, 1995) has proved highly successful. Its application has led to a number of new and interesting results on various topics including electron-impact electronic excitation (Branchett & Tennyson 1990; Noble & Burke 1992), analysis and prediction of resonances (Noble & Burke 1992; Stibbe & Tennyson 1997), dissociative recombination (Sarpal *et al*. 1994*b*) and electron-impact dissociation (Stibbe & Tennyson 1998). However, this code is built assuming the use of STOs and, for the reasons discussed above, is intrinsically limited to treating collisions with linear molecules.

A molecular R-matrix calculation can be broken down into a number of basic computational steps. These are the generation of integrals, the generation of a set of orthonormal molecular orbitals, the construction and diagonalization of the inner-region Hamiltonian matrix and solution of the outer-region scattering problem.

The most fundamental change in the new code is the use of GTOs to represent both the wavefunction of the target molecule and the continuum. This required the use of an entirely new integral code for which we have switched to the 'Molecule–Sweden' suite of codes developed by Almlof & Taylor (1984). The major advantage of GTOs over STOs is that, for GTOs, multicentred integrals can be evaluated analytically. However, quantum-chemistry codes assume that the integration is over an infinite range. This, of course, is not the case for the inner region of an R-matrix calculation, which is necessarily finite.

The main modification required to make a standard quantum-chemistry integral code suitable for R-matrix calculations is to restrict the range of spatial integration to a finite sphere. Instead of modifying the existing integrals code, we chose to subtract from the integrals over an infinite range, the contribution from the region outside the sphere. This has been implemented in a program GAUSTAIL, details of which are given in Morgan *et al*. (1997, 1998).

The only other entirely new code written for our polyatomic package is one to generate an orthonormal set of molecular orbitals. The difference here is that, as discussed above, the code uses a procedure based on symmetric orthogonalization to both orthogonalize the basis and remove linearly dependent functions. The diatomic code used a mixture of Lagrange and Schmidt orthogonalization for these tasks (Tennyson *et al*. 1987).

Hamiltonian construction and diagonalization is handled by the recently developed SCATCI program (Tennyson 1996*b*), which was written to handle scattering from both diatomic and polyatomic targets. This program makes explicit use of the structure of a scattering calculation in constructing the Hamiltonian matrix. For this task it is some 200 times faster than more conventional configuration-interaction (CI) procedures implemented in standard quantum-chemistry packages. The developments used in SCATCI had a number of parallels with those employed in the RMATRX II code of Burke *et al*. (1994) for greatly accelerating the Hamiltonian construction problem for electron–atom collisions.

For the electron diatomic-outer-region problem we have a well-established robust and flexible suite of programs (see Gillan *et al*. 1995). These have been generalized for polyatomic targets by writing a new module which interfaces to the inner-region codes. Once R-matrices, outer-region potentials and channels are defined, the electron–diatom, electron–polyatom and, indeed, the electron–atom outer-region problems all look very similar.

An overview of both the diatomic and polyatomic UK R-matrix codes is given in a recent publication (Morgan *et al*. 1998).

(*d*) *Models*

An important feature of the R-matrix method, which we have been careful to retain in our electron–molecule codes, is control over the models used in the calculation.

Any electron-scattering calculation requires the consideration of an N-electron target system and an $(N+1)$-electron collision complex. To get good results it is important that the treatment of both systems be balanced.

For a given fixed geometry, the inner-region wavefunction in the R-matrix method has the form

$$\psi_k = \sum_{ij} \phi_i(x_1, \ldots, x_N) u_{ij}(x_{N+1}) a_{ijk} + \sum_i \chi_i(x_1, \ldots, x_{N+1}) b_{ik}, \tag{2.1}$$

where the $u_{ij}(x)$ are the continuum orbitals discussed above and the ϕ_i are target wavefunctions, which themselves may be expressed in terms of a CI expansion. The χ_i are two-centre quadratically integrable (L^2) functions constructed from the target occupied and virtual molecular orbitals.

Obviously, the choice of target wavefunctions and continuum orbitals is important, but a key step in developing a reliable model is also the choice of the L^2 terms. These terms are important for both relaxing any imposed orthogonality constraint between the target and continuum orbitals, and for representing short-range polarization effects not included in the necessarily limited close-coupled expansion over target states. For single-determinant SCF targets, it is possible to make a rigorous distinction between static-exchange (SE) and static-exchange-plus-polarization (SEP) models according to how the L^2 terms are defined. However, this is not true for CI target wavefunctions. In this case great care must be taken over selecting these L^2 terms if a balanced calculation is to be retained (see, for example, Tennyson 1996*c*).

3. Results

We have performed calculations using the new electron–polyatomic program suite for a number of targets. Calculations have been performed for collisions with diatomic molecules, but these were largely for testing purposes and will not be considered here. So far most of our work has concerned collisions with molecules of atmospheric importance, in particular N_2O (Morgan *et al.* 1997), CO_2 (Morgan 1998*a*), O_3 and water (Morgan 1998*b*). Below we present some sample results.

(*a*) *Nitrous oxide*

N_2O is an important species in the upper atmosphere which plays a role in ozone destruction. N_2O lasers are also of interest. In both cases, electron collisions play an important role, though data on the various collision processes remain fairly scarce.

Electron–N_2O collision calculations for energies up to 10 eV were performed by Morgan *et al.* (1997), who considered N_2O only in its equilibrium geometry. This calculation was performed using only the ground electronic state of N_2O within both SE and SEP models. The difference between the SE and SEP models lies in the choice of L^2 terms in equation (2.1). Integrated cross-sections computed using these two models are compared in figure 1.

The SE calculation of Morgan *et al.* (1997) reproduced the results of a very similar calculation by Sarpal *et al.* (1996), who used the Bonn R-matrix code. Both SE calculations found a low-energy $^2\Pi$-shape resonance, which has a profound effect on the computed total cross-section. However, the two SEP calculations produced somewhat different results. Our calculation found the resonance at 2 eV, close to

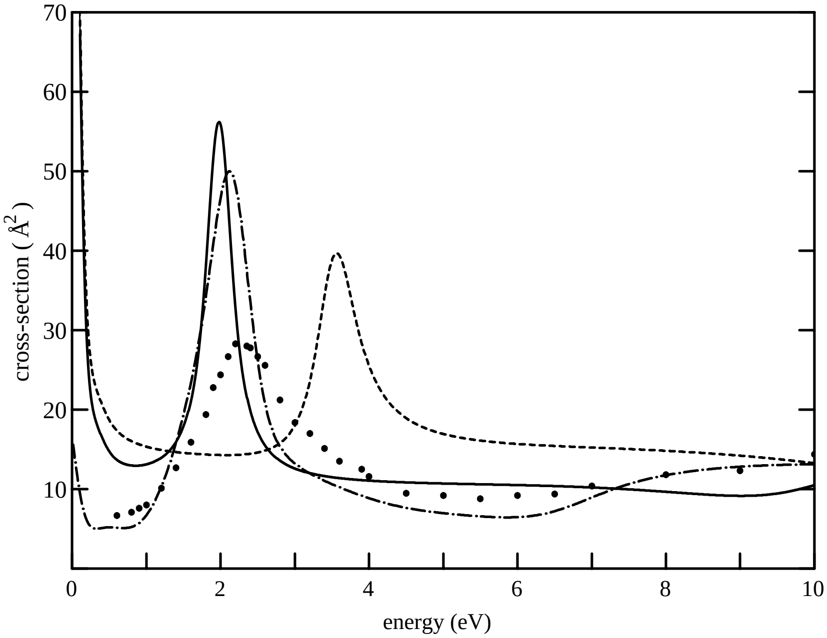

Figure 1. Integrated cross-sections for electron–N_2O: – – –, SE model; ——, SEP model; –·–·–, CI target model of Sarpal *et al.* (1996); · · · · · ·, experiment of Szmytkowski *et al.* (1984).

but slightly lower than experiment (Szmytkowski *et al.* 1984), but the Bonn SEP calculation placed the resonance at 0.8 eV. The difference between these calculations is entirely in the treatment of the L^2 terms. These are significantly less easy to control in the Bonn implementation of R-matrix theory, which makes no attempt to balance individual configurations in the CI expansion of equation (2.1).

(*b*) *Ozone*

A second system studied extensively by Sarpal *et al.* (1994*a*, 1998) using the Bonn code is ozone. Ozone is a key species for atmospheric studies, yet electron–ozone collisions remain poorly characterized. In particular, the location and symmetry of the various resonance features have not been firmly established.

We have performed a number of calculations for this system, results for which are presented in figure 2. This figure gives eigenphase sums for the resonant $^2A_1$ and $^2B_2$ symmetries. Resonances are characterized by a rapid rise in the eigenphase sum through π, although narrow resonances may not be fully resolved, in which case they appear as discontinuities in the eigenphase sum. Both SE calculations show low-lying, broad-shape resonances with $^2A_1$ and $^2B_2$ symmetry at *ca.* 8 eV and 11 eV, respectively. The Bonn SE calculation shows further resonances at *ca.* 17 eV in both symmetries but we find no evidence for these structures in our SE calculations.

As commented on already, the positions of shape resonances are sensitive to the treatment of polarization effects. Our SEP model lowers the shape resonances by 2–3 eV. However, for scattering energies above 8 eV the SEP calculations also show numerous narrow resonance features. These features are almost certainly ‘pseudo-resonances’, caused by the omission of electronically excited states from the calcu-

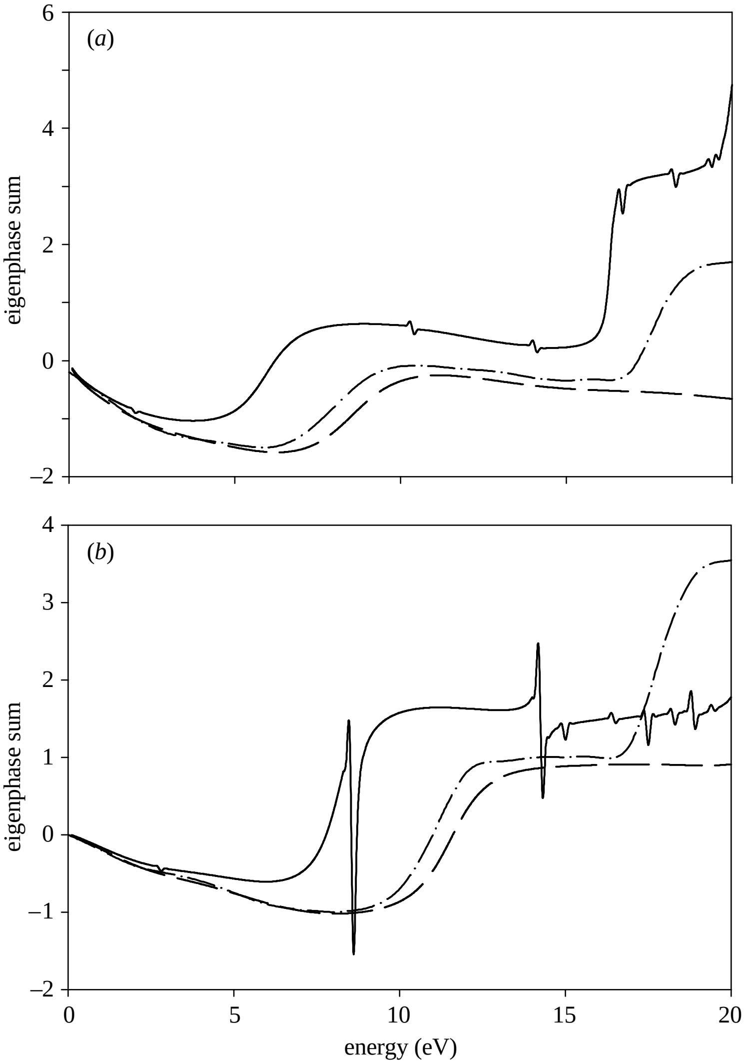

Figure 2. Eigenphase sums for electron–ozone collisions: (*a*) $^2A_1$ symmetry; (*b*) $^2B_2$ symmetry; – – –, SE model; –·–·–, SE model of Sarpal *et al.* (1994*a*); ——, SEP model.

lation. These features are common in scattering calculations performed at energies where open thresholds are omitted from the calculation (see Burke *et al.* (1987) for an excellent example). Ozone has a large number of low-lying electronic states, and so far no-one appears to have attempted to include these directly in a scattering calculation via a close-coupling expansion.

(*c*) *Water*

Water is not only an important atmospheric molecule, but is the major constituent of the human body. Knowledge of electron–water collision interactions are important

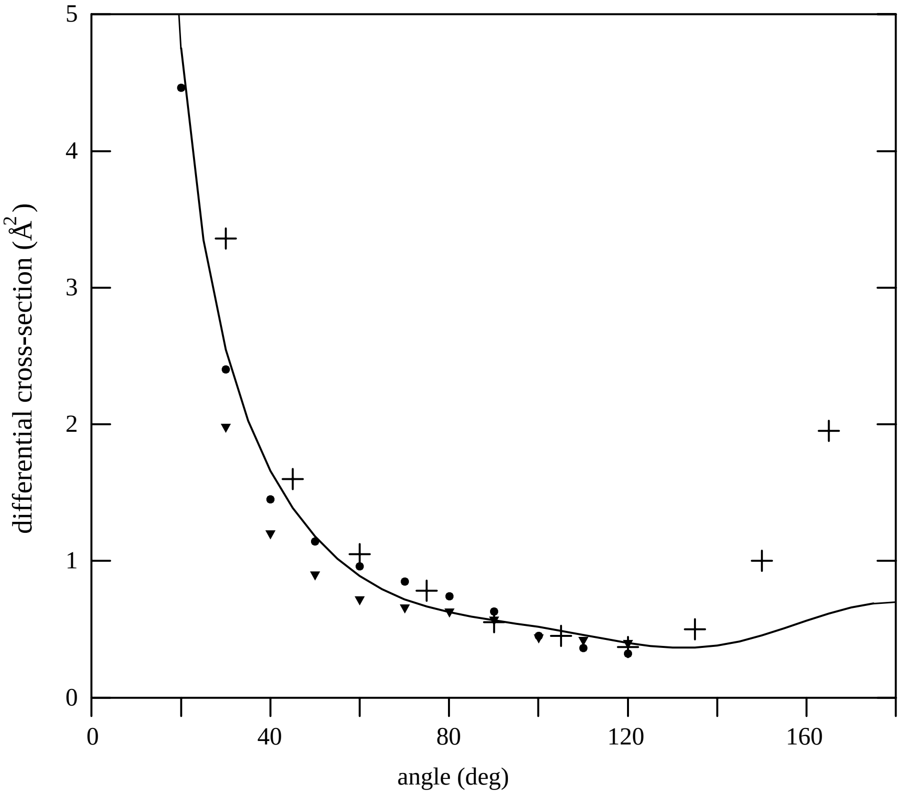

Figure 3. Differential cross-section for elastic electron–water collisions at 6 eV: ——, SEP model. Experimental results: ▾, Danjo & Nishimura (1985); ●, Johnstone & Newell (1991); +, Shyn & Cho (1987).

for models of radiation damage. Morgan (1998*b*) has recently completed a study of electron-impact excitation of water. Here we consider only the elastic cross-section.

Perhaps surprisingly it is remarkably hard to determine an accurate cross-section for elastic electron–water collisions. The reason for this is that water's large permanent dipole moment produces a differential cross-section that is very strongly forward peaked and, as a result, the total cross-section is completely dominated by small angles (Okamoto *et al*. 1993). This means that the most reliable cross-sections are from theory, and comparisons of large-angle scattering via the differential cross-section become the only way of benchmarking any theory against experiment. Figure 3 shows such a comparison.

Figure 3 presents results computed for electron–water at the SEP level using an SCF target. As this calculation only included low partial waves in the continuum ($l \leqslant 3$), higher partial waves, which dominate the forward scattering behaviour, were included using the (dipole) Born approximation. It can be seen that our results agree well with the experiment at angles of 120° and less. This level of agreement is found in other scattering calculations which treat the problem at a similar level (see, for example, Okamoto *et al*. 1993). It is unclear why our calculations underestimate the backscattering peak.

(*d*) *Carbon dioxide*

Morgan (1998*a*) recently reported a series of studies on electron–CO_2 scattering which found clear evidence for a virtual state in this system. Whereas resonances can be considered as poles in the S-matrix at complex values of the momentum k, and bound states as poles on the positive imaginary axis, virtual states are poles lying on the negative imaginary axis. A virtual state is not a physical state but a feature of the scattering system which can, if it lies sufficiently close to the origin, have a profound effect on the very-low-energy scattering cross-section. The manifestation of such a state, as predicted by model calculations, is a sharp rise in the cross-section as the scattering energy goes to zero (Morrison 1982). Although virtual states have been found in model calculations, none had previously been found in any detailed *ab initio* study.

Morgan's calculations did not show the effect of a virtual state in either the SE or SEP models. It was only when excited target states where introduced into the close-coupling expansion that a dramatic upturn was found in the cross-section at low energy. To demonstrate that this behaviour is indeed associated with a virtual state it is necessary to analyse the S-matrix as a function of complex k. Figure 4 shows the results of this analysis for the multistate model as a function of the CO_2 bending angle, θ. For linear geometries, $\theta = 180°$, the virtual state corresponds to the pole in the S-matrix at $k = -0.2\mathrm{i}$, which occurs for $^2\Sigma_\mathrm{g}$ symmetry. There is a second pole at $k = 0.6 - 0.03\mathrm{i}$ with $^2\Pi_\mathrm{u}$ symmetry. This pole corresponds to the 5 eV shape resonance. It is present in SE, SEP and close-coupling models, although as for other shape resonances, it is sensitive to the level of polarization included in the calculation.

As CO_2 is bent it develops a dipole. Figure 4 traces the behaviour of the two poles as a function of bending angle. The virtual state traces a parabola on the unphysical sheet of the complex momentum and reaches the origin at $\theta = 147.5°$. For angles less than 147.5°, it becomes a true bound state.

The $^2\Pi_\mathrm{u}$ shape resonance shows rather different behaviour as CO_2 is bent. Bending the molecule lifts the degeneracy and the state splits into $^2\mathrm{A}_1$ and $^2\mathrm{B}_2$ symmetry states. The resonance of $^2\mathrm{B}_2$ symmetry is largely unaffected by bending, moving slowly to lower energy and showing a slight increase in width. Conversely the $^2\mathrm{A}_1$ resonance moves rapidly away from the real axis so that inspection of the eigenphase sum for $\theta \leqslant 160°$ gives essentially no trace of any resonant behaviour.

4. Conclusion

R-matrix theory, as pioneered by Burke and his many co-workers for a whole range of electron-collision problems, is now being successfully applied to electron collisions with polyatomic systems. So far only a limited number of calculations have been performed with the newly developed UK polyatomic R-matrix code (Morgan *et al.* 1997, 1998), but this code is written in a general fashion and should provide many new results for some time to come.

It is a pleasure for us to acknowledge the profound influence Phil Burke has had on the whole area of electron-collision theory. In particular, he was responsible both for starting the UK attack on electron–molecule collisions using R-matrix theory and for stimulating both of our interests in this problem. We thank him for many years of advice, encouragement and helpful discussions.

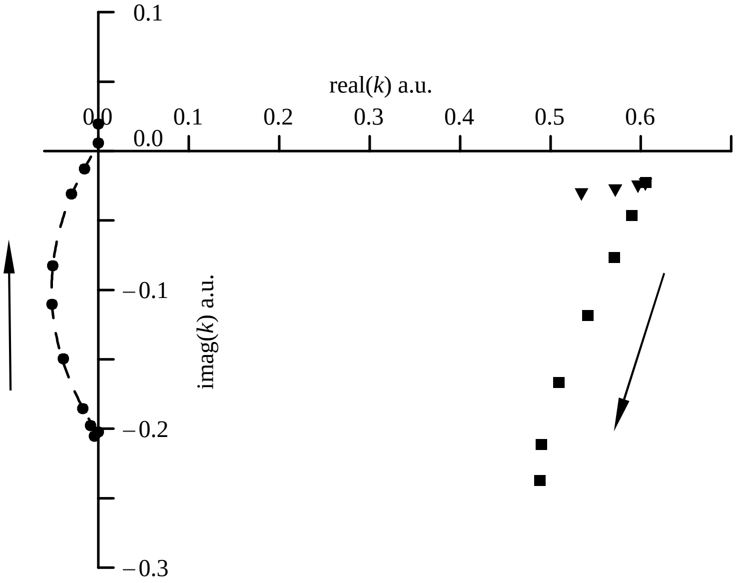

Figure 4. Location of S-matrix poles in the complex momentum (k) plane as a function of CO_2 bending angle. The arrows show the direction the poles move as CO_2 is bent from linear. The dots are for the virtual state and the dashed curve is a parabola fitted to those poles lying in the lower left-hand quadrant. The squares and triangles represent $^2A_1$ and $^2B_2$ symmetry poles, respectively. For linear CO_2 these become degenerate and correspond to a $^2\Pi_u$ shape resonance.

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