Multiple scattering approach to elastic electron collisions with molecular clusters

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Abstract. We revisit our multiple-scattering method to treat low energy elastic electron collisions with $(H_2O)_2$. Calculations are performed for different geometries of the water dimer with different dipole moments. The effect of the dipole moment of the cluster is analysed. The elastic cross sections are compared to R-matrix results. Good agreement is found above 1 eV for all geometries. Results confirm the validity of the technique.

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1. Introduction

As the spectrum of scientific and technological fields requiring information on electron collisions widens, the need for novel approaches to the theoretical study of these processes increases. The study of low energy electron collisions ‡ with atoms and molecules has been an active field of research for many years. However, until recently, the focus was on the development of ever more sophisticated, and therefore accurate, techniques and methods (see, for example, Khakoo et al. 2006). This effort was underpinned by fast increases in the computational resources available to scientists.

In recent years, however, interest in understanding the interaction of low energy electrons with bigger molecular targets has grown significantly. This interest stems, among other fields, from the study of biological radiation damage and the confirmation (Boudaïffa et al. 2000) that low energy electrons can damage DNA. The potential targets in this environment are larger than anything ever studied before: there is, of course, DNA but proteins and other macromolecules could be of relevance too. In addition, these targets are not isolated but are normally surrounded by other molecules. Up until now, most theoretical models have only considered collisions with isolated (gas phase) targets (one exception is the work of Fabrikant and collaborators; see, for example, Fabrikant & Hotop 2005).

‡ We define low energy collisions as those in which the kinetic energy of the scattering electron is lower than the ionization potential of the target.

Water is the main constituent of living organisms and therefore a highly relevant target when biological radiation damage is concerned. In addition, water tends to trap low energy electrons due to its large dipole moment; for this reason, it is expected to play an important role in electron induced processes (Garrett et al. 2005, Ptasinska & Sanche 2007). Extensive experimental and theoretical work has been carried out on collisions with water vapour (a recent compendium can be found in Itikawa & Mason 2005), but little is known about collisions with aggregated water. A few experimental studies of collisions with solid water have been reported (Rowntree et al. 1991, Simpson et al. 1997, Michaud et al. 2003, Herring-Captain et al. 2005). Work on attachment of slow electrons and formation of $(H_2O)_n^-$, aimed at elucidating the mechanism of electron solvation, has also been performed (Knapp et al. 1986, Knapp et al. 1987, Weber et al. 1999, Barnett et al. 1989, Lee et al. 1991).

Our aim is to develop a methodology to study electron scattering from clusters, and we have focused initially on water clusters. We believe that by understanding electron interactions with H_2O clusters, we will be able to contribute to the understanding of biological radiation damage. It is known that some of the solvation layers surrounding DNA do not have the characteristics of bulk water (Becker et al. 1997) but might be explained in terms of clustered water. Clusters composed of more than a few monomers are too big to be studied with the available *ab initio* computational implementations. We have therefore turned to a multiple scattering (MS) method to perform these studies. The multiple scattering method is based on the idea that it is possible to separate the potential of a complex target into regions with each region taken as a single scatterer. Thus, the cross section for large systems can be determined by combining information from its subunits hence making it possible to study collisions with large targets.

One of the first applications of multiple-scattering ideas to electron-molecule collisions was that of Dill and Dehmer (Dill & Dehmer 1974, Siegel et al. 1976). The application of their method to electronic collisions was abandoned in the 80s, probably because *ab initio* methods became computationally feasible and started producing good results. Kimura and collaborators published some work on electron collisions with water (Kimura et al. 2000) but, to the best of our knowledge, the details of their approach were never published nor was the method applied to other targets.

More recently, and again spurred by the interest in understanding electron interactions with DNA at sub-ionization energies, Caron and Sanche published a series of papers looking at collisions with a model helical molecule (Caron & Sanche 2003, Caron & Sanche 2004, Caron & Sanche 2005, Caron & Sanche 2006); in these works, the authors used accurate collisional information for atomic targets (inert gases). A more sophisticated approach was employed by Caron et al. (2008) who used collisional information for DNA subunits to build a picture of the electron interaction with a DNA fragment.

A similar technique had been used to study electron collisions with the water dimer (Bouchiha et al. 2008). In that paper, the elastic cross section calculated using the multiple scattering technique was compared to that obtained from a purely R-matrix calculation for the equilibrium geometry of the dimer. We have now extended this work to the study of scattering for several different geometries of the water dimer. Again, R-matrix calculations are used to

compare and test our MS results. The changes in geometry lead to changes in the relative orientation of the monomers and therefore in the total dipole of the dimer. It is to study how these changes affect the agreement between MS and *ab initio* cross sections, and therefore the validity of the method, that we have performed these new calculations.

All calculations have been carried out within the fixed-nuclei approximation. In addition, no attempt to complete the partial wave expansion by means of a Born-type correction or similar has been performed. Due to a bug in the program, some of the results presented in Bouchiha et al. (2008) were incorrect. The corrected results show a similar good agreement with the R-matrix cross sections, but some of the assumptions made in the previous paper have proved unsound. Atomic units are used throughout.

2. Theory

The multiple-scattering approach is based on the idea that the interaction potential (in our case, between the scattering electron and the target cluster) can be represented differently in different regions. More fundamentally, in the area close to the target, the potential can be approximated by a combination of the interaction potential with sub-units of the target. In earlier work, where the target was a molecule, these subunits were atoms. In our case, where the target is a cluster, the subunits correspond to the molecular monomers forming the cluster. This decomposition of the interaction potential enables us to determine collisional information for the whole (the cluster) by combining collisional information for the sub-units. The advantage of this approach is that the scattering information of the smaller sub-units can be determined using sophisticated methods, whereas their application to the whole target is not feasible due to computational limitations.

In our implementation of the MS technique, we use the R-matrix method (Burke & Berrington 1993) to determine the collisional information for the molecular monomers. The choice of this *ab initio* method is particularly appropriate as it is also based on the division of space, this time in two regions. These regions are separated by a sphere of radius a. The inner region contains all the electronic density of the target states included in the calculation. Inside it, the discretized states of the N-electron target + scattering electron wavefunctions are determined using quantum chemistry techniques that provide a good representation of exchange, correlation and polarization effects. In the outer region, exchange and correlation can be neglected and a single centre multipole expansion is employed to represent the electron-target interaction; a partial wave expansion is used for the wavefunction representing the scattering electron. This results in a set of coupled differential equations that are solved by means of a propagation technique in order to determine the radial part of the wavefunction describing the scattering electron. This propagation makes use of the multipole potential to the determination of the R-matrix for $r + \Delta r$ when said matrix is known for r. By matching the propagated functions to asymptotic analytical expressions, collisional information is obtained. The main advantage of using the R-matrix method to obtain scattering information for the monomers is that, in the propagation step, it is possible to "switch" on or off the interaction between electron and monomer for distances bigger than a.

Details of the derivation of our MS equations were provided in Bouchiha et al. (2008). Here, we present the main equations (using more explicit notation) and provide a brief explanation of their physical meaning. We label the monomers with the index n and define the position of their centre of mass with respect of the centre of mass of the cluster with $\vec{R}_n$. The relative position vector for the monomers is then $\vec{R}_{nn'} = \vec{R}_n - \vec{R}_{n'}$.

In order to calculate cross sections for elastic scattering from the cluster, we derive an expression for the T-matrix $\mathbf{T}^{\mathrm{tot}}$ of the cluster in terms of the T-matrix of the monomer:

$$\mathbf{T}^{\mathrm{tot}} = \mathbf{A} \cdot \mathbf{T} \cdot (\mathbf{I} - \mathbf{XT})^{-1} \cdot \mathbf{B} . \tag{1}$$

Here $\mathbf{A}$ and $\mathbf{B}$ are matrices that account for the transformation from the centre of mass of the monomer to that of the dimer and take the form:

$$\mathbf{A} = \left(\begin{array}{cccc} \mathbf{A}^1 & \mathbf{A}^2 & \cdots & \mathbf{A}^N \end{array} \right), \qquad \mathbf{B} = \left(\begin{array}{c} \mathbf{B}^1 \\ \mathbf{B}^2 \\ \vdots \\ \mathbf{B}^N \end{array} \right) \tag{2}$$

with N the total number of scatterers (in our case $N = 2$). $\mathbf{A}^n$ and $\mathbf{B}^n$ are also matrices whose elements are defined by:

$$A^n_{L_1 L_2} = \sum_{L'} i^{l_1 + l' - l_2} (-1)^{m_2} F^{l_1, l', l_2}_{m_1, m', -m_2} Y_{L'} \left(-\hat{R}_n \right) j_{l'} (\kappa R_n) , \tag{3}$$

$$B^n_{L_1 L_2} = \sum_{L'} i^{l_1 + l' - l_2} (-1)^{m_2} F^{l_1, l', l_2}_{m_1, m', -m_2} Y_{L'} \left(\hat{R}_n \right) j_{l'} (\kappa R_n) . \tag{4}$$

In these expressions, Y_L are spherical harmonics with $L = (l, m)$, j_l are spherical Bessel functions and $\kappa = \sqrt{E}$ with E the kinetic energy of the scattering electron. In addition:

$$F^{l_1, l_2, l_3}_{m_1, m_2, m_3} = [4\pi (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)]^{\frac{1}{2}} \left(\begin{array}{ccc} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{array} \right) \left(\begin{array}{ccc} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array} \right) \tag{5}$$

and $\left(\begin{array}{ccc} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array} \right)$ is the Wigner 3-j symbol.

$\mathbf{T}$ is a block-diagonal matrix that can be written as:

$$\mathbf{T} = \left(\begin{array}{cccc} \mathbf{T}^1 & & & 0 \\ & \mathbf{T}^2 & & \\ & & \ddots & \\ 0 & & & \mathbf{T}^N \end{array} \right), \tag{6}$$

where $\mathbf{T}^n$ are the monomer T-matrices that have been rotated to reflect the orientation of the monomers in the cluster. Knowing such orientations, it is possible to construct a rotation matrix $\mathbf{W}^n$ for each monomer (Messiah 1962), which is then applied to the T-matrix, $\mathbf{T}^{\mathrm{Rmat}}$, obtained in the R-matrix calculation:

$$\mathbf{T}^n = \mathbf{W}^n \cdot \mathbf{T}^{\mathrm{Rmat}} \cdot (\mathbf{W}^n)^{-1} . \tag{7}$$

Since our clusters are homogeneous, $\mathbf{T}^{\mathrm{Rmat}}$ is the same for all sub-units.

The term $(\mathbf{I} - \mathbf{XT})^{-1}$ in Equation (1) represents the multiple scattering between the two scatterers and $\mathbf{X}$ takes the form:

$$\mathbf{X} = \begin{pmatrix} \mathbf{X}^{11} & \mathbf{X}^{12} & \cdots & \mathbf{X}^{1N} \\ \mathbf{X}^{21} & \mathbf{X}^{22} & & \mathbf{X}^{2N} \\ \vdots & & \ddots & \vdots \\ \mathbf{X}^{N1} & \mathbf{X}^{N2} & \cdots & \mathbf{X}^{NN} \end{pmatrix} . \tag{8}$$

The elements of each $\mathbf{X}^{nn'}$ sub-matrix are:

$$\mathbf{X}^{nn'}_{L_1 L_2} = \frac{1}{2} \sum_{L'} i^{l'+l_1-l_2} (-1)^{m_2} F^{l',l_1,l_2}_{m',m_1,-m_2} Y_{L'}\left(\hat{R}_{nn'}\right) h^+_{l'}\left(\kappa R_{nn'}\right) , \tag{9}$$

where h^+_l are spherical Hankel functions. It should be pointed out that, for $n = n'$, $\mathbf{X}^{nn'} = \mathbf{0}$, which is consistent with the interpretation of the $(\mathbf{I} - \mathbf{XT})^{-1}$ term as the multiple scattering term. Following this, the diagonal blocks in equation (8) are zero.

Equation (1) tells us how to combine the monomer information in form of T-matrices but it says nothing about how these should be generated. That is, it does not prescribe what characteristics the R-matrix calculation to generate the monomer T-matrices should have. It is clear that to be consistent with the non-overlapping MS theory, the monomer data should represent the interaction with the electron in a volume as small as possible around it to minimise overlap. This implies running the R-matrix calculations for the smallest possible radius a. The other issue to take into account when choosing the parameters for the R-matrix calculation is how much of the long range interaction should be included. The most significant of these interactions for neutral clusters with a dipole moment (whose monomers also have a dipole moment) is with the dipole. But is this interaction well described by taking into account the electron interaction with the dipole moment of each monomer?

In practise, we have found (Bouchiha et al. 2008) that two different monomer T-matrices need to be used in Equation (1). One, $\mathbf{T}_{\mathrm{dip}}$, is determined by including in the R-matrix calculation the dipole interaction in the outer region. Failure to include this interaction leads to an underestimated cross section at low energies. The other T-matrix needs only to account for the very short range interaction and it is used in the MS term: $\mathbf{T}_c$ is calculated excluding the dipole interaction in the outer region. That is, we truncate the effect of the dipole at a certain radius a_c. In addition, a further truncation is necessary: a cut-off is applied on the angular momentum, and is used to include in the multiple scattering term only those partial waves that can overcome the angular momentum energy barrier $E(l,r) = \frac{l(l+1)}{r^2}$. The cut-off depends on the electron kinetic energy E_e and on the inter-molecular distance $d = R_{nn'}$; the partial waves with l_c such that:

$$E(l_c, d) = \frac{l_c(l_c+1)}{d^2} < E_e < E(l_c+1, d) = \frac{(l_c+1)(l_c+2)}{d^2} , \tag{10}$$

with the energies in Rydberg, should be retained.

With these two monomer T-matrices, the expression for the cluster T-matrix can be rewritten as:

$$\mathbf{T} = \mathbf{A} \cdot \mathbf{T}_{\mathrm{dip}} \cdot (\mathbf{I} - \mathbf{XT}_c)^{-1} \cdot \mathbf{B} . \tag{11}$$

To summarise: two R-matrix calculations need to be performed to obtain the monomer T-matrices. The inner region part is the same in both cases, but the outer region parameters differ. For $\mathbf{T}_{\text{dip}}$ we run the calculation including the dipole term in the multipole expansion potential whereas for $\mathbf{T}_c$ the interaction potential in the outer region is set to zero.

3. Characteristics of the calculation

Two different sets of R-matrix calculations were performed: the ones needed to generate the monomer T-matrices for the MS calculation and those to determine the *ab initio* elastic cross sections of the cluster for comparison purposes. We will briefly describe the characteristics of these as well as those of the MS calculation. Firstly, we describe the different dimer geometries chosen for the calculations.

3.1. Geometries

We run R-matrix calculations for five different geometries of $(H_2O)_2$; they all correspond to local minima in the potential energy surface. The geometry parameters have been taken from Park et al. (2001) (equilibrium geometry) and Huang et al. (2006) (all the others); some of these parameters are shown in Table 1 (the complete list can be found in the publications cited). We chose geometries with different properties, particularly with a range of different dipole moments, with the constraint that the geometry of the monomers was not heavily distorted from that of isolated water.

The geometry of the dimer in the MS calculation is 'built' by taking two identical monomers (in the equilibrium geometry) and rotating them (in fact, it is the T-matrices that are rotated) to reflect their relative orientation in the dimer. The distance between their centres of mass in the dimer is also an input parameter in the MS calculation. When the geometry used in the R-matrix calculation (directly constructed from the published parameters) includes monomers whose geometry is different to the equilibrium one, the conformation of the cluster in the MS calculation does not correspond exactly to the R-matrix one. Although small differences are unlikely to have a big effect, we tried to minimise these. For this reason, apart from the value of the dipole moment, the geometries we considered show similar characteristics.

The MS calculations are mostly influenced by the inter-monomer distance, their relative orientation and the total dipole moment; it is the latter that we are particularly interested in. One of the main objects of this work is to establish whether the global dipole interaction (i.e. that due to the dimer as a whole) is intrinsically taken into account in the cluster T-matrix of Equation (11), or whether a propagation as used by Bouchiha et al. (2008) is needed to include the dipole term explicitly.

On top of the equilibrium geometry (here labelled EQ), we studied collisions with the dimer in two configurations, labelled S and L, possessing a smaller and larger dipole moment respectively (1.77 Debye and 4.30 Debye) than the equilibrium geometry (2.73 Debye). In addition we chose two geometries for which the dimer has no dipole moment (labelled Z_1 and

Z_2) differing only in the relative position and orientation of the sub-units; the results would then be independent of the dipole interaction and from the comparison we would be able to look at other parameters influencing the calculation.

In some cases (see Table 1) the differences between the monomers in the dimer and the isolated one are not as small as in the equilibrium geometry, but they are never more than a few percents. It can be noted that in some cases the monomers lose the C_{2v} symmetry, having different O–H bond lengths, but the variation is always small. We believe that the geometry differences between the R-matrix and MS geometries will not affect significantly the results.

3.2. R-matrix calculations for the dimer

The R-matrix calculation was performed following previous work on electron scattering from isolated water (Gorfinkiel et al. 2002) and $(H_2O)_2$ (Gorfinkiel 2009) with some minor changes. As in the previous work, we used the double-zeta plus polarisation (DZP) Gaussian basis set of Dunning (1970) for O and the triple-zeta (TZ) basis of Dunning (1971) for H, augmented with a diffuse s function and two p functions extracted from the basis set used by Gil et al. (1994). However, since only the electronic ground state was included in the calculation, we decided not to generate natural orbitals as in previous work and we simply used the molecular orbitals from a Hartree-Fock self consistent field calculation.

These orbitals were then used in a CASCI (complete active space configuration interaction) calculation with 4 electrons frozen in two core orbitals, and including 11 active orbitals. The number of configurations generated was around 9000. The dipole moments obtained are compared to those calculated by Huang et al. (2006) in Table 2. Differences are smaller than 10% for all geometries. We deem the accuracy achieved sufficient for our purpose.

The radius of the R-matrix boundary was set to 13 a_0, following tests performed by Gorfinkiel (2009) for the dimer at the equilibrium geometry. We checked this radius for the other geometries considered here and it proved to be valid in all cases.

The continuum orbitals describing the scattering electron were expanded on a basis of Gaussian type orbitals (GTOs) centred on the centre of mass of the target, with l values up to 4. Including GTOS with higher l increases significantly the computational effort required. We used the set of GTOs optimised for an R-matrix sphere of radius 13 a_0 in Faure et al. (2002); it includes 13 functions of type s, 11 of type p, 10 of type d, 8 of type f and 6 of type g. A close-coupling configuration interaction calculation was performed to obtain the N + 1 wavefunctions in the inner region. The number of configurations generated was around 24000.

3.3. R-matrix calculation for the monomer

In order to produce the T-matrices required by the MS method we performed an R-matrix scattering calculation for the isolated water monomer. For the target description we made use of a similar basis set to that used for the water dimer description (DZP for the O, TZ for the H, with no extra s or p diffuse functions) and generated natural orbitals. In the CASCI model

we included a core orbital with two frozen electrons and 8 active orbitals. Again, only the electronic ground state was included in the calculations.

For these calculations, the R-matrix radius was set to 6 a_0, following the tests described in Caron et al. (2007). An appropriate continuum basis set was generated following Faure et al. (2002). Two T-matrices were obtained: $\mathbf{T}_{\mathrm{dip}}$, produced including the dipole interaction at all distances and $\mathbf{T}_c$ that only includes it up to $a_c = 6$ a_0 (see below).

3.4. Multiple Scattering calculations

Equation (11) shows how R-matrix gas phase data for monomers is combined in the MS theory to obtain electron-dimer cross sections. As explained in that section, $\mathbf{T}_c$ has to be trimmed, applying two cut-offs. One is a cut-off on the dipole, that is only included up to the radius a_c. This T-matrix therefore represents only the interaction of the scattering electron with the monomer sub-unit inside a small sphere around it, and neglects the long range interaction with its dipole. Caron et al. (2007) established that a value $a_c = 6$ a_0 was the optimum one when data on water molecules is used. This value, obtained in a study on ice, should depend only on the dipole moment of the sub-units, and should be valid also in our case, for all the dimer geometries considered.

The second cut-off is applied on the partial waves contributing to $\mathbf{T}_c$. To avoid discontinuities at energies where the number of partial waves included changes, a two-point interpolation on the parameter l between l_c and $l_c + 1$ is performed. In Bouchiha et al. (2008) an *ad hoc* correction term γ was introduced in Equation (10) to avoid including spurious features in the final cross section. In the present work, however, we have corrected the procedure used to generate the rotation matrices, and these spurious features (peaks) are no longer present for most of the dimer geometries. Nonetheless, the parameter is still necessary for the geometry labelled Z_2 and we have therefore performed all calculations with $\gamma=0.75$ such that:

$$\frac{l_c(l_c + 1)}{d^2} < \gamma E_e < \frac{(l_c + 1)(l_c + 2)}{d^2} \tag{12}$$

The monomer T-matrices produced in the R-matrix code need to be rotated; the Euler angles representing the rotations are obtained comparing the orientation of the water molecule as considered in the R-matrix calculation to that of each monomer in the dimer geometry. Since the dimerised monomers are not identical to the gas-phase monomers, no rotation can transform one into the other, so the elements we took into account to build the rotation matrices are the O–centre-of-mass direction and the H–O–H plane. There is no need for a third parameter since the water molecule is symmetric with respect to the cited symmetry elements.

Bouchiha et al. (2008) concluded that a propagation was required to include the electron-dimer dipole moment interaction. The R-matrix was obtained from the T-matrix (see their appendix) and then propagated from a radius of 9 a_0 to 50 a_0, where it was finally matched to the asymptotic Bessel functions to derive the propagated T-matrix and cross section. It must be pointed out that the procedure to obtain the R-matrix at a specific (non-asymptotic) distance

from the T-matrix is approximate: it assumes that the potential is zero for all electron-target distances bigger than the specified distance and this is clearly not the case for a polar molecule like water. In the present work we compared the propagated and unpropagated MS results, and concluded that the propagation step is not needed, since it increases the differences between the MS and R-matrix cross sections. This would imply that the interaction of the electron with the dipole moment of the cluster is already included in the global T-matrix of Equation (11).

4. Results and Discussion

In Figures 1 and 2 we present a comparison between cross sections obtained with the R-matrix suite and those obtained with the corrected version of MS code, for the five geometries considered. All the cross sections have been calculated up to an energy of 10 eV, above which non-physical resonances (pseudo-resonances) may appear.

The agreement between MS and R-matrix cross sections is very good down to 1 eV. Below this energy, the MS method overestimates the cross section for all geometries, except the one labelled L. At these low energies, the discrepancy is most significant in the Z_1 and Z_2 cases: the R-matrix cross section decreases approaching zero energy, as expected, while the MS curve displays the behaviour of a cross section describing a collision with a polar target. This would indicate that the effect of the electron interaction with a dipole moment, even if not explicitly taken into account by means of the propagation, is implicitly included, leading to an overestimation of the cross section, especially for $E \to 0$. It is to be expected that the less-rigorous MS method, in which the electron-dimer interaction potential is implicitly approximated with electron-monomer potentials, fares poorly at low energies. However, it is rather disappointing that the method fails to reproduce, even approximately, the shape of the cross section for those dimer geometries with no dipole moment.

Above 1 eV, the dimer geometry L presents the worst overall agreement; for this case, the MS method underestimates the cross section for all energies, thus implying that the effect of the dipole moment is underrepresented in this case. The S geometry shows a slightly better agreement between cross sections than EQ and the zero dipole moment ones. This dimer geometry possesses the dipole moment most similar to that of the water monomer.

For the dimer labelled L, for which the monomer geometries are most distorted in comparison to the isolated water (although this distortion is still small: the HOH angle of one of the monomers is reduced by less than 3%) we performed a test to investigate if this could be the cause of the disagreement between cross sections. We run a calculation in which one set of monomer T-matrices was calculated using a smaller HOH angle (the other set corresponded to the standard equilibrium geometry): the changes in the cross section were negligible. We have also tested that truncating the partial wave expansion at $l=5$ instead of $l=4$, both in the calculation of the R-matrix cross sections and in that of the T-matrices used to determine the MS cross section, has negligible effect on the agreement between them.

As mentioned before, use of the propagation procedure proposed in Bouchiha et al. (2008) does not improve the general agreement between MS and R-matrix cross sections. Similarly, a test for the equilibrium geometry in which $\mathbf{T}_{\mathrm{dip}}$ is generated neglecting the dipole

moment in the outer region produced an MS cross section that was too small below 5 eV. Other tests using different a_c or different R-matrix radii a in the calculation of $\mathbf{T}_{\mathrm{dip}}$ produced worse results or almost identical cross sections.

The cross section for electron scattering from a molecule with a permanent dipole moment is formally divergent in the fixed-nuclei approximation (Garrett 1971). This means that, in order to provide data that could be compared with experimental results, the cross sections for the EQ, L and S geometries would have to be 'corrected' using the dipolar Born approximation (Jain & Thompson 1983). This can be done in two ways: an approximate one that would require adding the same (energy dependent) correction to both cross sections and another that might potentially affect the R-matrix and MS cross sections significantly differently below 1 eV (Baluja et al. 2007). None of these will alter the conclusions derived here from the comparison, particularly as it is the cross sections for the geometries with μ=0 that show the bigger disagreement at very low energies.

Finally, it should be noted that the use of γ=0.75 has little effect on the MS cross sections. This parameter is, however, necessary to remove the spurious feature between 6-7 eV for the geometry labelled Z_2.

5. Conclusions

The multiple-scattering method first introduced to treat molecular clusters by Bouchiha et al. (2008) provides cross sections in good agreement with the more accurate R-matrix results for energies above 1 eV for several dimer geometries. Below 1 eV the MS technique seems to overestimate the effect of the electron-dipole moment interaction for four of the geometries considered and underestimate it for the one with a dipole moment more than twice as big as that of the monomer. For monomers with μ=0, the method fails to reproduce the correct behaviour of the cross section.

The method is computationally inexpensive once scattering data (T-matrices) are generated for the monomer. It requires, as most scattering calculations do, information on the geometry of the target cluster. In addition, the values of two parameters need to be established in order to determine $\mathbf{T}_c$: that of a_c, determining the extent to which the electron-dipole moment interaction is included, and γ, an *ad hoc* parameter required in the truncation of the partial wave expansion. The value for a_c was selected in a study of ice (Caron et al. 2007) and should only depend on the dipole moment of the molecular monomer. The value of γ is more of a puzzle: for the dimers presented here it is only needed in one case, to eliminate a non-physical feature. We chose γ=0.75 by comparing the MS and R-matrix cross sections for the Z_2 geometry: since no resonances are present in the R-matrix results, we concluded that the feature around 6.5 eV was non-physical and therefore needed removing. This γ value produces very little change in the cross sections when used for the other dimer geometries. The physical justification for the parameter is unclear: Caron et al. (2008) use $\gamma > 1$ linking it to a larger effective distance between unit scatterers, whereas in our case $\gamma < 1$. Nonetheless, preliminary work on $(H_2O)_3$ indicates that a γ=0.75 is also needed in that case to remove unphysical features. However, as we hope to extend this method to treating other clusters for

which no comparison will be possible and for which physical resonances may be present, a better way of determining the value of γ should be established.

Work is under way to apply the method to bigger molecular clusters and to dimers of other molecules.

Acknowledgments

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Tables and table captions

geometry	$R(O_1H_1)$	$R(O_1H_2)$	$\alpha(H_1O_1H_2)$	$R(O_2H_3)$	$R(O_2H_4)$	$\alpha(H_3O_2H_4)$	$R_{nn'}$
H_2O	1.81	1.81	104.5				
EQ	1.810	1.823	104.5	1.814	1.814	104.6	5.50
	[—]	[+0.013]	[—]	[+0.004]	[+0.004]	[+0.1]	
Z_1	1.816	1.822	104.82	1.816	1.822	104.82	5.37
	[+0.006]	[+0.012]	[+0.32]	[+0.006]	[+0.012]	[+0.32]	
Z_2	1.815	1.821	105.08	1.815	1.821	105.08	5.34
	[+0.005]	[+0.011]	[+0.58]	[+0.005]	[+0.011]	[+0.58]	
S	1.816	1.822	104.95	1.816	1.822	104.95	5.36
	[+0.006]	[+0.012]	[+0.45]	[+0.006]	[+0.012]	[+0.45]	
L	1.818	1.818	101.61	1.818	1.818	104.50	5.70
	[+0.008]	[+0.008]	[-2.82]	[+0.008]	[+0.008]	[—]	

Table 1. Bond lengths (in a_0) and angles (in degrees) of the isolated monomer and the five dimers considered. The values of the isolated monomer parameters are the same as in Gorfinkiel et al. (2002); those for the dimer geometry EQ are from Park et al. (2001) and those for the other dimers are from Huang et al. (2006). The difference between each parameter in the dimer and in the isolated monomer is also shown in square brackets. The inter-monomer distance ($R_{nn'}$) is also shown (measured in a_0).

geometry	sym	μ (Debye)	
		P	H
H_2O	C_{2v}	1.95	1.85
EQ	C_s	2.73	2.56
Z_1	C_i	0.00	0.00
Z_2	C_{2h}	0.00	0.00
S	C_2	1.77	1.65
L	C_{2v}	4.36	4.12

Table 2. Symmetries (point group) and dipole moments (in Debye) of the dimer geometries considered in this work. P denotes the values obtained in the R-matrix calculations and H indicates the dipole moments from Huang et al. (2006).

Figure captions
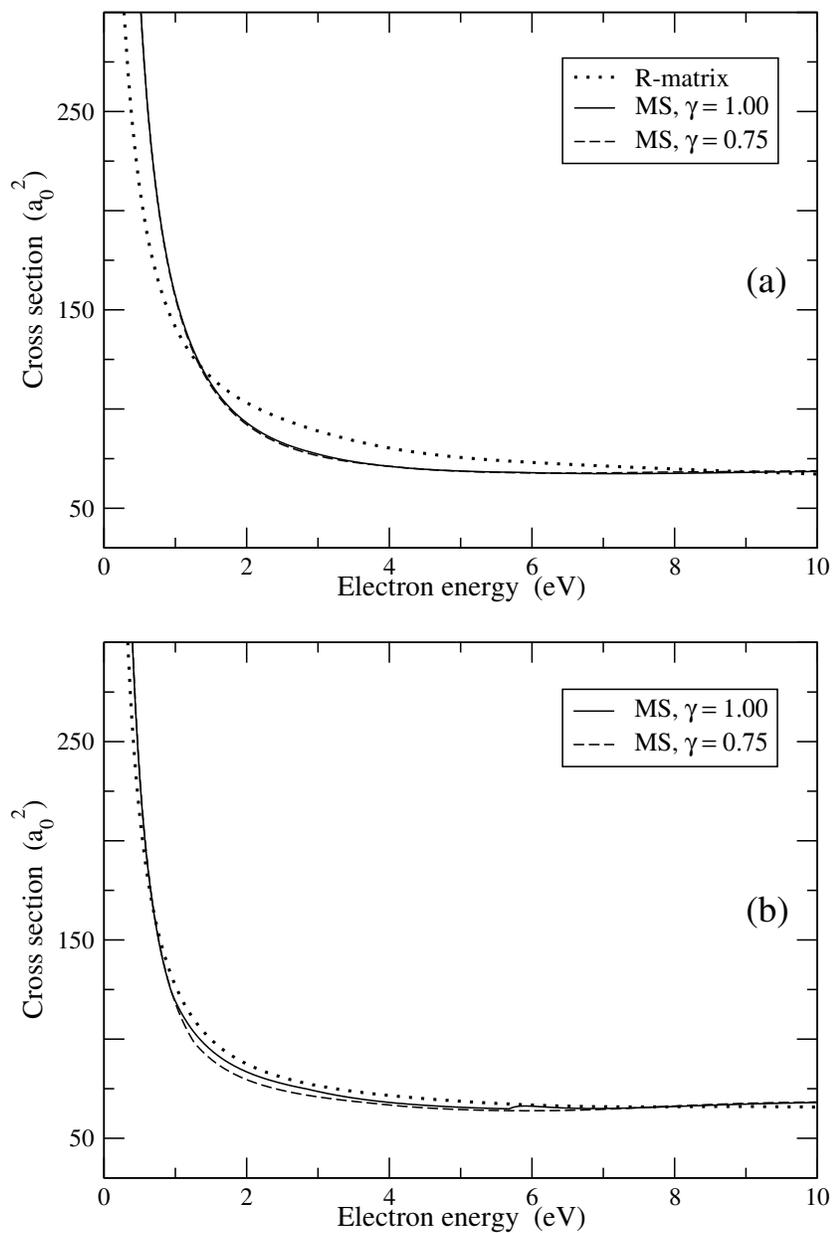
Figure 1. R-matrix and MS elastic cross sections for geometries EQ (a) and S (b) for two values of the parameter γ. The comparison for geometry S shows a very good agreement at all energies.
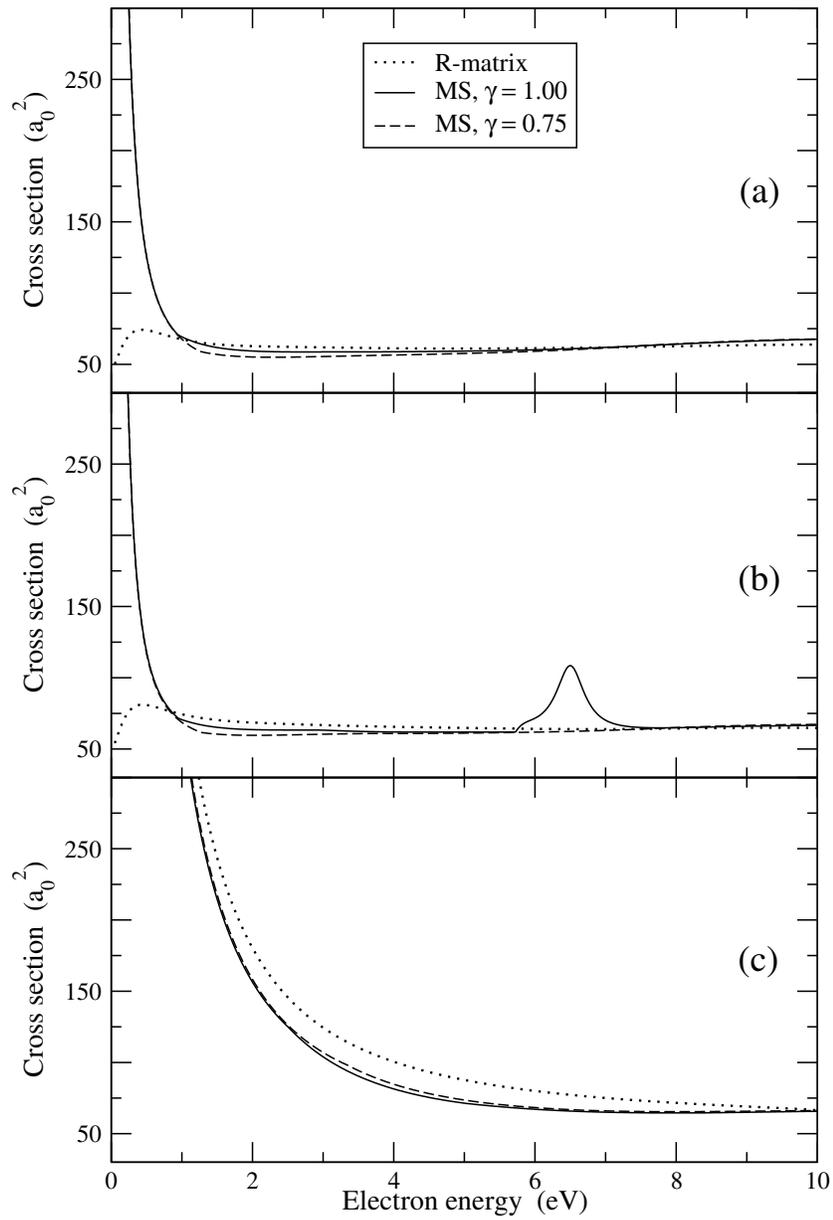
Figure 2. R-matrix and MS elastic cross sections for geometries Z_1 (a), Z_2 (b) and L (c) for two values of the parameter γ. The use of $\gamma = 1$ leads to the presence of an unphysical feature in the cross section for the Z_2 dimer in the 6-7 eV region.