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LETTER TO THE EDITOR

Electron–H_3^+ collisions at intermediate energies

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Abstract

A new procedure is presented for the *ab initio* study of electron–molecule collision at energies straddling the target ionization threshold. The *R*-matrix with pseudostates method, which allows for the inclusion of discretized continuum states in a close-coupling expansion, is adapted to molecular targets using even-tempered basis sets. Calculations for electron collisions with the H_3^+ molecular ion provide converged polarizabilities, electronic excitation and ionization cross sections.

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

Electron collisions with molecules are important for determining the behaviour of all low-temperature plasmas. The theoretical study of these collisions has greatly developed over the last 20 years. Low-energy processes (dissociative recombination, rotational excitation, excitation to low-lying electronic states, etc) are routinely investigated. Their study is not without problems, but a variety of well-tested methods, many of them *ab initio*, are available (Huo and Gianturco 1995). When the kinetic energy of the scattering electron is high, perturbative methods can be used for the study of electronic excitation and ionization.

In contrast, the intermediate energy regime has remained virtually untouched. This regime extends from below the first ionization threshold to a few hundred eV. The energy is too low for perturbative methods to be valid and *ab initio* methods based on close-coupling expansions require infinite numbers of channels. To date, only simple analytic expressions for ionization cross sections (Kim and Rudd 1994, Deutsch *et al* 2000, Huo 2001) are available and no method to study all possible electron impact processes has been implemented.

The intermediate energy problem also arises in the study of electron–atom collisions. For this, the *ab initio* convergent close-coupling (Bray *et al* (2002) and references therein) and intermediate energy *R*-matrix method (Burke *et al* 1987) proved highly successful for simple targets. More recently, other methods have been developed, among which the most significant are the *R*-matrix with pseudostates (RMPS) (Bartschat *et al* 1996), exterior complex scaling (Rescigno *et al* 1999) and time-dependent close-coupling (Pindzola and Robicheaux 2000) procedures. Of these methods, only the RMPS has been successfully applied to targets with many active electrons. Representing molecular continua is a more difficult task than

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representing atomic ones, due to the lower symmetry and multicentre nature of the potential. Pseudostates have been used in collision studies for more than 30 years as a way of completing the close-coupling expansion not only in electron and positron–atom collisions but also in ion–atom ones. Nevertheless, no systematic use of pseudostates for molecular systems has been reported.

Our aim is to develop an RMPS procedure to treat the general electron–molecule collision problem at intermediate energies as part of the UK *R*-matrix polyatomic code (Morgan *et al* 1998). In this letter, we report the first implementation of this procedure, which we call M-RMPS (molecular RMPS). We chose to first apply our method to H_3^+ because it is the simplest polyatomic ion. More significantly, H_3^+ is the dominant ion in low-temperature hydrogenic plasmas. It plays a fundamental role in interstellar chemistry and has been observed in planetary aurora and diffuse interstellar media (McCall *et al* 1998) where significant populations of energetic electrons are to be found. The interaction of H_3^+ with thermal (McCall *et al* 2003, Kokoouline and Greene 2003) and higher energy (Kalhori *et al* 2004) electrons remains an active area of study. However, there is no published information about collisions with intermediate energy electrons, although such experiments have been performed (El Ghazaly *et al* 2004).

The basic idea of the standard *R*-matrix method is the division of configuration space into two regions (see Huo and Gianturco (1995) for details). The boundary between the regions is defined by a sphere of radius a centred at the centre of mass of the molecule. In the inner region, exchange and correlation are taken into account using rigorous quantum chemistry methods. In the outer region, where these effects are negligible, the use of long-range multipole potentials suffices to describe the electron–molecule interaction. When the electronic part of the problem is very complex (as is the case at intermediate energies) *R*-matrix calculations are so far restricted to the use of the fixed-nuclei approximation. In this approximation, nuclear motion is neglected and the electronic wavefunctions are calculated at the ground state equilibrium geometry of the molecule. The neglect of the rotational motion is known to have little effect for non-dipolar systems; the effect of vibrational motion, however, might be more significant.

In the inner region, the basis states wavefunctions can be written as

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

where the $u_{ij}(x)$ are continuum orbitals and x_i are the spatial and spin coordinates of electron i; ϕ_i are target wavefunctions, which are expressed in terms of a configuration interaction (CI) expansion. The χ_i are multi-centre, quadratically integrable, L^2 functions constructed from the target occupied and virtual molecular orbitals (MOs), and are used to represent correlation and polarization effects. In the polyatomic *R*-matrix suite, both molecular and continuum orbitals are expanded in terms of Gaussian type orbitals (GTOs). The coefficients a_{ijk} and b_{ik} are obtained by diagonalizing the N+1 electronic Hamiltonian.

The RMPS method augments the close-coupling expansion of equation (1) with wavefunctions that represent target pseudostates. These states are not true eigenstates of the target, but if chosen correctly, they represent a discretized version of the electronic continuum. Transitions into the pseudostates whose energies are above the ionization threshold are assumed to represent ionization, although it may be necessary to project out the bound component of these states (Kernoghan *et al* 1995).

Normally, pseudostates are obtained by diagonalizing the target electronic Hamiltonian in a suitable basis. To represent the continuum these pseudostates must be able to reproduce the electron density of the ionized system (that is, of the target with an extra positive charge plus an electron that is no longer bound). This can be achieved by including the appropriate configurations in the CI expansion. For this purpose, we introduce in our calculations a new set of orbitals, that we will call pseudo-continuum orbitals (PCOs). These orbitals are used to describe the ionized electron. Then, on top of the usual configurations employed in the target description (where all the electrons occupy MOs) another set of configurations is included in which one of the target electrons occupies a PCO.

In our implementation, the PCOs are expanded in terms of GTOs centred at the centre of mass of the system using an even-tempered basis set (Schmidt and Ruedenberg 1992). In this type of basis sets, the exponents of the GTOs follow:

$$\alpha_i^{\mathrm{PCO}} = \alpha_0 \beta^{(i-1)} \qquad i = 1, \ldots, N. \tag{2}$$

An advantage of using even-tempered exponents is that different basis sets can be systematically generated by choosing different values for the parameters α_0 and β. This can be used for proving convergence and removing pseudoresonances (see below). It is a necessary condition for the R-matrix method to be valid that the electronic density of all the target states included in the expansion (1) is contained inside the R-matrix box. This means, in practice, that the amplitudes of the basis functions used to expand the MOs must be negligible at the boundary. This must also hold for the GTOs expanding the PCOs which puts a lower limit on the values of α_0 that can be employed.

The main practical problem that arises when including pseudostates in the calculation is that of linear dependence. In the standard R-matrix polyatomic treatment (Morgan *et al* 1998), the continuum orbitals are Schmidt orthogonalized to the already orthogonal MOs. The resulting set of continuum orbitals are then made orthogonal using a symmetric orthogonalization procedure. In this step, several continuum orbitals may be deleted; for this purpose a deletion threshold, δ_{thrsh}, must be provided. For standard R-matrix calculations δ_{thrsh} varies with a (and hence, with the continuum basis set) and is usually set to $\delta_{\mathrm{thrsh}} = 10^{-7}$ for $a = 10a_0$. To allow for the inclusion of PCOs we implemented an extra orthogonalization step: the PCOs are first Schmidt orthogonalized to the MOs and then symmetric orthogonalized among themselves (again, several PCOs may be deleted). The resulting set of MOs and PCOs is then treated as the MOs set in the standard calculation. The choice of β is dictated by two contradicting trends: smaller values provide a better distribution of pseudostates but make it more difficult to avoid linear dependence (a more detailed analysis can be found in Gorfinkiel and Tennyson (2004)). We find that use of $\delta_{\mathrm{thrsh}} \geqslant 5 \times 10^{-6}$ is required both for PCOs and continuum orbitals.

In our calculations, we restricted the PCO basis to $l \leqslant 2$ and used a radius of $a = 10a_0$. For the MOs, we followed Faure and Tennyson (2002) and used the basis set from Orel (1992) removing from it the two GTOs with the smallest exponents. For the continuum we adapted the basis set (with $l \leqslant 4$) from Faure and Tennyson (2002); the largest exponents were deleted so that

$$\alpha_i^{\mathrm{PCO}} \geqslant \alpha_j^{\mathrm{continuum}} \qquad \forall i, j. \tag{3}$$

This measure facilitates the orthogonalization and does not undermine the representation of the scattered electron since the PCO basis provides short range GTOs. In contrast to previous electron impact excitation studies, we built MOs corresponding to H_3^{2+}. In this way, we tried to ensure that configurations with single excitations into PCOs represented an electronic distribution similar to that of an ionized state of H_3^+. As a result, the excitation thresholds to the first three excited states were slightly lower than those predicted by more accurate calculations.

Many PCO bases were tested for our calculations. The criterion was to obtain a fairly homogeneous distribution of pseudostates while avoiding linear dependence problems. The first basis tested (with $\beta = 1.5$) had few pseudostates associated with the open channels in the

Table 1. Polarizabilities of H_3^+.

States in close-coupling expansion	$\alpha_\parallel$	$\alpha_\perp$
6 (physical target states)	−3.2848	−0.0638
28 (states up to IT, $E_{\text{cut}} = 33.47$ eV)	−3.4563	−2.0893
64 (states up to $E_{\text{cut}} = 45$ eV)	−3.5247	−2.2093
152 (states up to $E_{\text{cut}} = 132$ eV)	−3.5336	−2.2480
Accurate *ab initio* value[a]	−3.5978	−2.2454

[a] Accurate *ab initio* value from Augspurger and Dykstra (1998).

10 eV range above the ionization threshold. Furthermore, the first pseudostate corresponding to a continuum state was 2 eV above the ionization threshold. These calculations resulted in cross sections that showed a 'step' behaviour and displayed a threshold for ionization that was 2 eV above the true threshold. The best pseudostate distribution was obtained using the values $\beta = 1.3$ and $\alpha_0 = 0.14, 0.15, 0.16, 0.17$.

When using the standard R-matrix method, the computationally demanding part of the calculation corresponds to the diagonalization of the N+1 electronic Hamiltonian in the inner region. For electron rich systems, this can severely limit the quality of the target description. On the other hand, because only a few dozen channels are present, the calculation of the K-matrices in the outer region is computationally cheap, which allows very fine grids of incident energies to be studied. When the number of target states is increased, the number of channels rises significantly, even when the partial wave expansion is restricted to low l. As a result, the outer region becomes the most time-consuming part of the calculation. This puts a computational limit on the number of target states that can be included and the number of calculations with different basis sets for the PCOs that can be run.

Here we restrict our scattering calculations to those including 64 (bound and continuum) target states. The criterion was to include all states obtained in our target CI whose energy difference with the ground state was smaller than a certain value E_{cut}. From a full CI calculation, we determined the vertical ionization threshold (IT) of H_3^+ to be 33.47 eV. So $E_{\text{cut}} = 45$ eV was chosen to ensure that we would have a good representation of our system up to energies of 43 eV. With these characteristics, the 64 target states included in our H_3^+ calculation produced around 400 channels for each of the four irreducible representations of the C_{2v} point group used in the calculations.

An important result of our calculations is that the target polarizability converges when pseudostates are included in the close-coupling expansion. The slow convergence of these expansions is well known (Gil *et al* 1994); so is the importance of accurately representing the polarizability of the target for low energy collisions. Table 1 shows our results for the PCO basis set with $\beta = 1.3$ and $\alpha_0 = 0.14$. Inclusion of 64 target states brings both components of the polarizability to within 2% of the high accuracy result (Augspurger and Dykstra 1998). Tests showed that increasing the number of target states in the expansion without the use of pseudostates does not lead to convergence of $\alpha_\perp$: inclusion of a discretized representation of the target continuum is clearly essential for this convergence.

The use of pseudostates in a calculation introduces unphysical, spurious resonances above the IT known as pseudoresonances. For cationic targets, each pseudostate supports a series of Feshbach type pseudoresonances associated with the Rydberg series converging to them. Below the IT these pseudoresonances give an approximate representation of the real resonance series of the system. Several methods have been proposed to deal with above IT pseudoresonances in electron–atom collisions. In atomic RMPS calculations, they are eliminated by performing a weighted average of several calculations with different bases for the PCOs (Bartschat and Bray 1996). Due to the large number of sharp resonances in our case, this method was not effective. We found that a convolution procedure similar to the one proposed by Meyer *et al* (1995) followed by an averaging of the convoluted results is best suited to deal with the problem in the ionization cross section. A Gaussian function of variable width was used to convolute each cross section (for each PCO basis) and the results were then averaged to produce our final cross section:

$$\sigma^{\mathrm{ION}}(E) = \frac{1}{4\sqrt{\frac{\pi}{\sqrt{E}}}} \sum_{i}^{4} \int_{E_m}^{E_M} \mathrm{e}^{-\sqrt{E}(E'-E)^2} \sigma_i^{\mathrm{ion}}(E'; \alpha_{0i}) \, \mathrm{d}E' \tag{4}$$

E_m is taken to be $0.5E_h$ smaller than the IT and E_M is at least $0.5E_h$ bigger than the maximum energy for which σ^{ION} is presented. This method eliminates all resonances, including physical ones. We found no stable resonance whose position does not change with the change of basis in this energy range: that is, no physical resonances are present above the IT. This justifies the use of the convolution procedure, but a technique to preserve the physical resonances above IT would have to be devised for collisions in which they are present.

Our low energy eigenphase sums are in agreement with previous calculations (Orel and Kulander 1993, Faure and Tennyson 2002) which included only six bound target states. However, the positions of the low-lying Feshbach resonances are all shifted downwards corresponding to an increase in the quantum defect of about 0.05 compared to the previous studies. This result, which is of significance for processes such as ion-pair formation in the dissociative recombination of H_3^+ (Kalhori *et al* 2004), is probably a consequence of the correct representation of the polarizability.

The cross sections for excitation into the first two ($^3\mathrm{E}'$ and $^1\mathrm{E}'$) excited states are very similar to previous results for energies up to about 20 eV. However, with increasing incident energy, the 6-state and the pseudostate calculations differ: figure 1 shows the cross section for excitation into the first $^3\mathrm{E}'$ state. As can be seen, the 6-state calculation overestimates the cross section at higher energies. The four $\beta = 1.3$ bases for the PCOs give practically identical results below the IT so only one is shown in the figure for clarity. This indeed should be the case if the choice of basis for the PCOs is correct. Above the IT, the four cross sections differ in the position of the pseudoresonances and also slightly in magnitude. A cubic fit to the average of the four $\beta = 1.3$ pseudostate calculations is shown in figure 1 as our recommended value in this energy region.

Figure 2 presents our results for the ionization of H_3^+. The four different $\beta = 1.3$ PCO bases give cross sections that are similar in size but have different pseudoresonance structures. The convolution plus averaging procedure produces a smooth cross section, shown in figure 2(b). This cross section still shows some oscillations that we consider to be within our numerical error, and hence should not be seen as physical features.

Figure 2 also compares our results with the prediction given by the Wannier threshold law (Wannier 1953). Our unaveraged results give excellent agreement with this law for almost 1 eV above the IT. However, the Gaussian averaging procedure does not preserve this agreement and results in an unphysical cross section below IT. Also plotted in figure 2(b) is the cross section obtained with the pseudostate basis corresponding to $\beta = 1.5$, $\alpha_0 = 0.14$ and a slightly higher deletion threshold in the orthogonalization procedure. As mentioned before, this basis does not provide a good ionization cross section.

Cross sections for production of D^+ and D_2^+ in intermediate energy electron–D_3^+ collisions are currently being measured in Belgium. Comparison with these experiments will be given in a longer paper (Gorfinkiel and Tennyson 2004) which will also discuss in detail the more

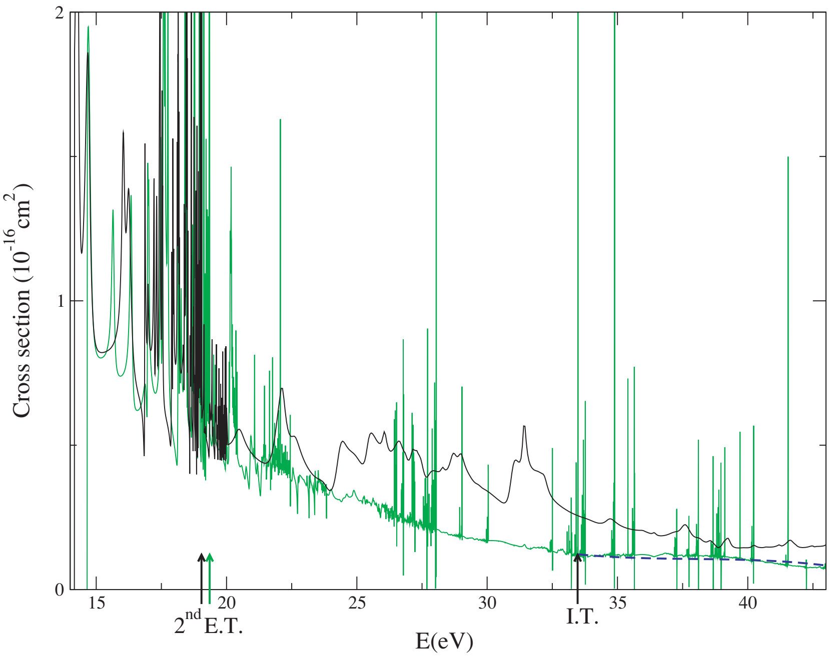

Figure 1. Integral cross section for excitation into the first excited electronic state (^{3}E$'$). Dark full line: 6-state calculation with no pseudostates. Light full line: 64-state calculation with PCO basis with $\alpha_0 = 0.14$ and $\beta = 1.3$. Dashed line: fit to the averaged cross section above ionization threshold (IT). Arrows indicate the second excitation threshold (ET) in each calculation and the IT.

technical aspects of our calculations. This comparison will allow us to test the validity of our results.

In conclusion, we have extended the energy range for which electron–molecule collision processes can be studied *ab initio* using a molecular *R*-matrix with pseudostate method (M-RMPS). We present the first *ab initio* electron–molecule cross sections at intermediate energies, including ionization cross sections. We show that the M-RMPS method allows us to obtain converged polarizabilities. This is the first time that proven converged polarizabilities have been obtained as part of an electron–molecule collision study. This opens the possibility of employing small bases of pseudostates optimized for the accurate representation of the polarizability in low energy calculations.

The M-RMPS method is fully general and has been implemented as part of the UK polyatomic *R*-matrix code (Morgan *et al* 1998). The implementation differs significantly from the atomic one. In the atomic RMPS, Sturmian-type functions (that form a complete set for hydrogenic systems) are used to describe the ionized electron. In our case, the use of Sturmians introduced too many numerical difficulties and hence we opted for the use of GTOs. These functions allow for an analytical solution of the integrals involved and hence a much higher accuracy. The orthogonalization steps are also different, since the atomic RMPS uses numerical continuum functions and the molecular case GTOs. In the atomic case, a Lagrange orthogonalization between continuum and target orbitals is first performed and then the continuum orbitals are Schmidt orthogonalized to the target orbitals and PCOs. The molecular case involves successive steps of Schmidt and symmetric orthogonalization procedures (see above).

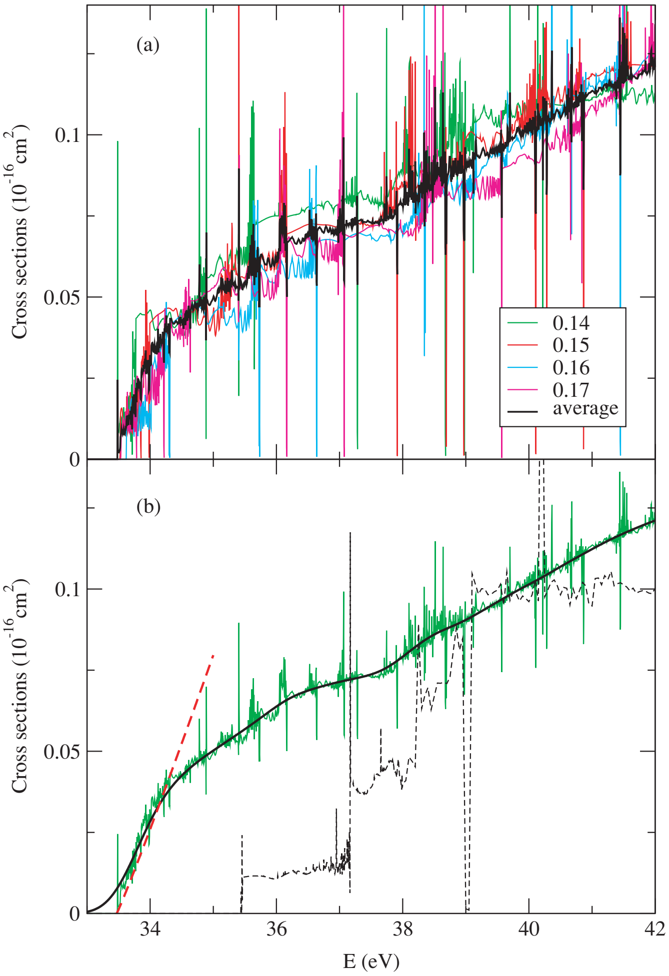

Figure 2. Total ionization cross section for different models. Panel (a) shows results for four different PCO bases with $\beta = 1.3$ and the α_0 values indicated in the graph; the black line corresponds to the averaging (with equal weights) of the four individual cross sections. In (b), the following cross sections are compared: average plus convolution result (dark full line); averaged (non-convoluted) cross section (light full line); unconverged result from the PCO basis set with $\alpha_0 = 0.14$ and $\beta = 1.5$ (thin dashed line) and a low energy fit following the Wannier threshold law: $\sigma \propto E^{1.05589}$ (thick dashed line).

The work presented here is a first approach to the problem. A lot remains to be done and calculations can definitely be improved. Other methods for treating the pseudoresonance problem could be tested. A projection method may be needed for more complex molecules (tests for H_3^+ showed no effect on the ionization cross section). Neutral molecules have much more diffuse electronic wavefunctions and consequently their study requires bigger R-matrix boxes (for example, $a = 20a_0$ for H_2 (Branchett and Tennyson 1990)). This in turn means that larger continuum and PCO basis sets are needed, increasing the number of channels in the outer region. Therefore, a parallel implementation of this part of the code is needed to study neutrals. Our M-RMPS method should allow the study of many new complex problems such as excitation to high lying electronic states and electron collisions with molecular anions.

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