DETERMINING IONIZATION CROSS SECTIONS WITH THE MOLECULAR R-MATRIX WITH PSEUDOSTATES METHOD

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The molecular R-matrix with pseudostates method (MRMPS) has been developed to calculate excitation and ionisation cross sections at energies straddling the first ionization threshold of the target. The method is fully general and has been implemented as part of the UK polyatomic R-matrix code [1]. This is the first *ab initio* method that provides information on molecular electron impact ionisation.

The MRMPS method, similar to the R-matrix with pseudostates method employed in electron-atom collisions [2], is based on the use of some states that represent a discretized continuum. These states, known as pseudostates, are eigensolutions of the molecular Hamiltonian within the basis set used but do not represent real eigenstates of the system. If chosen carefully, they will give a proper description of the continuum states of the target at short range. These pseudostates are included in the close-coupling expansion used to represent the basis states wavefunctions for the target plus electron in the inner region. Transition into the pseudostates that are above the ionization threshold can be interpreted as ionization. In practice, a projection technique may be required to extract the bound component from the pseudostates.

How to generate the pseudostates and ensure a good description of the ionized target is far from trivial. In our implementation, we use Gaussian Type Orbitals (GTOs) as basis functions for all (bound, continuum and pseudocontinuum) orbitals. This makes all integrals required analytical but leads to problems of linear dependence. A careful choice of exponents for the GTOs used to expand the pseudocontinuum orbitals can ensure that this linear dependence is avoided while at the same time providing a good distribution of pseudostates. We have chosen to use an even-tempered basis set for the pseudocontinuum orbitals, so their exponents follow: $\alpha_i = \alpha_0\beta^{(i-1)}$. However, no systematic strategy for the choice of α_0 and β has yet been found.

Another problem that arises in these calculations is the presence of non-physical resonances associated with the pseudostates. This problem is particularly severe in the case of cationic targets (e.g. H_3^+) as there are an infinite number of Rydberg states of H_3 that converge to each of the H_3^+ thresholds. A convolution plus averaging technique has been implemented to deal with this problem. This technique requires performing calculations for several sets of pseudostates.

The MRMPS method was first applied to H_3^+ [3, 4] and then to H_2 [4]. Agreement with experimental data for ionisation of H_2 is very good. Experiments for H_3^+ are currently being performed. Use of pseudostates in the close-coupling expansion produced a converged polarizability for both systems. This results can have significant relevance in low energy collisions where polarization effects are very important.

We will describe in detail how the MRMPS method has been applied to the calculation of ionisation cross sections. In particular, a projection method recently implemented and based on collisional calculations of the bound states of the target plus electron system, will be presented at the conference.

References

[1] L.A. Morgan, J. Tennyson and C. J. Gillan 1998 *Computer Phys. Commun.* **114** 120.

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