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Electron re-scattering from H_2 and CO_2 using R-matrix techniques

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The R-matrix method is being used to investigate electron (re-)scattering for the H_2 and CO_2 systems. This is being done computationally using the UK molecular R-matrix package. The similarity of re-scattering to electron–molecule scattering off the associated cations at geometries near to those of the neutral molecules forms the basis of our initial model. Preliminary cross-sections and eigenphase sums have been calculated for molecular hydrogen and carbon dioxide. These show highly resonant behaviour in the energy range studied and this is particularly pronounced as channel thresholds are approached. The initial results suggest that inclusion of resonance phenomena could be vital for interpretation of electron re-scattering experiments. Elastic differential cross-sections for symmetries relevant to experiments performed using linear polarization are also presented and prospects for a more realistic model are discussed.

1. Introduction

Electron re-scattering in conjunction with high harmonic generation can allow for time-resolved study of nuclear and electronic dynamics at subfemtosecond timescales with Ångstrom spatial resolution [1–5], see [6] for a general review of the attosecond physics area. In such experiments a molecule is ionized in a strong, few cycle, laser field. The changes in sign of the laser field during the cycle can cause the electron to re-collide with its parent molecular ion. Under these circumstances the electron can either recombine leading to high harmonic generation or it can be scattered. This scattering can be thought of as electron self-diffraction and the process has the potential to act as a detailed probe of the target molecule [2]. It is usual for such experiments to be performed on aligned molecules, as the alignment can modify the probability of re-collision.

It is important for the understanding and analysis of such experiments to have a physically sound theoretical model of re-scattering which is capable of treating quantum mechanically the complicated scattering dynamics of an electron–molecular ion collision. We use sophisticated *ab initio* quantum mechanical techniques to model this part of the re-scattering process. Previous theoretical models of the recollision problem have thus greatly simplified this aspect of the problem [1, 7, 8].

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In our preliminary model, re-scattering from a molecule is modelled as electron scattering from the corresponding molecular cation. The nuclear geometry is assumed to be frozen at the neutral molecule equilibrium value. Molecular alignment and strong field effects have not yet been included.

H_2 and CO_2 are two molecules well suited to experimental study (e.g. [9]) and have been our initial subjects. However the theoretical techniques being used offer great flexibility and can be applied to other small molecules of interest.

2. The R-matrix method

The R-matrix method is an *ab initio* and fully quantum theoretical technique particularly well suited to electron scattering problems [10]. It divides the configuration space of the molecular target into an inner and outer region. In the inner region the scattering electron interacts with the bound electrons through exchange and electron–electron correlation. Rigorous techniques from quantum chemistry are used to account for these interactions, giving energy independent wave functions. The outer region reduces to a potential scattering problem where a single electron moves in the long range multi-pole potential of the molecule. Only the outer region problem needs to be solved as a function of electron energy. This is of particular importance for problems, such as the ones considered here, involving electron collisions with molecular ions since the strong energy dependence of these collisions means that calculations need to be repeated for a large number of energies to obtain reliable results.

The UK molecular R-matrix codes [11] give a general implementation of the R-matrix method for low (and intermediate [12]) electron collision energies. It has been widely used to study electron collisions with a variety of molecular ions but at present has no facilities for orienting molecules or dealing with attosecond laser fields. The former should be fairly straightforward to implement, the latter much less so.

3. Results

3.1 *Molecular hydrogen*

Electron collisions with the H_2^+ ion have been well studied [13–17], indeed it is something of a benchmark problem. Our calculations are therefore standard [15], but we focus on the collision symmetries of importance to a re-scattering experiment using linearly polarized light.

H_2 is a homonuclear diatomic and a member of the $D_{\infty h}$ point group; its ground state is X $^1\Sigma_g^+$. In our calculation we consider a rigid molecule with the inter-nuclear separation frozen at $1.4\,a_0$. The close-coupling expansion includes the lowest three states of the H_2^+ target ion which are $^2\Sigma_g^+$, $^2\Sigma_u^+$ and $^2\Pi_u$ symmetry. Dipole selection rules mean that a $^1\Sigma_g^+$ state can be excited to a state of either $^1\Sigma_u^+$ or $^1\Pi_u$ total symmetry by a single photon. However linearly polarized light means that only

$\Sigma_g^+ \leftrightarrow \Sigma_u^+$ transitions will occur. This means that in the case of multiphoton, linearly polarized light the total collision symmetry must be either ${}^1\Sigma_g^+$, which requires an even number of photons to be absorbed, or ${}^1\Sigma_u^+$, which requires an odd number. We therefore only consider these two total symmetries.

Figure 1 shows the total cross-section for the (re-)collision of an electron with an H_2^+ target. In these figures the energy scale represents the energy of the free electron, so has to have the vertical ionization energy of H_2, 16.4 eV [18], added to it to give the total energy absorbed from the laser field. The most notable feature in both figures is the pronouced structures caused by the temporary capture of the electron into resonances. Table 1 tabulates the position and widths of the lowest of these resonances. The values given here are in good agreement with those from other studies, although use of more states and larger basis sets leads to a slight lowering in the resonance positions and decrease in the width [15, 17] in line with the variational principle.

We note that there are an infinity of resonance series each of which contains an infinite number of resonances of decreasing width. Our calculation only captures

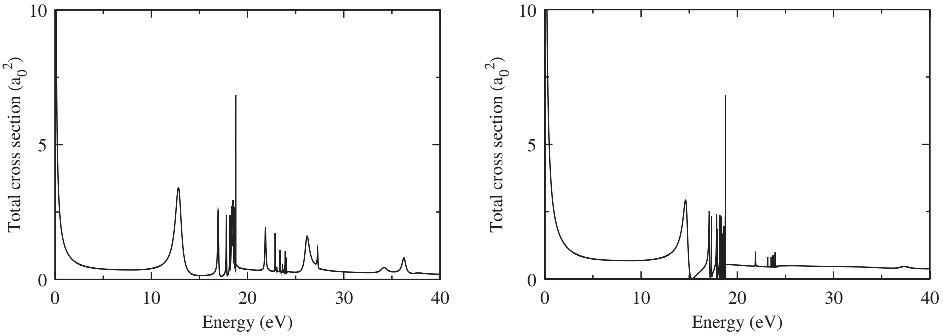

Figure 1. Total cross-section as a function of energy for the electron–H_2^+ collision problem: left-hand figure ${}^1\Sigma_g^+$ total symmetry, right-hand figure ${}^1\Sigma_u^+$ symmetry.

Table 1. Positions, widths and effective quantum numbers, ν, for low-lying H_2 resonances with ${}^1\Sigma_g^+$ and ${}^1\Sigma_u^+$ total symmetries.

E_r (eV)	Γ (eV)	ν	E_r (eV)	Γ (eV)	ν
${}^1\Sigma_g^+$			${}^1\Sigma_u^+$		
12.87	0.770	1.5191	14.76	0.553	1.8421
16.95	0.107	2.7386	17.11	0.084	2.8633
17.81	0.043	3.7584	17.32	0.015	3.0638
18.17	0.023	4.7650	17.86	0.034	3.8651
18.23	0.001	5.0110	17.95	0.006	4.0717
18.36	0.014	5.7771	18.19	0.017	4.8659
			18.24	0.003	5.0750
			18.37	0.010	5.8664
			18.40	0.002	6.0766

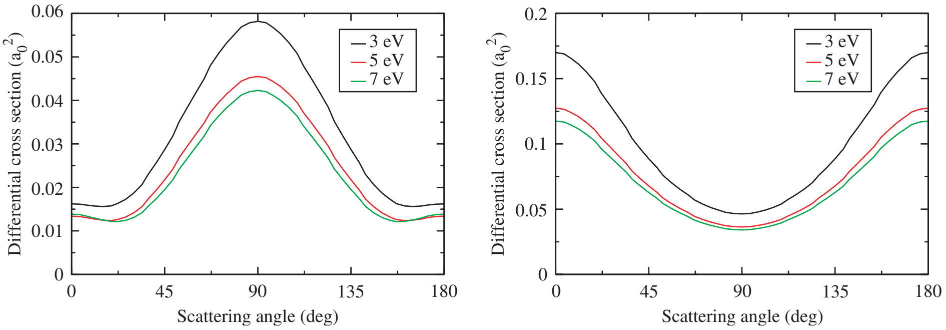

Figure 2. Differential cross-sections for electron–H_2^+ collisions for three electron collision energies: left-hand figure $^1\Sigma_g^+$ symmetry, right-hand figure $^1\Sigma_u^+$ symmetry. (The colour version of this figure is included in the online version of the journal.)

those series which converge on the two low-lying excited states of H_2^+ included in the calculation. Structure in our cross-sections which lie above the second of these states at our calculated vertical excitation energy of 24.1 eV must thus be treated with caution. To treat this region correctly requires a significant extension of the techniques used here [12, 19].

One question which has not been previously addressed is the symmetry dependent shape of the differential cross-section (DCS) for low-energy electron–H_2^+ collisions. Figure 2 shows differential cross-sections for three non-resonant collision energies separated by total symmetry. It is unusual to consider single symmetry contributions to the DCS since most scattering experiments cannot separate these contributions. For both symmetries at all three energies we find DCSs which are very symmetric about a 90° collision: for $^1\Sigma_g^+$ scattering this geometry represents a significant maximum, while for $^1\Sigma_u^+$ the scattering is strongly forward (0°) or backward (180°) peaked. Such symmetric differential cross-sections are typical of processes which are dominated by a single partial wave.

3.2 *Carbon dioxide*

CO_2 is a linear triatomic molecule and is also a member of the $D_{\infty h}$ point group with a ground state of X $^1\Sigma_g^+$ symmetry. In our calculation the two CO bond lengths were frozen at their equilibrium value of 2.196 a_0 [20]. The coupled-states expansion includes the lowest four states of the CO_2^+ target ion which have $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$ and $^2\Sigma_g^+$ symmetry respectively.

There has been little previous theoretical work on the electronically excited states of CO_2^+, see [20] for an exception. A 6-311G* basis set of Gaussian type functions was used to represent the CO_2^+ 'target' in our calculations. We test various target models based on the use of the complete active space (CAS) procedure to represent the configuration interaction (CI) of the valence electrons [21]. In order of increasing complexity the models used comprised 72 orbitals (model I), 83 orbitals (model II) and 93 orbitals (model III) which represents the full valence space. Models II and III, as could be expected, gave superior target energies but resulted in calculations which

Table 2. Comparison CO_2^+ target models (see text for details). Ground state energies are absolute energies, other calculated energies are vertical excitation energies. The experimental energies from [22] are abiabatic excitation energies and therefore systematically lower than the calculated ones. All energies are in eV.

	Model I	Model II	Model III	Model I + NOs	Expt.
X $^2\Pi_g$	−5093.94	−5097.00	−5097.12	−5094.07	
A $^2\Pi_u$	5.28	3.96	3.96	4.66	3.82
B $^2\Sigma_u^+$	5.72	4.62	4.61	5.39	4.30
C $^2\Sigma_g^+$	7.49	5.88	5.86	7.21	5.62

were too large to be tractable when the extra electron was added in the scattering part of the computation. As a compromise we used model I but employed state averaged (pseudo)-natural orbitals (NOs) to improve the target representation. These NOs were obtained from the standard model plus single excitations to all virtual orbitals and double excitations to selected virtual orbitals from each symmetry and weighed the $^2\Pi_g$ and $^2\Sigma_u^+$ states one and six respectively. Table 2 summarizes the results of target calculations with these models.

Unlike the electron–H_2^+ problem, there has been little previous work on electron collisions with the CO_2^+ molecular ion. There is experimental work on photoionization of CO_2 [22, 23]. The only previous theoretical studies we are aware of also concentrated on the photoionization problem [24, 25].

Our scattering calculation was performed using the UK R-matrix polyatomic code [11, 26] which employs Gaussian type orbitals to represent the continuum. Here we used an R-matrix radius of $10\,a_0$ and the corresponding set of continuum orbitals for ionic targets designed by Faure *et al.* [27]. The close spacing between the excited target states meant that it was necessary to propagate [28] to a large distance to get stable results. A distance of $250\,a_0$ was used for the calculations presented here.

As CO_2 has the same symmetry as H_2, the same dipole allowed selection rules apply for absorption of linearly polarized light by an oriented molecule. However the UK R-matrix polyatomic code does not handle $D_{\infty h}$ symmetry and the calculations were instead performed using $^1A_{1g}$ and $^1B_{1u}$ symmetries to represent $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetries respectively. Below we use the $D_{\infty h}$ symmetry labels for clarity but it should be remembered that the results will also contain (minor) contributions from higher (Δ and above) symmetries.

Figure 3 gives our $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetry total cross-sections for electron collisions with CO_2^+. Again one should remember that $^1\Sigma_g^+$ corresponds to absorption of an even number of photons and $^1\Sigma_u$ an odd number, and that the total energy of the photons absorbed is the (re)-collision energy plus the CO_2 vertical ionization energy of 13.78 eV [22].

Perhaps unsurprisingly given simple geometric considerations, the total (re)-collision cross-section for an electron with CO_2^+ is considerably larger than that for electron–H_2^+. Indeed it is more than an order-of-magnitude larger for the $^1\Sigma_u^+$ symmetry. Again the cross-sections below the target states included in the

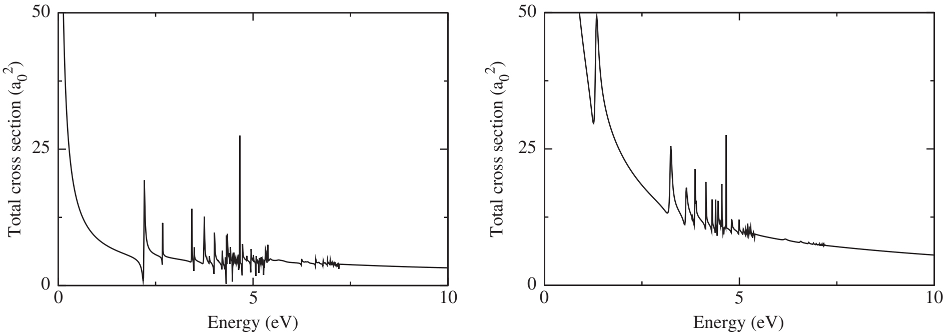

Figure 3. Total cross-section as function of energy for the electron–CO_2^+ collision problem: left-hand figure $^1\Sigma_g^+$ total symmetry, right-hand figure $^1\Sigma_u^+$ symmetry.

Table 3. CO_2 re-scattering resonances for $^1\Sigma_g^+$ and $^1\Sigma_u^+$ total symmetry.

E_r	Γ	ν	E_r	Γ	ν
$^1\Sigma_g^+$			$^1\Sigma_u^+$		
2.20	0.024	2.3537	1.31	0.085	2.0160
3.43	0.008	3.3271	3.23	0.059	3.0873
3.48	0.003	3.4030	3.63	0.040	3.6280
3.75	0.019	3.8596	3.79	0.001	3.9645
3.87	0.003	4.1594	3.86	0.013	4.1136
4.01	0.010	4.5735	4.14	0.008	5.1177
4.11	0.001	4.9939	4.30	0.005	6.1179
4.21	0.003	5.5014	4.39	0.004	7.1132
4.32	0.007	6.2922			
4.34	0.005	6.5035			

calculation are characterized by significant structure caused by resonances. Table 3 gives resonance parameters for the lowest of these.

4. Conclusions

We present initial calculations on electron (re-)scattering for the case of hydrogen and carbon dioxide molecules. The low-energy electron-molecular ion cross-sections show strong structures due to resonant behaviour near target excitation thresholds. This is because re-scattering from a neutral molecule is equivalent to electron–molecular cation scattering, and molecular cations display infinite series of resonances near threshold. This suggests there may be a need for the consideration of resonance phenomena in electron re-scattering. Further work is under way on refining the model to allow a closer representation of actual and potential re-scattering experiments.

To accurately model the experimental situation the initial model needs to be refined in several ways. The R-matrix codes should modified to include the effect of molecular orientation [29, 30]. The formalism for this has already been developed by Blum and co-workers [31, 32]. Our scattering amplitudes will be incorporated into a strong field model [2] for electron–parent molecule re-scattering or, more ambitious, use a time-dependent method to include laser field effects [33]. Finally our present calculations are constrained by the use of a close-coupled expansion to represent the target. This limits the energy range of the scattering procedure used here to below vertical ionization energy of the target system or the vertical second ionization of the neutral molecule being considered. The R-matrix with pseudostates method could be used to extend this energy range [12, 19].

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