Journal of Physics B: Atomic, Molecular and Optical Physics

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To cite this article: T Meltzer and J Tennyson 2020 *J. Phys. B: At. Mol. Opt. Phys.* **53** 245203

OPEN ACCESS
IOP Publishing
Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **53** (2020) 245203 (8pp)
https://doi.org/10.1088/1361-6455/abc3d1

Electron collisions with molecular hydrogen from electronically excited states using the R-matrix method

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Received 25 July 2020, revised 30 September 2020
Accepted for publication 22 October 2020
Published 20 November 2020

Abstract

Cross section data for electron impact electronic excitation of electronically excited states of H_2 are computed using fixed-nuclear R-matrix calculations. Specifically, there is a focus on transitions from the quasi-metastable excited states $a\ {}^3\Sigma_g^+$ and $c\ {}^3\Pi_u$. Data are compared with known theoretical data where available. Our calculations suggest that the published cross sections are generally too large in the low energy (<20 eV) collision region. The effect of shifting the electronic excitation thresholds to those given by essentially exact calculations is tested.

Keywords: R-matrix, electron collisions, electronic excitation, superelastic scattering, metastable states

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Electron collisions with molecular hydrogen are of practical importance for the semiconductor plasma industry (Bartschat and Kushner 2016) and magnetically confined fusion plasma reactors (Janev *et al* 2003). In addition, they have application in atmospheric and astrophysical modelling (Colonna *et al* 2012). This relevance is compounded by the ubiquity of molecular hydrogen which can be found across the Universe in stars, planets and interstellar medium. For example, it has long been know that electron–H_2 collisions are important in the upper atmosphere of Jupiter (Cravens 1987). More generally, it was shown recently that electron-molecule collisions were responsible for the emission lines observed in comet 67P/Churyumov-Gerasimenko as part of the Rosetta mission (Marinković *et al* 2017).

Despite the importance of electron–molecule cross section data, there are still few benchmark data available. This issue has been highlighted by many authors over the last decade (Yoon *et al* 2008, Anzai *et al* 2012, Song *et al* 2019). In fact, Fedus and Karwasz (2017) raised the important point that even where experimental or theoretical data are available they often do not converge to the same answer. Cross sections for electronically excited states present an additional layer of difficulty both for experiment and theory.

Molecules exhibit an increasingly dense collection of excited states below their threshold to ionisation. Experimentally, this makes it hard to separate the different contributions arising from each excited state when these states are close in energy. For theoretical studies the number of states that need to be included in the model, in order to capture the correct

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physics, increases with the number of states that are accessible for a given scattering energy. Therefore, molecules with densely packed excited states in the energy region of interest present significant computational challenges for full-scale close-coupling calculations.

To date, only a handful of theoretical studies have been carried out which provide integrated cross sections (ICS) for (de-)excitation starting from electronically excited states. Even for H_2, which is one of the simplest molecules, cross section data from excited states are hard to find. Available studies include calculations using the semi-classical impact parameter (IP) method by Celiberto *et al* (1996) which provided vibrationally resolved ICS for the $B\ ^1\Sigma_u^+ \rightarrow I\ ^1\Pi_g$ inelastic transition. This study was followed by Laricchiuta *et al* (2004) who used the same method to calculate ICS for the $a\ ^3\Sigma_g^+ \rightarrow d\ ^3\Pi_u$, $c\ ^3\Pi_u \rightarrow g\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u \rightarrow h\ ^3\Sigma_g^+$ triplet transitions. Typically the ICSs produced by the impact parameter method are valid for high scattering energies i.e., $E \gg I_\mathrm{p}$, where I_p is the ionisation potential of the molecule. For low to intermediate scattering energies, $E \sim I_\mathrm{p}$, really close-coupling calculations are required. However, close-coupling calculations are similarly scarce with the only known data being Schwinger multichannel (SMC) method calculations of the ICS from the $c\ ^3\Pi_u$ excited state (Sartori *et al* 1997), and differential and integral cross sections from the $a\ ^3\Sigma_g^+$ excited state (Sartori *et al* 1998). Joshipura *et al* (2010) carried out optical model potential calculations from the excited metastable $c\ ^3\Pi_u$ state. However, this approach is not capable of resolving individual electronic states—instead only a sum of the inelastic processes can be computed.

In recent work (Meltzer *et al* 2020), the R-matrix method was used to produce converged cross sections for electron impact electronic excitation of molecular hydrogen in the $X\ ^1\Sigma_g^+$ ground electronic state to the first ten electronic excited states. The R-matrix calculations were verified by a detailed comparison with recent experimental data, recommended cross sections (Yoon *et al* 2008) and the results of accurate molecular convergent close-coupling (MCCC) calculations carried out by Zammit *et al* (2017a). In this paper, we extend the previous work to address the need for accurate cross section data for electronic transitions starting from electronically excited states of molecular hydrogen. The $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$ electronic excited states are of particular interest as these states are quasi-metastable (Catherinot *et al* 1978). Although, it has been shown that collision data are required from all excited electronic states in order to effectively describe the electron energy distribution functions in a H_2 plasma, metastable or otherwise (Capitelli *et al* 1994). For this reason, ICS starting from other low-lying excited states are also provided.

2. Method

This work uses the R-matrix method as implemented in the UKRMol+ suite of codes (Mašín *et al* 2020) to obtain cross section data for electron collisions with H_2. The theoretical approach is well documented by numerous authors (Tennyson 2010, Burke 2011, Mašín *et al* 2020) and therefore a detailed description of the theory will not be given here. However, there are several key features of the R-matrix method, that have been leveraged to obtain the cross section data presented in this work, which will be discussed in the following.

Table 1. Absolute target energies, E (E_h), obtained from this work at an internuclear separation of $R = 2.00a_0$ compared with accurate electronic structure calculations.

State	E (E_h)		ΔE ($\times 10^{-3} E_\mathrm{h}$)
	RM[a]	Reference	
X $^1\Sigma_g^+$	-1.1368	-1.1381[b]	-1.37
b $^3\Sigma_u^+$	-0.8965	-0.8971[c]	-0.54
B $^1\Sigma_u^+$	-0.7512	-0.7521[d]	-0.84
c $^3\Pi_u$	-0.7367	-0.7375[c]	-0.75
a $^3\Sigma_g^+$	-0.7356	-0.7361[c]	-0.47
C $^1\Pi_u$	-0.7174	-0.7182[e]	-0.87
EF $^1\Sigma_g^+$	-0.7171	-0.7177[f]	-0.62
e $^3\Sigma_u^+$	-0.6827	-0.6832[c]	-0.43
B′ $^1\Sigma_u^+$	-0.6649	-0.6655[d]	-0.57
h $^3\Sigma_g^+$	-0.6600	-0.6606[c]	-0.56
GK $^1\Sigma_g^+$	-0.6599	-0.6604[f]	-0.53
d $^3\Pi_u$	-0.6597	-0.6607[c]	-1.01
g $^3\Sigma_g^+$	-0.6595	-0.6598[c]	-0.38

[a] This work;
[b] Kołos *etal* (1986);
[c] Staszewska and Wolniewicz(1999);
[d] Staszewska and Wolniewicz(2002);
[e] Wolniewicz and Staszewska(2003);
[f] Wolniewicz and Dressler(1994).

2.1. Target model

The target model used in this work has been adapted from previous work (Meltzer *et al* 2020). That is, a triply-augmented basis set t-aug-cc-pVTZ (tAVTZ hereafter) of Gaussian type orbitals (GTOs) is used to describe the target states (Dunning 1989, Woon and Dunning 1994). We use the full-CI method to obtain an exact solution to the Schrödinger equation within this given basis set. In D_{2h} symmetry, the target model can be expressed as $(19, 9, 9, 4, 19, 9, 9, 4)^2$, with 2 electrons occupying all of the spin-space symmetry-allowed combinations of molecular orbitals. This model was found to give accurate target states for all states dissociating into H(1s) + $\mathrm{H}(n\ell, n \leqslant 3)$ (Meltzer *et al* 2020). The ground state and the 12 lowest-lying target states obtained via this approach are given in table 1 for the internuclear separation of $R = 2.00a_0$. By comparison to the essentially exact data of Kołos *et al* (1986), Wolniewicz and Dressler (1994), Staszewska and Wolniewicz (1999), Staszewska and Wolniewicz (2002) and Wolniewicz and Staszewska (2003) (henceforth reference data) we obtain a maximum absolute energy difference of $|\Delta E| = 1.37 \times 10^{-3} E_\mathrm{h}$ and relative shifts all less than $10^{-3} E_\mathrm{h}$

For the current work an internuclear bond separation of $R = 2.00a_0$ is used. This separation corresponds approximately to the equilibrium bond length for the majority of electronically excited states considered in this work. Whilst target energies are only tabulated for the ground state and the first 12

Table 2. Parallel, $\alpha_{\parallel}$, and perpendicular, $\alpha_{\perp}$, polarizabilities of H_2 given in atomic units.

	Bond Length (a_0)	$\alpha_{\parallel}$	$\alpha_{\perp}$
Model from Meltzer et al (2020)	1.448	6.69	4.31
Kołos and Wolniewicz (1967)	1.45	6.72	4.74
Bridge and Buckingham (1966) (exp.)	—	6.94	4.82
This work	2.00	10.96	6.12
Kołos and Wolniewicz (1967)	2.00	10.96	6.51

Table 3. Continuum basis parameters for the continuum basis.

Property	Value
Number of B-splines (per l)	65
B-spline order	9
$l_{\max}$	6

electronically excited states, the scattering model uses all target states below the maximum scattering energy of 20 eV. For H_2 in D_{2h} symmetry this corresponds to 85 target states, which are included in the close-coupling expansion.

Another way to verify the suitability of the target model is to see how well it represents the dipole polarizability, α, of the molecule. Jones and Tennyson (2010) investigated how the polarizability of several molecules converged with increasing amounts of diffuse molecular orbitals via the use of pseudo-continuum orbitals (PCOs). In our model, we do not use PCOs, however, we include a large number of diffuse target orbitals that are generated from the triply-augmented tAVTZ basis set.

In table 2, parallel, $\alpha_{\parallel} \equiv \alpha_{zz}$, and perpendicular, $\alpha_{\perp} \equiv \alpha_{xx} = \alpha_{yy}$, polarizabilities computed using the UKRMol+ codes are compared with the accurate calculations of Kołos and Wolniewicz (1967) and the experimental data of Bridge and Buckingham (1966). In this work we have used the same sum-over-states method as described by Jones and Tennyson (2010). We provide polarizabilities for two different bond lengths. One close to the mean vibrational bond length, $R = R_0 = 1.448a_0$, which uses the target model from our previous work (Meltzer et al 2020) and another calculation using the target model from this work at $R = 2.00a_0$. The two theoretical calculations are in good agreement for the dipole polarizabilities in the parallel direction with acceptable agreement in the perpendicular direction. Comparing to the experimental data shows larger discrepancies however this is to be expected as the calculations are computed for a fixed geometry.

2.2. Scattering model

As with the target model, the scattering model is also based on the previous work (Meltzer *et al* 2020). That is, a B-spline type orbital (BTO) basis set is used to described the continuum. In general, the UKRMol+ code can support an arbitrary mixture of GTOs and BTOs as a continuum basis (Mašín *et al* 2020) but for this work we found that the BTO-only continuum basis performed best.

The previous R-matrix calculations (Meltzer *et al* 2020) were computed for scattering energies up to 30 eV. However, as noted by the authors, those R-matrix calculations did not include ionisation channels. To do so would require the use of pseudostates as described in the R-matrix with pseudostates method (Gorfinkiel and Tennyson 2005). Therefore, for scattering energies above the ionisation threshold the R-matrix calculation overestimates the cross section. This effect is small however, and was only noticeable for the smallest cross sections—typically dipole-forbidden transitions into highly-excited states e.g., $X\ ^1\Sigma_g^+ \rightarrow d\ ^3\Pi_u$ and $X\ ^1\Sigma_g^+ \rightarrow h\ ^3\Sigma_g^+$. This follows the general rule that neglecting target states which are energetically accessible leads to an overestimation of the cross section. This behaviour was also observed in the MCCC calculations of (Zammit *et al* 2017b) when only the bound states were used. Therefore, in this work we have restricted the energy range of the R-matrix calculations to 20 eV relative to the ground state.

Reducing the maximum scattering energy from 30 eV to 20 eV means that the size of the continuum basis set can also be reduced. The new continuum basis set is defined by the parameters in table 3. The only difference from previous work is that the number of B-splines per angular momentum symmetry has been reduced from 75 to 65. This reduces the computational cost for the R-matrix calculation both in terms of the memory required and the compute time, whilst still retaining completeness.

2.3. Target shifting

To verify the convergence of the ICS relative to the target states, we shift the target states obtained in the R-matrix calculation to the exact reference data shown in table 1. This is similar to the approach used by Branchett *et al* (1991) where thresholds were shifted to match exact reference data. The effect of shifting thresholds was particularly important for identifying the parent states of different resonances, see Stibbe & Tennyson (1997). For H_2, potential parent states could be separated by as little as 0.04 eV. For example, the $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$ states have thresholds at 10.94 eV and

10.90 eV, respectively, at a bond length of $R = 2.0a_0$. However, in contrast to Branchett *et al* (1991) we are applying threshold shifts of the order 0.01 eV compared to shifts of the order 0.1 eV used in their work.

There are several different ways to shift the target states, some of which are equivalent. Below we summarise three approaches that could have been used:

(I) Shift calculated threshold energies relative to the ground state to the thresholds of exact data.
(II) Shift calculated target energies to the absolute values of exact data.
(III) Shift calculated target energies to the exact absolute values (as done in case II) but then shift all target states by a constant so that the ground state remains unchanged.

In case I, the ground state is kept the same between calculations and only the thresholds for excited electronic states relative to the ground state are altered, where data are available. This method works particularly well for calculations that consider only a handful of target states. That is, when exact reference or experimental data are available for all target states considered. In this work however, our model uses all 85 target states. Exact reference data is only obtainable for the lower-lying states, accounting for approximately 25% of the states included. Therefore, at some point we will have neighbouring states that lie close in energy where one has been shifted to exact data and the other has not. It was found that this approach led to a switching in the ordering of states. This has negative implications for the scattering calculation which relies on the correct energy ordering of target states. Moreover, for molecules other than H_2 the situation will likely be worse. Perhaps only a handful of the electronic states will have accurate experimental or theoretical data available. For this reason we decided against this method for the current work.

Case II, like case I, will still have accurate thresholds but now the absolute energies are also adjusted, including the ground state. Because variational calculations lie above the exact answer, shifting to exact data should have the effect of lowering the target states. This removes the possibility of unshifted states becoming lower in energy than those that have been shifted. Therefore, it is possible to use this method when only a subset of the target states are known exactly. However, tests showed that altering the ground state energy led to numerical instabilities in the $N + 1$ scattering calculation. This in turn led to spurious artefacts in the ground elastic ICS.

Case III is essentially a combination of case I and case II. In case III, we first shift the energies of the target states where exact data are available. Then, we shift all (85) target states by the difference between the exact ground state and the calculated ground state. This keeps the benefit of case II which works when only a subset of exact data are available, and, does not alter the energy ordering of target states. Lastly, case III also retains the benefit of case I which does not alter the ground state, therefore eliminating the numerical instabilities caused by changing the ground state energy.

3. Results

In this section we present electron impact cross sections computed using the R-matrix method for electronic de-excitation and excitation from two metastable excited states, $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$. Our calculations are compared with the previous theoretical calculations of Sartori *et al* (1997), Sartori *et al* (1998) and Laricchiuta *et al* (2004). Only a subset of our results will be discussed explicitly, however, ICS data for all possible combinations of initial and final state from the list of states provided in table 1 are included as supplementary data (https://stacks.iop.org/JPB/53/245203/mmedia). That is, ICS data are provided for 169 separate transitions between the states; $X\ ^1\Sigma_g^+$, $b\ ^3\Sigma_u^+$, $B\ ^1\Sigma_u^+$, $c\ ^3\Pi_u$, $a\ ^3\Sigma_g^+$, $C\ ^1\Pi_u$, $EF\ ^1\Sigma_g^+$, $e\ ^3\Sigma_u^+$, $B'\ ^1\Sigma_u^+$, $h\ ^3\Sigma_g^+$, $GK\ ^1\Sigma_g^+$, $d\ ^3\Pi_u$ and $g\ ^3\Sigma_g^+$. The transition dipole moments for all allowed transitions have also been included in the supplementary data for two internuclear separations, $R = 1.448a_0$, using the model from our previous work (Meltzer *et al* 2020) and $R = 2.00a_0$ using the model from this work.

To test how the accuracy of the target states affects the accuracy of the computed ICS, we use two different sets of target states. Firstly we use the unaltered *ab initio* target states obtained by the diagonalisation of the N-electron Hamiltonian (RM data in table 1) to run a full scattering calculations. Secondly, using approach III detailed above, we shift the eigenenergies obtained in the diagonalisation of the N-electron Hamiltonian to the essentially exact reference data given in table 1. If we first consider cross sections for transitions from the state $a\ ^3\Sigma_g^+$, shown in figures 1(a)–(e), it can be seen that the shifting of target states to accurate reference data has a negligible effect. This demonstrates that the target states are sufficiently converged for the scattering calculation. This is to be expected as the target states are already in close agreement with the accurate reference data (see table 1).

In figures 1(a)–(d) the UKRMol+ calculations are compared with the SMC calculations of Sartori *et al* (1998). For the ground state (figure 1(a)) and the $b\ ^3\Sigma_u^+$ state (figure 1(b)) there is qualitative agreement although the SMC cross sections are up to a factor of 5 times larger across the energy range considered in this work. It is worth mentioning that the calculation of Sartori *et al* (1998) was performed at an internuclear separation of $R = 1.96a_0$ although as discussed by the authors the effect of changes to the internuclear separation on the ICS was small. Therefore, it is suitable to make a comparison between the two calculations. We suspect the data of Sartori *et al* (1998) overestimates the cross section and that the most likely cause is due to the difference in scattering model. That is, the SMC calculation only considers four target states, whereas the R-matrix calculation includes 85 target states. This is similar to the issue raised previously when comparing the R-matrix calculations to MCCC calculations above ionisation threshold. However, for the SMC calculations, not only are Sartori *et al* (1998) lacking ionisation channels but they are also neglecting a large number of target states that contribute to the close-coupling expansion. The effect of this is to significantly overestimate

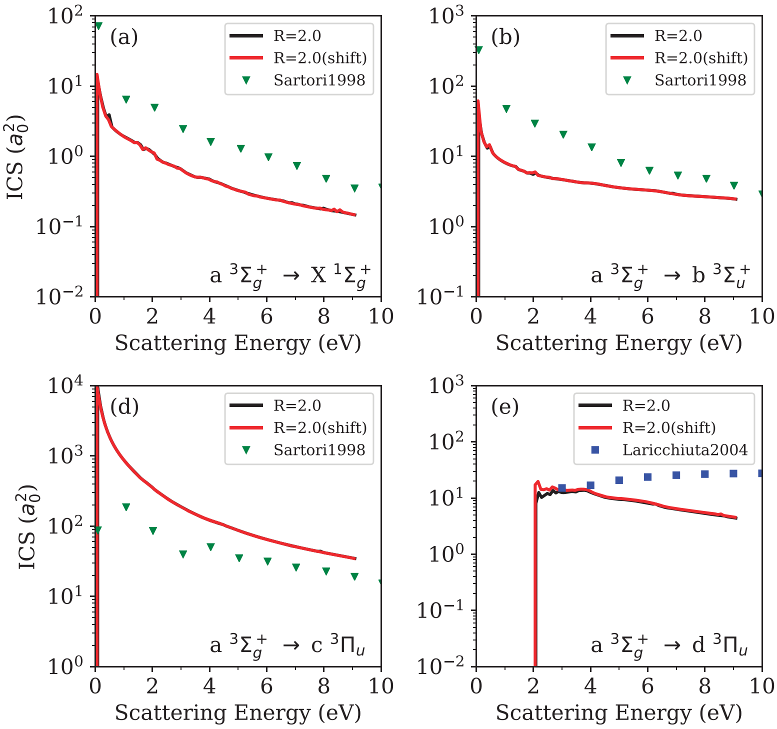

Figure 1. ICS for transitions starting from the electronically excited state $a\ ^3\Sigma_g^+$ to (a) the ground state $X\ ^1\Sigma_g^+$ and (b)–(e) the excited states $b\ ^3\Sigma_u^+$, $a\ ^3\Sigma_g^+$, $c\ ^3\Pi_u$ and $d\ ^3\Pi_u$ respectively. R-matrix data are shown for calculations that use unshifted target states (black) and target states shifted to accurate reference data (red) at an internuclear separation of $R = 2.0a_0$. The theoretical data of Sartori *et al* (1998) (green triangles) and Laricchiuta *et al* (2004) (blue squares) are plotted for comparison.

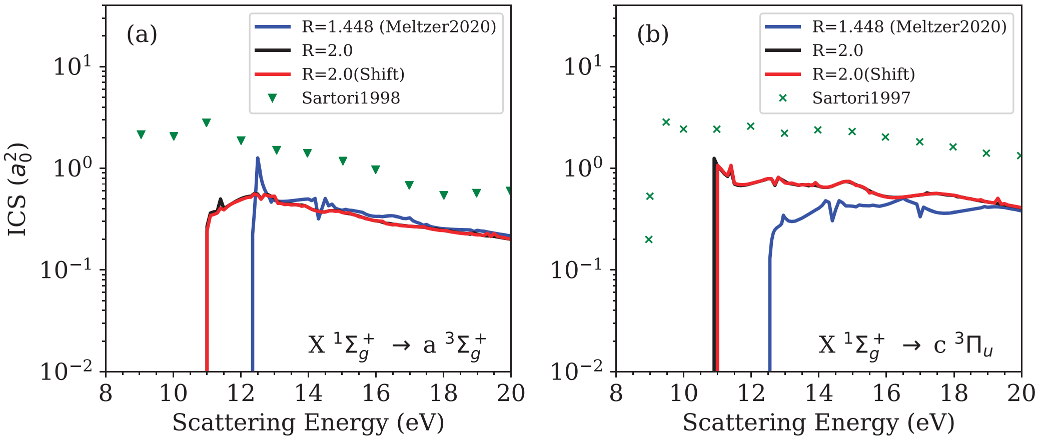

Figure 2. ICS for the (a) $X\ ^1\Sigma_g^+ \rightarrow a\ ^3\Sigma_g^+$ and (b) $X\ ^1\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ transitions. R-matrix data are shown for calculations that use unshifted target states (black) and target states shifted to accurate reference data (red) at an internuclear separation of $R = 2.0a_0$. R-matrix calculations from Meltzer *et al* (2020) are also provided for comparison at the internuclear separation of $R = 1.448a_0$ (blue). The R-matrix cross sections are compared with theoretical data from Sartori *et al* (1997) (green crosses) and Sartori *et al* (1998) (green triangles).

the cross section. In addition the target excitation energies obtained by and used in their model are 8.939 eV and 9.028 eV for the $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$ states, respectively (Sartori *et al* 1998). These energies differ from the accurate reference data by approximately 2 eV, however, the impact of this on the cross section is expected to be less significant.

The ICS of the elastic transition $a\ ^3\Sigma_g^+ \rightarrow a\ ^3\Sigma_g^+$ is shown in figure 1(c). For this transition the agreement is greatly improved between the SMC data of Sartori *et al* (1998) and the R-matrix data obtained in this work, with qualitative and quantitative agreement across the entire energy range considered. For the $a\ ^3\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ transition (figure 1(d)) there is again qualitative agreement across the scattering energy range considered, although the SMC method under predicts the ICS.

For the $a\ ^3\Sigma_g^+ \rightarrow d\ ^3\Pi_u$ transition we compare with the IP calculations of Laricchiuta *et al* (2004). The ICS provided by Laricchiuta *et al* (2004) are vibrationally resolved, however

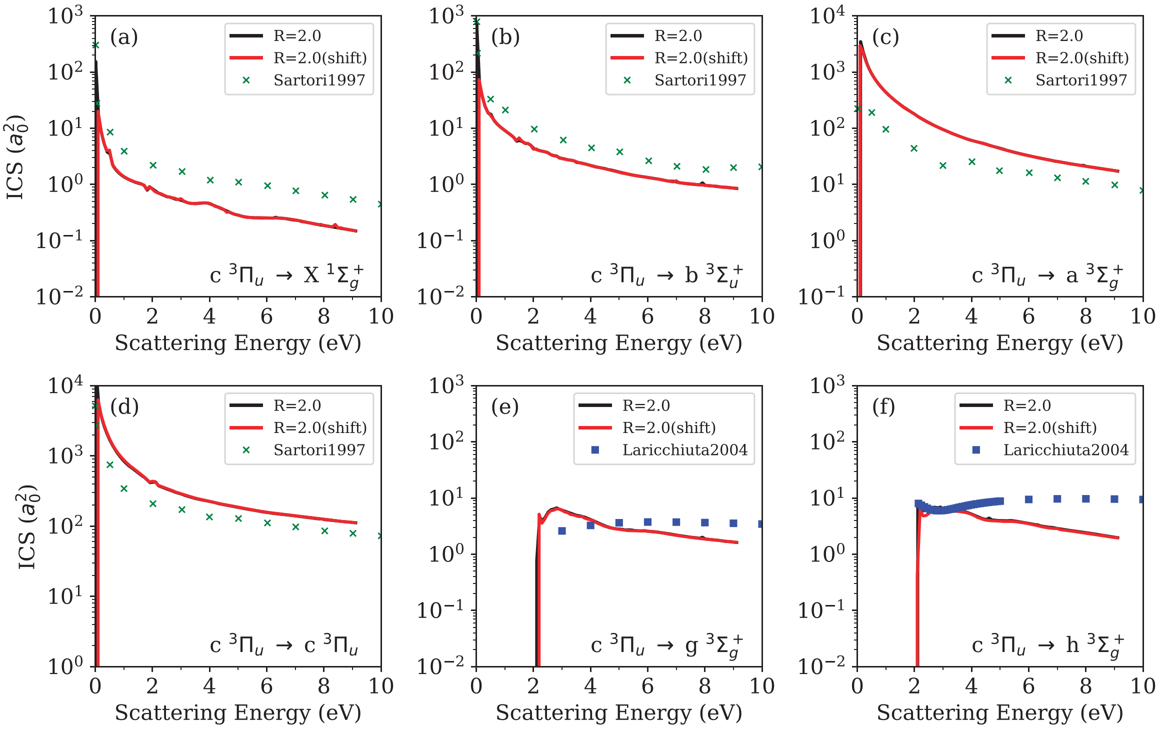

Figure 3. ICS for transitions starting from the electronically excited state $a\ ^3\Sigma_g^+$ to the (a) ground state $X\ ^1\Sigma_g^+$ and (b)–(f) the excited states $b\ ^3\Sigma_u^+$, $a\ ^3\Sigma_g^+$, $c\ ^3\Pi_u$, $g\ ^3\Sigma_g^+$ and $h\ ^3\Sigma_g^+$ respectively. R-matrix data are shown for calculations that use unshifted target states (black) and target states shifted to accurate reference data (red) at an internuclear separation of $R = 2.0a_0$. The theoretical data of Sartori *et al* (1997) (green crosses) and Laricchiuta *et al* (2004) (blue squares) are plotted for comparison.

for this work the ICS are purely electronic. In order to compare the two calculations, we take the ICS which have been summed over all final vibrational states from the ground initial vibrational state $\nu_i = 0$. Under the Franck–Condon principle this should approximately correspond to the purely electronic cross section (Hazi 1981).

The ICS obtained from IP calculations are shown in figure 1(e) alongside the R-matrix calculations. Here, the agreement between the two calculations is not so good. Whilst the two calculations agree close to threshold, as the scattering energy increases they disagree both quantitatively and qualitatively. There are a several reasons that could explain this difference. Firstly, it should be noted that the R-matrix calculations do not use a Born correction procedure (see e.g., Norcross and Padial (1982)). The effect of a Born correction is to top-up the calculated cross section using an analytic Born series that accounts for the infinite number of partial waves that were truncated into a finite expansion i.e., for this work a maximum angular momentum of $L_{\max} = 6$ was used. Although, as was demonstrated by Meltzer *et al* (2020), the ICS for dipole-allowed transitions from the ground state, $X\ ^1\Sigma_g^+$, into the $B\ ^1\Sigma_u^+$, $C\ ^1\Pi_u$ and $B'\ ^1\Sigma_u^+$ states were sufficiently converged without a Born top-up procedure. It was only in the differential cross sections that a noticeable effect could be observed. Therefore we suspect that there would be an increase in the ICS due to the Born top-up, although it would be small in comparison to the differences we are discussing here. Secondly, the IP method uses classical trajectories to model the scattering electron. This description is not accurate until much higher energies, as noted by Tapley *et al* (2018) who found that the IP results significantly overestimated the cross sections for dipole-allowed states below scattering energies of 100 eV. Thirdly, we have performed a fixed-nuclei calculation which is being compared to a vibrationally resolved cross-section. Nevertheless, based on the assumption that the initial vibrational state, $\nu_i = 0$, can be used as an approximation of the purely electronic cross-section we believe that it is likely that the impact parameter method overestimates the cross section in the energy range considered in this work.

In figures 2(a) and (b) the ICS for transitions from the ground state, $X\ ^1\Sigma_g^+$, to the metastable states, $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$ are shown, respectively. Figure 2(a) shows the data from three separate R-matrix calculations against the SMC results of Sartori *et al* (1998). At the internuclear separation of $R = 2.0a_0$ there are two datasets. The black curve show data obtained from the fully *ab initio* R-matrix calculation whereas the red curve show data obtained by shifting the target state energies to the accurate reference data. These two data sets essentially overlap highlighting again that the target states are sufficiently converged. The blue curve is the R-matrix ICS data taken from Meltzer *et al* (2020) which was carried out at the mean vibrational bond length, $R_0 = 1.448a_0$. This calculation was subject to a detailed comparison with recommended experimental data (Yoon *et al* 2008), recent experimental data and the theoretical MCCC calculations of Zammit *et al* (2017a). In that work Meltzer *et al* (2020) demonstrated good agreement between the MCCC ICS and the R-matrix ICS for both the $X\ ^1\Sigma_g^+ \to a\ ^3\Sigma_g^+$ and

$X\ ^1\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ transitions. It is not expected that the ICS would change by nearly an order of magnitude for such a small change in the internuclear separation i.e., $R = 1.448a_0$ to $R = 2.0a_0$. Therefore this indicates that the SMC data in figure 2(a) is approximately a factor of 5 times too large. A similar argument holds for the SMC data in figure 2(b). Using an argument of reciprocity, this also indicates that the superelastic transitions, $a\ ^3\Sigma_g^+ \rightarrow X\ ^1\Sigma_g^+$ and $c\ ^3\Pi_u \rightarrow X\ ^1\Sigma_g^+$, are also significantly overestimated by the SMC method.

In figure 3, again two separate R-matrix calculations are shown; one obtained without shifting the target states (black curve) and the other obtained by shifting the target states to the accurate reference data (red curve). In all cases (figure 3(a)–(f)) there is practically no difference between the two calculations with and without shifting the target states. Figure 3(a)–(d) compare the UKRMol+ data (computed at $R = 2.0a_0$) with that obtained via the SMC calculations of Sartori *et al* (1997) (computed at $R = 1.96a_0$). The superelastic SMC ICS, figure 3(a), is approximately 5 times greater than the R-matrix ICS, however, there is qualitative agreement between the two cross sections. Similarly, the superelastic $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ transition cross section, figure 3(b), is also in qualitative agreement but roughly twice as large as the ICS obtained in the R-matrix calculation. This is for the same reasons as mentioned previously. That is, due to the difference in scattering model we believe that the SMC data overestimate the ICS. For the quasi-elastic and elastic ICSs shown in figures 3(c) and (d) respectively, the agreement between the two theories is again in qualitative agreement, however both SMC cross sections are roughly a factor of two smaller.

ICS for inelastic transitions into the $h\ ^3\Sigma_g^+$ and $g\ ^3\Sigma_g^+$ states, figure 3(e) and (f) respectively, show the R-matrix data alongside the IP calculations of Laricchiuta *et al* (2004). At scattering energies near threshold, i.e., 2 eV to 4 eV, the two theories are roughly in agreement, however, the R-matrix calculations have a decreasing trend that qualitatively disagrees with the IP calculations over the energy range considered in this work. Again, making similar arguments to those discussed for the $a\ ^3\Sigma_g^+ \rightarrow d\ ^3\Pi_u$ transition, we believe that the IP data overestimate the cross section for the higher scattering energies considered in this work i.e., roughly 5 eV to 10 eV.

4. Conclusion

We provide ICS data that is of use for the plasma modelling community. ICS have been explicitly shown for the metastable states $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$, however, transitions from the ground state and 12 lowest-lying excited states have been included in supplementary material.

The effect of shifting the target states to exact reference data has been investigated. We find that shifting the target energies has very little effect on the ICS obtained. This suggests that the target model we have selected is already sufficiently converged for the scattering calculation.

Furthermore, our results suggest that previous SMC and IP calculations tend to overestimate the cross sections for electronic (de-)excitation from initially excited states. We believe that our model is at least the right order of magnitude based on the previous success of our model in obtaining accurate and converged ICS for electronically excited states of H_2 from the ground state. This implies that SMC and IP data overestimate the ICS by as much as a factor of 5 for certain transitions. For the SMC calculations this is particularly noticeable in the superelastic transitions from initial states $a\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u$ into the $X\ ^1\Sigma_g^+$ and $b\ ^3\Sigma_u^+$ states, when comparing the results with the R-matrix data. That being said, the SMC calculations did show qualitative agreement with our calculations for all transitions where data were available. For the quasi-elastic transitions, $a\ ^3\Sigma_g^+ \rightarrow c\ ^3\Pi_u$ and $c\ ^3\Pi_u \rightarrow a\ ^3\Sigma_g^+$, the agreement between SMC and R-matrix data is improved.

R-matrix ICS data for three inelastic transitions, $a\ ^3\Sigma_g^+ \rightarrow d\ ^3\Pi_u$, $c\ ^3\Pi_u \rightarrow h\ ^3\Sigma_g^+$ and $c\ ^3\Pi_u \rightarrow g\ ^3\Sigma_g^+$, were also compared with IP calculations. Of the three ICS, the agreement was closest for the $c\ ^3\Pi_u \rightarrow g\ ^3\Sigma_g^+$ transition. However, in general, both theories quantitatively and qualitatively disagreed, despite some quantitative agreement close to threshold. Impact parameter is essentially a high-energy scattering method, and so, close agreement was not expected at such low scattering energies.

This work demonstrates the need for large scale close-coupling calculations in order to obtain accurate cross sections for low energy electron collisions.

Acknowledgments

TM's studentship was funded by EPSRC grant EP/M507970/1; this work was also supported by UK Collaborative Computational Project Q (CCPQ) through EPSRC grant EP/M022544/2 and the UK-AMOR project through EPSRC grant EP/R029342/1. The authors acknowledge the use of the UCL Myriad High Throughput Computing Facility (Myriad@UCL), and associated support services, in the completion of this work

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