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Ola A. Al-Hagan

Chuangang Ning

Kate L. Nixon

Andrew James Murray

*et. al.* For a complete list of authors, see [http://scholarsmine.mst.edu/phys\\_facwork/1522](http://scholarsmine.mst.edu/phys_facwork/1522)

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## Recent theoretical progress in treating electron impact ionization of molecules

**<sup>1</sup>Ola Al-Hagan, Chuangang Ning<sup>2</sup>, Kate Nixon<sup>3</sup>, Andrew Murray<sup>3</sup>, Christopher Colyer<sup>4</sup>, Mark Stevenson<sup>4</sup>, Birgit Lohmann<sup>4</sup> and Don Madison<sup>1</sup>**

<sup>1</sup>Department of Physics, Missouri University of Science & Technology, Rolla, MO 65409, USA

<sup>2</sup>Department of Physics and Key Laboratory of Atomic and Molecular NanoSciences of MOE, Tsinghua University, Beijing 100084, People's Republic of China

<sup>3</sup>School of Physics & Astronomy, University of Manchester, Manchester M13 9PL, United Kingdom

<sup>4</sup>ARC Centre for Antimatter-Matter Studies, University of Adelaide, Adelaide, SA 5005, Australia

E-mail: oan6f@mst.edu

**Abstract.** (e,2e) ionization differential cross sections are presented for several molecules. We will compare experimental results with theoretical calculations using the molecular three body distorted wave (M3DW) approximations for H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and Formic Acid (FA) using better wave-function for the molecules than we had in previous works. Generally, good agreement is found between the M3DW approach and experiments.

### 1. Introduction

There has been impressive progress in the area of theoretical treatments of charge particle collisions with atoms and molecules in the last decade. There have been many (e, 2e) studies for ionization of atoms and this area is now fairly mature. There have been some experimental and theoretical studies performed for the (e, 2e) processes with molecular targets but most of these studies have been performed either for high incident energies or for small molecules [1-4]. Most recently, low to intermediate incident energies have been reported for relatively simple molecular systems [5-6]. For these cases the dynamics of the ionization collisions become important and therefore more sophisticated models are needed to get good agreement with the experimental data.

In this paper, we will use the molecular three-body distorted wave (M3DW) approximation method coupled with the orientation averaged molecular orbital (OAMO) approximation. We apply this treatment to calculate the triple differential cross section (TDCS) for a variety of electron angles and energies for H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and HCOOH (Formic Acid - FA) using better wave-function for the molecules than we had in previous works.

### 2. Theory

The molecular 3-body distorted wave (M3DW) approximation has been presented by our group in previous publications [7-9] so only a brief outline of the theory will be presented. The triple differential cross section (TDCS) for the M3DW is given by:

$$\frac{d^5\sigma}{d\Omega_a\Omega_b dE_b} = \frac{1}{(2\pi)^5} \frac{k_a k_b}{k_i} |T|^2 \quad (1)$$

Where  $\vec{k}_i$ ,  $\vec{k}_a$ , and  $\vec{k}_b$  are the wave vectors for the initial, scattered and ejected electrons. The amplitude is given by:

$$T = \left\langle \chi_a^-(\vec{k}_a, \mathbf{r}_1) \chi_b^-(\vec{k}_b, \mathbf{r}_2) C_{scat-eject}(r_{12}) | V - U_i | \phi_j^{OA}(\mathbf{r}_2) \chi_i^+(\vec{k}_i, \mathbf{r}_1) \right\rangle \quad (2)$$

Where  $r_1$  and  $r_2$  are the coordinates of the incident and the bound electrons,  $\chi_i$ ,  $\chi_a$ , and  $\chi_b$  are the distorted waves for the incident, scattered, and ejected electrons respectively, and  $\phi_j^{OA}(r_2)$  is the initial bound-state wave-function which is approximate as the orientation averaged molecular wave-function for the molecular orbital of interest. The molecular wave function was calculated by Ning using density functional theory (DFT) along with the standard hybrid B3LYP [10] functional by means of the ADF 2007 (Amsterdam Density Functional) program [11] with the TZ2P (triple-zeta with two polarization functions) Slater type basis sets. The present molecular wave-functions are better than the ones we used in previous works. The factor  $C_{scat-eject}(r_{12})$  is the Coulomb-distortion factor between the two final state electrons,  $V$  is the initial state interaction potential between the incident electron and the neutral molecule, and  $U_i$  is a spherically symmetric distorting potential which used to calculate the initial-state distorted wave for the incident electron  $\chi_i^+(\vec{k}_i, \mathbf{r}_1)$ .

The molecular distorted waves are calculated using a spherically averaged distorting potential as described in previous works [7-9]. The Schrödinger equation for the incoming electron wave-function is given by:

$$(T + U_i - \frac{k_i^2}{2}) \chi_i^+(\vec{k}_i, r) = 0 \quad (3)$$

where  $T$  is the kinetic energy operator. The initial state distorting potential contains three components  $U_i = U_s + U_E + U_{CP}$ , where  $U_s$  is the initial state spherically symmetric static potential which is obtained from the molecular charge density averaged over all angular orientations,  $U_E$  is the exchange potential of Furness-McCarthy [12] which approximates the effect of the continuum electron exchanging with the passive bound electrons in the molecule, and  $U_{CP}$  is the correlation-polarization potential of Perdew and Zunger [13,14].

The final state for the system is approximated as a product of distorted waves for the two continuum electrons times the average Coulomb-distortion factor. The final state distorted waves are calculated as the initial state except that the final state spherically symmetric static distorting potential for the molecular ion which is used for  $U_s$ .

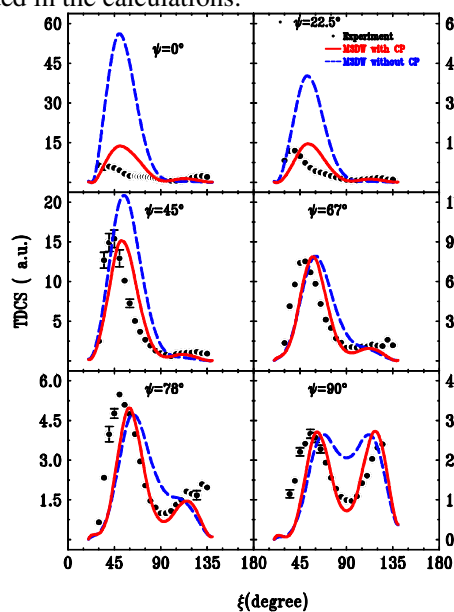
### 3. Results and discussion

#### 3.1. Molecular hydrogen ( $H_2$ )

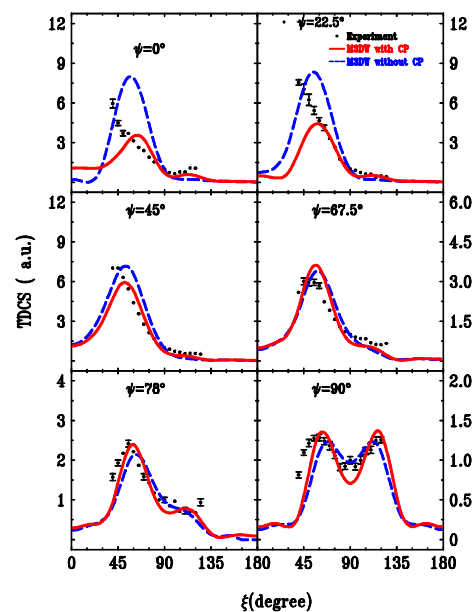
Our recent study using the M3DW method yielded good agreement with the experimental measurements for triply differential cross sections (TDCS) for ionization of both  $H_2$  and He by electron impact in a plane perpendicular to the incident beam direction with symmetric final state energies [15]. Figures 1 and 2 contain a comparison between our calculations and some recent experimental data [16] for ionization of  $H_2$  taken by Andrew Murray and Christian Kaiser at Manchester University. The Manchester apparatus is designed such that the angle between the

incident beam direction and the detection plane (defined as  $\psi$ ) can be varied. The scattering plane corresponds to  $\psi=0^\circ$  and the perpendicular plane corresponds to  $\psi=90^\circ$ . The TDCS results in figures 1 and 2 are plotted as a function of the half-angle between the two final state electrons in the detection plane (i.e.  $2\xi$  is the angle between the electrons in the detection plane). For low incident electron energies, we have found that using the full Coulomb-distortion factor  $C(r_{12})$  in M3DW calculations overestimates the effect of the final state electron-electron repulsion, normally called the post collision interaction (PCI), while the Ward-Macek average C-factor  $C(r_{12}^{ave})$  [17] yields better agreement with experimental data so we have used the Ward-Macek approximation.

Although the experimental data are not absolute, only one normalization factor is needed for the different  $\psi$  angles and we have chosen to normalize experiment to theory for  $\psi=90^\circ$ . Two different M3DW calculations are presented – one including the correlation polarization potential and one excluding it. As can be seen from figures 1 and 2, there is good agreement between the experiment and the theory for large values of  $\psi$  especially in the perpendicular plane when the correlation-polarization potential is included. At low  $\psi$  values, the agreement between the experiment and the theory is not as satisfactory. The largest experimental cross sections for both equal ( $E_a=E_b=10$  eV) and unequal ( $E_a=18$  eV,  $E_b=2$  eV) energy sharing were not in the scattering plane but rather in a plane where  $\psi=45^\circ$ . The M3DW also predicts the largest cross sections for the  $45^\circ$  plane if correlation and polarization is included in the calculations.



**Figure 1.** TDCS for electron impact ionization of  $H_2$  for equal final state energies  $E_a=E_b=10$  eV. See text for definition of angles. The measurements are compared with M3DW calculations obtained with and without the correlation-polarization potential.

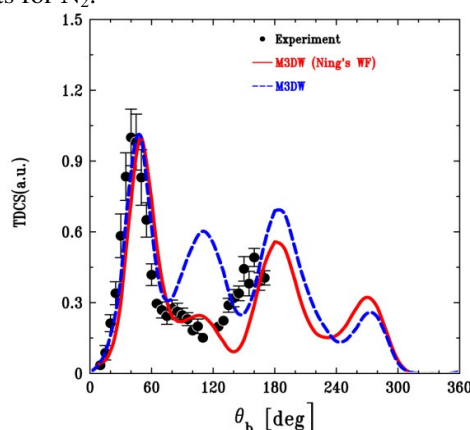


**Figure 2.** TDCS for the electron impact ionization of  $H_2$  for unequal final state energies  $E_a=18$  eV and  $E_b=2$  eV. See text for definition of angles.

### 3.2. Molecular nitrogen ( $N_2$ )

$N_2$  measurements are of particular interest due to the possibility of observing the effects of 2-center Young's-type interference terms in the cross sections [18]. Gao et al. [19] predicted a very strong Young's type interference effect for ionization of the  $3\sigma_g$  state of  $N_2$  for small projectile scattering angles when the ejected electron comes out at  $180^\circ$  (i.e. the backward beam direction) but this

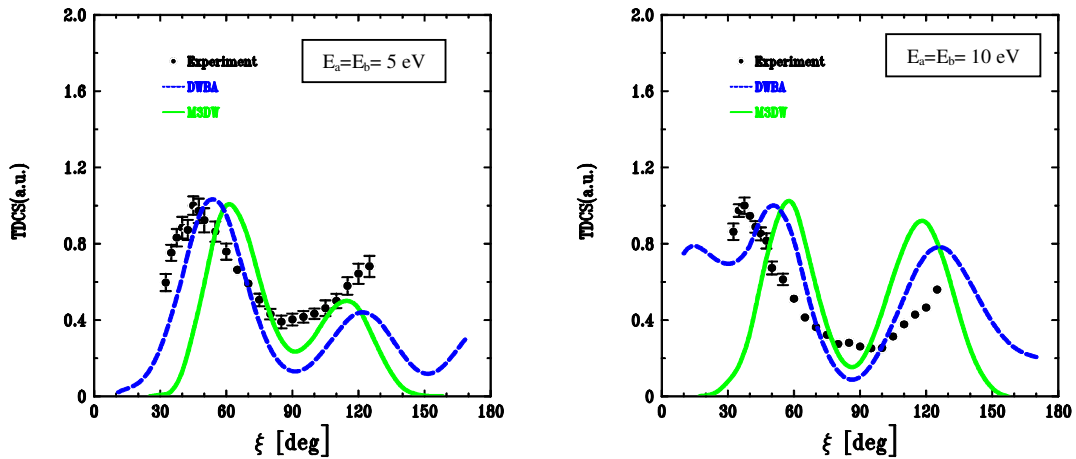
prediction is yet to be verified experimentally. This prediction resulted from a M3DW calculation using a polarization potential containing arbitrary cut-off parameters and a fairly elementary molecular orbital. We repeated these calculations using the M3DW method with an improved correlation-polarization potential [13-14] and improved molecular orbitals. The M3DW with the improved polarization potential and original molecular orbital is shown as the blue dotted line in figure 3 and the agreement with experiment improved but there was a predicted peak near  $100^\circ$  which is not seen in the experimental results. Then we did another M3DW calculation and this time we used a better wave-function calculated by Ning. The M3DW with Ning's wave-function is shown also as the solid red line. As can be seen from figure 3, the new calculation is in even better agreement with experimental data and the theory still predicts a Young's type interference peak around  $180^\circ$ . Since the agreement between theory and the experiment is fairly good, we are encouraged to think that the predicted  $180^\circ$  peak may be real. Until now, the existing experimental data is inconclusive concerning the existence of Young's interference effects for  $N_2$ .



**Figure 3.** TDCS for the  $3\sigma_g$  state of  $N_2$  with  $E_0=75.6$  eV,  $E_a=E_b=30$  eV and  $\theta_a=22^\circ$ . The experiment data are compared to two sets of M3DW. The dotted blue line is the M3DW using an old wave-function and the solid red line is the M3DW using an improved wave-function. The experimental data are those of Murray et al. [20].

### 3.3. Water ( $H_2O$ )

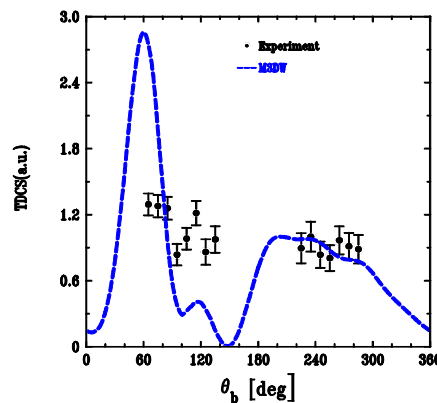
A couple years ago we compared the results of the M3DW method with experimental results for ionization of the  $1b_1$  state of  $H_2O$  [21] and we found qualitative agreement with experiment but the results were somewhat disappointing. We now believe that the disappointing results stemmed from the OAMO being invalid for the  $1b_1$  state. Kate Nixon and Andrew Murray have very recently measured triple differential cross sections for low incident energy electron-impact ionization of the  $3a_1$  molecular state of  $H_2O$  and the OAMO approximation should be much better for this state. They used the same experimental apparatus as for  $H_2$ . Figure 4 shows the experimental and theoretical TDCS for  $H_2O$  in the symmetric coplanar geometry with excess energy of 10 eV and 20 eV. There is a relatively good agreement between the experimental data and the M3DW (including the correlation-polarization potentials) and the DWBA calculations which is the same calculation as the M3DW except the PCI term is not included in the calculations. The DWBA without PCI has unphysically large cross sections for 20 eV excess energy when the two electrons leave the collisions in the same direction and this is a common failure of the DWBA. The agreement between experiment and theory found here for the  $3a_1$  state is better than we previously found for the  $1b_1$  state indicating that the OAMO approximation is much better for this state.



**Figure 4.** TDCS for electron impact ionization of  $\text{H}_2\text{O}$  in symmetric coplanar geometry as a function of  $\xi$  ( $2\xi$  is the angle between the two outgoing electrons). The cross sections are presented for excess energies of 10 eV and 20 eV.

### 3.4. Formic acid ( $\text{HCOOH}$ )

Birgit Lohmann's group at the ARC Center of Excellence for Antimatter-Matter studies at the University of Adelaide, Australia have recently measured (e,2e) ionization differential cross sections of formic acid ( $\text{HCOOH}$ ) for an incident electron energy of 100 eV and an ejected electron energy of 10 eV. This is a planar molecule with carbon near the center of mass which is of biological interest. The HOMO (highest occupied molecular orbital) is the  $10a'$  (ionization potential of 11.6 eV) and the next state is the  $2a''$  (ionization potential of 12.45 eV) and these two states cannot be resolved in the experiment so the experimental data represent a sum of the  $10a'$  and  $2a''$  states. Unfortunately the OAMO approximation is not valid for the  $2a''$  state so we can only calculate results for the  $10a'$  HOMO state.



**Figure 5.** Triple differential cross section of ionization of Formic Acid with  $E_0=100$  eV,  $E_b=10$  eV and  $\theta_a=10^0$  as a function of the ejected electron angle. The Experimental measurements represent a sum of the  $10a'$  and  $2a''$  states while the M3DW results are for the  $10a'$  state only.

Figure 5 shows a comparison between the experimental data and the M3DW results without the correlation-polarization potential. The experimental data have been normalized to theory in the recoil region. Although the M3DW agrees well with the shape of the recoil peak, the theory predicts a larger and more pronounced binary peak than found in the experimental data. Since the effect of the  $2a''$  is

unknown, it would be highly desirable to have experimental results which resolved the 10a' state to ascertain how well the M3DW works for a larger molecule such as this.

#### 4. Conclusions

In this paper, we presented TDCS for electron impact ionization of different molecules and compared the experimental results with the M3DW. Overall the theory is in reasonably good agreement with the experiments. Including the correlation polarization potential in the M3DW improved the agreement with the experiment for H<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. Replacing our old wave-function with Ning's wave-function has also improved the agreement with experiment for N<sub>2</sub> (the H<sub>2</sub> results did not change). We looked at two larger molecules – water and formic acid. We found better agreement with experiment for the 3a<sub>1</sub> state of H<sub>2</sub>O than we had previously found for the 1b<sub>1</sub> state. For formic acid, we found good agreement with the shape of the recoil peak but not the binary peak. However, the experimental data represented a sum of the 10a' and 2a'' states while we were only able to calculate results for the 10a' state so validity of the M3DW method using OAMO for large molecules has not been adequately tested.

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