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# Electron impact ionization of molecules at low to intermediate energies—A search for Young's double slit type interferences

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**Abstract**

Experimental and theoretical work studying the (e,2e) collision process from diatomic molecules is reported. In particular, recent work carried out from near threshold to ~100 eV incident electron energy ionizing $H_2$ and $N_2$ in coplanar symmetric and asymmetric geometries is compared to calculations using a molecular three body distorted wave model. Of interest is the possibility of observing the effects of Young's double slit-type interference terms in the measured cross-sections. There is considerable interest in this type of scattering, since simple models predict the effects should be equivalent to a modulation of the cross-section from individual atoms which constitute the molecule. Such effects have recently been inferred at 250 eV incident energy in an asymmetric geometry, however at lower energies the complexity of the scattering process and the requirement to integrate over all possible alignments of the targets means that these effects remain unclear. Experimental data and results from a molecular three-body distorted wave (M3DW) model are presented, and possible methods to experimentally align and detect the molecular direction prior to ionization are suggested.


*Keywords:* (e,2e) Spectroscopy; Molecules; Low energy electron collisions; Coplanar; Young's slit interference

## 1. Introduction

Low energy (e,2e) processes which study the single ionization of targets following electron collision have not extensively been carried out on molecular targets until recently. These experiments measure the scattered and ejected electrons emanating from the interaction region in coincidence, the time of flight of the electrons resulting in a time-correlated signal that can be measured to high precision. Since the momenta of the ingoing and outgoing electrons are determined, these are kinematically complete experiments. The experimentalist is free to select the energy balance between the electrons such that energy is conserved, and can choose a range of scattering geometries so as to probe different kinematic regions of the ionization process. In the experiments described here, the incident electron direction defines the $z$-axis, and a coplanar geometry is chosen where the ingoing and outgoing electrons form a plane. Both an asymmetric geometry (where one of the outgoing electrons is measured at a fixed polar angle $\theta_a$, with the correlated electron being detected for a range of angles $\theta_b$) and a symmetric geometry (where both electrons are measured over a range of polar angles such that $\theta_a = \theta_b$) are adopted, as shown in Fig. 1.

Whereas there has been a wide study of ionization in the low to intermediate energy regime (between threshold and ~100 eV above threshold) for atomic targets, there has been much less work carried out ionizing molecules. Recent experimental work has been carried out in this regime by the Manchester group using $CO_2$ [1], $H_2$ [2,3], $N_2$ [4,5] and $H_2O$ targets [6], and there has been new theoretical work by the Rolla group which considers these scattering processes for $H_2$ and $N_2$ [7–9]. In particular, there has been considerable interest in the possibility of observing 'double scattering' effects from diatomic molecules, which is similar to a Young's double slit experiment in optics. In this simple model, each atom that constitutes the molecule produces a coherent scattered wave such that interference maxima and minima are produced. The atoms act like individual slits in the optical analogy, and the cross-section is modulated by an angular function representing these interferences.

Unlike optical experiments where the double slits are accurately separated and are fixed in space, it is not yet possible to control the alignment of the target molecules with respect to the scattering geometry. Hence, the interference contributions from

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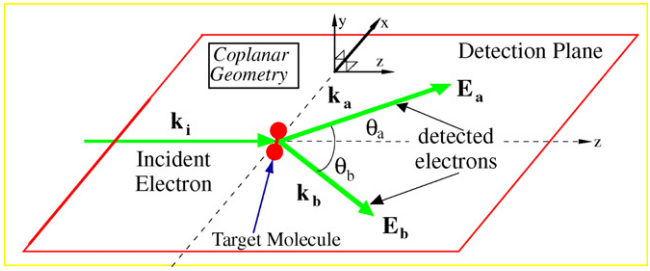


Fig. 1. Coplanar symmetric geometry, showing the direction of the scattered and ejected electrons following the collision.

each constituent atom must be integrated over all possible molecular directions. If ionization is *independent* of the molecular direction, this interference term may not be completely eliminated in the signal. Using a plane wave approximation in an asymmetric geometry, the molecular cross-section is then given by the constituent atomic cross-section modulated by an angular factor $M(E_{\mathrm{inc}}, \theta_a, \theta_b)$. This factor can be written [10]:

$$M(E_{\mathrm{inc}}, \theta_a, \theta_b) = 2\left(1 + \frac{\sin|\boldsymbol{\chi}||R|}{|\boldsymbol{\chi}||R|}\right) \quad (1)$$

where $\boldsymbol{\chi} = \mathbf{k}_a + \mathbf{k}_b - \mathbf{k}_i$ and $\mathbf{R}$ is the vector representing the internuclear axis.

The plane wave approximation is most accurate at high energies, and there is some evidence that equation (1) is applicable at these energies [11]. For the low to intermediate energy range as studied here, distorted waves must be used, and effects such as polarization of the target, exchange and post-collisional interactions have to be carefully considered.

In this paper, recent experimental and theoretical results for ionization of $H_2$ and $N_2$ in both a symmetric and asymmetric geometry are presented. Experimental results for $H_2$ are compared with those from He where the outgoing electrons carry the same energy. Results from a molecular three body distorted wave (M3DW) theory developed to study ionization from molecular systems are also presented, and it is seen that theory predicts the general structure of the scattering process at higher energies. This theory was extended to the ionization of $N_2$ molecules, and strong double slit type interference effects were predicted for an asymmetric geometry. These predictions have now been tested by experiment, and the results of this comparison are presented here.

Finally, limitations of the experiment for producing detailed results from molecular systems are explored. The first limitation results from the use of a target which is rotationally hot, as produced from an effusive beam. The second arises from the lack of alignment of the molecules prior to ionization. In the final section of this paper, these limitations are discussed, and possible solutions to these problems are suggested for the future.

## 2. The experimental setup

Fig. 2 depicts the experimental apparatus that is used in Manchester. The (e,2e) spectrometer is fully computer controlled and computer optimised, and can access all geometries from the perpendicular plane ($\psi = 90°$) through to a coplanar geometry ($\psi = 0°$). The electron source is a two-stage gun that produces a 1 mm diameter beam of electrons ranging in energy from 10 eV through to 300 eV, with zero beam angle at the interaction region and current of up to 5 μA. The electron analysers consist of a three-element zoom lens which images the interaction region onto a real aperture at the entrance of a hemispherical energy analyser operating at a pass energy of 15 eV. The combined energy resolution of the spectrometer is therefore ~500 meV.

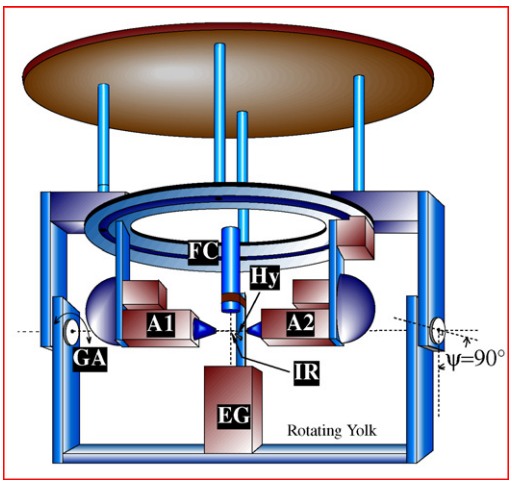


Fig. 2. The (e,2e) spectrometer in Manchester. The electron gun (EG) is shown in the perpendicular plane ($\psi = 90°$), and can rotate around the gun axis (GA) to a coplanar geometry ($\psi = 0°$). Analysers A1, A2 rotate in the horizontal detection plane with an axis through the interaction region (IR). The gas effuses from a hypodermic needle (Hy), the electron beam being dumped into a Faraday cup (FC).

The target molecular beam is produced from an effusive nozzle constructed from a platinum–iridium hypodermic needle of internal diameter 0.6 mm. The molecules are rotationally active, since they are sourced from a gas bottle held at room temperature. For $H_2$ targets, the ground state rotational levels which are significantly populated range from $J = 0$ to 5, whereas for $N_2$ levels from $J = 0$ to 28 are populated.

To enhance the angular range of the (e,2e) spectrometer, a magnetic angle changing (MAC) device [12] has also been installed. This device uses a well controlled magnetic field produced from a set of coils to steer electrons into and out of the scattering region, so that their direction at the interaction region changes (Fig. 3). The coils are designed so that no magnetic field penetrates into the electron analysers, nor into the electron gun. This field localization allows the spectrometer to be operated with the MAC device switched both off and on without changing the focussing conditions of the electron optics. The variation in angle of the electrons produced by the MAC device was ascertained by observing the angular shift of well defined structures in the elastic cross-section from argon. By using this device, the angular range of the spectrometer was increased in these experiments from $35° \leq \theta_{a,b} \leq 145°$ to $10° \leq \theta_{a,b} \leq 170°$.

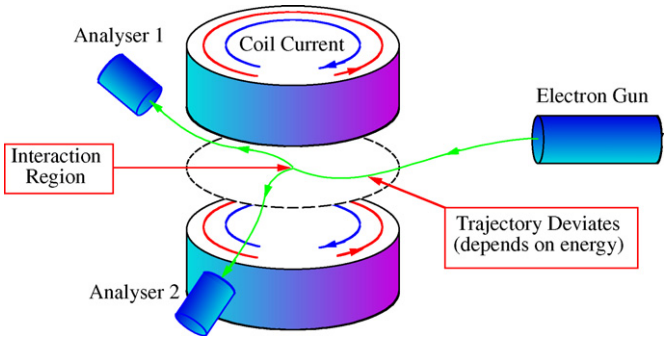


Fig. 3. The MAC device installed into the spectrometer. The coils are wound such that the magnetic field at the gun and analysers is zero. The field deviates incident and outgoing electrons according to their velocity, and so allows the angular range of the spectrometer to be extended.

## 3. Comparison of He and $H_2$ cross-sections

Fig. 4 compares experimental results for ionization of helium and $H_2$ in a symmetric geometry at excess energies $(E_a + E_b)$ ranging from 10 eV through to 40 eV [13,2]. The theoretical results from the M3DW model are shown for $E_a + E_b$ from 20 eV through to 40 eV [7]. The data are presented on a logarithmic scale, and are all normalised to unity at $\theta_a = \theta_b = 45^\circ$ since no absolute or relative data were taken with respect to energy. In this geometry, the MAC device was not used as it cannot increase the angular range of the experiment.

The results for helium show a typical double lobe structure, with a peak in the forward direction at $\theta \approx 45^\circ$ and a peak in the backward scattering direction at $\theta \approx 135^\circ$. The forward peak is considered as being due to a binary collision between the incident electron and one of the valence electrons, with the core playing only a minor role. In this case, since both electrons have equal energy, the electrons are expected to emerge at a mutual angle of 90°, as is seen. The peak in the backward direction is considered as due to multiple scattering, where the incident electron initially scatters from the core, then a binary collision occurs. In this case, the electrons are expected to emerge in the opposite direction again with a mutual angle between the electrons of 90°, as is observed. It can be seen that backward

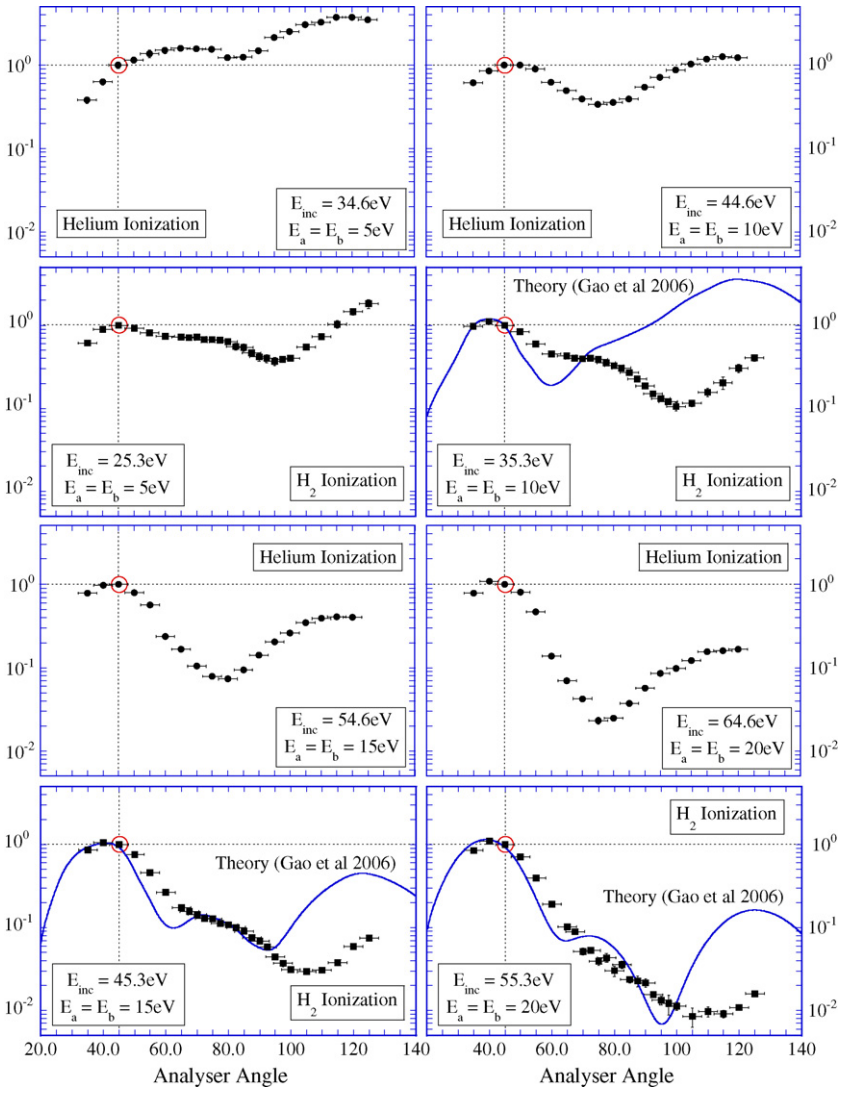


Fig. 4. Helium and $H_2$ cross-sections in a symmetric geometry, compared to results from the M3DW model. For details, see text.

scattering has a higher probability at low energies, and that as the energy increases, forward scattering becomes the dominant mechanism. In all cases, there is a clear distinction between forward and backward scattering events.

The results from an $H_2$ target have similarities and differences to helium. $H_2$ and helium are electronically similar, since there are two protons and two electrons in each target. The main difference is that the protons in helium are located in a single scattering centre (the nucleus), whereas the protons in $H_2$ are separated by the inter-nuclear distance $R$. For He the scattering process has spherical symmetry with respect to the ionic core, however for $H_2$ this symmetry is no longer applicable. The valence electrons in helium also have spherical symmetry, whereas in $H_2$ the electrons distribute themselves so as to ensure stability of the molecule, and so have a high probability of being between the nuclei.

One of the key differences between $H_2$ and He seen in Fig. 4 is the presence of a third peak in the cross-section for $H_2$ at $\theta \approx 80^\circ$. The backward scattering cross-section once more dominates at low energies for this target, although the peak is outside the angular range of the measurements. The additional peak at $\theta \approx 80^\circ$ is clearest at low energies. As the energy increases, this third structure is observed at all energies, apart from at the highest energy. By contrast to helium, the $H_2$ cross-section in the backward direction at the highest energy is a factor of 100 times smaller than the forward scattering peak, indicating that the effects of multiple scattering diminish more rapidly for this target.

The theoretical calculations from the M3DW model are also shown compared to experimental data, for excess energies from 20 eV through to 40 eV. The model predicts a forward and backward scattering peak with a peak at $\theta \approx 80^\circ$ as in the experiment, but this is clearest at higher energies. At 20 eV excess energy theory and experiment strongly disagree, especially in the backward direction where it is predicted the cross-section should be much higher than in the forward direction, in direct contrast to experiment. In fact, the theory is more similar to the experimental results for helium with a secondary double-scattering peak near $\theta \approx 135^\circ$ which is larger than the binary peak for low energies. As the energy increases, the agreement improves, however the theory continues to predict a backward double scattering peak while it is not seen in the experiment. The forward and middle peak are much more closely predicted by the model at the higher energies. The interesting question concerns the source of the peak at $\theta \approx 80^\circ$. One possibility is that this peak is a signature of a Young's type double slit interference. However, we think that this is unlikely since Eq. (1) does not predict a peak at $\theta \approx 80^\circ$ and there is no evidence in the theoretical results which would suggest such an origin for this peak. Although the general trends are present in the theory, improvements to the model are clearly required. Further experiments are also desirable so that a more detailed analysis of the features present can be made.

## 4. Measurements from nitrogen

The ability to model electron impact ionization from a non-centro-symmetric target as developed by the Rolla group is a significant advance on previous theories, however the computational requirements are extremely demanding. As such there are approximations that must be made in the model to make the calculations tractable. One of these which has already been discussed is the integration of the cross-section over the different alignments of the target prior to the collision. A further study on $H_2$ in an asymmetric geometry at an incident energy of 75.3 eV was carried out recently in a collaboration between the Rolla and Manchester groups [3]. This study produced much closer agreement between theory and experiment than shown in Fig. 4.

Since the M3DW model appears more accurate at higher energies and in an asymmetric geometry, it was decided to further test the predictions of the model by studying the ionization of $N_2$. Madison and co-workers predict that the effects of two-centre scattering from $N_2$ should be far stronger than for $H_2$, and generated theoretical results for an asymmetric geometry with $\theta_a = 1^\circ$, $10^\circ$ and with each electron carrying the same energy [9]. The model predicts very strong effects in the backward direction that are a direct consequence of two-centre interference.

The spectrometer at Manchester cannot access these very forward scattering geometries, and so the Rolla group re-calculated the cross-section for an asymmetric geometry with $\theta_a = 22^\circ$, which is the smallest angle that can be accessed in the experiment. Very strong two-centre interference effects were once again predicted using both a 3DWA and a distorted wave impulse approximation (DWIA). A MAC device was installed into the spectrometer to allow an increased angular range to be accessed, as discussed above.

Fig. 5 shows the results from the theoretical calculations compared to experiment, normalised to unity at $\theta_b = 45^\circ$. Theory predicts three large peaks in the cross-section, with peaks at $\theta_b \approx 45^\circ$, $110^\circ$, $190^\circ$. In [9], the peak at $\theta_b \approx 190^\circ$ was attributed to a double scattering interference process in which the active electron back scattered from two nuclei aligned parallel to the beam axis and the peak at $\theta_b \approx 110^\circ$ was attributed to a secondary Youngs'-type interference peak. The cross-sections

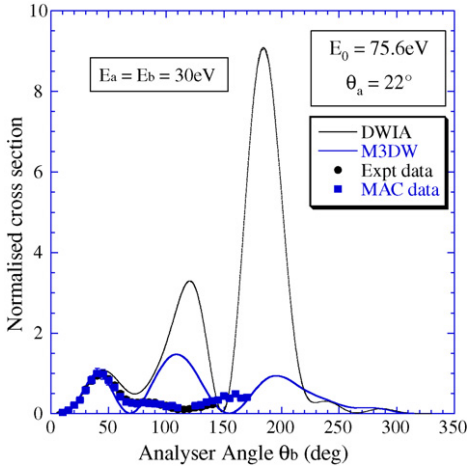


Fig. 5. Comparison of theory and experiment for coplanar asymmetric ionization studies from $N_2$. The experimental data was collected both with and without the MAC device operating. The calculation shows the results for a distorted wave impulse approximation (DWIA) and a molecular three-body distorted wave approximation (M3DW). Agreement between theory and experiment is poor, except for forward scattering.

for this molecular orientation were sufficiently dominant that the interference pattern persisted even after averaging over all molecular orientations. The DWIA calculation predicts a very large peak at the highest angle. This reduces in the M3DW model but is still very clear. The peak at $\theta_b \approx 110^\circ$ reduces by a factor of two for the M3DW model compared to the DWIA model, whereas the forward peak narrows.

The experimental results do not agree well with theory. The results are shown for experiments with and without the MAC device operating, and it can be seen that there is a good overlap between these data. The forward peak at $\theta_b \approx 45^\circ$ seems to match the M3DW theory quite well, however experiment shows a minimum in the cross-section at $\theta_b \approx 110^\circ$, in contrast to either model. There is a small backward scattering peak in the data which appears to have reached a maximum at $\theta_b \approx 160^\circ$, rather than at $\theta_b \approx 190^\circ$ as predicted. Even with higher angles being measured, it is unlikely that the comparison between theory and experiment will improve.

An important effect that has not been well represented in the theory is that of polarization of the target. Very recent calculations have begun where this effect is added in a non-ab initio way, and this inclusion indicates that polarization is a very important effect for this target. Preliminary results suggest that polarization effects will significantly reduce the $\theta_b \approx 110^\circ$ peak while the $\theta_b \approx 190^\circ$ remains. Consequently, larger angle measurements would be very valuable. The dramatic difference presented in Fig. 5 clearly shows that additional work in both theory and experiment is required to clarify where these discrepancies arise.

## 5. Present limitations and possible solutions

The poor comparison between theory and experiment in these low to intermediate energy ionization regimes is not entirely unexpected, given the complexity of the model, the approximations that must be made and the difficulties and limitations of the experiments. There is still much to be learned in this energy regime for atomic targets, although there has been great advances in recent years as new experimental data has been produced and theory has improved. Distorted wave approximations for the ingoing and outgoing channels, exchange, post-collisional interaction terms and the effects of polarization have all been included into the most sophisticated models to steadily improve their accuracy. Ionization experiments from more complex atomic targets have also now been made [14], allowing further refinement of the models which are pushed to lower energies. Discrepancies still remain, however the understanding of ionization from atoms in this regime is becoming clearer.

The ionization of a molecular target adds considerably to the complexity of these models. In particular, the need to adopt a non-spherically symmetric geometry puts great demands on computer requirements, and so additional approximations must be made as discussed above. Increased computational power and speed will alleviate many of these restrictions, and as found for atomic targets, these improvements are likely to predict cross-sections that begin to converge onto the experimental data.

More serious restrictions arise in the experiments, which need to be resolved if accurate knowledge of these important ionization processes is to be known. One restriction of current experiments is that the molecular ensemble is rotationally hot. This can be eliminated by using a supersonically cooled jet of molecules, rather than by producing the target beam from an effusive nozzle. The disadvantage of this technique is that the experiment has to be operated in a pulsed mode, to allow the vacuum pumps to recover after the gas load is released into the vacuum chamber. The coincidence experiment can then only operate at an effective rate of ~100 Hz in this pulsed mode, and so data accumulation time will increase. By also including an ortho to para converter prior to supersonic expansion [15], it is possible to produce >95% of all molecules which are in the $[v, J] = [0,0]$ ground state.

The more significant experimental limitation arises due to the random directions of the target molecular axes prior to ionization. Even the most sophisticated theory must integrate over all possible alignments to compare with present experiments, thereby losing critical information about the scattering process and the effects of quantum interferences from the two scattering centres. An experimental method to align the molecules prior to the ionization occurring is therefore highly desirable.

Whereas techniques to align certain polar molecules are possible using hexapole fields [16], these cannot be applied to non-polar targets such as $H_2$ and $N_2$ where Young's double slit type interference effects are expected. An alternative method may be to use a high power fs laser beam to efficiently dissociate the target molecules prior to ionization occurring [17]. By adopting two orthogonal laser beams, it should be possible to dissociate with high efficiency all molecules whose inter-nuclear axis aligns with the polarization vector of the laser beams. In this way, the remaining molecules will all be aligned in the same direction with respect to the scattering geometry. If the molecules are also cooled to $J = 0$ in the expansion of the jet, they should then provide an aligned, non-polar molecular target beam for ionization experiments. The disadvantage of this method is that most of the target beam density will be lost during dissociation, however as the supersonic jet has a high initial density, this should not result in a large loss of signal compared to conventional experiments. Such experiments are currently being considered.

## 6. Conclusions

Experimental and theoretical results have been presented for the ionization of $H_2$ and $N_2$ targets in both a symmetric and asymmetric geometry. The results from theory have been found to agree with experiment at higher energies for $H_2$, however large differences have been found for $N_2$. These disagreements appear to be largely due to the polarization of the target which is not included in the calculation. The apparatus used to produce these results has been described, and the limitations of both the theory and experiment which allows exacting comparison using these targets has been detailed. Improvements in both theory and experiment are needed, and a possible way forward to elucidate more detailed information has been discussed.

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