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Dynamical (e,2e) Studies of Bio-Molecules

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Observations always involve theory.
∼ Edwin Hubble (1889-1953)

1 Introduction

In 1911, Rutherford performed a famous experiment which involved scattering α and β particles through a thin gold foil. By measuring the angular distribution of the scattered particles, Rutherford found that he could obtain information relating to the internal structure of the target [1]. From the information obtained in such a manner, Rutherford detailed what is known as the Rutherford model of the atom, in which a very small positively charged nucleus, containing much of the atom's mass, was orbited by low-mass electrons.

As can be seen from the example above, understanding the collision process in atomic physics is of fundamental importance if we are to develop a complete model for our physical universe. Electron impact ionisation is one such collision process, and is considered by some to be one of the most fundamental [2]. Through the use of collision experiments, significant knowledge of the ionisation process may be obtained, which has many uses: from the study of fusion plasmas, to materials research and even medical research.

Returning to the history of the field, Ramsauer in 1921 used a single electron beam to measure a total electron-atom collision cross section [3], in what is considered by many to be the first electron scattering experiment. Further early electron scattering experiments were performed in 1922 by Townsend and Bailey. They discovered that the effect of an electron collision with a target (in this case argon) is dependant upon the velocity of the electron [4].

Subsequently, in 1928, Langmuir and Jones performed the first experimental electron impact ionisation experiment, specifically measuring the energy lost by the incident electron during a collision with gas molecules [5]. Using their results, they were able to provide the resonance energies and ionisation potentials of a series of gases, including H_2, N_2, He, Ne, Ar and Hg. Rudberg performed similar energy loss experiments upon molecular nitrogen in 1930, in an attempt to provide more accurate ionisation and resonance energy measurements [6].

Later in that same year, Bethe employed the First Born Approximation (FBA) to calculate theoretical cross sections for both elastic and inelastic collisions as well as ionising collisions [7].

Up until this point in history, most experiments had focused on measuring cross sections that were differential only in energy. However this was changed by Hughes and McMillen in 1932, who measured the Double Differential Cross Section (DDCS) of argon for a range of electron energies between 50eV and 550eV [8]. The DDCS provides more information about the ionisation process because unlike previous measurements that were differential in only energy, the DDCS is differential in either the angle or the energy of the outgoing electrons.

However useful the DDCS may be, it still only provides somewhat limited information as a number of parameters of the collision process remain undetermined. The Triple Differential Cross Section (TDCS) provides a solution to this problem, as it becomes possible to fully investigate the ionisation process with respect to all kinematics of the outgoing electrons. The most common manner by which to measure the TDCS is through what is known as the (e,2e) technique.

1.1 (e,2e) Spectroscopy

(e,2e) spectroscopy refers to a type of electron impact experiment which involves "firing" a beam of electrons at a beam of target atoms or molecules. These two beams are directed to cross one another to form a spatially defined interaction region [9]. The beam of incident electrons ionise the target species, thus leading to an electron being ejected from the target. A number of detectors then collect both the ejected and the previously incident (now scattered) electron and measure them in temporal coincidence. This allows for the measurement of the TDCS, which tells us the probability of two outgoing electrons, of specific energy and momenta, being scattered in particular directions after an ionisation event. As we shall see later in Section 2.4, there are many possible configurations under which (e,2e) measurements might be conducted. In this thesis, we are interested in those configurations giving rise to what has been termed dynamical (e,2e) experiments. As a consequence, a large volume of work from Electron Momentum Spectroscopy (EMS) is not included here. The reader should consult the book from Weigold and McCarthy [2] for a dissertation of that work.

The first to propose a TDCS experiment was Smirnov *et al.* [10, 11]. Subsequently, in 1969, the first experimental (e,2e) results were published simultaneously by both Ehrhardt *et al.* [12] and Amaldi [13]. From these initial

experiments the (e,2e) coincidence technique quickly became a powerful tool for investigating the dynamics of the ionisation process. Through such investigations theoretical models were developed and tested, and eventually a satisfactory agreement between the models for simple atomic systems (such as H and He) was found [14]. However, the current theoretical models still appear to have fallen short when describing the complex interactions that occur when low to intermediate energy electrons ionise molecules. Note that (e,2e) experiments using these kinematics are generally known as dynamical (e,2e) experiments.

Unlike atomic dynamical (e,2e) spectroscopy, the literature on molecular measurements is rather limited due to the difficulties in using (e,2e) techniques with molecular targets [15]. These difficulties arise from the high densities of molecular states, as they can be quite close in energy which can prove to be quite a challenge to resolve using (e,2e) spectroscopy. Indeed the energy resolution of (e,2e) spectroscopy is generally inferior to that of photoelectron spectroscopy, and other similar techniques [2] (see Section 3.3.1). However the benefits in applying (e,2e) spectroscopic techniques to molecular systems are significant, as they can elucidate effects responsible for perturbations in the molecular cross section [16, 9]. Currently, experimental molecular (e,2e) results are available for molecules including H_2 [16], N_2 [16, 17, 18, 19, 20, 21, 22, 23], CO_2 [17, 24], He [25, 26], CO [18], O_2 [27], N_2O [28], C_2H_2 [29], H_2O [9, 30, 31], CH_4 [26, 32, 33, 34], formic acid [15, 35], tetrahydrofuran [15, 36] and thymine [15]. In addition, as a result of this research, pyrimidine [37] and α-tetrahydrofurfuryl alcohol [38] have also been published.

The first molecular (e,2e) experiment was performed by Jung *et al.* and was published in 1975 [16]. That experiment involved using 100eV or 250eV incident electrons to ionise H_2 under kinematic conditions referred to as coplanar asymmetric (see Section 2.4 for more details). Furthermore the ejected electrons measured had energies of either 4.5eV or 9eV, and the scattered electrons were measured over the angular range between $-4°$ and $-25°$. It was observed that molecular targets had smaller recoil peaks when compared to those for atomic targets, for the species thus far investigated. Jung *et al.* also performed (e,2e) coincidence measurements on N_2 at the same time [16]. Using the same coplanar asymmetric kinematic geometry as before, Jung *et al.* employed 100eV incident electrons and measured ejected electron energies of 3eV or 4eV at the scattered electron angles of $-8°$, $-15°$ and $-25°$. The results from this experiment were much the same as the H_2 results, again showing a relatively smaller recoil peak.

Following this, Chérid *et al.* also performed (e,2e) experiments on H_2 under the

coplanar asymmetric kinematic conditions [39]. However, Chérid *et al.* made use of 4087eV incident electrons and detected either 20eV or 100eV ejected electrons. The purpose of this experiment was to compare the First Born Approximation (FBA) and the Plane Wave Impulse Approximation (PWIA) theoretical results to the experimental results. What was found was that the FBA provided good agreement with the experimental results, while the PWIA failed to predict either the shape or the magnitude of the measured TDCS. This development was expected for the 20eV ejected electron measurements as the impulse conditions were not met. However, with the 100eV ejected electrons the bound Bethe conditions were met (see Section 2.4) and previous comparisons drawn with He had shown excellent agreement between the theory and experiment.

Avaldi *et al.* studied the 1σ orbital of C_2H_2 using a coplanar asymmetric kinematic geometry [29]. The incident electron energy was 1500eV, the ejected electron had energies of either 9.6eV or 41eV and all measurements were performed at small scattering angles. The experimental results showed that the TDCS was not symmetrical around the momentum transfer vector, as well as the recoil peak being of a larger magnitude than for an atomic target measured under the same kinematic conditions. The results were also compared to those from FBA calculations and they were not found to be in good agreement, most likely due to the FBA lacking Post Collision Interaction (PCI) terms.

An interesting point to note at this stage is that the experimental TDCS results were not measured on an absolute scale. Indeed it is still quite a common practice to scale the experimental results to the theoretical calculations, due to the difficulty in measuring absolute TDCSs. Avaldi *et al.* sought to remedy this by providing absolute N_2 TDCSs in 1992 [40]. Those experiments were performed using a coplanar asymmetric geometry, 300eV incident electrons with 10eV ejected electrons and the scattered electrons measured at angles of 3° and 3.5°, and then with 18.4eV ejected electrons and scattered electron angles of 7.2° and 8°. However the experimental TDCS results were unable to be compared to a theoretical model, and it appears that the procedure proposed to set the absolute scale was not embraced by the community.

Later in 1996, Doering and Yang also measured the TDCS of N_2, now particularly focusing on the $3\sigma_g$ and $1\pi_u$ orbitals [19]. Once again using the coplanar asymmetric geometry, the TDCS was measured with 100eV incident electrons for a range of ejected electron energies between 3eV and 13eV, and at scattered electron angles less than 5°. The results from this experiment were interesting, as they showed that there was a shift in the position of the binary and recoil

peaks, away from the momentum transfer direction (κ). It was further noted that TDCSs measured for the two different orbitals had distinctive differences from one another, indicating that the TDCSs, under these kinematic conditions, were sensitive to the initial and final states of the molecular target.

Further (e,2e) measurements on the molecular orbitals of N_2 were performed by Rioual *et al.* in 1996 [18]. These measurements were performed under the coplanar symmetric kinematic geometry, with incident electron energies ranging between 90eV and 400eV. The experimental apparatus used had a 1.2eV energy resolution allowing additional features to be observed although, once again, it was found that the PWIA calculations did not provide good agreement with the measured data.

Rioual *et al.* also performed dynamical (e,2e) measurements on the 5σ, 1π, 4σ and 3σ orbitals of CO [18]. As for their measurements on N_2, the (e,2e) spectrometer they used was set up to exploit the coplanar symmetric kinematic regime and used incident electrons with energies ranging from 90eV to 400eV. Much like their N_2 measurements, the higher resolution allowed satellite structures, resulting from final-state configuration interaction effects, to be observed in the cross section. However, the PWIA calculations again fell short in describing the TDCS.

Cavanagh and Lohmann collected several N_2O TDCSs using a coplanar asymmetric (e,2e) spectrometer, with an incident electron energy of 900eV and an ejected electron energy of 25eV [28]. The measurements were performed on the 2π (valence) orbital at scattered electron detection angles of $-2°$, $-5°$ and $-10°$, as well as the inner-shell 4σ orbital at a scattered electron detection angle of $-5°$. At the scattered electron angle of $-10°$, the 2π orbital displayed a pronounced double-lobe structure in the binary region, while at $-5°$ this binary lobe structure was barely discernible. Also of note was that at $-2°$, the recoil peak had a higher magnitude than expected as well as the maxima of both binary and recoil peaks being shifted with respect to κ and $-\kappa$ (see Equation 2.8), much like what was observed by Doering and Yang for N_2 [19]. Additionally, the inner-shell 4σ orbital measurements showed a smaller binary-to-recoil ratio than was expected, which may have been due to the ejected electrons interacting with the molecular target as they escaped.

Doering and Yang additionally performed a series of dynamical (e,2e) measurements on the $1\pi_g$, $1\pi_u$ and $3\sigma_g$ orbitals of O_2 in 2001 [27]. Using 100eV incident electrons, ejected electron energies of either 3.5eV, 6eV or 11eV and at

a scattered electron angle of 4°, the experiment was performed under coplanar asymmetric kinematic conditions. The collected data were compared to their previous N_2 results [19], due to both molecules sharing the same orbital symmetry types, although the order of the orbital energies is reversed. Broadly speaking, it was found that in the binary region the TDCSs were largely the same, although a greater shift away from the momentum transfer direction was observed in O_2. This suggested that the shape of the orbital has a significant effect on the TDCS. In addition the recoil peak behaviour was vastly different between the two molecules, with the physical reason for this particular observation remaining an unanswered question even today.

Hussey and Murray also performed (e,2e) measurements on N_2, using electrons with incident energies of 25.6eV or 76.7eV [20]. Their measurements were performed upon the $3\sigma_g$ and $1\pi_u$ orbitals and their results suggested that, as for asymmetric kinematics, cross sections measured under the symmetric kinematic regime are sensitive to contributions from configuration interaction effects.

The $1b_1$, $1b_2$, $2a_1$ and $3a_1$ molecular orbitals of H_2O were investigated by Milne-Brownlie *et al.*, under the coplanar asymmetric kinematic geometry configuration [9, 30]. All measurements were performed using 250eV incident electrons and 10eV ejected electrons, while the scattered electron detection angle was held at 15°. Those results were compared to corresponding results from Distorted Wave Born Approximation (DWBA) calculations, which proved to be an inadequate model as their recoil peak was of significantly higher magnitude than what was observed.

Gao *et al.* published DWBA and Molecular 3-body Distorted Wave (M3DW) results for the $3\sigma_g$ orbital of N_2 in 2005 [21]. Those calculations were performed for both coplanar symmetric and asymmetric kinematic regimes, and for the symmetric arrangement the M3DW results were found to give a better agreement with the experimental data. However, compared to data from Distorted Wave Impulse Approximation (DWIA) calculations averaged over all molecular orientations (DWIAOA) [22], the M3DW and DWBA results were still modest. This was not the case under the asymmetric kinematic arrangement, as the M3DW calculations accurately predicted both the shape and relative magnitude of the experimental data, while the DWBA failed to predict the relative magnitude.

The experimental results of Rioual *et al.* [18] and Hussey and Murray [20], for ionisation from the $3\sigma_g$ orbital of N_2, were then compared to corresponding

DWIAOA TDCSs calculated by Gao *et al.* [22]. At high incident electron energies, the DWIAOA calculations were in good agreement with the experimental results, although the agreement deteriorated for the lower incident electron energies. Comparatively, the DWIAOA showed better agreement with the experimental results than the PWIA calculations, especially at intermediate incident electron energies. From those results, Gao *et al.* suggested that the DWBA would be a better theory to model molecular (e,2e) results.

Hussey and Murray also performed a set of (e,2e) measurements on the $1\pi_g$ and $4\sigma_g$ orbitals of CO_2 in 2005 [24]. As before, they worked under the coplanar symmetric kinematic arrangement and used incident electron energies between 25eV and 100eV. No theoretical results were available for CO_2 at the time and so the experimental results were compared to their previous N_2 results [20], which were unsurprisingly different.

Naja *et al.* made dynamical (e,2e) measurements on N_2 under the coplanar asymmetric kinematic geometry regime in 2007 [23]. Using 600eV incident electrons, and 74eV ejected electrons, Naja *et al.* presented measurements that were the sum of the $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ (outer) orbitals as well as a separate measurement for the inner $2\sigma_g$ orbital. Much like previous measurements performed on molecular nitrogen, the local maxima of the binary and recoil peaks were shifted away from the momentum transfer vector, while the recoil peak displayed a higher magnitude than expected.

Kaiser *et al.* published a series of experimental results for H_2O, using both coplanar symmetric and asymmetric geometries [31]. The incident electron energies for those measurements were between 15eV and 95eV and the $1b_1$ molecular orbital was studied. The results were compared to those from a DWBA calculation, which incorporated final state PCI, and a good agreement was found with the experimental results at low and intermediate incident energies. However at high incident electron energies, agreement was marginal.

The $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ (outer-valence) orbitals, as well as the inner-valence $2\sigma_g$ orbital, of N_2 were studied once again by Lahmam-Bennani *et al.* in 2009 [17]. Much like the experiment undertaken by Naja *et al.* in 2007 [23], the measurements were performed under the coplanar asymmetric geometry and with 600eV incident electrons, although instead now either looking at 37eV or 205eV ejected electrons. These measurements were compared to a set of results from First Born Approximation-Two Centre Continuum (FBA-TCC) calculations, which once again failed to reproduce the experimental results. In the

same paper, Lahmam-Bennani *et al.* also published (e,2e) results for the $1\pi_g$ orbital of CO_2 [17]. Those experiments were performed with incident electron energies between 500eV and 700eV, and ejected electron energies of either 37eV or 74eV. A scattered electron angle of $-6°$ was chosen, in order to ensure that the recoil peak would be large, and it was noted that the cross sections exhibited narrow binary peaks located at around the momentum transfer direction.

Methane, CH_4, was investigated by Lahmam-Bennani *et al.* in 2009, the focus of which were the $1t_2$ (outer) and $2a_1$ (inner) valence orbitals [26]. These measurements were performed under coplanar asymmetric kinematics, with incident electron energies of 5000eV, at a scattered electron angle of $-6°$, and for the ejected electron energies of 12eV, 37eV or 74eV. The recoil peak was once again observed to be of a greater magnitude than expected, relative to the binary peak. This proved to be a problem for the Brauner, Briggs and Klar (BBK) model, as well as the 1-Coloumb Wave (1CW) model, as neither were able to reproduce the observed recoil peak magnitude. The BBK model was, however, able to reproduce the shape of the binary peak satisfactorily.

In 2009, Colyer *et al.* measured TDCSs for the outer valence, $10a'$, orbital of formic acid (CHOOH) [35]. These measurements were performed with a coplanar asymmetric kinematic geometry, using 100eV or 250eV incident electrons, detecting 10eV ejected electrons and at scattered electron detection angles of $-5°$, $-10°$ and $-15°$. Their results were compared to M3DW, and Molecular 3-body Distorted Wave with Correlation-Polarisation-Exchange terms (M3DW-CPE), calculations which were both found to give reasonably good agreement with the experimental results.

Nixon *et al.* also studied H_2O, specifically focusing on the $3a_1$ orbital, using both coplanar symmetric geometry and an out-of-plane configuration [41]. Under this specific kinematic regime, the angle of the incident electron beam, with respect to the scattering plane, is varied. For this set of measurements, the incident electrons had energies between 4eV and 40eV above the $3a_1$ orbital ionisation threshold, and there was both equal and unequal energy sharing between the final state electrons. Superficially the collected results were similar to those of Kaiser *et al.* [31], although with the noticeable absence of a secondary peak in the forward ejected electron angular region. Their results were also compared to two M3DW calculations, with a varying degree of success. Specifically, it was found that the M3DW that was calculated to only include PCI terms to the first order performed much better than the M3DW calculations including PCI terms to all orders.

Furthermore, Nixon *et al.* also performed some dynamical (e,2e) measurements on CH_4 and Ne under the coplanar symmetric kinematic geometry [33, 34]. These measurements were performed on the $1t_2$ (HOMO) and $2a_1$ (NHOMO) molecular orbitals for CH_4, and on the $2s$ shell of Neon. The outgoing electrons were measured at having energies ranging from 2.5eV up to 20eV. The results of these measurements were compared to one another, as well as DWBA results [34] and M3DW results [33].

Colyer *et al.* produced a set of dynamical (e,2e) measurements on tetrahydrofuran (THF) in 2010, measuring the TDCSs of the combined outer-most valence orbitals, $12a' + 9b$ [36]. 250eV incident electrons were used, along with 10eV ejected electrons being detected, at the scattered electron angles of $-5°$, $-10°$ or $-15°$ under the coplanar asymmetric kinematic geometry. The experimental results were once again compared to those from M3DW calculations. This comparison showed good agreement, except at the scattered electron angle of $-5°$ where the measured recoil peak was of significantly larger magnitude than that predicted by theory. We note that the work of Colyer *et al.* [36] probably represents the first dynamical (e,2e) investigation on a large polyatomic molecule, and one which can also be considered as a prototype for a biomolecule.

The TDCSs of the unresolved inner valence $14a' + 2a''$ orbitals of thymine, were published in 2012 by Bellm *et al.* [42]. These measurements were performed using coplanar asymmetric kinematics with 250eV incident electrons, 20eV ejected electrons were detected and with the scattered electrons collected at angles of $-10°$ or $-15°$. Curiously the measured recoil peaks were relatively small in magnitude compared to their binary peaks, and the FBA calculations performed were found to be in very good agreement with these measurements.

1.2 Project Significance

In 1953 Watson and Crick discovered the structure of deoxyribonucleic acid, more commonly known as DNA [43]. This complicated molecule's existence was foreshadowed from as early as 1865, with Mendel's famous pea inheritance studies [44]. Life, in its most basic form, can be considered to be the simple manipulation and eventual transference of genetic information from one generation to the next [45]. DNA is the transport medium for this information and it is essential for life to continue. The information stored within the structure of DNA is used to construct the components of cells, the primary amongst which are the proteins.

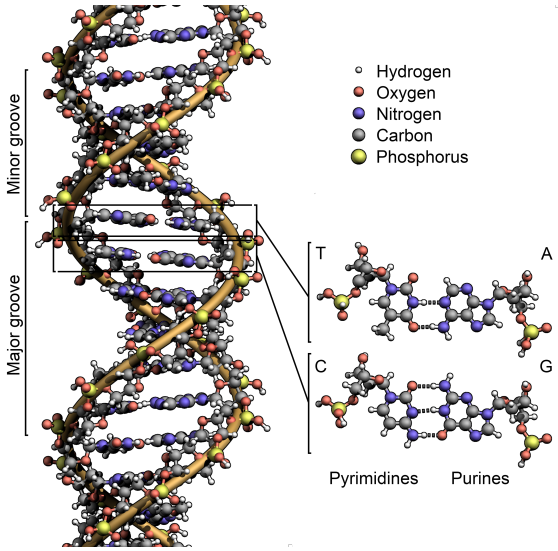

Figure 1.1: *A three dimensional model of a segment of DNA [46].*

Structurally, DNA primarily consists of two long polymer chains composed of what is referred to as nucleotides, which are held together by a 'backbone' of sugars and phosphates that are in turn held together by cyclic ester units [47]. "Hanging off" the sugars, on these two anti-parallel polymer chains, are four molecular structures, called nucleobases or informally bases, with the entire structure being stabilised through hydrogen bonds [47]. Four nucleobases encode the information on the DNA: adenine (A), cytosine (C), guanine (G) and thymine (T). These four bases form complementary pairs along the two polymer chains: adenine with thymine and guanine with cytosine. In the case of ribonucleic acid (RNA), uracil (U), an additional fifth base, takes the place of thymine. Figure 1.1 shows a three dimensional model of DNA, making particular note of the nucleobases [46].

DNA is a fragile molecule and damage can be caused to it quite easily. Ionising radiation (e.g. photons, electrons, positrons, protons, etc) is one such source of damage, which is widely used in medicine, as both a diagnostic probe and as a treatment. As the ionising radiation passes through the biological medium, it interacts with it in a series of elastic and inelastic collisions that, in turn, produce secondary 'species'. Until quite recently it was thought that the damage caused by ionising radiation, to biological systems, was primarily due to high-energy ballistic impacts by the initial ionising particle. However, in recent years, experiments, simulations and theoretical calculations have indicated that the secondary species produced by the high-energy ballistic impacts have a more significant role in biological radiation damage than was previously thought [48].

One of the secondary species produced in such a way are electrons, and a single high-energy ionising particle can create an extremely large number of electrons with energies in the 0eV to 20eV range. These electrons can then interact with the components of the biological medium, including H_2O [49], the sugars [50], organic acids [51] and the DNA bases [52, 53, 54, 55, 56, 57].

Boudaïffa *et al.* originally showed that electrons with energies lying between 3eV and 20eV (inclusive) can cause significant damage to DNA [58], while Martin *et al.* extended these energies to cover the 0eV to 4eV range [59]. Nikjoo and Goodhead also performed a set of calculations to indicate the extent of the role played by secondary electrons in radiation damage [60]. The damage caused by the secondary electrons is due to the process of dissociative attachment, which can lead to single or double strand breaks in the DNA, as well as the formation of ionic products or free radicals, which can in turn cause further degradation of the DNA strand and the surrounding biological medium. The majority of cellular damage due to high-energy ionising radiation is now thought to be due to these particular processes [54].

As such, modelling the behaviour of high-energy radiation, and any secondary species produced, is highly desirable so that the process may be understood and eventually controlled. One manner by which this is achieved is through the use of charged particle track structures, in which the paths of the primary and secondary species are simulated. Figure 1.2 shows an example of the output of a typical charged particle track structure simulation, with an overview of charged particle track structures and their use in determining radiation damage being given by Hill [61].

Charged-particle track structures are fundamentally based upon Monte Carlo simulations, which are used to determine individual ionisation, etc., events that occur along the path of the incident ionising radiation. These Monte Carlo simulations are often based upon cross sections which are either experimental, or theoretical if no measurements are available. However, due to the biological medium being primarily made up of water ($> 75\%$), and the distinct lack of experimental cross sections for the larger biomolecules, the calculations usually only use water cross section data, implicitly assuming that all biological matter is water. A further twist on this assumption is that nearly all current water cross section data is measured while the water is in a gaseous phase, and there has been some contention as to whether this accurately portrays the behaviour in liquid phase water [63, 64].

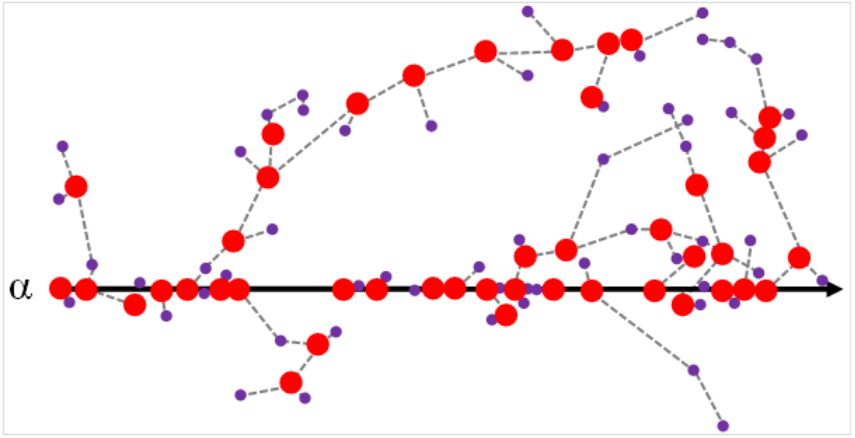

Figure 1.2: *An example of the output from a Charged-particle Track Structure Analysis simulation [62]. The straight black line represents the path of a 4MeV incident α-particle, the large red circles indicate ionisation events and the small purple circles are excitation events. The grey dashed lines indicate the paths of the secondary electrons that arise due to the ionisation events.*

Pyrimidine, α-tetrahydrofurfuryl alcohol (THFA), tetrahydropyran (THP), tetrahydrofuran (THF) and 1,4-dioxane were chosen as subjects for the present study, as they are analogues of some larger molecules that are of biological significance. It is very difficult to perform reliable measurements and calculations for cross section data for electron scattering directly from large molecules, such as DNA [35]. As such there is limited information available on the various biomolecules, but there is also a need for such information in order to better model the effects of radiation upon biological systems. Therefore, studies on analogue systems, such as those presented in this thesis, are vital. In addition, it is unlikely that experiment will be able to produce all the relevant data needed for the simulation studies. Only theory will be able to fufil that role. As such it is also vital to provide data that can benchmark theory, which is another of the aims of the measurements reported in this thesis.