



Flinders

UNIVERSITY

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

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That theory is worthless. It isn't even wrong!

~ Wolfgang Pauli (1900-1958)

2

Definitions and Theory

2.1 Introduction

An (e,2e) experiment involves the collision of an incident electron with a target atom or molecule. After this collision, one or more electrons are removed from the target particle, resulting in a process which is known as electron impact ionisation. Electron impact ionisation is one of the many potential scattering processes that can occur. It is classed as an inelastic collision: a collision event in which the target particle's internal structure is changed. Other collision processes are super-elastic scattering (e.g. a laser excites the target particle, which is then de-excited by the incident electron that scatters with increased energy), and elastic scattering (no internal structural change to the target particle due to the collision). While inelastic scattering also covers discrete excitation events (e.g. rotational, vibrational or electronic-state excitation), this thesis focuses on the inelastic ionisation process.

The ionisation process may be categorised in a number of different ways:

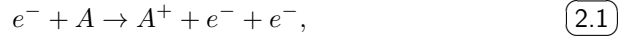
- Direct versus resonant
Direct ionisation occurs when one or more electrons are removed from the target particle with minimal interaction with the target core. Resonant ionisation occurs via a resonant process followed by the ionisation (eg autoionisation).
- Single versus multiple
Single ionisation occurs when only a single electron is ejected from the target particle as a result of the collision. During multiple ionisation, many electrons can be ejected (eg the Auger effect).
- Inner shell versus outer shell

CHAPTER 2. DEFINITIONS AND THEORY

During the ionisation process, an electron is usually ejected from either the inner electron shell of the target particle or the outer electron shell. However, if the incident projectile has a high enough energy then core-electron ionisation can also occur.

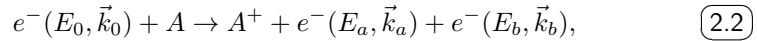
2.2 Ionisation

The direct single ionisation of a target particle (A), by an electron collision event, can be described by the following equation:



where A^+ represents the positive ion produced by the collision. The most likely result of this event is the ejection of an electron (e^-) from the valence shell of the target.

The motion of the target can be neglected as its mass is much larger than that of the electron. Therefore, Equation 2.1 can be rewritten as:



where E_0 , E_a , E_b are the kinetic energies, and \vec{k}_0 , \vec{k}_a , \vec{k}_b are the momenta of the incident, scattered and ejected electrons, respectively.

For the ionisation process to comply with the law of conservation of energy:

$$E_0 = \epsilon_i + E_a + E_b, \quad (2.3)$$

where ϵ_i is the ionisation potential of an electronic orbital in the target species. As the recoil energy of the resultant ion is small compared to that of the electrons, it is neglected.

Furthermore, for the process to comply with the law of conservation of momentum the momentum imparted (\vec{q}) to the ionised target particle is:

$$\vec{q} = \vec{k}_0 - \vec{k}_a - \vec{k}_b. \quad (2.4)$$

As the system is comprised of three free moving particles, four types of cross section can be defined: the single, double and triple differential cross sections and the total cross section.

2.3 Differential Cross Sections

A cross section measures the probability that a given collision process will occur under specific kinematic conditions [65]. Of the four cross sections that will be discussed in this thesis, the Total Ionisation Cross Section (TICS) yields the least information. It is represented by the symbol $\sigma(E_0)$. Unlike other cross sections, the TICS is dependent only upon the incident electron energy (E_0). It provides a measure of the total number of ions produced by the collision process. The TICS can simply be calculated by integrating each of the single differential cross sections and then summing them together [66].

2.3.1 Single Differential Cross Sections

The Single Differential Cross Section (SDCS) is a measure of the energy distribution of the two outgoing electrons after the collision process. The SDCS is represented by:

$$\frac{d\sigma}{dE} \tag{2.5}$$

Since, from a quantum mechanical perspective, the two outgoing electrons are indistinguishable, a specific naming convention is necessary. The “fast” outgoing electron, i.e. the electron that has energy close to the excess energy ($E = E_0 - \epsilon_i$), is referred to as the scattered electron. The “slow” outgoing electron with an energy relatively closer to zero is referred to as the ejected electron.

The SDCS cannot usually be measured directly, unless specific techniques are used. It must be obtained by numerical integration of the double differential cross section with respect to all angles of emission of the outgoing electrons [67]. Another form of SDCS can be obtained by numerically integrating the double differential cross section with respect to all energies [66]. However, this latter form has little physical meaning and so is rarely used.

2.3.2 Double Differential Cross Sections

The Double Differential Cross Section (DDCS) is a measure of the energy and angular distribution of either the ejected, or scattered, electron after the collision event. The DDCS can be measured using what is known as a “crossed beam experiment”; an experiment in which a beam of electrons, of a specified energy, cross a target atomic (or molecular) beam at an angle of 90° . After interaction, a single outgoing electron is detected according to either its energy or angle.

The DDCS is represented by the following formula:

$$\frac{d^2\sigma}{d\Omega dE}. \quad (2.6)$$

High energy incident electrons tend to scatter from the target in a narrow angular range centred around the unscattered electron beam. Lower energy incident electrons tend to scatter from the target isotropically in all directions [67]. High energy ejected electrons can reveal information about the target's electronic structure in the cross section, due to a binary collision between the incident electron and an electron from the target.

In the DDCS there is significant uncertainty in the observed ionisation process and state, for a given energy. Hence the theories that are used to describe the DDCS must include all processes and states that could possibly contribute to the cross section. This makes them very awkward to employ. However, they can be simplified by determining the energies and momenta of the outgoing electrons. This allows a specific process to be selected. Such information can be obtained using the triple differential cross section.

2.3.3 Triple Differential Cross Sections

The Triple Differential Cross Section (TDCS) is a measure of the probability that an incident electron of energy E_0 and momentum \vec{k}_0 will produce two electrons, of energies E_a and E_b , momenta of \vec{k}_a and \vec{k}_b and at solid angles $d\Omega_a$ and $d\Omega_b$, upon undergoing a collision with a target species [2]. The TDCS is represented by:

$$\frac{d^5\sigma}{d\Omega_a d\Omega_b dE_a}. \quad (2.7)$$

A useful feature of the TDCS is its ability to fully determine the ionisation process, excluding the spin of the electrons involved. Hence theories formulated to describe the process do not have to be summed over unobservable parameters. This allows a good comparison to be easily drawn. This remarkable feature of the (e,2e) technique arises because the scattered and ejected electrons are measured in temporal coincidence. The electrons can therefore be connected to a specific ionisation event.

The momentum imparted to the ion, and the momentum transfer vector, are two of the most important kinematic parameters required in understanding the ionisation collision process. The amount of momentum imparted to the ion is

2.3. DIFFERENTIAL CROSS SECTIONS

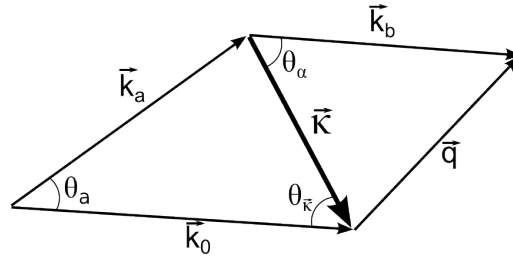


Figure 2.1: *Vector diagram illustrating the transfer of momentum during an ionisation event. In this diagram, θ_a is the angle of the scattered electron, relative to the incident electron; $\theta_{\vec{\kappa}}$ is the angle in which the momentum is transferred; and $\theta_\alpha = \theta_{\vec{\kappa}} - \theta_b$, where θ_b is the angle of the ejected electron, relative to the incident electron.*

easily calculated using the conservation of momentum equation (Equation 2.4). The momentum transfer vector is defined as the momentum change between the incident electron and the outgoing scattered electron [67] (refer to Figure 2.1), and is given by:

$$\vec{\kappa} = \vec{k}_0 - \vec{k}_a. \quad (2.8)$$

The amount of momentum that is transferred during the collision event is of particular importance. If a TDCS is performed with a high incident electron energy, and small momentum transfer (i.e. $\kappa < 1\text{a.u.}$), the collision process behaves like a photoionisation event [68]. Thus the final cross section produced is dependent upon the configuration of the ejected electron, prior to the ionisation event. Furthermore, structural details of the target molecule (e.g. orbital ionisation potentials, orbital momentum distributions, target and ion correlations and orbital-specific momentum densities) can be determined when measuring the TDCS of this kinematic configuration. By measuring such a TDCS, a clear picture of the electron momentum distribution around the target's nucleus emerges [69].

However, when the kinematics are arranged to collect such structural information, the ionisation process acts merely as a tool for this purpose alone. Little, or no, information about the dynamics of the ionisation process can be obtained [67, 70]. If a TDCS is performed with a medium to large momentum transfer ($\kappa > 1\text{a.u.}$), information relating to the dynamics of the collision event can be obtained. This information includes any distortion effects which relate to the process, and details of the interaction that occurs between the particles. In summary, the cross section is dependent upon the configuration of the electronic structure of the target particle, prior to ionisation [67].

2.4 Kinematics

There are a number of different kinematic parameters that can be varied when measuring a TDCS; each of which can provide information about different physical properties of the electron ionisation process. The differing configurations of the kinematic parameters are collectively known as kinematic geometries and can be categorised into five major groups: coplanar symmetric, non-coplanar symmetric, coplanar asymmetric, non-coplanar asymmetric and coplanar mutual angle (refer to Figure 2.2).

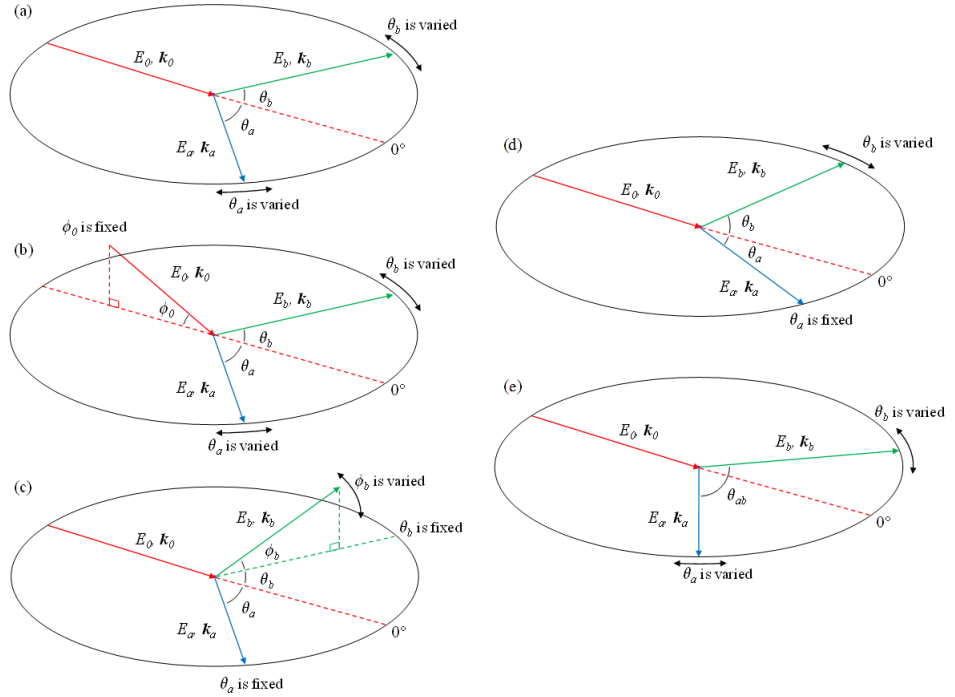


Figure 2.2: Illustration of the various kinematic geometries most commonly employed in $(e, 2e)$ measurements [15]: (a) coplanar symmetric, (b) non-coplanar symmetric, (c) non-coplanar asymmetric, (d) coplanar asymmetric, and (e) mutual constant angle. Furthermore it should be noted that: 1. for symmetric geometries $\theta_a = \theta_b$; 2. for the constant angle case it is θ_{ab} that remains constant; and 3. for the non-coplanar case either ϕ_0 or ϕ_b may be out of plane.

A coplanar kinematic geometry is one in which the incident, scattered and ejected electrons are all detected in the same plane, commonly referred to as the scattering plane. A non-coplanar kinematic geometry on the other hand, is one in which one of the types of electrons is detected *outside* of the scattering plane, or originates from outside the scattering plane, at an angle of ϕ . These two kinematic geometries provide ‘different’ TDCS measurements due to the

influence of the recoil momentum, \vec{q} , acting in a plane perpendicular to the incident electron momentum, \vec{k}_0 .

A symmetric kinematic geometry represents the least probable ionisation process, as the outgoing electrons have equal energies and angle (i.e. $E_a = E_b$ and $\theta_a = \theta_b$) [9]. Asymmetric geometry, however, is a kinematic geometry in which the scattered electron is detected at a fixed forward angle (relative to the incident electron beam) while the ejected electron is detected over multiple different angles within the scattering plane. In a mutual constant angle geometry, the angle between the ejected and scattered electrons being measured remains constant.

2.4.1 Symmetric Kinematics

As mentioned above, the symmetric kinematic geometry is the least probable ionisation process, due to an equal energy sharing between the two outgoing electrons (i.e. $E_a = E_b$). While this in practice makes measuring that cross section difficult, the effort is worthwhile as it provides unique information about the target's valence electronic structure. Note, however, that in certain circumstances dynamical information (e.g. distortion effects) can also be extracted from this geometry [71]. Symmetric kinematic geometry has also been used recently in low energy incident electron experiments, in order to study the dynamics of the (e,2e) collision [33, 34]. As almost half of the incident electron's momentum is transferred to the bound electron, the momentum transfer vector ($\vec{\kappa}$) is large. The momentum transfer, in this case, is defined as:

$$\vec{\kappa}^2 = \vec{k}_0^2 + \vec{k}_a^2 - 2|\vec{k}_0||\vec{k}_a| \cos(\theta_a). \quad (2.9)$$

Three main factors determine the observed behaviour of a TDCS measured under symmetric kinematic geometry [72]:

- i) the Coulomb density-of-state factors,
- ii) binary collisions, and
- iii) quantum interference between different contributions to the total transition amplitude.

Electron Momentum Spectroscopy (EMS) experiments are generally measured in non-coplanar symmetric kinematic geometries [2] (see Figure 2.2.c).

2.4.2 Asymmetric Kinematics

TDCSs measured under asymmetric kinematic geometry can be broken down into three incident electron energy regions, the lower, the intermediate and the higher energy regimes. Depending on the energy region utilised, either structural or dynamical information may be obtained [67]. The low incident electron energy region lies within the range $1.5\epsilon_i \leq E_0 \leq 5\epsilon_i$. In this region the exchange process plays an important role, because the individual particles involved have time to interact [67]. When the incident electron energy lies within the range $5\epsilon_i \leq E_0 \leq 20\epsilon_i$, it is referred to as the intermediate energy region. Although the exchange processes are now negligible, the higher order terms in the interaction potential still have relevance [73]. The high energy region is defined by $E_0 \geq 20\epsilon_i$, where the relatively high energy results in particles with little time to interact with one another during the collision process [67].

A TDCS measured under the asymmetric kinematic geometry typically comprises two distinct peaks [36], located around the momentum transfer direction, $\vec{\kappa}$ and $-\vec{\kappa}$. The first peak (the binary peak) is located near $\vec{\kappa}$. It is produced by binary collisions involving only the incident and bound electrons. Such binary collisions can also occur under what is known as the Bethe ridge condition, under which all momentum is transferred to the ejected electron (i.e. $|\vec{\kappa}| = |\vec{k}_b|$) [69]. The second peak (the recoil peak) is located near $-\vec{\kappa}$. It is caused by an initial binary collision followed by a secondary collision with the target nucleus [69]. Figure 2.3 shows a typical example of an asymmetric kinematic TDCS, with the binary and recoil peaks being highlighted [15].

The shape of the TDCS is determined by the target valence electronic structure and/or the dynamical conditions of the collision process [67]. A TDCS measurement of an atomic s or p electron shell, that uses high energy incident electrons (in a low magnitude momentum transfer regime), will produce binary and recoil peaks that are symmetric around $\vec{\kappa}$ and $-\vec{\kappa}$, respectively [67]. However if the incident electron has an intermediate energy, and interacts with an s orbital electron, the recoil peak will be smaller than the binary peak [67]. That said, under these same kinematics a p -shell orbital electron will produce a double peak in the binary region, the resolution of which is dependent upon how close those kinematics conform to the Bethe ridge condition. Intermediate energy incident electrons also appear to cause a shift in both the binary and recoil peaks, thus removing the symmetry around $\vec{\kappa}$ and $-\vec{\kappa}$ [67]. Low incident electron energies generally lead to TDCSs that are symmetrical around the momentum transfer directions, yet retain the single and double binary peak formations of the s -shell

2.5. FORMAL SCATTERING THEORY

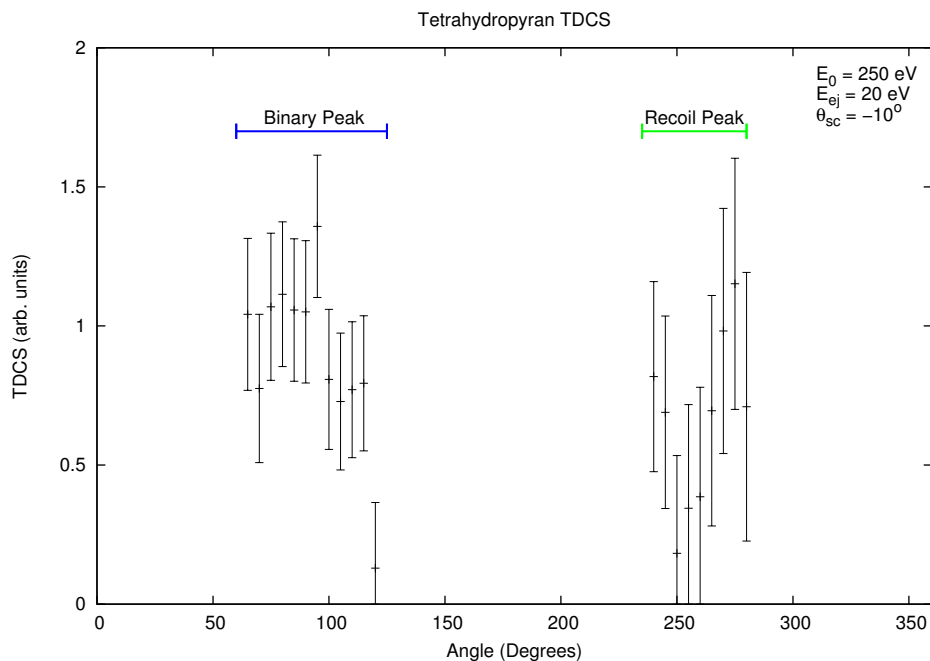


Figure 2.3: A tetrahydropyran triple differential cross section, measuring a p -type orbital under coplanar asymmetric kinematics with an intermediate incident electron energy. All the major features have been labelled.

and p -shell orbital electrons, respectively [67].

2.4.3 Mutual Constant Angle Kinematics

As with the symmetric case, in a mutual angle kinematic geometry the outgoing electrons each have the same energy (i.e $E_a = E_b$). It consequently possesses some of the physical properties of the symmetric regime. However, unlike the symmetric regime, the angle between the two outgoing electrons, θ_{ab} , remains constant. When that angle is chosen such that $\vec{k}_0 \cdot \vec{k}_b = 0$, the contributions of the singlet and triplet two electron states to the TDCS are enhanced and the Coulomb density-of-state factors are no longer dependent upon the angle of the outgoing electrons, θ_{ab} . Thus the dynamical collision effects are highlighted by this particular kinematic geometry [72].

2.5 Formal Scattering Theory

Much of science relies on theoretical modelling that attempts to predict experimental outcomes from a set of input parameters. Scattering theory provides a model for collisions occurring between incident projectiles and target species within an interaction region. At present a complete theoretical description for all the possible kinematic parameters is unavailable [9]. However, more simpli-

CHAPTER 2. DEFINITIONS AND THEORY

fied models that provide an understanding of the ionisation process do exist.

The rules that govern the dynamics of collision systems are quantum mechanical in nature. The Hamiltonian, \mathcal{H} , is the observable parameter of the system. It corresponds to the total energy, and is described by:

$$\mathcal{H} = \mathcal{K} + \mathcal{V}, \quad (2.10)$$

where \mathcal{K} is the kinetic energy and \mathcal{V} is the interaction potential.

Every free moving particle has an associated wavefunction, ψ , that in turn has associated eigenstates, $|\Psi\rangle$. These are the quantum states of the system. The Schrödinger equation is the eigenvalue equation for the Hamiltonian. It is given by:

$$(E - \mathcal{H})|\Psi\rangle = 0, \quad (2.11)$$

where E is the energy state of Ψ . The asymptotic wavefunction, Φ , which is an eigenstate of the kinetic energy, \mathcal{K} , can be obtained from:

$$(E - \mathcal{K})|\Phi\rangle = 0. \quad (2.12)$$

The cross section for a collision system can in principle be calculated by using the time-independent Schrödinger equation, which assumes that the system has reached a stationary state. Furthermore, in a standard scattering experiment, the incident electron beam can be considered to be continuous, as the electron gun (see Section 3.1.3) usually runs for an extended period of time and produces a stable electron current over that time. Thus the time-independent Schrödinger equation is given by:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi(r) = E\psi(r), \quad (2.13)$$

where $V(r)$ is the scattering potential, and E is the energy of the electron, classically defined as:

$$E = \frac{1}{2}mv^2, \quad (2.14)$$

where v is the velocity.

2.5. FORMAL SCATTERING THEORY

The stationary scattering wave function is a solution to Equation 2.13. It satisfies the asymptotic boundary conditions: $V(r)$ tends towards zero faster than $\frac{1}{r}$, as $r \rightarrow \infty$. The stationary scattering wave function can be described by:

$$\psi(r)_{r \rightarrow \infty} = A \left(e^{i\vec{k}_i \cdot \vec{r}} + f(k, \theta, \phi) \frac{e^{ikr}}{r} \right), \quad (2.15)$$

where A is a normalisation constant (independent of r and the angles θ and ϕ), and the function f is the scattering amplitude.

In theory the differential cross section is proportional to the scattering amplitude (f) (i.e. $\frac{d\sigma}{d\Omega} \propto |f(k, \Omega)|^2$), which in turn is dependant upon the energy of the particle, E , and the scattering angles θ and ϕ .

The asymptotic behaviour of the scattering wave function (Equation 2.15) is related to the magnitude of the scattering in a particular direction by the scattering amplitude, f . Using Dirac notation, the scattering amplitude may be defined as:

$$f = -2\pi^2 \langle \Phi_{k_f} | \mathcal{V} | \Psi_{k_i} \rangle, \quad (2.16)$$

where Ψ_{k_i} is the incident wavefunction, Φ_{k_f} is the final wavefunction and \mathcal{V} is the scattering potential describing the interaction between the incident electron and the target.

Equation 2.16 can be written in terms of a collision matrix, which relates the past and future states of the wavefunction (Ψ_{k_i} and Φ_{k_f} , respectively) [65]. There are several forms of the collision matrix, including the S-matrix, R-matrix, K-matrix and T-matrix; the latter of which will be employed in our further discussion in this section of the thesis.

Otherwise known as the transition matrix, the T-matrix element (T_{if}) is representative of the transition between the past and future states of the wavefunction, and is defined as:

$$T | \Phi_{k_f} \rangle = \mathcal{V} | \Psi_{k_i} \rangle. \quad (2.17)$$

Using Equation 2.17, Equation 2.16 can be expressed in terms of the T-matrix thus:

$$f = -2\pi^2 \langle \Phi_{k_f} | T | \Psi_{k_i} \rangle. \quad (2.18)$$

The TDCS (measured in atomic units) can be calculated by applying this same approach to the specific case of electron impact ionisation:

$$\frac{d^5\sigma}{d\Omega_a d\Omega_b dE_a} = (2\pi)^4 \frac{\vec{k}_a \vec{k}_b}{k_0} \Lambda |T_{if}|^2, \quad (2.19)$$

where Λ is the average over all spin orientations and magnetic sublevels for the final state of the target.

As a complete and practical theoretical description of the ionisation process does not yet exist, one of a number of available approximations must be used to evaluate the T-matrix. Two that are worthy of further discussion, in the context of this thesis, are the Distorted Wave Born Approximation and the Molecular 3-body Distorted Wave approximation. Fundamental to an understanding of these approximations is the Lippmann-Schwinger equation, which we now briefly describe.

2.5.1 The Lippmann-Schwinger Equation

The wavefunction Ψ may be solved using the Lippmann-Schwinger equation, which takes the boundary conditions of the scattering problem into account [74]. The time-independent Schrödinger equation can be rewritten as:

$$[\nabla^2 + k^2]\Psi(r) = V(r)\Psi(r), \quad (2.20)$$

where the general solution to this equation is:

$$\Psi(r) = \Phi(r) + \int G_O(r, r') V(r') \Psi(r') dr'. \quad (2.21)$$

Here $\Phi(r)$ is a solution to the homogeneous equation:

$$[\nabla^2 + k^2]\Phi(r) = 0, \quad (2.22)$$

and $G_O(r, r')$ is the Green's function for the incoming and outgoing waves (symbolised by + and - respectively). The Green's function can be rewritten in Dirac notation:

$$G_O^{(\pm)}(r, r') \equiv \langle r | \mathcal{G}_O^{(\pm)} | r' \rangle, \quad (2.23)$$

2.5. FORMAL SCATTERING THEORY

where the Green's function operator ($\mathcal{G}_O^{(\pm)}$), otherwise known as the resolvent operator, is defined as:

$$\mathcal{G}_O(E^{(\pm)}) := \frac{1}{E^{(\pm)} - \mathcal{K}}. \quad (2.24)$$

By making use of the resolvent operator, $\mathcal{G}_O^{(\pm)}$, the wavefunction can be rewritten as:

$$\Psi(r) = \Phi(r) + \mathcal{G}_O^{(\pm)} \mathcal{V} \Psi^{(\pm)}, \quad (2.25)$$

This is the Lippmann-Schwinger equation, a formalism which can be used instead of the Schrödinger equation [74]. This substitution will be employed in the later discussion of the various theoretical TDCS approximations, that are relevant to the experiments described later.

2.5.2 Born Approximations

Calculation of a general solution to the Schrödinger equation (Equation 2.21), begins with a zero-order approximation. The number of orders in the approximation is then increased to produce a series of functions:

$$\begin{aligned} \Psi_0(r) &= \Phi(r) \\ \Psi_1(r) &= \Phi(r) + \int G_O(r, r') V(r') \Psi_0(r') dr' \\ &\vdots \\ \Psi_n(r) &= \Phi(r) + \int G_O(r, r') V(r') \Psi_{n-1}(r') dr'. \end{aligned} \quad (2.26)$$

Assuming that this sequence of functions converges to an exact solution, the Born series can be derived. The Born series is defined as a perturbation type expansion of the wavefunction (or scattering amplitude) in powers of the interaction potential [74]. The Born series is thus represented by:

$$\Psi(r) = \Phi(r) + \int G_O(r, r') V(r') \Psi_0(r') dr' + \int G_O(r, r') V(r') \Psi_1(r') dr' + \dots \quad (2.27)$$

Hence, by substituting the Lippmann-Schwinger equation into the Born series, we produce an expression for the scattering amplitude:

$$f = -2\pi^2 \langle \Phi_{k_f} | \mathcal{V} + \mathcal{V} \mathcal{G}_O^{(\pm)} \mathcal{V} + \mathcal{V} \mathcal{G}_O^{(\pm)} \mathcal{V} \mathcal{G}_O^{(\pm)} \mathcal{V} + \dots | \Phi_{k_i} \rangle. \quad (2.28)$$

CHAPTER 2. DEFINITIONS AND THEORY

First Born Approximation

An approximate quantum mechanical prediction for the differential cross section, for a particle scattered in three dimensions by a potential $V(r)$, can be calculated using the First Born Approximation (FBA). The FBA scattering amplitude (and thus ultimately the cross section) is the first term of the Born series (Equation 2.28). *Id est*:

$$f_{FBA} = -2\pi^2 \langle \Phi_{k_f} | \mathcal{V} | \Phi_{k_i} \rangle. \quad (2.29)$$

The elastic scattering process is very illustrative in regard to the FBA, as here the incident and scattered electrons can be described using plane waves:

$$\Phi_{k_i}(r) = e^{i\vec{k}_i \cdot \vec{r}} \quad (2.30)$$

$$\text{and } \Phi_{k_f}(r) = e^{i\vec{k}_f \cdot \vec{r}}, \quad (2.31)$$

where Φ_{k_i} is the incident wave and Φ_{k_f} is the scattered wave. Thus the scattering amplitude (Equation 2.29) may be written as:

$$\begin{aligned} f_{FBA} &= 2\pi^2 \int e^{i(\vec{k}_i - \vec{k}_f) \cdot \vec{r}} V(r) dr \\ &= 2\pi^2 \int e^{i\vec{k} \cdot \vec{r}} V(r) dr, \end{aligned} \quad (2.32)$$

where \vec{k} is the usual momentum transfer vector (see Equation 2.8). Equation 2.32 indicates that the f_{FBA} is proportional to the Fourier transform of the potential. Furthermore the scattering amplitude is proportional to differential cross section (i.e. $|f_{FBA}|^2 \propto \frac{d\sigma}{d\Omega}$, refer to Section 2.5), so that this equation provides a mechanism for calculating the elastic scattering cross section (note this can be generalised for inelastic processes). However, the FBA is only able to reproduce experimental cross section results at high incident electron energies, as it does not include all of the possible interactions that can occur during the collision event.

Plane Wave Born Approximation

Since the (e,2e) system now contains three bodies rather than two, the FBA must be modified to make it applicable to the (e,2e) reaction. That modification, known as the Plane Wave Born Approximation (PWBA), involves redefining the Hamiltonian to suit a three body system. As previously defined, the

2.5. FORMAL SCATTERING THEORY

Hamiltonian for a two body system is given by Equation 2.10:

$$\mathcal{H} = \mathcal{K} + \mathcal{V}.$$

However, in the case of the (e,2e) process, the kinetic energy of the system, \mathcal{K} , is made up of three bodies, and is now given by:

$$\mathcal{K} = (K_1 + U_1) + (K_2 + v_2), \quad (2.33)$$

where K_1 and K_2 are the kinetic energies of the incident/scattered and bound/ejected electrons respectively, U_1 is the distorting potential of the target particle and v_2 represents the interaction between the incident/scattered electron and the target particle.

Likewise, the potential energy of the system, \mathcal{V} , must be modified to accommodate for three bodies. Thus:

$$\mathcal{V} = v_1 + v_3 - U_1, \quad (2.34)$$

where v_1 and v_3 are the interactions between the bound/ejected and incident/scattered electrons and the target particle respectively. By substituting Equations 2.33 and 2.34 into Equation 2.10, we arrive at the Hamiltonian for a three body problem:

$$\begin{aligned} \mathcal{H} &= \mathcal{K} + \mathcal{V} \\ &= (K_1 + U_1) + (K_2 + v_2) + v_1 + v_3 - U_1 \\ \therefore \mathcal{H} &= K_1 + K_2 + v_1 + v_2 + v_3. \end{aligned} \quad (2.35)$$

In the PWBA the incident wavefunction, Φ_i , describes the incident electron and target particle, while the final wavefunction, Φ_f , describes the scattered and ejected electrons as well as the ionised target particle. They are defined as:

$$|\Phi_i\rangle = |\psi_i \vec{k}_0\rangle, \quad (2.36)$$

and

$$|\Phi_f\rangle = |\psi_f \vec{k}_a \vec{k}_b\rangle. \quad (2.37)$$

CHAPTER 2. DEFINITIONS AND THEORY

In Equations 2.36 and 2.37, ψ_i and ψ_f represent the target particle in its electronic ground state and final target state, respectively. \vec{k}_0 , \vec{k}_a and \vec{k}_b represent the incident, scattered and ejected electron plane waves, respectively. Substitution of Equations 2.36 and 2.37 into the FBA scattering amplitude (Equation 2.29), produces the scattering amplitude for the PWBA:

$$f_{PWBA} = -2\pi^2 \langle \psi_f \vec{k}_a \vec{k}_b | \mathcal{V} | \psi_i \vec{k}_0 \rangle. \quad (2.38)$$

If it is assumed that the ion (the final target state) is in its ground electronic state, ψ_f can be omitted. The theoretical TDCS for the PWBA then becomes:

$$\frac{d^5\sigma}{d\Omega_a d\Omega_b dE_a} = (2\pi)^4 \frac{\vec{k}_a \vec{k}_b}{k_0} \Lambda |\langle \vec{k}_a \vec{k}_b | \mathcal{V} | \psi_i \vec{k}_0 \rangle|^2, \quad (2.39)$$

where, as noted earlier, Λ is the average over all spin orientations and magnetic sublevels for the final state of the target.

As the PWBA only includes the first term of the Born series (see Equation 2.28), it is only capable of yielding the binary peak of the TDCS. The higher order terms of the Born series account for possible multiple scattering processes, such as the interaction that must occur for a recoil peak to form.

Distorted Wave Born Approximation

Introducing higher order terms from the Born series into an approximation, greatly increases the complexity of the functions and therefore the degree of difficulty in calculating them. A far simpler approach is to describe the initial and final wavefunctions with distorted waves; a technique known as the Distorted Wave Born Approximation (DWBA). A local central potential U , called the distorting potential, is selected and the scattering amplitude (Equation 2.16) is reformulated in terms of the distorting wave eigenstate of U , rather than in terms of plane waves. Starting with the Hamiltonian (Equation 2.10) and partitioning it as follows:

$$\mathcal{H} = (\mathcal{K} + U) + (\mathcal{V} - U), \quad (2.40)$$

and now substituting Equation 2.40 into the Schrödinger equation (Equation 2.13), gives an inhomogeneous equation:

$$(E^{(\pm)} - \mathcal{K} - U) |\Psi^{(\pm)}\rangle = (\mathcal{V} - U) |\Psi^{(\pm)}\rangle. \quad (2.41)$$

2.5. FORMAL SCATTERING THEORY

Here $\mathcal{K} = \mathcal{K}_0 + \mathcal{H}_t$, where \mathcal{K}_0 is the kinetic energy operator of the incident electron and \mathcal{H}_t is the Hamiltonian of the target particle. Thus the homogeneous equation, using distorted waves, is:

$$(E^{(\pm)} - \mathcal{K}_0 - U - \mathcal{H}_t)|j\chi_j^{(\pm)}\rangle = 0, \quad (2.42)$$

where $|j\chi_j^{(\pm)}\rangle$ is the distorted wave channel state. Furthermore $|\chi_j^{(\pm)}\rangle$ represents the distorted waves for the incident or outgoing waves, which replace the plane waves \vec{k}_j in Equations 2.36 and 2.37 [66]. Finally, j is an index that represents particular channels, namely $j = 0, a, b$ corresponds to the incident, scattered and ejected electron channels, respectively. As such, Equation 2.42 can then be further separated into projectile and target operators:

$$(E^{(\pm)} - \mathcal{K}_0 - U)|\chi_j^{(\pm)}\rangle = 0, \quad (2.43)$$

$$\text{and } (\epsilon_i - \mathcal{H}_t)|j\rangle = 0. \quad (2.44)$$

For the electron impact ionisation of a target particle, the one-electron distorted waves are defined as:

$$(E_0 - \mathcal{K}_1 - U_1)|\chi^{(+)}(\vec{k}_0)\rangle = 0, \quad (2.45)$$

$$(E_a - \mathcal{K}_1 - U_1)|\chi^{(-)}(\vec{k}_a)\rangle = 0, \quad (2.46)$$

$$(E_b - \mathcal{K}_2 - v_2)|\chi^{(-)}(\vec{k}_b)\rangle = 0, \quad (2.47)$$

$$\text{and } (\epsilon_i - \mathcal{K}_2 - v_2)|\alpha\rangle = 0, \quad (2.48)$$

where α is the state or orbital of the bound electron, i.e. the target state.

By substituting the plane waves for distorted waves in Equations 2.36 and 2.37, the T-matrix element becomes:

$$\langle \vec{k}_a \vec{k}_b | T_{if} | \psi_i \vec{k}_0 \rangle = \langle \chi^{(+)}(\vec{k}_a) \chi^{(-)}(\vec{k}_b) | U_1 | \alpha \chi^{(+)}(\vec{k}_0) \rangle. \quad (2.49)$$

The ground state average of the projectile-target potential forms the optimum choice for the distorting potential U_1 . *Id est*:

$$U_1 = \langle \alpha | v_1 + v_3 | \alpha \rangle. \quad (2.50)$$

It is important to note that $v_1 - U_1$ and the states $|\alpha\rangle$ and $|\chi^{(-)}(\vec{k}_b)\rangle$ of the bound/ejected electron are orthogonal, i.e. the central potential does not contribute to the aforementioned states [66]. Hence, the DWBA uses a first order

two-body Coulomb potential,

$$v_3 = \frac{1}{\vec{r}_a - \vec{r}_b}, \quad (2.51)$$

where \vec{r}_a and \vec{r}_b are the position vectors of the scattered and ejected electrons, respectively. Finally the TDCS, under the DWBA, is:

$$\frac{d^5\sigma}{d\Omega_a d\Omega_b dE_a} = (2\pi)^4 \frac{\vec{k}_a \vec{k}_b}{\vec{k}_0} \Lambda |\langle \chi^{(+)}(\vec{k}_a) \chi^{(-)}(\vec{k}_b) | v_3 | \alpha \chi^{(+)}(\vec{k}_0) \rangle|^2. \quad (2.52)$$

2.5.3 Molecular 3-body Distorted Wave Approximation

While the Molecular 3-body Distorted Wave (M3DW) approximation shares many properties with the DWBA, it differs in one particularly significant way. Specifically, the M3DW approximation contains a term describing the Post-Collision Interaction (PCI) between the scattered and ejected electrons to all orders of perturbation theory [75]. By contrast, the DWBA merely calculates the PCI to first order [21]. Consequently, TDCSs computed using M3DW calculations show a greater promise in describing the ionisation process than other existing approximations.

As with the DWBA, the scattering amplitude in the M3DW needs to be reformulated in terms of the distorting wave eigenstate of U rather than plane waves. The reformulated homogeneous Schrödinger equation is thus given by:

$$\left(\mathcal{K} + U_i - \frac{k_i^2}{2} \right) \chi_0^{(+)}(\vec{k}_0) = 0. \quad (2.53)$$

Substituting the plane waves in Equations 2.36 and 2.37 with distorted waves, gives the scattering amplitude for M3DW as:

$$f_{M3DW} = \langle \chi_a^{(-)}(\vec{k}_a) \chi_b^{(-)}(\vec{k}_b) | C_{scat-eject} | V - U_i | \chi_0^{(+)}(\vec{k}_0) \rangle, \quad (2.54)$$

where $C_{scat-eject}$ is the Ward-Macek average Coulomb distortion factor between the two final electron states [76]. $C_{scat-eject}$ is explicitly given by:

$$C_{scat-eject} = e^{-\frac{\pi\gamma}{2}} \Gamma(1 - i\gamma) {}_1F_1(i\gamma, 1, -i(k_{ab}r_{ab} + \vec{k}_{ab} \cdot \vec{r}_{ab})), \quad (2.55)$$

where γ is the Sommerfeld parameter (a measure of the strength of the Coulomb interaction between two electrons), $\Gamma(1 - i\gamma)$ is the gamma function, ${}_1F_1$ is a confluent hypergeometric function, and \vec{k}_{ab} is the product of the reduced mass for two electrons (μ) and the relative velocity between the two electrons (v_{ab}).

2.5. FORMAL SCATTERING THEORY

Thus the TDCS under the M3DW formulation is written as:

$$\frac{d^5\sigma}{d\Omega_a d\Omega_b dE_b} = \frac{1}{(2\pi)^5} \frac{\vec{k}_a \vec{k}_b}{k_0} \Lambda |\langle \chi_a^{(-)}(\vec{k}_a) \chi_b^{(-)}(\vec{k}_b) C_{scat-eject} | V - U_i | \chi_0^{(+)}(\vec{k}_0) \rangle|^2 \quad (2.56)$$

The proper way to average over molecular alignment is to calculate cross sections for different molecular alignments and average the cross sections [77]. However, due to the limited processing power available, such a method has not been possible to achieve until quite recently [78]. As such, Gao *et al.* suggested the Orientation Averaged Molecular Orbital (OMAO) method, in which the molecular wavefunction is averaged, rather than the cross sections [79]. Analytically, this can be shown to work for highly symmetric sigma gerade states (i.e. “s-type” orbitals), if the angular momentum transferred to the nucleus is less than one [77]. However, in the case of asymmetric sigma gerade states (i.e. “p-type orbitals”), the average can be zero, and so it is necessary to instead average the absolute value of the molecular wavefunction, so that the asymmetric contributions don’t cancel each other out [77]. This does mean that the resulting wavefunction requires renormalisation after, as the norm is not conserved through the calculation [77].

It should be noted at this time, that none of the theoretical results presented later in Chapters 4 - 6 were undertaken as part of this Masters thesis. Rather, these results were generated by Professor Don H. Madison and his group at the Missouri Science and Technology University in the U.S.A. Nonetheless, so this document could be self-contained, a brief introduction to the relevant theoretical formulations has been given here in the latter part of this chapter.