Electron Correlation and Spin-Dependent Effects in the Electron Impact Excitation of Zinc Atoms

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January 16, 2009

This thesis is presented for the degree of Doctor of Philosophy of
The University of Western Australia
Abstract

This work investigated electron correlation and spin-dependent effects in electron scattering from zinc for incident electron energies from the lowest excitation threshold at 4.003 eV to 50 eV. Experiments were performed using a crossed-beams electron impact spectrometer, which included an unpolarised electron gun, and also a spin-polarised electron gun. The apparatus was tested, and shown to be operating well, by repeating past studies of electron scattering from helium and argon.

Emission cross sections for the $4s4p^3P_1$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d, 5d, 6d^3D_{1,2,3}$ and $4s4d, 5d^1D_2$ states were measured from the respective thresholds to 50 eV. These were compared with Convergent Close-Coupling (CCC) and B-spline R-matrix (BSRM) calculations of the $4s4p^3P_1$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d^1D_2$ and $4s4d^3D_{1,2,3}$ emission cross sections. There are serious discrepancies between the theories, and between the theories and experiment, which indicates strong continuum coupling and innershell excitation effects in the electron excitation of zinc.

The differential elastic scattering signal at scattering angles of 30°, 54°, 90° and 110° was measured for incident electron energies from just below the lowest excitation threshold at 4.003 eV, to the ionisation threshold at 9.394 eV. Some assignments given by Sullivan et al. [1] and Zatsarinny and Bartschat [2] were confirmed by the present experiment. An area of disagreement in the literature concerning the nature of a feature observed at the $4s4p^1P_1$ threshold at 5.796 eV was resolved in favour of Zatsarinny and Bartschat, who assign the feature as a cusp.

The differential elastic scattering signal and the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ electron excitation functions at scattering angles of 15°, 30°, 54°, 90° and 110° were measured for incident electron energies from the ionisation threshold to 14 eV. All were strongly affected near 11 eV by negative-ion resonances based on innershell-excited, $3d^94s^24p$ parent states. The electron transmission study of Burrow and Michejda [3] indicates that there are at least eight negative-ion resonances in the near-11 eV region, and the dominant negative-ion resonances in the differential elastic scattering signal are $3d^64s^24p^2D_{3/2,5/2}$. The differential elastic scattering signal and the electron excitation functions show that negative-ion resonances with another, odd-parity configuration may be present. Spin asymmetry functions between 10 eV and 12.5 eV were measured for $4s4p^3P_{0,1,2}$ state excitation at scattering angles of 30°, 54° and 90°, and for $4s4p^1P_1$ state excitation at 54°. These measurement showed the spin-dependence introduced by resonance scattering, and the possible influence of Mott scattering and the spin-coupling effect.

Photon excitation functions for the $4s4p^3P_1$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d, 5d, 6d^3D_{1,2,3}$ and $4s4d, 5d^1D_2$ states were measured for incident electron energies from their respective thresholds to 16 eV. Below the ionisation threshold, the $4s4p^3P_1$ photon excitation function supports the assignment of the near-$4s4p^1P_1$ threshold feature as a cusp. Some of the overlapping negative-ion resonances which were observed near 7.5 eV in the $4s4p^3P_1$, $4s4p^1P_1$ and $4s5s^3S_1$ photon excitation functions were assigned with the assistance of the BSRM calculations of Zatsarinny and Bartschat. However, continuum coupling effects...
above 8 eV seem to cause the theoretical negative-ion resonance predictions to break down. Above the ionisation threshold, the near-11 eV negative-ion resonance effects depend on the configuration $n, L$ and $S$ of the neutral state excitation observed. This may be due to the properties of the mixed negative ion component states. Postcollision interaction (PCI) effects the $4s5s^3S_1, 4s4d, 5d, 6d^3D_{1,2,3}$ and $4s4d, 5d^1D_2$ photon excitation functions. The PCI mechanism can populate the $4s4d, 5d, 6d^3D_{1,2,3}$ and $4s4d, 5d^1D_2$ states because the scattered and ejected electrons have a similar energy, and can thus exchange a large amount of orbital angular momentum.

The present work demonstrates that electron correlation effects, especially those associated with innershell excitation, are very significant in electron scattering from zinc. Existing theoretical models of electron scattering from zinc inadequately treat electron correlations, and as a result of this are inaccurate, as shown here. The studies presented here should guide the development of models that accurately describe the innershell excitation effects, which are important for zinc and a great many other atoms.
Acknowledgements

I would like to thank my supervisors, Prof. Jim Williams and Dr Danica Cvejanović, for all the assistance and guidance they have given me during my time at the Centre for Atomic, Molecular and Surface Physics.

To my co-workers Dr Tony Sergeant, Dr Sergey Samarin, Paul Guagliardo and Peter Wilkie, thanks for your help and companionship. Special thanks to my fellow zine victim Dr Luka Pravica for showing me how it should be done.

I’d like to acknowledge Prof. Igor Bray, A/Prof. Dimitri Fursa, Prof. Klaus Bartschat, Dr Oleg Zatsarinny, Prof. Bob McEachran and Prof. Paul Burrow, who generously provided their data in electronic form.

To Mum and Piers, Dad and Mary Anne, Paddy, Gran and Grandad, Nana and Pop, Klaas and Ainslie; thanks for everything you’ve done for me as I’ve gone about this nutty business.

And most of all, to Bron, whose love and support got me through it all.
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Chapter 1

Introduction

This work investigates the role of electron correlations and spin-dependent interactions in the atomic structure of zinc, and in collisions between zinc atoms and electrons. The intensity and momentum of scattered electrons and atomic decay photons, as well as photon polarisation, were measured after the collision of free zinc atoms with an incident probe electron beam. Focus was placed on studying electron correlation phenomena such as negative-ion resonances and postcollision interaction, which have a sharp energy dependence. All measurements were made as a function of incident electron energy and, for some studies, spin polarisation.

The co-ordinate system used throughout this work is shown in Figure 1.1. The incident electron momentum vector $\mathbf{k}_{\text{in}}$ defines the positive $z$-axis, with the $x$-axis lying in the so-called “scattering plane” defined by $\mathbf{k}_{\text{in}}$ and the scattered electron momentum vector $\mathbf{k}_s$. The $y$-axis normal to the scattering plane was the quantisation axis for the transversely spin-polarised electron beam, using the right-hand co-ordinate convention. Scattered electrons were detected at an angle $\theta$ to the incident electron momentum vector $\mathbf{k}_{\text{in}}$, with $+\theta$ lying to the left of $\mathbf{k}_{\text{in}}$ as shown in Figure 1.1. The photon detection and polarisation analysis system accepted radiation emitted in the direction of the positive $y$-axis.

Both atomic structure and the present atom-electron collisions, which occur at energies sufficient to alter the quantum state of electrons only, are governed by electromagnetic interactions involving the electrons and the nucleus, and should be described exactly by the Dirac equation. There will be a vanishingly small influence from the weak interaction, and thus parity will be conserved. The magnetic interactions between the electrons and the nucleus are small, with, for example, a hyperfine splitting on the order of $10 \, \mu\text{eV}$ for the $4s4p^3P_2$ state of the Zn$^{67}$ isotope, with nuclear spin $I = 5/2$ [4]. In addition, zinc isotopes which comprise 95.3 % of total abundance have no nuclear spin. Hyperfine interactions are neglected in this work, and the total electronic angular momentum $J$ is considered to be conserved. With these considerations in mind, the Hamiltonian containing the interactions relevant for both atomic structure and atom-electron collisions is given by

$$H = H_o + H_{\text{rel}}$$  \hspace{1cm} (1.1)
with $H_o$ the non-relativistic Hamiltonian, which contains kinetic energy terms and terms describing the electrostatic interactions between the electrons and between the electron and the nucleus. It is given by

$$H_o = \sum_i^{N+1} \left( -\frac{\hbar^2}{2m} \nabla_i^2 r_i - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \sum_{i<j} e^2 \frac{1}{4\pi\varepsilon_0 r_{ij}}$$

with $r_i$ the radial coordinate of the $i$th electron in the system, and

$$r_{ij} = |r_i - r_j|$$

the separation between the $i$th and $j$th electrons in the system. The summation here is taken over the $N$ atomic plus 1 incident electrons of a collision system. There is no dependence on orbital $L$ or spin angular momentum $S$, which in the absence of other interactions means that $L$ and $S$ will be conserved, and the atomic states will be well $LS$-coupled.

Of the relativistic parts of the overall Hamiltonian, the most significant is due to the spin-orbit interaction. An electron with spin $s$ and orbital angular momentum $l$ experiences a magnetic momentum due to the rotating charge distribution it views in its rest frame. The spin-orbit Hamiltonian $H_{so}$ is given by

$$H_{so} = \sum_i^{N+1} \frac{1}{2m_e c^2} \frac{1}{r_i} \frac{dV}{dr_i} l_i s_i$$

The spin-orbit interaction introduces $L$ and $S$ dependence, which makes possible a transfer of angular momentum between $L$ and $S$, and leads to a breakdown of $LS$-coupling. A complete relativistic Hamiltonian will also contain terms accounting for the interactions between electron spins and between electron spins and the orbits of other electrons, as well as relativistic corrections to energy and a Darwin term for electrons with $l = 0$. However, the energies characteristic of these interactions and corrections are much smaller than those of the spin-orbit interaction, and so they are not considered further here.

In practice, the Dirac equation is intractable for atomic systems, and so appropriate approximations need to be made. In its simplest treatment, the problem is reduced to solving the Schrödinger equation, with the potential that of the dominant electrostatic interactions. These are simplified by describing them as the electron-nucleus interaction modified by core-electron screening through which the electron-electron interactions, or electron correlations, are included. If the spatial separation between an outer or probe electron and the electron core is large, so $r_{ij} = |r_i - r_j| \approx r_i$, it experiences an approximately central field, and the “central field approximation” can be applied. However, if there is significant penetration of an outer or probe electron into the core, the degree of independence between outer or probe electrons and the core electrons that is implied by a central field approximation ceases to be accurate.

The role of electron correlations is particularly prominent in the atomic structure of zinc, which has an outermost ground state electron configuration of $3d^{10}4s^2$. An energy level diagram for zinc is shown in Figure 1.2. Electron-electron interactions between $3d$
Figure 1.1: The co-ordinate system used throughout this thesis, with the x, y and z axes relating to the incident electron linear momentum $k_{in}$ and spin angular momentum $S$ as shown.
and 4s electrons cause a departure from the general electron configuration energy-ordering expected from a central field approximation, and this evident from an examination of trends across the periodic table. In the same period as zinc, and just prior to the transition metals, is calcium ($Z = 20$), which has a $4s^2$ outermost electron configuration. Moving from Ca across the transition metals sees progressive filling of the $3d$-subshell, to $3d^34s^2$ for V ($Z = 23$). However, the trend is broken for Cr ($Z = 24$), where the expected $3d^44s^2$ ground state is an excited state lying 0.96 eV above the true $3d^54s$ ground state. The pattern resumes for Mn ($Z = 25$), which has a ground state configuration of $3d^54s^2$, and continues up to Ni ($Z = 28$). It breaks down again for Cu ($Z = 29$), where the $3d^94s^2$ ground state configuration expected is an excited state lying 1.389 eV above the $3d^{10}4s$ true ground state. This demonstrates the interdependence of $4s$ and $3d$ electrons, a result of which is a natural bias against ground state configurations with the large angular momentum of a $d$-subshell one electron short of being half-filled or filled. To add another example specific to zinc, the $4s4d^1D_2$ state lies 38 meV below the $4s4d^3D_1$ state in contradiction to the usual case where, due to the greater spatial separation required by the exclusion principle, triplet states have a lower energy than singlets with the same $n$ and $L$ quantum numbers. Departures from the expected energy orderings, such as the above, point to the presence of configuration interaction [5].

If the central field approximation is applied and spin-orbit interaction neglected, an atomic state can be considered to have a single configuration constructed from independent particle configurations of given $n$ and $l$, and definite $L$ and $S$ in addition to definite parity and $J$. However, if the central field approximation is not valid a true atomic state may be more accurately described as an admixture of configurations with the same parity, $J$, $L$ and $S$ with independent particle configurations as a starting point but also with continuum, core-excited and multiply excited configurations. Since this structural effect is caused by electron-electron interactions, it is this admixture which describes the correlations. Also, if there is significant spin-orbit interaction the atomic states will no longer have definite $L$ and $S$. In this case a better description would be an admixture of states with different $L$ and $S$ or, if $LS$-coupling ceases to be valid, states of given $J$ derived from intermediate $jLS$ or full $j$ coupling.

This basic approach has underpinned previous studies of neon by Yu et al. [6] in which incident spin-polarised electrons enabled observation and interpretation of the angular momentum parameters. That study showed, for example, cross-sections and atomic decay photon polarisations different from those expected given the dominant $LS$ component of an excited state. This was due, in part, to the possibility of non-exchange excitation of triplet states from a singlet ground given a significant singlet component in the excited state. Some other important illustrative examples of configuration interaction in atomic systems can be found in the studies of Penttila et al. [7], Mansfield and Newsom [8] and Ueda et al. [9]. Penttila et al. measured the $3p$ photoelectron spectrum and subsequent Auger decay spectrum of Mn, and performed both single and multiconfiguration calculations. The problem was treated as a two step process, and it was observed that while the
single configuration approach adequately described the photoionisation, multiple configurations were used to reproduce the Auger spectrum. So, for the $3p^53d^54s^2$ configuration, with a $3p$-hole but half-full $3d$-subshell and full $4s$-subshell, electron correlations were not as important as for configurations such as $3d^34s^2$ and $3d^44s$ with less-than-half-full $3d$-subshells. For strontium, which has a $4p^65s^2$ outer electron configuration, Mansfield and Newsom found the absorption spectrum was complicated due to configuration mixed $4p$-core excited states. Following this study Ueda et al. measured branching ratios for the autoionising decay of the $4p^55s^24d$ states of Sr. The most significant decay routes were those that required the least rearrangement of electron configuration, namely Sr$^+$ $4p^65s$ (66%) and $4p^64d$ (23%). However, there was a significant contribution (8%), from the seemingly more complicated decay to Sr$^+$ $4p^65p$, and this was attributed to mixing of the Sr $4p^65s^24d$ and $4p^65s5p^2$ configurations.

The present observations indicate that, upon the opening of the $3d$-core electron excitation channel, correlations in zinc become pronounced and have a significant influence on electron scattering. Experimental evidence indicates that $3d^34s^24p$ autoionising states and $3d^{10}4snl$ below-ionisation state excitation probabilities are comparable over a range of energies and scattering angles. This has been observed in the photon impact studies.
of Marr and Austin [12] and Kuntze et al. [13], as well as the electron impact studies of Back et al. [14] and Predojević et al. [15]. In addition these states have also been shown by the structure calculations of Mansfield [11] to have a strong mixing of different $L, S$ and electron configuration. For example, the observed energy ordering of the optically allowed $3d^94s^24p^3P_1, 3D_1$ and $^1P_1$ states observed by Marr and Austin et al. could be obtained only if perturbation mixing with the $3d^{10}4s4p$ configuration was included in the theory. Thus, it is reasonable to expect that the $3d^94s^24p$ states of zinc provide fertile ground for the exploration of electron correlations.

Most theoretical scattering calculations for zinc have not treated $3d$-core electron excitation, either explicitly or through the inclusion of $3d$-hole states in the target description. An exception is the work of Zatsarinny and Bartschat [2], who used a $B$-spline $R$-matrix (BSRM) method with term dependent, non-orthogonal target orbitals, an approach given in detail by Zatsarinny and Froese Fischer [16]. Their multi-configuration target description included $3d^9n_i\pi^l\pi^l'$ pseudostates, where $\pi$ denotes a correlated, rather than physical, orbital. These calculations were presented in tandem with another $R$-matrix calculation, referred to as RM25, which used only valence-electron excited states and a semi-empirical core polarisation potential in the target description. However, it is doubtful that such a model adequately describes the core-valence correlations, especially because the authors found that the $3d^94s^24p\ ^1P_1$ state made the second greatest contribution (2.289 $a_0^3$), after the $4s4p\ ^1P_1$ state (31.952 $a_0^3$), to the polarizability of the ground state. Perhaps this is why the BSRM were in excellent agreement with the transmission experiment of Burrow et al. [17], while there were some discrepancies with the RM25 calculations. Zatsarinny and Bartschat also presented integral cross sections for elastic and inelastic scattering and for negative-ion resonance parameters which will be discussed in detail in Chapters 4, 5 and 6. An area in which the BSRM approach requires development is in its description of the target continuum, which the pseudostates must span in order to describe the target accurately. Limitations on the BSRM model are expected where coupling to the target continuum is important, which is expected to be the case for the excitation of states with a small cross section, for example optically-forbidden states, above 10 eV.

In a recently published zinc theoretical and experimental cross-section study, Fursa et al. [18] presented $4s4p, 5p\ ^1P_1$ state cross-sections between 15 and 60 eV and angles of $10^\circ$ and $150^\circ$. The experiment extended the $0^\circ$ to $12^\circ$ low angle scattering study of Panajotović et al. [19], while the calculations were performed using the Convergent Close Coupling (CCC) approach, which has been reviewed by Fursa and Bray [20]. The CCC approach is expected to describe adequately the target continuum, but it does rely on the “frozen-core approximation” which, for zinc, assumes that the $4s$ and incident electrons will be active outside an inert $3d$-core. Like the RM25 model, core-excited states were not included in the target description, and core-valence correlations were accounted for with a polarisation potential, which was varied to reproduce the expected ionisation energy and $4s^2\ ^1S_0 \rightarrow 4s4p\ ^1P_1$ optical oscillator strength. However, the latter was also accurately reproduced by the RM25 model, and so may not be an appropriate criterion for assessing
core-valence correlation models. The agreement between the new experiment and theory presented in Fursa et al. is good for low angles, but overall the authors noted that the agreement was “not perfect”, and further work is required to account for the observed discrepancy. There was poor agreement between the most recent work and both the previous experiment of Williams and Bozinis [21] and the Relativistic Distorted Wave Approximation (RDWA) calculations of Kaur et al. [22]. The RWDA approach is able to calculate spin-dependent quantities to be discussed below, but assumes a frozen core and limited coupling between states other than the initial and final states of the transition.

Excited states which lie below the ionisation threshold will decay by photon emission, with the strongest, electric dipole mechanism having a transition rate on the order of 10^8 s⁻¹. On the other hand, discreet excited states with energies that lie above the ionisation threshold are degenerate to, and interact strongly with, continuum states, and so will generally decay by autoionisation to an ionic state and an unbound, “ejected”, electron. This process proceeds at a much faster rate than decay by dipole radiation emission, typically 10^{15} s⁻¹. Selection rules which depend on the interaction which mediates the transition also apply to autoionisation, but generally are not as restrictive as the dipole selection rules because the ejected electron can take any orbital angular momentum value.

Autoionisation mediated by the electrostatic interaction conserves L and S, so in the absence of other interactions an autoionising state can only decay to a coupled ion and continuum electron with the same overall orbital and spin angular momentum, as well as parity and J. A transition can also be mediated by the spin-orbit interaction, which allows ΔL = 0, ±1 and ΔS = 0, ±1, but decay rates are on the order of 10^6 times smaller than those of electrostatic decay [5]. Much more appreciable is the role that spin-orbit interaction plays due to its mixing of different L and S states. This allows electrostatic decay to proceed through a variety of mixed-state components. Autoionising decay transition rates through this mechanism can be appreciable, and much even for slight mixing [5].

In the present measurements, the target zinc atom is perturbed with an incident electron which participates in the subsequent correlations. As a result two types of effects are observed here, both dependent on the electron correlations which influence structure and the scattering dynamics, and both observable at energies near excited state thresholds. The first is the formation and decay of negative-ion resonances, which result when the scattered electron is temporarily bound to the atom to form a complex which then decays to a neutral bound state plus an unbound electron. The second is the postcollision interaction (PCI), where scattered and ejected electrons resulting from the excitation and decay of an autoionising state exchange energy via the Coulomb interaction, which modifies their trajectories and final energies. By observing these effects, the present work aims to characterise electron correlations in zinc structure and electron scattering.

Negative-ion resonances are often described using the so-called “parent” and “grandparent” models introduced by Schulz [23]. For a X^+nln'l' negative-ion, the parent state is X^+nl and the grandparent state is X^+. If the coupling between the outer nln'l' electrons is weaker than between the nl and X^+ core, the parent model is appropriate. If
the coupling between the outer $nl/nl'$ electrons is stronger than between the $nl$ and $X^+\text{core}$, the grandparent model is appropriate. Mechanisms for negative-ion formation can be envisaged in terms of phenomena of wider applicability in physics, namely shape and Feshbach resonance, and are outlined by Schulz. For a shape resonance, the continuum electron tunnels through a potential barrier, in the atomic scattering case a centrifugal barrier associated with the parent state, then tunnels out again. Shape resonances lie energetically above their parent states, and so are able to decay into them by autoionisation, as described above. This decay into parent states tends to be quite strong, and so shape resonances are generally quite short-lived and energetically broad (typically above 100 meV). On the other hand, a Feshbach resonance forms when the incident electron deposits energy and momentum into the target, and is then bound until it regains sufficient energy to escape. Feshbach resonances usually occur at energies between 0 and 0.5 eV below that of their parent states, and so cannot decay into them. So, the decay of Feshbach resonances requires a greater rearrangement of electron configuration, with the result that they are longer-lived and energetically more narrow (typically 10 meV). However, since the distinction between these two types of scattering is sometimes unclear, a classification based on identifying shape or Feshbach resonances can be of limited applicability. For example, the so-called “b” resonances with a configuration $np^5[(n+1)s(n+1)p^3P]$ can be described consistently across a range of different atoms using the grandparent model, but appear at energies both below and above their parent states [24].

In the present work we investigate the situation in which, after the negative-ion decays by electron emission, the atom is left in a state lying below the ionisation threshold. Negative-ion resonance provides an alternative elastic and inelastic scattering mechanism, which can be observed due to its interference with direct scattering. The theory for interference between direct and resonance processes was given by Fano [25], specifically for the case of photoionisation through the excitation of an autoionising state. However, this theory is also applicable to the present case and other instances of resonance phenomena, such as the direct and resonance transport through quantum dots observed by Clerk et al. [26], atom-atom scattering of laser-cooled rubidium observed by Courteille et al. [27], and the formation of Efimov states in neutron scattering from $^{19}\text{C}$ observed by Mazumdar et al. [28]. In cross section measurements, the interference produces an asymmetric profile given by

$$\sigma = \sigma_o + \sigma_r \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$$  \hspace{1cm} (1.5)

where $\sigma$ is the total cross-section, $\sigma_o$ is the direct excitation cross-section, $\sigma_r$ is the resonance cross-section, the shape parameter $q$ quantifies the interference between the direct and resonant processes and

$$\varepsilon = \frac{2(E - E_r)}{\Gamma}$$  \hspace{1cm} (1.6)

with $E$ the incident electron energy, $E_r$ the resonance energy and $\Gamma$ the resonance energy width, which is related to the negative-ion lifetime through the uncertainty principle.

The assignment of negative-ion resonance configurations and angular momentum properties usually proceeds after first identifying possible $X^+nl$ parent states in the vicinity
of the resonance energy. Arguments based on a resonance energy can also be used to give
the negative ion a spectroscopic term assignment, especially if assisted by observation of
several terms in the negative-ion resonance series [29]. An assignment can also be made
by observing the angular momentum properties of the incident and scattered electrons, by
measuring partial wave behaviour, incident electron spin dependence or scattered electron
polarisation. Combining these measurements with knowledge of the angular momentum
properties of the target state under observation, and applying the appropriate angular
momentum conservation principles, will lead to a resonance assignment. However, for
inelastic scattering and elastic scattering from $J \neq 0$ targets, such a procedure may be
complicated because multiple partial waves may be involved in the autoionisation process.

The experimental and theoretical work on negative-ion resonances, including those
observed for zinc, has been reviewed by Buckman and Clark [24] and Schulz [23]. The
majority of information for zinc is limited to negative-ion resonances below the ionization
threshold. Optical excitation functions conducted by the Uzhgorod group [30, 31, 32, 33]
for the $4s4p^3P_1$, $4s5s^3S_1$, $4s4d$, $5d$, $6d^1D_2$, $4s4d$, $5d^3D_{1,2,3}$ and $4s6s^1S_0$ states, above and
below the ionization threshold, show negative-ion structures with moderate detail. In
scattered electron studies by the same group [34], negative-ion structure was also shown
to affect the total scattering cross section and the $4s4p^1P_1$ integral cross section. However,
apart from showing the presence of numerous negative-ion resonance structures, partic-
ularly in the vicinity of the $3d^04s^24p$ autoionising state thresholds, collectively the work
presented by the Uzhgorod group provides little information regarding resonance ener-
gies or spectroscopic assignments. Electron transmission experiments presented by Bur-
row et al. [17] and Sullivan et al. [1] detect and assign configurations to some negative-ion
resonances below the ionisation threshold. Sullivan et al. also includes the only pre-
vious angle-differential negative-ion resonance study in zinc, which confirmed a $d$-wave
nature and $4s4p^22D$ assignment for a negative-ion resonance just above the $4s4p^3P_{0,1,2}$
state threshold. Stokes polarization parameter measurements conducted by Pravica et
al. [35] have also observed negative-ion resonances above the ionisation threshold, and
will be discussed below. Existing theoretical negative-ion resonance calculations using
the BSRM method [2] give resonance energies and assignments, but are limited to below
8.5 eV. Experimental evidence of negative-ion resonances based on $3d^04s^24p$ parent states
exists in the work of the the Uzhgorod group, and is supported by the present work. It
is reasonable to expect the existence of such negative-ion resonances given the electron
correlation effects evident from the strong mixing and core-polarisation associated with
these states [11, 2]. However, zinc negative-ion resonances associated with the excitation
of a $3d$ electron have not been modelled.

In the present context, PCI involves the exchange of energy and momentum between
scattered and ejected electrons after the decay of an autoionising state excited near thresh-
old. Energy is transferred to the faster, ejected electron from the slower, scattered electron.
The effect is more significant for short-lived autoionising states [36], because the scattered
electron interacts with the ejected electron and ion core for a greater length of time. If
the energy transfer is sufficiently large, the scattered electron may become bound to the residual ion, resulting in the population of neutral states below the ionisation threshold. This is the class of PCI that is observed here.

PCI can be identified because it characteristically affects the excitation of higher-lying states, and PCI structures present in \( nL^{2S+1} \) state excitation functions shift upwards in energy with increasing \( n \). Models of these PCI effects have been presented by King et al. [36], Barker and Berry [37], Morgenstern et al. [38] and van de Water and Heideman [39]. The effect has been observed and analysed in detail for the electron scattering from helium by King et al. and van Ittersum et al. [40]. King et al. have put forward a model which they term “shake-down” in analogy to the “shake-up” and “shake-off” Auger processes. In this approach the sudden change in field experienced by the scattered electron after autoionisation leads to it becoming bound. If initially the scattered electron has a continuum wavefunction of \( \psi_{kl}^{(2)} \), using the sudden approximation the probability \( P_{nl} \) that after autoionisation the electron will become bound in the state \( \psi_{nl}^{(1)} \) is given by

\[
P_{nl} = \int \psi_{kl}^{(2)*} \psi_{nl}^{(1)} d \mathbf{r} \tag{1.7}
\]

This approach neglects interference between the direct and resonance excitation processes, which is uncertain given that PCI structures do not appear to have a Fano profile [36]. However, PCI can produce peaks as well as dips in a cross section, for example the \( 1s^{n}n\ell \), \( n = 6,7,8 \) states of helium [36], and is not analogous to the incoherent cascade population of excited states by electric dipole transitions. Also neglected is the interaction between the scattered and ejected electrons, which is reasonable for helium where, in the decay to the \( 1s^{2}S_{1/2} \) ground state of \( \text{He}^{+} \), ejected electron energies are greater than 33.2 eV. In the case of zinc, ejected electrons emitted in the decay to the \( 4s^{2}S_{1/2} \) ground state of \( \text{Zn}^{+} \) can have an energy as low as 0.55 eV. For near-threshold autoionising state excitation both the scattered and ejected electrons are slow, and spend a relatively long time in the field of the \( \text{Zn}^{+} \) ion. They resemble two Wannier electrons [41], that is two low energy electrons in the field of a residual ion after near-threshold ionisation. A similar situation, for an excited ion with a vacancy in an inner-shell, was described by Kuchiev [42]. As a consequence the probability for energy exchange and the exchange of angular momentum is enhanced.

The present apparatus was able to resolve electron spin-dependence in the scattering process. A spin-polarised electron beam with an energy resolution of 120 meV was available for use, while the quasi-two electron Zn atoms could not be spin polarised. The spin-polarised work detailed here involved angle differential measurements of scattered electron intensity, but not spin-polarisation, and measurements of decay photon polarisation. The spin polarisation of an electron beam is defined as

\[
P_e = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} \tag{1.8}
\]

where \( N_\uparrow/N_\downarrow \) is the number or current of electrons with their spin vector oriented along the positive/negative direction of a reference axis. In this work only transversely polarised
electron beams were used, so the spin vector direction was defined relative to the $y$-axis. Below is an outline of mechanisms which result in spin dependence in atomic collision systems, and which are relevant to the measurements detailed in this work. More detailed treatments are given by Kessler [43] and Hanne [44], on which the following summary is based.

The spin-orbit interaction, the Hamiltonian of which is given by Equation 1.4, results in an effect on the continuum electron known as Mott scattering. Through the $l_s$ term, the sign of the spin-orbit potential depends on the relative orientation of $l$ and $s$. For a fixed incident electron spin orientation, an electron with $+l$ defined relative to the positive $y$-axis (i.e. one that passes to the right of the atom and is scattered through a positive angle $\theta$) experiences a different potential from an electron with $-l$ (i.e. one that passes to the left of the atom and is scattered through a negative angle $\theta$). Equivalently, an incident electron with a fixed orbital angular momentum orientation experiences a different potential depending on whether it has spin-up or spin-down. The interaction provides a mechanism by which the spin of continuum electron can flip during an elastic collision, and so the scattering process is described by direct and spin-flip scattering amplitudes, $f$ and $g$, respectively. We define $I_\uparrow(\theta)$ and $I_\downarrow(\theta)$ as the intensities of scattered electrons detected at an angle $\theta$ for incident spin up and down electrons, respectively. The relative difference between $I_\uparrow(\theta)$ and $I_\downarrow(\theta)$, or the asymmetry $A(\theta)$, is related to the incident electron polarisation $P_e$ by [43]

$$A(\theta) = \frac{I_\uparrow(\theta) - I_\downarrow(\theta)}{I_\uparrow(\theta) + I_\downarrow(\theta)} = S_A(\theta)P_e$$  \hspace{1cm} (1.9)

with $S_A(\theta)$ the asymmetry function, which for elastic scattering is identical to the Sherman function $S(\theta)$ which is defined in terms of the scattering amplitudes $f$ and $g$ as

$$S(\theta) = \frac{fg^* - f^*g}{|f|^2 + |g|^2}$$  \hspace{1cm} (1.10)

The Sherman function gives the polarisation which will be obtained by an initially unpolarised electron beam after Mott scattering. It is the asymmetry function $S_A(\theta)$, obtained by dividing the measured asymmetry $A(\theta)$ by the independently measured $P_e$, which is presented here. For elastic Mott scattering, the spin up/down asymmetry will be the same as the left/right asymmetry measurements, where the incident spin polarisation vector is kept constant while the relative difference between scattering signal at $\pm\theta$ is measured. Spin up/down asymmetries, spin left/right asymmetries and Sherman function measurements will also be equivalent for inelastic scattering, provided Mott scattering is the only spin-dependent mechanism at play. If inelastic scattering is considered as a two-step mechanism, Mott scattering can either involve both the incident electron in field of ground-state atom, or the scattered electron in the field of the excited atom. Generally, inelastic scattering is affected by the other spin-dependent effects outlined below, and so the equivalence of asymmetry and scattered electron polarisation measurements does not hold in general.

Spin-dependence can also be introduced by exchange scattering. It is possible to transfer spin angular momentum between the target and the incident electron, for example
in the excitation of a triplet state from singlet state. However, this effect is not mediated by the spin-orbit interaction and so, unlike Mott scattering, spin and orbital angular momenta are conserved overall. Information regarding the magnitude and phase of the amplitudes $f$ and $g$ (which have a physical meaning different from those defined for Mott scattering) can be extracted through electron and target polarisation analysis. However, exchange scattering can only introduce a spin up/down asymmetry if the target atoms are spin polarised, which was not the case here and there will be no left/right asymmetry because there is no dependence on whether the electron passes to the left or the right of the atom.

The fine structure effect results from a combination of spin-orbit interaction, acting within the target to split $J$ levels, and exchange scattering [44]. It can lead to an observable spin up/down asymmetry, given by Hanne, provided the fine structure is resolved. However, the 120 meV energy resolution of the present experiment was insufficient to do so, and so the observed sum over statistically populated $J$ levels will have no asymmetry due to the fine structure effect. Hanne also discusses the spin-orbit coupling effect, which is similar to the fine structure effect in that it results from a combination of spin-orbit interaction in the target and exchange scattering. The difference between the two is that the spin-orbit coupling effect arises through $LS$-mixing in the target. Such mixing means that $J$ levels of the target atom are not statistically populated, and so the spin-orbit coupling effect can result in an observable spin up/down asymmetry even if fine-structure is not resolved.

Negative-ion resonances may also produce spin-asymmetry and scattered electron polarisation, and are a very important consideration for the studies presented here. As an illustrative example, consider a $^2P_{3/2,5/2}$ resonant state, with the resonance energy of fine structure components split by some energy, excited from a $^1S_0$ ground state by spin-polarised electrons. Let the resonance structure be observed by detection electrons elastically scattered through positive angles $\theta$. By applying angular momentum conservation it can be seen that the $J = 1/2$ negative ion will be excited by $p$-wave, spin-down incident electrons, while the $J = 3/2$ negative ion will be excited by $p$-wave, spin-up incident electrons. As a result, negative-ion resonances will produce observable scattered electron polarisation and spin up/down left/right asymmetries. They are equivalent because scattered electrons with positive $l$ are detected at positive $\theta$, and scattered electrons with negative $l$ are detected at negative $\theta$. The sign of the asymmetry will depend on the nature of the interference between direct and resonant scattering.

Compared to other atomic targets, for example helium and mercury, there have been relatively few zinc studies and there is little information indicating when relativistic effects need to be taken into account for the present observations of this medium-sized atom. Fine structure splitting in zinc is much smaller than in mercury, with the lowest neutral excited states $4s4p^3P_{0,1,2}$ separated by 72 meV, compared to the 793 meV separation between the $6s6p^3P_{0,1,2}$ states of mercury. The spin-orbit interaction pushes some of the core excited $5d^96s^26p$ states below the first ionization threshold of 10.44 eV, for example the
$5d^96s^2\{^2D_{5/2}\}^3P_2$ state located at 8.54 eV. Such fine structure effects in mercury negative-ion resonances are large compared to zinc, and have been resolved by a number of electron impact studies, for example Newman et al. [45]. Unlike mercury, the $3d^44s^2nl$ states of zinc all lie above the first ionization threshold at 9.394 eV. For zinc, interactions with the core will not be dominated by spin-orbit effects as they are in mercury, and there will be a finer interplay between magnetic and electrostatic interactions.

The spin-polarised incident electron Stokes parameter measurements of Pravica et al. [35] investigated spin dependence in the vicinity of the $3d^94s^24p$ states, and found negative-ion resonance structures affecting polarisation. Stokes parameters defined as

$$P_1 = \frac{I_{0^\circ} - I_{90^\circ}}{I_{0^\circ} + I_{90^\circ}} \quad P_2 = \frac{I_{45^\circ} - I_{135^\circ}}{I_{45^\circ} + I_{135^\circ}} \quad P_3 = \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}} \quad (1.11)$$

where $I_\theta$ is the intensity of light polarised at an angle $\theta$ to the incident electron beam and $I_{\sigma^+}/I_{\sigma^-}$ is the intensity of left/right-hand circularly polarised light with photons detected along the positive $y$-axis. Stokes parameters measured without coincident detection of scattered electron are known as integrated Stokes parameters, and only these will be presented here. For unpolarised electron impact excitation, symmetry arguments show that the intensities $I_{45^\circ}$ and $I_{135^\circ}$ are equivalent, as are $I_{\sigma^+}$ and $I_{\sigma^-}$. So, for this case, $P_2$ and $P_3$ must vanish. However, by introducing an incident electron beam with a preferential spin direction, or spin polarisation, the symmetry is broken and $P_2$ and $P_3$ can be non-zero.

Non-zero values of $P_2$ and $P_3$ are indicative respectively of spin-orbit interaction, and exchange scattering or spin-orbit interaction [46]. Pravica et al. found that negative-ion resonances in the vicinity of the $3d^94s^24p$ autoionising states resulted in small, but statistically significant non-zero values for both $P_2 (= -0.007 \pm 0.001)$ and $P_3 (= -0.017 \pm 0.001)$. The effect of spin-orbit interaction in scattering from zinc was somewhat unexpected, since it is generally considered that zinc is too small for spin-orbit interaction to be significant. The fact that spin-orbit interaction is observable in this instance may be due to the higher angular momentum of the open $3d$ core compared to the outer electrons. Kuhn [5] showed that the spin-orbit effect is stronger in configurations in which electrons with lower energy have higher $l$, for example the $3p4s$ state of silicon. The increased penetration effects in configurations of this type lead to an increased importance of spin-orbit interaction.

Similar measurements to up/down asymmetries were conducted for zinc by Bartsch et al. [47]. They measured the left/right asymmetry in elastic scattering as a function of scattering angle for a number of fixed incident electron energies between 2 and 14 eV. They observed a significant left-right asymmetry as a result of Mott scattering with, for example, $S_A = -0.4$ at an incident energy of 14 eV and an observed scattering angle of 80°. Overall the measured asymmetries were smaller than for larger atoms such as mercury, for which the spin-asymmetry in elastic scattering at 18 eV and an observed scattering angle of 90° is greater than 0.7 [48]. Although they investigated near the $3d^94s^24p$ thresholds, because their asymmetries were measured as a function of scattering angle at a wide energy mesh, the experiment was not sensitive to negative-ion resonances. However, fluctuation of the 90° asymmetry between 0.2 at 9 eV and -0.3 at 11 eV seems to suggest an influence of the the negative-ion resonances observed by Pravica et al.. Kumar et al. [49] used
a relativistic approach to calculate $S(\theta)$, with the interaction potential including static, exchange and polarisation terms. These calculations showed very good agreement with experiment at 2, 3, 4 and 5 eV, but not at 9 and 14 eV, while the asymmetry at 11 eV was not calculated. The disagreement of these two previous studies at these energies suggests significant spin-dependent effects due to $3d$-core activated electron correlation, which was not included in the theory.

This thesis presents a series of studies which investigated elastic scattering, and excitation of the $4s^2p^3P_{0,1,2}$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d$, $4s5d$, $4s6d^3D_{1,2,3}$ and $4s4d$, $4s5d^1D_1$ states of zinc. The incident electron energy ranged from below the first excitation threshold at 4.01 eV to 50 eV, but with a focus on the energy region between first ionisation threshold at 9.34 eV and 17 eV, where previous work, for example that of Mansfield, suggests significant correlation effects. Investigation of a diverse range of states exploited the $n$, $L$ and $S$ dependent behaviour of the correlation effects, and because of variable exit channel coupling separated different contributions to the complex interference structures. An array of different techniques were employed, namely emission cross section measurements, photons excitation functions, electron energy-loss spectroscopy, differential elastic scattering measurements, electron excitation functions and spin-asymmetry measurements. Using these techniques, the present work sought to characterise cross sections, map and identify negative-ion resonance and PCI effects, and examine spin-dependent behaviour. It attempts to describe and understand how and why these features appear for electron scattering from zinc, and thus assist an extension of the current approach to scattering phenomena to include a more accurate treatment of non-dominant interactions.

The outline of this thesis is as follows. Chapter 2 details the experimental apparatus, and how it was operated. The results of experimental studies undertaken to verify the performance of the apparatus and prepare it for zinc studies are presented in Chapter 3. The results of these zinc studies are the subject of Chapters 4-7. Chapter 4 presents the results of the emission cross section studies, Chapter 5 presents the results of the differential elastic scattering and electron excitation function studies, Chapter 6 presents the results of the photon excitation function studies, and Chapter 7 presents the results of the spin asymmetry measurements. Each of these chapters contains a detailed discussion of the present data and the relevant literature, and some conclusions drawn from the discussion. Conclusions which apply to the thesis as a whole are presented in Chapter 8.
Chapter 2

The Experimental Apparatus

Isolated atom-electron scattering events were generated in the present experiment using the crossed-beams method. Two different types of electron beams were available for use, one spin-polarised and the other unpolarised. Both electron guns incorporated electrostatic energy selectors to control the incident electron energy resolution. An electron beam was crossed with a beam of ground state atoms which, during zinc studies, emanated from a heated oven. The volume in which the beams crossed will be referred to here as the interaction region. Scattered electron intensity was measured as a function of scattering angle and residual energy using a rotatable electron analyser, and the intensity and polarisation of wavelength-selected atomic decay photons was measured by a fixed-position detection system. The vacuum conditions necessary to perform this type of experiment were maintained using a system of vacuum chambers, turbomolecular pumps and rotary pumps.

2.1 Vacuum System

Figure 2.1 shows a simplified representation of the vacuum system. Part (a) is the interaction chamber, which consisted of a 550 mm tall, 500 mm diameter cylinder with a base plate which could be lowered to give access to the internal components. A pressure of $2 \times 10^{-7}$ Torr was maintained by a KYKY F250 turbomolecular pump. Connected to the interaction chamber was a differentially pumped transport region, marked (b), 400 mm long, 80 mm in diameter and pumped by a Pfeiffer TMU 065 turbomolecular pump. High voltage electron optics used to transport the spin-polarised electron beam to the interaction chamber were contained here. The transport region was connected to the ultra-high vacuum (UHV) spin-polarised electron source chamber, marked (c), via a pneumatic valve, marked (g). With the pneumatic valve closed the transport region pressure was $5 \times 10^{-8}$ Torr, and with it open the pressure was $8 \times 10^{-9}$ Torr.
Figure 2.1: The vacuum and gaseous target atom delivery systems, showing (a) interaction chamber, (b) differentially pumped beam transport region, (c) spin-polarised electron source chamber, (d) turbomolecular pumps, (e) foreline valve and alumina sorption trap, (f) rotary backing pump, (g) pneumatic valve, (h) gaseous target atom delivery system leak valve and (i) bypass line valve. All valves are marked × and the μ-metal shielding is marked with the heavier dashed line, with the lighter dashed line showing outlines of the spin-polarised electron gun, the Faraday cup and internal photon optics.
The spin-polarised electron source chamber, or more simply the “source chamber” as it will be referred to throughout this work, was a 150 mm 6-way cross pumped by a Pfeiffer TMU 521 turbomolecular pump. UHV pressures, on the order of $2 \times 10^{-10}$ Torr, were necessary to operate the source of spin-polarised electrons. The components contained in the source chamber were carefully designed and manufactured from UHV-compatible materials to avoid virtual leaks caused by gas traps and materials with a high vapour pressure. Despite these measures, the source chamber pressure was limited by the emission of water vapour and other atmospheric constituents absorbed by the chamber walls and internal components whilst open to air. To reach the required low pressure, water vapour was removed by baking the chamber at 180°C for around 24 hours using fibreglass heating strips.

All turbomolecular pumps were backed by Edwards E2M12 foreline pumps, with foreline pressures typically 0.02 Torr. Backstreaming of oil from these pumps was minimised using activated alumina sorption traps. Pressures below $1 \times 10^{-4}$ Torr were monitored by ionisation gauges controlled by a Vacuum Generators IPGC1 ion-gauge controller. The ion gauge within the interaction chamber was covered by an aluminium shield which prevented photons from the gauge head being detected, while also allowing sufficient gas flow. Pressures above $1 \times 10^{-2}$ Torr were measured by PVG5KF pirani gauges also controlled by the ion gauge controller.

An Extor mass spectrometer was used to monitor the progress of bakes, and also to check for leaks, and some example mass spectra are shown in Figure 2.2. Mass spectrometry was employed to identify the partial pressure of molecular species present within the vacuum chamber. This was valuable diagnostic tool because a prevalence of certain molecules indicated specific problems with the vacuum system. A case in point is the spectrum shown in Figure 2.2d, in which an external leak is indicated by large N$_2$ and O$_2$ peaks, at 28 a.m.u. and 32 a.m.u. respectively, with relative partial pressures similar to their relative atmospheric abundance. As a further example, though not one seen in any of the spectra here, a peak at a high a.m.u might indicate the presence of a non-UHV compatible plastic material outgassing large hydrocarbon molecules. In the mass spectrum taken before baking, shown in Figure 2.2a, the dominant peaks at 16, 17 and 18 a.m.u. are due to H$_2$O and its fragments OH and O. During baking the water vapour partial pressure is elevated as shown in Figure 2.2b. Baking allows water vapour to be removed more quickly than it would otherwise. After baking the partial pressure of water vapour is much diminished, as can be seen in Figure 2.2c, and the overall pressure is on the order of $1 \times 10^{-10}$ Torr.

2.2 Unpolarised Electron Gun

Figure 2.3 shows the unpolarised electron gun, labelled (a), and the configuration of the apparatus whilst operating in unpolarised incident electron mode. The most notable characteristic of this instrument was its ability to produce beams with good energy resolution
Figure 2.2: Mass spectrometry vacuum diagnostics for the UHV spin-polarised electron source chamber. (a) Mass spectrum taken before baking with dominant peaks due to H$_2$O and its fragments OH and O. (b) Mass spectrum taken during baking showing the elevated partial pressure of H$_2$O within the chamber. (c) Mass spectrum taken after baking showing a significantly diminished water vapour partial pressure. (d) Mass spectrum with enhanced N$_2$, and O$_2$ peaks indicating an external leak. Note the change of scale between spectra.
2.2. UNPOLARISED ELECTRON GUN

Figure 2.3: The arrangement of components used in unpolarised incident electron studies. Housed inside the interaction chamber are (a) the unpolarised electron gun, (b) the metal vapour source, only the nozzle is shown, (c) the internal lens of the photon detection system, (d) the electron analyser and channel electron multiplier (CEM), (e) the removable gas jet and (f) the liquid nitrogen cooled zinc vapour collection plate. A Faraday cup mounted inside the chamber opposite the electron gun is not shown. Mounted outside the chamber is the remainder of the photon analysis and detection system (c) comprising of, from the bottom up, the Liquid Crystal Variable Retarder (LCVR), the linear polariser, an interference filter, the external lens and the Photomultiplier tube (PMT).
and current while operating at low incident energies, between 3 and 20 eV. Electrons were produced thermionically in the electron gun using a thoriated tungsten V-shape filament operating at 2.4 A. The emitted electrons were extracted through a 1 mm diameter aperture, then shaped into a beam by a series of 5 electrostatic lens elements. Following these was a 35 mm-mean radius, 127° cylindrical electrostatic energy selector with 1 mm diameter entrance and exit apertures which narrowed the energy spread of the electron beam from its initial thermal distribution. After the energy selector the electrons passed through a set of deflectors and two lens elements which steered and focused the beam into the interaction region, 25 mm from the electron gun exit. All lens elements were aperture lenses made from 0.1 mm thick molybdenum sheet, while the energy selector and the deflectors were made from copper. All of these elements were graphite coated to reduce surface potential effects. The unpolarised electron gun was turntable-mounted, however its position was kept fixed.

Theoretically, under optimal operating conditions the Full Width at Half Maximum (FWHM) $\Delta E_g$ of the approximately Gaussian energy distribution obtained from a 127° energy selector is a function of its mean radius $R_g$, the width of its input and output apertures $\Delta R_g$ and its pass energy $E_{pg}$. The resolving power $\Delta E_g/E_{pg}$, derived from Roy et al. [50] for conditions of optimal beam current, is

$$\frac{\Delta E_g}{E_{pg}} = \frac{3 \Delta R_g}{2 R_g}$$  \hspace{1cm} (2.1)

Lowering $E_{pg}$ narrowed the electron beam energy distribution, but decreased its current. So, the pass energy was varied according to needs of the particular experiment being performed, with consideration given to the resolution required and the overall data collection efficiency. Typically, with an $E_{in} = 10$ eV incident energy, a $E_{pg} = 15$ eV pass energy produced a $\Delta E_g = 350$ meV beam with 500 nA current, a $E_{pg} = 5$ eV gave $\Delta E_g = 210$ meV and 40 nA, and a $E_{pg} = 2$ eV pass energy gave $\Delta E_g = 80$ meV and 0.5 nA. These resolutions were determined from measurements of near-threshold zinc 4s4d$^1D_2$ state excitation, which will be more fully detailed in Sections 3.4.1 and 6.1.4. The observed energy resolutions are all within ±10 meV of what would be expected given an initial energy spread of 400 meV from the electron source, applying Equation 2.14 to be discussed later. This value is a reasonable estimate of the initial energy spread, given that when the gun was operated with a high pass energy $E_{pg}$, the incident beam resolution was approximately 400 meV.

The need to install a zinc vapour collection system, which will be described in Section 2.7, restricted space within the interaction chamber. In order to save space, the final lens elements of the spin-polarised electron gun were removed from the interaction chamber during unpolarised incident electron studies. Likewise, during spin-polarised incident electron studies the unpolarised electron gun was removed. This permitted the electron analyser to be rotated through 0° to +110° during both types of studies.
2.3. ELECTRON ANALYSER

2.2.1 Faraday Cup

The majority of the electron beam was left unscattered after passing through the interaction region, and was collected by a Faraday cup, shown in Figure 2.4, mounted 40 mm from the interaction region and opposite the electron gun in use. The current collected by the Faraday cup was monitored to assist tuning of the electron guns, and recorded during some experimental studies as a measure of energy-dependent electron gun transmission. It consisted of a 20 mm diameter copper plate maintained at a potential of 36 V relative to ground, mounted within a 25 mm diameter grounded cylindrical copper housing. The front opening of the housing was covered by 80% transparency molybdenum mesh, which maximised the Faraday cup collection area whilst preventing electric field penetration into the unipotential interaction region. The Faraday cup was raised into and out of position from outside the chamber using a mechanism connected to a rotary feedthrough, which allowed the electron analyser to move into scattering angles smaller than 60°.

2.3 Electron Analyser

The electron analyser, labelled (d) in Figure 2.3, was constructed from the same materials as the unpolarised electron gun. Electrons scattered within ±2° the observed scattering angle passed through a 3 mm entrance aperture located 50 mm from the interaction region. Accepted electrons were focused and steered by 4 aperture lens elements and a deflector, then passed through a 127° cylindrical energy selector with a mean radius of 65 mm and 1 mm diameter entrance and exit apertures. This allowed only scattered electrons with residual energies within a narrow range to be detected by the Photonis 719 channel electron multiplier (CEM), which was mounted within a grounded housing above the energy selector exit aperture. Ortec 459 bias supplies maintained the front of the CEM at 300 V, and the back at 2.5 kV. These optimum voltages were determined by a pulse height analysis, similar to that shown in Figure 2.5, as those which maximised the CEM signal to noise ratio by best separating the signal and noise pulse height distributions. Outside the vacuum chamber, signal was de-coupled from the CEM high-voltage supply cable using a 1 nF, 5 kV rated capacitor. The apparatus was mounted on a turn-table.
the position of which could be controlled outside the vacuum chamber using a rotary feed-
through. Space-restrictions within the interaction chamber meant that only scattering
angles within the range $0^\circ$ to $+110^\circ$ could be observed.

The electron analyser energy resolution was estimated by measuring the width of sharp
negative-ion resonance structures, for example the $1s^22s^22S_{1/2}$, $\Gamma = 9$ meV [51] helium
negative-ion resonance at 19.36 eV, discussed in detail in Section 3.2. The observed reso-
nance width, along with knowledge of the incident beam resolution, allowed the electron
analyser resolution to be determined from Equations 2.12 and 2.14, which will be discussed
below. Setting the analyser pass energy $E_{pa}$ to 10, 5 and 2 eV resulted in FWHM analyser
resolutions of $E_a = 200$ meV, 130 meV and 60 meV respectively. For a 127$^\circ$ analyser
with the present geometry, Equation 2.1 predicts resolutions of 230 meV, 115 meV and
46 meV for pass energies of 10, 5 and 2 eV respectively, in reasonable agreement with what
was observed. As for the the unpolarised electron guns, the energy resolution was varied
according to needs of the particular experiment being performed, with consideration given
to the resolution required and the overall data collection efficiency.
Figure 2.5: Pulse height analysis of the CEM output, with an applied voltage of 2.5 kV. The CEM output pulses were amplified by an Ortec VT120A pre-amplifier. (a) Pulse height analysis with electrons incident upon the CEM, showing a larger signal pulse peak on the right well separated from the smaller noise peak to the left. (b) Pulse height analysis with no electrons incident on the CEM, showing only the noise peak.
Figure 2.6: The spin-polarised electron gun, showing details of the (a) 813 nm laser diode, (b) linear polariser, (c) Liquid Crystal Variable Retarder, (d) left-hand circularly polarised light passing through the chamber window, (e) GaAs crystal mounted in its molybdenum holder with Caesium dispensers above and tungsten filament below, (f) 90° electrostatic deflector, from which emerges an electron beam with linear momentum and polarisation vectors as shown, (g) the spin-source optics mounting, (h) spin-source chamber containing the crystal, lens elements, the 90° electro-static deflector and the 180° hemispherical energy selector, (i) the pneumatic valve, (j) the high voltage, differentially pumped transport region, (k) final spin-polarised gun lens elements fixed inside the interaction chamber.
2.4 Spin-Polarised Electron Gun

The spin-polarised electron gun is shown in Figure 2.6. Polarised electrons were obtained by photoemission from a Gallium Arsenide (GaAs) crystal, specially prepared in UHV conditions, illuminated by circularly polarised laser light. Electrons were transported into the interaction region by electron-optical elements, which included a 90° bender and a 180° hemispherical energy selector. Spin-up and spin-down incident electrons, as defined in Chapter 1, were produced by left-hand and right-hand circularly polarised laser light respectively. A computer-controlled Liquid Crystal Variable Retarder (LCVR) allowed automated control of the incident spin-polarised electron beam polarisation vector.

2.4.1 Laser Optics

The photon optics used for the spin-polarised electron source laser are shown in Figure 2.6, parts (a), (b) and (c). Photo-emission from the GaAs crystal was produced using a Schafter-Kirchoff 813 nm laser diode and SK 9733C controller. The laser power required for normal operation was 2 mW which gave an photo-emission current of 4 $\mu$A from the GaAs crystal. Laser power was increased to 5 mW for short time periods in instances where the scattering signal was very low, or where a higher emission current made the alignment and calibration procedures described below more accurate. The laser beam was circularly polarised by passing it through a linear polariser, then a Liquid Crystal Variable Retarder (LCVR) with its fast axis at 45° to the linear polariser axis. A computer controlled, Meadowlark B1020 A.C. voltage supply controlled the birefringent properties of anisotropic nematic liquid crystal (NLC) molecules contained within the LCVR. The LCVR was oriented so that 1/4 and 3/4-wave retardance produced right-hand and left-hand circularly polarised photons respectively.

2.4.2 Production of Spin-Polarised Electrons from a GaAs Crystal

GaAs spin-polarised electron sources are discussed in detail by Pierce and Meyer [52]. As shown in Figure 2.7, circularly polarised photons incident on a GaAs crystal excite electrons from the $P_{3/2}$ valence band, across the $E_g = 1.52$ eV bandgap and into the $S_{1/2}$ conduction band. In the present experiment, where quantisation is along the $y$-axis, the transitions must obey $\Delta m_j = +1$ or $-1$ for incident photons with spin aligned with the positive and negative $y$-axes respectively. Assuming incident photons with positive spin, the following transitions are possible for the unstrained-type crystal used here

$$P_{3/2}, m_j = -3/2 \rightarrow S_{1/2}, m_j = -1/2$$
$$P_{3/2}, m_j = -1/2 \rightarrow S_{1/2}, m_j = +1/2$$ (2.2)

The probability of the first transition relative to the second is 3:1, which results in a polarisation of $(3 - 1) / (3 + 1) = 0.5$, or 50%, in the opposite direction to the incident photon spin. However, depolarisation caused by scattering from defects and impurities and exchange scattering in the caesium-oxygen layer results in final electron polarisations
Figure 2.7: Top: energy bands of GaAs near the centre of the Brillouin zone. Adapted from Pierce and Meyer [52]. a) The energy gap $E_g$ and the spin-orbit splitting $\Delta$ between the $P_{3/2}$ and $P_{1/2}$ valence bands, b) transitions allowable with absorption of spin-up photons (solid lines) or spin-down photons (dashed lines). The numbers within the circles indicate the relative transition probabilities. Bottom: the band structure of GaAs with different surface treatments. a) No treatment, b) with a caesium surface layer lowering the vacuum level to the conduction band, c) with a cesium oxide surface layer lowering the vacuum level below the conduction band.
2.4. SPIN-POLARISED ELECTRON GUN

![Graph showing emission current vs. time with labels for Cs, O2, and CsO2]

Figure 2.8: The GaAs photo-emission current during the activation process. At points marked Cs caesium deposition commenced and the oxygen dispenser was off, while at points marked O2 oxygen deposition commenced and the caesium dispenser was switched off. The fluctuations in emission current after 30 minutes are due to small adjustments being made to the caesium dispenser current to find stable operating conditions.

of ~30% for the unstrained crystal. Thus the electron beam polarisation was $P_e \approx 0.3$, aligned with the positive y-axis, or spin-up, for 3/4-wave LCVR retardance, and aligned with the negative y-axis, or spin-down, for 1/4-wave retardance.

The conduction band in an untreated GaAs crystal lies $\chi = 4$ eV below the vacuum level, where $\chi$ is the electron affinity. Photoemission can be achieved using photons with an energy $h\nu = E_{gap} + \chi$, but in this case it would also be possible for photoexcited electrons to scatter inelastically from electrons below the Fermi energy to produce an electron-hole pair. Thus the photo-excited electron could lose energy and not be emitted, reducing the quantum efficiency of the process. This problem can be circumvented by applying a surface treatment of Cs2O, or “activating the crystal”, which reduces $\chi$ to 0 or negative values as shown in Figure 2.7.

Caesium was deposited using resistively heated evaporative dispensers placed above the crystal, driven by a current of 3.5 A during activation. After approximately 2 minutes of caesium deposition, a photo-emission current from the crystal on the order of 10 nA was observed. The variation of GaAs crystal emission current during the various stages of activation is shown in Figure 2.8. Caesium deposition continued until the emission current started to decrease, at which point the caesium deposition was stopped, O2 was permeated through a heated silver tube connected to the chamber, and the emission current started to increase again. Once the emission current had again started to decrease, O2 deposition was stopped, caesium deposition recommenced, then the process was repeated until an emission current of ~8 µA was reached. Maintaining a stable emission current required a continuous supply of Cs to maintain the Cs2O layer, so lastly the caesium dispenser
current was adjusted within the range 2.5 A and 3 A until the emission current remained steady.

The GaAs crystal surface must be atomically clean prior to activation. Before installation, most surface contaminants were removed by an ultra-sonic cleaning procedure using, in turn, ammonia, distilled water, methanol and acetone. Then, immediately preceding each activation, the crystal was cleaned further by heating it to 600°C for 30 minutes using a tungsten filament fixed below the molybdenum crystal holder. An n-type thermocouple attached to the crystal holder was used to monitor temperatures during the crystal baking. After cleaning, the crystal was left to cool to below 40°C before activation commenced.

Prior to their first use after opening the source chamber, the caesium and oxygen dispensers were outgassed by heating them to their maximum operating temperatures. During degassing, the temperatures of these components were increased slowly so that the chamber pressure remained below 10⁻⁸ Torr. The caesium and oxygen dispensers were outgassed with the chamber walls still hot from baking, and with the crystal at a temperature of 300°C, to ensure the species released were pumped from the system and did not contaminate the crystal.

2.4.3 Electron Optics

Electrons were extracted from the crystal surface by a 2 mm diameter aperture, which was held at a potential 80 V higher than the crystal. Once extracted, the initially longitudinally-polarised electrons, which have their preferential spin direction parallel or anti-parallel to their momentum, passed through a 90° electrostatic bender. Here, the linear momentum vector of electrons was rotated by 90° while the spin-polarisation vector was unaffected. Electrons leaving the 90° electrostatic bender were transversely polarised, that is their preferential spin direction was perpendicular to their linear momentum. Following the bender was a deflector then 5 lens elements. These, and all other lenses and deflectors in the spin gun, were copper cylinders with an internal diameter of 15 mm. The electrons then passed through a 180° hemispherical energy selector with 1 mm entrance and exit apertures, and a mean radius of 80 mm. After the selector were 2 deflectors and 3 lens elements leading into the 0.5 m long transport region. In the transport region the kinetic energy of the electrons was increased to ∼1 keV to reduce the divergence of the beam, as governed by the Helmholtz-Lagrange invariant [53]

\[ E^{1/2} \theta r = \text{constant} \]  

where \( E \) is the beam energy, \( \theta \) the beam pencil angle and \( r \) its radial extent. The final elements of the spin-polarised electron gun were housed inside the interaction chamber and consisted of 5 lens elements and a deflector. These were fixed to the turn-table base plate, but were not rotatable.

From Kuyatt and Simpson [54], a hemispherical energy selector with a mean radius \( R_s \), entrance and exit aperture widths \( \Delta R_s \) and pass energy \( E_{ps} \) has a resolving power

\[ \frac{\Delta E_s}{E_{ps}} = \frac{\Delta R_s}{R_s} \]  

(2.4)
2.4. SPIN-POLARISED ELECTRON GUN

where $\Delta E_s$ is the FWHM resolution of the hemispherical energy selector. Since for the pilot spin-polarised electron study presented here it was important to maximise the statistical accuracy, and thus the incident beam current, the pass energy was kept quite high at $E_{ps} = 25$ eV. The FWHM resolution of electrons obtained directly from the crystal was 300 meV, which combined with the hemispherical energy selector, using Equation 2.14, gave an overall incident electron beam energy resolution of 220 meV.

2.4.4 Spin Source Calibration

The laser diode produced a partially linearly-polarised beam, and so the linear polariser was oriented so that its axis was aligned with the beam polarisation axis, and the emission current was maximised. Once the linear polariser was correctly oriented, the LCVR controller voltages needed to produce 1/4 and 3/4-wave retardances were determined. A device consisting of a photodiode fixed behind a spinning linear polariser was placed after the LCVR. The linear polariser axis rotated relative to the polarisation axis of photons emerging from the LCVR, which resulted in a sinusoidal output voltage from the photodiode. When the LCVR was set at 1/4 or 3/4-wave retardance, and thus produced circularly polarised light, the intensity of light reaching the photodiode did not change as the linear polariser rotated. In this case the photodiode produced a flat voltage output. An oscilloscope was used to monitor the photodiode voltage output, while the LCVR voltage was increased from zero until the settings which produced flat waveform were found. The smaller voltage corresponded to 3/4 wave retardance.

In practice the waveforms seen at 1/4 and 3/4-wave LCVR retardance were not perfectly flat, since light from the LCVR was not perfectly circularly polarised. So, after the procedure above fine adjustments were made to the LCVR fast axis position and the 1/4 and 3/4 retardance voltages until the 1/4 and 3/4-wave retardance photodiode waveform amplitudes were the same. This was necessary to ensure that the degree of circular polarisation produced by the LCVR, as well as the GaAs crystal emission current, was the same for 1/4 and 3/4-wave retardance. If the emission current was not constant with changing retardance, then spurious non-zero values will be measured for the asymmetry function $S_A$, defined in Chapter 1, even in the absence of spin-dependant scattering effects. The emission current was monitored while the LCVR retardance was changed, and it was observed to remain constant.

The spin-polarisation of the incident beam $P_e$ was measured using the method of Eminyan and Lampel [55]. The spin-polarisation $P_e$ and the integrated Stokes parameter $P_3$ for the $4s5s^3S_1 \rightarrow 4s4p^3P_2$ transition in zinc have the following relationship

$$P_3 = -\frac{P_e}{2}$$

(2.5)

If the degree of circular polarisation is not the same for 1/4 and 3/4-wave retardance, then neither is the degree of spin-polarisation for incident spin-up and spin-down electrons. In this case the observed and actual values of $S_A$ will differ, if spin-dependant effects are present. Incident spin-up electrons yielded $P_3 = -0.145 \pm 0.005$, and incident spin-down
electrons yielded \( P_3 = +0.142 \pm 0.005 \). So, the spin-up and down spin-polarisations were the same within the uncertainty. Averaging the spin-up and down measurements gives \( P_e = 0.287 \pm 0.004 \). Also, the fact that \( P_3 \) had the expected sign gave confidence that both the spin-polarised electron source LCVR and the photons analysis LCVR, which will be described below, had been correctly oriented as per the manufacturers specification to produce or accept photons with the expected circular polarisation.

### 2.5 Photon Detection

Figure 2.3 part (c) and Figure 2.9 show the photon analysis system. Atomic decay photons emitted into a 0.12 sr solid angle centred on the positive \( y \)-axis were admitted through a 4 mm aperture 10 mm above the interaction region, then shaped into a parallel beam by a \( f = 50 \) mm lens placed with the interaction region at its focal point. Photons then passed through a chamber window, a LCVR computer-controlled using a Meadowlark D1040 Digital Interface, a linear polariser, a narrow band interference filter and a \( f = 100 \) mm lens which focused them onto the photo-cathode of an Electron Tubes 9863-350QB photomultiplier tube (PMT). The PMT was cooled to -15° C inside an EMI FACT 50 Mk III housing, which reduced the PMT dark counts to \( \sim \)2 per second, as shown in Figure 2.10. A pulse height analysis, similar to that conducted for the CEM and shown in Figure 2.5, determined the PMT operating voltage for optimum signal-noise separation to be 1.8 kV, which was applied using a Canberra 3105 power supply. When polarisation studies were not being conducted the LCVR and linear polariser were removed from the photon detection system to improve counting rates and allow the detection of wavelengths below their \( \sim 450 \) nm transmission limit. All lenses and windows were UV-grade fused silica which allowed UV-photons, such as 214 nm radiation from the decay of the zinc \( 4s^4p^1P_1 \) state, to be studied.

In the present experimental configuration, the Stokes parameters \( P_1, P_2 \) and \( P_3 \) can be measured using the combination of linear polariser and LCVR orientations and retardances detailed by Hayes et al. [56]. \( P_1 \) and \( P_3 \) are measured with the LVCR fast axis at 135° to the incident electron momentum vector \( \mathbf{k}_{in} \), and the linear polariser axis aligned with \( \mathbf{k}_{in} \). \( I_{0^\circ} \) and \( I_{90^\circ} \) are measured with the LCVR at 0 and 1/2-wave retardance respectively and \( I_{\sigma^+} \) and \( I_{\sigma^-} \) are measured with the LCVR retardance at 3/4 and 1/4-wave respectively. \( P_2 \) was not measured here, but can be with the LCVR fast axis at 90° to \( \mathbf{k}_{in} \), and the linear polariser axis at 135° to \( \mathbf{k}_{in} \). In this case \( I_{45^\circ} \) and \( I_{135^\circ} \) are measured with the LCVR retardance at 1/2 and 0-wave respectively.

The internal and external lens positions were adjustable \textit{in situ} so that they could be accurately placed with the interaction region or photo-cathode at their respective focal points. Optimisation of the lens positions is discussed in detail in Section 2.9 below. The internal lens holder, shown in Figure 2.9 part (b), screwed onto the end of a threaded aluminium tube fixed to the chamber roof, and was connected by a train of gears to a rotary feedthrough to permit external up/down position adjustment. As shown in Figure 2.9 part
Figure 2.9: The photon analysis and detection system, showing details of part (c) in Figure 2.3; (a) interaction region, (b) internal lens and mount allowing up/down position adjustment from outside the vacuum chamber using the mechanism shown, (c) the interaction chamber wall, (d) uv-transmittion, fused-silica chamber window, (e) LCVR, (f) linear polariser, (g) interference filter, (h) external lens and mount allowing up/down position adjustment using the mechanism shown, (i) PMT inside its cooled housing with a quartz window.
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Figure 2.10: The dark counts produced by the photomultiplier as a function of its housing temperature.

Figure 2.11: Calibration of the linear polariser angle via measurements of 667 nm photons from the $1s3d^1D_2 \rightarrow 1s2p^1P_1$ transition in helium, using the method described in the text. (a) Detected photon intensity as function of linear polariser orientation, (b) Detected photon intensity as function of linear polariser orientation between ±30°, which is used to determine the correct orientation of the linear polariser. The bars indicated the statistical uncertainty of each point.
Figure 2.12: Calibration of the Liquid Crystal Variable Retarder, using the method described in the text. The voltages corresponding to 0, 1/4, 1/2 and 3/4 wave retardances are shown.

Figure 2.13: The dependence of the helium decay photon signal on the vertical displacement of the lenses from their optimal positions, measured by detecting 667 nm photons from the $1s3d^1D_2 \rightarrow 1s2p^1P_1$ transition in helium. • external lens position, □ internal lens position.
(h), the external lens was mounted on a hollow PVC cylinder free only to move vertically, threaded into a tapped PVC spacer. The lens could be raised and lowered by rotating the spacer. Figure 2.13 shows the sensitive dependence of the photon signal on the lens positions. The counting rate of decay photons from the $1s3d^1D_2 \rightarrow 1s2p^1P_1$ transition in helium was measured as a function of lens position, with an impact energy of 25 eV, and a helium partial pressure of $3 \times 10^{-5}$ Torr. As can be seen in the Figure, a shift of 3 mm away from the optimal lens position decreased the signal by a quarter.

Stokes parameter measurements relied on the linear polariser axis being at either $0^\circ$ or $135^\circ$ to the incident electron momentum vector. The uncalibrated linear polariser was initially oriented with its axis at an angle $\delta$ to the incident electron momentum vector $k_{in}$. Letting $\alpha$ be the angular displacement of the linear polariser from this initial orientation, the calibration procedure involved observing the intensity of polarised light from an atomic transition as $\alpha$ was increased through to $360^\circ$. Figure 2.11 shows the photon intensity as function of polariser angle for 667 nm photons from the $1s3d^1D_2 \rightarrow 1s2p^1P_1$ transition in helium which has a polarisation of $P_1 = 0.4$ near 25 eV [57]. The data were fitted with the function $I = I_0 + P \cos 2(\alpha - \delta)$, which determined $\phi$ and thus allowed the linear polariser axis to be aligned with $k_{in}$.

The LCVR retardance is wavelength dependent, and so a fresh LCVR calibration was required before a different atomic transition could be studied. Linearly polarised light was passed into the interaction chamber through a side window, and this was ensured to be the only appreciable source of photons within the interaction chamber. With the LCVR fast axis at $45^\circ$ to the linear polariser axis, the lab PC scanned the LCVR voltage whilst simultaneously recording the intensity of photons detected by the PMT. An example calibration curve is shown in Figure 2.12. The first extremum, in this case a maximum, corresponds to a 0-wave retardance and the second extremum, in this case a minimum, corresponds to a 1/2-wave retardance. The two points where the observed photon intensity is mid-way between these extrema correspond to 3/4 and 1/4-wave retardances, with the 3/4-wave retardance voltage setting the lower of the two. After calibration, $P_1$ for the $1s3d^1D_2 \rightarrow 1s2p^1P_1$ transition in helium was remeasured to check the polarisation analysis system.
Figure 2.14: A simplified representation of the circuit used to control electron optical elements in the unpolarised electron gun, spin-polarised electron gun and electron analyser, showing (a) computer controlled voltage supply, (b) connection between the unpolarised electron gun, spin-polarised electron gun and the electron analyser, (c) voltage defining the incident beam energy for the electron guns, (d)-(f) system of voltage supplies and potentiometers controlling the lens element and deflector potentials. For simplicity, the voltmeter and ammeter used to monitor the electron optical elements potentials and currents are not shown.
2.6 Electronics

2.6.1 Electron Optics Control

A diagram showing a simplified representation of the circuit used to control the unpolarised electron gun, spin-polarised electron gun and electron analyser is shown in Figure 2.14. The potentials applied to electron-optical elements within the electron guns and the electron analyser were controlled by a system of stabilised voltage supplies and potentiometers. Using the switch, shown near (a) in the diagram, the individual electron spectrometer circuits could either be connected directly to ground or float on a computer controlled (CC), GW GPS-3030 30 V power supply. The computer controlled supply permitted automated control of the incident electron beam energy, and which part of the scattered electron residual energy spectrum was detected by the electron analyser CEM. The same computer controlled supply was used for the unpolarised electron gun, spin-polarised electron gun and electron analyser, as shown by (b) in the diagram.

The incident beam energy was set by applying a voltage to the unpolarised electron gun filament, or the crystal holder for the spin-polarised electron gun. Since, as discussed in Section 2.8 below, the interaction region was grounded, a negative voltage was applied to the filament and the crystal holder. The actual beam energy differed from the applied voltage due to contact potentials, and so it was necessary to perform the energy calibration procedure described in Section 3.4.1. The pass energy and thus resolution of the 127° cylindrical and 180° hemispherical energy selectors was set using the entrance/exit aperture and inner/outer cylinder or hemisphere voltage controls are shown at (f) in Figure 2.14. Lens element and deflector potentials were controlled using the the system of potentiometers at (d) in the diagram. To simplify the presentation, not all lens control potentiometers are shown. Suitable lens and deflector potentials were determined from a SIMION simulation. These initial settings were refined over the course of years by careful tuning of the electron guns to maximise the photon signal, and the electron analyser to maximise the inelastically scattered electron signal. Due to the different contact potentials, the optimal tuning of the apparatus was strongly dependent on whether zinc or noble gas targets were used. For zinc studies the electron guns and electron analyser were tuned using the scattered electrons and 214 nm photons resulting from excitation of the 4s4p1P1 state. The voltage applied to, and current incident upon, the various elements was monitored using a Keithley 197A multimeter.

Ideally, the voltages applied to electron optical elements in the present experiment would have no AC components, or ripple, because these have a detrimental effect on beam focusing and energy resolution. The voltages applied to the electron optical elements of the unpolarised gun, spin polarised gun and electron analyser were checked using an oscilloscope and all found to have acceptably small ripple voltages of < 50 mV in electron lenses, and < 5 mV in energy selectors.
2.6. ELECTRONICS

Figure 2.15: The electron and photon detection electronics. The specific components used, all outside the vacuum chamber, are as follows; Ortec VT120A Pre-amplifiers, Ortec 935 Quad Constant Fraction Discriminator (CFD), NIM to TTL converter made in-house, Canberra 2143 Time-to-amplitude converter (TAC), Ortec 8075 multichannel buffer (MCB), Powerdaq Data acquisition card (DAQ), Ortec 541 Ratemeters, (An Ortec 872 Counter/Timer was also used to monitor count rates), Keithley 197A Autoranging multimeter.
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2.6.2 Detection Electronics

The system used to process and record CEM and PMT output pulses is shown in Figure 2.15. Nanosecond pulses from the output of the PMT and the CEM decoupling circuits were passed through Ortec VT120A preamplifiers, then an Ortec 935 Quad Constant Fraction Discriminator (CFD). The discriminator level was set 20% above that which reduced to 2 counts/s the spurious counts present with the incident electron beam, ion-gauge head and metal vapour source switched off. The negative NIM pulses from the CFD were converted into positive pulses by a NIM - TTL converter, then counted by a Powerdaq data acquisition card and finally recorded by the lab PC. Signal counting rates were monitored using an Ortec 872 Counter/Timer and Ortec 541 Ratemeters, which accepted output from the NIM-TTL converter, and the shape of the signal pulses was monitored using a Tektronix Type 454 Analog Oscilloscope. The lab PC displayed and recorded the data using software created in-house. To check the operation of the electronics, a Hewlett Packard 8082A pulse generator producing 10 ns negative pulses was connected in place of the CEM and PMT, and the output of each device was viewed in turn using an oscilloscope. The correct type and rate of pulses were verified as being produced, recorded or discriminated out, and there were no pulse reflections as a result of poor impedance matching.

During the course of the project, some preliminary coincidence studies were undertaken to assess the potential for a full scale study to proceed using the present apparatus. These are presented in detail in Section 3.3. A Canberra Model 2143 Time Analyser accepted electron and photon signals from the CFD. The signal with the slower counting rate provided the start pulse, and the other was delayed by 100 ns before providing the stop pulse. This delay was appropriate for the helium $1s3d^1D_2 \rightarrow 1s2p^1P_1$ study undertaken, given that the lifetime of this state is 16.7 ns [58] and an incident electron energy of 40 eV was used. The Time Analyser output was passed through an Ortec 926 ADCAM multichannel buffer (MCB), and then into the lab PC where time information was displayed as a histogram using Ortec Maestro multichannel analyser emulator software.

2.7 Target Atom Sources

Two different classes of atomic targets were used in this study. The noble gases helium and argon were used to test, tune and optimise the apparatus because the electron impact excitation of these targets has been extensively studied, and because, unlike zinc, they do not have a degrading effect on the apparatus. However, the principle focus of the project was electron impact excitation of free zinc atoms, which was achieved by delivering zinc into the interaction region in the form of a vapour.

2.7.1 Gaseous Target Source

The system used to deliver gaseous atomic targets into the interaction chamber is shown partially in Figure 2.1, parts (h) and (i). Helium and argon were delivered into the interaction chamber via a feed-through from gas cylinders outside the vacuum. A needle
valve was used to control the density of target atoms in the interaction region, and the target gas partial pressure was varied between $1 \times 10^{-6}$ Torr and $3 \times 10^{-5}$ Torr, as measured by the interaction chamber ion gauge. Target gas was formed into a beam and directed in the positive $y$-direction by a gas jet, shown in Figure 2.3, which had a 5 mm long, 0.3 mm inner diameter exit nozzle, and a tip lying 3 mm below the interaction region. The gas jet was made from aluminium, with an Electrical Discharge Machining (EDM) machined nozzle, and graphite coated to minimise surface potentials and photon and electron reflection. Screws fixed the gas jet into a recess in the top turn-table plate, which accurately located the jet nozzle, and the join was sealed using a viton o-ring. A reliable method to accurately and repeatedly locate the gas jet was necessary because it was used to define the interaction region position during alignment, but it was removed during zinc experiments to prevent zinc deposits on its tip from blocking the electron beam.

Before the first operation of the gas delivery system after opening the interaction chamber, or before changing the target gas, the gas lines outside the vacuum chamber were evacuated using an Edwards E2M12 rotary pump. Gas in lines within the vacuum was evacuated through a large diameter bypass line, which avoided having to pump gas through the constrictive gas jet and so made the evacuation process much faster. Once the target gas was evacuated, the bypass line was closed.

2.7.2 Metal Vapour Source

The metal vapour source is shown in Figure 2.16. Pellets of 99.999% purity zinc were vaporised within the main cavity of a thermally heated oven. A 150 mm long nozzle, welded to the top of the oven and at an angle of 30° to the scattering plane, directed the free atom vapor down through the interaction region, which was 7 mm from the 1 mm inner diameter, 4 mm long nozzle tip. The oven and nozzle were heated independently using cylindrical copper sleeves with embedded twin filament Thermocoax heater elements. Oven temperatures were varied between 500 and 530°C depending on the available signal, which had the dependence on oven temperature shown in Figure 2.17, whilst the nozzle temperature was maintained 50°C hotter to prevent zinc from condensing on and clogging the nozzle tip. Maintaining these temperatures required the oven and nozzle heaters to be driven at 0.4 A and 0.5 A respectively. The oven and nozzle temperatures were monitored using $n$-type thermocouples fixed onto the copper sleeves. After $\sim$300 hours of operating time the zinc shot was replenished using an opening in the top of the oven, which was sealed with a plug and copper gasket. The measured interaction chamber pressure was unaffected by operation of the zinc oven, because almost all zinc vapour condensed on surfaces within the chamber before it reached the ion-gauge head. For studies detecting elastically scattered electrons, a 5 mm diameter molybdenum plate connected to the Faraday cup raising/lowering mechanism, described in Section 2.10.3, was used to temporarily block the oven so that the electron signal due to elastic scattering from residual gases and surfaces could be measured.

The majority of the source was constructed from 316-grade stainless steel, with molyb-
Figure 2.16: The metal vapour source, showing (a) stainless steel screw, (b) stainless steel housing, (c) stainless steel oven, (d) copper clamp, (e) molybdenum plug, (f) stainless steel nozzle, (g) molybdenum light shield, (h) copper sleeves with embedded heaters, (i) molybdenum crucible, (j) macor insulation.
2.7. TARGET ATOM SOURCES

Figure 2.17: The performance of the metal vapour source, determined by detection of the 636 nm $4s4d^1D_2 \rightarrow 4s4p^1P_1$ decay photon signal (a) The atomic decay photon signal as a function of oven temperature with the oven shield in place, (b) the detection rate of 636 nm thermal photons produced by the oven as a function of oven temperature for • an unshielded oven, □ with the molybdenum oven shield installed.
Figure 2.18: The zinc vapour collection system, (a) copper, liquid nitrogen cooled zinc collection plate fixed to the turntable top plate, (b) liquid nitrogen reservoir, (c) reservoir stand fixed to the turntable base plate, (d) reservoir vent, (e) reservoir inlet, connected to the self-pressurising dewar. Note that part (a) here is the same as part (f) of Figure 2.3.
molybdenum used for the plug and to line the inside of the oven cavity. Molybdenum was chosen for these parts because it is not reactive with molten zinc [59]. It also has a thermal conductivity of 138 Wm$^{-1}$K$^{-1}$, which is $\sim$8 times greater than that of 316-grade stainless steel [60], and for this reason an earlier version of the source was constructed entirely of molybdenum. However, the thermal conductivity of the oven material was found to be a secondary consideration compared to the quality of the oven-nozzle join. Molybdenum could not be welded using the workshop equipment available because of its high melting point of 2623°C, and its high propensity for forming brittle molybdenum oxide at temperatures above 816°C. Instead, the oven and nozzle were joined using silver solder. This joint deteriorated with exposure to zinc vapour, causing it to leak and become brittle enough after a year of operation to snap during regular maintenance. The welded join between the stainless steel oven and nozzle has not presented this problem.

The metal vapour source was contained inside a stainless steel housing, from which it was thermally isolated by Macor blocks. This housing, as well as a 4 mm diameter cylindrical molybdenum shield extending 3 mm past the nozzle tip, prevented the detection of thermal photons produced by the oven. The detection rate of 636 nm photons thermally produced by the oven before and after the molybdenum oven shield was installed is shown in Figure 2.17. Before installation of the shield, measurements of 636 nm photons from the $4s4d^1D_1 \rightarrow 4s4p^1P_1$ transition, which has the longest wavelength of any photons studied here, were difficult because the thermal photon counting rate was comparable to the decay photon counting rate. However, installing the shield and coating all other potentially reflective surfaces with graphite soot reduced the 636 nm thermal photon counting rate to 10 counts/s at an operating temperature of 500°C. The whole assembly was fixed onto a mounting with in-built position manipulators which allowed the source nozzle to be precisely aligned with the interaction region. The nozzle tip was placed as

Figure 2.19: Cooling of the zinc vapour collection plate from room temperature to the operating temperature of -140°C.
close as possible to the interaction region without the oven shield blocking the entrance aperture to the photon optics.

2.7.3 Zinc Vapour Collection

Once the zinc beam had passed through the interaction region it was critical to collect as much of it as possible because of its degrading effect on the apparatus. For example, the photon signal was reduced by optical lenses becoming zinc-coated, and both the electron guns and electron analyser were made inoperative by zinc deposits on electrical insulators which connected electron lens elements to each other or to ground. To fix these problems the vacuum chamber needed to be opened so that the apparatus could be cleaned, so the rate of zinc deposition onto sensitive elements put an upper limit on the running time of the experiment. The collection system exploited the high sticking coefficient for zinc vapour incident on cold copper surfaces.

The zinc vapour collection system is shown in Figure 2.18. A 140 mm diameter, liquid nitrogen cooled copper plate was placed opposite the oven nozzle to collect zinc vapour. Liquid nitrogen was gravity-fed to the plate from a 6 L internal reservoir filled using an external, self-pressurising 160 L dewar. Both the plate and the reservoir were made as large as possible to minimise boil-off by maximising the volume of liquid nitrogen kept well thermally insulated within the vacuum chamber. Also, maximising the surface area of cold surfaces maximised the overall cryopumping ability of the system. The reservoir was filled and vented via a feedthrough consisting of two 1/4” stainless-steel pipes welded onto a 2 3/4” conflat flange. As shown in Figure 2.19, with the external dewar pressurised to 130 kPa it took 15 minutes to fill the initially room temperature reservoir, and a further 35 minutes for the copper plate to reach its minimum temperature of -140°C. A solenoid valve controlling the flow of liquid nitrogen from the dewar was connected to the mains supply through a timer, which automatically opened the valve for 5 minutes every hour to top-up the reservoir. The cooling system could be operated continuously for 60 hours before the external dewar needed to be re-filled. After the liquid nitrogen cooling system was installed, the maximum running time of the experiment was extended from around 24 hours to 200 hours.

2.7.4 Apparatus Cleaning

Zinc accumulation within the apparatus restricted the total operating time of each data run to ∼200 hours, when one of the many insulators usually had become sufficiently coated in zinc to become conductive. When this occurred, the apparatus was opened to atmosphere and components were cleaned as necessary.

Zinc deposits on metallic elements such as the chamber walls, the turn-tables, the spectrometer shield and the lens cap were removed with a Kim-wipe. Zinc deposition onto these surfaces did not hinder operation of the apparatus, but keeping them as clean as possible prevented zinc flakes from peeling off and lodging in more sensitive areas, such as high-voltage feed-throughs. Also, regular cleaning made it easier to notice oven leaks
through the large increase in general zinc deposition they produced. Windows and lenses were also cleaned with a Kim-wipe, but after being cleaned in this fashion 2 or 3 times these elements no longer collected zinc deposits. Zinc was removed from the collection system using heavy duty Scotch-Brite scourer pads. A vacuum cleaner was used to suction zinc as it was being removed to prevent zinc flakes from peeling off and lodging in sensitive areas, and also to remove stray zinc flakes that had collected in feed-throughs.

Once shorted internally by zinc deposits, the Faraday cup, electron gun and electron analyser were removed from the interaction chamber for cleaning. After these elements were stripped down, zinc was removed from insulators using a scourer pad, and removed from lenses using a Kim-wipe. The elements were then re-assembled and re-aligned using the procedure described in Section 2.9.

Exposure to zinc vapour for more than $\sim 400$ hours caused problems for the Faraday cup raising/lowering mechanism, the internal lens positioning mechanism and the ion gauge head. A small amount of zinc gathered in the mechanisms caused them to jam. This was rectified by resurfacing contacting surfaces with wet-and-dry sandpaper, and applying some molybdenum disulphide dry lubricant. Zinc deposits onto insulators within the ion gauge head caused it to produce erratic pressure readings. As these deposits were not removed easily using abrasives, zinc was removed instead by submerging the ion gauge in a 0.03 mol/L hydrochloric acid solution for 1 minute, then rinsing it thoroughly with water. The acid concentration of this dilute solution was sufficient to remove the reactive zinc, but components of the ion gauge did not react.

A similar amount of zinc vapour exposure also caused problems for the CEM. After several experimental runs, the CEM started to produce $\sim 20000$ counts/s of pulses that were not associated with any source of electrons, such as the electron guns, the ion gauge filament or possible sparks from nearby conducting elements. The noise persisted even when all elements within the chamber except the CEM were grounded. Noise pulses from the CEM viewed using the analogue oscilloscope had the same shape and size as regular signal pulses, so they could not be discriminated out using the CFD. It was only possible to get rid to the noise by reducing the high voltage applied to the CEM, or by letting the CEM rest overnight without any zinc vapour in the vacuum chamber. Since, except in this last aspect, the noise pulses had identical properties to signal pulses, it was thought that they were caused by electron discharge or breakdown in the circuits connected to the CEM, or between the front of the CEM and its grounded metal housing. All cables part of this circuit were exchanged and extra insulation was added around the CEM but this did not get rid of the noise. Finally, the CEM was replaced which fixed the problem, but only in the short term. Given the evidence above, it was hypothesised that current-conducting zinc deposits within the CEM were causing small electron discharges, which were then amplified to produce $\sim 1.3$ V pulses after amplification by the Ortec VT120A pre-amplifier as per the normal operation demonstrated in Figure 2.5. A novel method was used to remove these deposits; ultra-sonically cleaning the CEM in a solution of toothpaste and distilled water, then rinsing it in acetone. Toothpaste contains small particles of silicon...
dioxide, which act as fine abrasive during ultra-sonic cleaning. This approach did in fact succeed in eliminating the noise and extending the CEM working life.

Long term exposure to zinc had a detrimental effect on another two key elements of the experiment, the turn-tables and the interaction chamber turbomolecular pump. In the early stages of the project, before an effective zinc collection device had been installed, the turn-tables became jammed due to zinc deposits in ball-bearing tracks, while the turbomolecular pump overheated and stopped running due to zinc deposits onto blades and bearings. Both elements needed to be removed from the chamber for repairs, which in the case of the turn-tables was especially inconvenient as a comprehensive apparatus realignment, discussed in Section 2.9 was then necessary. They were stripped down, cleaned, re-machined where necessary and re-assembled by a workshop technician, before finally being re-installed in the vacuum chamber.

2.8 Electric and Magnetic Field Minimisation

This experiment investigated electron-atom collisions in a field free region. A field free interaction region makes it simpler to control the incident electron energy and scattering angle accepted by the electron analyser, and the focusing and polarisation vector of the incident electron beam. In addition, external electric and magnetic fields remove the degeneracy of magnetic sub-levels through the Stark and Zeeman effects, and an external magnetic also causes the Hanle effect, where a phase shift between coherently excited atomic magnetic sublevels results in decay radiation depolarisation.

All elements close to the interaction region were grounded to the vacuum chamber, or shielded by a well grounded cover. This included the electron optical elements, which were all contained within grounded shields. The vacuum chamber in turn was grounded to the building’s copper water pipes. No insulating materials were placed close to the interaction region as they may become charged by absorbing electrons or ions.

All components and fixings within the vacuum chambers were made of non-magnetic 316 stainless steel, aluminium, copper, molybdenum, tantalum or ceramics. The Earth’s natural field was reduced inside the vacuum chambers by enclosing them in very high magnetic permeability shields made from 1.5 mm thick mu-metal sheet. These shields were positioned as shown shown in Figure 2.1. Magnetic flux lines pass preferentially through areas of high magnetic permeability, and so volumes enclosed by mu-metal are shielded from external magnetic fields. To remove remnant magnetisation before installation, the shields were heated in a hydrogen atmosphere to a temperature above the mu-metal Curie temperature ($1200^\circ\text{C}$). However, knocks to the shields that were unavoidable during the normal operation of the experiment induced magnetisation, and so it was necessary to periodically demagnetise the shields. This was done by passing 7 A a.c. through a 1 m diameter 78 turn coil placed over the shields. Repeatedly reversing the applied field direction resulted in fewer domains being aligned with the initial magnetisation after each cycle.
The magnitude of the magnetic field inside the lab was measured to be 580 mG using an Applied Physics Systems 520A fluxgate magnetometer, zeroed inside a demagnetised triple layer mu-metal shield. Initially, a field of 11.4 mG was measured in the interaction chamber. This field was countered using external 19 turn Helmholtz coils separated by 500 mm and aligned with the largest component of the field, which was in the direction of the $y$-axis defined in Figure 1.1. A current of 0.84 A in these coils reduced the field inside the chamber to 2.4 mG.

2.9 Alignment of the Apparatus

2.9.1 Turn-Table Alignment

As mentioned in Section 2.7.4 above, at an early stage of the project the turn-tables were removed from the scattering chamber for repair. Once repaired, the turntables were checked to ensure they were running parallel to each other and the fixed turntable base, and that the gas jet tip was at the centre of their rotation. The turntables were then re-installed in the chamber and aligned with the spin source optics. The last lens elements of the spin-polarised gun, marked (j) in Figure 2.6 were re-attached to the turntables and aligned with the interaction region, the position of which was marked 3 mm above the gas jet tip on a drill bit inserted into the gas jet. The vacuum chamber was closed and, by reaching into the chamber through a large open port, the turntables were moved horizontally and raised by inserting shims until a neat fitting brass rod could be pushed through the last spin lenses and into the transport optics. At this point the turn-tables, and therefore the interaction region, were aligned with the spin-polarised electron gun.

2.9.2 Spin Source Laser Alignment

Crystal emission current was strongly dependent on the alignment of the laser, and how well it was focused on the crystal surface. The laser was fixed onto a workbench, and then its lens position was adjusted until light was focused onto a screen placed at the same distance as that between the mounted laser and the crystal. Once mounted, the laser was aligned using position manipulators incorporated into the mounting, shown in Figure 2.6 part (g), which moved the laser in the plane parallel to the crystal surface. Using an Optical Systems FJW spectroscope to view the infra-red beam, the laser was positioned until a beam spot was seen on the crystal surface. This alignment procedure was sufficient to produce photo-electrons from an activated crystal. Once an emission current of 1 $\mu$A was reached during activation, the laser alignment was optimised by making fine adjustments to its position while simultaneously monitoring the emission current.

2.9.3 Electron Spectrometer Alignment

Once the unpolarised electron gun, the last elements of the spin polarised gun or the electron analyser were re-mounted in the vacuum chamber, they were aligned using small
pointed PVC rods that were slid into their ends. Their positions were adjusted until the pointed ends of these rods were aligned with the interaction region, the position of which was marked as above with a drill bit inserted into the gas jet. Their respective mountings permitted left/right position manipulation, and they could be raised or lowered by adding or removing shims. A small spirit level was used to check that the rotatable elements remained parallel to the turntables.

2.9.4 Metal Vapour Source Alignment

Oven alignment was found to be more critical than the alignment of any other element of the experiment, due to the strong influence it had on the observed signal and because, unlike the electron sources with their deflector plates, misalignment could not be compensated for using controls outside the interaction chamber. The oven was also the most often removed and replaced element of the experiment, and so an accurate, simple and repeatable alignment procedure was necessary.

The small diameter drill bit used to align the electron spectrometers was inserted into the gas jet, and another, 1 mm drill bit was inserted into the end of the oven. The oven was then aligned so that these drill bits crossed at the point on the gas jet drill bit marking the interaction region. The oven drill bit was marked in millimetre intervals, making it possible to accurately set the distance from the oven to the interaction region. To assist the collection of the metal vapour beam, the angle between the oven and the scattering plane was made as large as was possible without hitting the photon optics mounted above the interaction region. Larger angles increased the proportion of the zinc beam collected by the plate below the interaction region.

2.9.5 Photon Detection System Alignment

The alignment of the photon detection system was a critical factor affecting photon counting rates. It was essential to have the optical axes of the lenses aligned with each other, the interaction region and the photocathode of the PMT. To ensure this, the internal lens housing was fitted with a screw-on brass cap with the non-threaded end tapered to a sharp point. The internal housing was then moved until the point was directly over the top of the gas jet, and thus aligned with the interaction region. The tapered cap was removed and replaced with a cap having a well centred 0.25 mm aperture. Outside the chamber, two concentric apertures spaced by 150 mm were mounted in place of the PMT and the optical elements, within the assembly used to locate them. The position of this assembly was manipulated until light from a lamp positioned close to the interaction region could be seen to pass through all three apertures.

Lens Optimisation

Figure 2.13 shows the dependence of photon counts on the lenses positions. It was important to accurately position the lenses, because ± 3 mm displacements resulted in 25%
increases/decreases in the signal. First, the external lens was positioned in approximately
the correct position with no other optical elements in place. This was done with the inter-
action chamber open to atmosphere, using a weak light-source placed 1.5 m from the lens
and so producing an approximately parallel beam at the lens. With no other light sources
in the laboratory, the external lens position was adjusted until the photon counting rate
from the PMT was maximised, indicating that the PMT photo-cathode was positioned
approximately at the external lens focal point. With the interaction chamber closed, the
internal lens was placed in approximately the correct position above the gas jet, ± 3 mm,
using a gauge. The interaction chamber was then evacuated, and the internal lens position
adjusted to maximise the atomic decay photon counting rate from helium. Final, small
position adjustments within a ± 2 mm range were made to each lens in turn, until both
lens were at an optimal position.

2.10.1 Photon Excitation Function, Emission Cross Section and Stokes
Parameter Measurements

Studies detecting photons, compared to studies only detecting electrons, more efficiently
isolate products resulting from the excitation of a particular state because of the superior
resolution available using interference filters. For this reason, in the present work, a far
more diverse range of states were investigated in photon detection studies compared to
electron detection studies. For the photon-detection measurements, the electron gun in
use was connected to the CC voltage supply to allow automated control of the incident
electron energy, which was swept up then down across a predefined range. An energy
mesh of 20 or 25 meV was used for the photon excitation function measurements, and
an energy mesh of 1 eV was used for the emission cross section measurements. For high
energy-resolution Stokes parameter measurements an energy mesh of 50 meV was used,
and for low energy-resolution Stokes parameter measurements an energy mesh of 1 eV was
used. The non-atomic decay photon background was measured before the first sweep by
accumulating counts with the incident electron energy below the threshold of the excited
state being investigated. This background was subtracted from the final data. For one
sweep, photon counts at each incident electron energy were accumulated for a total of 8
seconds, with counts being accumulated for 4 seconds on the upwards voltage ramp, and
another 4 seconds on the downwards voltage ramp.

The emission cross section studies measured cross section shapes for incident electron
energies between threshold and 50 eV, and were put on an absolute scale by normali-
sation to the theoretical calculations either of Fursa and Bray [61], or Zatsarinny and
Bartschat [2]. As described in more detail in Chapter 4, during emission cross section
measurements the current collected by the Faraday cup as a function of the incident
electron energy was recorded and used to normalise the data. Where possible, photon
polarisation was measured to account for the spatial distribution of atomic decay photons
using Equation 4.1. The uncertainties which must be considered in these measurements, for example due to variation of zinc oven flux between separate scans, are discussed in Chapter 4.

High energy-resolution photon excitation function measurements were used to characterise threshold behaviour, negative-ion resonance and PCI effects, and were not intended to be put on an absolute scale. In this context the uncertainty in the photon intensity measurements was statistical, and was judged from the precision with which energies could be assigned to the observed features. The energy resolution of these measurements was the same as the the energy resolution of the electron gun in use, that is $\Delta E_g$ for the unpolarised, and $\Delta E_s$ for the spin-polarised electron gun. The specific resolutions and uncertainties in each experiment will be discussed more completely in Chapters 6.

Extensive measurements of the Stokes parameter $P_1$ were undertaken for 636 nm photons from the $4s4d^1D_2 \rightarrow 4s4p^1P_1$ transition in zinc. Also, as mentioned in Section 2.4.4, the Stokes parameter $P_3$ for 480 nm photons from the $4s5s^3S_1 \rightarrow 4s4p^3P_2$ transition was also measured to quantify the polarisation of the spin-polarised electron beam. The method used to measure Stoke parameters which will now be described applies directly to $P_1$. It is the same method as that used to measure $P_2$ and $P_3$, with two exceptions. First, for $P_2$ the intensities $I_{45^\circ}$, $I_{135^\circ}$ were measured and for $P_3$ the intensities $I_{\sigma^+}$ and $I_{\sigma^-}$ were measured, using the LCVR orientations described in Section 2.5. Second, during a sweep the photon polarisation was measured first with spin-up incident electrons, then spin-down incident electrons, at each point on the incident electron energy mesh.

The intensity and polarisation of the photon background was measured before starting a Stokes parameter scan. This was done by reducing the incident electron energy below threshold, then accumulating photon counts for 10 seconds for each decay photon polarisation orientation. The background intensities for each photon polarisation orientation were $I_{\text{back},0^\circ}$ and $I_{\text{back},90^\circ}$. During a Stokes parameter sweep, the software set the beam energy, set LCVR retardance to measure $I_{0^\circ}$, let the system settle for 0.5 s, then accumulated counts for 4 seconds. The software then changed the LCVR to measure $I_{90^\circ}$, allowed the system to settle again, then accumulated and recorded counts for another 4 seconds. The incident electron energy was then stepped, and the process was repeated. The individual sweeps were summed to obtain the raw total intensities $I_{\text{raw},0^\circ}$ and $I_{\text{raw},90^\circ}$, at each incident electron energy on the mesh. The background intensities $I_{\text{back},0^\circ}$ and $I_{\text{back},90^\circ}$ were subtracted from these raw intensities to give

$$I_{0^\circ} = I_{\text{raw},0^\circ} - \frac{t}{10} I_{\text{back},0^\circ}$$
$$I_{90^\circ} = I_{\text{raw},90^\circ} - \frac{t}{10} I_{\text{back},90^\circ}$$

where $t$ was the total accumulation time of $I_{\text{raw},0^\circ}$ and $I_{\text{raw},90^\circ}$, and the background counts were accumulated for 10 seconds. $P_1$ was then calculated from $I_{0^\circ}$ and $I_{90^\circ}$ using Equation 1.11. Stoke parameters are a ratio of intensity measurements, and so self-normalise to variations in experimental conditions such as beam current, optics transmission and target atom flux. The total uncertainty in $P_1$ comes from combining counting measurements $I$...
with statistical uncertainties given by $\Delta I = \sqrt{I}$. If the statistical uncertainty in $I_{0^\circ}$ is $\Delta I_{0^\circ}$, and the statistical uncertainty in $I_{90^\circ}$ is $\Delta I_{90^\circ}$, then

$$
\Delta I_{0^\circ} = \sqrt{I_{raw,0^\circ} + \frac{t}{10} \sqrt{I_{back,0^\circ}}} \quad (2.8)
$$

$$
\Delta I_{90^\circ} = \sqrt{I_{raw,90^\circ} + \frac{t}{10} \sqrt{I_{back,90^\circ}}} \quad (2.9)
$$

(2.10)

the uncertainty in $P_1$, $\Delta P_1$, is

$$
\Delta P_1 = \left| \frac{dP_1}{dI_{0^\circ}} \right| \cdot \Delta I_{0^\circ} + \left| \frac{dP_1}{dI_{90^\circ}} \right| \cdot \Delta I_{90^\circ}
$$

$$
= \frac{2}{(I_{0^\circ} + I_{90^\circ})^2} \left( I_{90^\circ} \Delta I_{0^\circ} + I_{0^\circ} \Delta I_{90^\circ} \right) \quad (2.11)
$$

This formula was used to calculate the Stokes parameter uncertainties referred to throughout this thesis.

### 2.10.2 Electron Energy Loss Spectroscopy

For electron energy loss spectroscopy, the intensity of scattered electrons is measured as a function of residual energy, with the incident electron energy and observed scattering angle fixed. An energy loss spectrum shows which scattering processes can be isolated in the electron detection channel, and also their relative cross sections. An electron energy loss spectrum was also used to determine the electron analyser potential settings needed to detect either elastically scattered electrons, or inelastically scattered electrons associated with a particular state of interest. For this purpose, taking an electron energy loss spectrum was a necessary precursor to the other electron detection studies conducted here.

The incident electron energy was kept constant by disconnecting the electron gun from the CC supply. The electron analyser was set at a particular angle, and connected to the CC voltage supply to allow automated control. Sweeps across a predefined scattered electron residual energy range were conducted in the same manner as for the photon excitation functions. The data obtained was displayed as a function of $E_{loss}$, which is related to the incident electron energy $E_{in}$ and the scattered electron residual energy $E_{res}$ by

$$
E_{loss} = E_{in} - E_{res} \quad (2.12)
$$

This transformation is made so that peaks in the spectrum are at the energy of their corresponding excited state. For example, a peak at 5.796 eV in a zinc electron energy loss spectrum will be due to scattered electrons that have excited the $4s4p^1P_1$ state.

The FWHM energy resolution of these measurements depends on both the electron gun resolution $\Delta E_g$ and the electron analyser resolution $\Delta E_a$ through the relationship [62]

$$
\Delta E_{1/2} = \sqrt{\Delta E_g^2 + \Delta E_a^2} \quad (2.13)
$$

which is expected for the convolution of two Gaussian distributions with FWHMs of $\Delta E_g$ and $\Delta E_a$.  


2.10.3 Differential Cross Sections, Electron Excitation Functions, and Spin Asymmetry Measurements

Some differential cross section measurements using argon targets were conducted to test the angular response of the electron analyser and to calibrate its angular position. These studies are detailed in Section 3.1. The data was collected by fixing the incident electron energy and the observed scattered electron residual energy, then measuring the electron intensity as a function of scattering angle. There was no automated control of the electron analyser position.

Electron excitation function measurements were used to observe the scattering angle dependence of negative-ion resonance profiles. Elastic scattering was also investigated using the electron excitation function method, but since the atom was not left in an excited state these are referred to here as angle differential elastic scattering signal measurements. Data was obtained with the electron analyser at a fixed angle, and with the electron gun and analyser both connected to the CC supply to allow the incident electron energy, $E_{\text{in}}$, and the residual energy of the detected electrons, $E_{\text{res}}$, to be scanned together. The apparatus was operating in “constant energy loss” mode, as can be seen from Equation 2.12, and so measured a quantity proportional to the incident electron-energy dependent, differential cross section for elastic scattering or for exciting a particular state. Sweeps across a predefined incident electron energy range were conducted in the same manner as for photon excitation function measurements, and an energy mesh of either 20 meV or 25 meV was used.

The scattered electron background was measured and subtracted from the raw data. For inelastic scattering studies, the background was estimated by measuring the energy loss peak of the state of interest at a number of incident electron energies within the range studied. The signal in the wings of the energy loss peak was taken to be the scattered electron background present at a particular incident energy. The background was assumed to vary slowly and smoothly with energy, and so the electron backgrounds at other energies within the range studied were interpolated from these measurements. For elastic scattering this method was unreliable because it did not account for elastic scattering from surfaces and residual gases. Instead, the background was measured by operating the apparatus in the constant energy loss mode, with electron counts measured as a function of incident energy, without a target atom beam present. For the helium study detailed in Section 3.2, the target atom beam was stopped by shutting off the external leak valve shown at Figure 2.1 part (h). For zinc studies, a small strip of molybdenum, placed 4 mm in front of the oven nozzle, was raised to block the target beam. The molybdenum strip was connected to the Faraday cup raising/lowering mechanism, which allowed it to be moved from outside the chamber.

The FWHM energy resolution of electron excitation functions depends on the electron gun energy resolution $\Delta E_g$ and the electron analyser $\Delta E_a$, and is given by [62]

$$\Delta E_{1/2} = \frac{\Delta E_g \Delta E_a}{\sqrt{\Delta E_g^2 + \Delta E_a^2}}$$  (2.14)
which is what is expected for the multiplication of two Gaussian distributions with FWHMs of $\Delta E_g$ and $\Delta E_a$. This relationship has also been applied above to the case where the electron energy distribution obtained from the unpolarised and spin-polarised electron sources was narrowed by a 127° cylindrical or 180° hemispherical energy selector. As for photon excitation functions, the uncertainty in electron intensity measurements was statistical and best judged from the precision with which energies could be assigned to the observed features. The specific energy resolutions and uncertainties in each experiment will be discussed more completely in Chapters 5 and 7.

The method for obtaining spin asymmetries was almost the same as that used to obtain electron excitation functions, except that during a sweep the scattered electron intensity at each point in the energy mesh was measured first with incident spin-up electrons, then with incident spin-down electrons. Summing multiple scans gave the raw total intensities $I_{\text{raw,}↑}$ and $I_{\text{raw,}↓}$. The electron backgrounds for incident spin-up and spin-down electrons were measured separately using the method described for electron excitation functions. The measured background counts $I_{\text{back,}↑}$ and $I_{\text{back,}↓}$ were accumulated for 60 seconds. These background intensities were subtracted from the raw total intensities to give

$$I↑ = I_{\text{raw,}↑} - \frac{t}{60}I_{\text{back,}↑} \quad (2.15)$$
$$I↓ = I_{\text{raw,}↓} - \frac{t}{60}I_{\text{back,}↓} \quad (2.16)$$

where $t$ was the total accumulation time of $I_{\text{raw,}↑}$ and $I_{\text{raw,}↓}$, and the background counts were accumulated for 60 seconds. $S_A$ was then calculated from $I↑$, $I↓$ and the measured incident spin-polarisation $P_e = 0.287 \pm 0.004$, using Equation 1.9. The total statistical uncertainty in the asymmetry $A$ comes from combining counting measurements $I$ each with statistical uncertainties $\Delta I = \sqrt{I}$. It the statistical uncertainty in $I↑$ is $\Delta I↑$, and the statistical uncertainty in $I↓$ is $\Delta I↓$, then

$$\Delta I↑ = \sqrt{I_{\text{raw,}↑}} + \frac{t}{60}\sqrt{I_{\text{back,}↑}} \quad (2.17)$$
$$\Delta I↓ = \sqrt{I_{\text{raw,}↓}} + \frac{t}{60}\sqrt{I_{\text{back,}↓}} \quad (2.18)$$

The uncertainty in $A$, $\Delta A$ is

$$\Delta A = \left| \frac{dP_e}{dI↑} \right| \cdot \Delta I↑ + \left| \frac{dP_e}{dI↓} \right| \cdot \Delta I↓$$
$$= \frac{2}{(I↑ + I↓)^2} \left( I↑ \Delta I↑ + I↓ \Delta I↓ \right) \quad (2.19)$$

and it was this value that was used to judge the statistical accuracy of the data. Since $S_A = A/P_e$, the uncertainty $\Delta S_A$ also affected by the uncertainty $\Delta P_e = 0.004$. So,

$$\Delta S_A = \left| \frac{dS_A}{dA} \right| \cdot \Delta A + \left| \frac{dS_A}{dP_e} \right| \cdot \Delta P_e$$
$$= \frac{1}{P_e} \cdot \Delta A + \frac{A}{P_e^2} \Delta P_e$$
$$\simeq \frac{1}{P_e} \cdot \Delta A + O(10^{-3}) \quad (2.20)$$

This formula was used to calculate the asymmetry function uncertainties referred to throughout this work.
A series of studies were conducted to verify and assess the apparatus performance and to enable zinc studies to commence. The studies included argon differential cross section measurements and helium differential elastic scattering measurements. These were conducted to assess the energy-dependent transmission of the unpolarised electron gun and electron analyser, and the angular response of the electron energy analyser. A coincidence experiment was also conducted using helium to determine the feasibility of conducting this type of experiment with the present apparatus. Before the zinc studies commenced, an accurate energy calibration technique was found, checks made to ensure no atomic beam-density dependent effects were present, and electron energy loss spectra were taken to determine which excited states could be resolved in the scattered electron channel.

3.1 Argon Differential Cross Section

Elastic differential cross sections for argon were measured between 20° and 110°, at incident electron energies of 10 eV, 20 eV and 40 eV. These measurements were compared with the previous experimental studies of Williams and Willis [63], Panajotović et al. [64], Srivastava et al. [65] and DuBois and Rudd [66], and the theoretical Relativistic Distorted Wave (RDW) calculations of McEachran [67]. The results of the present and previous studies are shown in Figure 3.1, with the present measurements placed on an absolute scale by normalising to the theoretical calculations at 40°. The present elastic differential cross section measurements served two purposes. First, they allowed the angular resolution and angular response of the electron analyser to be checked. Second, it permitted the electron analyser angle to be calibrated using the sharp dip in argon elastic differential cross section near 68° which is present at an incident electron energy of 40 eV.

The present data was taken with an incident beam current of 500 nA and an argon partial pressure of $5 \times 10^{-6}$ Torr, which resulted in an electron counting rate of 30000 counts/s at 20°. The present data in Figure 3.1 are the combination of three scans taken on separate days. In each scan, the electron counts at each scattering angle were accumulated
Figure 3.1: Argon Elastic Differential Cross Sections at (a) 10 eV incident electron energy, (b) 20 eV incident electron energy and (c) 40 eV incident electron energy; • present data, □[63], × [64], + [65], △ [66], — Relativistic Distorted Wave calculations of [67]. The present data is normalised to the theory at 40°, and the uncertainty is within the data markers.
Figure 3.2: Phase shift analysis of the 10 eV argon elastic differential cross section, with □ the present data, — phase shift fit. At the bottom are $\chi^2$ surface and contour maps used to find the optimal fit parameter values.
for two minutes. The scattered electron background was measured at each angle and for each scan using the method described in Section 2.10.3, and subtracted from the raw final data.

There is an obvious deviation of the present study from theory and previous experiments in the vicinity of the sharp angular structures in Figure 3.1 due to differences in angular resolution. For example, the 40 eV differential cross section measured by [63] is 406 times larger at 40° than at it is at 68°. The present 40 eV differential cross section is only 30 times larger at 40° than at it is at 68°. The greatest angular acceptance of all the other studies presented in Figure 3.1 was ±1°. As discussed in Section 2.3, from purely geometric considerations the angular acceptance of the present electron analyser was approximately ±2°. The effective acceptance angle may have been greater because the lens effects of the electron-optics, and also because of scattering from the inside surface of nose cones which were placed in front of the electron analyser entrance aperture to prevent zinc vapour from entering. However, the high angular resolution of, for example, Williams and Willis was unnecessary for the planned zinc studies which aimed to uncover structures with a sharp energy dependence, but not necessarily a sharp angular dependence. Angular resolution was a less important consideration than energy resolution, rapid data accumulation and apparatus protection. The present resolution was sufficient to calibrate the electron analyser angle to ±2° and determine the partial wave contribution to negative-ion structures, and this was all that was required.

To quantify the shape of the present differential cross sections and thus the angular response of the electron analyser, a phase shift analysis was conducted for the present data and the results compared with those presented by Williams [68]. The theory of phase shift analysis is presented in more detail by Mott and Massey [69]. If the incident electron spin-dependent effects are negligible, as they should be in the case of the argon scattering processes observed here, then the differential elastic cross section is given by

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2$$  \hspace{1cm} (3.1)

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l + 1) \left[ \exp(2i\eta_l) - 1 \right] P_l(\cos \theta)$$  \hspace{1cm} (3.2)

where $f$ is the scattering amplitude, $k$ is the wavenumber of the incident electron, $P_l$ are Legendre polynomials and $\eta_l$ are scattering phase shifts. A phase shift analysis determines these phases from experimental differential cross sections by a least squares fitting procedure. The phases can also be calculated using, for example, the first Born approximation, which is accurate for the higher partial waves which do not penetrate the inner part of the atom and thus only experience its long-range dipole field. For elastic scattering from argon at incident electron energies of 10 eV, 20 eV and 40 eV, only the $\eta_0$, $\eta_1$, $\eta_2$ and $\eta_3$ phase shifts need to be determined from the data, because the phase shifts for the higher partial waves are accurately calculated using the Born approximation [68]. Phase shifts were fitted using the function

$$2ikf(\theta) = c_L(\theta) + \sum_{l=0}^{L} (2l + 1) \left[ \exp(2i\eta_l) - 1 \right] P_l(\cos \theta)$$  \hspace{1cm} (3.3)
3.1. ARGON DIFFERENTIAL CROSS SECTION

with

\[ c_L(\theta) = 2i\pi\alpha k^2 \left[ \frac{1}{3} - \frac{1}{2} \sin \frac{\theta}{2} - \sum_{l=1}^{L} \frac{1}{(2l+3)(2l+1)} P_l(\cos \theta) \right] \]  

(3.4)

where phase shifts are determined for the first \( L \) partial waves, and \( c_L \) gives the contribution to the cross section from partial waves greater than \( L \) as calculated using the first Born approximation. Strictly speaking, phase shifts only have physical significance below the first inelastic excitation threshold, which for argon is 11.548 eV, where the elastic scattering amplitude can be expanded into angular momentum components. However, phase shift analysis is a useful method by which a differential cross section shape can be characterised, as has been done here.

Equation 3.4 was fitted to the experimental data using the non-linear, least-squares Marquardt-Levenberg algorithm fitting function of the GNUPLOT program. Appropriate parameter starting values were determined by calculating \( f(\theta) \) across a grid of values of \( \eta_0 \) and \( \eta_1 \), with all other phase shifts those given by the Born approximation. The \( \chi^2 \) variance between these trial cross sections and the experimental data was calculated for each \( \eta_0 \) and \( \eta_1 \) combination using a FORTRAN program, and plotted as a surface in GNUPLOT. The \( \eta_0 \) and \( \eta_1 \) values which produced the global minima in this plot were used as starting values for the fitting procedure, while the starting points for the other parameters were their values calculated using the Born approximation.

Phase shifts were obtained for the present argon data, and also to the data of Williams [68] to check the fitting method. The result of the phase shift analysis for 10 eV incident electron energy is shown alongside the present data in Figure 3.2, and the present phase shift analysis results is compared with those of Williams in Table 3.1. The best agreement is for the 10 eV differential cross section, where there are no sharp angular features, and so there is no difference due to the better angular resolution of the previous experiment. For 10 eV, \( \eta_1, \eta_2 \) and \( \eta_3 \) agree within the error of the fit. There is disagreement between the \( \eta_0 \) phases, because the two experimental data sets were differently normalised. From this analysis it was concluded that the angular response of the electron analyser was acceptable.

Table 3.1: A comparison between the present phase shift analysis results, and those of [68]

<table>
<thead>
<tr>
<th>Phase Shift</th>
<th>10eV Present</th>
<th>[68]</th>
<th>20eV Present</th>
<th>[68]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_0 )</td>
<td>-1.18 ± 0.03</td>
<td>-1.098 ± 0.02</td>
<td>-1.56 ± 0.02</td>
<td>-1.70 ± 0.05</td>
</tr>
<tr>
<td>( \eta_1 )</td>
<td>-0.54 ± 0.02</td>
<td>-0.528 ± 0.01</td>
<td>-0.88 ± 0.02</td>
<td>-1.07 ± 0.04</td>
</tr>
<tr>
<td>( \eta_2 )</td>
<td>0.92 ± 0.02</td>
<td>0.936 ± 0.08</td>
<td>1.83 ± 0.07</td>
<td>1.41 ± 0.05</td>
</tr>
<tr>
<td>( \eta_3 )</td>
<td>0.13 ± 0.02</td>
<td>0.093 ± 0.02</td>
<td>0.40 ± 0.04</td>
<td>0.12 ± 0.02</td>
</tr>
</tbody>
</table>
Figure 3.3: Elastic electron excitation function measurements of the $1s2s^2 2S_{1/2}$ negative-ion resonance in helium, showing both the present measurement and the previous measurements of [70]. The present data have been normalised to those previous measurements.
3.1. ARGON DIFFERENTIAL CROSS SECTION

Figure 3.4: The three stages of the negative-ion resonance fitting procedure; (a) Background interpolation, • observed total signal, − interpolated background; (b) • resonance contribution, − fitted Shore parametrisation function; (c) • observed total signal, − fitted Fano function.
3.2 Helium Differential Elastic Scattering Study

The performance of the apparatus when operating in the electron excitation function mode was tested by repeating measurements of the helium $1s2s^22^S_{1/2}$ negative-ion resonance at 19.366 eV conducted by Brunt et al. [70]. The differential elastic scattering signal was measured at scattering angles between 33° and 100°, and these measurements are shown alongside the previous work in Figure 3.3. The energy resolution of the present study was $\Delta E_{1/2} = 120$ meV.

For an isolated negative-ion resonance, like the $1s2s^22^S_{1/2}$ helium negative-ion resonance, the resonance energy, apparent width, and interference parameter $q$ can be determined by fitting a Fano-profile, given by Equation 1.5, to the data. The following procedure was used to fit a Fano-profile to the $1s2s^22^S_{1/2}$ helium negative-ion resonance, and isolated negative-ion resonances which were observed in electron scattering from zinc.

The observed negative-ion resonance profile depends on the shape of the non-resonance background, and so to obtain accurate resonance parameters it is necessary to fit both simultaneously. However, the negative-ion resonance profile and the non-resonance background were separately fitted at first to determine appropriate parameter starting values for the final combined fit. The non-resonance contribution to the signal was estimated by fitting a polynomial function to the wings of the resonance. The order of the fitted polynomial function was that which minimised $\chi^2$ without the error of the fitted coefficients exceeding 10%. This interpolated background was then subtracted from the data, to isolate the resonance contribution.

Next, the isolated resonance contribution was fitted using the Shore parametrisation [71]

$$\sigma_r = \frac{a\varepsilon + b}{1 + \varepsilon^2}$$

(3.5)

where $\sigma_r$ is the resonance signal, $a$ and $b$ are shape parameters and

$$\varepsilon = \frac{2(E - E_r)}{\Gamma}$$

(3.6)

where $E_r$ is the resonance energy and $\Gamma$ the apparent resonance width. The Shore parametrisation was used because it does not include a non-resonance contribution. The final fit, to the combined resonance and non-resonance signal, used the Fano equation [25], given in Chapter 1 but repeated here

$$\sigma = \sigma_o + \sigma_r \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$$

(3.7)

where $\sigma_o$, $\sigma_r$ and $\sigma$ are the non-resonance, resonance contributions and total cross sections. A polynomial function was used to fit $\sigma_o$, and the starting parameters for this polynomial function were those obtained from the non-resonance signal fitting described above. The starting value for the $q$ shape parameter was determined from $a$ and $b$ by

$$q = \frac{b \pm \sqrt{a^2 + b^2}}{a}$$

(3.8)
and \( \text{sign}(q) = \text{sign}(a) \), and the starting values of \( E_r \) and \( \Gamma \) were values of these parameters determined from the Shore parametrisation fit. The various stages of the fitting procedure are shown in Figure 3.4.

Table 3.2: A comparison the resonance parameters for the \( 1s^2s^2 2S_{1/2} \) negative-ion resonance in helium obtained from the present data, and from the data of [70]

<table>
<thead>
<tr>
<th>Angle</th>
<th>Present</th>
<th>[70]</th>
</tr>
</thead>
<tbody>
<tr>
<td>33°</td>
<td>( q = 0.89\pm0.03 )</td>
<td>( q = 0.717\pm0.04 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma = 117\pm4 \text{ meV} )</td>
<td>( \Gamma = 22\pm2 \text{ meV} )</td>
</tr>
<tr>
<td>54°</td>
<td>( q = 0.61\pm0.01 )</td>
<td>( q = 0.53\pm0.01 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma = 115\pm2 \text{ meV} )</td>
<td>( \Gamma = 21\pm1 \text{ meV} )</td>
</tr>
<tr>
<td>70°</td>
<td>( q = 0.41\pm0.02 )</td>
<td>( q = 0.31\pm0.03 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma = 112\pm3 \text{ meV} )</td>
<td>( \Gamma = 26\pm2 \text{ meV} )</td>
</tr>
<tr>
<td>90°</td>
<td>( q = 0.20\pm0.01 )</td>
<td>( q = 0.04\pm0.04 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma = 120\pm4 \text{ meV} )</td>
<td>( \Gamma = 23\pm2 \text{ meV} )</td>
</tr>
<tr>
<td>100°</td>
<td>( q = -0.03\pm0.02 )</td>
<td>( q = -0.07\pm0.03 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma = 112\pm4 \text{ meV} )</td>
<td>( \Gamma = 25\pm2 \text{ meV} )</td>
</tr>
</tbody>
</table>

The results of Fano-profile fits to the present data and those of Brunt et al. [70] are presented in Table 3.2. As can be seen from Figure 3.3, the present experiment is able to reproduce the angle-dependent negative-ion resonance shapes apparent in Brunt et al.. This is also demonstrated in Table 3.2, where the \( q \) values obtained from both data sets are of similar magnitude, decrease with increasing angle and become negative at 100°. The 20 meV resolution of the previous experiment was significantly better than the 120 meV resolution of the present experiment, and this was reflected in the discrepancy between the resonance widths obtained. The authors of the previous work state that the current of their incident beam was less than 1 nA. However, in zinc experiments the operating time is restricted, so low currents are not ideal for obtaining data with sufficiently small statistical uncertainty. The present measurements indicate that even with a 120 meV energy resolution the present apparatus was able to characterise the angle-dependent behaviour of negative-ion resonances. When the present study of the helium \( 1s^2s^2 2S_{1/2} \) negative-ion resonance was undertaken, a resolution of 120 meV was the best that the apparatus could achieve. Further tuning over the course of months obtained the better energy resolution demonstrated in the work presented in Chapters 5-7.

### 3.3 Coincidence Measurements

The coincident detection of electrons and photons originating from the same scattering event is a powerful experimental technique. Photon measurements are not integrated over all scattering angles, and so through analysis of their polarisation or spatial-distribution one can directly measure the angle-dependant scattering amplitudes, which are the fun-
Figure 3.5: Time spectra taken during preliminary coincidence measurements. (a) Time spectrum for the 1s3d^1D_2 state of helium excited by 40 eV scattered through 40°, showing the fit to the data of Equation 3.9. (b) A random spectrum taken to ensure instrumental artefacts were not present. The solid line is the a linear fit to the spectrum, the dashed line is mean counts per channel.
damental quantities by which the scattering event is described. Particular excited states are more easily resolved than in studies detecting only scattered electrons, because an interference filter is used. The coincidence technique can therefore be used to measure differential cross sections, electron excitation functions and spin asymmetry functions for states which cannot be resolved in an electron energy loss spectrum. However, counting rates in electron-photon coincidence experiments are generally less than 20 counts/s, which makes them extremely time-consuming compared to the types of measurements described above. A preliminary coincidence study of the $1s3s{^1}D_2$ state of helium excited by 40 eV incident electrons was conducted to see if the present apparatus was suitable to conduct a coincidence experiment for zinc.

For this coincidence study, the photon and electron signal pulses were processed in the same manner described in Section 2.6.2, until after the CFD. After this point the signal with the lower counting rate was used to provide the START signal of a Time-to-Amplitude Converter (TAC). The other signal was passed through a delay. In the present study, where the state lifetime was 16.7 ns, a delay of 100 ns was used. The delayed signal provided the TAC STOP signal. Pulses from the TAC, which have an amplitude directly proportional to the time separation between the START and STOP pulses, were height analysed using an Ortec Multichannel Buffer (MCB) and Maestro software. The resulting information was displayed as a histogram, an example of which is shown in Figure 3.5.

Given the time required to obtain a statistically significant coincidence spectrum can be on the order of days, it is especially important to verify the performance of the electronics and software used, to ensure time is not wasted obtaining a spectrum influenced by instrumental effects. The measures taken to verify the electronics were also used in non-coincidence studies are discussed in Section 2.6.2. For the coincidence electronics, output pulses from the PMT were used to provide both the START and the STOP signal, with the STOP pulse delayed relative to the START pulse. Using an oscilloscope, the TAC output pulses were verified as being positive square pulses with a width of 10 $\mu$s and a height up to 10 V directly proportional the STOP pulse delay applied in accordance with the manufacturers specifications. Keeping this set-up, the MCB/Maestro software combination was tested to ensure that the time separation between the START and STOP pulses was the same as that displayed, and that all PMT pulses were counted. Lastly, a spectrum was obtained using completely uncorrelated signals to provide the START and STOP pulses, in this case PMT signals from the present and a completely separate apparatus. This produced the spectrum shown in Figure 3.5b along with the a linear fit to the data. The background is not perfectly flat, and as a result the line of best fit varies by $\pm 0.2\%$ across the spectrum. However, the slope was within the 0.5% standard deviation of the data and so was considered to be acceptable.

A coincidence spectrum was measured for excitation of the $1s3d{^1}D_2$ state of helium. Inelastically scatted electrons with an energy loss of 23.07 eV were detected at a scattering angle of 40° in coincidence with 667 nm photons from the $1s3s{^1}D_2 \rightarrow 1s2p{^1}P_1$ transition. The incident electron energy was 40 eV, and the target gas partial pressure was $3 \times$
10^{-6} \text{Torr. The electron and photon signals were approximately 4000 counts/s and 1500 counts/s respectively, which generated TAC pulses at a rate of around 1 per second. The resulting spectrum shown in Figure 3.5 was obtained over 100 hours. In the previous 1s3d^1D_2 state coincidence experiment of Cvejanović et al. [72], spectra with much better statistical accuracy were obtained in around 24 hours. Fitted to the data is the function given by Gale [73]

\[
Y(t) = A + B \left[ \left( 1 + \text{erf} \left( \frac{ht - \frac{1}{2h\tau}}{\sqrt{2}} \right) \right) \exp \left( \frac{-t^2}{4h^2\tau^2} \right) \right]
\]  

(3.9)

which results from the convolution of a gaussian apparatus function with the exponentially decaying curve which describes the probability for a state with a radiative lifetime \(\tau\) emitting a photon at time \(t\). \(A\) and \(B\) describe the size of the background and the peak respectively, and \(h\) is the standard deviation of the gaussian apparatus function. The fit yielded a lifetime \(\tau\) of 18.7\pm1.1 \text{ ns} which is slightly higher than the accepted lifetime of 16.7\pm0.8 \text{ ns} [74]. Also, the signal to noise ratio in this spectrum of 1.4, calculated integrating the signal and noise contributions under the peak in Figure 3.5a, suggests that significant optimisation is required before the present apparatus can be used to perform any coincidence studies. It was decided that coincidence studies should not proceed for two reasons. First, pilot photon and electron excitation studies had already been conducted, and had revealed a great deal of interesting phenomena which could be investigated more efficiently using non-coincidence techniques. Second, the use of zinc targets and the associated restriction on experimental running times for the present experiment were unfavourable for a coincidence study of this atom.
3.4 Initial Zinc Measurements

3.4.1 Energy Calibration

The incident electron energy was calibrated using photon excitation function measurements of the zinc 4s4d$^1D_2$ state, which has a step-like cross section at its threshold. Photon excitation functions measured around the 4s4d$^1D_2$ state threshold at 7.744 eV were fitted with the theoretical, BSRM integral cross section of Zatsarinny and Bartschat [2], convoluted with a Gaussian experimental apparatus function accounting for the finite experimental energy resolution. The parameters of this fit were the energy difference between the theory and the uncalibrated experiment, the FWHM width of the Gaussian apparatus function, and the normalisation factor required to bring the photon excitation function onto an absolute scale. Both the energy difference, and the energy width were determined to within an accuracy of ±10 meV. In the example calibration shown in Figure 3.6, the electron beam resolution was 80 meV. Calibrations were performed before and after each individual experimental study, then averaged to account for energy drifts, which have been found to occur in metal vapour studies [75]. The average difference between before and after calibrations was 20 meV, and so the energy uncertainty due to energy drifts is estimated as ±10 meV, but the exact energy calibration error for each individual experimental study will be detailed separately in each of the Chapters 4-7. These energy drifts resulted in the nominal energy resolution of the apparatus being better than that which was apparent in the data. Again, the exact energy resolution for each study will be detailed in the chapters that follow.

3.4.2 Checks for Atomic Beam Density Effects

If the target atom beam is too dense the probability of effects such as radiation trapping, collisional depolarisation or multiple electron scattering may become significant. Radiation trapping occurs if radiation emitted in the decay of an excited atomic state is reabsorbed by a nearby atom. In an experiment such as the present, where atoms in the beam are almost entirely in the ground state, radiation trapping is most likely to effect studies of states with a direct transition to ground and a large photon excitation cross section, for example the 4s4p$^1P_1$ state of zinc. Radiation trapping will modify the observed decay photon polarisation, and the apparent radiative lifetime of an affected state, measured using coincidence techniques, will be longer than the actual lifetime. If an electron-impact excited atom subsequently collides with another atom, the additional energy and momentum transfer process will modify the excited state wavefunction and may result in de-excitation without photon emission. This leads to a decrease in intensity and a “collisional depolarisation” of the photon signal with increasing beam density.

In zinc studies the atomic beam density was controlled by the oven temperature, and so measurements of photon intensity and polarisation as a function of oven temperature were used to test whether the types of processes outlined above were affecting the present study. These measurements of the intensity of 214 nm photons from the 4s4p$^1P_1 \rightarrow 4s^2^1S_0$
transition and the intensity and polarisation of 636 nm photons from the \(4s4d^1D_2 \rightarrow 4s4p^1P_1\) transition across the oven operating temperature range are shown in Figure 3.7. A decrease in the photon polarisation with increasing oven temperature, which is indicative of collisional depolarisation, was not detected. Neither was a change in the ratio of 636 nm to 214 nm photon intensities, which one might expect if \(4s4p^1P_1\) state excitation was affected by radiation trapping.

Photon excitation function measurements of the \(4s4p^3P_1\) state of zinc, which are detailed in Section 6.1.1, revealed a sharp increase in the intensity of decay photons around an incident energy of 8 eV. This energy is roughly twice the 4.003 eV energy of the lowest, \(4s4p^3P_0\) excited state. The BSRM calculations of Zatsarinny and Bartschat [2] indicate that near-threshold excitation of the \(4s4p^3P_{0,1,2}\) states has the largest cross section of any inelastic electron scattering process in zinc, so it was suspected that the observed enhancement was due to the onset of double scattering. If double scattering were significant, so too would be the probability that a single incident electron could result in the detection of two 307 nm photons. The probability of a single scattering event occurring is proportional to the atomic beam density, so the probability for a double scattering event occurring is proportional to the atomic beam density squared. Thus, if double scattering were responsible for the peak, the peak’s size relative to the below 8 eV region would increase linearly with increasing beam density. The double scattering hypothesis was tested by remeasuring the photon excitation function for a range of different oven temperatures. Figure 3.8
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Figure 3.8: A test for double electron scattering, detecting 307 nm photons from the $4s4p^3P_1 \rightarrow 4s^2 1S_0$ transition with an oven temperature of (a) 450°C and (b) 520°C. The ratios displayed indicate that double scattering was insignificant.
Figure 3.9: An example zinc electron energy loss spectrum, taken at a scattering angle of 30° and an incident electron energy of 10 eV. Also shown are the energies of the 4s4l, n = 4, 5, 6 l = s, p, d states.

shows that as the oven temperature was increased the 8 eV peak grew in proportion to the rest of the spectra, and so double scattering was not its cause. Given the cross sections calculated by Zatsarinny and Bartschat [2], if, within range of the oven temperatures used, double scattering was insignificant for 4s4p3P1 excitation at 8 eV incident energy, then it was almost certainly insignificant for all other inelastic processes.

3.4.3 Electron Energy Loss Spectroscopy

Figure 3.9 shows a zinc electron energy loss spectrum taken at a scattering angle of 30° and an incident electron energy of 10 eV, along with the energies of the 4s4l, n = 4, 5, 6 l = s, p, d states. The strongest contribution is due to the 4s4p1P1 state at 5.797 eV, followed by the contributions from the 4s4p3P0,1,2 states. The other two peaks in this spectrum contain overlapping contributions from several excited states. The lower energy peak near 7.74 eV has contributions from the 4s4d1D2, 4s4d3D1,2,3, 4s5p1P1 and 4s5p3P0,1,2 states, and the peak near 8.49 eV has contributions from the 4s5d1D2, 4s5d3D1,2,3, 4s6p1P1 and 4s6p3P0,1,2 states.

A least squares, Gaussian fit to the 4s4p1P1 peak in Figure 3.9 determined the energy resolution during this particular scan to be $\Delta E_{1/2} = 275$ meV. This was sufficient to isolate the 4s4p3P0,1,2 and 4s4p1P1 states, but insufficient to resolve other states or the J levels of 4s4p3P0,1,2. The best unpolarised electron gun and electron analyser resolutions achieved in the present experiment were $\Delta E_g = 80$ meV and $\Delta E_a = 60$ meV, which, from
Equation 2.13, give an energy loss resolution of $\Delta E_{1/2} = 100$ meV. This resolution is also insufficient to isolate the $J$ levels of $4s4p^3P_{0,1,2}$, which are separated by 30 meV, or the $4s4d^1D_2$, $4s4d^3D_{1,2,3}$ and $4s5p^1P_1$ states, which are separated by 50 meV. Newell and Ross [76] measured zinc electron energy loss spectra with a 35 meV resolution for incident electron energies above 50 eV, and scattering angles below 11°. Higher resolutions are obtained at the expense of signal strength, so this degree of resolution was impractical for the present work where, because lower incident electron energies were used and higher scattering angles were investigated, there was already a smaller beam current and available signal. The present apparatus was used for photon emission studies, in which complete state selection is easily achieved optically, so it was unnecessary to completely resolve in the electron detection channel all states intended for study. On the basis of electron energy loss spectrum measurements it was decided to restrict scattered electron studies to investigations of elastic scattering, $4s4p^1P_1$ excitation and $4s4p^3P_{0,1,2}$ excitation, albeit with unresolved $J$ states in the last case.

3.5 Conclusion

The studies presented in this chapter showed that, within its capabilities, the apparatus worked well. In particular, the fact that it was able to accurately reproduce the $1s2s^22S_{1/2}$ helium negative-ion resonance profile and angular dependance validates the similar studies conducted with zinc detailed in Chapters 5-7. The limitations of the apparatus were also shown, for example its unsuitability for electron-photon coincidence studies. These factors combined demonstrate that in the zinc studies that followed, the apparatus was being operated in an optimum fashion, and that it was being put to its best uses.
Chapter 4

Emission Cross Section Measurements

This chapter details emission cross sections measured for the $4s^4p^3P_1$, $4s^4p^1P_1$, $4s5s^3S_1$, $4s4d$, $5d$, $6d^3D_{1,2,3}$ and $4s4d, 5d^1D_1$ states for incident electron energies from their respective thresholds to 50 eV. The energies of these states and the wavelengths of the transitions studied are presented in Figure 4.1. The purpose of the measurements was to expand experimental cross section studies beyond investigations of the $4s4p, 5p^1P_1$ states, to include a greater range of orbital and spin angular momentum states.

An emission cross section is the total cross section for producing photons associated with the decay of a particular excited state populated either directly, or by cascades. Emission cross sections can be obtained through photon intensity measurements. In this work the intensity of photons emitted into a small solid angle was measured as a function of the incident electron energy. The measurements were corrected to account for any energy-dependence of the decay photon spatial distribution to make them proportional to emission cross sections. Photons were detected at 90° to the incident electron beam. For dipole radiation, Percival and Seaton [77] give the relationship between the photon intensity at 90° due to the decay of a particular state, $I(90°)$, and the total photon intensity integrated over all solid angles, $I$, to be

$$I = 4\pi I(90°) \left(1 - \frac{P_1}{3}\right)$$

(4.1)

where $P_1$ is the integral Stokes parameter defined in Equation 1.11. For incident electron energies below the threshold for cascades the emission cross section is identical to the integral cross section of the state being investigated. Above the cascade threshold emission cross sections are a sum of the direct and cascading state cross sections. The contribution from each cascading state is weighted by the branching ratio for its decay into the upper state of the transition.

Each state was scanned twice, with the individual scans taken on different days. During each scan photon counts were accumulated for two minutes at each point on the energy mesh. The incident beam current was also recorded for each data point, and then later used to normalise the data. It was important to do this because the incident beam current
was energy dependent and affected the overall shape of the experimental emission cross section. The electron gun was operated and tuned to minimise the variation of current across each scan. The smallest current variations were achieved by operating the electron gun with a $127^\circ$ energy selector pass energy of 10 eV, resulting in an energy resolution of $\Delta E_g = 250$ meV resolution and a beam current of 210 nA at 20 eV. There was a $\pm 20\%$ variation of current across the incident energy range studied under these conditions, as shown in Figure 4.2. However, the beam current was most dependent on the incident energy below 15 eV, and above this energy the variation in beam current was $\pm 4\%$.

A 1 eV energy mesh was used for these emission cross section studies, so the energy calibration did not have to be as accurate as for the studies detailed in Chapters 5-7. 4s4d$^1D_2$ threshold calibration scans were taken more quickly to save time, and the resulting statistical accuracy and wider than usual energy resolution gave a total estimated energy uncertainty of 100 meV.

Unlike the beam current, some factors were independent of the incident beam energy but varied between scans taken on different days. For example there was some difference in oven flux between scans, and decreasing Faraday cup collection efficiency and lens or window transmission over time due to zinc deposition. It was necessary to normalise the two scans to each other to account for this. The normalisation factor was the ratio of the photon signal for each scan summed over all energies. Once normalised, the scans were averaged to give the final data. The variation between individual scans was much greater than that given by the usual counting statistics. The uncertainty in the experiment was quantified by calculating the percentage difference between the two scans at each data point, and finding the average percentage difference across all data points for all states studied. The average percentage difference, and the resulting estimated uncertainty of the photon intensity measurements, was 12%.
Figure 4.2: Variation of electron beam current in emission cross section studies for incident energies between 5 and 50 eV.

The present measurements are compared with the BSRM theory of Zatsarinny and Bartschat [78], and the CCC theory of Fursa and Bray [61]. As previously discussed, these models have distinct strengths and weaknesses. The BSRM theory includes 3\textit{d}-subshell excited states in its target description, but there is some inadequacy in its treatment of the continuum. The CCC model adequately describes the continuum, but relies on a frozen core approximation. Given the large cross section for 3\textit{d}\textit{3s}^{2}\textit{4p} states [19] this is not likely to be valid. Emission cross section calculations have the added complication of requiring the inclusion of cascades, which is another point where the two theories can differ. Accurate predictions of the cascade contributions to a particular state requires accurate calculations of high \textit{n} and \textit{L} state cross sections, which are likely to be strongly effected by the different target state descriptions of the two theories.

CCC and BSRM calculations which do not include cascades, continuum coupling or 3\textit{d}-excited target states are in almost perfect agreement. This is demonstrated by Figures 4.3 and 4.4, which show CCC-29 and BSRM-23 integral cross section calculations for the 4\textit{s}4\textit{p}^{1}\textit{P}_{1} and 4\textit{s}4\textit{d}^{3}D_{1,2,3} states. The vertical axes are labelled “Cross Section” because these calculations are intended to show underlying agreement between the two models, but not to accurately calculated integral cross sections. Apart from not including coupling to the continuum or 3\textit{d}-excited target states, these two calculations used the same method as the equivalent theories presented below. Therefore, a comparison between experiment and theory will indicate to some extent the relative importance of coupling to the continuum or 3\textit{d}-excited target states in scattering from zinc.

The photon intensity measurements were normalised to a single point of one of the calculations, to allow a direct comparison between experiment and theory. The appropri-
Figure 4.3: Comparison of theoretical calculations of the $4s4p^1P_1$ integral cross section, neglecting the effects of coupling to the continuum and inner-shell excitation; $\text{--- CCC-29 integral cross section, } \text{--- BSR-23 integral cross section.}$

Figure 4.4: Comparison of theoretical calculations of the $4s4d^1D_2$ integral cross section, neglecting the effects of coupling to the continuum and inner-shell excitation; $\text{--- CCC-29 integral cross section, } \text{--- BSR-23 integral cross section.}$
4.1. RESULTS AND DISCUSSION

4.1.1 4s4p 3P1 State

The experimental 4s4p 3P1 state emission cross section is shown alongside CCC and BSRM emission cross section calculations in Figure 4.5, with the experiment normalised to the CCC theory at 6 eV. This state has a threshold energy of 4.030 eV, and was investigated by detecting 308 nm photons from the 4s4p 3P1 → 4s2 1S0 transition, using a 12 nm
Figure 4.6: Percentage cascade contribution to theoretical $4s4p^3P_1$ state emission cross sections from threshold to 50 eV. Also shown are the thresholds of $n = 4, 5, 6$ states which can decay into the $4s4p^3P_1$ state via dipole radiation transition. – CCC emission cross section, −−− BSRM emission cross section.

bandwidth interference filter with a centre wavelength of 309 nm and 18% transmission at $\lambda = 308$ nm. The $4s4p^3P_1$ state decays to the ground state via an intercombination transition, and has a lifetime of 20 $\mu$s [79]. The radiation resulting from its decay is completely depolarised because of this, and so no polarisation correction was required.

Cascades affect the $4s4p^3P_1$ state emission cross section from 6.655 eV onwards. In Figure 4.6, the percentage cascade contribution to the CCC and BSRM emission cross section calculation is shown alongside the threshold energies of $n = 4, 5, 6$, $4sns^3S_1$ and $4snd^3D_{1,2,3}$ states which can decay directly into $4s4p^3P_1$. However, there will be a significant contribution of multi-step cascades from the whole triplet manifold into this, the lowest triplet state. For CCC, the peak cascade contribution of 39% occurs at 10.5 eV, and from 9.5 eV to 40 eV cascades comprise more than 30% of the emission cross section. Cascade contributions to the BSRM calculation are similar to CCC up to 10 eV, but above this energy range between 37% and 65%. Since the entire triplet manifold will cascade into one of the $4s4p^3P_{0,1,2}$ $J$-components, this discrepancy shows that in general the BSRM calculations predict larger triplet state cross sections for incident energies above the ionisation threshold. The $4s5s^3S_1$ and $4s4d^3D_{1,2,3}$ emission cross sections shown below support this conclusion, because BSRM is larger than CCC above 12 eV in both cases. A special situation arises relating to excitation of the $4s6s^3S_1$ state, which has a threshold energy of 8.11 eV. This state can decay via the $4s6s^3S_1 \rightarrow 4s4p^3P_1$ transition with the emission of 304 nm photons. The filter used had 13% transmission at this wavelength,
4.1. RESULTS AND DISCUSSION

Figure 4.7: (a) Emission cross section measurements for the $4s4p^1P_1$ state from threshold to 50 eV: • present experimental data with indicated uncertainty, — CCC emission cross section, --- BSRM emission cross section. (b) CCC Stokes parameter $P_1$ calculations, — with cascades and — without cascades.
so the excitation of one atom into the \(4s6s^3S_1\) state had the potential to result in two photons being detected.

Of all the states studied, the agreement between experiment and the two theories is best for \(4s4p^3P_1\), albeit with an expected discrepancy due to the near-11 eV negative-ion resonances. One interpretation of this fact is that neither coupling to the continuum nor coupling to excited 3d-electron states is important in this particular process. However, given the strong influence of negative-ions associated with 3d\(^9\)4s\(^2\)4p states, the latter conclusion in particular is questionable. Both theories are, in a sense, incomplete. Their agreement with any of the experimental data given here may be coincidental, and may mask underlying problems.

### 4.1.2 \(4s4p^1P_1\) State

The experimental \(4s4p^1P_1\) state emission cross section is shown alongside CCC and BSRM emission cross section calculations in Figure 4.7a, with the experiment normalised to the BSRM theory at 40 eV. This state has a threshold energy of 5.796 eV, and was investigated by detecting 214 nm photons from the \(4s4p^1P_1 \rightarrow 4s2^1S_0\) transition. The interference filter used had 16\% transmission at this wavelength, a centre wavelength of 214 nm and a bandwidth of 9 nm. Photons from the decay of the \(4s4p^3P_1\) state should be highly polarised, and so a polarisation correction to the data was required. However, the 214 nm wavelength of the decay photons was below the polarisation analysis system’s transmission.
4.1. RESULTS AND DISCUSSION

Instead, the polarisation correction was applied using CCC calculations of $P_1$ which included the effect of cascades. The CCC $P_1$ calculations, with and without cascade effects, are shown in Figure 4.7b.

Cascade contributions to the $4s4p^1P_1$ state emission cross section are present from 6.917 eV onwards. In Figure 4.8, the cascade contribution to the CCC and BSRM emission cross section calculations is shown alongside the threshold energies of $n = 4, 5, 6$, $4sns^1S_0$ and $4snd^1D_2$ states, which can decay directly into $4s4p^1P_1$. Percentage cascade contributions to the $4s4p^1P_1$ state are small, between 10% and 24% across the affected region, when compared to $4s4p^3P_1$ and the other states studied here. This is due to its large cross section for direct excitation, and also because higher lying singlet states can decay into $n \geq 5$, $4snp^1P_1$ states which themselves will decay strongly to the ground state. As was the case for the $4s4p^3P_1$ state, BSRM predicts a larger cascade contribution. The BSRM model predicts a larger $4s4d^1D_2$ emission cross section, as discussed below, which may explain the larger predicted cascade contribution.

For the $4s4p^1P_1$ state, there is quite good agreement between the normalised experimental cross section magnitudes and both theories, which lie within or just outside the experimental uncertainty across the whole incident electron energy range. There is, however, disagreement regarding the general cross section shape. In particular, it seems both theories overestimate the relative size of the cross section between 10 eV and 30 eV. The CCC and BSRM calculations agree well up to approximately 12 eV. Above 12 eV there is a striking difference as CCC remains approximately 20% lower than BSRM. This is somewhat unexpected, given that excitation of the optically-allowed $4s4p^1P_1$ state by 14 eV - 50 eV incident electrons has a large cross section and should not be strongly influenced by coupling to the continuum or to inner-shell excited states. Consequently, one might expect the two models to be in close accord. Some insight into why the two models disagree may be gained from a comparison with Figure 4.3. The experimental data and BSRM emission cross section are both quite similar to the CCC-29 and BSRM-23 integral cross section. However, the CCC emission cross section is markedly different, peaking around 16 eV and having a flatter shape above this energy than all the other data. This would suggest that coupling to the continuum and 3d-excited states is small for $4s4p^1P_1$ excitation, but there is an underlying problem in the CCC emission cross section calculation.

4.1.3 $4s5s^3S_1$ State

The $4s5s^3S_1$ state emission cross section is shown alongside CCC and BSRM emission cross section calculations in Figure 4.9, with the experiment normalised to the CCC theory at 8 eV. This state has a threshold energy of 6.655 eV, and was investigated by observing 481 nm photons from the $4s5s^3S_1 \rightarrow 4s4p^3P_2$ transition. The photons were selected by an interference filter with 61% transmission at this wavelength, a centre wavelength of 482 nm and a bandwidth of 10 nm.

Cascade contributions will be due to the $4snd^3P_{1,2,3}$ states, with the $n=5$ threshold at 7.594 eV. The cascade contribution to the $4s5s^3S_1$ state emission cross section is very large,
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Figure 4.9: Emission cross section measurements for the $4s5s^3S_1$ state from threshold to 50 eV: • present experimental data with indicated uncertainty, — CCC emission cross section, —— BSRM emission cross section.

Figure 4.10: Percentage cascade contribution to theoretical $4s5s^3S_1$ state emission cross sections from threshold to 50 eV. Also shown are the thresholds of $n = 5, 6, 7$ states which can decay into the $4s5s^3S_1$ state via dipole radiation transition. — CCC emission cross section, —— BSRM emission cross section.
as is demonstrated by Figure 4.10 which shows the percentage cascade contribution to the
CCC and BSRM emission cross sections. Above 8 eV, the CCC calculation suggests that
the cascade contributions comprise over 60% of the observed signal. Cascade contributions
to the BSRM calculation are even higher, peaking at 87% at 40 eV. Direct excitation of
the 4s5s\(^3\)S\(_1\) state results in a zero decay photon polarisation \(P_1\). There will be some
polarisation due to the influence of cascades but it will be small, as shown by Pravica [80]
who measured \(P_1 \approx 0.01\) for the 4s5s\(^3\)S\(_1\) \(\rightarrow\) 4s4p\(^3\)P\(_2\) transition at an incident electron
energy of 8.5 eV. No correction was made to account for this small polarisation.

Near threshold, both theoretical emission cross sections show a rapid oscillatory na-
ture, and this is also seen in the high resolution photon excitation function measurements
detailed in Chapter 6. It is difficult to compare with the present low-resolution experiment
in this energy region but, aside from data points at 9 eV and 10 eV, both theories are
within the experimental uncertainty up to 13 eV. At 9 eV and 10 eV the experimental
emission cross section is higher than predicted by the theories. Above 13 eV there is good
agreement between the shape of the experimental and CCC emission cross sections, but
the experimental cross section is consistently smaller for incident electron energies above
15 eV. The BSRM emission cross section is significantly higher than both experiment and
CCC for energies between 13 eV and 40 eV. This is, for example, approximately twice
as large as the CCC cross section at 20 eV. A comparison of Figures 4.9 and 4.10 sug-
ests that the difference between the theories is due to the larger cascade contribution to
BSRM. Given the significant influence of cascades it is difficult to assess which model is
more accurate for 4s5s\(^3\)S\(_1\) excitation. However, coupling to the continuum may suppress
the \(n \geq 5, 4snp\(^3\)P\(_{1,2,3}\) state cross sections above 12 eV, bringing the CCC emission cross
section into closer agreement with the experiment.

4.1.4 4s4d, 5d\(^1\)D\(_2\) States

The 4s4d\(^1\)D\(_2\) emission cross section is shown in Figure 4.11a along with CCC and BSRM
emission cross section calculations. The present data were normalised to the BSRM cal-
culation at 40 eV. The 4s4d\(^1\)D\(_2\) state, which has a threshold energy of 7.744 eV, was
investigated by detecting 636 nm photons from the 4s4d\(^1\)D\(_2\) \(\rightarrow\) 4s4p\(^1\)P\(_1\) transition. The
interference filter used had 65% transmission at this wavelength, a centre wavelength of
638 nm and a bandwidth of 10 nm. A polarisation correction was made to the 4s4d\(^1\)D\(_2\)
data using \(P_1\) measurements taken between threshold and 50 eV, shown in Figure 4.11b
alongside CCC and BSRM \(P_1\) calculations. Of these two \(P_1\) calculations, only the CCC
included cascade effects.

Since 4snp\(^1\)P\(_1\) states will decay predominantly to the ground state, cascade contribu-
tions to 4s4d\(^1\)D\(_2\) will come mostly from 4snf\(^1\)F\(_3\) states, with the \(n=4\) threshold at
8.53 eV. The percentage cascade contribution to the CCC and BSRM emission cross sec-
tions is shown in Figure 4.12. The estimated cascade contribution are approximately 10%
for both calculations across most of the energy range studied. Cascade contributions to
CCC are generally larger, and have a peak of 22% near 10 eV. These cascades seem to be
Figure 4.11: Emission cross section and polarisation measurements for the $4s4d^1D_2$ state from threshold to 50 eV: (a) Emission cross section, • present experimental data with indicated uncertainty, − CCC emission cross section, −−− BSRM emission cross section. (b) Stokes parameter $P_1$, • present experimental data with indicated uncertainty, − CCC with cascade effects included, −−− BSRM without cascade effects included.
4.1. RESULTS AND DISCUSSION

Figure 4.12: Percentage cascade contribution to theoretical $4s4d^1D_2$ state emission cross sections from threshold to 50 eV. Also shown are the thresholds of $n = 4, 5, 6, 7$ states which can decay into the $4s4d^1D_2$ state via dipole radiation transition. — CCC emission cross section, —— BSRM emission cross section.

Figure 4.13: Comparison of $4d^1D_2$ and $5d^1D_2$ emission cross section shapes from threshold to 50 eV; • $4s4d^1D_2$ data with indicated uncertainty, ○ $4s5d^1D_2$ data with indicated uncertainty.
CHAPTER 4. EMISSION CROSS SECTION MEASUREMENTS

associated with the peak in the CCC emission cross section near 12 eV.

There is excellent overall agreement between the experimental and BSRM cross section shapes. In particular, experiment and the BSRM theory both have a broad peak in the cross section which has its maximum value near 20 eV. The BSRM calculations are within the experimental uncertainty across the whole energy range. The agreement with CCC is good from the step-like threshold up to 14 eV, but there is significant disagreement between the theories above this energy. Both calculations predict similar cascade contributions, and so for 4s4d^{1}D_{2} it is easier to judge which model more accurately describes the target. Comparing Figures 4.4 and 4.11, inclusion of innershell excited states into the BSRM target description removes the unphysical peak at 14 eV, and enhances the relative size of the cross section above 20 eV. These changes bring the BSRM calculations into better agreement with the experiment. There is not such a large difference between the two CCC calculations, but the inclusion of continuum coupling also removes an unphysical peak near 14 eV. Therefore, for 4s4d^{1}D_{2} excitation, coupling to the excited 3d-electron states is possibly more important than coupling to the continuum.

For the P_{1} measurements shown in Figure 4.11b, there is agreement between experiment and theory regarding the shape, but not the magnitude, near threshold. This may be due to the experimental energy resolution, not being sufficient to resolve the near-threshold structures apparent in the theory. There is also obvious disagreement between 9 and 15 eV, where the polarisation is affected by the near-11 eV negative-ion resonances. The effect of these negative-ion resonances on photon polarisation measurements will be discussed in more detail in Chapter 6. As a general observation, the measured P_{1} is lower than theory across the whole energy region studied, but above 16 eV there is good agreement with at least one of the calculations. Between 16 and 40 eV the experiment agrees best with the BSRM P_{1} calculation, which does not include cascades. Above 40 eV experiment agrees best with CCC, where the cascade effects included in CCC perhaps compensate for an inadequate treatment of 4s4d^{1}D_{2} excitation overall.

The 4s5d^{1}D_{2} state, which has a threshold energy of 8.473 eV, was investigated by detecting 463 nm photons from the 4s5d^{1}D_{2} \rightarrow 4s4p^{1}P_{1} transition. The interference filter used had 15\% transmission at this wavelength, a centre wavelength of 458 nm and a bandwidth of 9 nm. No polarisation correction was made for the 4s5d^{1}D_{2} state because the transmission of 458 nm photons by polarisation analysis was low. This compromised the ability to measure this relatively small emission cross section.

In Figure 4.13 the 4s5d^{1}D_{2} emission cross section shape is compared with a CCC 4s5d^{1}D_{2} integral cross section, and the experimental and theoretical 4s4d^{1}D_{2} state emission cross sections presented above. The vertical axis is labelled “Cross Section” because the figure presents a mixture of integral and emission cross sections. The 4s5d^{1}D_{2} emission cross section was normalised to CCC calculations at 9 eV. One might expect the 4s5d^{1}D_{2} and 4s4d^{1}D_{2} emission cross sections to have a similar shape, but this appears not to be the case. The 4s5d^{1}D_{2} cross section peaks at 12 eV, approximately 10 eV below the energy at which the 4s4d^{1}D_{2} emission cross section is at its maximum. It then
4.1. RESULTS AND DISCUSSION

Figure 4.14: Emission cross section measurements for the $4s4d^3D_{1,2,3}$ state from threshold to 50 eV; • present experimental data with indicated uncertainty, — CCC emission cross section, —— BSRM emission cross section.

decreases quite rapidly as one might expect a triplet state cross section to do. The cross section at 50 eV is 2% of the peak cross section, compared to 80% for $4s4d^1D_2$. However, the $4s5d^1D_2$ cross section does not decay as rapidly as the $4s5d^3D_{1,2,3}$ cross section shown below, which at 30 eV is only 0.2% of its peak cross section. The difference between the $4s4d^1D_2$ and $4s5d^1D_2$ emission cross sections may be due to a strong singlet-triplet mixing of the $n = 5$ state. This would result in a depression relative to the $4s4d^1D_2$ cross section because the probability for exchange excitation of the $4s5d^1D_2$ state decreases rapidly with increasing energy. However, the influence of direct excitation will mean the cross section will not decrease as rapidly as that of the $4s5d^3D_{1,2,3}$ state.

4.1.5 $4s4d, 5d, 6d^3D_{1,2,3}$ States

The $4s4d^3D_{1,2,3}$ emission cross section is shown in Figure 4.14, along with CCC and BSRM emission cross section calculations. The present data were normalised to the CCC calculation at 9 eV. The $4s4d^3D_{1,2,3}$ state, the $J$ components of which have threshold energies of 7.782 eV, 7.783 eV and 7.783 eV respectively, were studied by detection of photons from the $4s4d^3D_{1,2,3} \rightarrow 4s4p^3P_{0,1,2}$ transitions. These give rise to six closely spaced lines with wavelengths between 328 and 335 nm. The 11 nm bandwidth interference filter used was centred on 334 nm with 14% transmission at 328 nm and 34% at 335 nm. The lines resulting from the $4s4d^3D_{1,2,3} \rightarrow 4s4p^3P_{0,1,2}$ transitions were detected, but with different efficiencies. Photon polarisation was not measured for this state, because the wavelengths were below the transmission limit of the photon polarisation analysis system. Significantly depolarised photons would be expected to be detected due to the
Figure 4.15: Percentage cascade contribution to theoretical $4s4d^3D_{1,2,3}$ state emission cross sections from threshold to 50 eV. Also shown are the thresholds of $n = 4, 5, 6, 7$ states which can decay into the $4s4d^3D_{1,2,3}$ state via dipole radiation transition. — CCC emission cross section, --- --- BSRM emission cross section.

Figure 4.15 shows the percentage cascade contribution to the CCC and BSRM $4s4d^3D_{1,2,3}$ state emission cross sections. Also shown are the thresholds for $n = 4, 5, 6, 7$, $4snp^3P_{0,1,2}$ and $4snf^3F_{2,3,4}$ states which can decay directly into $4s4d^3D_{1,2,3}$. Cascades will be present for incident electron energies above 8.840 eV. Compared to $4s4d^1D_2$, there is a greater cascade contribution to the $4s4d^3D_{1,2,3}$ state emission cross section. This may be because, unlike their singlet equivalents, $4snp^3P_{0,1,2}$ states do not have an allowed transition to the ground state. The cascade contributions predicted by the two theories are similar up to 14 eV, but those for CCC are larger and peak at 44% at 10.5 eV. Above 14 eV cascade contributions to the BSRM calculations are considerably larger, oscillating around 35% while the CCC cascade contributions remain around 20%.

The experimental emission cross section shape is most like that of the CCC calculation, which is within the experimental uncertainty for energies from threshold to 13 eV. Above this energy the experimental emission cross section is consistently much smaller than CCC, with the experiment approximately one-third of the CCC prediction at 20 eV. The BSRM calculation is in poor agreement with both the experiment and CCC for energies above 12 eV, both in terms of magnitude of the cross section and its overall shape. For example unlike the experiment, between 10 eV and 16 eV the BSRM cross section does not decrease with increasing energy. Consequently, the BSRM emission cross section is much larger than experiment and CCC between 14 eV and 40 eV. At 20 eV, the BSRM
4.1. RESULTS AND DISCUSSION

Figure 4.16: Comparison of $4s4d^3D_{1,2,3}$, $4s5d^3D_{1,2,3}$ and $4s6d^3D_{1,2,3}$ emission cross section shapes from threshold to 30 eV; • $4s4d^3D_{1,2,3}$ data with indicated uncertainty, ○ $4s5d^3D_{1,2,3}$ data with indicated uncertainty, + $4s6d^3D_{1,2,3}$ data with indicated uncertainty.
emission cross section is around six times greater than the CCC emission cross section. A comparison of Figures 4.14 and 4.15 would suggest that the disagreement is due in part to an overestimation of the $4snf^3F_{2,3,4}$ cross sections by BSRM. For the case of the $4s5s^3S_1$ emission cross section, it appeared that coupling to the continuum suppresses the $n \geq 5$, $4snp^3P_{0,1,2}$ state cross sections above 12 eV. The apparent overestimation of cascades into the $4s4d^3D_{1,2,3}$ state by BSRM may be because coupling to the continuum also suppresses the excitation of $4snf^3F_{2,3,4}$ states.

For the $4s5d^3D_{1,2,3}$ states, which all have threshold energies of 8.503 eV, the six lines resulting from the $4s5d^3D_{1,2,3} \rightarrow 4s4p^3P_{0,1,2}$ transition are spread from 276 to 280 nm. The 10 nm bandwidth interference filter used was centred on 283 nm with 5% transmission at 276 nm and 16% at 280 nm. For the $4s6d^3D_{1,2,3}$ states, which all have threshold energies of 8.829 eV, the six lines resulting from the $4s6d^3D_{1,2,3} \rightarrow 4s4p^3P_{0,1,2}$ transition are spread from 257 to 261 nm. The 9 nm bandwidth interference filter was centred on 262 nm with 10% transmission at 257 nm and 20% at 261 nm.

The $4s4d^3D_{1,2,3}$, $4s5d^3D_{1,2,3}$ and $4s6d^3D_{1,2,3}$ states emission cross section shapes are compared in Figures 4.16. The $4s5d^3D_{1,2,3}$ and $4s6d^3D_{1,2,3}$ data have been normalised at 10 eV to CCC integral cross sections, which are also presented. As the figures present a mixture of integral and emission cross sections, the vertical axes are labelled “Cross Section”. The $4s5d^3D_{1,2,3}$ and $4s6d^3D_{1,2,3}$ emission cross sections were not measured above 30 eV, because there was insufficient signal above this energy. As may be expected, the cross section shape for these states are similar and typical of non-optically allowed states, that is a rapid onset peaking near-threshold is followed by a rapid decrease. All three have their peak cross section near 10 eV. At 30 eV, the $4s4d^3D_{1,2,3}$ emission cross section is 2% of its peak value, and the $4s5d^3D_{1,2,3}$ emission cross section is 0.2% its the peak value, the $4s6d^3D_{1,2,3}$ emission cross section is 0.5% of the peak value. As is also the case for the $4s4d^3D_{1,2,3}$ state, the $4s5d^3D_{1,2,3}$ and $4s6d^3D_{1,2,3}$ cross sections decay more rapidly with increasing energy than is predicted by CCC.

### 4.2 Conclusion

Generally speaking, there is sporadic agreement between the experimental data and the CCC and BSRM emission cross section calculations. The aspects unique to each theory, namely an expansive treatment of the target continuum in CCC and the inclusion of excited 3d-electron states in BSRM, clearly have a significant impact on the calculations. This suggests that these effects are important in electron scattering from zinc. The differences between the models are compounded by the need to include cascades in emission cross section calculations. For the higher-lying, small cross section cascading states the respective effects included in CCC and BSRM should have a more significant impact than on, for example, a low-lying optically allowed state with a large cross section. Perhaps as a result of this, the percentage cascade contributions made to CCC and BSRM emission cross sections are, in general, significantly different.
The best agreement between the experiment and the two theoretical models is seen for the $4s4p^3P_1$ emission cross section. Unexpectedly, the agreement is not as good for the $4s4p^1P_1$ state, which is the lowest optically allowed state, and accordingly has a relatively large cross section across the energy range studied. While the BSRM emission cross section calculation agrees well with the experimental data, there appears to be an underlying problem in the CCC model’s treatment of the continuum. For the $4s4d^1D_2$ state there is good agreement between the experimental data and BSRM, and this appears to be the only case investigated here where it is clear that coupling to the excited $3d$-electron states is more important than coupling to the continuum. There are large cascade contributions to the $4s4d^3D_{1,2,3}$ emission cross section, and different estimations of their significance seem to be the root of disagreement between the theories. However, both theoretical approaches appear to overestimate the relative size of the $4s4d^3D_{1,2,3}$ cross section above 14 eV. The greatest disagreement between the experiment and theory is for the $4s5d^1D_2$ state. This state appears to have a significant triplet component, which results in the relative size of the cross section above 14 eV being smaller than expected. The $4s5d^3D_{1,2,3}$ and $4s6d^3D_{1,2,3}$ state emission cross sections are very similar in shape to that of the $4s4d^3D_{1,2,3}$ state, and it appears that CCC overestimates the relative size of their cross sections at higher energies.
Chapter 5

Electron Excitation Functions and Differential Elastic Scattering Studies

All the states of zinc investigated in this work were strongly affected by negative-ion resonances. This chapter details angle-differential scattered electron studies which aimed to characterise these negative-ion resonances from below the first excitation threshold at 4.006 eV, to 14 eV, just above the $3d^94s^24p$ autoionising state thresholds. The work includes differential elastic scattering signal measurements from 3 eV to 14 eV incident electron energy, and $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ state electron excitation function measurements taken with incident electron energies from near the first ionisation threshold at 9.394 eV to 14 eV.

Of particular interest are the negative-ion resonances which occur near the threshold of the $3d^94s^24p$ innershell-excited states. Elastic scattering and excitation of the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ states are all very strongly affected by these negative-ion resonances, with, for example, the resonance structure comprising approximately half of the $4s4p^3P_{0,1,2}$ differential cross section at some angles. These very strong negative-ion resonances provide an excellent opportunity to investigate and characterise the significant electron correlation effects associated with creation of the $3d$-hole.

Angle-differential scattered electron studies of negative-ion resonances allow resonance configurations and $LS$-terms to be assigned through an application of parity and angular momentum conservation. This is possible because these measurements resolve partial wave behaviour. From Mott and Massey [69], an application of the partial waves method, including spin-orbit effects, gives the elastic scattering cross section as

$$\sigma = |f|^2 + |g|^2$$

(5.1)

where

$$f(k, \theta) = \frac{1}{2i\hbar} \sum \left[ (l + 1) \{ e^{2i\delta^+} - 1 \} + l \{ e^{2i\delta^-} - 1 \} \right] P_l(\cos \theta)$$

(5.2)

$$g(k, \theta) = \frac{1}{2i\hbar} \sum \{ e^{2i\delta^+} - e^{2i\delta^-} \} P_l^1(\cos \theta)$$

(5.3)
$f$ and $g$ are the direct and spin-flip scattering amplitudes in Mott scattering defined in Chapter 1, $k$ and $l$ are the linear and orbital angular momenta of the incident electron, $\delta_i^\pm$ are the phase shifts referring to states with total angular momenta $l \pm 1/2$, and $P_l, P_1^l$ are the Legendre and associated polynomials respectively.

Only incident electrons with a specific parity and total angular momentum $j$ will excite a particular negative-ion resonance. If the effect of Mott scattering is not significant, then the phase shifts of the partial waves not involved in exciting the negative are given by

$$\delta_i^+ = \delta_i^- = \delta_i$$

(5.4)

The spin-orbit interaction will split the fine-structure components of a negative-ion resonance with a given configuration, $L$ and $S$. A particular component will be excited by incident electrons with either $j = l + 1/2$, or $j = l - 1/2$, but not both. The phase shifts of the partial waves affected by a negative-ion resonance are given by

$$\delta_l^\pm = \delta_l + \delta_{l, \text{res}}^\pm$$

(5.5)

$$\delta_{l, \text{res}}^\pm = \arccot \left( \frac{2(E_{\text{res}}^\pm - E)}{\Gamma} \right)$$

(5.6)

where $\delta_{l, \text{res}}^\pm$ is the phase shift associated with the $J = l \pm 1/2$ negative ion, $E$ is the incident electron energy, $E_{\text{res}}^\pm$ is the energy of the $J = l \pm 1/2$ negative ion, and $\Gamma$ is the resonance width. Mott scattering is again assumed to be insignificant, and so any difference between $\delta_i^+$ and $\delta_i^-$ will be considered to be due only to negative-ion resonances.

The negative-ion resonance effects contained within the scattering amplitudes $f$ and $g$ will be scaled by $P_l(\cos(\theta))$ and $P_1^l(\cos(\theta))$ respectively. Therefore, these functions determine how the magnitude of a negative-ion resonance profile depends on the scattering angle observed. Take for example the $np^5(n + 1)s^2 2P_{1/2,3/2}$ negative-ion resonances observed in the noble gases below the lowest excitation threshold, which is exited from a $np^6$ ground state by $p$-wave incident electrons. These have been observed in neon ($n = 3$) by Heindorff et al. [81], in argon ($n = 4$) by Williams and Willis [63], and in argon and krypton ($n = 5$) by Weingartshofer et al. [82] and Williams and Willis [63]. For neon, the $J = 3/2$ component is 131 meV lower than the $J = 1/2$ component, and the resonance width is 1.4 meV. The resonance width compared to fine-structure splitting is similarly small for argon and krypton. As a result, there will be a significant difference between the $\delta_i^+$ and $\delta_i^-$ phases from just below $E_{\text{res}}^+$ to just above $E_{\text{res}}^-$. The $P_l(\cos(\theta))$ and $P_1^l(\cos(\theta))$ polynomials combine such that the $np^5(n + 1)s^2 2P_{1/2,3/2}$ negative-ion resonance profiles are not observable at a scattering angle of $80^\circ$.

Here, the negative-ion resonances were observed in inelastic scattering, and elastic scattering above the lowest excitation threshold, so, strictly speaking, a partial wave treatment is not applicable. Inelastic scattering will also have the complication of the incident and scattered electrons associated with a negative-ion resonance being in different partial waves. However, if the physical origin a of negative-ion resonance induced, spin-flip scattering amplitude $g$ remains the same, that is fine-structure splitting within the negative-ion resulting in an incident electron spin dependence, then $g$ should be small
Table 5.1: The Legendre polynomials $P_l \cos(\theta)$ up to $f$-wave ($l = 3$). Also shown are the scattering angles $\theta$ at which $P_l \cos(\theta) = 0$.

<table>
<thead>
<tr>
<th>Partial Wave</th>
<th>$P_l \cos(\theta)$</th>
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</tr>
</thead>
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<td>$s$-wave ($l = 0$)</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>$p$-wave ($l = 1$)</td>
<td>$\cos(\theta)$</td>
<td>$90^\circ$</td>
</tr>
<tr>
<td>$d$-wave ($l = 2$)</td>
<td>$\frac{1}{2}(3 \cos^2 \theta - 1)$</td>
<td>$54.7^\circ, 125.3^\circ$</td>
</tr>
<tr>
<td>$f$-wave ($l = 3$)</td>
<td>$\frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta)$</td>
<td>$39.2^\circ, 90^\circ, 140.8^\circ$</td>
</tr>
</tbody>
</table>

for zinc negative-ion resonances observed here. As will be seen below, the zinc negative-ion resonances observed by the present work are generally not isolated, and have resonance widths on the order of the negative-ion fine structure splittings. The profiles of the $J$ components of a negative-ion resonance will therefore have a significant overlap, meaning that at a given energy there will be little difference in the effects acting on incident spin-up and spin-down electrons.

Given this, the angular-dependent behaviour of the zinc negative-ion resonance profiles should depend strongly on the Legendre polynomials $P_l(\cos(\theta))$, and relatively weakly on the associated polynomials $P_l^1(\cos(\theta))$. The Legendre polynomials $P_l(\cos(\theta))$ are given in Table 5.1, along with the values of $\theta$ for which $P_l(\cos(\theta)) = 0$. By identifying the scattering angle or angles at which a negative-ion resonance is absent, one can determine the parity, $J$, and possibly $L$ and $S$ of the negative-ion.

Nominally, the elastic scattering studies were conducted with an energy resolution of $\Delta E_{1/2} = 50$ meV. However, this was degraded by the presence of energy drifts, as discussed in Section 3.4.1, and so the apparent resolution of the elastic scattering data is closer to 80 meV. Owing to the smaller available signal, studies of the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ states were conducted with a nominal resolution of $\Delta E_{1/2} = 100$ meV, but because of energy drifts the apparent resolution was 120 meV.

The observed negative-ion resonances were characterised using one of a few different methods. If the negative-ion resonance was isolated, it was fitted with a Fano profile as per the procedure detailed in Section 3.2, which extracted a resonances energy and width. If negative-ion resonances overlapped, as was the case for all incident electron energies above 7 eV, the procedure was not as simple because overlapping Fano profiles could not be fitted to the data with an acceptable precision. Instead, negative-ion resonance contributions to the observed signal were isolated by subtracting a least squares polynomial fit to the slowly varying non-resonance background. The relative size of the various resonance structures as well as details of their shape become more apparent by subtracting a background. It is particularly important to see clearly the finer details in the case of overlapping negative-ion resonances, because this helps to identify the presence of multiple resonance structures. Several overlapping negative-ion resonances were observed between 7 eV and 8.5 eV, but the statistical accuracy of the data made any analysis difficult. In this case, information was extracted largely through a comparison between the previous experimental data of
Sullivan et al. [1], and the BSRM calculations of Zatsarinny and Bartschat [2]. The negative-ion resonances above the ionisation threshold, near 11 eV were observed with a high degree of statistical accuracy. As shown by Fano [25], there can be both constructive and destructive interference across a resonance, resulting in a structure which generally comprises a peak and a dip. However, the energies of the numerous overlapping negative-ion resonances near-11 eV were characterised only by the positions of peaks determined using a peak-fit, not true resonance energies. This approach was chosen because the near-11 eV negative-ion resonances generally appear to be overlapping peaks which enhance the observed cross sections, and also because it was a simple method which allowed the energy of the various structures to be characterised in a consistent fashion. However, it did not determine the true number of negative-ion resonances, or true resonance energies. For each feature, the resonance energies or resonance peak energies given in Tables 5.2-5.6 were obtained by averaging the Fano profile or peak fit energy determinations across the observed angles. Also indicated in the tables is the total energy uncertainty for each feature, which included an uncertainty of ±20 meV due to energy calibration and energy drifts, and the additional uncertainty due to the fit.

5.1 Elastic scattering below the ionisation potential

The results of differential elastic scattering studies between 3.5 eV and 9 eV are shown in Figures 5.1 and 5.2, while structures that have been observed in this energy region are shown in more detail in Figures 5.3-5.8. Almost all these structures are negative-ion resonances, the only exception being a structure a 5.80 eV which may be a “cusp”. These occur at an excited state threshold, where the effect of a new excitation channel becoming energetically accessible can result in a structure in the cross sections of open scattering channels. The energies of the observed structures extracted by a Fano or peak fitting procedure are given in Table 5.2. Also shown in the table are the energies and widths of negative-ion resonances observed by the experiment of Sullivan et al. [1], and predicted by the BSRM calculations of Zatsarinny and Bartschat [2].

Figures 5.3 and 5.4 show details of the structures observed for incident electron energies between 3.5 eV and 5.5 eV, at scattering angles of 30°, 54°, 90° and 110°. The dominant negative-ion resonance is associated with d-wave scattered electrons, as can be judged by the lack of structure at 54°. The previous experiment of Sullivan et al. detected a weak negative-ion resonance at 3.82 eV, and the “elbow” near 4 eV at 54° may perhaps be due to this negative-ion resonance. At other angles this weak negative-ion resonance appears to be masked by the very strong effect of the dominant negative-ion resonance, which is approximately 28% of the interpolated background at 30°, 83% of the interpolated background at 90° and 110% of the interpolated background at 110°. The average energy and apparent width of the dominant negative-ion resonance, with the data from each scattering angle weighted according to the precision of its Fano profile fit, were 4.26±0.02 eV and 409±7 meV respectively. Compared to 30° and 110° the Fano profile fit
to the 90° data was not as precise, because the non-resonance background did not appear to vary linearly with incident electron energy. This may also explain why the resonance energy and width determined by the 90° fit was higher and wider than at the other angles.

Figures 5.5 and 5.6 show details of the structure observed at 5.80 eV at scattering angles of 30, 54°, 90° and 110°. The feature is not visible at 90°, which indicates that it is associated with p-wave scattered electrons. The size of the feature is approximately 5% of the interpolated background at 30°, 3% of the interpolated background at 54° and 9% of the interpolated background at 110°. Although this structure may not be a negative-ion resonance a Fano profile fit was used to determine its energy and apparent width. If this structure is a negative-ion resonance then the fit parameters extracted will have their usual relationship to the energy, lifetime and interference with direct scattering of a negative ion state. If it is a cusp this will not be the case, but given the present structure has a similar shape to a negative-ion resonance a Fano fit will be a valid method to characterise its energy and width. With the data from each scattering angle weighted according to the precision of its Fano profile fit, these were determined as 5.80±0.02 eV and 110±10 meV respectively. Compared to 30° and 54°, at 110° the Fano profile fit was less precise due to poorer counting statistics, which may explain why the extracted resonance energy was 40 meV higher than at the other angles.

Figures 5.7 and 5.8 show the contribution of overlapping negative-ion resonance structures observed near 7.6 eV as a percentage of the estimated non-resonance background at 30°, 54°, 90° and 110°. Also marked, with bars and numerical labels, are the positions of negative-ion resonances observed in the photon excitation function measurements presented in Chapter 6, and by Sullivan et al.. At their peak, the features comprise approximately 1.6% of the interpolated background at 30° and 54°, 15% of the interpolated background at 90° and 10% of the interpolated background at 110°. The presence of several overlapping negative-ion resonances prevented Fano profile fitting, and this combined with the poorer statistics compared to the rest of the present data made it difficult to extract consistent resonance energies and to identify the partial wave behaviour of the structures. However, some conclusions can be drawn from a comparison with the more statistically accurate, photon excitation function data presented in Chapter 6, as well as the work of Sullivan et al. and Zatsarinny and Bartschat which will be discussed further below.
Figure 5.1: Differential elastic scattering signal at a scattering angle of (a) 30°, (b) 54°. The features near 4.26 eV, 5.80 eV and 7.60 eV are shown in greater detail in Figures 5.3-5.8.
5.1. ELASTIC SCATTERING BELOW THE IONISATION POTENTIAL

Figure 5.2: Differential elastic scattering signal at a scattering angle of (a) 90°, (b) 110°. The features near 4.26 eV, 5.80 eV and 7.60 eV are shown in greater detail in Figures 5.3-5.8.
Electron Counts

$E_r = 4.23 \pm 0.02$ eV

$\Gamma = 405 \pm 3$ meV

$y = (-9.3966 \times 10^5 + 4.8784 \times 10^5 \times E + \ldots) \times 10^{-6}$

<table>
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<tr>
<th>Error Value</th>
<th>Chisq</th>
<th>R</th>
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<tr>
<td>NA</td>
<td></td>
<td>0.010934</td>
</tr>
</tbody>
</table>

Figure 5.3: Differential elastic scattering signal in the vicinity of the 4.26 eV negative-ion resonance at a scattering angle of (a) 30°, (b) 54°. • present data, — a combined polynomial background and Fano profile fit to the negative-ion resonance which obtained the resonance energy and width displayed. The size of the resonance, where present, as a percentage of the non-resonance background is also indicated.
Figure 5.4: Differential elastic scattering signal in the vicinity of the 4.26 eV negative-ion resonance at a scattering angle of (a) 90°, (b) 110°. • present data, — a combined polynomial background and Fano profile fit to the resonance structure which obtained the resonance energy and width displayed. The size of the resonance, where present, as a percentage of the non-resonance background is also indicated.
Figure 5.5: Differential elastic scattering signal in the vicinity of the 5.80 eV feature at a scattering angle of (a) 30°, (b) 54°. • present data, — a combined polynomial background and Fano profile fit to the negative-ion resonance which obtained the resonance energy and width displayed. The size of the resonance, where present, as a percentage of the non-resonance background is also indicated.
Figure 5.6: Differential elastic scattering signal in the vicinity of the 5.80 eV feature at a scattering angle of (a) 90°, (b) 110°. • present data, — a combined polynomial background and Fano profile fit to the negative-ion resonance structure which obtained the resonance energy and width displayed. The size of the resonance, where present, as a percentage of the non-resonance background is also indicated.
Figure 5.7: Percentage resonance contributions to the differential elastic scattering signal in the vicinity of the near-7.6 eV negative-ion resonance group at a scattering angle of (a) 30°, (b) 54°. Marked with numbers are the energy positions of resonance structures observed in photon excitation function measurement, detailed in Chapter 6.
Figure 5.8: Percentage resonance contributions to the differential elastic scattering signal in the vicinity of the near-7.6 eV resonance group at a scattering angle of (a) 90°, (b) 110°. Marked with numbers are the energy positions of resonance structures observed in photon excitation function measurement, detailed in Chapter 6.
Table 5.2: Energies, widths and spectroscopic assignment of negative-ion resonances observed in the differential elastic scattering signal below the ionisation threshold. The total uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The numbers in the leftmost column refer to the labels used throughout this work to identify negative-ion resonances below the ionisation threshold at 9.394 eV. The energies, widths and assignment of resonances given in previous electron transmission [1] and BSRM studies [2] are included. All energies are in units of eV.

<table>
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<th>Label</th>
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<th>$54^\circ$</th>
<th>$90^\circ$</th>
<th>$110^\circ$</th>
<th>Transmission</th>
<th>BSRM</th>
<th>Assignment</th>
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<td>4.29±0.04</td>
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<td>4.25 (4s4p$^2$2D)</td>
<td>4.234 (4s4p$^2$2D)</td>
<td>$4s4p^2D$</td>
</tr>
<tr>
<td></td>
<td>$\Gamma=0.405±0.002$</td>
<td>-</td>
<td>$\Gamma=0.460±0.01$</td>
<td>$\Gamma=0.380±0.006$</td>
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</tr>
<tr>
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<td>-</td>
<td>5.83±0.04</td>
<td>5.79 (4s4p$^2$2S)</td>
<td>5.796 (cusp)</td>
<td>cusp</td>
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<td>0.097±0.009</td>
<td>-</td>
<td>0.110±0.02</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
5.1 Discussion

The negative-ion resonance spectrum seen here below the ionisation threshold has many similarities to the negative-ion spectra of cadmium and mercury. Mercury negative-ion resonances have been well studied both experimentally and theoretically, for example by Burrow et al. [83], Sullivan et al. [1], Newman et al. [45], Bartschat and Burke [84] and references within Buckman and Clark [24]. Most experimental investigations of mercury, cadmium and zinc negative-ion resonances have used either electron transmission or metastable atom detection techniques, which generally have excellent energy resolution, but are hindered by not resolving scattered electron angular distributions. Sullivan et al. have performed measurements of negative-ion resonances in differential elastic scattering, as have Albert et al. [85].

All these studies have detected several negative-ion resonances in the vicinity of the \( {n}{s}{n}{p}^2 {P}_{0,1,2} \) state thresholds, which have been assigned a \( {n}{s}{n}{p}^2 \) electron configuration, with \( n = 4 \) for zinc, \( n = 5 \) for cadmium and \( n = 6 \) for mercury. The \( {4}{P} \) terms of this configuration are the lowest, and Burrow et al. [83] observe all three \( J \)-components in mercury, with \( J = 1/2 \) having the lowest energy and \( J = 5/2 \) the highest. Also, the splitting between the \( J = 1/2 \) and \( J = 3/2 \) components was observed to be 120 meV, while the \( J = 3/2 \), \( J = 5/2 \) splitting was 243 meV. For cadmium, Sullivan et al. [1] detected only the \( J = 3/2 \) and \( J = 5/2 \) components, split by 60 meV, while in their zinc electron transmission study the \( 4s4p^2 {2}{P}_{1/2,3/2,5/2} \) negative-ion resonances produced a barely discernible structure at 3.82 eV, and no fine structure was resolved. It was suggested above that there may be a weak negative-ion resonance near 4 eV, which can be seen only as an elbow-like structure in the \( 54^\circ \) spectrum. Parity and total angular momentum conservation requires that the \( 4s4p^2 {2}{P}_{1/2} \) negative ion decays to the ground state by \( s \) emission, and the \( 4s4p^2 {4}{P}_{3/2,5/2} \) negative ion decay by \( d \)-wave emission. Therefore, only the \( 4s4p^2 {4}{P}_{1/2} \) negative-ion resonance can be observed at \( 54^\circ \). However, this negative-ion resonance is not observed for cadmium, which suggests that it is the weakest of the three components and should also not be seen for zinc. The other negative-ion resonances have the same partial wave behaviour as the strong, broad negative-ion resonance at 4.26 eV, and so will probably be completely masked in the present measurements.

The present observations of the 4.26 eV negative-ion resonance in zinc are in excellent agreement with the electron transmission and differential elastic scattering studies of Sullivan et al.[1] and the BSRM calculations of Zatsarinny and Bartschat [2]. Both assign the negative-ion resonance as \( 4s4p^2 {2}{D}_{3/2,5/2} \). The experiment measured a resonance energy of 4.25 eV, and the theory predicted a resonance energy of 4.234 eV and resonance width of 372 meV. The present experiment determined a resonance energy of 4.26 ± 0.02 eV and a width of 409 ± 7 meV, so the previous experiment is within the uncertainty of the present experiment, while the theoretical resonance energy and width are both lower than determined here. This resonance energy discrepancy is small, with the theoretical prediction lying only 6 meV outside the bounds of uncertainty for the present experiment. However, the difference between the predicted and measured resonance width is more significant,
and is not due simply to the finite, $\Delta E_{1/2} = 80$ meV experimental energy resolution. Taking Equation 2.13 as the approximate relationship determining the width of a convoluted structure, a $\Delta E_{1/2} = 80$ meV resolution should broaden a 372 meV resonance width by only 9 meV. As is apparent by examination of the narrow structure at 5.80 eV, the experimental energy resolution was certainly less than $\Delta E_{1/2} = 170$ meV, which is roughly what is required to broaden a resonance width from 372 meV to 409 meV. Both the present experiment and Sullivan et al. [1] showed the resonance profile to be absent at 54°, which is consistent with the positive parity, and total angular momentum $J = 3/2$ or $J = 5/2$ of a 4s4p $^2$D $3/2,5/2$ negative ion. Also supporting this assignment in preference to other nsnp $^2$ terms with $J = 3/2$ or $J = 5/2$ is the fact that strong, broad negative-ion resonances with a nsnp $^2$D $3/2,5/2$ assignment have also been observed near the nsnp $^3$P $0,1,2$ thresholds of cadmium and mercury. Burrow et al. [83] observed a splitting of 400 meV between the lowest, $J = 3/2$ component and the $J = 5/2$ component, but Sullivan et al. [1] did not resolve the fine structure of this negative ion for cadmium or zinc.

There are some marked disagreements within the literature regarding the existence or otherwise of the remaining, nsnp $^2$P $1/2,3/2$ and nsnp $^2$S $1/2$ terms of the nsnp $^2$ mercury, cadmium and zinc negative ion configuration. Newman et al. [45] claimed to have identified small, broad structures in their mercury metastable state excitation functions due to the 6s6p $^2$P $1/2,3/2$ negative-ion resonances, but as noted by Sullivan et al. [1] these negative-ion resonances have not been predicted by theoretical calculations. Of particular interest here are the sharp structures in mercury, cadmium and zinc which coincide almost exactly with the nsnp $^1$P excited state thresholds. Such a structure in zinc is seen here at 5.80 eV, and has also been observed by Sullivan et al., and in the photons excitation functions detailed in Chapter 6. Similar structures have also been observed for cadmium at the 5.417 eV threshold of the 5s5p $^1$P state, and for mercury at the 6.702 eV threshold of the 6s6p $^1$P state [1, 24, 45]. Almost all the previous experimental works have assigned the structure a nsnp $^2$S $1/2$ negative-ion resonance. One notable exception is Burrow et al. [17], who observed the near-nsnp $^1$P threshold structure in electron transmission studies of mercury, cadmium and zinc, and claim that is it almost certainly a cusp. Also, Sullivan et al. [1] assign the feature as a nsnp $^2$S $1/2$ negative-ion resonance, but also suggest that it may instead be a cusp. However, a theoretical time delay analysis conducted by Zatsarinny and Bartschat [2] was not so equivocal, and determined that the zinc feature was a cusp, not a negative-ion resonance. That time-delay analysis technique, described in detail in [86], includes checking partial waves for the $\pi$ phase-shifts, which occur across a resonance.

The present angle differential measurements clearly show that the 5.80 eV feature disappears at 90°, which indicates that, if it is a negative-ion resonance, it decays to the ground state by $p$-wave electron emission. Thus, the parity conservation requirement means that this feature cannot be a 4s4p $^2$S $1/2$ negative-ion resonance. Of the previous experimental investigations of this feature, only the cadmium differential elastic scattering signal measurements of Sullivan et al. [1] resolved partial waves. They concluded that the feature was observable at all scattering angles, which supported the 5s5p $^2$S $1/2$ assign-
ment since this negative-ion resonance will decay to the ground state by s-wave emission. However, upon closer inspection of their data, one would suggest that at 90° there is no statistically significant structure, especially when compared with the quite obvious structure resolved at 24°, 54° and 120°. If this structure is due to a negative-ion resonance, its configuration would most likely be $nsnpd$ or $nsnp(n + 1)s$, since its energy strongly suggests that it is based on a $4s4p$ parent state. All of the terms derived from these configurations will have fine structure, which should be observed for mercury. The fact that even in mercury the structure is observed to be a single and narrow suggests that it is not a $nsnpd$ or $nsnp(n + 1)s$ negative-ion resonance. Furthermore, Zatsarinny and Bartschat [2] do not predict any negative-ion resonances with these configurations.

The theory of cusps is set out in detail by Wigner [87], who showed that cross sections affected by a cusp have the functional form

$$\sigma = a + b |E - \epsilon_n|^\frac{1}{2} + O(E - \epsilon_n)$$

where $E$ is the incident electron energy, $\epsilon_n$ is the threshold energy of the opening scattering channel and $a$ and $b$ are constants. As can be seen from Equation 5.7, cusps result in the cross section having a infinite derivative at $\epsilon_n$. The derivative can be positive or negative on either side of the threshold, and so cusps can be associated with a peak, a dip or a rounded step [88]. The shape of the near-$6s6p^1P_1$ threshold feature in the mercury metastable atom excitation functions of Newman et al. [45] is consistent with a cusp, as is the near-$5s5p^1P_1$ threshold feature in the cadmium electron transmission spectrum of Sullivan et al.[1]. The zinc differential scattering signal in Figures 5.5 and 5.5 show that the feature quite possibly has a discontinuous derivative at the $4s4p^1P_1$ threshold, but the present energy resolution is insufficient to make a definitive assessment of the structure’s shape.

Lastly, the observation of a $p$-wave nature for the structure further strengthens the claim that it is a cusp, since it is this partial wave which is responsible for near-threshold excitation of the $4s4p^1P_1$ state. In addition, Zatsarinny and Bartschat [2] predict a $p$-wave nature for the structure. Based on the available evidence it appears the the 5.80 eV feature seen here for zinc is most likely a cusp, as are the equivalent structures in mercury and cadmium.

Elastic scattering between 7 eV and 8.5 eV appears to be influenced by many different negative-ion resonances. BSRM calculations predict 11 negative-ion resonances in this energy region, built on the parent configurations of $4s5p$, $4s4d$, $4s6s$, $4s7s$ and $4s6d$, and having a range of different symmetries. Multiple negative-ion resonances in this energy region have also been identified in electron transmission by Sullivan et al.[1], and in the photon excitation function studies detailed in Chapter 6. As can be seen in Figures 5.7 and 5.8, there is a reasonable correspondence between the present differential elastic scattering measurements, and the three negative-ion resonances identified by Sullivan et al.[1]. The discussion here will be restricted to a comparison of these two experiments and the calculation of Zatsarinny and Bartschat [2]. There is also reasonable correspondence between the present elastic scattering data and the negative-ion resonances marked (4), (5) and (6).
which are observed in photon excitation functions. However, these will not be included in this discussion. Elastic scattering is the dominant scattering process and so will have the largest impact on electron transmission, meaning that these two sets of data are therefore more closely related than inelastic and elastic scattering.

The lowest energy negative-ion resonance observed in electron transmission is at 7.40 eV, and was assigned a $4s5s4d$ configuration. Such a configuration will give rise to $^4D_{1/2,3/2,5/2,7/2}$ and $^2D_{3/2,5/2}$ terms, for which the dominant decay mechanism to the ground state will be $d$-wave emission. This suggests that the corresponding structure in differential elastic scattering should be absent at 54°. Zatsarinny and Bartschat do not predict any negative-ion resonances within 100 meV of 7.40 eV. The next highest negative-ion resonance in electron transmission is observed at 7.55 eV, and has been assigned a $4s4d^2$ configuration. This configuration gives rise to many components, which can decay to the ground state by $s$, $d$ and $g$-wave emission. On the other hand, Zatsarinny and Bartschat [2] also predict a $4s5p^22S_{1/2}$ negative-ion resonance at 7.524 eV and a $4s5p^22D_{3/2,5/2}$ negative-ion resonance at 7.570 eV. The former negative ion will decay to the ground state by $s$-wave emission, and the corresponding structure in differential elastic scattering should be present at all angles. On the other hand, the latter negative ion will decay to the ground state by $d$-wave emission, and the corresponding structure in differential elastic scattering should be absent at 54°. The highest energy negative-ion resonance observed in electron transmission is at 7.65 eV, and has been assigned $4s5p^22D_{3/2,5/2}$. For this negative ion the decay mechanism to the ground state will be $d$-wave emission, and the corresponding structure in differential elastic scattering should be absent at 54°. Zatsarinny and Bartschat predict two near-by negative-ion resonances, a $4s4p5p^22F_{5/2,7/2}$ negative-ion resonance at 7.615 eV, and a $4s4d5s^22D_{3/2,5/2}$ negative-ion resonance at 7.725 eV. These negative ions will decay to the ground state by $f$-wave emission and $d$-wave emission respectively. The emission of an $f$-wave electron requires a large centrifugal barrier to be overcome, which suggests that perhaps the $4s4d5s^22D_{3/2,5/2}$ negative-ion resonance is more likely to affect elastic scattering, resulting in a lack of negative-ion resonance structure at 54°.

By inspection of Figures 5.7 and 5.8, and allowing some margin for error due to the ±0.03 eV energy uncertainty of the present experiment, it appears that the 7.55 eV negative-ion resonance structure is present at all angles. This supports a $4s5p^22S_{1/2}$ assignment for this negative-ion resonance. The partial wave behaviour of the other negative-ion resonances is not as clear. The 7.40 eV negative-ion resonance seems to be associated with a dip in the elastic cross section which is present at all angles except 110°. The 7.65 eV negative-ion resonance seems to be associated with a peak at 30°, but at the other scattering angles it is difficult to determine whether it is associated with a peak or a dip, or if it is absent. Generally speaking, it is very difficult to analyse data such as these where there are numerous closely spaced and relatively weak negative-ion resonances. The energy resolution and counting statistics also make it difficult to determine the partial wave behaviour. So although the present measurements show a strong angular dependence, the amount of information which can be extracted from the data is
limited. However, some further negative-ion resonances assignments will be made in this energy region using the photon excitation function measurements detailed in Chapter 6. These measurements exploited the $L$ and $S$ dependance of negative-ion decay and so were better able to isolate overlapping negative-ion resonances.

## 5.2 Elastic scattering above the ionisation threshold

As has already been mentioned several times, negative-ion resonances have a large effect on zinc elastic and inelastic cross sections near 11 eV. The negative-ion resonances are quite broad, on the order of 100 meV, and overlap to form a large structure with three main peaks, but within these peaks there also appear to be doublet and multiplet structures. This is particularly apparent in the photon excitation function measurements presented in Chapter 6, where different components of the resonance structure affect the excitation of states with different $L$ and $S$. In the present scattered electron measurements, multiple negative-ion resonance contributions are apparent as the shoulders on the observed peaks.

To assist the interpretation of the present work, shown in Figure 5.9a is the result of a previous experimental study by Burrow and Michejeda [3]. These data were obtained using the electron transmission technique described by Schulz [23] (and references therein), which measures the derivative of transmitted current with respect to energy and so is highly sensitive to negative-ion resonances. The electron transmission approach is also conducive to high energy resolution studies and producing data with excellent statistical accuracy. Of the experiments performed to date, this is the best able to show the number and width of negative-ion resonances present. However, transmission studies do not have the state selectivity or angular resolution of the present experiment.

There is excellent agreement between the transmission study, which had an energy resolution of 35 meV, and the present differential elastic scattering data presented in Figures 5.9a-5.11. Both experiments show three main negative-ion resonance groups, but the doublet structure of the two lowest energy groups suggested in the present data is obvious in the transmission study. For the third and highest energy group, shoulders suggest the presence of multiple broad and overlapping negative-ion resonances. Both the present and the transmission experiments also show a relatively small peak, marked $d$ in Figures 5.9a and c, at an energy of 11.61 eV.

To allow a more direct comparison with the present results, the transmission data were manipulated to make them approximately equivalent to cross section measurements. First, the transmission data were integrated, because they are differential with respect to energy. Next, the resonance contributions to this integrated transmission signal were isolated by subtracting a least squares polynomial fit to the the slowly varying non-resonance background. Lastly, the data were inverted because increases/decreases in the transmitted current correspond to decreases/increases in the scattering signal. The manipulated transmission data is shown in Figure 5.9b. The effects observed in the transmission data are summed over all scattering channels, but one would expect small angle elastic scattering
Figure 5.9: (a) The derivative of transmitted current, (b) transmission data manipulated as described in the text and (c) differential elastic scattering signal at 15° between 9 eV and 14 eV. For (c), • present data, − transmission data, − a polynomial fit to the slowly varying non-resonance background, • the percentage resonance contribution to the data.
Figure 5.10: Differential elastic scattering signal at (a) 30°, (b) 54°. • present data, — transmission data, − a polynomial fit to the slowly varying non-resonance background, -— the percentage resonance contribution to the data.
Figure 5.11: Differential elastic scattering signal at (a) 90°, (b) 110°. • present data, — a polynomial fit to the slowly varying non-resonance background, - - - the percentage resonance contribution to the data.
5.2. ELASTIC SCATTERING ABOVE THE IONISATION THRESHOLD

to dominate since its signal was by far the greatest in this energy region. Accordingly, to permit a direct comparison, the manipulated transmission data is placed above the 15° elastic differential scattering signal in Figure 5.9c. Again, there is excellent agreement between the two experiments. Doublet structure, though still apparent in the manipulated transmission data, is not as obvious which highlights the sensitivity of the energy differential experimental technique. Also, the structure present near 11.6 eV clearly resolved in the differential data is only a shoulder after integration. Lastly, structures in the manipulated transmission are at least approximately 100 meV wide, and so much larger than the 35 meV resolution of the experiment. This confirms that the negative-ion resonances here have a large natural width. So, for the present electron and photon excitation function measurements, the ability to resolve all the negative-ion resonances is limited by their large natural width and close spacing, not by the resolution of the experiment.

The combined information gathered from the elastic scattering and transmission studies presented here, and the photon excitation functions presented in Chapter 6, suggest that at least eight negative-ion resonances are present in the near-11 eV region. Throughout this work, the near-11 eV negative-ion resonances are labelled using the following system. The labels A, B and C are used to distinguish the three groups of large negative-ion resonances. The individual structures produced by structures within these groups are distinguished with primes, for example the two structures produced by the A-group resonances are marked a and a'. The negative-ion resonance structure near 11.61 eV is marked d. These labels are used to associate resonance structures seen at the same energy in different channels, and to clarify which negative-ion resonances affect a particular excitation mechanism. Labels for the a and a' resonance structures are marked at 10.75 and 10.80 eV, which are the energies of the a and a' resonance structure peaks in the manipulated transmission. Labels for the b and b' resonance structures are marked at 11.01 and 11.09 eV, and labels for the c, c' and c'' resonance structure peaks in photon excitation functions. The label for the d resonance structure is marked at 11.61 eV, which is the energy of the d resonance structure peak in the differential elastic scattering signal at 15°. The a, a', b, b', c, c', c'' and d resonance structures are not referred to as negative-ion resonances because the present electron and photon excitation function measurements indicate that they may be comprised of several negative-ion resonances.

The differential elastic scattering signals from 15° to 110° are shown in Figures 5.9a-5.11, with the interpolated background and the isolated resonance contributions. The energies of resonance structures observed in the differential elastic scattering signal above the ionisation threshold are given in Table 5.3. Doublet and multiplet structures, though perhaps suggested by the width of the peaks and the presence of shoulders, are not resolved clearly. There is a lack of structure at 54°, which implies that the dominant negative-ion resonances have a d-wave nature. The A-group resonances are not apparent at 90°, which perhaps suggests that these negative-ions have a p-wave nature. For the d resonance structure it is difficult to distinguish partial wave behaviour because it is relatively weak.
Table 5.3: Energies of resonance structures observed the differential elastic scattering signal above the ionisation threshold. The total uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The letters in the leftmost column refer to the resonance labels used to identify negative ion resonances throughout this paper. All energies are in units of eV.

<table>
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<th>a</th>
<th>a’</th>
<th>b</th>
<th>b’</th>
<th>c</th>
<th>c’</th>
<th>c''</th>
<th>d</th>
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<td>11.24±0.03</td>
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<td>-</td>
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and masked by contributions from the near-by dominant peaks. The significant strength of negative-ion resonances can be seen in their contributions to the overall elastic cross section. The peak contributions are approximately 10% at 15° and 30°, and approximately 30% at 90° and 110°.

5.2.1 Discussion

As shown in Figure 5.10b, negative-ion resonance structure almost completely disappears at 54°, indicating that the dominant negative-ion resonances decay to the ground state by the emission of a d-wave electron. Thus, these negative ions have positive parity, total angular momentum of $J = 3/2$ or 5/2, and a significant $2D$ component.

Between the energies of 10.2 eV and 12 eV, the calculations of Mansfield [11] predict that there are twelve $3d^94s^24p$ states, compared to two $3d^{10}4p^2$ states. Furthermore, the ejected electron spectra of Back et al. [14] indicate that the 3d-core excited states have the greater cross section. So, is most likely that the negative ions are based on $3d^94s^24p$ parent or $3d^94s^2$ grandparent states. The configurations which obey the positive parity restriction and lie in the vicinity of the negative-ion resonances include $3d^{10}4p^24d$, $3d^94s^24p^2$ and $3d^94s^24p4f$. One might possibly expect the 4f electron capture to be less likely than the capture of a 4p electron, as is generally the case for higher angular momentum electrons because a larger centrifugal barrier is involved. So, the elastic electron scattering results seem to suggest a $3d^94s^24p^2$ configuration for the negative ions.

Having established the likely, $3d^94s^24p^2$ negative ion configuration associated with the observed resonances, appropriate momentum coupling schemes and the manifold of expected state energies will now be considered. Although so far this discussion has been based on distinct electron configurations, it is quite likely that this concept may not be applicable when describing these negative-ion states. Ideally, a discussion would proceed using models which take configuration mixing into account, which as noted above is indicated by Mansfield [11] to be essential for reproducing the correct energy ordering of the $3d^94s^24p$ states. Mansfield also showed the $3d^94s^24p$ to be strongly mixed, with the
strongest $LS$ component of one state having a weight of only 49%. One would expect negative ions based on these parent states to be even more strongly mixed, given that the size of the spin-orbit interaction relative to the central field potential will be greater for two 4$p$ electrons outside a 3$d^9 4s^2$ Zn$^+$ core than for one 4$p$ electron outside a 3$d^9 4s^2$ Zn$^+$ core. In the absence of theoretical modelling for 3$d^9 4s^2 4p^2$ negative-ion resonances in zinc, a comparison between the resonance energies listed in Table 5.3 and spectroscopic data on 3$d^9 4s^2 4p^2$ autoionizing states of neutral gallium obtained by Connerade [89], which is isoelectronic to Zn$^-$, will be used as a basis for further interpretation.

The energy spectrum and assignments of the optically-allowed 3$d^9 4s^2 4p^2$ autoionising states of gallium [89, 10] are shown in Figure 5.12. Connerade [89] performed unrestricted Hartree-Fock configuration average calculations using the MCHF72 code of Froese-Fischer [90] and approximate $LS$-coupling. The results of these Ga calculations are in reasonable agreement with observed transition energies, but not always with observed intensities. Also shown in Figure 5.12 are the zinc a,$a'$, b,$b'$, c,$c'$, $c''$ and d resonance structure energies, and the energy of zinc autoionising states with 3$d^{10} 4p^2$ and 3$d^9 4s^2 4p$ electron configuration [11, 10].

When $LS$-coupling is applied to the 4$p$ electron pair and restrictions imposed by the Pauli principle taken into account, the three states, $1D$, $3P$ and $1S$ [91, 5] can be formed. $LS$-coupling of the electron pair to the $2D$ ion core leads to the optically allowed states of gallium observed in the absorption spectra of Connerade [89] [10], displayed in Figure 5.12. Arrows indicate from which electron pair symmetry the observed states are derived, and the doublets resulting from fine structure components are connected with horizontal bars. The 3$d^9 4s^2 4p^2$ states of Ga are ordered with a $3P$ outer electron pair having the lowest energy, followed by $1D$ and $1S$. The energy difference between these outer electron states is large enough that the terms arising from coupling of different outer electron states to the core are well separated in energy. However, the various terms that result from the coupling of a particular outer electron state to the core are sufficiently close in energy that their fine-structure components are intermingled. For zinc negative ions, which have $Z = 30$ instead of $Z = 31$ like Ga, the difference in energy between outer electron states is likely to be smaller, because they experience a smaller central potential. Verification of this can be found by comparing the energy separation between terms arising from the 3$d^{10} 4p^2$ configurations of Zn and Ga$^+$, where the separations between the $1D$, $3P$ and $1S$ states of Zn are significantly smaller than for Ga$^+$ [10]. It might be expected that the zinc 3$d^9 4s^2 4p^2$ negative-ion resonances arising from a $3P$ outer electron pair states would have the lowest energy, and those arising from a $1S$ outer electrons pair states would have the highest energy. However, smaller energy separations compared to Ga will result in intermingling of resonances associated with negative ions having different outer electron states, as well as different $J$.

The $2D$ core and $1D$, $3P$ and $1S$ outer electrons can also couple to produce non-optically allowed quartet and $F$ states, which are given in Table 5.4. This table shows all states with $J = 3/2$ or $5/2$ which are derived from $LS$-coupling of the 3$d^9 2D_{3/2,5/2}$
core to $4p^2 \, 1S, \, 3P, \, 1D$ outer electrons. There are 16 states in total, and these are likely to mix strongly with each other, and perhaps also with states derived from other configurations with the same parity, such as $4s4p^2$ and $4p^24d$. Altogether, there are six possible $3d^94s^24p^2D_{3/2,5/2}$ states arising from $LS$-coupling, and so probably six real, mixed states with a dominant $2D$ character. However, together the transmission and electron scattering data suggests that there are at least eight negative-ion resonances, most of which appear to decay to the ground state by $d$-wave emission. There is a small anomaly in the electron scattering data which suggests that the $a$ and $a'$ resonance structures may perhaps decay by $p$-wave emission, which will be discussed later. However, if this behaviour is spurious, then it would seem that at least two of the negative ions decay via a non-dominant $LS$ component. This will be necessary because, of the partial waves which comply with the parity restriction, only $d$-wave electrons will ensure that $J$ is also conserved. As a result their decay via a non-dominant $LS$-component, at least two of the negative ions may be longer lived, and therefore produce resonances which are narrower than the other negative-ion resonances.

Negative-ion resonances with a $(n-1)d^9ns^2np^2$ configuration were also observed in the mercury $(n=6)$ metastable atom excitation function measurements of Newman et al. [45]. Six negative-ion resonances observed at energies between 8.854 eV and 10.90 eV were assigned this configuration, but several negative-ion resonances within and just above this energy range were not assigned a configuration, and may also be $5d^96s^26p^2$. The negative-ion resonances were assigned using the $j-j$ coupling scheme, which Connerade et al. [92] showed was the appropriate scheme to classify the levels of the isoelectronic Tl. Newman et al. observed a large, approximately 1 eV energy separation between the mercury negative ions based on a $2D_{5/2}$ core, and those based on a $2D_{3/2}$ core, which is significantly larger than the 337 meV splitting between the $3d^9(2D_{5/2})4s^2$ and $3d^9(2D_{3/2})4s^2$ levels of $Zn^+$. The zinc negative-ion resonances will therefore not be as well separated by $3d^9$ core fine structure. Also, the $6p$ outer electrons of the mercury negative-ion resonances are $j-j$ coupled. This is unlike the $4p$ outer electrons of the zinc negative-ion resonances, which level assignments of isoelectronic gallium by Connerade[89] suggest will be approximately $LS$-coupled. These considerations mean that it is difficult to use the mercury negative-ion resonances as a guide to assign the present zinc negative-ion resonances.

Based on the discussion above, there appears to be an anomaly in the elastic scattering data at 90° where the $A$-group resonances are not present. This seems to suggest that these negative ions decay by $p$-wave emission, and should therefore be present in the elastic scattering signal at 54°. The dip structure at 54°, shown in Figure 5.10b, coincides approximately with the $a$ and $a'$ observation energies. A negative-ion resonance could appear radically different in the absence of overlapping contributions from other structures, and so it is possible that the $a$ and $a'$ resonance structures, which seem associated with a peak at 30°, may appear as a dip at 54°. If the $a$ and $a'$ resonance structures do decay to the ground state by $p$-wave electron emission, they must be associated with odd parity negative ions having total angular momentum of $J = 1/2$ or $3/2$. Possible electron configurations
Figure 5.12: Observed energy levels of Ga, Zn and Zn\(^{-}\). Upper energy scale; the \(^3d^94s^24p^2\) autioionising states of gallium [10]. Assignments are based on the LS coupling scheme [89]. Lower energy scale; zinc negative ion, and \(^3d^94s^24p\) autoionising state energies [11].
Table 5.4: Possible 3d-core excited negative ion states, of the configuration 3d$^9$4s$^2$4p$^2$ and $J = 3/2$ or 5/2, or 3d$^9$4s$^2$4p4d and $J = 1/2$ or 3/2, derived from LS-coupling.

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</tr>
<tr>
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<tr>
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</tr>
<tr>
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<td>2D$<em>{3/2}$, 2P$</em>{1/2,3/2}$, 2S$_{1/2}$</td>
</tr>
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<td>4F$<em>{3/2}$, 4D$</em>{1/2,3/2}$, 4P$<em>{1/2,3/2}$, 4S$</em>{3/2}$, 2D$<em>{3/2}$, 2P$</em>{1/2,3/2}$, 2S$_{1/2}$</td>
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</table>
would therefore include $3d^{10}4p^3$, $3d^{10}4p^24f$, $3d^94s4p4d$ and $3d^94s4p4g$ and $43d^94s^24p5s$. The $3d^94s4p4d$ configuration seems the most likely given the density of $3d^94s4p$ states in the vicinity of the negative-ion resonances, the simplicity of an autoionisation process where the 3$d$-hole could be filled by a 4$d$ electron, and the generally smaller probability for the capture of higher angular momentum electrons. The possible states derived from $LS$ coupling of a $3d^94s4p4d$ configuration are shown in Table 5.4. If $a$ and $a'$ are associated with $3d^94s4p4d$ configuration negative ions, that these are the lowest energy negative-ion resonances in this region may point to a significant interaction between the 3$d$ hole and the 4$d$ outermost electron resulting in a higher binding energy.

However, there could be another reason for the apparent disappearance of the $A$-group resonances at 90°. The $a$ and $a'$ resonance structures could, for example, have profiles at 90° which when superimposed on each other and the other negative-ion resonances could lead to them being “cancelled out”. It is also possible that there is some interference between the negative-ion resonances which may cause the lack of $A$-group resonance structure at 90°. Also, the angular behaviour of negative-ion resonance profiles can deviate from that of the Legendre polynomials $P_l(\cos(\theta))$ if the spin-flip scattering amplitude $g$, defined in Equation 5.3, is significant. This could occur if the fine-structure splitting of the negative ion is much greater than its width, or if there is a significant background spin-orbit interaction. However, as was shown, for example, by Weingartshofer et al. [82], this spin-dependent effect causes negative-ion resonance profiles to be present at angles where $P_l(\cos(\theta)) = 0$, and to be absent at angles nearby. This is not seen in the present case, where the anomalous absence of structure at 90° corresponds to a zero of the $P_l(\cos(\theta))$ Legendre polynomial.

Another feature of interest in the elastic scattering data is the broad dip in the cross section between 10 and 13 eV evident at 90° and 110°. This may indicate a significant number of unresolved, overlapping, short-lived, and therefore energetically broad, negative-ion resonances. The density of possible $3d^94s^24p$ parent states in this energy region lends support to this idea, especially given the apparent significance of electron correlations associated with this configuration. Factors which may result in short negative ion lifetimes have been discussed by Read et al. [29]. Briefly, if the rearrangement during negative-ion decay involves only changes in principle quantum $n$, a shorter negative-ion lifetime is expected. The lifetimes are also shorter the lower the angular momentum of the ejected electron because the centrifugal barrier it experiences will be smaller. There are five states derived from $LS$-coupling of the $3d^94s^24p^2$ configuration with $J = 1/2$. Of these, one arising from coupling of the $^2D$ core to $^1D$ outer electrons has a $^2S$ character, and so would be expected to have a strong decay to ground via $s$-wave emission mediated by the electrostatic interaction. The other terms with $J = 1/2$ may be mixed with the $^2S$ state, allowing them to also decay to the ground state by $s$-wave emission. However, negative-ions based on pure $3d^94s^24p^2$ configurations cannot decay to the $3d^{10}4s^2$ ground state without a change in $n$ for at least one electron, which would be expected to result in a longer negative ion lifetime. On the other hand, Mansfield [11] has shown that configu-
ration mixing is significant for the $3d^94s^24p$ states of zinc, so less complicated negative-ion decay mechanisms may proceed through components other than the dominant configuration. For example, given the mixing of $3d^94s^24p$ and $3d^{10}4s4p^2$ configurations predicted by Mansfield, the $3d^94s^24p^2$ and $3d^{10}4s4p^2$ negative-ions may be also be mixed. A $3d^{10}4s4p^2$ negative-ion can couple to form a $2S$ state which will also decay to the ground state without a change of $n$ for any of the atomic electrons. Configuration mixing provides a mechanism by which negative ions, formed by strong correlations involving a $3d^9$ core, may decay to $3d^{10}4s4l$ states with only minor rearrangements in electron configuration. If the the broad dip in the cross section between 10 and 13 eV is due to very short lived negative ions, then it is likely to be a signature of configuration mixing.

5.3 $4s4p^3P_{0,1,2}$, $4s4p^1P_1$ electron excitation functions

The affect of near-11 eV negative-ion resonances on the excitation of the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ states was found to be very significant, especially for $4s4p^3P_{0,1,2}$ excitation where at some scattering angles negative-ion resonance contributions were over 50% of the observed signal. The results of electron excitation function studies for the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ states of zinc in the vicinity of the near-11 eV negative-ion resonances are shown in Figures 5.13-5.17. For comparison, elastic differential scattering signal in the same energy region is also shown in these figures. In all figures the estimated background is shown as a solid line with the resonance structure contributions as a percentage of the interpolated background. Also shown are markers indicating the averaged observed energies of the $a$-$d$ resonance structures. The energies of the features observed are shown in Tables 5.5 and 5.6.

Like the elastic scattering study, the $4s4p^3P_{0,1,2}$ electron excitation function shows three dominant structures. Resonance contributions to this state were clearly at a minimum at 90°, indicating a dominant role of $p$-wave electron emission in the decay process, and approximately 50% at all the other angles observed. However, the $4s4p^1P_1$ electron excitation function is very different, particularly at 15° and 30°, where negative-ion resonances are associated with a broad, single dip. The $4s4p^1P_1$ electron excitation functions lack significant structure at any angle due to the $A$-group resonances. Resonance contributions as a percentage of the observed signal were also smaller, ranging between 12% at 15° to 35% at 110°. In addition to the features observed in elastic scattering, at 15° both the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ state excitation functions display a feature near 10 eV. Given the limited amount of available data regarding these structures, labelled $x$ and $y$ in Figures 5.13 b and c, it is difficult to enter into a detailed analysis. However, these features occur near the thresholds of the lowest energy, $3d^{10}4p^23P_{0,1,2}$ autoionising states at 9.940, 9.968 and 10.017 eV. The structures may be cusps or negative-ion resonances associated with the $3d^{10}4p^23P_{0,1,2}$ states.
Figure 5.13: Electron excitation functions taken at a scattering angle of 15° in the vicinity of the near-11 eV negative-ion resonances; (a) elastic signal, (b) present 4s4p $^3P_{0,1,2}$ data (c) present 4s4p $^1P_1$ data. • present data, — polynomial fit to the slowly varying non-resonance contribution, • the percentage resonance contribution to the data.
Figure 5.14: Electron excitation functions taken at a scattering angle of 30° in the vicinity of the near-11 eV negative-ion resonances; (a) elastic signal, (b) present 4s4p$^3P_{0,1,2}$ data (c) present 4s4p$^1P_1$ data. • present data, — polynomial fit to the slowly varying non-resonance contribution, - the percentage resonance contribution to the data.
Figure 5.15: Electron excitation functions taken at a scattering angle of 54° in the vicinity of the near-11 eV negative-ion resonances; (a) elastic signal, (b) present 4s4p\(^3\)P\(_{0,1,2}\) data (c) present 4s4p\(^1\)P\(_1\) data. • present data, — polynomial fit to the slowly varying non-resonance contribution, - • the percentage resonance contribution to the data.
Figure 5.16: Electron excitation functions taken at a scattering angle of 90° in the vicinity of the near-11 eV negative-ion resonances; (a) elastic signal, (b) present 4s4p^3P^{0,1,2} data (c) present 4s4p^1P data. • present data, - polynomial fit to the slowly varying non-resonance contribution, --- the percentage resonance contribution to the data.
Figure 5.17: Electron excitation functions taken at a scattering angle of 110° in the vicinity of the near-11 eV negative-ions; (a) elastic signal, (b) present 4s4p3P0,1,2 data (c) present 4s4p1P1 data. • present data, — polynomial fit to the slowly varying non-resonance contribution, —— the percentage resonance contribution to the data.
5.3.1 Discussion

In the case of inelastic scattering, the emitted electron is not restricted to a single partial wave, because the atom is generally left in a state with non-zero angular momentum after the decay of the negative ion. The negative ions associated with the dominant resonance observed in elastic scattering have \( J = 3/2 \) or \( 5/2 \) and positive parity, can decay to the \( 4s4p^3P_{0,1,2} \) or \( 4s4p^1P_1 \) states by the emission of a \( p \) or \( f \)-wave electron. Contributions from both \( p \)-wave and \( f \)-wave electrons will be zero at \( 90^\circ \), and \( f \)-wave contributions will also be zero at \( 39.2^\circ \) and \( 140.8^\circ \). Both the \( 4s4p^3P_{0,1,2} \) and \( 4s4p^1P_1 \) electron excitation functions have significant structure at \( 90^\circ \). One explanation could be that, as discussed above, the spin-dependence of the scattering could result in deviations from the angular behaviour expected from the Legendre polynomials \( P_l(\cos \theta) \). Another explanation is the presence of negative ions which decay to the \( 3d^{10}4s4p \) configuration by \( s \) or \( d \)-wave electron emission.

Parity conservation requires that these resonances cannot have a \( 3d^3 \) or \( 3d^9 \) configuration.

An alternative negative ion configuration is \( 3d^94s^24p4d \), and it was suggested above that resonances associated with negative ions having this configuration may cause the anomalous absence of the \( A \)-group resonances in the \( 90^\circ \) differential elastic scattering signal. However, for elastic scattering the contribution of negative-ion resonances with a \( 3d^94s^24p4d \) or any other negative parity configuration is almost completely masked by the \( 3d^94s^24p^2 \) negative-ion resonances. Perhaps the relative strength of odd-configuration negative-ion contributions to the \( 4s4p^3P_{0,1,2} \) and \( 4s4p^1P_1 \) is large because the negative ion is mixed with the \( 3d^{10}4s4p4d \) configuration. If so, the negative ion can decay via \( 3d^{10}4s4p4d \) to the \( 4s4p^3P_{0,1,2} \) or \( 4s4p^1P_1 \) state by emission of a \( d \)-wave electron, with almost no rearrangement of electron configuration.

For \( 4s4p^3P_{0,1,2} \) state excitation, the \( B \) and \( C \)-group negative-ion resonances are smaller at \( 90^\circ \) than at the other angles, as can be seen in Figures 5.13-5.17. For example, at \( 90^\circ \) the structure due to the \( C \)-group negative-ion resonances peaks at 18% of the interpolated background, whereas at \( 110^\circ \) it peaks at 52%. This means that there is a large contribution of \( p \)-wave scattered electrons to these structures, and therefore also a large contribution from \( 3d^94s^24p^2 \) negative-ion resonances. But compared to the differential elastic scattering signal at \( 54^\circ \), there still is a significant structure at \( 90^\circ \) due to the \( B \) and \( C \)-group resonances. There are possibly \( s \) or \( d \)-wave scattered electron contributions to these structures, or both, and therefore contributions from negative-ion resonances with an odd electron configuration, such as, for example, \( 3d^94s^24p4d \). The \( 4s4p^3P_{0,1,2} \) electron excitation function supports the suggestion put forward above that the \( A \)-group resonance structure is due to negative ions with a \( 3d^94s^24p4d \) configuration. The size of the \( a \) resonance structure, measured from the point where the electron excitation function starts to increase near 10.6 eV, to the point where the \( a \) structure peaks near 10.75 eV, is 38% of the interpolated background at \( 15^\circ \), 32% at \( 30^\circ \), 28% at \( 54^\circ \), 22% at \( 90^\circ \), and 41% at \( 110^\circ \). The fact that the size of the \( A \)-group resonance structure is lowest at \( 90^\circ \) suggests that there is some contribution from \( p \)-wave electrons. Compared to the \( B \) and \( C \)-group negative-ion resonances, the size of the \( A \)-group negative-ion resonances is relatively
constant across the angular range studied. This is consistent with a large contribution from s-wave electrons resulting from the decay of a 3d\textsuperscript{0}4s\textsuperscript{2}4p4d negative ions.

For the 4s4p\textsuperscript{1}P\textsubscript{1} state, the peak size of negative-ion resonance structures relative to the interpolated background is 12\% at 15\degree, 15\% at 30\degree, 26\% at 54\degree, 29\% at 90\degree and 36\% at 110\degree. The increase in negative-ion resonance contributions with increasing scattering angle might be expected because the non-resonance excitation of singlet states is generally forward peaked. However, the similar size of negative-ion resonance structures in the 54\degree, 90\degree and 110\degree electron excitation functions indicates that they are not dominated by p-wave electron contributions. Also of note is that, for the 4s4p\textsuperscript{1}P\textsubscript{1} state electron excitation functions, only the 54\degree and 90\degree data have a near-11 eV negative-ion resonance structure comprised of multiple peaks. At 15\degree, 30\degree and 110\degree there are only single broad structures near 11 eV. The structures at 15\degree and 30\degree are dips, with respective FWHM of 350 meV and 440 meV, while the 110\degree structure is a 400 meV FWHM peak. As shown in Table 5.6, the extrema of the 15\degree, 30\degree and 110\degree structures at all due to C\texttext{-group negative-ion resonances. At 54\degree and 90\degree, d-wave and p-wave will be respectively zero. That multiple peaks should be present only at these angles, and that at other angles the single structures are very broad, suggests that many negative-ion resonances, with both odd and even configurations, affect 4s4p\textsuperscript{1}P\textsubscript{1} state excitation near 11 eV with a similar strength. Numerous closely spaced and overlapping negative-ion resonances with a similar strength could produce the single broad structures at 15\degree, 30\degree and 110\degree. The absence of some odd configuration negative-ion resonance contributions at 54\degree, and all even configuration negative-ion resonance contributions at 90\degree would allow the structure due to negative ions of opposite parity to become apparent in the electron excitation functions.

This interpretation begs two questions. First, why are p-wave resonance contributions smaller relative to s and d-wave resonance resonance contributions for 4s4p\textsuperscript{1}P\textsubscript{1} as opposed to 4s4p\textsuperscript{3}P\textsubscript{0,1,2}? And second, if 4s4p\textsuperscript{1}P\textsubscript{1} excitation is affected relatively strongly by 3d\textsuperscript{0}4s\textsuperscript{2}4p4d negative ions, why are contributions from the A\texttext{-group negative-ion resonances so small? Given that there is evidence even in elastic scattering that the A\texttext{-group has a strong contribution from 3d\textsuperscript{0}4s\textsuperscript{2}4p4d negative-ion resonances, it might be expected that the A\texttext{-group has a large effect on the 4s4p\textsuperscript{1}P\textsubscript{1} state. Answers to these questions may perhaps be derived from knowledge of which LS terms comprise the mixed negative-ion resonance states.

Turning to the first question, if there are relatively small p-wave resonance contributions to the 4s4p\textsuperscript{1}P\textsubscript{1} state, it is probably because the 3d\textsuperscript{0}4s\textsuperscript{2}4p\textsuperscript{2}, J = 3/2, 5/2 negative ions do not decay as strongly to this state. Observations of these negative-ion resonances in elastic scattering suggest that they have a strong \textit{2D LS} character, but they will probably be strongly mixed with some of the terms given in Table 5.4. Some of these are quartet terms, which will have a strong, \textit{LS-coupling allowed transitions into the 4s4p\textsuperscript{3}P\textsubscript{0,1,2} state, but not the 4s4p\textsuperscript{1}P\textsubscript{1} state. A similar argument, applied to the 3d\textsuperscript{0}4s\textsuperscript{2}4p4d configuration, may answer the second question. If the negative-ion resonances which comprise the A\texttext{-group are strongly mixed with quartet terms given in Table 5.4, they would de-
Table 5.5: Energies of resonance structures observed in differential electron excitation functions for the $4s^3P_{0,1,2}$ states above the ionisation threshold. The total uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The letters in the leftmost column refer to the resonance labels used to identify negative-ion resonances throughout this paper. All energies are in units of eV.

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<th>b</th>
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Table 5.6: Energies of resonance structures observed in photon excitation functions for the $4s^1P_1$ state above the ionisation threshold. The total uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The letters in the leftmost column refer to the resonance labels used to identify negative-ion resonances throughout this paper. All energies are in units of eV.

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cay preferentially to the $4s^3P_{0,1,2}$ state. However, the $A$-group negative-ion resonances also contribute strongly to elastic scattering from the singlet ground state. The electron configuration rearrangement required for decay into the ground state is different from the decay into the $4s^3P_{0,1,2}$ or $4s^1P_1$ state. The decay into the ground state perhaps occurs through a configuration component of the mixed negative-ion which has a doublet, as opposed to quartet, nature.

### 5.4 Conclusion

Structures in the differential elastic scattering signal below the ionisation threshold were grouped into three energy regions. The present observation of the 4.26 eV negative-ion resonance are in agreement of the resonance energy and width reported by Sullivan et al.\cite{1}, and the $4s4p^22D_{3/2,5/2}$ assignment made in that work, and the theoretical work of Zatsarinny and Bartschat \cite{2}. The 5.80 eV feature was observed to have a $p$-wave nature, which is definitive proof that it is not a $4s4p^22S_{1/2}$ negative-ion resonance, as assigned by Sullivan et al. It follows that the similar features observed for mercury
(n = 6) and cadmium (n = 5) are not $nsnp^2 2S_{1/2}$ negative-ion resonances either, which contradicts assignments made by Sullivan et al. and Newman et al. [45]. The most obvious alternate negative ion configurations are $nsnpnd$ and $nsnp(n + 1s)$, but the lack of any observed fine structure in the mercury feature seems to rule both out. On the other hand, the energy position, shape and $p$-wave nature of this feature are all consistent with the cusp assignment made by Zatsarinny and Bartschat. Multiple overlapping negative-ion resonances are observed near 7.5 eV, three of which coincide with negative-ion resonances observed by Sullivan et al.. The 7.50 eV negative ion seems to decay to the ground state by $s$-wave emission, which supports a $4s5p^2 2S_{1/2}$ assignment made by Zatsarinny and Bartschat. The statistical accuracy of the present data is insufficient to assign other negative-ion resonances observed in this energy region.

The differential elastic scattering signal is in excellent agreement with the transmission data of Burrow and Michejeda [3], which indicates the presence of at least eight negative-ion resonances in the near-11 eV region. These negative-ion resonances display a dominant $d$-wave behaviour, which suggests that they have a $3d^94s^24p^2$ configuration, $J = 3/2, 5/2$ and a significant $2D$ $LS$ character. A comparison with the energy level structure of the isoelectronic gallium atom suggests that the negative ions are approximately $LS$-coupled, and are ordered in energy depending on whether the $4p$ outer electrons are in a $^3P$ (lowest energy), $^1D$, or $^1S$ (lowest energy) state. The $A$-group negative-ion resonances are absent from the elastic scattering signal at 90°. This may be because overlapping negative-ion resonances cancel at this energy, or because there is a deviation from the expected partial wave behaviour due to spin-dependence as was shown by Weingartshofer et al. [82]. Another possible explanation is that the $A$-group structures seen in elastic scattering are due to negative-ion resonances with a $3d^94s^24p4d$ configuration. Finally, it was suggested that the large, broad depression in the 90° and 110° elastic scattering signals may be due to shortlived negative-ion resonances, which decay to the ground state by $s$-wave emission, through a $4s4p^2$ component of the mixed negative ion configuration.

Negative ions with a $3d^94s^24p^2$ configuration can decay into the $4s4p^3P_0,1,2$ or $4s4p^1P_1$ state by $p$ or $f$-wave emission. The $p$ and $f$-wave scattered electron contributions are both zero at 90°, so no structure would be expected at this angle near 11 eV if just the $3d^94s^24p^2$ configuration negative ions affect $4s4p^3P_0,1,2$ and $4s4p^1P_1$ excitation in this energy region. This is not the case, and furthermore resonance contributions to the $4s4p^1P_1$ electron excitation function are relatively strong at 90°. Negative ions with a $3d^94s^24p4d$ configuration, which will decay to the $4s4p^3P_0,1,2$ and $4s4p^1P_1$ states by $s$ or $d$-wave emission, are possibly responsible for this. If they are responsible, the near-11 eV region contains more negative-ion resonances than is apparent even in the high resolution transmission experiment of Burrow and Michejeda [3], and these resonances must be derived from at least two different negative ion configurations.
Photon Excitation Functions

Photon excitation functions have an advantage over electron excitation functions because, through the use of interference filters, they are better able to isolate particular states of interest. Compared to the present electron excitation function measurements, a more diverse range of excited states were investigated with photon excitation functions. These included the $4s4p^3P_1$ fine structure component, which was unresolved in the electron excitation function measurements, and $n \geq 5$ states. However, photon excitation functions are angle-integrated measurements affected by cascades, meaning that information regarding angle dependence is lost, and different structures present in the excitation of different states are intermingled. Perhaps the only benefit of cascade effects is that they result in a sensitivity to the excitation of high-$n$ and $l$ states. These states have small cross sections, making them difficult to study individually, but the combined cascades from a high-$l$ Rydberg series into a lower-lying, low-$l$ state may be significant.

The photon excitation functions allow an investigation of how strongly a particular negative-ion decays to a neutral state, depending on the neutral state’s configuration, $n$, $L$ and $S$. This provides information regarding the configuration, $J$, $L$ and $S$ of the negative-ion, or, as is probably important for the near 11 eV negative-ion resonances, information regarding the configuration, $L$ and $S$ of the mixed component states of the negative-ion. The extent of any mixing, and which states are mixed, characterises how electron correlations affect the negative-ion structure, and the dynamics of its decay mechanism. The photon excitation functions also reveal another dynamic, electron correlation effect: postcollision interaction (PCI). This was possible in this study through measurements of the $4s4d, 5d, 6d^3D_{1,2,3}$ states, which identify PCI structures by their characteristic $n$-dependence.

This chapter reports on negative-ion resonances below and above the ionization threshold, and PCI structures above the ionisation threshold, observed in photon emission from the $4s4p^3P_1$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d, 5d^1D_2$ and $4s4d, 5d, 6d^3D_{1,2,3}$ states of zinc. The observed transitions and associated photon wavelengths, threshold energies and cascade contributions for each of these states are detailed in Chapter 4. Most of the studies here were conducted with a nominal energy resolution of $\Delta E_{1/2} = 80$ meV, except for scans of the $4s5d^1D_2$ and $4s6d^3D_{1,2,3}$ states which were conducted with an energy resolution of
\[ \Delta E_{1/2} = 120 \text{ meV} \] owing to lower available signal. However energy drifts decreased the apparent energy resolution, which also varied between scans.

The energies of structures were extracted from the photon excitation function data using the same methods employed in Chapter 5. Isolated resonances were fitted with a Fano-profile, but overlapping structures were isolated by subtracting the non-resonance background, before resonance structure energies were determined by a peak fit. Unlike the electron excitation functions presented in Chapter 5, below the ionisation threshold the energy position of peak and dips within overlapping-resonance structures were determined. This was done because it was uncertain whether negative-ion resonances in this energy region produced peaks or dips in the cross section. Above the ionisation threshold, the near-11 eV negative-ion resonances were characterised by the peak energies, in keeping with the electron excitation function analysis. The PCI structure energies were also characterised by the peak energies, because PCI appeared to enhance the cross sections of states investigated here. As noted in Chapter 5, this approach did not determine the true number of resonances or their energies, so a comparison between the various data should not be made exclusively by inspection of the tables. Also, comparisons between different exit channels are complicated by varying resonance contributions and interference effects, which can result in a different appearance for the same resonance in different states. The energies of observed structures are shown in Tables 6.1-6.3, alongside any energies given in previous experimental or theoretical studies. The total energy uncertainty for each feature, which included the ±20 meV calibration and energy drift uncertainty, and the uncertainty due to the fit, is indicated in the tables.

### 6.1 Below First Ionisation Threshold

The energies of structures observed below the ionisation threshold are listed in Table 6.1 with \(P\) indicating a peak and \(D\) a dip, along with features in previous photon excitation functions [31, 33], transmission experiments [1] and BSRM calculations [2]. Structures in the table are labelled with the numbers referred to throughout this work.

#### 6.1.1 Excitation of the \(4s4p^3P_1\) state

Figures 6.1 and 6.2 show the negative-ion resonances which affect excitation of the \(4s4p^3P_1\) state up to the ionisation threshold. Cascades will be present above the \(4s5s^3S_1\) threshold at 6.655 eV, and, as shown in Chapter 4, the calculations of Zatsarinny and Bartschat [2] and Fursa and Bray [61] predict a large effect of direct and multistep cascades from the whole of the triplet manifold into this, the \(J = 1\) component of the lowest triplet state.

Figure 6.1 shows the cascade free region up to the \(4s5s^3S_1\) state threshold at 6.654 eV. The position of the 4.26 eV negative-ion resonance observed in the differential elastic scattering signal is marked (1). The large, 409 meV width of this \(4s4p^2^2D\) shape resonance shows that it decays strongly into its \(4s4p^3P_{0,1,2}\) parent state. Although a clear Fano-profile due to the \(4s4p^2^2D\) negative-ion resonance is not seen in the \(4s4p^3P_1\) photon
6.1. BELOW FIRST IONISATION THRESHOLD

Figure 6.1: Photon excitation function for the $4s4p^3P_1$ state of zinc from threshold to 6.7 eV; • present data, — a combined polynomial background and Fano profile fit to the resonance structure which obtained the resonance energy and width displayed. Also shown is the resonance contribution as a percentage of the total signal.

excitation function, it does seem to produce the rapid rise in the near-threshold cross section. Like the elastic scattering study detailed in Chapter 5, a sharp feature, marked (2) in Figure 6.1, is observed at 5.80 eV. For $4s4p^3P_1$ excitation this feature is a peak, while in elastic scattering it is a dip. As was discussed in Chapter 5, previous assignments of this feature as a $4s4p^22S_{1/2}$ negative-ion resonance have been ruled out in favour of an assignment as a cusp. Nonetheless, a Fano-profile was fitted to determine the energy and width of the feature. As for the feature in elastic scattering, this was done because convoluted cusps and negative-ion resonances have a similar shape, and so Fano-profile fitting gave a reasonable estimate of the feature’s width and energy.

Observations from 6.5 eV to the ionisation threshold are shown in Figure 6.2. Prominent in the data is an isolated, 81 meV wide negative-ion resonance at 7.66 eV, marked (6). Above 8 eV there is a complicated structure which indicates the presence of several overlapping negative-ion resonances. All structures in the $4s4p^3P_1$ excitation function above 6.654 eV have a corresponding feature in a higher triplet state excitation function reported here, except the dip at 8.67 eV, marked (14). Therefore, it is not possible to distinguish which structures are due to resonances decaying directly into the $4s4p^3P_1$ state, and which appear through cascades. Also, special consideration is required for the $4s6s^3P_1$ state, the threshold of which at 8.11 eV is marked (⋆) in Figure 6.2. As discussed in Chapter 4, excitation of this state could potentially result in two photons being detected. However, one would expect a relatively small cross section for the $4s6s^3P_1$ state, and therefore a
Figure 6.2: Photon excitation function for the $4s4p^3P_1$ state of zinc from 6.7 eV to the ionization threshold; • present data, — a combined polynomial background and Fano profile fit to the resonance structure which obtained the resonance energy and width displayed. Also shown is the resonance contribution as a percentage of the total signal. The threshold of the $4s6s^3S_1$ state is marked (*).
6.1. BELOW FIRST IONISATION THRESHOLD

The 4s4p\(^1\)P\(_1\) state photon excitation functions below the ionisation threshold are shown in Figures 6.3 and 6.4. Cascades will be present above the 4s5s\(^1\)S\(_0\) threshold at 6.917 eV, but, as shown in Chapter 4, the calculations of Zatsarinny and Bartschat \[2\] and Fursa and Bray \[61\] predict a relatively small cascade contribution. This may be due to the large cross section for direct 4s4p\(^1\)P\(_1\) excitation, and because other states within the singlet manifold have a direct transition to ground. 4s4p\(^1\)P\(_1\) state excitation below the ionisation threshold was chosen to make a comparison between the present experiment and the negative-ion resonance sensitive BSRM calculations of Zatsarinny and Bartschat due to the small cascade contributions, and the low likelihood of significant continuum coupling effects.

Figure 6.3 compares the present, near-threshold data to the 4s4p\(^1\)P\(_1\) BSRM integral cross section of Zatsarinny and Bartschat \[2\]. The calculations have been convoluted with an apparatus function of width \(\Delta E_{1/2} = 100\) meV, which was determined to be the best estimate of resolution for this particular scan by comparing experiment and the theory convoluted with a range of apparatus functions. The BSRM calculations predict that the 4s4p\(^1\)P\(_1\) cross section is finite at its 5.796 eV threshold, marked (2). The result is a “threshold resonance”, like that observed for the near-threshold excitation of the
Figure 6.4: Photon excitation function for the 4s4p$^1P_1$ state of zinc in the energy region from 6.5 to 8.8 eV; (a) • present data, — fit to the background obtained using the method described in the text; (b) • resonance contribution to the present data, obtained by subtracting the estimated background, — the resonance contribution to the estimated BSRM emission cross section, obtained by subtracting a background estimated in the same manner as for the experimental data. See text for details.
6.1. BELOW FIRST IONISATION THRESHOLD

$1s2s^3S_1$ state of helium by Ehrhardt et al. [93], and analysed by Herzenberg and Ton-That [94], which produces a sharp peak at the threshold, followed by a dip. For helium, this threshold resonance is associated with a cusp in elastic scattering [88], a threshold feature is suggested by a shoulder structure in the experimental data, but the structure is less prominent than the peak in the convoluted theory.

In the higher energy region shown in Figure 6.4 there is a dominant dip at 7.60 eV, marked (6), within a complex structure extending from 6.5 eV to 8.5 eV. To compare the complicated resonance structures observed by the experiment and predicted by theory in this energy region, first the $4s4p^1P_1$ BSRM emission cross section was convoluted with a $\Delta E_{1/2} = 80$ meV apparatus function. The theoretical resonance structures were then isolated by subtracting a fit to the smoothly varying background, as was done for the experimental data, and the results are presented in Figure 6.4b. The general shape of the experimental and theoretical structures are in excellent agreement, with the average energy discrepancy between corresponding features being 17 meV.

6.1.3 Excitation of the $4s5s^3S_1$ state

The photon excitation function for the $4s5s^3S_1$ state in Figure 6.5 and the resonance contribution to the data. As shown in Chapter 4, the calculations of Zatsarinny and Bartschat [2] and Fursa and Bray [61] predict a very large cascade contribution to this state, from the $4s5p^3P_0$ threshold at 7.594 eV onwards. A steady onset from the 6.65 eV threshold is followed by a large dip at 7.50 eV then peak at 7.64 eV, marked (5) and (6) respectively. The 42% deviation of the dip (5) from the the interpolated background is the largest for any feature below the ionisation threshold. These features are near the onset of cascades, but the BSRM $4s5s^3S_1$ integral cross sections contain a similar feature near 7.60 eV. This suggests that the step-like behaviour in the emission cross section is due at least in part to a negative-ion resonance affecting direct $4s5s^3S_1$ excitation. The coincidental onset of cascades may serve to heighten the resonance structure. There are three other features in this spectra, a dip marked (7) at 7.78 eV, a peak marked (8) at 7.88 eV and a dip marked (9) at 8.15 eV. Feature (7) coincides with a peak in the $4s4p^1P_1$ spectrum, feature (8) coincides with a peak in the $4s4d^3D_{1,2,3}$ spectrum and feature (9) coincides with a dip in the $4s4d^3D_{1,2,3}$ spectrum and a peak in the $4s4d^1D_2$ spectrum.

6.1.4 Excitation of the $4s4d, 5d^1D_2$ states

Figures 6.6 a and b show the photon excitation function and resonance contribution for the $4s4d^1D_2$. As shown in Chapter 4, the calculations of Zatsarinny and Bartschat [2] and Fursa and Bray [61] predict relatively small cascade contributions, coming mostly from the $4snf^1F_3$ states which have their onset at 8.534 eV. There will also be contributions from high-$n$ and $l$ singlet states, which will cascade into $4s4d^1D_2$ through $4snf^1F_3$ states. The calculations and the experiment show a step-like onset at threshold, and so a convoluted step-function was included in the background fit subtracted from the raw data. Strong resonances are clearly visible up to 8.64 eV, producing alternating peaks and dips.
Figure 6.5: Photon excitation function for the $4s5s^3S_1$ state of zinc in the energy region from threshold to 9.5 eV; (a) • present data , — a fit to the background obtained using the method described in the text; (b) -•- resonance contribution to the present data, obtained by subtracting the estimated background.
Figure 6.6: Photon excitation function for the 4s4d\(^1\)\(D_1\) state from threshold to 10 eV:
(a) • present data, − fit to the background using the method described in the text.
(b) • the resonance contribution to the present data; (c) − BSRM integral cross section
convoluted with a \(\Delta E_{1/2} = 80\) meV apparatus function, • present data normalized to
theory.
Figure 6.7: Photon excitation function for the $4s5d^1D_1$ state from threshold to 9.5 eV.

Excitation of the $4s4d,^1D_2$ state from the ground state is a not optically allowed, and so one might expect $4s4d,^1D_2$ excitation to be more significantly affected by coupling to the continuum than excitation of the $4s4p,^1P_1$ state. Since it is also predicted that cascade population of the $4s4d,^1D_2$ state is relatively insignificant compared to the other states studied, this photon excitation function was compared with the BSRM calculation of Zatsarinny and Bartschat to their resonance predictions in an instance where their model may not be appropriate. Figure 6.6 c compares the present data with the BSRM integral cross section calculations, convoluted with a $\Delta E_{1/2} = 80$ meV apparatus function. A peak in the BSRM integral cross-section due to the 8.122 eV resonance corresponds almost exactly with an experimental feature at 8.15 eV, marked (9) in Figure 6.6. There is fair agreement between theory and the experimental feature peaking at 8.40 eV, but above this energy the calculation deviates from experiment, and shows several resonance structures which were not observed.

Figure 6.7 shows the $4s5d^1D_1$ state photon excitation function. Theoretical cascade predictions for this state were not presented in Chapter 4, but the states which cascade into $4s5d^1D_1$ will be similar to those which cascade into $4s4d^1D_1$. Cascade contributions to the $4s4d^1D_1$ state will probably be larger because it is lower-lying, but the significance of cascades in the $4s5d^1D_1$ state photon excitation function may be greater because it has a lower direct excitation cross section. The threshold behavior and general shape is very similar to the $4s4d^1D_2$ state, albeit with a slower onset due to the lower resolution. However, no discernible resonance features were detected. This may be due to the lower energy resolution with which the $4s5d^1D_1$ study was conducted, but the negative-ion
resonances lying just above the 4s5d\(^1\)D\(_1\) threshold are weaker than those lying just above the 4s5d\(^1\)D\(_1\) threshold, as can be seen in the 4s4p\(^3\)P\(_1\), 4s4p\(^1\)P\(_1\) and 4s5s\(^3\)S\(_1\) photon excitation functions.

6.1.5 Excitation of the 4s4d, 5d, 6d\(^3\)D\(_{1,2,3}\) states

The photon excitation function for the 4s4d\(^3\)D\(_{1,2,3}\) state is shown in Figure 6.8a, along with the resonance contribution to the data shown in Figure 6.8b. As shown in Chapter 4, the calculations of Zatsarinny and Bartschat [2] and Fursa and Bray [61] predict quite significant cascade contributions, coming mostly from the 4snf\(^3\)F\(_{2,3,4}\) states which have their onset at 8.534 eV. There will also be contributions from high-n and l singlet states, which will cascade into 4s4d\(^3\)D\(_{1,2,3}\) through 4snf\(^3\)F\(_{2,3,4}\) states.

A steep onset to the experimental data reaches a local maximum 90 meV above the 7.78 eV threshold, but it is uncertain whether this peak is due to a negative-ion resonance or the shape of the near-threshold, non-resonance cross section. This peak is followed by a second, sharp peak at 8.24 eV, marked (10) in Figure 6.8. Both peaks are observed in cascade free energy region, which extends to the 4s6p\(^3\)P\(_{0,1,2}\) state threshold at 8.44 eV. The energies of the lowest three structures correspond well in energy with structures in the 4s4d\(^1\)D\(_2\) photon excitation function, but the peaks in 4s4d\(^1\)D\(_2\) excitation function appear as dips in 4s4d\(^3\)D\(_{1,2,3}\) function and vice versa. This observation may indicate negative-ion resonances effecting both 4s4d\(^1\)D\(_2\) and 4s4d\(^3\)D\(_{1,2,3}\) states, but having different interference effects depending on the spin of the neutral state. This apparent spin dependence is not limited to the 4s4d\(^1\)D\(_2\) and 4s4d\(^3\)D\(_{1,2,3}\) states. Both the 4s4d\(^3\)D\(_{1,2,3}\) and 4s4p\(^3\)P\(_1\) photon excitation functions exhibit a peak at 8.26 eV and a dip at 8.40 eV, marked (10) and (11) in Figures 6.2 and 6.8. Conversely, the 4s4p\(^1\)P\(_1\) and 4s4d\(^1\)D\(_2\) states have a dip at 8.26 eV and a peak at 8.38 eV.

A comparison of Figures 6.8 and 6.2 indicates that cascade from the 4s4d\(^3\)D\(_{1,2,3}\) state excited near threshold has little affect on the 4s4p\(^3\)P\(_1\) photon excitation function. The sharp onset of the 4s4d\(^3\)D\(_{1,2,3}\) state ends 200 meV before, and is therefore not associated with the sharp onset of the cascade influenced 4s4p\(^3\)P\(_1\) photon excitation structure which begins at 8.2 eV. Perhaps the vertical onset and threshold peak in 4s4d\(^3\)D\(_{1,2,3}\) are due entirely to the J = 3 state, which does not decay to 4s4p\(^3\)P\(_1\).

Figures 6.9a and b show the 4s5d\(^3\)D\(_{1,2,3}\) photon excitation function and resonance contribution to the data. Figure 6.10 shows the 4s6d\(^3\)D\(_{1,2,3}\) photon excitation function. Theoretical cascade predictions for these states were not presented in Chapter 4, but the states which cascade into 4s5d, 6d\(^3\)D\(_{1,2,3}\) will be similar to those which cascade into 4s4d\(^3\)D\(_{1,2,3}\). Cascade contributions to the 4s4d\(^3\)D\(_{1,2,3}\) state will probably be larger because it is lower-lying, but the significance of cascades in the 4s5d, 6d\(^3\)D\(_{1,2,3}\) state photon excitation functions may be greater because it has a lower direct excitation cross section. The threshold behavior and general shape of the 4s5d\(^3\)D\(_{1,2,3}\) photon excitation function
Figure 6.8: Photon excitation function for the $4s4d^3D_{1,2,3}$ state from threshold to 10 eV; (a) • present data, – a fit to the background obtained using the method described in the text. (b) •• resonance contribution to the present data.
6.1. BELOW FIRST IONISATION THRESHOLD

Figure 6.9: Photon excitation function for the $4s5d^3D_{1,2,3}$ state of zinc from threshold to 10 eV; (a) • present data , – a fit to the background obtained using the method described in the text; (b) •• resonance contribution to the present data.
is very similar to the $4s4d^3D_{1,2,3}$ state. A sharp onset at threshold is followed by a dip at 8.75 eV then a peak at 8.80 eV, marked (15) and (16) respectively in Fig. 6.9. The threshold behavior and general shape of the $4s6d^3D_{1,2,3}$ photon excitation function are also very similar to those of the $4s4d^3D_{1,2,3}$ state, albeit with a slower onset due to the lower resolution, but no discernible resonance features were detected.
Table 6.1: Energies of structures observed in $4s^3p^1$, $4s^4p^1 P_1$, $4s^5s^3 S_1$, $4s^4d^3D_{1,2,3}$, $4s^4d^1D_2$ and $4s^5d^3D_{1,2,3}$ state photon excitation functions below the first ionization threshold. Results from BSRM theory [2] and previous transmission [1] and photon excitation function [31] experiments are presented for comparison. P indicates a peak, D a dip and F a Fano fitted structure. Unless otherwise stated, the present energy uncertainty is ±30 meV. † a weak structure only observed after background subtraction with an energy uncertainty of ±60 meV, ‡ mean value from different transitions.

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6.1.6 Discussion

Several characteristics of the 5.80 eV feature observed in the $4s4p^3P_1$ photon excitation function, and marked (2) in Figure 6.1, support the feature being designated as a cusp. It lies at the $4s4p^1P_1$ threshold, within the experimental energy uncertainty, and its shape is consistent with a cusp peak. It also has an appearance almost identical to the cusp in the BSRM $4s4p^3P_{0,1,2}$ integral cross section of Zatsarinny and Bartschat [2], bearing in mind the finite experimental energy resolution. Also of note is the similarity between the present $4s4p^3P_1$ photon excitation function, and the mercury metastable atom excitation function of Newman et al. [45], which near the $6s6p^1P_1$ threshold is sensitive only to the $6s6p^3P_{0,2}$ states. The peak seen at the $6s6p^1P_1$ threshold is identical in shape to that seen in the $4s4p^3P_1$ photon excitation function near the $4s4p^1P_1$ threshold. There seems, therefore, to be overwhelming evidence that the features observed in elastic scattering and $nsnp^3P_{0,1,2}$ excitation near the $nsnp^1P_1$ thresholds in zinc ($n = 4$), cadmium ($n = 5$) and mercury ($n = 6$) are cusps.

Zatsarinny and Bartschat [2] present BSRM calculations of the partial wave contributions to the $4s4p^3P_{0,1,2}$, $4s4p^1P_1$ and $4s5s^3S_1$ integral cross sections. These predictions will be used here to assign terms to some of the overlapping negative-ion resonances observed above 7 eV. This will be done by matching the shape of an observed resonance structure to that of a negative-ion resonance excited by a particular partial wave, but will be restricted here to excitation below 8.4 eV, where confidence in the theory is greatest.

For $4s4p^3P_1$ excitation, the resonance (6) at 7.66 eV shown in Figure 6.2 corresponds best in shape and energy to a resonance which produced a peak in the $^2D_e$ partial wave (see Figure 3 of [2]). This suggests that either the $4s5p^22^2D$ resonance at 7.570 eV or the $4s4d5s^2D$ resonance at 7.725 eV contributes most strongly to this feature. A $4s5p^22^2S$ resonance at 7.524 eV and a $4s4d5p^2P$ resonance at 7.595 eV also affect the BSRM calculations, both producing dips, but no corresponding structures are observed in the experiment. This is possibly because they are masked by the stronger $4s5p^22^2D$ or $4s4d5s^2D$ resonance. No significant resonance structure is predicted between 7.60 eV and 8.5 eV, which suggests that the photon excitation function structures in this energy range are heavily influenced by cascades.

The $4s4p^1P_1$ data shown in Figure 6.4b has its strongest feature at 7.60 eV, marked (5). The shape of this resonance in the $f$-partial wave, suggesting that it is due to the $4s4d5p^22F$ resonance at 7.615 eV. Likewise, the peak in the experimental data at 7.44 eV, marked (4) in Figure 6.4, could be due to the $4s5p^22^2D$ resonance at 7.57 eV, and the peak at 8.36 eV, marked (10) in Figure 6.4, could be due to a combination of the $4s7s^22^2S$ and $4s5d6p^22F$ resonances.

The $4s5s^3S_1$ is heavily influenced by cascades from the $4snp^3P_{0,1,2}$ states, and so a large number of the negative-ion resonances observed in the $4s5s^3S_1$ photon excitation function will be due to cascading states for which partial wave contributions are not presented by Zatsarinny and Bartschat. However, the sharp dip at 7.50 eV, marked (5), and the peak at 7.64 eV, marked (6), are probably due to direct $4s5s^3S_1$ excitation. BSRM
Below First Ionisation Threshold

predicts many, overlapping resonances affecting $4s5s^3S_1$ excitation in this energy region, and there are resonances in several partial waves with shapes similar to the structures observed in the photon excitation function. The $4s4d5p^2P$ resonance at 7.595 eV and the $4s5p^2^2D$ resonance at 7.570 eV produce a dip similar to that observed at 7.50 eV. These two resonances also produce a peak similar to that observed at 7.64 eV, as does the $4s4d5p^2F$ resonance at 7.615 eV.

The agreement between the present and previous experiments is generally within expected limits of deviation, given the present ±30 meV energy uncertainty and the different experimental methods used in some previous studies. In particular, the photon excitation function measurements by Shpenik et al. [31, 33] seem to contain negative-ion resonance effects similar to those observed here. The electron transmission studies of Sullivan et al. [1] present the derivative of the transmitted current with respect to energy and include effects from all scattering channels, so resonance shapes and energies are not always easy to compare with photon emission data. However, there appears to be good agreement with this experiment. Neither the present photon excitation functions, nor the scattered electron studies presented in Chapter 5, agree with $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ integral cross section measurements of Shpenik et al. [34]. This previous study detected the excitation of all $4s4p^3P_{0,1,2}$ state J levels, but the resulting curve does not show any structures below 6.5 eV corresponding to feature (2) shown in Figure 6.1. The $4s4p^1P_1$ photon excitation function shows resonant structures below the ionization threshold in agreement with Shpenik et al. [31]. However, the relative resonance contributions of up to 50% are much greater than in the present experiment.

Negative-ion resonance structures in the present data correspond well with resonance energies and profiles obtained by Zatsarinny and Bartschat [2] below ∼8 eV, and there is also reasonable agreement regarding the near-threshold cross section behaviour for the $4s4p^1P_1$ and $4s4d^1D_2$ states, shown in Figures 6.3 and 6.6c. For $4s4p^1P_1$ excitation, the good agreement between the experimental and theoretical resonance contributions extends to 8.5 eV, as can be seen in Figure 6.4. BSRM calculations also closely reproduced the transmission curve of Sullivan et al. [1], which will be most strongly influenced by elastic scattering, between 3.5 eV and 10 eV. However, Figure 6.6c shows the BSRM cross-section for $4s4d^1D_2$ state excitation fluctuating relative to the experimental shape above 8.2 eV, indicating a loss of accuracy for higher energies. This is expected because, as has been stated in Chapter 4, Zatsarinny and Bartschat note that their approach is most reliable in the near-threshold regime, due to its limited treatment of the target continuum.

For helium, $1s3s^3S_1$ and $1s3s^1S_0$ state integral cross section studies of Stepanovic et al. [95] showed a remarkable agreement between experiment and 69 state B-spline R-matrix (BSRM-69) calculations (69 coupled states with $S$, $P$, $D$ and $F$ symmetry). This theoretical method produced both the general cross-section shape and the finer details seen by the experiment throughout the $n = 3, 4$ and 5 resonance manifold, demonstrating its excellent predictive capability. However, the BSRM model has trouble treating the stronger and more complex electron correlation effects active in zinc excitation.
6.2 Above First Ionisation Threshold

The energies of the negative-ion resonance structures observed above the ionisation threshold are shown in Table 6.2, and the energies of PCI structures observed in the $4s5s^3S_1$, $4s5d^1D_2$ and $4snd^3D_{1,2,3}$ photon excitation functions are shown respectively in Tables 6.3, 6.4 and 6.5. The near-11 eV resonance structures are labelled with the letters $a$-$d$ using the system described in Chapter 5. Structures observed in $4snd^3D_1$ state excitation functions, and identified as PCI effects by their $n$ dependence, are labeled with numbers in order of increasing energy positions. Also, structures in the $4s5s^3S_1$ excitation function observed in the energy region above 12 eV may be due to PCI, and are labelled in a similar fashion. The number is preceded by the letter $T$ for features observed in $4snd^3D_{1,2,3}$ excitation functions, the letter $S$ for features observed in $4snd^1D_2$ excitation functions and $U$ for features observed in $4s5s^3S_1$ excitation function.

6.2.1 Excitation of the $4s4p^3P_1$ state

The photon excitation function and percentage resonance contributions for the $4s4p^3P_1$ state in the energy region from 10.3 eV to 12.8 eV are shown in Figures 6.11a and b. The data contains three strong resonance structures, which peak at energies corresponding to the $a$-structure at 10.76 eV, the $b'$-structure at 11.09 eV and the $c''$ structure at 11.42 eV, each with a height close to 30% of the interpolated background. Shoulders on the 11.42 eV peak at 11.34 eV and 11.66 eV indicate contributions from the $c'$ and $d$ resonance structures.

Compared to the $4s4p^3P_{0,1,2}$ electron excitation functions, presented in Section 5.3, the $A$ and $B$-group negative-ion resonances have a much larger effects relative to the $C$-group structure. Within the $B$-group, the $b'$ resonance structure has a greater prominence in the photon excitation function, as does the $c''$ resonance structure within the $C$-group. These negative-ion resonance structures could have a much stronger effect outside the $15^\circ - 110^\circ$ scattering angle range of the electron excitation function measurements, but the differential cross sections within this range are likely to have the greatest weight in the angle-integrated photon excitation functions. Cascade contributions may also cause resonance structures in the photon excitation functions, or make them more prominent. For the $4snd^3D_{1,2,3}$ photon excitation functions, the $c''$ resonance structure is the most prominent within the $C$-group, and so the enhancement of the $c''$ structure in the $4s4p^3P_1$ photon excitation function may be due to cascades. However, cascades cannot explain the larger $A$-group negative-ion resonances and $b'$ resonance structure, because neither of these are as prominent in the $4s5s^3S_1$ or $4snd^3D_{1,2,3}$ photon excitation functions as they are in the $4s4p^3P_1$ photon excitation function. Therefore, the $A$-group negative-ion resonances and $b'$ resonance structures are more significant in the $4s4p^3P_1$ photon excitation function than in the $4s4p^3P_{0,1,2}$ electron excitation function because the photon measurements did not observe the $J = 0, 2$ components. This implies either that negative ions corresponding to the $A$-group and the $b'$ structure decay more strongly to $4s4p^3P_1$, or that negative
Figure 6.11: The photon excitation functions for the $4s4p^3P_1$ state of zinc from 10.2 eV to 12.8 eV; (a) • present data, − estimated smoothly varying background; (b) ● resonance contributions as a percentage of the total signal.
ions corresponding to the $b$ resonance structure and the $C$-group resonances decay more strongly to $4s4p^3P_0$, $4s4p^3P_2$, or both.

PCI effects predominantly the excitation of higher energy and higher $n$ neutral states [96], and so should not influence direct excitation of the $4s4p^3P_1$ state. As will be seen below, PCI structures were prominent in the $4s5s^3S_1$ and $4snd^3D_{1,2,3}$ photon excitation functions, so PCI will affect the $4s4p^3P_1$ photon excitation function through cascades. However, no structures were observed in the $4s4p^3P_1$ photon excitation function which could be associated clearly with PCI effects.

### 6.2.2 Excitation of the $4s4p^1P_1$ state

The $4s4p^1P_1$ state excitation function and percentage resonance contribution from 10.3 to 12.8 eV are shown in Figure 6.12a and b. Also shown, in Figure 6.13, is a small negative-ion resonance observed near 16 eV. There are fewer negative-ion resonances observed in the near-11 eV energy region than for $4s4p^3P_1$, and the height of the largest peak is only 8% of the interpolated background. The $A$-group resonances are associated with a shoulder at 10.74 eV, a peak corresponding to the $b$ resonance structure is present at 11.00 eV, and a peak corresponding to the $c$ resonance structure is present at 11.22 eV. The significant dip in intensity near 11.5 eV may be related to the $c''$ or $d$ resonance structures, or perhaps simply the trailing edge of a resonance profile. A comparison with the $4s4p^3P_1$ excitation function suggests that, of the closely spaced components of the $B$ and $C$-groups, negative ion associated with the lower energy structures decay predominantly into the singlet state, and negative ions associated with the higher energy structures decay predominantly into the triplet state.

There is a marked difference between the $4s4p^1P_1$ photon excitation functions and electron excitation functions. Fursa et al. [18] have shown that the $4s4p^1P_1$ differential cross section is very forward peaked, as would be expected for this optically-allowed state. Given this, the effect of the near-11 eV negative-ion resonances on the $4s4p^1P_1$ integral cross section and the low-angle $4s4p^1P_1$ electron excitation functions should be similar. The near-11 eV negative-ion resonances produce a single, broad dip in the $4s4p^1P_1$ electron excitation functions at 15° and 30°, but the $4s4p^1P_1$ photon excitation function has peaks corresponding to the $b$ and $c$ resonance structures. There are some structures in the 54° and 90° $4s4p^1P_1$ electron excitation functions due to $B$ and $C$-group negative-ion resonances, and these will be enhanced in the photon excitation functions by cascades from the $4snd^1D_2$ states, discussed below, and the $4sns^1S_0$, $n \geq 5$ states which have not been studied here.

The small negative-ion resonance shown in Figure 6.13 has a size equal to 1.3% of the interpolated background, and has been labelled $e$. Since the structure appeared to be an isolated negative-ion resonance, a Fano profile was fitted using the method described in Section 3.2 which yielded a resonance energy of 16.16 eV and an apparent width of $\Gamma=460$ meV. A negative-ion resonance with an energy of 16.18 eV and width of 390 meV has previously been observed in the $4s5d, 6d^1D_2$ photon excitation functions of Shpenik et
Figure 6.12: Photon excitation function for the $4s4p^1P_1$ state of zinc between 10.2 eV and 12.8 eV; (a) • present data, — estimated smoothly varying background; (b) ● resonance contributions as a percentage of the total signal.
CHAPTER 6. PHOTON EXCITATION FUNCTIONS

7.55
7.6
7.65
7.7
7.75
15.5 16 16.5 17 17.5
10^5 Photon Counts
Incident Electron Energy (eV)
1.3% of signal
\[ E_r = 16.16 \pm 0.04 \text{ eV} \]
\[ \Gamma = 460 \pm 29 \text{ meV} \]

Figure 6.13: The photon excitation function for the 4s4p^1P_1 state of zinc near 16 eV; • present data, — a combined polynomial background and Fano profile fit to the resonance structure which obtained the resonance energy and width displayed.

All the optically allowed states of neutral zinc within 0.5 eV of the negative-ion resonance have a 3d^0 4s^2 np, \( n = 5, 6, 7 \) or 3d^0 4s^2 nf, \( n = 4, 5 \) configuration [10]. There are multiple negative-ion resonances associated with the 3d^0 4s^2 4p autoionising states, and so there may be multiple negative-ion resonances associated with the 3d^0 4s^2 np, \( n = 5, 6, 7 \) or 3d^0 4s^2 nf, \( n = 4, 5 \) autoionising states. If so, the dip at 16.16 eV may be due to several overlapping negative-ion resonances, not a single, broad negative-ion resonance.

As for the 4s4p^3P_1 state, PCI effects should not influence direct excitation of the 4s4p^1P_1 state. As will be seen below, PCI structures were prominent in the 4s5d^1D_2 photon excitation function, so PCI will affect the 4s4p^1P_1 photon excitation function through cascades. However, no structures were observed in the 4s4p^1P_1 photon excitation function which could be associated clearly with PCI effects.

6.2.3 Excitation of the 4s5s^3S_1 state

The photon excitation function for the 4s5s^3S_1 state in the energy region between 10 and 16 eV is shown in Figure 6.14a, alongside percentage contributions from negative ion resonances and possible PCI structures in Figure 6.14b. As discussed above, cascades are predicted to strongly affect the 4s5s^3S_1 state photon excitation function, more than any of the other photon excitation functions measured. Therefore, the structures observed indicate negative-ion resonance effects on direct excitation of the 4snp^3P_0,1,2 states, and the 4s5s^3S_1 state. The A-group resonances produce a shoulder at 10.79 eV, there is a peak at 10.98 eV which corresponds to the b resonance structure, and the C-group resonances
Figure 6.14: Photon excitation function for the $4s5s^3S_1$ state of zinc from 10 eV to 16 eV; (a) • present data, — estimated smoothly varying background; (b) •• the percentage resonance and PCI structure contribution to the data.
produce a small, broad peak at 11.27 eV with unresolved contributions from the $c, c'$ and $c''$ resonance structures. Given the strong cascade contributions from $4snp^3P_{0,1,2}$ states, and the large effect which $A$ and $C$-group negative-ion resonances have on $4s4p^3P_{0,1,2}$ excitation, it is notable that $A$ and $C$-group negative-ion resonances do not produce significant structures in the $4s5s^3S_1$ photon excitation function. This could be because $A$ and $C$-group negative-ion resonances may produce dips in the $4s5s^3S_1$ integral cross section and peaks in the $4snp^3P_{0,1,2}$ integral cross sections, or vice versa. If this is the case, then the competing negative-ion resonance structures could cancel out. Another possible explanation is that the $A$ and $C$-group negative-ion resonances do not decay into the $4s5s^3S_1$ or $4snp^3P_{0,1,2}$ states. Given the large effect which $A$ and $C$-group negative-ion resonances have on $4s4p^3P_{0,1,2}$ excitation, significant $n$-dependence in the decay of the near-11 eV negative-ion resonances may be present.

At energies above 12 eV a series of enhancements were observed. Six peaks having heights up to around 20% of the interpolated background are resolved, and are marked $U1$ to $U6$ in Figure 6.14. The estimated position of the peak for each structure is shown in Table 6.3. Although only one $4sns^3S_1$ state, and thus no $n$ dependence, has been observed, the presence of PCI in other states in this energy region suggests the PCI may also be affecting the spectra here. However, the binding energy of the $4s5s^3S_1$ state is greater than the $4s4d^3D_{1,2,3}$ and $4s4d^1D_2$ states, in which PCI effects are either small or barely resolved. This suggests that any PCI structures may be due to cascades from $4snp^3P_{0,1,2}$ $n \geq 6$ states, which have thresholds of 8.44 eV and above. The $U1$-$U4$ structures are broader than the other PCI structures identified, and the large overlap between adjacent structures made it difficult to quantify the width and onset of the individual peaks. The broad nature of these peaks may be due to all members of the $4snp^3P_{0,1,2} n \geq 6$ series cascading into $4s5s^3S_1$. As has been stated, PCI structures shift upwards in energy with increasing $n$, meaning that when the $4snp^3P_{0,1,2} n \geq 6$ states are summed, the PCI structures will be smeared out. The $U5$ and $U6$ structures at 15.11 eV and 15.49 eV are sharper, and are at energies slightly higher than those where PCI structures have been seen in the other states investigated. They may be negative-ion resonances. The optically allowed states of neutral zinc within 0.5 eV of these structures have configurations of $3d^{10}4ns, n \geq 7, 3d^{10}4pnd, n \geq 5$ or $3d^{9}4s^2np, n = 5, 6$ [10].

6.2.4 Excitation of the $4s4d, 5d^1D_2$ states

The photon excitation functions for the $4s4d, 5d^1D_2$ states in the energy region between 10 and 16 eV are shown in Figure 6.15, while percentage contributions from negative-ion-resonances and PCI structures in Figure 6.16. Both have peaks which correspond to the $b'$ and $c'$ resonance structures, at 11.10 and 11.31 eV in the $4s4d^1D_2$ photon excitation function, and 11.06 eV and 11.29 eV in the $4s5d^1D_2$ photon excitation function. The $A'$-group negative-ion resonances do not appear to affect either state. Figure 6.16 shows that the near-11 eV negative-ion resonances are much better resolved and more prominent in the $4s4d^1D_2$ excitation function, where the negative-ion resonance structures are 15% of
6.2. ABOVE FIRST IONISATION THRESHOLD

the interpolated background compared to 8% for the $4s5d^1D_2$ excitation function. This is in agreement with the study of Shpenik et al. [33], whose $4s4d^1D_2$ state resonance energy data are included in Table 6.2. In that study, the near-11 eV negative-ion resonances had a significant effect on the $4s4d^1D_2$ photon excitation function, a relatively small effect on the $4s5d^1D_2$ photon excitation function, and almost no effect on the $4s6d^1D_2$ photon excitation function. The $4snf^1F_3$ states will cascade preferentially to $4s4d^1D_2$ because it has lower energy compared to $4s5d^1D_2$ and $4s6d^1D_2$. This greater cascade contribution may explain why the near-11 eV negative-ion resonances are more prominent in the $4s4d^1D_2$ photon excitation function. Another possible explanation is that the near-11 eV negative-ion resonances decay to $n=4$ states more strongly.

The experiment of Pravica et al. [35] suggests that, of the $B$-group resonances, those associated with the $b$-resonance structure affect $4s4d^1D_2$ excitation more strongly. These spin-polarised incident electron measurements observed a negative-ion resonance in $P_1$, $P_2$ and $P_3$ Stokes parameters with an average energy of 10.98±0.02 eV. It is possible that a contribution from the $b$ resonance structure is masked in the $4s4d^1D_2$ photon excitation function by the steep rise in photon counts due to the negative-ion resonances associated with the $b'$ structure. The second negative-ion resonance observed at 11.33 eV in the Stokes parameters coincides with the $c'$ resonance structure, which is the most prominent in the photon excitation function.

The spin-dependent behaviour and different negative-ion resonance shapes apparent in the Stokes parameters indicate that it is not straightforward to compare them with the present photon intensity measurements. A further complication is that the Stokes parameters were measured with a resolution of 250 meV, which is much lower than the 80 meV resolution used here. To make a clearer comparison between the two experiments, the $P_1$ measurements of Pravica et al. were repeated using the present, unpolarised incident electron beam. As noted in Chapter 1, the integral Stokes parameters $P_2$ and $P_3$ are by definition zero for unpolarised incident electrons. The present $P_1$ measurement, shown in Figure 6.17, demonstrates that the same overlapping negative-ion resonances can produce different structures, with different energies, in photon excitation functions and Stokes parameters. Resonances produce two dips in the polarisation, one at 11.05 eV corresponding equally well with the $b$ and $b'$ resonance structures, and one at 11.45 eV corresponding best with the $c''$ resonance structure. These energies do not agree with the resonance energies quoted by Pravica et al., but their resonance energies were obtained by fitting two overlapping Fano-profiles to the data. This may not be appropriate, since this study has shown that there appear to be at least eight negative-ion resonances in the near-11 eV energy region. Also, an inspection of the data presented by Pravica et al. shows that the $P_1$ spectrum has dips at 10.97 and 11.42 eV, which is in closer agreement with the observations here.

In the PCI affected energy region above 12 eV, the $4s4d^1D_2$ and $4s5d^1D_2$ state excitation functions differ significantly from each other and from the $4s4d, 5d, 6d^3D_{1,2,3}$ state excitation functions presented below. As can be seen in Figure 6.16a, the $4s4d^1D_2$ pho-
Figure 6.15: Photon excitation functions between 10 eV and 16 eV for the, (a) 4s4d$^1D_2$ and (b) 4s5d$^1D_2$ states of zinc; • present data, — estimated smoothly varying background.
	on excitation function shows a broad peak centered around 12.6 eV approximately 1.5 eV wide. There are weak undulations between 13.2 and 14.2 eV, but they do not appear to be statistically significant. Shpenik et al. [33] report three structures in their 4s4d$^1D_2$ state excitation function at 12.45, 14.48 and 14.89 eV, but these are not visible clearly in their published data. In contrast to the 4s4d$^1D_2$ state, the present 4s5d$^1D_2$ excitation function shows three well pronounced peaks, S1 at 11.94 eV, S2 at 12.90 eV and S3 at 13.60 eV, followed by indication of another structure S4 at 14.16 eV. The positions of these structures are in good agreement with structures observed by Shpenik et al., which are listed in Table 6.4.
Figure 6.16: Percentage resonance and PCI structure contributions to the (a) $4s4d^1D_2$ and (b) $4s5d^1D_2$ photon excitation functions.
There are clearly resolved PCI structures in the 4s4d3D1,2,3 excitation function throughout this energy region, as shown in Figure 6.19a. The binding energies of 4s4d1D2 and 4s4d3D1,2,3 differ by less than 40 meV, and so one may expect 4s4d1D2 to also be affected by PCI. A lack of structure may be because the PCI interference in 4s4d1D2 direct excitation varies such that, when integrated over all scattering angles, the PCI structures disappear. The PCI structures observed here seem to enhance cross sections rather than diminish them, so this explanation is probably invalid. The 4s4d1D2 state has a larger cross section than 4s4d3D1,2,3, and so PCI contributions similar to those present in the 4s4d3D1,2,3 photon excitation function may appear small in the 4s4d1D2 photon excitation function. Cascades from the 4snf1F3 and 4snf3F2,3,4 states respectively, which will may have PCI contributions, will also be more significant for the 4s4d1D2 photon excitation function compared to the 4s4d3D1,2,3 photon excitation function. Another possibility is that the PCI mechanism favours the population of triplet, rather than singlet, states.

6.2.5 Excitation of the 4s4d, 5d, 6d3D1,2,3 states

The photon excitation functions for the 4s4d, 5d, 6d3D1,2,3 states in the energy region between 10 and 16 eV are shown in Figure 6.18, alongside percentage contributions from negative-ion resonances and PCI structures in Figures 6.19. For n=4 there is a peak at 10.79 eV which corresponds to the a’ resonance structure, but the A-group negative-ion resonances do not influence the other two states. The a’ resonance structure in the 4s4d3D1,2,3 photon excitation function could be due to cascades from the 4snf3F2,3,4
6.2. ABOVE FIRST IONISATION THRESHOLD

states, which will cascade preferentially into the lowest \(n\) state. Alternatively, the \(A\)-group negative ions may only decay strongly into neutral states with \(n = 4\). For the \(B\)-group negative-ion resonances, favourable relative contributions to the \(4s5d^3D_{1,2,3}\) photon excitation function and a lack of drifts during this particular scan led to a double peak structure being resolved, with peaks at 11.03 eV and 11.11 eV corresponding to the \(b\) and \(b'\) resonance structures. A \(B\)-group double peak was not resolved in the \(4s4d^3D_{1,2,3}\) photon excitation function, which has a peak at 11.05 eV lying halfway between the \(b\) and \(b'\) resonance structures, suggesting that both are present. The peak in the \(4s6d^3D_{1,2,3}\) photon excitation function at 11.08 eV corresponds with the \(b'\) resonance structure. A third structure is observed around 11.47 eV in all three states, which corresponds to the \(c''\) resonance structure. The \(n = 5, 6\) states also appear to be affected by negative-ion resonances associated with the \(c'\) and \(d\) resonance structures.

At energies above 12 eV a series of broad enhancements are observed in the \(4s4d, 5d, 6d^3D_{1,2,3}\) photon excitation functions, which, because they shift upwards in energy with increasing \(n\) of the state observed, have been conclusively attributed to PCI. As shown in Figures 6.19a, b and c, two peaks, \(T1\) and \(T2\), are resolved clearly in all spectra and have heights up to around 30\% of the interpolated background. A third peak, \(T3\), is not so well resolved for the \(4s4d^3D_{1,2,3}\) and \(4s6d^3D_{1,2,3}\) states, and not resolved at all for the \(4s5d^3D_{1,2,3}\) state. The estimated position of the peak for each structure is shown in Table 6.5. As \(n\) of the observed state increases, the peaks not only shift upward in energy but also appear to become narrower. As a result, the PCI structures change from broad enhancements overlapping each other and the near-11 eV negative-ion resonances in the \(4s4d^3D_{1,2,3}\) spectrum, to peaks well separated from the negative-ion resonances and each other in the \(4s6d^3D_{1,2,3}\) spectrum. The PCI peaks in the \(4s5d^3D_{1,2,3}\) and \(4s6d^3D_{1,2,3}\) photon excitation functions could be narrower due to smaller cascade effects, which may smear out structures in the \(4s4d^3D_{1,2,3}\) photon excitation function. Another explanation is that, because the \(4snd^3D_{1,2,3}\) states become more closely spaced with increasing \(n\), the band into which the energy of a scattered electron must fall in order to populate a \(4snd^3D_{1,2,3}\) state by the PCI mechanism narrows with increasing \(n\).
Figure 6.18: Photon excitation functions for the (a) $4s4d^3D_{1,2,3}$, (b) $4s5d^3D_{1,2,3}$ and (c) $4s6d^3D_{1,2,3}$ states of zinc from 10 eV to 16 eV; • present data, – estimated smoothly varying background.
Figure 6.19: Percentage resonance and PCI structure contributions to the (a) \( 4s4d^3D_{1,2,3} \), (b) \( 4s5d^3D_{1,2,3} \) and (c) \( 4s6d^3D_{1,2,3} \) photon excitation functions from 10 eV to 16 eV.
Table 6.2: Energies of resonance structures observed in photon excitation functions for the $4s4p^3P_1$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d$, $5d$, $6d^3D_{1,2,3}$ and $4s4d$, $5d^1D_2$ states. The total energy uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The letters in the leftmost column refer to the resonance labels used to identify negative-ion resonances throughout this paper. Elastic scattering data and data from previous photon excitation functions [33] are presented for comparison. All energies are in units of eV.

<table>
<thead>
<tr>
<th>Res. Label</th>
<th>Present experiment</th>
<th>Ref. [33]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>10.76±0.04</td>
<td>-</td>
</tr>
<tr>
<td>$a'$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$b$</td>
<td>10.99±0.04</td>
<td>-</td>
</tr>
<tr>
<td>$b'$</td>
<td>11.09±0.04</td>
<td>-</td>
</tr>
<tr>
<td>$c$</td>
<td>11.24±0.03</td>
<td>-</td>
</tr>
<tr>
<td>$c'$</td>
<td>11.33±0.03</td>
<td>-</td>
</tr>
<tr>
<td>$c''$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$d$</td>
<td>11.61±0.04</td>
<td>-</td>
</tr>
<tr>
<td>$e$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6.3: Energies of peaks observed in photon excitation functions for the $4s5s^3S_1$ state possibly due to PCI. The total energy uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The labels $U1$ to $U6$ are used to identify the individual peaks throughout this work. All energies are in units of eV.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>$U1$</th>
<th>$U2$</th>
<th>$U3$</th>
<th>$U4$</th>
<th>$U5$</th>
<th>$U6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4s5s^3S_1$</td>
<td>12.19±0.06</td>
<td>12.71±0.04</td>
<td>13.36±0.04</td>
<td>13.84±0.04</td>
<td>15.11±0.04</td>
<td>15.49±0.04</td>
</tr>
</tbody>
</table>

6.2.6 Discussion

Negative-ion resonances

Whether or not a particular near-11 eV negative-ion resonance structure is observed in the present photon excitation functions is strongly dependent on the $n$, $L$ and $S$ of the observed state. This can be explained in a number of different ways. The photon excitation functions are angle-integrated measurements, and so a structure which produces a peak in the differential cross section at some angles and a dip at others may not produce any structure in the integral cross section. The Fano profile of a negative-ion resonance depends on the excitation channel in which it is observed, and overlapping negative-ion resonances may appear as a peak or dip in one photon excitation channel, but cancel out in another. Similarly, negative-ion resonance effects in cascades can cancel those in direct excitation, and as a result no structure would be observed in the photon excitation function. There is also a possibility that adjacent resonances affecting the excitation of particular state may destructively interfere.

Another consideration, and perhaps the most important, is that the strength with which a particular negative ion decays into a neutral state depends on their respective parity, total angular momentum $J$, electron configuration, $L$ and $S$. As was stated in Chapter 1, negative ion decay must conserve parity and total angular momentum $J$. Therefore, autoionising transitions which also conserve $L$ and $S$, even those occurring via a non-dominant component of a mixed state, are much more likely than those which do not [5]. However, there are additional factors which make an autoionisation process more or less favourable. As a guiding principle, given by Fano and Lichten [97], the autoionisation channel requiring the least energy transfer is the most likely. Accordingly, autoionisation rates are faster if only the principle quantum number $n$ of the electrons is altered. The autoionisation rates are also faster the lower the $l$ of the ejected electron, because the centrifugal barrier which needs to be overcome is smaller. These last two principles were applied by Read et al. [29] to classify negative-ion resonances observed for the noble gases. Also, the probability for two-electron autoionisation, an example of which is $1s2p^3 \rightarrow 1s^22p + e\,s$ transition, is much greater than that of three-electron autoionisation, an example of which is $1s2p^3 \rightarrow 1s^22s + e\,p$ transition [98]. There must be a balance of these factors for a negative-ion resonance to be observed. If a negative ion can only decay
Table 6.4: Energies of peaks observed in photon excitation functions for the $4s5d^1 D_2$ state possibly due to PCI. The total energy uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The labels $S1$, $S2$, $S3$ and $S4$ are used to identify the individual peaks throughout this paper. Previously published peak energies for the $4s5d^1 D_2$ state photon excitation function [33] are presented for comparison. All energies are in units of eV.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>PCI structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5d^1 D_2$ (present)</td>
<td>$S1$</td>
</tr>
<tr>
<td></td>
<td>$S2$</td>
</tr>
<tr>
<td></td>
<td>$S3$</td>
</tr>
<tr>
<td></td>
<td>$S4$</td>
</tr>
<tr>
<td>$5d^1 D_2$ (Shpenik et al.)</td>
<td>12.03</td>
</tr>
</tbody>
</table>

Table 6.5: Energies of peaks observed in photon excitation functions for the $4d, 5d, 6d^3 D_{1,2,3}$ states attributed to PCI. The total energy uncertainty due to energy calibration, energy drifts and the peak fitting is indicated for each structure. The labels $T1$, $T2$ and $T3$ are used to identify the individual peaks throughout this paper. All energies are in units of eV.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>PCI structures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T1$</td>
</tr>
<tr>
<td></td>
<td>$T2$</td>
</tr>
<tr>
<td></td>
<td>$T3$</td>
</tr>
<tr>
<td>$4s4d^3 D_{1,2,3}$</td>
<td>12.10±0.04</td>
</tr>
<tr>
<td></td>
<td>13.12±0.05</td>
</tr>
<tr>
<td></td>
<td>13.69±0.04</td>
</tr>
<tr>
<td>$4s5d^3 D_{1,2,3}$</td>
<td>12.53±0.04</td>
</tr>
<tr>
<td></td>
<td>13.44±0.05</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$4s6d^3 D_{1,2,3}$</td>
<td>12.68±0.04</td>
</tr>
<tr>
<td></td>
<td>13.65±0.05</td>
</tr>
<tr>
<td></td>
<td>14.38±0.07</td>
</tr>
</tbody>
</table>
6.2. ABOVE FIRST IONISATION THRESHOLD

Table 6.6: A comparison of the near-11 eV negative-ion resonance configurations with the configurations of the observed neutral states, showing the partial waves which must be emitted in a decay to each neutral state, and possible components of the mixed negative ion state through which the autoionisation may occur. If no mixed configuration is given, autoionisation can proceed through the dominant negative ion configuration with a change only in the \( n \) quantum numbers of the electrons.

<table>
<thead>
<tr>
<th>Neutral State ( 3d^{10} )</th>
<th>( 3d^{9}4s^24p^2, J = 3/2, 5/2 )</th>
<th>( 3d^{9}4s^24p^4d, J = 1/2, 3/2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Partial Wave</td>
<td>Mixed Configuration</td>
</tr>
<tr>
<td>( 3d^{10}4nsn )</td>
<td>s-wave</td>
<td>( 3d^{9}4s^24d5s, 3d^{10}4s^25s )</td>
</tr>
<tr>
<td></td>
<td>d-wave</td>
<td>( 3d^{9}4s^24d^2, 3d^{10}4s^24d )</td>
</tr>
<tr>
<td>( 3d^{10}4snp )</td>
<td>p-wave</td>
<td>( 3d^{9}4s^24p^24d, 3d^{10}4p^25s )</td>
</tr>
<tr>
<td></td>
<td>f-wave</td>
<td>( 3d^{9}4s^24p^24f, 3d^{10}4p^25s )</td>
</tr>
<tr>
<td>( 3d^{10}4snd )</td>
<td>s-wave</td>
<td>( 3d^{9}4s^24d^2, 3d^{10}4d^25s )</td>
</tr>
<tr>
<td></td>
<td>d-wave</td>
<td>( 3d^{9}4s^24d^2, 3d^{10}4d^25s )</td>
</tr>
<tr>
<td>( 3d^{10}4snf )</td>
<td>p-wave</td>
<td>( 3d^{9}4s^24d4f, 3d^{10}4f^25s )</td>
</tr>
<tr>
<td></td>
<td>f-wave</td>
<td>( 3d^{9}4s^24d^24f, 3d^{10}4f^25s )</td>
</tr>
</tbody>
</table>

electrostatically via a significant electron configuration rearrangement and emission of a high-\( l \) electron, then it will be long-lived and the associated negative-ion resonance will be small and very narrow and thus difficult to resolve. On the other hand, if a negative ion can decay electrostatically by \( s \)-wave electron emission with changes only to electron \( n \), then it will be short-lived and the associated resonance will be very broad and thus also difficult to resolve.

There is conclusive evidence in the differential elastic scattering signal that a large number of the near-11 eV negative-ion resonances are due to \( 3d^{9}4s^24p^2 \) negative ions with \( J = 3/2, 5/2 \). There is also some evidence, in the differential elastic scattering signal and the \( 4s4p^3F_{0,1,2} \) and \( 4s4p^1P_1 \) electron excitation functions, of resonances due to negative ions with odd parity, and it has been suggested that these negative ions have a \( 3d^{9}4s^24p^4d \) configuration and \( J = 1/2, 3/2 \). Table 6.6 compares these configurations with the configurations of the the excited states which were observed here, including cascading states. As can be seen from the table, the decay of a \( 3d^{9}4s^24p^2 \) or \( 3d^{9}4s^24p^4d \) negative ion into a \( 3d^{10}4nsn \) neutral state is generally a complicated process, requiring one or more electrons to change their \( l \) quantum number. The decay of \( 3d^{9}4s^24p^2 \) into the \( 3d^{10}4snd \) states is especially complicated, as it is a three-electron autoionisation process, and at least two of these electron are required to change their \( l \) quantum number. One might expect therefore that the \( 3d^{9}4s^24p^2 \) negative-ion resonances do not affect the excitation of the \( 3d^{10}4snf \) states. However, this is probably not the case because very strong structures observed in \( 3d^{10}4snf \) state photon excitation functions correspond closely to structures in the differential elastic scattering signal due to the \( 3d^{9}4s^24p^2 \) negative-ion resonances.

The \( 3d^{9}4s^24p^2 \) and \( 3d^{9}4s^24p^4d \) negative ions may decay strongly into \( 3d^{10}4snl \) states,
despite this being a seemingly complicated process, because they are a mixture of configurations and LS terms. As mentioned in Chapter 1, a similar argument has been used by Penttila et al. [7] and Ueda et al. [9] to explain the significant influence of relatively complicated autoionisation processes in magnesium and strontium. Conversely, if either a 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{2} or 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}d negative ion does not decay strongly into a particular neutral state observed here, it could be because the negative ion is not mixed with a configuration through which a simple decay into the neutral state can occur. Some configurations which may be mixed with 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{2} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}d are shown in Table 6.6. The mixed state configurations were chosen because they can decay to their corresponding neutral state and partial wave with alterations of only two electron \textit{n} quantum numbers. The mixed configurations given are an illustrative sample, and not an exhaustive or accurate list of the configurations which may comprise the negative ions and assist their decay. Only two possible mixed configurations are listed for each combination of negative ion configuration, neutral state and partial wave, with preference given to 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{2} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}d configurations. These were selected because, compared to 3\textit{d}\textsuperscript{10}4\textit{s}\textit{n} states, they are closer in energy to the 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{2} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}d configurations, and therefore might be expected to interact more strongly with them. In some cases no 3\textit{d}\textsuperscript{10}4\textit{p}\textit{n} configurations fulfil the stated criteria, and so a 3\textit{d}\textsuperscript{10}4\textit{s}\textit{n} configuration is suggested instead. There may be a significant mixing between the 3\textit{d}\textsuperscript{10}4\textit{s}\textit{n} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{2} or 3\textit{d}\textsuperscript{10}4\textit{s}\textit{n} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}d configurations, given that Mansfield predicted mixing between the 4\textit{s}\textit{p}\textsuperscript{1}P\textsubscript{1} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{1}P\textsubscript{1} states [11].

The strength of 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{2} and 3\textit{d}\textsuperscript{9}4\textit{s}\textsuperscript{2}4\textit{p}\textsuperscript{4}d negative-ion resonances also depends on the \textit{n} and \textit{S} of the neutral states observed. The clearest example here relates to the A-group resonances, which produce a clear structure in the 4\textit{s}\textit{p}\textsuperscript{3}P\textsubscript{0,1,2} and 4\textit{s}\textit{d}\textsuperscript{3}D\textsubscript{1,2,3} electron and photon excitation functions, and the differential elastic scattering signal, but do not affect any other states observed here. This includes the 4\textit{s}\textit{p}\textsuperscript{3}P\textsubscript{0,1,2} states, and the 4\textit{snp}\textsuperscript{3}P\textsubscript{0,1,2} states which strongly influence the 4\textit{s}\textit{p}\textsuperscript{3}S\textsubscript{1} photon excitation function. The observed \textit{n}-dependence shows that the near-11 eV negative ions interact more strongly with \textit{n} = 4 neutral states. The spin dependence of the near-11 eV negative-ion resonances is not general, because negative ions which appear not to decay into the 4\textit{s}\textit{p}\textsuperscript{1}P\textsubscript{1} and 4\textit{s}\textit{p}\textsuperscript{1}D\textsubscript{2} states decay strongly into the 4\textit{s}\textsuperscript{2}1S\textsubscript{0} ground state. The present observations show that there is a spin dependence in negative ion decay only to certain neutral state configurations. Again, this could be due to the role of mixing in negative ion decay. Observable negative-ion resonances will be due to autoionisation processes which conserve \textit{L} and \textit{S}. The strength of decay into a given neutral state will depend on the configuration of the mixed negative ion states, and their \textit{LS} character. If decay of a negative ion into a particular neutral state configuration occurs through a quartet, \textit{S} = 3/2 mixed component, then there is an \textit{LS}-allowed transition to the triplet neutral state, but not to the singlet neutral state.
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PCI effects

Due to the high density of autoionizing states it is not a trivial task to identify which are associated with the observed PCI structures, and to extract information from the observed energy shifts. To gain some insight into which autoionizing states are strongly excited near threshold, one may examine the ejected electron spectra data of Back et al. [14], taken at an electron impact energy of 16 eV and an ejected electron angle of 60°, combined with autoionizing state energies [11, 10]. Of all the spectra taken by Back et al., the one used here was obtained under conditions closest to our experiment. The energies, assignments and angular momentum compositions given here for the autoionizing states observed by Back et al. are from the ab initio calculations of Mansfield [11].

Information regarding near threshold autoionizing state excitation can also be extracted from energy loss spectra obtained using incident electron energies slightly above the autoionizing state energies. Indeed, several such energy loss spectra were taken during the course of the project including the examples shown in Figure 6.20. However, in this case the energy loss spectra will be complicated by two factors. First, scattered and ejected electrons will have similar energies and overlap in the energy loss spectrum. Secondly the shift of scattered and ejected electron energies due to the PCI will smear out energy loss structures making their identification difficult. All of the spectra in Figure 6.20 were taken at a scattering angle of 40°, but the incident electron energy decreasing from 20 eV in Figure 6.20a, to 13.4 eV in Figure 6.20c. At 20 eV, ejected electron peaks due to $3d^94s^24p$ autoionising states are completely separated from the scattered electron, energy loss peaks marked with vertical bars in Figure 6.20a. However, with decreasing incident energy the ejected electron peaks, marked with arrows in Figures 6.20b and c, begin to overlap with the energy loss peaks. Thus, while energy loss peaks are clear and easily identified in the 20 eV spectrum, at 13.4 eV overlapping energy loss and ejected electron peaks smeared by PCI complicate any analysis.

The experiment of Back et al. indicates that the highest ejected electron yield in the energy region of interest here is associated with the decay of autoionizing states arising from the $3d^94s^24p$ electron configuration. This is true at both low and higher incident electron energies, indicating that the excitation of one inner 3d electron into the first unoccupied p orbital has a much larger probability than the excitation of two 4s electrons into any combination of higher orbitals. Furthermore, their spectra indicate that, of the autoionising states, only those with a $3d^94s^24p$ configuration incident electron energy of 20 eV. Consequently, it would be reasonable to expect states with a $3d^94s^24p$ electron configuration to be associated with the PCI effects observed here.

The structures in the $4snd^3D_{1,2,3}$ state photon excitation functions will be used to identify autoionising states which may be associated with the observed PCI effects. These states were chosen because PCI structures are seen clearly in the lowest, $4s4d^3D_{1,2,3}$ state. However, one would expect that PCI structures with a similar energy in the $4snd^3D_{1,2,3}$, $4snd^1D_2$, $4s5s^3S_1$ and $4snp^3P_{0,1,2}$ states would be associated with the same autoionising state. The energy of an autoionizing state associated with a PCI structure should be close
Figure 6.20: Electron energy loss spectra taken at 40° for incident energies of (a) 20 eV, (b) 15 eV and (c) 13.4 eV. Also indicated are the position of energy loss and 3d⁹4s²4p autoionising state ejected electron peaks.
to, but not higher than the onset of the structure in the lowest neutral state in which it is observed. Considering this, autoionizing states which could be associated with the PCI structures were identified from the ejected electron spectra of Back et al. (see Table 1 and Figure 3 of this reference). The relevant autoionizing states and state energies are indicated in Figure 5.12. Relative ejected electron intensities were then used to assess which of these autoionizing states were most likely to be associated with the PCI structures. It should be noted, however, that this approach assumes that the relative ejected electron intensities and therefore autoionizing state cross sections are not significantly different closer to threshold or at different ejected electron angles, which may not be the case.

From Figure 6.19, the onset of the T1 and T2 structures are 11.64 eV and 12.68 eV respectively. The T3 structure was not clearly resolved in all spectra, so will not be discussed. Below 11.64 eV, the 3d94s24p3P0,1,2 states at 10.974, 11.187 and 11.379 eV respectively, the 3d104p5s1S0 state at 11.504 eV, the 3d104s24p3D3 state at 11.539 eV and the 3d94s24p1D2 state at 11.619 eV, have been observed in the ejected electron spectra. By far the strongest contribution is from the 3d94s24p3P1 state, the 3d94s24p1D2 state is barely resolved, and the others are approximately a third to a sixth of the intensity of the strongest peak.

Considering now the T2 structure, in addition to those above the states observed below 12.68 eV in the ejected electron spectra are the 3d94s24p1F3 state at 11.669, the 3d94s24p3D1 state at 11.799, the 3d94s24p1P1 state at 11.884 and the 3d104p5s3P1 at 12.654 eV. The latter state produces a very weak peak in the ejected electron spectra, with an intensity approximately 20 times smaller than that associated with the 3d94s24p3P1 state. The other three states in this group appear to have appreciable cross sections, with their associated ejected electron peaks having intensities between approximately a quarter and a half of that for the 3d94s24p3P1 state.

The analysis of Mansfield also shows that most states likely to be associated with the observed PCI structures are strongly mixed. For example, the 3d94s24p state at 11.186 eV which produces the largest ejected electron peak has been assigned as 92%3P + 4%1P + 3%3D. Even stronger mixing is present in the high angular momentum 3d94s24p(36%1F + 33%3D + 31%3F) state at 11.669 eV, which produces the second largest ejected electron peak. Furthermore, the autoionizing states with the largest cross section at higher energies and in photoionization are the 3d94s24p(73%3D + 20%1P + 6%3P) + 3d104s4p(0.5%1P) state at 11.799, and the 3d94s24p(73%1P + 24%3D + 1%3P) + 3d104s4p(2%1P) state at 11.884, are an admixture of different configurations with large 3D and 1P characters for both states. Given this strong mixing, it is uncertain which autoionizing states, or even which components of these states, decay most strongly via the PCI to the neutral states which we observe. However, if the PCI structures are caused by the most strongly excited states, then the T1 structure is probably associated with autoionisation of the 3d94s24p3P1 state at 11.186, and the T2 structure is probably associated with autoionisation of the 3d94s24p1F3 state at 11.669 eV and, or, the 3d94s24p3D1 state at 11.799 eV.

The 3d94s24p autoionising states will decay to the 3d104s2S1/2 ground state of the
Zn$^+$ ion by the ejection of a $p$ or $f$-wave electron. Autoionisation by $p$-wave ejection requires the $l$ of one electron to change, whereas autoionisation by $f$-wave ejection will require the $l$ of two electrons to change. Both are two-electron autoionisation processes, and therefore much simpler than the decay of $3d^94s^24p^2$ and $3d^94s^24p^4d$ negative ions into some of the observed neutral states. Given this, configuration mixing may not be important in autoionisation of the $3d^94s^24p$ states. The $3d^94s^24p^3P_1$ state at 11.186 eV will decay to $3d^{10}4s^2S_{1/2}$ by $p$-wave emission, and the $3d^94s^24p^1F_3$ state at 11.669 eV will decay to $3d^{10}4s^2S_{1/2}$ by $f$-wave emission. The $3d^94s^24p$ state at 11.799 eV does not have an $LS$ allowed transition through its dominant $^3D_1$ component, but may decay to $3d^{10}4s^2S_{1/2}$ through its $^1P_1$ component by $p$-wave emission.

The PCI effects occur near the autoionising state thresholds, and so the scattered electron will have low energy, and therefore low orbital angular momentum. This means that there must be a significant transfer of orbital angular momentum between the scattered and ejected electrons to populate the $4snd^3D_{1,2,3}$ and $4snd^1D_2$ states by the PCI mechanism. This leads to a consideration which is important to this discussion of PCI in zinc, namely that for near-threshold excitation of the lowest autoionising states the scattered and ejected electrons will have similar energies. This situation is similar to that in which Wannier-type correlations can be expected [41]. Another consequence is that a large exchange of orbital angular momentum between the scattered and ejected electrons is possible.

The fundamental principles of large angular momentum transfer in electron scattering from atoms have been discussed by Fano [99], specifically for the case of high $\ell$ state excitation. Subsequently, Fano’s arguments were applied to PCI in the excitation of Rydberg states [40] in helium, and angular momentum exchange between outgoing scattered and ejected electrons was also reported in [100]. According to Fano, high values of angular momentum are transferred via a torque which one electron exerts on the other in an interaction lasting for a time comparable to the orbital period of the excited state. Although Fano’s analysis applies to ionization in the Wannier regime, the correlated motion of two electrons and the escape or capture of one of them into a bound orbit is the same as reported here and is governed by the same type of correlations. The result essential to the current discussion is that the torque which determines the maximum momentum which one of the electrons can attain depends inversely on the velocity $v$ of the faster electron. This implies a significant difference between the amount of orbital momentum which can be transferred by PCI in zinc compared to helium. The zinc autoionizing states of interest here occur within 2.5 eV of the first ionization threshold. So, for near-threshold autoionizing state excitation the ejected electron will have an energy below 2.5 eV, but will be faster than the scattered electron. An order of magnitude estimate of the maximum possible exchange of orbital momentum [99, 40] gives

$$\Delta J \leq e^2/4\pi\epsilon_0v$$ \hspace{1cm} (6.1)

For an ejected electron energy of 2 eV, the estimate above gives a value of $\Delta J \leq 2.61h$, so up to two units of orbital momentum ($\ell=2$) can be transferred by PCI for any of the
autoionizing states considered.

6.3 Conclusion

The 5.80 eV feature observed in the differential elastic scattering signal is also observed in the $4s4p^3P_{0,1,2}$ photon excitation function, where its appearance is consistent with that of a cusp peak. It is very similar to a feature in the BSRM $4s4p^3P_{0,1,2}$ integral cross section calculated by Zatsarinny and Bartschat [2], who assign the feature as a cusp. The 5.80 eV feature in the $4s4p^3P_{0,1,2}$ photon excitation function is also very similar to another which was observed in the mercury metastable atom excitation function of Newman et al. [45] near the $6s6p^1P_1$ threshold. This supports the claim that the features observed at the $nsnp^1P_1$ thresholds of zinc ($n = 4$), cadmium ($n = 5$) and mercury ($n = 6$) are cusps. Zatsarinny and Bartschat also predicted that the $4s4p^1P_1$ state integral cross section is finite at its threshold, but this is not supported by the present data. Between 7 eV and the ionisation threshold a large number of overlapping negative-ion resonance effect the $4s4p^3P_1$, $4s4p^1P_1$, $4s5s^3S_1$, $4s4d^3D_{1,2,3}$, $4s4d^3D_2$ and $4s5d^3D_{1,2,3}$ photon excitation functions. The $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ partial wave calculations of Zatsarinny and Bartschat were used to assign some of the negative-ion resonances affecting these states. For $4s4p^3P_1$, the negative-ion resonance (6) at 7.66 eV was assigned $4s5p^22D$ or $4s4d5s^2D$. For $4s4p^1P_1$, the negative-ion resonance (4) at 7.44 eV was assigned $4s5p^22D$, resonance (5) at 7.60 eV was assigned $4s4d5p^2F$ and the negative-ion resonance (10) at 8.36 eV was assigned $4s7s^22S$ or $4s5d6p^2F$.

The near-11 eV negative-ion resonances influence all the photon excitation functions presented here, but the strength of some negative-ion resonances was observed to be dependent on the $n$, $L$ and $S$ of the observed neutral state. The decay of $3d^94s^24p^2$ or $3d^94s^24p^4d$ negative ions into some of the neutral states observed is seemingly very complicated, with, for example, decay of $3d^94s^24p^2$ negative ions into the $3d^{10}4s4d$ configuration requiring three electrons to become active, and two electrons to have a change in $l$. It was suggested that the complicated autoionisation processes required for the $3d^94s^24p^2$ and $3d^94s^24p^4d$ negative ions to decay into the neutral states observed here are possible because the negative ions are strongly mixed. It was observed that, within a given neutral state configuration, some negative-ion resonances affect the triplet state, but not the singlet state. This could occur if the decay of a negative ion into a given neutral state configuration occurs via a mixed state with a quartet nature. In this case there will be a LS-allowed decay only to the triplet neutral state.

PCI structures were identified in the $4s4d, 5d, 6d^3D_{1,2,3}, 4s5d^1D_2$ and $4s5s^3S_1$ photon excitation functions in the energy range between 12 eV and 15 eV, although the structures in the $4s5s^3S_1$ photon excitation function are probably due to the $4snp^3P_{0,1,2}$ states. The energy of these structures in the $4s4d^3D_{1,2,3}$ photon excitation functions, and the ejected electron spectra of Back et al. [14] suggest that the PCI structures near 11.64 eV are due to the $3d^94s^24p^3P_1$ state at 11.186, and the PCI structures near 12.68 eV are due to the
$3d^9 4s^2 4p^1 F_3$ state at 11.669 eV and, or, the $3d^9 4s^2 4p^3 D_1$ state at 11.799 eV. For the $4snd^3 D_{1,2,3}$ and $4snd^1 D_2$ states to be populated by the PCI mechanism, there must be a large transfer of orbital angular momentum between the scattered and ejected electrons. This is possible for zinc because, unlike most other instances in which PCI has been investigated, the scattered and ejected electrons have a similar energy.
Chapter 7

Spin-Polarised Electron Studies

This study was conducted to establish whether the near-11 eV resonances have a significant impact on the spin asymmetry function. As discussed in Chapters 1 and 5, negative-ion resonances introduce a spin dependence into the scattering process by only affecting incident electrons with their spin oriented such that $J$ conservation is obeyed. However, there are complicating factors in the present case. The negative-ion resonances are energetically broad and overlap each other, and so spin asymmetry contributions from different negative-ion resonances may cancel out. There may also be competing spin dependent behaviour due to the different negative ion configurations, with different partial wave behaviour, which are possibly observed near 11 eV. Lastly, experimental spin-polarised electron studies are demanding, especially when zinc targets are used. Accordingly, these studies concentrated on $4s4p^3P_{0,1,2}$ state excitation, where as a proportion of the total scattering signal the negative-ion resonances in the unpolarised incident electron functions were greatest. It was thought, therefore, that this state provided the best opportunity to observe spin asymmetries. After the successful measurement of asymmetries for the $4s4p^3P_{0,1,2}$ state, the $4s4p^1P_{1}$ state spin asymmetry function was measured at $54^\circ$ to make a comparison between states with different spin angular momentum.

The results of spin asymmetry function measurements in the vicinity of the near-11 eV negative-ion resonances for the $4s4p^3P_{0,1,2}$ state are shown in Figures 7.1 - 7.3, and results for the $4s4p^1P_{1}$ state are shown in Figure 7.5. These studies were conducted with an energy resolution of $\Delta E_{1/2} = 120$ meV. For each scattering angle investigated, the spin-up incident electron and spin-down incident electron scattering signals are shown separately, alongside the spin asymmetry function $S_A$ calculated using Equation 1.9. The energy positions of the $a, a', b, b', c, c', e''$ and $d$ negative-ion resonance structures determined from the photon and electron excitation functions are also indicated. The value of $S_A$ at these resonance energies is indicated in Table 7.1 for each scattering channel and angle investigated.
Figure 7.1: Spin asymmetry function $S_A$ for the $4s4p^3P_{0,1,2}$ state at $30^\circ$ in the vicinity of the near-11 eV negative-ion resonances; (a) • differential electron excitation function taken with spin up incident electrons, △ differential electron excitation function taken with spin down incident electrons, (b) • spin asymmetry function $S_A$, with the indicated uncertainty.
Figure 7.2: Spin asymmetry function $S_A$ for the $4s4p^3P_{0,1,2}$ state at 54° in the vicinity of the near-11 eV negative-ion resonances; (a) • differential electron excitation function taken with spin up incident electrons, △ differential electron excitation function taken with spin down incident electrons, (b) ● spin asymmetry function $S_A$, with the indicated uncertainty.
Figure 7.3: Spin asymmetry function $S_A$ for the $4s4p^3P_{0,1,2}$ state at $90^\circ$ in the vicinity of the near-11 eV negative-ion resonances; (a) • differential electron excitation function taken with spin up incident electrons, △ differential electron excitation function taken with spin down incident electrons, (b) • spin asymmetry function $S_A$, with the indicated uncertainty.
7.1 Results

For $4s4p^3P_{0,1,2}$ state excitation, shown in Figures 7.1-7.3, all four of the negative-ion resonance structure groups identified in unpolarised electron excitation function measurements also appears to influence the asymmetry. Also of interest is the non-zero background asymmetry present at 30° and 54°. This non-zero background was further characterised by measuring $S_A$ as a function of scattering angle at an incident electron energy of 12 eV. The results of this investigation are shown in Figure 7.4. Combined with the other $4s4p^3P_{0,1,2}$ state asymmetry measurements, the data suggest that the magnitude of the background asymmetry is small for large angles, increases to a maximum near 20°, then decreases as $\theta$ approaches 0°. The sign of the asymmetry also changes with the sign of $\theta$, which is indicative of spin-orbit interaction. It should be stressed however that these are preliminary measurements, as perhaps can best be judged by the size of the error bars in Figure 7.4. Another aspect of the data indicating the need for further studies is that $S_A \theta \neq -S_A(\theta)$, which is not in keeping with the behaviour expected for Mott scattering. This may indicate the presence of a spin-coupling effect, which through exchange scattering will result in a spin up/down asymmetry, but not a left/right asymmetry [44].

In the $4s4p^3P_{0,1,2}$ state asymmetry function at 30°, both the $a$ and $a'$ resonance structures appear within a double peak. Therefore, the spin-sensitivity may permit the negative-ion resonances within the $A$-group to be resolved, despite the same energy resolution being insufficient to do so in the unpolarised incident electron measurements discussed in Chapter 5. Relative to the background, $S_A$ is positive at the $b$ resonance structure and
Figure 7.5: Spin asymmetry function $S_A$ for the $4s4p^1P_1$ state at 54° in the vicinity of the near-11 eV negative-ion resonances; (a) • differential electron excitation function taken with spin up incident electrons, △ differential electron excitation function taken with spin down incident electrons, (b) • spin asymmetry function $S_A$, with the indicated uncertainty.
negative at the $b'$ resonance structure, but there is not a distinct structure associated with either. The $c$ and $c'$ resonance structures are associated with a dip in $S_A$ which is followed by a prominent peak in the vicinity of the $c''$ and $d$ resonance structures. The maximum asymmetry of approximately -0.1 occurs near the $c$ and $c'$ resonance structures, but the maximum deviation from the background asymmetry of approximately 0.12 is associated with the $c''$ and $d$ resonance structures.

The resonance structures in the $4s4p^3P_{0,1,2}$ spin asymmetry function at $54^\circ$, shown in Figure 7.2, are very similar to those measured at $30^\circ$. There are, however, some obvious differences. The double peak structure is not resolved for the $A$-group resonances. The $B$-group resonances produce a distinct structure, namely a peak corresponding to the $b$ resonance structure with a shoulder possibly associated with the $b'$ resonance structure. Last, the background asymmetry of -0.02 is smaller than that seen at $30^\circ$. At $54^\circ$ the largest value of $S_A$ is approximately -0.24, and occurs near the $c$ and $c'$ resonance structures.

The greatest difference between the spin-up and spin-down signals is seen at $90^\circ$. This is not surprising, since the greatest asymmetry is usually seen where the scattering signal is smallest. Of the angles investigated the $4s4p^3P_{0,1,2}$ state scattering signal was smallest at $90^\circ$. Comparing Figures 7.1-7.3, at $54^\circ$ and $30^\circ$ the spin-up and spin-down scattering signals are quite similar. However, at $90^\circ$ there are significant differences, most strikingly that the $b$ and $b'$ structures are absent from the spin-down signal. The spin-up signal has structures corresponding to the $a$, $a'$, $b$, $b'$, $c''$ and $d$ resonance structures, while the spin-down signal has structures corresponding to the $a$, $c$, $c'$ and $c''$ resonance structures. As a result, in the asymmetry function $S_A$ shown in Figure 7.3 there is a peak incorporating the $a$, $a'$, $b$ and $b'$ resonance structure, followed by a dip incorporating the $c$, $c'$ and $c''$ resonance structures. There is perhaps a small positive asymmetry at the $d$ resonance structure, but the statistical accuracy of the data is not sufficient to make a conclusive judgement. The background asymmetry at $90^\circ$ is negligible, and the largest asymmetry of approximately 0.34 occurs in the vicinity of the $b$ and $b'$ resonance structures.

The spin asymmetry function for $4s4p^1P_1$ state excitation was measured only at $54^\circ$, and the results of this study are shown in Figure 7.5. Unpolarised incident electron excitation functions for the $4s4p^1P_1$ state at $54^\circ$, presented in Chapter 5, show peaks due to the $B$-group resonances, a narrow dominant peak at the $c'$ resonance structure and a shoulder at the $d$ resonance structure. In the asymmetry function shown in Figure 7.5, there is perhaps a small peak at the $a$ and $a'$ resonance structures but given the statistical accuracy of the data it is not possible to say with certainty. The $b$ and $b'$ resonance structures do not seem to be associated with any asymmetry structures, but there is a dip in the asymmetry between the $b'$ and $c$ resonance structures. This is followed by a large peak incorporating the $c$, $c'$ and $c''$ resonance structures, and a dip at the $d$ resonance structure. There is a negligible background asymmetry, and the maximum asymmetry is approximately 0.12, compared to -0.24 for the $4s4p^3P_{0,1,2}$ state at the same angle.
Table 7.1: Spin asymmetry function $S_A$ for excitation of the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ states in the vicinity of the near-11 eV resonances and for the non-resonance background between 10 and 10.5 eV, with indicated uncertainties. The numbers in brackets indicate the difference between the asymmetry at the resonances and the non-resonance background.

<table>
<thead>
<tr>
<th>State</th>
<th>Angle</th>
<th>Back.</th>
<th>a</th>
<th>a'</th>
<th>b</th>
<th>b'</th>
<th>c</th>
<th>c'</th>
<th>c''</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4s4p^3P_{0,1,2}$</td>
<td>30°</td>
<td></td>
<td>0.01 ± 0.02</td>
<td>0.00 ± 0.02</td>
<td>-0.03 ± 0.01</td>
<td>-0.08 ± 0.01</td>
<td>-0.09 ± 0.01</td>
<td>-0.08 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.07)</td>
<td>(0.06)</td>
<td>(0.03)</td>
<td>(-0.02)</td>
<td>(-0.03)</td>
<td>(-0.02)</td>
<td>(0.07)</td>
<td>(0.09)</td>
</tr>
<tr>
<td>$4s4p^3P_{0,1,2}$</td>
<td>54°</td>
<td></td>
<td>0.07 ± 0.02</td>
<td>0.08 ± 0.02</td>
<td>0.11 ± 0.02</td>
<td>0.04 ± 0.02</td>
<td>-0.21 ± 0.02</td>
<td>-0.20 ± 0.01</td>
<td>-0.01 ± 0.01</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.09)</td>
<td>(0.10)</td>
<td>(0.13)</td>
<td>(0.06)</td>
<td>(-0.19)</td>
<td>(-0.18)</td>
<td>(0.01)</td>
<td>(0.04)</td>
</tr>
<tr>
<td>$4s4p^3P_{0,1,2}$</td>
<td>90°</td>
<td></td>
<td>0.00 ± 0.04</td>
<td>0.07 ± 0.04</td>
<td>0.14 ± 0.04</td>
<td>0.27 ± 0.04</td>
<td>0.23 ± 0.03</td>
<td>-0.04 ± 0.03</td>
<td>-0.22 ± 0.03</td>
<td>-0.13 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.07)</td>
<td>(0.14)</td>
<td>(0.27)</td>
<td>(0.23)</td>
<td>(-0.04)</td>
<td>(-0.22)</td>
<td>(-0.13)</td>
<td>(0.02)</td>
</tr>
<tr>
<td>$4s4p^1P_1$</td>
<td>54°</td>
<td></td>
<td>0.04 ± 0.03</td>
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<td>(0.07)</td>
<td>(0.14)</td>
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<td>(-0.04)</td>
<td>(-0.22)</td>
<td>(-0.13)</td>
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</tbody>
</table>
7.2 Discussion

Similar measurements to those presented here have been performed for mercury by Bartschat et al. [101]. That study measured the energy dependence of the asymmetry in excitation of the 6s6p \(^3P\) and 6s6p \(^1P\) states of mercury between the respective threshold energies and 22 eV. The fine structure levels of the mercury 6s6p \(^3P\) state were resolved, unlike in the present study where the fine structure of the zinc 4p4 \(^3P\) states was not resolved. Both studies displayed significant spin asymmetries due to negative-ion resonances. An explanation for the negative-ion resonance induced asymmetries observed by Bartschat et al. was provided by Kessler [43]. Kessler notes that, when picking out the electrons of the dominant partial wave, with orbital angular momentum \(l\), we must take into account that transversely polarised electrons which are scattered to the left have total angular momenta \(j\) different from those of the electrons scattered to the right, since the orbital angular momenta are opposite. Kessler concludes that, for a given incident electron spin polarisation, either electrons scattered to the right or to the left, but not both, may have \(j\) suitable to excite the compound state and to exhibit a negative-ion resonance. Therefore, in the present measurements in which electrons scattered to the left only were detected, either spin-up incident electrons or spin-down incident electrons, but not both, may have \(j\) suitable to excite the negative-ion resonance.

To demonstrate the effect a negative-ion resonance will have on the spin asymmetry, consider a negative-ion resonance which enhances the cross section of the observed state, and is excited by incident electrons with orbital angular momentum \(l\). If the observation is made at a positive scattering angle \(\theta\), and if this negative-ion resonance produces a positive spin-up/down asymmetry, it means that spin-up incident electrons excite the negative ion, which therefore has a total angular momentum \(J = l + 1/2\). Likewise, if this negative-ion resonance produces a negative spin-up/down asymmetry, spin-down incident electrons will excite the negative ion, which therefore has a total angular momentum \(J = l - 1/2\). Obviously, a negative-ion resonance will not generally enhance a cross section, because it may interfere destructively as well as constructively with the non-resonance cross section. Whether a particular negative-ion resonance produces a positive or negative asymmetry will depend on its Fano profile, as well as its parity and \(J\). In principle, spin asymmetry measurements can resolve overlapping negative-ion resonances with different \(J\), even if because they have large natural width they cannot be resolved in unpolarised electron excitation function experiments. Therefore, high-resolution spin asymmetry function measurements, which are possible with the present apparatus, should provide data of great use for classifying the near-11 eV negative-ion resonances.

As discussed in Chapter 5, it appears that 3d\(^0\)4s\(^2\)2p\(^2\) and 3d\(^0\)4s\(^2\)4p\(^4\)d configuration negative-ion resonances decay into the 4s4p \(^3P\) \(_{0,1,2}\) and 4s4p \(^1P\) \(_1\) states. Negative ions with a 3d\(^0\)4s\(^2\)2p\(^2\) configuration are most likely excited by d-wave incident electrons, as was observed in elastic scattering, can decay to the 4s4p \(^3P\) \(_{0,1,2}\) or 4s4p \(^1P\) \(_1\) states by \(p\) or f-wave electron emission. Negative ions with a 3d\(^0\)4s\(^2\)4p\(^4\)d configuration will most likely be excited by p-wave incident electrons, and can decay to the 4s4p \(^3P\) \(_{0,1,2}\) or 4s4p \(^1P\) \(_1\)
states by $s$ or $d$-wave electron emission. The $4s4p^3P_{0,1,2}$ state is most strongly affected by $3d^94s^24p^2$ negative-ion resonances, but the negative-ion resonance structure present in the $4s4p^3P_{0,1,2}$ state electron excitation function at $90^\circ$ indicates $s$ and or $d$-wave contributions from $3d^94s^24p4d$ configuration negative ions. For the $4s4p^1P_1$ state, the effect of $3d^94s^24p4d$ negative-ion resonances is comparable to that of the $3d^94s^24p^2$ negative-ion resonances.

The sign of the relative asymmetry for each structure, which is given in Table 7.1, shows whether it is predominantly composed of negative-ion resonances excited by incident spin-up or spin-down electrons. Given that the near-11 eV negative-ion resonances appear to enhance the cross section, a positive relative asymmetry should be associated with a $J = l + 1/2$ negative ion excited by spin-up incident electrons, while a negative relative asymmetry should be associated with a $J = 1 - 1/2$ negative ion excited by spin-down incident electrons. At $90^\circ$, $p$ and $f$-wave scattered electron contributions, and therefore also $3d^94s^24p^2$ configuration negative-ion resonances, should be absent. Positive relative asymmetries should indicate a predominance of $J = 3/2$, $3d^94s^24p4d$ configuration negative-ion resonances excited by spin-up, $p$-wave incident electrons. On the other hand, a negative asymmetry should indicate a predominance of $J = 1/2$ negative-ion resonances, excited by spin-down incident electrons. At $54^\circ$ there will be no contributions of $d$-wave scattered electrons, but contributions from $s$, $p$ and $f$-wave scattered electrons. This means that resonances due to $3d^94s^24p^2$ or $3d^94s^24p4d$ configuration negative ions can be observed. A positive asymmetry can indicate a $J = 3/2$, $3d^94s^24p4d$ negative-ion resonance excited by a spin-up $p$-wave incident electron, or a $J = 5/2$, $3d^94s^24p^2$ negative-ion resonance excited by a spin-up $d$-wave incident electron. Likewise, a negative asymmetry can indicate a $J = 1/2$, $3d^94s^24p4d$ negative ion excited by a spin-down $p$-wave incident electron, or a $J = 3/2$, $3d^94s^24p^2$ negative ion excited by a spin-down $d$-wave incident electron. This will also be the case at $30^\circ$, where there will also be $d$-wave contributions from $3d^94s^24p4d$ negative-ion resonances. If negative-ion resonances derived from only one configuration affect the $90^\circ$ asymmetry, while possibly two affect the $30^\circ$ and $54^\circ$ asymmetries, then this is in keeping with the observation that the $90^\circ$ scattering signals have a clearer incident electron spin dependence.

Table 7.1 shows that the sign of the relative asymmetry at a given resonance structure is very consistent across the scattering angles and states studied. The hypothesis that $3d^94s^24p^2$ and $3d^94s^24p4d$ configuration negative-ion resonances affect the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ states near 11 eV was put forward in Chapter 5 to explain the nature of the electron excitation functions as being due to the different states having different scattering angle-dependent sensitivities to negative-ion resonances associated with different configurations. Given this, one might not expect the relative asymmetry at a given resonance structure to be so consistent across the scattering angles and states studied. The fact that they are, if the multiple resonance-configuration hypothesis is accurate, indicates that the $3d^94s^24p^2$, $J = 3/2$ negative-ion resonance energies coincide with the $3d^94s^24p4d$, $J = 1/2$ negative-ion resonance energies, as do those for $3d^94s^24p^2$, $J = 5/2$ and $3d^94s^24p4d$,
$J = 3/2$. A simpler explanation of the consistent asymmetry behaviour is that only negative-ion resonances due to the $3d^94s^24p^2$ configuration are present, and the deviation from the expected angle-dependent behaviour observed in the $4s4p^3P_{0,1,2}$ and $4s4p^1P_1$ electron excitation functions are due to something else. It appears from Figure 7.4 that Mott scattering is significant for $4s4p^3P_{0,1,2}$ excitation below 54°. Equation 5.3 shows that a significant spin-flip amplitude $g$ will make the scattering angle dependent behaviour of the negative-ion resonance dependent on the associated Legendre polynomial $P_1^l(\cos \theta)$. Mott scattering was shown to have an effect on the krypton negative-ion resonances observed by Weingartshofer et al. [82]. However, the electron excitation functions which suggest two overlapping negative-ion resonance configurations were those for the $4s4p^1P_1$ state excitation, and those for the $4s4p^3P_{0,1,2}$ state excitation at scattering angles above 54°, and Mott scattering does not appear to be significant for any of these.

7.3 Conclusion

The primary objective of this study was to measure spin asymmetries for electron scattering from zinc, which is a demanding experimental task. The successful measurement of these quantities demonstrates the capabilities of the apparatus and the operator. Furthermore, these studies established that the near-11 eV negative-ion resonances have a significant affect on the spin asymmetry function $S_A$, and that such measurements should be further pursued given the complex behaviour displayed. The most obvious immediate improvement for the present apparatus would be to use the 180° hemispherical energy selector to improve the incident electron energy resolution, possibly to study elastic scattering for which the analysis will be more straightforward. The analysis here was complicated by the 120 meV energy resolution, which was insufficient to separate negative-ion resonances within the $A$, $B$ and $C$ resonance groups or the $d$ resonance structure, the observation of inelastic scattering and the resultant contribution of more than one partial wave, and the possible presence of both $3d^94s^24p^2$ and $3d^94s^24p^4d$ configuration negative-ion resonances. Preliminary studies also indicate a non-zero spin asymmetry for the $4s4p^3P_{0,1,2}$ state, seemingly unrelated to any negative-ion resonances. These asymmetries may be due to Mott scattering, but some aspects of the data indicate the presence of a spin-coupling effect as well.
Chapter 8

Conclusions

This work studied the significance of electron correlation and spin-dependent phenomena in the electron impact excitation of zinc, using a variety of experimental approaches. Electron correlation effects were found to have a significant influence on elastic and inelastic scattering for incident electron energies between the first excitation threshold at 4.003 eV, and 20 eV. Negative-ion resonances and PCI associated with inner-shell excitation were found to be particularly strong, and need to be included in any accurate theoretical model of electron scattering from zinc. With some modification, the apparatus used here could be used to provide more incisive data regarding the complex negative-ion and PCI structures observed between the ionisation threshold and 16 eV, to further develop an understanding of the inner-shell activated electron correlation effects. It would be best if the development and interpretation of these future experimental investigations is assisted by appropriate theoretical modelling. The results presented here offer the best available guide for these future studies, which are necessary to extend the accurate treatments of electron-atom scattering beyond the simplest targets.

Emission cross sections, shown in Chapter 4, were measured because they could be compared directly to theoretical calculations. There is excellent agreement between the CCC calculations of Fursa and Bray [61] and BSRM the calculations Zatsarinny and Bartschat [78] if they are simplified to exclude coupling to the continuum and the influence to inner-shell excited states. However, there are significant differences between full CCC calculations, which rely on a frozen core approximation but adequately treat the target continuum, the full BSRM calculations, which do not adequately treat the target continuum but include 3d inner-shell excited states in the target description, and the experimental emission cross sections. There is reasonably good agreement between experiment and both theories for the $4s4p^3P_{0,1,2}$ emission cross section, but the theories diverge for all the other emission cross sections, and which of the calculations agrees better with experiment depends on the excited state. This might suggest that, of the two effects which are differently treated by the CCC and BSRM models, coupling to the continuum is more important in the excitation of the $4s5s^3S_1$ and $4s4d^3D_{1,2,3}$ states, while the influence of 3d-innershell excited states is more important in excitation of the $4s4p^1P_1$ and $4s4d^1D_2$ state. Neither of the theories predict the strong negative-ion resonances and
PCI associated with the $3d^94s^24p$ states which are observed for incident electron energies between the ionisation threshold and 16 eV. As a result there is a consistent discrepancy between the experimental and theoretical emission cross sections in this energy range. This demonstrates that neither theoretical approach adequately treats the electron-zinc scattering problem, and that zinc cross section calculations must include inner-shell excitation effects in order to be accurate, particularly at energies between the ionisation threshold and 20 eV.

Of the zinc negative-ion resonances, only those present below the ionisation threshold have previously been studied with any rigour, either experimentally or theoretically, by assigning resonance energies, widths, configurations and $LS$-terms. The present investigations of zinc negative-ion resonances below the ionisation threshold, conducted by measuring the differential elastic scattering signal and photon excitation functions, verified some conclusions of the previous studies, and resolved a disagreement between them. The comparison between the present experiment and the BSRM calculations of Zatsarinny and Bartschat [2] also showed that the simplest zinc negative-ion resonances, which are based on $3d^{10}4snl$ parent states, are quite well understood. The present experiment, the experiment of Sullivan et al. [1] and the BSRM calculations of Zatsarinny and Bartschat are in agreement that the wide resonance observed here at 4.26 eV is due to a $3d^{10}4s^24p^{2}D$ negative ion. An area of disagreement in the literature, concerning the feature observed at the $4s^24p^1P_1$ threshold of zinc, has been resolved by the present differential elastic scattering signal and $4s^24p^3P_1$ photon excitation function measurements in favour of Zatsarinny and Bartschat, who assign the zinc feature as a cusp. This finding suggests that similar features observed in the excitation of mercury and cadmium by Newman et al. [45] and Sullivan et al. are also cusps. Between 7 eV and 8.5 eV numerous overlapping negative-ion resonances are observed here, and though it is not straightforward to make comparisons, there appears to be good agreement between the present differential elastic scattering and $4s^24p^1P_1$ photon excitation function measurements, and the work of Zatsarinny and Bartschat and Sullivan et al. As discussed in Chapter 6, the BSRM calculations were also used to assign some of the negative-ion resonances observed in the $4s^4p^3P_1$, $4s^4p^1P_1$ and $4s^5s^3S_1$ photon excitation functions. However, BSRM negative-ion resonance predictions for the $4s^4d^1D_2$ state break down above 8 eV, indicating a growing influence of coupling to the continuum.

The near-11 eV negative-ion resonances in zinc are very significant, and so afford an excellent opportunity to study inner-shell excitation effects. These will generally be important in the electron impact excitation of atoms, but have been the subject of relatively few experimental or theoretical studies. The differential elastic scattering signal and the transmission study of Burrow and Michejda [3] suggest that there are at least eight negative-ion resonances in the near-11 eV region, with $3d^94s^24p^2^2D_{3/2,5/2}$ negative-ion resonances predominant. The $a$-group resonances are absent from the $90^\circ$ differential elastic scattering signal, and many negative-ion resonances effect the $90^\circ$ $4s^4p^3P_{0,1,2}$ and $4s^24p^1P_1$ electron excitation functions. This contradicts what would be expected if all the
near-11 eV negative-ion resonances had a $3d^94s^24p^22D_{3/2,5/2}$ assignment, but interference effects, overlapping negative-ion resonance profiles or spin-dependence may explain the observations. Another explanation is that negative-ion resonances due to a different, odd parity configuration were observed, and it was suggested here that this other negative ion configuration is $3d^94s^24p4d$. Observations of the near-11 eV negative-ion-resonances in photon excitation functions indicate that the negative ions decay most strongly into $n = 4$ states, and that, within the $4s4p$ and $4s4d$ neutral state configurations, some negative-ion resonances only effect the triplet states. This may be because $3d^94s^24p^2$ and $3d^94s^24p4d$ negative ions decay into the observed neutral states occurs through a component of the mixed negative ion, and that the observed spin dependence is due to the decay of some negative ions into the $4s4p$ and $4s4d$ configurations occurring through a quartet state.

The present experimental evidence does not show conclusively that $3d^94s^24p4d$ negative-ion resonances are present, or that mixing has a significant influence on which neutral states are effected by a particular negative-ion resonance. These explanations were advanced, in the absence of appropriate theoretical guidance, to explain the complicated behaviour which has been observed. The fact that the numerous, overlapping negative-ion resonances in the near-11 eV region appear to be energetically broad, even in the high-resolution transmission study of Burrow and Michejda [3], indicates that it may be impossible for experiments to resolve all the negative-ion resonances. Given this, theoretical models are needed to determine how many negative-ion resonances are present, what the assignments of these negative-ion resonances are, how strongly the negative ions are mixed and how mixing influences their decay, the interference between overlapping negative-ion resonances, and the extent to which spin-dependent interactions affect the negative-ion resonances. Because the negative-ion resonances are associated with $3d$-innershell excitation, the present theoretical models will require significant development before they are able to adequately treat the near-11 eV negative-ion resonances and reproduce the present observations.

The PCI structures observed for zinc in the energy region between 12 eV and 16 eV are large compared to those observed for other atoms. In the case of zinc the scattered and ejected electrons have a similar energy, which permits a large transfer of orbital angular momentum and the population through PCI of the $L = 2$, $4snd^1D_2$ and $4snd^3D_{1,2,3}$ states, as is observed here. Neither the BSRM or the CCC emission cross sections include PCI effects, but they will need to be treated in accurate calculations of the $n \geq 5$ state cross sections. Most of the previous experimental studies of PCI have investigated situations where the ejected electron has much more energy than the scattered electron, and the “shake-down” model of King et al. [36] is appropriate. A different theoretical model needs to be developed to describe the zinc PCI structures, and this model would also, ideally, characterise the interference between direct and PCI excitation.

The greatest limitations on the present experiment were due to run-times being restricted by zinc deposition onto sensitive parts of the apparatus. Extending operating times would allow higher energy resolution experiments, result in more statistically ac-
curate data, and permit more difficult experimental techniques, such as electron-photon coincidence and \((e,2e)\), to be used. The apparatus was originally used for studies of electron scattering from noble gases. Experiments using zinc vapour targets were made possible by the installation of an oven and a liquid-nitrogen cooled, zinc vapour collection plate. Several refinements can be made to the apparatus. The oven could be positioned so that the zinc vapour beam is directed along the positive \(y\)-axis. This would result in less deposition onto the electron gun, the electron analyser, and the turbomolecular pump, but would require the photon detection system to be moved, or perhaps protected from zinc deposition by heating. Zinc vapour would be more effectively collected if the beam was directed into a liquid-nitrogen cooled shroud surrounding the interaction region, which would have slits and apertures to allow the passage of the incident electron beam, scattered electrons and decay photons. The deposition of zinc onto the electron gun and electron analyser could also be reduced by heating them, and also replacing their macor insulating components with teflon or glass, which are both less prone to accumulating zinc.

This improved apparatus could be used to remeasure the \(4s4p^3P_{0,1,2}\) and \(4s4p^1P_1\) spin asymmetry function with high energy resolution and possibly a greater degree of incident electron beam spin polarisation, and to extend these measurements into elastic scattering. Given the large number of apparently broad negative-ion resonances near 11 eV, exploiting the spin-dependence of resonance scattering in a high energy resolution experiment may be the only way in which the negative-ions can be assigned without theoretical modelling. The apparatus could also be used to measure the ejected electron spectrum of zinc at energies lower than those investigated by Back et al. [14]. Such an investigation could be a precursor to \((e,2e)\) studies, which will be possible with the present apparatus if the unpolarised electron gun is replaced by a second electron analyser. It would be particularly interesting to conduct an \((e,2e)\) investigation of PCI affecting zinc at incident electron energies between 12 eV and 15 eV, where the scattered and ejected electrons associated with the \(3d^94s^24p\) autoionising states have a similar energy.

The experimental investigations of inner-shell excitation phenomena in zinc could also be extended to include other atomic targets. Perhaps the most obvious target atom is cadmium. The similar electron configuration and energy level structure means that there will be a direct correspondence between observations of cadmium and zinc. However, fine structure splitting will be greater in cadmium, which means that, if there are negative-ion resonance associated with the \(4d^95s^25p\) autoionising states of cadmium, they should be easier to assign than the near-11 eV negative-ion resonances in zinc. As discussed in Chapter 1, the \(3d^44s^2\) and \(3d^94s^2\) low-lying excited states of chromium and copper seem to be associated with significant electron correlation effects, and so they may be associated with significant negative-ion resonance effects. A drawback of experiments of the electron impact excitation of chromium or copper is that very high temperatures, on the order of 2180 K for chromium and 1358 K for copper, will be required to create an adequately dense metal vapour beam. These temperatures cannot be achieved by the present oven.
The present work is the most thorough investigation of electron correlation phenomena in electron scattering from zinc which has been undertaken to date. Of particular note is the amount, and diversity of data obtained to characterise 3d-innershell excitation effects. Apart from indicating the significance of these effects for zinc, their complex \( n \), \( L \) and \( S \) dependent properties, and the possibly important role of configuration interaction, the present study also provides ample opportunity for testing theoretical models. In doing so, it assists the extension of present theoretical treatments of electron-atom scattering to include an good treatment of inner-shell excitation, which is vitally important to accurately describe scattering from all but the most simple atomic targets. The achievements of the present work are numerous, and especially notable given the great difficulties presented by metal vapour experiments. Nonetheless, the strength, variety and complexity of the electron correlation effects in zinc, which have been demonstrated here, make their experimental investigation very attractive. The present work provides a comprehensive guide for any future studies.
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