Theory of Ultrafast Interatomic
(Intermolecular) Electronic Decay
Processes in Polyatomic Clusters

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Abstract

This thesis is devoted to the study of the non-radiative process of Interatomic (Intermolecular) Coulombic Decay (ICD) in clusters. The aims of this thesis are two-fold: firstly we study ICD in the inner-valence-ionised endohedral fullerene complexes, such as \((2s^1)\text{Ne}^+@C_{60}\), where it is ultrafast due to the many available decay channels. We investigate the open question of the dependence of the ICD rate on the location of the endohedrally confined ion. Qualitative analysis shows that once the symmetry of the endohedral system is lowered by the departure of a rare gas atom from its equilibrium position in the centre of the cage, multipole plasmon resonances can be excited by energy transfer from the inner-valence-ionised ion to the cage. Nevertheless, our quantitative analytical and \textit{ab initio} numerical studies lead to the conclusion that the total ICD width is remarkably stable across broad range of geometries. It turns out that the multipole plasmon excitation is negligible and the well-known dipole fullerene plasmon is the one defining the ICD time scale.

Secondly we focus our attention onto inner-valence vacancies that are not energetic enough to decay via ICD. We propose that under such conditions, an ICD-like electronic process may still be induced by an incident photon. We call the new process single photon laser-enabled ICD (spLEICD). We for the first time investigate spLEICD in a series of van der Waals and hydrogen-bonded clusters. Our results demonstrate that the spLEICD cross-sections in hydrogen-bonded systems are larger than in van der Waals ones, whereas polyatomic van der Waals clusters lead to a more efficient spLEICD process than the van der Waals diatoms. We analyse the dependence of the spLEICD cross-section on the inter-atomic distance in a cluster showing analytically that it obeys the \(1/R^6\) law at large distances. This analysis is confirmed by our \textit{ab initio} numerical calculations. This strong distance-dependence may allow spLEICD to be used as a novel spectroscopic technique for the study of processes which occur in different spatial regions of molecules or clusters.
The true sign of intelligence is not knowledge but imagination.

Albert Einstein

Declaration

I hereby certify that the material of this thesis, which I now submit for the award of Doctor of Philosophy of Imperial College London, is entirely my own work unless otherwise cited or acknowledged within the body of the text.

Laila Bahmanpour
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Chapter 1

Introduction

This thesis investigates Interatomic/Intermolecular Coulombic Decay (ICD) as well as the single photon laser-enabled ICD (spLEICD) in selected Van der Waals and hydrogen-bonded clusters. ICD takes places in weakly bound clusters with a vacancy on the inner subshell of the valence shell. The recombination of a valence electron on the cluster sub-unit with the inner-valence vacancy into the vacancy causes valence ionisation on a neighbouring cluster sub-unit as a result of electronic correlation, i.e. the Coulomb repulsion between electrons. An inner-valence ionised cluster is said to be ICD-inactive if the energy of the vacancy is below the double ionisation potential (DIP) of the cluster. However, as we have found, an incident external photon may provide the required additional energy thus enabling ICD in a process referred to as single photon Laser Enabled ICD (spLEICD).

This thesis is divided into six chapters: the background material on ICD and related phenomena is provided in this chapter. Sections 1.1 to 1.5 are devoted to the introduction of non-radiative electronic bound-free transitions including ICD, while in section 1.6 we introduce fullerenes and endohedral fullerenes (see below). Chapters 2 and 3 lay the mathematical groundwork as well as the computational and theoretical approximation tools necessary for the study of ICD and spLEICD.

Chapter 4 is dedicated to the study of ICD in endohedral fullerenes where we will
use both a semi-analytic and a numerical method in order to calculate the rate of ICD. In chapter 5 we investigate $sp$LEICD in selected NeAr and ammonia clusters by numerically calculating photoionisation cross sections which characterise the process.

### 1.1 Non-Radiative Electronic Bound-Free Transitions

Atoms possess infinite number of bound electronic states. The most stable of these states is called the ground state. An external energy source can disturb the ground state by either exciting an electron to a higher, more energetic, bound state, or by promoting the electron into the continuum in a process called ionisation. The latter is referred to as a bound-free transition, and can be induced by shining light on the atom, a process referred to as photoionisation [1].

Photoionisation of an atom results in the creation of a vacant orbital, which in turn can lead to the rearrangement of electrons inside the atom in order to re-establish a favourable potential energy landscape. The aim of this thesis is to investigate the dynamics that unfolds following the creation of a vacancy in the inner subshell of the valence shell — from here on referred to as an inner-valence vacancy — on an atom, molecule, or a cluster. Depending on the environment in which the resulting ion is placed, the vacancy may take one of two main decay routes, (1) Photo-emission, which takes place on nanosecond ($10^{-9}$ s) time scales, and (2) Non-radiative electronic decay processes, which can proceed on femto- (fs, $10^{-15}$ s) to attosecond (as, $10^{-18}$ s) time scales. The former process involves an outer-valence electron filling in the vacancy and releasing the extra energy as a photon. This thesis will be mainly concerned with the properties of the latter process, which can be either intra- or inter-atomic in nature.

Intra-atomic non-radiative decay processes are most commonly found in core-
ionized atoms. Auger decay [2] is an example of an intra-atomic non-radiative decay process which takes place when a core-vacancy is annihilated by an outer electron, while another outer electron escapes into the continuum as a result of electronic correlation. We will look more closely at this process in section 1.2.

Autoionisation is another type of intra-atomic non-radiative decay mechanism that usually takes place when a bound electron has been photo-excited into a high-lying Rydberg state. An example of this process will be presented in section 1.3.

Not all vacancies have enough energy to overcome the double ionisation potential (DIP) of the ion and decay via electron emission. An isolated ion with an inner-valence vacancy whose energy lies below the DIP of the ion may only decay via the slow (ns) process of photo-emission. Place this ion in the environment of a weakly bound cluster and a much faster decay channel (few fs time scales) may become available. This process is called Interatomic Coulombic Decay (ICD) [3–7], and involves an outer-valence electron on the atom with the initial vacancy recombining into the vacancy, while a valence electron on a neighbouring atom escapes into the continuum as a result of the Coulomb repulsion between the electrons. The primary focus of the present thesis is ICD in weakly bound clusters. More detailed explanation of ICD and resonant ICD will be given in section 1.4. The latter process is concerned with excitation rather than ionisation as a way of creating the inner-valence hole, and the excited electron may also be involved in the resonant ICD processes. A more formal explanation of the theory behind ICD and related phenomena can be found in chapters 2 and 3.

1.2 Auger Decay

Auger decay is an efficient intra-atomic non-radiative decay process that follows sudden ionisation of a core orbital. It involves the recombination of an electron from a higher shell into the core vacancy. The released energy is transferred onto another
outer-shell electron causing it to escape into the continuum. This process leaves behind a doubly ionised species and an electron in the continuum.

Fig. 1.1 is a schematic diagram for one of the channels of the Auger process in 1s-ionised neon. A 2s electron fills the 1s vacancy, while a 2p electron is released into the continuum as a result of electron correlation. The lifetimes of core vacancies that are prone to Auger decay are generally between about 1 to 10 femtoseconds and may also reach sub-femtosecond time scales [2].

\[
\text{Ne}^+ \quad \text{continuum} \quad \text{Ne}^2+ + e^-
\]

Figure 1.1: Auger decay of Ne(1s) vacancy into the $^3P$ final state of Ne$^{2+}$: A 2s electron drops into the vacancy, while a 2p electron escapes into the continuum, leaving behind Ne$^{2+}$.

An interatomic Auger process [8,9] is switched on as a core hole is created within an ionic compound. In this process, valence electrons from a nearest neighbour in the compound take part in the Auger process instead of, or alongside, those in the atom with the initial vacancy. This happens because of the valence electron deficit on the cation of ionic compound that precludes the standard intra-atomic Auger decay. A related process of interatomic Coulombic decay in inner-valence-ionised clusters that happens due to the insufficient energy of the electronic vacancy will be discussed in section 1.4.
1.3 Autoionisation

Autoionisation is the preferred intra-atomic mechanism expected to take place in core or inner-valence-excited atoms. As an example, consider the doubly excited helium, He($2p^2$). This is a highly excited bound state that overlaps with the continuum, and only a small “kick” is required in order for an electron in this state to make the transition from the bound to a continuum state. As one of the excited electrons drops into the 1s orbital, the Coulomb repulsion between the electrons enables the bound-free transition of the excited electron, leaving behind He$^+$. 

Autoionisation is also a possible decay pathway in inner-valence excited clusters that are prone to resonant ICD (see section 1.3). Fig. 1.2 is a schematic diagram of such a process in the excited Ne$^+$Mg cluster: A 2p electron fills in the 2s vacancy, while the energy of this transition enables the excited 3p electron to escape into the continuum.

\[ \text{Ne}^* \rightarrow \text{Ne}^+ + \text{Mg} \]

![Figure 1.2: Schematic representation of autoionisation in NeMg dimer as one of the non-radiative decay pathways following photo-excitation of a Ne-2s electron into Ne-3p orbital. Ne(2p→2s) transition causes the excited 3p electron to escape into the continuum, leaving behind Ne$^+$Mg.](attachment:image.png)
1.4 Interatomic/Intermolecular Coulombic Decay (ICD)

Interatomic Coulombic Decay (ICD) [3–7, 10–13] has an underlying mechanism similar in essence to the interatomic Auger process (section 1.2), except that the initial vacancy is an inner-valence (iv) vacancy instead of a core vacancy. This vacancy is not energetic enough to cause local second-ionisation as in the Auger process. Therefore in an isolated system, this vacancy would decay through the slow (nanosecond) process of photo-emission. But if the iv-vacancy were on an atomic/molecular subunit within a cluster, it could decay by ionising a neighbouring cluster subunit. This is a result of the lower double ionisation potential of the cluster due to the possibility of spatial separation between the final vacancies on different cluster subunits [4].

The mechanism works in the following way: an outer-valence (ov) electron on the cluster subunit that hosts the initial iv-vacancy recombines into the vacancy. The energy released as a result of this recombination is transferred onto a valence electron on a neighbouring cluster subunit, leading to its ionisation (Fig. 1.3). This leaves behind a doubly ionised cluster which can go through disintegration, referred as a Coulomb explosion, if the positive charges are not positioned in a favourable geometry. Thus some of the energy of the initial inner-valence vacancy goes to the kinetic energy of the positively charged fragments that fly off in opposite directions, and the rest to the kinetic energy of the ICD electron in the continuum [14].

ICD can proceed in weakly-bound systems such as hydrogen-bonded and Van der Waals clusters [3]. This is because an essential requirement for ICD is zero overlap between the orbitals that are involved in the process [15]. We will take this requirement into account as we investigate ICD in noble gas endohedral fullerenes [16, 17] in chapter 4. In the following subsection we will look at some aspects of ICD more closely by considering neon dimer.
ICD can proceed because the double ionisation threshold of the cluster is lowered due to a sharing of the positive charge across the nearest neighbours within the cluster [3]. The rate of ICD is on the order of few femtoseconds, and depends on the number of the neighbouring species and therefore the number of available decay channels. The quantity that measures the ICD rate is the decay width, $\Gamma$, the theoretical details of which will be discussed in chapter 3. Once $\Gamma$ is known, the lifetime $\tau$ of the initial inner-valence vacancy may be found using $\tau = \hbar / \Gamma$.

1.4.1 ICD in Neon Dimer

Neon dimer is the most extensively studied system when it comes to ICD [12,18,19]. It consists of two Neon atoms bound by the weak Van der Waals force with a binding energy of 2 meV [20]. Neon has the electronic configuration $1s^22s^22p^6$. For an inner-valence vacancy on an isolated neon, Auger decay is energetically forbidden because the energy of $2s^12p^6$ configuration (48.5 eV) lies below the double ionisation threshold of neon. In other words the energy released as a result of Ne $2p \rightarrow 2s$ transition (26.84 eV [12]) is not enough to enable another $2p$ electron to escape into the continuum. However in the presence of a neighbouring neon there is the possibility of charge separation between the cluster subunits. This significantly lowers the double ionisation threshold of the cluster, thus allowing ICD to proceed. Fig. 1.3 is a schematic representation of ICD in neon dimer.

This process can be summarized in three main steps in the following way [19]:

$$\hbar \omega + Ne_2 \rightarrow Ne_2^+(i.v.) + e^-$$
$$\rightarrow Ne_2^{2+}(o.v.) + e^- + e_{ICD}^-$$
$$\rightarrow Ne^+ + Ne^+ + e^- + e_{ICD}^-$$

which means that the photoionisation of Ne$_2$ produces an iv-vacancy which successively decays to create a doubly ionised cluster with an outer-valence (ov) vacancy on each neon. The repulsion between the two ov-ionised cluster sub-units leads to
Figure 1.3: Schematic representation of the mechanism of Interatomic Coulombic Decay in neon dimer: 

a. A $2p$ electron on a 2s-ionised neon recombines to fill in the vacancy. The Coulomb interaction between this electron and a $2p$ electron on the neighbouring atom causes outer-valence ionisation of that atom. The blue wavy line represents a virtual photon thought to be responsible for the energy transfer between the two atoms in the dimer (see chapter 4). 

b. Two positively charged neon ions that remain behind repel each other leading to disintegration of the cluster in a Coulomb explosion.

The Coulomb explosion of the system into two Ne$^+$ fragments. These fragments are emitted back to back with a total kinetic energy that is referred to as Kinetic Energy Release (KER), and whose value corresponds to their inter-nuclear distance at the instant of ICD. Thus a signature of ICD is the coincidental detection of three particles: two back to back ions and one electron whose kinetic energies add up to 5.37 eV, which is the total energy released as a result of ICD in neon dimer [18].

1.4.2 Resonant Interatomic Coulombic Decay- RICD

Interatomic Coulombic Decay, as explored so far, is initiated by ionisation which creates an inner-valence vacancy. Electronic excitation into an unoccupied orbital can also create a hole in the iv orbital. This gives rise to resonant ICD processes [21–23], first observed by Barth et al. in large neon clusters [21]. Gokhberg et al. [24] have further explored the different types of RICD by looking at Ne($2s \rightarrow 3p$) excitation in MgNe clusters. Magnesium is a particularly suitable neighbour for neon as it has low single and double ionisation thresholds compared to the inner-valence ionisation potential of neon. Two groups of final states result from RICD, namely, singly and doubly ionised final states. Below we will consider the possible decay channels that
lead to singly ionised MgNe clusters only.

**pRICD**

The *participator* Resonant ICD involves relaxation of the 3\(p\) electron into the 2\(s\) vacancy, causing ionisation of the 3\(s\) shell on Mg. The term *participator* points to the active role of the excited electron in the process. The resulting species is NeMg\(^+\). (Fig. 1.4)

![Figure 1.4: Schematic representation of pRICD](image)

**sRICD**

In the *spectator* Resonant ICD process, the excited 3\(p\) electron remains where it is as a spectator, while a 2\(p\) electron on Ne drops into the 2\(s\) vacancy, causing 3\(s\) ionisation on Mg. The resulting species is Ne\(^*\)Mg\(^+\), with Ne(2\(p\)−13\(p\)) as the excited state configuration. (Fig. 1.5)

Among the many possible varieties of RICD channels available for the decay of Ne(2\(s\)\(^−\)1)Mg state (see [24] for other decay channels) there are only a selection of channels that actually make the most substantial contribution to the decay width, \(\Gamma\). Gokhberg *et al.* [24] have approached this problem by calculating partial decay width of several of these channels using the Wigner-Weisskopf approximation (section 3). According to their results, the largest contribution to the decay width comes from autoionisation (section 1.3), followed by sRICD and pRICD. The reason behind this
Figure 1.5: Schematic representation of sRICD: Ne-2s vacancy is filled in by a Ne(2p) electron, while a Mg(3s) electron escapes into the continuum. Ne(3p) excited electron has no active role. The process leaves behind an excited Ne\(^*\)Mg\(^+\) state.

is that the process of autoionisation is based solely on a single centre, in this case neon, where orbital overlap helps speed up the process of decay. However in the case of pRICD and sRICD, recombination into the 2s vacancy occurs on neon while ionisation happens on the neighbouring centre, i.e. magnesium. The much lower decay width of pRICD as compared to the other two decay channels stems from the fact that sRICD involves an intra-shell recombination, Ne(2p → 2s), which is a much faster process than a pRICD with an inter-shell recombination, Ne(3p → 2s).

Similar processes to RICD exist where a metastable excited atom collides with a ground state atom, molecule, or condensed matter leading to the de-excitation of the colliding atom into the ground state and single ionisation of the target species. An example of such processes is the Penning ionisation represented by the following reaction

\[
A^* + B \rightarrow A + B^+ + e^- \tag{1.1}
\]

where \(A^*\) stands for the excited atom, and \(B\) is the target species. Penning ionisation proceeds only if the excitation potential of the excited atom were larger than the ionisation potential of the target species. For such metastable excited atoms, transition to the ground state is optically forbidden and the non-radiative process of Penning ionisation would the fastest de-excitation channel available. An example of Penning
ionisation can be illustrated using the diagram we presented in Fig. 1.4 above for the mechanism of pRICD; an excited Ne atom collides with a ground state magnesium atom. As a result of this collision Ne* gets de-excited and Mg gets singly ionised. The most important difference between the Penning ionisation and pRICD is that the latter is an energy transfer process while in Penning ionisation it is collision of the excited atom with the target atom that that leads to ionisation of the target atom.

1.5 Electron Transfer Mediated Decay, ETMD

In section 1.4 we introduced Interatomic/Intermolecular Coulombic Decay as an efficient non-radiative mechanism for the decay of inner-valence vacancies in clusters of atoms or molecules. We specifically considered the fate of an inner-valence vacancy in the homonuclear neon dimer. In this section we extend our attention onto weakly bound heteronuclear rare gas dimers, where an additional non-radiative interatomic decay channel becomes available as a result of differing energetics of the monomers, as will be explained below. This process is termed Electron Transfer Mediated Decay (ETMD), as it proceeds via electron transfer between the monomers, as opposed to ICD which is based on energy transfer [25].

Fig. 1.6 is a schematic representation of ETMD in Ne+[Ar] with a 2s vacancy on neon. The energy of this vacancy lies above the double ionisation threshold of argon. Therefore an outer-valence electron from argon drops into the neon vacancy, while another one of argon’s outer-valence electrons escapes into the continuum, leaving behind NeAr2+. ETMD is suppressed if there is the possibility of the faster process of ICD (see [26] and references therein). Zobeley et al. [25] have carried out a detailed theoretical investigation into the contributions to decay width, Γ, of ETMD and ICD at different NeAr geometries. The partial contribution of ICD to the decay width is more substantial than that of EMTD at all internuclear distances. Nevertheless the contribution

22
of ETMD towards the total decay width becomes larger faster as the internuclear distance decreases. This is because there must be orbital overlap between the two monomers in order for ETMD to proceed, and a larger overlap between the inner-valence vacancy on Ne and the Ar 3p orbitals is achieved with decreasing internuclear distance. The first unambiguous evidence for ETMD came through the study of triply ionised argon dimer Ar^{3+}-Ar [27].

### 1.5.1 Resonant Electron Transfer Mediated Decay

In section 1.4.2 we briefly touched upon different types of resonant ICD processes that take place in NeMg following a 2p → 3p electronic excitation on neon. Another possible decay channel for such a system is through the process of resonant ETMD [24]. Fig. 1.7 shows the schematics of resonant ETMD process in singly excited Ne^{*}Mg dimer: an Mg 3s electron fills the Ne 2s vacancy, while another Mg 3s electron is ejected into the continuum as a result of electronic correlation. The resulting cluster is the exotic species Ne^{-}Mg^{++}. 

Figure 1.6: Schematic representation of electron transfer mediated decay in Ne^{+}Ar; Ne 2s vacancy has enough energy to doubly ionise the neighbouring argon via the following process: an outer-valence electron from argon drops into the neon vacancy, while another one of argons outer-valence electrons escapes into the continuum. This process leaves behind NeAr^{2+}.
1.6 Fullerenes and Endohedral Fullerenes

Fullerenes were accidentally discovered in 1985, when Robert Curl, Richard Smalley, and their two students from Rice University in Texas set out to study the chemical reactivity of small (2 to 30 atoms) carbon clusters [28]. This study was stimulated by a question put forward by H. W. Kroto from the University of Sussex, which involved understanding the mechanism of formation of long-chain carbon molecules in circumstellar shells. They were initially looking to find out whether some or all of the species of carbon were similar to these long linear carbon chains which were known to be abundant in the interstellar space [29]. They used a combination of laser vaporization technique with pulsed supersonic nozzle technology, a method that involved laser vaporization of carbon species from the surface of a solid graphite disk into a high-density helium flow [28].

The resulting spectra [30] had succeeded in detecting clusters of up to 190 atoms, and for clusters of more than 40 atoms, only even-numbered ones were observed ($C_n$, $n$ even and greater than 40). The prominent, but not completely dominant, peak in these spectra belongs to the $C_{60}$ molecule. Kroto et al. [28] modified the clustering conditions until the $C_{60}$ peak became the dominant one, about 40 times larger than neighbouring clusters.
The even-numbered clusters form closed spheroidal structures which have been called fullerenes. Carbon atoms arranged in hexagons form the flat sheet of graphite. Adding one pentagonal defect [31] to this planar structure results in bending and curling of the structure. Adding exactly 12 pentagons creates enough curvature for the sheet to curl up into closed spheroidal structures, called fullerenes. The C\textsubscript{60} molecule is the prototypical fullerene which has 12 isolated pentagons evenly distributed over its surface, each one surrounded by a ring of hexagons. This highly symmetrical structure is a truncated icosahedron with a 12-fold icosahedral symmetry I\textsubscript{h}. The smallest fullerene, the C\textsubscript{20} molecule, also possesses icosahedral symmetry and consists only of 12 pentagons. But the fact that all these pentagons are direct neighbours of each other causes strain which makes C\textsubscript{20} extremely unstable. In C\textsubscript{60} this strain has been overcome by evenly distributing the pentagons over the surface and is thus a very stable cluster. Both C\textsubscript{60} and its close neighbour C\textsubscript{70} obey the isolated pentagon rule which states that no two pentagons should be next to each other in order for the fullerene structure to be stable [29].

There are two classes of bonds in the C\textsubscript{60} molecule; double bonds that connect the five-membered rings, and single bonds within each of the pentagons. C\textsubscript{60} belongs to the class of the so-called conjugated systems, where carbon compounds have alternating single and double C-C bonds.

Only even-numbered clusters can form fullerenes. This is because odd-numbered clusters will always end up with an extra un-bonded atom which is dangling off the structure. This makes them too reactive to survive in a condensing carbon vapour. In contrast, C\textsubscript{60} and all even-numbered clusters with number of atoms > 40 are virtually inert and therefore very stable, which provides enough evidence as to their closed structure (see ref [29] and references therein).

C\textsubscript{60}’s Highest Occupied Molecular Orbital (HOMO) is five-fold degenerate and
accommodates 10 electrons. There is a 1.9 eV energy gap between HOMO and Lowest Unoccupied Molecular Orbital (LUMO), which is three-fold degenerate, that can be overcome relatively easily by optical excitation [32].

1.6.1 Endohedral Fullerenes

One week after the discovery of the special stability of C\textsubscript{60}, Heath et al. [33] succeeded at placing a single Lanthanum atom inside the cage structure. La@C\textsubscript{60} was found to be as stable as an empty C\textsubscript{60} molecule, although other less stable La@C\textsubscript{n} endohedrals were also observed. The name convention, X@C\textsubscript{n}, was first put forward by reference [34], who were also the first to suggest a method for bulk production of endohedral fullerenes.

Heath et al. used a laser vaporization technique similar to the one used to make C\textsubscript{60} fullerene, but with the graphite disk impregnated with lanthanum. The resulting spectra yielded a prominent peak for La@C\textsubscript{60}. Because of its metallic characteristics, Lanthanum donates three electrons to the C\textsubscript{60} fullerene, i.e. La\textsuperscript{3+}@C\textsubscript{60}\textsuperscript{3−}. Other elements have also been successfully encaged within some fullerene structures, among which are some of the alkali and alkaline earth metals, other rare earth metals, N, O, P and F@C\textsubscript{60}, and rare gas elements. C\textsubscript{28} is the smallest fullerene cage that successfully traps metal atoms inside the cage [32]. He@C\textsubscript{60} and Ne@C\textsubscript{60} were first produced by Saunders et al. [35], followed by entrapment of other rare gas elements down the periodic table [36]. Unlike metallofullerenes which form ionic bonds with the cage structure, rare gas atoms sit mostly near the center of C\textsubscript{60} interacting with the cage only through the weak Van der Waals forces. Molecules such as Sc\textsubscript{3}N and La\textsubscript{2} have also been trapped in the larger clusters [32].

In this chapter we have qualitatively introduced the non-radiative processes of Interatomic Coulombic Decay (ICD) which is the main focus of this thesis. We have also covered some properties of endohedral fullerenes. ICD in endohedral fullerenes will be investigated in chapter 4. Because of their highly symmetric structure endo-
hedral fullerenes such as Ne@C_{60} offer shorter lifetimes for the initial inner-valence vacancy on neon than the Auger process in an isolated Ne^+ (2s^1). That is why we consider such a system for our theoretical investigations.

...LEICD— a novel single photon laser enabled ICD process will be introduced in chapter 5 for the first time and investigated in selected weakly bound systems such as NeAr and protonated ammonia dimer. The next two chapters will cover some mathematical aspects of ICD as well as a selection of computational quantum chemistry approximation methods which will be implemented in chapters 4 and 5.
Chapter 2

Theory I: Approximations for the Many-Electron Schrödinger Equation

2.1 The Time Independent Schrödinger Equation

Determining electronic structures of atoms and molecules is one of the main goals of quantum chemistry. The starting point is the Time Independent Schrödinger Equation (TISE), which is generally written as

\[ \hat{H}\Psi(r, R) = E\Psi(r, R), \] (2.1)

where \( r \) and \( R \) are position vectors of the electrons and the nuclei respectively, \( \Psi(r, R) \) is the wavefunction describing the system, and \( E \) is the total energy of the system. \( \hat{H} \) is the full Hamiltonian of a system of \( N \) electrons and \( M \) nuclei represented, in atomic units, as

\[ \hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}, \] (2.2)
where $Z_A$ and $M_A$ are the atomic number and the ratio of the mass of nucleus $A$ to the mass of an electron respectively. $\nabla^2$ is the Laplacian operator defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

$r_{iA} = |r_{iA}| = |r_i - R_A|$ is the distance between the $i^{th}$ electron and the $A^{th}$ nucleus, $r_{ij} = |r_i - r_j|$ is the distance between the $i^{th}$ and the $j^{th}$ electrons, and $R_{AB} = |R_A - R_B|$ is the distance between the $A^{th}$ and the $B^{th}$ nuclei.

The first term in the above representation describes the total kinetic energy of the electrons, the second term the total kinetic energy of the nuclei, the third term is the Coulomb attraction between the electrons and the nuclei, while the fourth and the fifth terms correspond to the Coulomb repulsion between the electrons and the nuclei respectively.

Eq. 2.1 is an eigenvalue equation that can only be solved exactly for the case of the hydrogen atom. However for many-electron systems electronic correlation introduces complications and the only way to solve the TISE would be to resort to methods of approximation. The Hartree-Fock approximation is one of these methods, as well as being a stepping stone towards more accurate methods of approximation such as the Møller-Plesset Many Body Perturbation Theory. We will discuss these approximation methods in this chapter, after setting the scene below by introducing the notation and some underlying theories.

### 2.1.1 The Born-Oppenheimer Approximation

The electrons are much lighter than the nuclei, and therefore their response to the displacement of nuclei is almost instantaneous. The electrons could therefore, to a good approximation, be considered to be moving in the electric field due to a fixed spatial arrangement of the much heavier nuclei. This is the Born-Oppenheimer approximation. It allows us to neglect the kinetic energies of the nuclei, and to consider the repulsion between the nuclei as a constant. Eq. 2.2 describing the full
Hamiltonian is therefore reduced to the electronic Hamiltonian

\[ \hat{H} = - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}. \]  

(2.3)

We can also write the electronic Schrödinger equation

\[ \hat{H} \Psi(r; R) = E \Psi(r; R), \]  

(2.4)

where \( \Psi \) is the electronic wavefunction that depends parametrically on the positions \( R \) of the nuclei. The energies can be calculated for a range of nuclear coordinates and hence potential energy plots for the nuclei could be obtained. These plots are referred to as potential energy surfaces which can predict the nuclear motion.

From this point forward we will simply refer to \( \Psi(r; R) \) as \( \Psi \).

### 2.2 The Variational Theory

The variational theory allows us to calculate an upper bound to the true energy of the system described by the Hamiltonian

\[ \hat{H} \Psi_\alpha = E_\alpha \Psi_\alpha \quad \alpha = 0, 1, \ldots, \]  

(2.5)

where \( \Psi_\alpha \) are a set of exact solutions to the Schrödinger equation, labelled by the index \( \alpha \), and

\[ E_0 \leq E_1 \leq E_2 \leq \ldots \leq E_\alpha \leq \ldots. \]  

(2.6)

\( E_0 \) is the lowest eigenvalue.

For this system, the Rayleigh ratio, \( \mathcal{E} \), is defined as

\[ \mathcal{E} = \frac{\int \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} d\tau}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} d\tau} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle}, \]  

(2.7)

30
where the trial function $\psi_{\text{trial}}$ is of the form
\[ \psi_{\text{trial}} = \sum_i c_i \psi_i. \]  
(2.8)

The variation theorem states that, for any trial function $\psi_{\text{trial}}$ that satisfies the correct boundary conditions of the problem, $E \geq E_0$.

The proof goes as follows: given the eigenvalue equation Eq. 2.5 for $n = 0$, and the definition for the trial wavefunction Eq. 2.8, consider the integral
\[ I = \int \psi_{\text{trial}}^* (\hat{H} - E_0) \psi_{\text{trial}} d\tau. \]  
(2.9)

Substitution for the trial wavefunction and using $\hat{H} \psi_j = E_j \psi_j$ leads to
\[ I = \sum_{i,j} c_i^* c_j (E_j - E_0) \int \psi_i^* \psi_j d\tau. \]  
(2.10)

We now apply the orthonormality condition which states that $\int_{-\infty}^{\infty} \psi_i^* \psi_j d\tau = \delta_{ij}$ where $\delta_{ij}$ is the kronecker delta. This reduces the sum to
\[ I = \sum_i |c_i|^2 (E_i - E_0) \geq 0, \]  
(2.11)

which is always positive or zero because $E_i \geq E_0$ and $|c_i|^2 \geq 0$. This means that
\[ \int \psi_{\text{trial}}^* (\hat{H} - E_0) \psi_{\text{trial}} d\tau \geq 0. \]  
(2.12)

Multiplying out the bracket and rearranging gives
\[ \frac{\int \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} d\tau}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} d\tau} \geq E_0. \]  
(2.13)
The left hand side of the above relation is just $\mathcal{E}$ as given by Eq. 2.7, therefore

$$\mathcal{E} \geq E_0,$$

which is the statement of the variational principle.

### 2.3 Many Electron Wavefunctions

#### 2.3.1 Orbitals

As a first approximation, we can neglect the contribution to the electronic Hamiltonian of electron-electron repulsion and write $\hat{H}$ as a sum of one-electron Hamiltonians $h_i$

$$\hat{H}^0 = \sum_{i=1}^{N_e} h_i, \quad (2.14)$$

where $h_i$ is the hydrogenic Hamiltonian for the $i^{th}$ electron in the presence of a nucleus of charge $Z_e$ and absence of all other electrons, and $N_e$ is the total number of electrons in the system under consideration. Since the Hamiltonian is expressed as a sum of $N_e$ independent one-electron terms, $\Psi^0$ can be written as a product of one-electron wavefunctions (orbitals):

$$\Psi^0 = \psi^0_1(1)\psi^0_2(2)\ldots \psi^0_{N_e}(N_e), \quad (2.15)$$

where $\psi^0_m(i)$ are the solutions of the one-electron equation

$$h_i \psi^0_m(i) = E^0_m \psi^0_m(i), \quad (2.16)$$

and $E^0_m$ is the energy of an electron in orbital $m$. The act of writing the total wavefunction as a product of one-electron wavefunctions is called the orbital approximation.
2.3.2 Spinorbitals

The many electron Hamiltonian only depends on the electrons’ spatial coordinates and takes no consideration of the electronic spin. But the inclusion of spin is essential to a full description of an electron. We do this by introducing spin functions $\alpha(\omega)$ and $\beta(\omega)$, corresponding to spin up and spin down respectively ($\omega$ is an unspecified spin variable). The two spin functions are orthonormal.

\[ \int d\omega \alpha^*(\omega)\alpha(\omega) = \int d\omega \beta^*(\omega)\beta(\omega) = 1, \quad (2.17) \]

\[ \int d\omega \alpha^*(\omega)\beta(\omega) = \int d\omega \beta^*(\omega)\alpha(\omega) = 0. \quad (2.18) \]

Using these spin functions we can therefore define \textit{spinorbitals} to be the product of a spatial orbital, $\psi(r)$, and either of the spin functions $\alpha(\omega)$ and $\beta(\omega)$

\[ \chi(x) = \begin{cases} 
\psi(r)\alpha(\omega) \\
\psi(r)\beta(\omega) 
\end{cases} \quad (2.19) \]

The electronic wavefunction $\Psi$ would thus be a function of the spatial coordinates $r_i$ as well as the spin variable $\omega$ which together define the coordinates $x_i$ of a spinorbital.

Because electrons are indistinguishable particles the many electron wavefunction must be antisymmetric with respect to interchange of any two electrons. This is the antisymmetry principle and requires that for any pair of indices, for example 1 and 2

\[ \Psi(x_1, x_2, ..., x_N) = -\Psi(x_2, x_1, ..., x_N). \quad (2.20) \]
A Slater determinant can be used as a tool to enforce the antisymmetry requirement

\[ \Psi(x_1, x_2, ..., x_N) = (N!)^{\frac{1}{2}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \ldots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \ldots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \ldots & \chi_k(x_N) \end{vmatrix}, \quad (2.21) \]

where the rows are labelled by electrons, and the columns by spinorbitals. If two electrons were to occupy the same spinorbital, two columns of the determinant would be equal, and the determinant zero. Thus the requirement of antisymmetry principle (or Pauli principle) is enforced. This can also be worded in terms of the Pauli exclusion principle, which states that no two electrons can occupy the same spinorbital. As a shorthand notation, we can only write the diagonal elements of the Slater determinant, i.e.

\[ \Psi(x_1, x_2, ..., x_N) = |\chi_i\chi_j...\chi_k\rangle, \quad (2.22) \]

where the electron labels are always chosen to be in the order \( x_1, x_2, ..., x_N \), and the normalisation constant is included. The N-electron Slater determinants obey the following orthonormality relation:

\[ \langle ...\chi_m...\chi_n|...\chi_p...\chi_s\rangle = \delta_{mp}\delta_{ns} - \delta_{ms}\delta_{np}. \quad (2.23) \]

### 2.4 Hartree-Fock Approximation

The purpose of the Hartree-Fock approximation [37, 38] is to find the best possible single Slater determinant approximation for the total electronic wavefunction. It does this by minimising the energy of the single Slater determinant using the variational principle. In order to find the best spinorbitals that help minimize the said energy we use an eigenvalue equation called the Hartree–Fock equation, which is defined for
electron $i$ in the following form

\[
\left[ h(i) + \sum_{j \neq i} J_j(i) - \sum_{j \neq i} K_j(i) \right] \chi_i(i) = \epsilon_i \chi_i(i) \tag{2.24}
\]

where $j$ indicates the electronic tag of all other electrons in the many-electron system that are not the $i^{th}$ electron. $h(i)$ is defined as the sum over the kinetic energy of electron $i$ and the nuclear potential energy

\[
h(i) = -\frac{1}{2} \nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}}. \tag{2.25}
\]

$J_j(i)$ is the Coulomb operator that takes account of the local potential experienced by electron 1 at position $x_1$ due to electron 2 at $x_2$. It is defined as:

\[
J_j(x_1) = \int \chi_{j}^*(x_2) \frac{1}{r_{12}} \chi_j(x_2) dx_2, \tag{2.26}
\]

where $1/r_{12}$ is the two-electron potential. $K_j(i)$ is the exchange operator which takes into account the effect of spin correlation, and arises due to the antisymmetric nature of the single determinant. It is defined by its effect when operating on a spinorbital $\chi_i$ corresponding to electron 1 at $x_1$:

\[
K_j(x_1) \chi_i(x_1) = \int \chi_{j}^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) dx_2 \chi_j(x_1). \tag{2.27}
\]

We can write an equation similar to Eq. 2.27 for the Coulomb operator:

\[
J_j(x_1) \chi_i(x_1) = \int \chi_{j}^*(x_2) \frac{1}{r_{12}} \chi_j(x_2) dx_2 \chi_i(x_1) \tag{2.28}
\]

The two-electron potential $1/r_{12}$ gives the interaction between electrons 1 and 2 due to the *instantaneous* position $x_2$ of electron 2. In Eq. 2.26 by integrating over $x_2$, we obtain the total potential felt by electron 1 at $x_1$ due to electron 2. In order to obtain the total averaged potential acting on electron 1 in $\chi_i$ due to the $N-1$ electrons in all the other spinorbitals, we sum over all $j \neq i$. This gives us the one-electron Coulomb
potential \[37\]

\[
\sum_{j \neq i} \int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_j(x_2) dx_2.
\]  \tag{2.29}

The summation in Eq. 2.24 is over \(j\) electrons where \(j \neq i\), and therefore varies for every choice of \(i\) where \(i\) denotes the electron whose corresponding optimal spinorbital \(\chi_i\) is to be found. This means that the operator in square brackets in Eq. 2.24 is different for every \(\chi_i\). In order to remove this dependence on the index \(i\) we can make use of the following property that results from Eq. 2.28 and Eq. 2.27:

\[
[J_i(i) - K_i(i)] \chi_i(i) = 0 \tag{2.30}
\]

This allows us to define a one-electron Hamiltonian known as the Fock operator, \(f\), where

\[
f(i) = h(i) + \sum_j [J_j(i) - K_j(i)], \tag{2.31}
\]

which is expressed in terms of the one-electron operator \(h(i)\), the Coulomb operator \(J_j(i)\), and the exchange operator \(K_j(i)\). Eq. 2.31 is a general definition of the Fock operator which is based on a spinorbital form of the Hartree–Fock equation. In subsection 2.4.1 we shall define a slightly different form of the Fock operator which is valid for closed-shell systems (where there are an even number of electrons in the system, all electrons are paired up and occupy orbitals of lowest energies). Using Eq. 2.31 the Hartree–Fock equation (Eq. 2.24) thus reduces to

\[
f(i) \chi_i = \epsilon \chi_i, \tag{2.32}
\]

\subsection*{2.4.1 Roothaan-Hall Equations}

Above we presented the Fock operator (Eq. 2.31) in its general spinorbital form. Here we will define the Fock operator for the case of a closed-shell N-electron molecule. Such a system has \(N/2\) occupied spatial orbitals each of which accommodates two electrons of opposite spins. In other words we will integrate out the spin functions in the Fock operator. This allows the development of an analytical technique, developed
by Roothaan [39], for solving the Hartree-Fock equations. The closed-shell form of the Hartree–Fock equation (Eq. 2.24) can be obtained by integrating over the spin functions. This results

\[ f(i)\psi_i(r_1) = \epsilon_i\psi_i(r_1), \tag{2.33} \]

where \( \psi_i(r_1) \) is the spatial part of the molecular orbital for electron at the spatial coordinate \( r_1 \), \( \epsilon_i \) is the electronic energy, and \( f(i) \) is the Fock operator for a closed shell system defined as

\[ f(i) = h(i) + \frac{N}{2} \sum_j [2J_j(i) - K_j(i)], \tag{2.34} \]

This definition of the Fock operator is very similar to that in Eq. 2.31 except that the sum is now over \( N/2 \) electrons and there is a factor of 2 in front of the Coulomb operator \( J \). We now expand the spatial part of the molecular orbitals, \( \psi_i(r) \), in a basis of atomic orbitals (AOs) \( \phi(r) \)

\[ \psi_i(r) = \sum_{\nu=1}^{L} C_{\nu i} \phi_\nu(r) \quad i = 1, 2, ..., L. \tag{2.35} \]

The one-electron atomic orbitals \( \phi_\nu(r) \) are known as basis functions. Therefore in the above case we are expanding a spatial molecular orbital in terms of \( L \) basis functions. We will use the Greek letters \( \nu \) and \( \mu \) to label these basis functions. \( C_{\nu i} \) are expansion coefficients. We now substitute Eq. 2.35 into the Hartree–Fock equation (Eq. 2.33),

\[ f \sum_\nu C_{\nu i} \phi_\nu(r) = \epsilon_i \sum_\nu C_{\nu i} \phi_\nu(r). \tag{2.36} \]

We can obtain a matrix equation by multiplying the above equation on the left by \( \phi_\mu^*(r) \) and integrating. This yields

\[ \sum_\nu C_{\nu i} \int \phi_\mu^*(r)f\phi_\nu(r)dr = \epsilon_i \sum_\nu C_{\nu i} \int \phi_\mu^*(r)\phi_\nu(r)dr. \tag{2.37} \]
This allows us to define the overlap matrix $S$ whose elements are

$$S_{\mu\nu} = \int \phi_\mu^*(r)\phi_\nu(r)dr,$$  \hspace{1cm} (2.38)

and the Fock matrix $F$ whose elements are

$$F_{\mu\nu} = \int \phi_\mu^*(r)f\phi_\nu(r)dr.$$  \hspace{1cm} (2.39)

The dimensions of both the overlap and the Fock matrices are $L \times L$ and both matrices are Hermitian. Using $S$ and $F$ we can now rewrite the integrated Hartree–Fock equation (Eq. 2.37) as

$$\sum_\nu F_{\mu\nu}C_\nu = \epsilon_i \sum_\nu S_{\mu\nu}C_\nu \hspace{1cm} i = 1, 2, ..., L.$$  \hspace{1cm} (2.40)

These are the Roothaan equations. By defining an $L \times L$ square matrix of expansion coefficients $C$, and a diagonal matrix $E$ whose elements are orbital energies $\epsilon$, we can write Eq. 2.40 in matrix form as

$$FC = SCE.$$  \hspace{1cm} (2.41)

This matrix equation is the starting point for determining the Hartree–Fock molecular orbitals $\{\psi_i\}$ and orbital energies $\epsilon_i$, and can be solved, among other methods, by using a computational technique known as the Self-Consistent Field (SCF) procedure. The SCF procedure is carried out by making a first guess at orbitals that go into Eq. 2.41, and subsequently solving the said equation iteratively. In chapters 4 and 5 of this thesis we will use the quantum chemistry software MOLCAS [40] which makes use of the SCF procedure in order to calculate Hartree-Fock molecular orbitals and energies for weakly bound systems. The names SCF procedure and Hartree–Fock approximation/method will be used interchangeably.

The Hartree-Fock approximation does not take into account the correlation between
electrons except through the Pauli Exclusion Principle for electrons with the same spin. It completely ignores the Coulomb repulsion between electrons, i.e. electronic correlation, by placing each electron in the average field of all other electrons and the nuclei in a given system. Other approximation methods such as the Møller-Plesset perturbation theoretical approximation (MP2) discussed in section 2.6 take correlation energy into account and thus provide more accurate solutions to the TISE than the Hartree–Fock (HF) method.

In chapter 4, ground state energies of the endohedral fullerene Ne@C_{60} are computed using the HF approximation as implemented in MOLCAS software. Corrections to the HF ground state energy are made by using the MP2 theory within MOLCAS. Similar calculations using the HF and MP2 theories are carried out for selected weakly bound clusters in chapter 5. The resulting energetic information help further computations of the rate of Interatomic Coulombic Decay (ICD) process in an endohedral fullerene in chapter 4 or photoionisation cross sections for laser enabled ICD in weakly bound clusters in chapter 5.

2.4.2 Basis Sets

Ab initio (from first principles) calculations of molecular systems require a suitable set of basis functions that are both easy to integrate and describe the physics of the problem accurately (i.e., cusp at the nucleus and exponential decay at large distances away from the nucleus). Here we will only consider Slater-type and Gaussian-types functions as candidates for use in basis sets.

Slater Type Orbitals (STOs) can be used as an approximation for atomic orbitals. For an orbital with quantum numbers $n, l, m$ belonging to a nucleus of atomic number $Z$, STOs have the analytical form

$$\psi_{nlm}(r, \theta, \phi) = Nr^l e^{-\frac{z_{\text{eff}}}{2r}} Y^m_l(\theta, \phi),$$

(2.42)
where \((r, \theta, \phi)\) defines spherical polar coordinates of a point in space, \(N\) is the normalisation constant, \(Y^m_l(\theta, \phi)\) the spherical harmonics functions characterising the angular dependence of the orbital. Since we are dealing with many-electron systems we use \(Z_{\text{eff}}\) \[41\] to denote the effective nuclear charge “felt” by an electron that is shielded from the full effect of the nuclear charge by the other electrons in the atom. We can also define the effective principal quantum number \(n_{\text{eff}}\) which is related to the true principal quantum number \(n\) \[41\] by

\[
n \rightarrow n_{\text{eff}}: \quad 1 \rightarrow 1 \quad 2 \rightarrow 2 \quad 3 \rightarrow 3 \quad 4 \rightarrow 3.7 \quad 5 \rightarrow 4
\]

The orbital exponent \(\zeta\) is therefore defined as

\[
\zeta = \frac{Z_{\text{eff}}}{n_{\text{eff}}}. \quad (2.43)
\]

We will make use of STOs as basis functions in chapter 4.

Despite the ability of STOs at accurately describing the cusp at the nucleus and the exponential tail of the true electronic wavefunction, the integrals involving STOs are difficult to evaluate when it comes to molecular orbital calculations. Therefore in \textit{ab initio} calculations Gaussian Type orbitals (GTOs) are commonly used. These have the form

\[
x^a y^b z^c \exp(-\alpha r^2), \quad (2.44)
\]

where the exponential is the Gaussian function, with \(\alpha\) characterising the extent of the function. The powers \(a, b,\) and \(c\) are integers whose sum determines the order of the Gaussian-type functions - So \(a + b + c = 0\) and \(a + b + c = 1\) give a zeroth- and first-order function respectively.

The Gaussian functions do not have a cusp at the origin and quickly die off with distance, which is a disadvantage when compared to STOs. However, by representing each atomic orbital as a linear combination of Gaussian functions one can approximately emulate a STO. Two parameters characterise this linear expansion:
a coefficient and an exponent. If a calculation allows the variation of both these parameters then it is said to use primitive Gaussian functions. If however the said parameters are pre-defined and remain constant throughout the calculation, then the Gaussian functions are referred to as being contracted. In this thesis we make use of two different types of basis sets - split valence basis sets [42] specifically 6-31G, and Dunning’s correlation-consistent basis sets [43] cc-pVQZ and cc-pV5Z.

In the split-valence 6-31G basis set six primitive Gaussian functions are used to describe the core orbitals, three contracted GTOs describe the inner part of the valence orbitals, and one primitive GTO represents the outer orbitals.

The cc-pVXZ (X=D, T, Q, 5 etc for double, triple, quadruple, 5 etc) stands for correlation-consistent polarised valence only X-zeta, and takes into account the correlation between valence electrons by adding polarisation functions.

2.4.3 The Slater-Condon Rules for Matrix Elements
There are certain rules that apply when evaluating matrix elements $\langle K | O | L \rangle$ between two single Slater determinants $| K \rangle$ and $| L \rangle$ depending on whether $O$ is a sum of one-electron operators $O_1$, or two-electron operators $O_2$. For a one-electron operator such as $h$

$$\langle i | h | j \rangle = \int \chi_i^*(x_1) h(r_1) \chi_j(x_1) dx_1 \quad (2.45)$$

And for a two-electron operator $1/r_{12}$

$$\langle ij | 1/r_{12} | kl \rangle = \int \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_k(x_1) \chi_l(x_2) dx_1 dx_2 \quad (2.46)$$
For two identical single Slater determinants \( |K\rangle = |L\rangle = |...mn...\rangle \):

\[
\langle K|O_1|L\rangle = \sum_{m}^{N} \langle m|h|m\rangle \\
\langle K|O_2|L\rangle = \frac{1}{2} \sum_{m}^{N} \sum_{n}^{N} \langle mn|\frac{1}{r_{12}}|mn\rangle
\]

(2.47)  

(2.48)

For two single Slater determinants that vary by one spinorbital, i.e. for

\[
|K\rangle = |...mn...\rangle \\
|L\rangle = |...pn...\rangle
\]

(2.49)

we have

\[
\langle K|O_1|L\rangle = \langle m|h|p\rangle \\
\langle K|O_2|L\rangle = \sum_{n}^{N} \langle mn|\frac{1}{r_{12}}|pn\rangle
\]

(2.50)

For two single Slater determinants varying by two spinorbitals, i.e. for

\[
|K\rangle = |...mn...\rangle \\
|L\rangle = |...pq...\rangle
\]

(2.51)

we have

\[
\langle K|O_1|L\rangle = 0 \\
\langle K|O_2|L\rangle = \langle mn|\frac{1}{r_{12}}|pq\rangle
\]

(2.52)  

(2.53)

For determinants varying by three or more spinorbitals both matrix elements are
zero. These are the Slater-Condon rules for matrix elements.

2.5 Excited Determinants and Configuration Interaction

The Hartree-Fock ground state is in a single-determinant form

$$|\Psi_0\rangle = |\chi_1\chi_2\ldots\chi_i\ldots\chi_j\ldots\chi_N\rangle$$ (2.54)

where $N$ is the total number of electrons in the system. The above wavefunction is the best variational approximation to the ground state. But there are $\binom{2L}{N}$ more possibilities for single determinants that could be formed from $2L$ spinorbitals, where

$$\binom{2L}{N} = \frac{(2L)!}{N!(2L-N)!}$$ (2.55)

is the binomial coefficient. The Hartree-Fock ground state is just one of those determinants. We can use the HF ground state as a reference state and classify other possible determinants by comparing them to this reference state. This means that we state which occupied orbitals will get replaced by which virtual orbitals. We will label occupied orbitals by the indices i, j, k, ... and refer to them by the set $\{\chi_i\}$. Virtual orbitals will be labelled by the indices r,s,t, ... and the set $\{\chi_r\}$. Determinants formed in this way form approximate single, doubly, triply, or higher excited states of the system, formed by exchanging corresponding numbers of occupied with virtual spinorbitals. For example, if the HF ground state were represented by the single Slater determinant

$$|\Psi_0\rangle = |\chi_1\chi_2\ldots\chi_i\chi_j\ldots\chi_N\rangle.$$ (2.56)
then we can write a singly excited state as

$$|\Psi_r^i\rangle = |\chi_1\chi_2...\chi_r\chi_j...\chi_N\rangle,$$ \hspace{1cm} (2.57)

where an electron from the occupied spinorbital $\chi_i$ has been promoted to the virtual spinorbital $\chi_r$. The doubly excited state would be

$$|\Psi_{ij}^{rs}\rangle = |\chi_1\chi_2...\chi_r\chi_s...\chi_N\rangle.$$ \hspace{1cm} (2.58)

An exact wavefunction for an $N$-electron system may thus be written as a linear combination of all $\binom{2L}{N}$ possible Slater determinants representing ground and excited states. The form of the exact wavefunction is

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ri} c_i^r |\Psi_r^i\rangle + \sum_{i<j,r<s} c_{rs}^{ij} |\Psi_{ij}^{rs}\rangle + ...$$ \hspace{1cm} (2.59)

where for doubly excited states, $i < j$ means we sum over all unique pairs of occupied spinorbitals, and $r < s$ means the same for virtual orbitals. In this way, the infinite set of $N$-electron determinants $\{|\Psi_i\rangle\} = \{|\Psi_0\rangle, |\Psi_r^i\rangle, |\Psi_{ij}^{rs}\rangle, ...\}$ forms a complete set which could be used for the expansion of any $N$-electron wavefunction.

The above procedure for finding the exact wavefunction is called configuration interaction (CI). In practice a CI expansion of the wavefunction is truncated to only include a finite number of excitation classes, for example only singly and doubly excited states. Truncation has to be done because of the factorial scaling of the full CI expansion.
2.6 Time Independent Perturbation Theory

In this section we discuss perturbation theory in order to set the scene for a more accurate approximation technique than the HF, referred to as the Møller-Plesset perturbation theory, which takes electronic correlation into account when solving the TISE. When the system experiences an external time independent perturbation, one can partition the Hamiltonian of the system into the unperturbed Hamiltonian $\hat{H}_0$ whose eigenvalues and eigenfunctions are known and the perturbation $\hat{V}$.

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$ (2.60)

where $\lambda$ is the perturbation parameter.

We want to find the solutions for

$$(\hat{H}_0 + \lambda \hat{V}) \Phi_n = E_n \Phi_n$$ (2.61)

where $\Phi_n$ and $E_n$ are the eigenfunctions (in this case molecular orbitals) and eigenvalues of the perturbed system respectively. Through a Taylor series expansion in $\lambda$ we can express these as

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$|\Phi_n\rangle = |\Psi_n^0\rangle + \lambda |\Psi_n^{(1)}\rangle + \lambda^2 |\Psi_n^{(2)}\rangle + \cdots$$ (2.62)

where $E^{(m)}$ and $\Psi^{(m)}$ for $m > 0$ are $m^{th}$ order energy and wavefunction corrections to their corresponding unperturbed values $E^0$ and $\Psi^0$ respectively. $E_n^0$ and $\Psi_n^0$ are the eigenvalues and eigenfunctions of the unperturbed Hamiltonian $\hat{H}_0$ respectively.

We can find expressions for the above $m^{th}$ order corrections by substituting Eq. 2.62 into Eq. 2.61 and identifying powers of $\lambda$. Therefore the first order corrections
to energy and wavefunction read as

\[ E^{(1)}_n = \langle \Psi_0^n | \hat{V} | \Psi_0^n \rangle \]

(2.63)

The higher order energy corrections are

\[ E^{(2)}_n = \langle \Psi_0^n | \hat{V} | \Psi^{(1)}_n \rangle \]

\[ E^{(3)}_n = \langle \Psi_0^n | \hat{V} | \Psi^{(2)}_n \rangle \]

(2.64)

The evaluation of these higher order energy corrections requires a knowledge of the wavefunction corrections, for which we resort to the Møller Plesset (MP) perturbation theory.

### 2.6.1 Møller-Plesset Perturbation Theory

In Møller Plesset Perturbation Theory the unperturbed Hamiltonian is expressed as a sum over \(N\) electrons of the one-electron Fock operators

\[
\hat{H}_0 = \sum_{i=1}^{N} f(i) = \sum_{i=1}^{N} \left( h(i) + \sum_{j=1}^{N} (J_j(i) - K_j(i)) \right),
\]

(2.65)

where \(J_j(i)\) and \(K_j(i)\) are the Coulomb and the exchange operators respectively, and \(h(i)\) is defined as the sum over the kinetic energy of electron \(i\) and nuclear potential energy experienced by that electron. The perturbation \(\hat{V}\) is expressed as the difference between the “full” Hamiltonian \(\hat{H}\) and the unperturbed Hamiltonian \(\hat{H}_0\). It is given by

\[
\hat{V} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \sum_{j=1}^{N} (J_j(i) + K_j(i))
\]

(2.66)

where the first term with the double sum represents the exact electronic correlation.
The Hartree-Fock wavefunction, $\Psi_0^0$, is the eigenfunction of the unperturbed Hamiltonian $\hat{H}_0$ operator. The zeroth-order energy $E_0^0$ is the sum over the occupied molecular orbital energies

$$E_0^0 = \sum_{i=1}^{\text{occupied}} \epsilon_i$$  \hspace{1cm} (2.67)$$

The Hartree-Fock energy is equal to the sum over the zeroth- and the first-order energies, $E_0^0 + E_1^0$. Therefore in order to obtain a more accurate estimation of the true energy of the system we require access to at least second-order corrections to the energy which in turn requires access to the first-order corrections to the wavefunction. This level of accuracy is referred to as MP2, and requires evaluation of $\langle \Psi_i^0 | \hat{V} | \Psi_i^{(1)} \rangle$ for the second-order energy correction. The first-order correction to the ground state wavefunction obeys

$$\langle \Psi_i^0 - \hat{H}_0 | \Psi_i^{(1)} \rangle = (\hat{V} - E_i^{(1)}) | \Psi_i^0 \rangle = (\hat{V} - E_i^{(1)}) | \Psi_i^0 \rangle.$$  \hspace{1cm} (2.68)$$

$|\Psi_i^{(1)}\rangle$ can be expanded in terms of the eigenfunctions of $\hat{H}_0$, $|\Psi_n^0\rangle$, which form a complete orthonormal set

$$|\Psi_i^{(1)}\rangle = \sum_n c_n^{(1)} |\Psi_n^0\rangle.$$  \hspace{1cm} (2.69)$$

Multiplying both sides of Eq. 2.68 by $\langle \Psi_n^0 |$ and using the orthogonality of zeroth-order wavefunctions we get

$$\langle \Psi_n^0 | (\hat{V} - E_i^{(1)}) | \Psi_i^{(1)} \rangle = \langle \Psi_n^0 | \hat{V} | \Psi_i^0 \rangle$$  \hspace{1cm} (2.70)$$

Finally, the second-order energy correction is expressed as

$$E_i^{(2)} = \langle \Psi_i^0 | \hat{V} | \Psi_i^{(1)} \rangle = \sum_n \frac{\langle \Psi_i^0 | \hat{V} | \Psi_n^0 \rangle^2}{E_i^0 - E_n^0}$$  \hspace{1cm} (2.71)$$

where the sum excludes the term with $n = i$.

Higher order MP calculations such as MP3 and MP4 are also possible, but get
far more complicated as well as computationally costly. Within the MP2 level of theory the computational cost scales as $K^4$ for $K$ basis functions, so a balance between the computational cost and the size of the basis function must be found. Another downside is that MP2 is a perturbation theory method and does not make use of the variational principle. Therefore the resulting energies could be lower than the “true” energies.

In chapters 4 and 5 the MP2 theory is implemented in the quantum chemistry software MOLCAS [40] which, alongside the first order Hartree–Fock (HF) theory (section 2.4) computes ground state energies. The resulting energetic information are required for further computations of ICD rates in a noble gas endohedral fullerene (chapter 4) or photoionisation cross sections for a laser enabled ICD process in selected weakly bound clusters (chapter 5). The next chapter is mainly concerned with the theoretical approximation methods that allow computation of decay width for the process of ICD as well as photoionisation cross sections for the process of $sp$LEICD.
Chapter 3

Theory II: Theoretical and Computational Techniques for Decay Widths and Photoionisation Cross Sections

In chapter 2 we presented methods for approximately solving the time independent Schrödinger equation for many-electron systems. In this chapter we will focus on the application of the tools of many-electron theory for the prediction of ICD decay widths and photoionisation cross sections relevant to the process of ICD. Examples will include atomic/molecular systems that weakly interact with an external electromagnetic field and whose interaction will lead either to transitions characterised through the Wigner-Weisskopf expression for the decay width (section 3.1) or the photoionisation cross section (section 3.2). In sections 3.4 and 3.5 we introduce methods of approximately describing the initial bound and final continuum states of the transitions caused by weak interaction of an atomic/molecular system with an electromagnetic field.
3.1 The Wigner-Weisskopf Approximation

The time-dependent Schrödinger equation is given as

\[ i\hbar \frac{d|\Psi(t)\rangle}{dt} = \hat{H}|\Psi(t)\rangle, \]  

(3.1)

where \( \hat{H} \) is the Hamiltonian operator. The wavefunction \( |\Psi(t)\rangle \) carries all the time-dependence of the system under consideration. This approach of taking account of the time development of the system is referred to as the Schrödinger picture of quantum dynamics [44]. An equivalent way of taking account of the time development of a system is to partition the time-dependence into both the wavefunction and the operator, as is done within the interaction picture of quantum dynamics. We will be using the interaction picture in this chapter as it is most well-suited to the problem of time dependent perturbation theory. The following transformation from the Schrödinger picture apply when developing the interaction picture

\[ |\tilde{\Psi}(t)\rangle = \exp \left( i\hbar \hat{H}_0 t \right) |\Psi(t)\rangle, \]  

(3.2)

where \( \hat{H}_0 = \hat{H} - \hat{V} \) with \( \hat{V} \) denoting the perturbation and \( \hat{H}_0 \) the unperturbed Hamiltonian, and the use of tilde points to the fact that we are in the interaction picture. Therefore the time-dependent Schrödinger equation in the interaction picture is

\[ i\hbar \frac{d|\tilde{\Psi}(t)\rangle}{dt} = \tilde{V}(t)|\tilde{\Psi}(t)\rangle, \]  

(3.3)

where \( \tilde{V}(t) \) is the time-dependent interaction operator defined as

\[ \tilde{V}(t) = \exp \left( \frac{i}{\hbar} \hat{H}_0 t \right) \hat{V} \exp \left( -\frac{i}{\hbar} \hat{H}_0 t \right). \]  

(3.4)
Introducing the time development operator in the interaction picture allows the time evolution of a state vector $|\tilde{\Psi}(t_0)\rangle$ at time $t_0$ to a later time $t$

$$|\tilde{\Psi}(t)\rangle = \tilde{T}(t, t_0)|\tilde{\Psi}(t_0)\rangle. \quad (3.5)$$

The time development operator satisfies the following integral equation

$$\tilde{T}(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} \tilde{V}(t') \tilde{T}(t', t_0)dt' \quad (3.6)$$

and allows us to write the transition matrix elements between eigenstates $(f, s)$ of the unperturbed Hamiltonian as

$$\langle f | \tilde{T}(t, t_0) | s \rangle = \delta_{fs} - \frac{i}{\hbar} \sum_n \int_{t_0}^{t} \exp(i\omega_{fn}t') \langle f | V(t') | n \rangle \langle n | \tilde{T}(t', t_0) | s \rangle dt', \quad (3.7)$$

where we have used the resolution of identity $\sum_n |n\rangle \langle n|$, and $\omega_{fn} = \frac{E_f - E_n}{\hbar}$. This equation is solved by iteration [44] to give the transition amplitude approximated to the first-order in perturbation theory

$$\langle f | \tilde{T}(t, t_0) | s \rangle = -\frac{i}{\hbar} \int_{t_0}^{t} \langle f | V(t') | s \rangle \exp(i\omega_{fs}t') dt', \quad (3.8)$$

where $s \neq f$ and $E_s < E_f$. $\langle f | V(t') | s \rangle$ is the perturbation matrix element. Eq. 3.8 is a valid approximation only for short time intervals $(t_0, t)$ and a sufficiently small perturbation $V$. If we assume the perturbation $V$ to be time-independent and $t_0 = 0$, then the above expression can be integrated to yield

$$\tilde{T}_{f\leftarrow s} = \langle f | \tilde{T}(0) | s \rangle = \frac{\langle f | V | s \rangle}{E_f - E_s} \left(1 - \exp(i\omega_{fs}t)\right), \quad (3.9)$$

where we have used $\omega_{fs} = \frac{E_f - E_s}{\hbar}$. The probability of this transition is simply the absolute value squared of the transition amplitude (Eq. 3.9):

$$P_{f\leftarrow s} = \left|\tilde{T}_{f\leftarrow s}\right|^2 = 2 \left|\langle f | V | s \rangle\right|^2 \frac{1 - \cos(\omega_{fs}t)}{(E_f - E_s)^2}. \quad (3.10)$$
The bound state, $|s\rangle$, can be considered to be embedded in a continuum of final states with final state density $\rho(E_f)$. The total probability of the decay of $|s\rangle$ would therefore be a sum over transition probabilities to all final states $|f\rangle$:

$$\sum_f P_{f\leftarrow s}(t) = 2\int \left|\langle f|V|s\rangle\right|^2 \frac{1 - \cos(\omega_{fs}t)}{(E_f - E_s)^2} \rho(E_f) dE_f,$$

(3.11)

where the integral is over all final states whose energy $E_f \approx E_s$. A bound state such as $|s\rangle$ that is coupled to a continuum in this way is called a resonance state, $\Psi_r$. The resonance state $\Psi_r$ decays exponentially, i.e., the probability that the system will be in the initial bound state $|s\rangle$ at time $t$ is given by

$$P_s(t) = \exp(-\Gamma t),$$

(3.12)

where $\Gamma$ is the width for the Interatomic Coulombic Decay (ICD) of the initial state $|s\rangle$ to the final state $|f\rangle$ and is proportional to the square of the matrix element of the perturbation $V$:

$$\Gamma = 2\pi|\langle f|\hat{V}|s\rangle|^2$$

(3.13)

In chapter 4 the initial state $|s\rangle$ will constitute an orbital vacancy in the inner sub-shell of the valence shell in neon, where neon is confined within a $C_{60}$ cage (the system is referred to as an endohedral fullerene). The final state $|f\rangle$ that is the result of ICD in this system will consist of an orbital vacancy on the outer sub-shell of the valence shell on neon and one on $C_{60}$, and also an electron in the continuum, referred to as $|k\rangle$. The final states $|f\rangle = |\phi_E\rangle$ must obey the following energy normalisation condition

$$\langle \phi_E|\phi_{E'}\rangle = \delta(E - E'),$$

(3.14)

where $\delta(E - E')$ is the Dirac delta function. Here it must be noted that the directionality of the continuum state $|k\rangle$ is not taken into consideration within the framework of the Wigner–Weisskopf approximation. We only calculate the total ICD width using this approximate theory without taking into account any angular distributions. This
is because we are using $L^2$ (square-integrable) wavefunctions which are zero at large radii and therefore not representative of true continuum states. In order to overcome this problem we will introduce the Stieltjes Imaging technique (see section 3.5) which renormalizes these $L^2$ wavefunctions to delta functions in energy with no directionality.

Eq. 3.13 is a rather general Wigner-Weisskopf expression for the decay width. Averbukh et al. [15] have derived a more complete expression for the total ICD width, $\Gamma_{ICD}$ which takes into account contribution to the decay width from all possible open channels with either singlet or triplet final states (where singlet and triplet only refer to bound unpaired electrons.). The derivation is cumbersome and will not be included here (see [15]). We only include the final expression here, which is:

$$\Gamma_{ICD} = 3\pi \sum_{k,ov_1,ov_2} |V_{ov_1,ov_2,k,iv} - V_{ov_1,ov_2,k,iv}|^2 \delta(\Delta E_{\text{triplet}})$$

$$+ \pi \sum_{k,ov_1,ov_2} |V_{ov_1,ov_2,k,iv} + V_{ov_1,ov_2,k,iv}|^2 \delta(\Delta E_{\text{singlet}})$$  (3.15)

where $ov_1$, $ov_2$ and $k$ refer to the final state of the decay with two outer-valence ($ov$) holes on either of the species involved in ICD and an electron in the continuum represented by the wavefunction $k$. $V_{ov_1,ov_2[iv,k]} = V_{ov_1,ov_2,iv,k} - V_{ov_1,ov_2,k,iv}$ is the total two-electron Coulomb integral expressed as the difference between the direct and the exchange integrals respectively [45]. If we ignore the electron in the continuum, the final state could either be a triplet or a singlet with respect to the spin orientation of the unpaired electrons in the bound orbitals of the resulting dication. Therefore the first term in Eq. 3.15 refers to the triplet and the second term to the singlet states of the final doubly ionised cluster. The purpose of the delta functions is to impose energy conservation conditions. $\Delta E_{\text{triplet}}$ and $\Delta E_{\text{singlet}}$ are each different combinations of the energies of the orbitals that are involved in ICD (See [15]).

In chapter 4 Eq. 3.15 will be implemented within a computer code whose purpose
is to numerically evaluate ICD rates in an endohedral fullerene system. The next section is concerned with introducing a rather general formula for the photoionisation cross section. In chapter 5 we will adapt this formula to the case of single photon laser enabled ICD (spLEICD) in selected weakly bound clusters in order to numerically compute the rate of such a process.

3.2 Photoionisation Cross Section

Photoionisation, the process of removing a bound electron from an atom, molecule, or a cluster by a photon of light, takes place when a photon provides the bound electron with energy larger than or equal to the binding energy of that electron, $\mathcal{E}_b$. The minimum required energy to ionise an atom is called the ionisation potential, $I_p$, which is equal in magnitude to the electron binding energy ($I_p = -\mathcal{E}_b$). The theoretical aspects of photoionisation have been extensively reviewed by Fano and Cooper in the large-wavelength regime [46]. In this regime both the photon momentum and Compton scattering [47] can be neglected as the wavelength of radiation is much larger compared to the size of the atom it interacts with.

The probability that photon absorption would lead to a bound-bound or bound-continuum transition is represented by the oscillator strength which is a dimensionless quantity. The concept of oscillator strength goes back to the times when classical electrons were thought to occupy well-defined positions within the atom. Therefore in response to weak external disturbances such as the electromagnetic radiation the electrons would oscillate in a pendular fashion about their equilibrium positions with an angular frequency $\omega_s$. With the rise of Quantum Mechanics and the concept of electronic position as a probability distribution, the oscillator strength found a rather evolved definition: it represents the fraction of electrons that take part in a resonance created via interaction with an external radiation [48].

The oscillator strength may be expressed in terms of the dipole matrix element
taken between the ground state $\Psi_0$ and the final continuum state $\Psi_E$ [49,50]. In the length gauge, this is

$$\frac{df(E)}{dE} = \frac{2mE}{3\hbar^2} \left| \left\langle \Psi_E \left| \sum_j \vec{r}_j \right| \Psi_0 \right\rangle \right|^2,$$  

(3.16)

where $j$ is the electronic index, $E$ is electronic energy, $m$ is the mass of an electron, and $\Psi_E$ obeys the following normalisation condition

$$\langle \Psi_E | \Psi_{E'} \rangle = \delta(E - E').$$  

(3.17)

The oscillator strength in the momentum gauge is

$$\frac{df(E)}{dE} = \frac{4}{3} \frac{1}{2mE} \left| \left\langle \Psi_E \left| \sum_j \vec{p}_j \right| \Psi_0 \right\rangle \right|^2.$$  

(3.18)

The photoionisation cross section is related to the oscillator strength through the following formula

$$\sigma(\omega) = \frac{2\pi^2 e^2 \hbar}{mc} \frac{df}{dE}.$$  

(3.19)

Using equations 3.16 and 3.18 in the formula for the photoionisation cross section leads to the cross section in the length and momentum gauge respectively

$$\sigma_{\text{length}}(\omega) = \frac{4\pi^2 e^2 E}{3\hbar c} \left| \left\langle \Psi_E \left| \sum_j \vec{r}_j \right| \Psi_0 \right\rangle \right|^2,$$  

(3.20)

$$\sigma_{\text{momentum}}(\omega) = \frac{4\pi^2 e^2 \hbar}{3m^2 cE} \left| \left\langle \Psi_E \left| \sum_j \vec{p}_j \right| \Psi_0 \right\rangle \right|^2.$$  

(3.21)

Both formulations 3.20 and 3.21 would yield the same results only when $\Psi_0$ and $\Psi_E$ are exact solutions of the Schrödinger equation [51]. In the case of many-electron systems where we only deal with approximate wavefunctions we must therefore always choose to work with one gauge only for the sake of consistency. In this thesis we consider cross section in the length gauge only. This is because we use Gaussian
Type Orbitals (GTOs) as basis sets for describing the wavefunctions involved in any given decay process: the incorrect behaviour of GTO’s near zero for the cross section given in the momentum gauge deems this gauge unsuitable for quantum chemical calculations [52].

In chapter 5 we develop Eq. 3.20 into an equation that specifically describes the process of single photon laser enabled ICD (spLEICD) in NeAr cluster.

### 3.3 Second Quantization

In this section we introduce the formalism of second quantisation, a mathematical tool that is a prerequisite to the material in section 3.4. We start by introducing the creation and annihilation operators - the creation operator, $c_i^\dagger$, is responsible for creating an electron in the spinorbital $\chi_i$. Thus

$$c_i^\dagger |\chi_k \ldots \chi_l\rangle = |\chi_i\chi_k \ldots \chi_l\rangle$$  \hspace{1cm} (3.22)

where $|\chi_k \ldots \chi_l\rangle$ is an arbitrary Slater determinant. On the other hand, the annihilation operator, $c_i$, removes or annihilates an electron in spinorbital $\chi_i$

$$c_i |\chi_k \ldots \chi_l\rangle = |\chi_k \ldots \chi_l\rangle$$  \hspace{1cm} (3.23)

Note that both the creation and annihilation operators add and remove an electron to or from the spinorbital immediately to the left of the corresponding Slater determinants. The creation and annihilation operators satisfy the following anticommutation relations

$$\{ c_i^\dagger, c_j^\dagger \} = \{ c_j, c_i \} = 0$$  \hspace{1cm} (3.24)

$$\{ c_i, c_i^\dagger \} = 1,$$  \hspace{1cm} (3.25)
where
\[ \{A, B\} = AB + BA. \] (3.26)

The Pauli exclusion principle follows from equation (3.24) for \( i = j \):
\[ \{c_i^\dagger, c_i^\dagger\} = c_i^\dagger c_i^\dagger + c_i^\dagger c_i^\dagger = 0 \]

Therefore
\[ c_i^\dagger c_i^\dagger = -c_i^\dagger c_i^\dagger = 0. \] (3.27)

This implies that
\[ c_i^\dagger c_i^\dagger |\chi_k \ldots \chi_l \rangle = c_i^\dagger |\chi_i \chi_k \ldots \chi_l \rangle = |\chi_k \chi_l \rangle = 0, \] (3.28)
i.e. no two electrons can occupy the same spinorbital \( \chi_i \). The antisymmetry property of the Slater determinant allows us to deal with situations such as
\[ c_i |\chi_k \chi_l \rangle = -c_i |\chi_i \chi_k \rangle = -|\chi_k \chi_l \rangle. \] (3.29)

Let us now use the formalism of second quantization in order to define a Slater determinant. We do this by introducing the vacuum state, \( |\rangle \), the state with no electrons. This state is normalized to unity and has the following property
\[ c_i |\rangle = 0, \] (3.30)
which means that the annihilation operator \( c_i \) cannot remove an electron from a state that contains no electrons. Using the vacuum state we can write the Slater
determinant in the formalism of second quantization:

\[
c_i^\dagger c_k^\dagger \ldots c_l^\dagger |\rangle = |\chi_i\chi_k\ldots\chi_l\rangle
\]  

(3.31)

The formalism of second quantisation will be used in chapter 5 within the framework of the Algebraic Diagrammatic Construction (ADC) (see section 3.4) which will be implemented in the code that calculates the cross section for a laser enabled Interatomic Coulombic Decay process.

3.4 ADC within the Framework of the Intermediate State Representation

Algebraic Diagrammatic Construction (ADC) is a one-particle Green’s function method used for the calculation of ionisation and electron-attachment spectra [53,54]. In this thesis, in order to construct (N-1)-electron wavefunctions, we resort to a scheme within ADC referred to as ADC(2)x which uses the Intermediate State Representation (ISR) [55]. The ISR formulation of ADC treats the (N-1)-electron \([G^-](\omega)\) and the (N+1)-electron \([G^+(\omega)\] parts of the electron propagator \(G(\omega)\) separately,

\[
G(\omega) = G^-(\omega) + G^+(\omega).
\]  

(3.32)

In this thesis we are only interested in the ionisation problem and therefore only concerned with the (N-1)-electron part, \(G^-(\omega)\), whose non-diagonal representation is

\[
G^{-}(\omega) = f^\dagger(\omega - K - C)^{-1} f,
\]  

(3.33)

where \(f\) is the matrix of transition amplitudes between the exact N-electron ground state \(|\Psi_0^N\rangle\) and the so-called “intermediate states” \(|\tilde{\Psi}_I^{N-1}\rangle\)

\[
f_{I,q} = \langle \tilde{\Psi}_I^{N-1}\rangle_{c_q}|\Psi_0^N\rangle,
\]  

(3.34)
where \( c_q \) is the destruction operator with \( q \) representing a general (hole or particle) state (see below). \( \mathbf{K} + \mathbf{C} \) is the secular matrix which for an exact N-electron ground state energy \( E_0 \) represents the shifted Hamiltonian \( \hat{H} - E_0 \) in terms of the intermediate states

\[
(K + C)_{IJ} = -\langle \tilde{\Psi}_N^{-1} \hat{H} - E_0 | \tilde{\Psi}_N^{-1} \rangle. \tag{3.35}
\]

These intermediate states are derived from the correlated excited states \( |\Psi_0^J\rangle \)

\[
|\Psi_0^J\rangle = \hat{C}_J |\Psi_0^N\rangle, \tag{3.36}
\]

where \( |\Psi_0^N\rangle \) can be written within the MP approximation method (chapter 2) as the following perturbation expansion

\[
|\Psi_0^N\rangle = |\Phi_0^N\rangle + |\Psi_0^{(1)}\rangle + |\Psi_0^{(2)}\rangle + |\Psi_0^{(3)}\rangle + \ldots. \tag{3.37}
\]

\( |\Phi_0^N\rangle \) is the HF ground state. The “physical” excitation operators

\[
\{\hat{C}_J\} = \{c_k; c_k^\dagger c_k c_l, k < l; \ldots\} \tag{3.38}
\]

are formed by a manifold of second quantisation operators. The indices \( i, j, k, \ldots \) and \( a, b, c, \ldots \) refer to occupied and unoccupied orbitals respectively (or hole and particle states respectively). Therefore the excitation class \( c_k \) represents a hole \((h)\) state, and the excitation class \( c_k^\dagger c_k c_l \) a two-hole-one-particle \((2h1p)\) state.

The essential step for obtaining the intermediate states from the correlated excited states is the Gramm-Schmidt orthogonalization between the excitation classes, followed by symmetrical orthonormalisation within each class. The exact \((N-1)\)-electron states can thus be written as a sum over the orthonormal intermediate states using a transformation matrix \( Y \):

\[
|\Psi_m^{N-1}\rangle = \sum_J Y_{jm} |\tilde{\Psi}_J^{N-1}\rangle \tag{3.39}
\]
The transition matrix element of any arbitrary operator $\hat{O}$ can therefore be written as

$$O_{mn} = \langle \Psi_{m}^{N-1} | \hat{O} | \Psi_{n}^{N-1} \rangle = \sum_{I,J} Y_{m}^{*} \langle \tilde{\Psi}_{I}^{N-1} | \hat{O} | \tilde{\Psi}_{J}^{N-1} \rangle Y_{nJ}, \quad (3.40)$$

where the matrix elements $\tilde{O}_{IJ} = \langle \tilde{\Psi}_{I}^{N-1} | \hat{O} | \tilde{\Psi}_{J}^{N-1} \rangle$ belong to the matrix $\tilde{O}$ which is the intermediate state representation of the operator $\hat{O}$. The explicit expression for $\tilde{O}_{IJ}$ will be provided in chapter 5 in connection with transition dipole matrix elements that define the photoionisation cross section.

In this thesis we are interested in $(N-1)$-eigenstates, $|\Psi^{N-1}\rangle$, which can be expressed as a sum over $1h$ and $2h1p$ states

$$\Psi^{(N-1)} = \sum_{i} c_{i} \phi_{i} + \sum_{ija} c_{ija}^{a} \phi_{ija}. \quad (3.41)$$

This equation will be used in chapter 5 for the calculation of the $spLEICD$ cross section. The above wavefunction is not correctly normalised in the continuum. In the next section we develop the tool necessary for normalising such a wavefunction.

### 3.5 The Stieltjes Imaging Technique

The $2h1p$ wavefunctions constructed using the ADC(2)$x$ method of approximation are not correctly normalised. Correctly energy-normalised continuum states $k_{E}$ can be approximated by making use of a discrete set of $L^{2}$ functions derived using the Stieltjes-Chebyshev moment theory [56–58] also referred to as the Stieltjes Imaging technique [51,59–61].

This method is based on projecting the Hamiltonian of the system so as to create a final state Hamiltonian, $\hat{H}_{f} = \hat{P} \hat{H} \hat{P}$, whose eigenstates are the final states of the
decay $k_E$. The role of the operator $\hat{P}$ [62] is to project $k_E$ onto a subspace that is spanned by the discrete and $L^2$-normalised eigenstates. These eigenstates are orthogonal to the initial bound states $\Psi_r$ which define $\hat{Q} = |\Psi_r\rangle\langle\Psi_r|$ where $\hat{P} = \hat{1} - \hat{Q}$. This method is based on the calculation of the final states of the decay using $L^2$ boundary conditions. In this way the continuum is discretised and forms a pseudospectrum, however the discrete final states $\tilde{k}_E$ calculated in this way are not correctly normalised and cannot be used to calculate $\Gamma$ directly.

In order to overcome this problem one can define spectral moments $\mu_k$:

$$\mu_k = \langle \Psi_r | \hat{V} \hat{H}_f^k \hat{V} | \Psi_r \rangle$$

(3.42)

Considering the whole spectrum of $\hat{H}_f$ including both bound and continuum states, the resolution of identity $\sum_j |k_{E_j}\rangle\langle k_{E_j}| + \int_{E_T}^{\infty} |k_E\rangle\langle k_E| dE$ could be inserted into the above equation yielding

$$\mu_k = \sum_i E_i^k \langle \Psi_r | \hat{V} | k_i \rangle^2 + \int_{E_T}^{\infty} E^k \langle \Psi_r | \hat{V} | k_E \rangle^2 dE,$$

(3.43)

where $E_T$ denotes the ionisation energy. Using the resolution of identity of the pseudospectrum $\tilde{k}_E$, we get

$$\mu_k \approx \sum_j (\tilde{E}_j)^k \langle \Psi_r | \hat{V} | \tilde{k}_{E_j} \rangle^2 \quad k = 0, 1, \cdots, 2n - 1.$$  

(3.44)

Here we have assumed that $\hat{V}$ has a finite radius of influence and therefore it can be resolved in the discrete eigenstates $\tilde{k}_{E_j}$. These spectral moments are computed using negative values of $k$ ($k \leq 0$) because the moments diverge for $k > 2$ [51]. The set of $j$ couplings is thus defined as $\gamma_j = 2\pi \langle \Psi_r | \hat{V} | \tilde{k}_{E_j} \rangle^2$ with corresponding energies $\tilde{E}_j$. These are used as input for the Stieltjes imaging procedure which then uses them to calculate the spectral moments until convergence is achieved. An approximate value of the width $\Gamma^n$ can therefore be obtained by adding the spectral moments calculated
up to order $n$ using

$$
\Gamma^n(E_r) = \frac{1}{2} \frac{\gamma_j^{n+1} + \gamma_j^n}{E_{j+1}^n - E_j^n}, \quad E_{j+1}^n < E_r < E_j^n.
$$

(3.45)

A similar formula to the one above exists for the photoionisation cross section [59].

The Stieltjes imaging technique is an efficient method that could be used in conjunction with efficient quantum chemistry methods such as the Wigner-Weisskopf and the ADC approximation in order to evaluate properties such as the decay width [63] and photoionisation cross section [49,50].

Having introduced the theoretical background to the subject of this thesis, we may now move on to the research chapters, i.e. chapter 4 where we investigate the process of Interatomic Coulombic Decay (ICD) in the endohedral fullerene Ne@C$_{60}$, and chapter 5 where we introduce the novel process of laser enabled ICD in weakly bound clusters.
Chapter 4

Interatomic Coulombic Decay in Endohedral Fullerenes

4.1 Introduction

So far we have covered the theoretical basis for ICD and its place in relation to other types of radiation-less decay mechanisms. In this chapter, we will explore ICD in the highly symmetric environment of an endohedral fullerene (see chapter 1), under lowered symmetry conditions as the confined atom moves away from the centre. Specifically we will calculate, by both analytical and numerical means, the ICD rate in $2s$-ionized neon inside $C_{60}$, from here on referred to as $(2s^1)\text{Ne}^+ @ C_{60}$. In such a system, ICD is expected to be ultrafast due to the 60 carbon atoms that are symmetrically positioned around the central neon. Since ICD mostly involves participation from outer-valence electrons ($2p$ in the case of carbon), and there are 180 such electrons that make up the $C_{60}$ electronic shell, any one of those is prone to ionisation by ICD. This means that there are almost 180 available ICD channels in $(2s^1)\text{Ne}^+ @ C_{60}$, and this is what makes this process ultrafast (few femtoseconds time scale). We will further explore ICD in endohedral fullerenes using a more formal approach in section 4.2.

The above-mentioned 180 electrons that belong to the $C_{60}$ exhibit a collective
behaviour due to the strong electronic correlations that they experience as a result of the inter-electronic Coulombic repulsion [64]. Incident optical radiation can set the electrons off on an oscillatory motion with respect to the surface of C\textsubscript{60}. The fundamental mode of these oscillations is referred to as the giant plasmon\textsuperscript{1} resonance, and is dipole in nature. The existence of a giant plasmon resonance in C\textsubscript{60} was first predicted by Bertsch \textit{et al.} [64] and later observed by Hertel \textit{et al.} [65]. As Fig. 4.1 shows, the giant resonance has a peak energy of about 20 eV, which turns out to be close to the energy released following the Ne\textsuperscript{+}(2p \rightarrow 2s) transition during the course of ICD in (2s\textsubscript{1})Ne\textsuperscript{+}@C\textsubscript{60}. Ne\textsuperscript{+} with a 2s2p\textsuperscript{6} configuration has an energy of about 48.5 eV\textsuperscript{2} above the ground state of the neutral neon, while the energy of Ne\textsuperscript{+} with a 2s\textsuperscript{2}2p\textsuperscript{5} configuration is about 21.6 eV. Therefore the recombination of a 2p electron into the 2s vacancy on neon with the former electronic configuration releases 26.9 eV, all of which is most likely transferred onto the C\textsubscript{60}. Around 7.6 eV [66] of this energy goes into the repulsive interaction between the positive charge on Ne and that on the C\textsubscript{60} with (2p\textsuperscript{5})Ne\textsuperscript{+}@C\textsubscript{60}\textsuperscript{+} as the final state of ICD. The remainder of this energy is used to excite the giant plasmon resonance.

The endohedral atom, in our case neon, also referred to as the confined atom, does not always sit exactly at the centre of the C\textsubscript{60} cage, rather it moves about the centre due to thermal effects. This calls for a study into whether the loss of spherical symmetry of the system as neon moves away from the centre brings the higher modes of plasmon oscillations into the picture. Is there the possibility that ICD in “off-centre” Ne\textsuperscript{+}@C\textsubscript{60} [67–70] may excite the so-called multipole plasmon oscillations?

We will approach this problem via two separate methods: (1) an analytical method which culminates in graphs that bear the contribution of each mode of plasmon oscillation to the possible enhancement of the ICD rate, (2) a numerical method based

\textsuperscript{1}The quantum mechanical unit of the plasma oscillations is referred to as a plasmon, an energy quantum with a value that equals \(\hbar \omega_p\), where \(\omega_p\) is the angular frequency of the plasma oscillations [48]. In this chapter, we will be using the terms \textit{plasmon} and \textit{plasma oscillations} interchangeably.

\textsuperscript{2}Energies are adapted from the NIST atomic energy levels database; \url{http://physics.nist.gov/PhysRefData/ASD/levels_form.html}
Figure 4.1: Photoionisation cross-section of C\(_60\) exhibits a large feature that peaks at about 20 eV. The excitation energy for this resonance is much higher than the ionisation potential of C\(_60\) (7.6 eV), and single ionisation of C\(_60\) is therefore unavoidable. [Figure adapted with permission from [65]]

on the Wigner-Weisskopf theory used for the calculation of the final ICD rate. Both our methods assume that the carbon atoms are fixed within the C\(_60\) cage. This is because the amplitude of vibrations of C\(_60\) atoms are small compared to the amplitude of neon’s vibration inside the cage and thus can be ignored in our approximate approach.

We will henceforth refer to the spherically symmetric case as the “at-centre” Ne\(^+\)@C\(_60\) (see [71] and references therein). We expect that only when the symmetry of the system has been lowered as in the off-centre case, ICD may set off the higher modes of C\(_60\) plasmon into oscillation. The reason behind this will become clear later in this chapter as we lay out the theoretical formulation of our methods. Briefly, our analytical approach involves manipulating the expression for the ICD width, \(\Gamma\), derived in chapter 3 using the Wigner-Weisskopf approximation, which results in an expression where \(\Gamma\) is directly proportional to the photoionisation cross-section of C\(_60\). This new expression allows us access to the possible correlation between C\(_60\) plasma
oscillations and the ICD rate. By replacing the neon orbitals that are involved in ICD with an infinite expansion in spherical harmonics, we re-define these orbitals with respect to the centre of the cage. This opens up the possibility of a one-to-one correlation of spherical harmonics corresponding to both the multipole plasmon oscillations and neon’s ICD orbitals.

4.2 ICD in \((2s^1)\text{Ne}^+@C_{60}\)

As already pointed out in the introduction, the purpose of this investigation is to find out whether and how ICD in the at-centre and off-centre \((2s^1)\text{Ne}^+@C_{60}\) may cause excitation of the multipole fullerene plasmon oscillations. We approach this problem first analytically and later numerically by adapting the Wigner-Weisskopf expression for \(\Gamma_{\text{ICD}}\) that we derived in chapter 3, to the case of \((2s^1)\text{Ne}^+@C_{60}\). The expression for \(\Gamma_{\text{ICD}}\) is

\[
\Gamma = 2\pi |V|^2, \tag{4.1}
\]

where \(V\) is the (direct) Coulomb potential matrix element,

\[
V = \langle ov_1(1)ov_2(2) | \frac{1}{r_{12}} | iv(1)\kappa(2) \rangle, \tag{4.2}
\]

with \(iv(1)\) and \(ov_1(1)\) respectively representing the inner-valence and and outer-valence orbitals on the “recombination” site i.e. on the atom/molecule with the original inner-valence vacancy, where an outer-valence electron recombines to fill in the inner-valence vacancy. \(ov_2\) and \(\kappa\) are the outer-valence and continuum orbitals on the “ionisation” site respectively, where an electron is ejected from the atom/molecule into the continuum as a result of the Coulomb interaction with the recombining electron, represented by the Coulomb operator \(1/r_{12} = 1/|r_1 - r_2|\). The numbers 1 and 2 are the electronic tags. Eq. 4.2 is only the “direct” contribution to the total ICD width. We will refer to it as the ICD matrix element from this point forward. As already touched upon in chapter 3, since the electrons are indistinguishable particles,
Figure 4.2: a. Ne(2s) orbital of neon shows hardly any overlap with the wall of C\textsubscript{60} as it resides at the centre of the cage while, b. Ar(3s) orbital largely overlaps with the wall of the cage (Figures were simulated using MOLCAS [40] and plotted in MOLDEN)

there is also an exchange contribution

\[ V_{\text{exchange}} = \langle ov_1(2)ov_2(1)\frac{1}{r_{12}}|iv(1)\kappa(2)\rangle, \quad (4.3) \]

where the electron tags are swapped in the \textit{bra} part of the matrix element. The direct process takes place as a result of the long-range effect of the Coulomb force, while the exchange process requires overlap between the valence orbitals of the two species involved in the process, and manifests the short-range effect of the Coulomb force.

Since neon is a small atom compared to the dimensions of C\textsubscript{60}, when it occupies the centre of the cage or even manoeuvres about the centre up to a certain radius, there is hardly any orbital overlap with the wall of the cage. This allows us to ignore the exchange process in our analytical derivations below. Later when we evaluate the ICD width numerically using the WW approximation, the contribution from the exchange process will be fully taken into account.

Our analytical treatment is only valid for small confined atoms such as neon. Larger atoms, for instance argon whose 3s orbital greatly overlaps with the wall of C\textsubscript{60} as shown in Fig. 4.2, do not offer this analytical simplification. Fig. 4.3 contains 3D plots of of the Ne 2p orbital inside C\textsubscript{60} which illustrate the range of motion available.

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Figure 4.3: 3D plots illustrating the degree of overlap of Ne(2p) orbital with the C\textsubscript{60} cage, at displacements $D$ of a. 1\textit{a}\textsubscript{0} where there is hardly any overlap, b. 2\textit{a}\textsubscript{0} with overlap beginning to appear, and c. 2.5\textit{a}\textsubscript{0} where overlap becomes rather significant. (Figures were simulated using MOLCAS and plotted in MOLDEN)

to neon before it overlaps with the cage at a distance of around 2\textit{a}\textsubscript{0} (where \textit{a}\textsubscript{0} is the atomic unit of length) from the centre of C\textsubscript{60}. Panel (a.) in this figure corresponds to displacement $D = 1\textit{a}\textsubscript{0}$, which is the turning point for neon as it experiences thermal vibrations at room temperature about its equilibrium position [72], i.e. the centre of C\textsubscript{60}. It is necessary to take these thermal vibrations into account when investigating the possible excitation of fullerene plasmon oscillations due to ICD in (2s\textsuperscript{1})Ne\textsuperscript{+}@C\textsubscript{60}. This is because this motion introduces the breaking of spherical symmetry of the system, which may excite the higher modes of plasmon oscillations for reasons that will become clear later in this section. Since these thermal vibrations are possibly the only type of motion that neon experiences under normal conditions, i.e. without the presence of any external disturbances, and since there is no overlap with the cage at or below the maximum radius of these vibrations (1\textit{a}\textsubscript{0} at room temperature [72]), we can ignore the exchange contribution to the ICD matrix element throughout this section.

Fig. 4.4 is a plot of the potential energy of Ne@C\textsubscript{60} with respect to the energy of the at-centre Ne@C\textsubscript{60} as a function of distance from the centre of the cage. This graph clearly illustrates that neon should mostly occupy a small sphere centred at its equilibrium position as the potential energy starts rising rather steeply for distances above 1.0\textit{a}\textsubscript{0}.  

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Figure 4.4: Plot of potential energy for Ne@C$_{60}$ with respect to the energy of the at-centre Ne@C$_{60}$ as a function of neon’s displacement $D$ from the centre of the cage, calculated numerically using both SCF and MP2 approximation methods, the latter offering more accurate results. The energy remains almost constant up to about 1.0 $a_0$ where it starts to rise. The arrow points to neon’s turning point for thermal vibrations (Energies were calculated using MOLCAS [40]).

We now return to the ICD matrix element as defined by Eq. 4.2. We choose to single out the orbital $p_z$ from which recombination of an electron into the 2$s$ vacancy takes place. We can do this since the three spatial directions are equivalent as a result of the spherical symmetry of our system. We will refer to the ICD matrix element corresponding to the $2p_z \rightarrow 2s$ transition as $V_z$. Let us re-write Eq. 4.2 in terms of the Ne and C$_{60}$ orbitals that are involved in ICD. We use the notation $r = (r, \theta, \phi)$ to represent the spherical polar coordinates.

$$V_z = \langle 2p_z(r)\Psi_{C_{60}}(r_{C_{60}})|\frac{1}{|r-r_{C_{60}}|}|2s(r)\kappa(r_{C_{60}})\rangle, \quad (4.4)$$

where the electron tags are replaced by the position vectors, in spherical polar coordinates, of those electrons with respect to the centre of C$_{60}$. $\Psi_{C_{60}}$ represents the orbital of the outer-valence electron on C$_{60}$ which during ICD escapes into the continuum, represented by the wavefunction $\kappa(r_{C_{60}})$. The orbitals $2s(r)$ and $2p(r)$ belong to neon, and correspond to $iv(1)$ and $ov(1)$ in Eq. 4.2 respectively.
Fig. 4.5 is a schematic diagram of neon inside C\textsubscript{60}, where neon is represented by a \textit{p} orbital directed along the \textit{z} axis. This is because in our later derivations we only consider the electronic density that takes part in ICD, i.e. a product of the 2\textit{s} and 2\textit{p} (in this case 2\textit{p}\textsubscript{z}) orbitals of neon only.

We use hydrogenic wavefunctions adapted to many-electron systems \cite{74} in order to approximate neon’s orbitals. Within the hydrogenic approximation, for Ne(2\textit{s}) and Ne(2\textit{p}\textsubscript{z}) orbitals with quantum numbers \((n,l,m) = (2,0,0)\) and \((n,l,m) = (2,1,0)\) respectively, these are written as

\begin{equation}
2\textit{s}(\textit{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{2}\right)^{\frac{3}{2}} (1 - \frac{Zr}{2}) e^{-\frac{Zr}{2}}, \tag{4.5}
\end{equation}

and

\begin{equation}
2\textit{p}\textsubscript{z}(\textit{r}) = \frac{1}{\sqrt{4\pi}} \cos\theta \left(\frac{Z}{2}\right)^{\frac{3}{2}} (Zr) e^{-\frac{Zr}{2}}. \tag{4.6}
\end{equation}

where \(Z\) is the atomic number. It is convenient to re-express the above equations in terms of Slater Type Orbitals (STOs) (see chapter 2). The reason for this will become clear later when we derive \(\Gamma_{\text{ICD}}\) for the off-centre \((2s^1)\text{Ne}^+\oplus\text{C}_{60}\). A STO is defined as

\begin{equation}
\psi_{nl}^{m}(\textit{r}) = r^{(n-1)} e^{-\zeta r} Y_{l}^{m}(\theta, \phi), \tag{4.7}
\end{equation}

where \(\zeta\) is a measure of the effective nuclear charge “felt” by an electron in an atom after taking into account the shielding by lower-lying electrons and the distance of that electron from the nucleus. It is defined as

\begin{equation}
\zeta = \frac{Z_{\text{eff}}}{n} \tag{4.8}
\end{equation}

with \(Z_{\text{eff}} = Z - s\), where \(s\) is the screening constant \cite{41}. Replacing \(Z\) in equations 4.5 and 4.6 with \(Z_{\text{eff}}\) and using \(n = 2\) allows us to redefine these equations in terms of \(\zeta\)

\begin{equation}
2\textit{s} = \frac{1}{\sqrt{\pi}} (\zeta)^{\frac{3}{2}} (1 - \zeta r) e^{-\zeta r}, \tag{4.9}
\end{equation}

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Figure 4.5: Schematics of Ne@C$_{60}$: The fullerene electronic shell, here drawn as the grey circular shell, is small compared to the radius of C$_{60}$ [73]. The shape labelled as Ne 2s2p that resembles a 2p orbital represents the product of the electronic wavefunctions $2s(r)$ and $2p(r)$ in the notation of this thesis. This product corresponds to the charge density of the recombining electron on neon. $r$ and $r_{C_{60}}$ are position vectors of the recombining electron on neon and the ionising electron on C$_{60}$ respectively. The inverse magnitude of their difference $r - r_{C_{60}}$ is the Coulomb operator that represents the long-range Coulomb interaction responsible for the process of ICD.
and

\[ 2p_z = \frac{1}{\sqrt{\pi}} (\zeta)^\frac{5}{2} e^{-\zeta r} \cos(\theta) \quad (4.10) \]

These expressions already look similar in form to the STO defined by Eq. 4.7. We can calculate \( \zeta \) using Eq. 4.8. In order to calculate the screening constant \( s \), we could use the Slater’s rules [41], i.e., for the \((2s,2p)\) shell we multiply the number of electrons in the shell (6 in the case of singly ionised neon) by 0.35, and the number of electrons in the lower shell (\(1s\) group) by 0.85. However this method only takes into account the contribution from lower-lying electrons. Clementi and Raimondi [75] have found that the outside electrons also influence the value of the screening constant. The authors have computed the SCF functions for most of the elements in the periodic table and have optimised the values of the orbital exponent \( \zeta \). The resulting value of zeta for neon \( 2s \) and \( 2p \) orbitals according to Clementi and Raimondi is \( \zeta = 2.8792 \). We will use this value throughout the rest of this chapter in our later derivation of \( \Gamma_{ICD} \) for the off-centre \((2s^1)\)Ne\(^+\)@C\(_{60}\).

Now that we have stated our assumptions and defined our orbitals, let us turn our attention to the ICD matrix element, and re-express it in terms of quantities that belong to Ne and C\(_{60}\) separately, and not to both at the same time. We can do this because based on the zero overlap assumption the position of the electron on C\(_{60}\), i.e. \( r_{C_{60}} \), is always larger than that of the electron on neon, i.e. \( r \). We can therefore express the Coulomb operator in terms of a multipole expansion \[76\].

\[
\frac{1}{|r - r_{C_{60}}|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{r_{C_{60}}^{l+1}} Y_l^m(\theta_{C_{60}}, \phi_{C_{60}}) Y_l^m(\theta, \phi) \quad (4.11)
\]

Substituting this multipole expansion back into the ICD matrix element leads to the decomposition of \( V \) into a product of two matrix elements, one purely belonging to neon, with a dipole operator that describes the recombination of a \( 2p \) electron into the \( 2s \) orbital vacancy, and the other purely describing the ionisation on C\(_{60}\) as a
result of the former process.

\[ V_z = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \langle 2p_z(r) | r^l Y_l^m(\theta, \phi) | 2s(r) \rangle \cdot \langle \Psi_{C_{60}}(r_{C_{60}}) | Y_{l+1}^{m+1}(\theta_{C_{60}}, \phi_{C_{60}}) \rangle | \kappa(r_{C_{60}}) \rangle \]  

(4.12)

Since we have made use of hydrogenic orbitals for neon, where \( 2p \propto Y_1^0 \) and \( 2s \propto Y_0^0 \), and since \( Y_0^0 \) is just a constant, \( Y_1^0 \) determines the values of \( l \) and \( m \) that survive following the application of the orthonormality condition for the spherical harmonics. The above sum therefore reduces to a single term

\[ V_z = \frac{4\pi}{3} \langle 2p_z(r) | r Y_1^0(\theta, \phi) | 2s(r) \rangle \cdot \langle \Psi_{C_{60}}(r_{C_{60}}) | \frac{Y_0^0(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^2} | \kappa(r_{C_{60}}) \rangle \]  

(4.13)

In order to simplify our derivation we use Cartesian coordinates which are related to the spherical polar coordinates, for the \( z \) direction, through \( z = r \cos \theta \). This would lead to an expression for the partial \( \Gamma \) corresponding to the recombination of a neon \( p_z \) electron into the 2s vacancy. Later, in order to find the total ICD width, benefiting from the spherical symmetry of our system, we can just multiply \( \Gamma_z \) by a factor 3 in order to take into account the \( x \) and \( y \) spatial directions as well.

Using \( Y_1^0 = \sqrt{\frac{3}{4\pi}} \left( \frac{z}{r} \right) \), the above expression reduces to

\[ V_z = \langle 2p_z(r) | z | 2s(r) \rangle \cdot \langle \Psi_{C_{60}}(r_{C_{60}}) | \frac{z_{C_{60}}}{r_{C_{60}}^2} | \kappa(r_{C_{60}}) \rangle \]  

(4.14)

If we consider the thickness of the \( C_{60} \) shell to be \( \Delta \), \( r_{C_{60}} \) spans \( R - \Delta/2 \) to \( R + \Delta/2 \) where \( R \) is the \( C_{60} \) radius. Therefore for \( \Delta << R \) we can approximate \( r_{C_{60}} \approx R \). We can therefore replace \( r_{C_{60}} \) in the operator for the \( C_{60} \) matrix element with the constant \( R \),

\[ V_z \approx \langle 2p_z(r) | z | 2s(r) \rangle \cdot \langle \Psi_{C_{60}}(r_{C_{60}}) | \frac{z_{C_{60}}}{R^2} | \kappa(r_{C_{60}}) \rangle \]  

(4.15)

where \( z_{Ne} \) and \( z_{C_{60}} \) represent the matrix elements. Substituting this approximate
expression for $V_z$ back into Eqn. 4.1 yields an expression for $\Gamma_z$

$$\Gamma_z = 2\pi |V_z|^2$$

$$= 2\pi \frac{z^2_{Ne} \cdot z^2_{C_{60}}}{R^6}$$

(4.16)

Hence, for the total ICD width, we have

$$\Gamma_{total} = 3\Gamma_z$$

$$= 6\pi \frac{z^2_{Ne} \cdot z^2_{C_{60}}}{R^6}$$

(4.17)

Matthew and Komninos [77] came up with a similar expression to the one above for a process they refer to as *inter-intra Auger decay*, or what we here refer to as ICD, in a diatom. They used expressions that allowed them to re-write the decay rate, $\Gamma_{ICD}$ in terms of the radiative lifetime $\tau$ of the vacancy on the recombination site, and the total photoionisation cross-section $\sigma$ for the ionisation site. The recombination site in our case is Ne where $2p \rightarrow 2s$ transition takes place, and the ionisation site where an electron is ionised from $C_{60}$. Here we use an adaptation of their final expression as given by Amusia for the case of Auger decay in endohedral fullerenes [69]

$$\Gamma = \frac{3\hbar}{4\pi} \left( \frac{c}{\omega} \right)^4 \tau_{Ne}^{-1} \frac{\sigma_{C_{60}}}{R^6},$$

(4.18)

where $c$ is the speed of light. This expression provides us with a simple interpretation of the mechanism behind the energy transfer in the course of ICD, where a “virtual” photon of frequency $\omega$ is emitted as a result of the annihilation of the inner-valence vacancy on the recombination site. This virtual photon will then get transferred to the ionisation site where it causes the release of an outer-valence electron into the continuum. This is called the virtual photon transfer mechanism, and was proposed to be valid for the ICD process by Thomas *et al.* [78] (see also [15]). The usefulness of Eq. 4.18 lies in the fact that both $\tau_{Ne}^{-1}$ and $\sigma_{C_{60}}$ are atomic/molecular (as opposed

---

3This expression varies from that derived by Matthew and Komninos by a factor of $3/4\pi$. See Ref. [63], under reference 25.
to cluster) quantities that are well-known and could be measured, and help verify theoretical results for the ICD rate in various systems.

4.2.1 ICD in \((2s^1)\text{Ne}^+@C_{60}\): A semi-analytic approach at determining the effect of neon’s vibrations inside the fullerene on the ICD rate

Our main concern so far has been the derivation of an expression for \(\Gamma_{\text{ICD}}\) that is valid for the at-centre \((2s^1)\text{Ne}^+@C_{60}\). This expression (Eq. 4.18) relates the ICD rate to the total photoionisation cross-section, \(\sigma_{C_{60}}\), of the fullerene, and thus to its (dipole) surface plasmon oscillations. This correlation exists because the vacancy decay on neon is a dipole transition which classically acts as a time-dependent dipole. It therefore makes sense to expect that the dipole mode of plasmon oscillations would interact with the neon vacancy which also has a dipole character. As mentioned earlier in this section, the radius of \(C_{60}\), \(R\), is much larger than the dimensions of neon. This means that we can treat the recombining electron on neon and the electron that gets ionised on \(C_{60}\) as localised charge densities. This assumption allows us to re-write the ICD matrix element, Eq. 4.12, in the following form

\[
V = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \int 2p_s(r_{Ne}) 2s(r_{Ne}) \cdot \frac{r_{Ne}^l Y_{l}^{m}(\theta_a, \phi_a) \cdot Y_{l}^{m*}(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^{l+1}}
\cdot \Psi_{C_{60}}^r (r_{C_{60}}) \kappa(r_{C_{60}}) dV_{Ne} dV_{C_{60}}
\]  

(4.19)

where \(r_{Ne}\) represents the position vector of the recombining electron with respect to the centre of the displaced neon, which itself has a position vector \(D = (D, \theta_D, \phi_D)\) with respect to the centre of \(C_{60}\) (Fig. 4.6), and

\[
dV_{Ne} = r_{Ne}^2 dr_{Ne} sin\theta_{Ne} d\theta_{Ne} d\phi_{Ne}
\]

\[
dV_{C_{60}} = r_{C_{60}}^2 dr_{C_{60}} sin\theta_{C_{60}} d\theta_{C_{60}} d\phi_{C_{60}}
\]
The products $2p^*(r_{Ne})2s(r_{Ne})$ and $\Psi_{C_60}^*(r_{C_60})\kappa(r_{C_60})$ correspond to the charge densities that are localised on Ne and C$_{60}$ respectively. The above equation is a two-centre integral, because position vectors $r_{Ne}$ and $r_{C_60}$ originate from two different centres, namely, in that order, one that is located at the nucleus of the displaced neon, and one located at the centre of the C$_{60}$ cage. Evaluating two-centre integrals is a complicated process. It would be convenient if we could define all our functions with respect to a single centre, in our case, the one belonging to C$_{60}$. This coordinate transformation will pave the way for what we set out to investigate in the first place, i.e. the possible excitation of multipole C$_{60}$ plasmon oscillations as a result of ICD in the off-centre $(2s^1)\text{Ne}^+@C_{60}$.

We perform the coordinate transformation of neon orbitals using an analytical
method devised by Silverstone [79] for expressing Slater Type Orbitals relative to a displaced origin. Our aim is to find the spherical harmonic expansion of the function $\Psi(r-D)$, where $(r-D) = r_N$. This function corresponds to the wavefunction of the recombining electron on the displaced neon, now defined with respect to the centre of $C_{60}$. In order to do this, we adapt the following result from Silverstone to our specific case

$$\Psi(r-D) = \sum_{l=0}^{\infty} \sum_{\lambda=|L-l|}^{L+l} v_{l,\lambda,L}(r, D) \sum_{m=-l}^{l} \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}} c^\lambda(L, M; l, m) Y^M_{\lambda-m}(\theta_D, \phi_D) Y^m_l(\theta, \phi)$$

(4.20)

where

$$v_{l,\lambda,L}(r, D) = \frac{i^{\lambda-l}}{\pi} \int_{-\infty}^{\infty} k^2 j_\lambda(kD) j_l(kr) \bar{\psi}(k) dk$$

(4.21)

is the term that carries all the radial character of our wavefunction, and

$$\sqrt{\frac{2\lambda + 1}{4\pi}} c^\lambda(L, M; l, m) = \int Y^M_{\lambda-m*}(\theta, \phi) Y^m_l*(\theta, \phi) Y^M_L(\theta, \phi) d\Omega$$

(4.22)

are referred to as the Gaunt coefficients [76], with $d\Omega = \sin\theta d\theta d\phi$. These coefficients are non-zero only if the sum $\lambda + l + L$ is an even number. $L$ and $M$ are the orbital angular momentum and the magnetic quantum numbers, in that order, corresponding to the original orbital that is to undergo coordinate transformation, i.e. the one that is defined within neon’s system of coordinates. Since $Y^0_0$ is just a constant, the values of $(L, M)$ are decided by $Y^0_1$, and therefore $(L, M) = (1, 0)$.

In Eq. 4.21, $j_\lambda(kD)$ and $j_l(kr)$ are the spherical Bessel functions of orders $\lambda$ and $l$ respectively, $k = (k, \theta_k, \phi_k)$ represent the spherical polar coordinates only in this case, and

$$\bar{\psi}(k) = 2\pi i^{L-1} \Gamma(n - L + 1)(-k)^L \left( \frac{1}{k} \frac{d}{dk} \right)^L \frac{1}{k} [ (\zeta - ik)^{L-n-1} - (\zeta + ik)^{L-n-1} ].$$

(4.23)

The term $\Gamma(n - L + 1)$, where $n$ is the principal quantum number corresponding to
\( \Psi(r) \), is the gamma function\(^4\), not to be mistaken with the decay width \( \Gamma \).

For the displaced neon orbitals defined with respect to the centre of \( C_{60} \), Eq. 4.19 therefore reads

\[
V_D = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \int \Psi^* (r-D) \frac{Y_l^m(\theta, \phi) \cdot Y_l^{m*}(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^{L+1}} \Psi^*_{C_{60}} (r_{C_{60}}) \kappa (r_{C_{60}}) dV_{C_{60}}
\]

(4.24)

now with \( dV = r^2 \sin \theta d\theta \ d\phi \). The charge density on the displaced neon is expressed as a product of equations 4.9 and 4.10.

\[
2s2p_z = \frac{\zeta^4}{\pi} \left[ r_{Ne} - \zeta r_{Ne}^2 \right] e^{-2\zeta r_{Ne} \cos \theta}
\]

(4.25)

The above product is actually a combination of two STOs, one with \( n=2 \), and one with \( n=3 \). Let us fully write out the two STOs for simplicity

\[
2s2p_z = \frac{\zeta^4}{\pi} r_{Ne} e^{-2\zeta r_{Ne} \cos \theta} - \frac{\zeta^5}{\pi} r_{Ne}^2 e^{-2\zeta r_{Ne} \cos \theta}
\]

(4.26)

As mentioned previously, Silverstone’s equation, Eq. 4.20, has been devised for a single “bare” STO as defined by Eqn. 4.7. Therefore we need to initially exclude the normalisation factors that precede each STO in the above equation, displace each STO separately, multiply the resulting displaced STO’s by their corresponding normalisation constants, and finally add them up in order to find the total displaced wavefunction, \( \Psi(r-D) \)

\[
\Psi(r-D) = \frac{\zeta^4}{\pi} (\Psi_{n=2}^2 (r-D) - \zeta \Psi_{n=3}^2 (r-D))
\]

(4.27)

All we need from Eq. 4.26 in order to evaluate \( \Psi_{n=2}(r-D) \) and \( \Psi_{n=3}(r-D) \) are the values of \( n \) and the orbital exponent \( \zeta \). Both of the individual displaced STOs must be evaluated at \( 2\zeta \). Let us take a look at Eq. 4.20 again: the only place where \( n \) and \( \zeta \) appear is in the radial coefficient, Eq. 4.21, inside the function \( \tilde{\psi}(k) \) (Eq. 4.23). But since \( \zeta \) is the same for both STOs, the only difference between \( \Psi_{n=2}(r-D) \) and

\(^4\) \( \Gamma(w) = (w-1)! \), if \( w \) is a positive integer.
\( \Psi_{n=3}(r - D) \) is in fact in the values of \( n \). Let us write them out explicitly. For the STO with \( n = 2 \)

\[
\Psi_{n=2}^{2c}(r - D) = \sum_{l=0}^{\infty} \sum_{\lambda=|1-l|}^{1+l} v_{l,\lambda,1}^{n=2}(r, D) \sum_{m=-l}^{l} \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}} c^\lambda(1,0;l,m) \]

\[
\cdot Y_{\lambda}^{-m}(\theta_D, \phi_D) Y_{l}^{m}(\theta, \phi), \quad (4.28)
\]

and for the STO with \( n = 3 \)

\[
\Psi_{n=3}^{2c}(r - D) = \sum_{l'=0}^{\infty} \sum_{\lambda'=|1-l'|}^{1+l'} v_{l',\lambda',1}^{n=3}(r, D) \sum_{m'=-l'}^{l'} \left( \frac{2\lambda' + 1}{4\pi} \right)^{\frac{1}{2}} c^{\lambda'}(1,0;l',m') \]

\[
\cdot Y_{\lambda'}^{-m'}(\theta_D, \phi_D) Y_{l'}^{m'}(\theta, \phi). \quad (4.29)
\]

Let us introduce a few constraints on the parameters within Eq. 4.20 that will greatly simplify the evaluation of this and later equations. As we mentioned earlier, the Gaunt coefficients require the value of the sum \( \lambda + l + L \) to be an even number. We have already established that \( L = 1 \). This implies that, in order for the evenness requirement to be met, \( \lambda + l \) must also be an odd number. Since \( \lambda \) only takes integer values between and including \(|L - l|\) and \( L + l \), and since \( L = 1 \), therefore

\[
|1 - l| \leq \lambda \leq 1 + l, \quad (4.30)
\]

which means that for every value of \( l \), there are three values of \( \lambda \). We also require that \( \lambda \neq l \) for \( \lambda + l \) to be an odd number, which would mean that only two values of \( \lambda \) remain valid. Also, we know that \( m \) must satisfy \(-l \leq m \leq l\). But if we consider the case where \( M = 0 \) in \( Y_{\lambda}^{M-m} = Y_{\lambda}^{-m} \), \( m \) must eventually satisfy

\[
|m| \leq \lambda \quad (4.31)
\]

Keeping these constraints in mind, we evaluated the radial functions \( v_{l,\lambda,L}(r, D) \) (Eq. 4.21) by numerical means in MATLAB. Let us now substitute Eq. 4.27 into Eq.
\[ V_D = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \int \left( \frac{\zeta^4}{\pi} \left( \Psi_{n=2}^*(r - D) - \Psi_{n=3}^*(r - D) \right) \right) \cdot \frac{r^l \cdot Y_l^m(\theta, \phi) \cdot Y_l^{m*}(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^{l+1}} \cdot \Psi_{C_{60}}^*(r_{C_{60}}) \kappa(r_{C_{60}}) dV dV_{C_{60}} \] (4.32)

Substituting for the displaced wavefunctions using equations 4.28 and 4.29 yields

\[ V_D = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \left( \frac{\zeta^4}{\pi} \int \left[ \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} v_{l',m',1}^{(n=2)}(r, D) \sum_{l''=-l''}^{l''} \left( \frac{2\lambda + 1}{4\pi} \right)^{1/2} c^{\lambda'}(1, 0; l', m') \right] \cdot Y_{l'}^{-m'}(\theta, \phi) \right) \]

\[ \cdot Y_{l'}^{-m'}(\theta_D, \phi_D) \cdot Y_{l''}^{m''}(\theta, \phi) \]

\[ -\zeta \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} v_{l',m',1}^{(n=3)}(r, D) \sum_{m''=-l''}^{l''} \left( \frac{2\lambda' + 1}{4\pi} \right)^{1/2} c^{\lambda''}(1, 0; l'', m'') \]

\[ \cdot Y_{l''}^{-m''}(\theta_D, \phi_D) \cdot Y_{l''}^{-m''}(\theta, \phi) \]

\[ = \frac{r^l \cdot Y_l^m(\theta, \phi) \cdot Y_l^{m*}(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^{l+1}} \cdot \Psi_{C_{60}}^*(r_{C_{60}}) \kappa(r_{C_{60}}) dV dV_{C_{60}} \] (4.33)

This is a rather complicated equation, but the spherical symmetry of our system allows us to simplify it by integrating over \((\theta, \phi)\), i.e. the direction of the electron measured with respect to the coordinate system whose origin is defined at the centre of \(C_{60}\). The following orthonormality relation hold when integrating

\[ \int_{\theta,\phi} Y_l^m Y_l^{m*} \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'} \] (4.34)
Therefore Eq. 4.33 reduces to

\[
V_D = \sum_{l=0}^{\infty} \frac{4s^4}{2l+1} \sum_{\lambda=1-|l|}^{1+l} \sum_{m=-l}^{l} \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}} e^{i\lambda(1, 0; l, m)} Y_{\lambda}^{-m*}(\theta_D, \phi_D)
\]

\[
\cdot \int \left[ v_{l,\lambda,1}^{(n=2)*}(r, D) - \zeta v_{l,\lambda,1}^{(n=3)*}(r, D) \right] r^{l+2} dr
\]

\[
\cdot \int \Psi_{C_{60}}^*(r_{C_{60}}) \frac{r_{C_{60}}^{l} Y_{l}^{m*}(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^{2l+1}} \cdot \kappa(r_{C_{60}}) dV_{C_{60}}
\]  

(4.35)

which is a much simpler equation. We have multiplied the top and bottom of the ratio in the second integral by \( r_{C_{60}}^l \) so that the numerator is now a function of the form \( r^l Y_{l}^m(\theta, \phi) \). This function represents the multipole field of the fullerene plasmon [80], which interacts with that of the recombining electron on neon (see Eq. 4.33 for the multipole field of neon.). As mentioned before we can take advantage of the fact that \( r_{C_{60}} \approx R \), where \( R \) is the radius of \( C_{60} \), and move \( r_{C_{60}}^{2l+1} \approx R^{2l+1} \) outside of the integral (see Eqn. 4.37). We can not do the same with \( r_{C_{60}}^l \) that sits in the numerator as it is essential to the definition of the multipole field of \( C_{60} \).

The two integrals in Eq. 4.35 characterise the ICD process in the following way: the first integral corresponds to the decaying inner-valence vacancy on neon, while the second integral represents single ionisation on \( C_{60} \) as a result of the neon vacancy decay. The collection of all the terms that precede this integral, from here on referred to as \( P_{\lambda}^m(D) \), have all the information we will need in order to determine the behaviour of plasmon oscillations that may accompany ICD in \((2s^1)\text{Ne}^+@C_{60}\). We can therefore re-write Eq. 4.35 as

\[
V_D = \sum_{l=0}^{\infty} \sum_{\lambda=1-|l|}^{1+l} \sum_{m=-l}^{l} P_{\lambda}^m(D) \cdot \int \Psi_{C_{60}}^*(r_{C_{60}}) \frac{r_{C_{60}}^{l} Y_{l}^{m*}(\theta_{C_{60}}, \phi_{C_{60}})}{r_{C_{60}}^{2l+1}} \cdot \kappa(r_{C_{60}}) dV_{C_{60}}.
\]  

(4.36)
where \( P_{l\lambda}^m(D) \) now carries all the displacement-dependent character of \( V_D \).

\[
P_{l\lambda}^m(D) = \frac{1}{R^{2l+1}} \frac{4\zeta^4}{2l+1} \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}} c^\lambda(1,0;l,m) Y_{\lambda}^{-m*}(\theta_D, \phi_D)
\]

\[
\cdot \int [v_{l,\lambda,1}^{(n=2)*}(r,D) - \zeta v_{l,\lambda,1}^{(n=3)*}(r,D)] r^{l+2} dr
\]

(4.37)

Eq. 4.36 thus reduces to

\[
V_D = \sum_{l=0}^{\infty} \sum_{\lambda} \sum_{m=-\lambda}^{\lambda} P_{l\lambda}^m(D) \cdot \int \Psi_{C_{60}}^*(r_{C_{60}}) \cdot r_{C_{60}}^l Y_{l}^{m*}(\theta_{C_{60}}, \phi_{C_{60}}) \cdot \kappa(r_{C_{60}}) dV_{C_{60}}
\]

(4.38)

where \( \lambda = |1-l|, 1+l \).

We can further simplify by fixing the direction of neon’s displacement to be along the z-axis, i.e. \( D = (D, 0, 0) \). This would reduce the values of \( m \) into \( m = 0 \) only. The reason for this is that \( Y_l^m \propto (\sin \theta)^n \) for all \( m \neq 0 \), and \( \sin 0 = 0 \). Therefore for the moment, we will be only dealing with \( P_l^0(D) \), where

\[
P_l^0(D) = \sum_{\lambda} P_{l\lambda}^0(D) = \frac{1}{R^{2l+1}} \frac{4\zeta^4}{2l+1} \sum_{\lambda} \left( \frac{2\lambda + 1}{4\pi} \right)^{\frac{1}{2}} c^\lambda(1,0;l,m) Y_{\lambda}^0(\theta_D, \phi_D)
\]

\[
\cdot \int [v_{l,\lambda,1}^{(n=2)*}(r,D) - \zeta v_{l,\lambda,1}^{(n=3)*}(r,D)] r^{l+2} dr
\]

(4.39)

with \( \lambda = |1-l|, 1+l \).

In order to evaluate Eq. 4.39, once again we must resort to numerical integration tools in MATLAB. Some of the Gaunt coefficients (Eq. 4.22) are listed in Ref. [76]. We developed a numerical code for the evaluation of Eq. 4.22 which allows us to compute all the other coefficients \( c^\lambda(L, M; l, m) \).

Fig. 4.7 is a plot of \( |P_l^0/R^l| \) as a function of the displacement \( D \) for \( l = 0 - 5 \). \( R \) is the radius of \( C_{60} \) and the purpose of \( 1/R^l \) is to cancel out the units of \( P_l^0 \) (which
Figure 4.7: Plot of $P^0_l/R^l$ (R is the C$_{60}$ radius) in the log scale as a function of displacement of neon in the $z$ direction, evaluated numerically using MATLAB. The contribution for all $l > 1$ is negligible. Only $l=0,1$ make significant contributions. The monopole $l = 0$ is not important as the corresponding integral with the monopole term of C$_{60}$ in Eq. 4.36 vanishes. The dipole term does not change with displacement $D$, and interacts with C$_{60}$’s dipole term, thus giving rise to dipole plasmon oscillations on the surface of the fullerene.
Figure 4.8: Plot of $P^{0}_l / R^l$ (R is the C$_{60}$ radius) in the log scale as a function of displacement of neon in the $x$ direction, evaluated numerically using MATLAB. Only the dipole term with $l = 1$ makes a significant contribution to $\sum_{m=-\lambda}^{\lambda} P^m l(D)$ (Eq. 4.36). This term remains constant with displacement and has the same value as in Fig. 4.7.
has units of length). This plot shows that the only significant contributions to $P_l$ come from $l = 0$ and $l = 1$. The former corresponds to the degree of excitation of the monopole plasmon oscillation, while the latter represents that of the dipole plasmon oscillation. The dipole contribution remains constant with displacement, which is what we expected to happen as the motion of a dipole inside another dipole should not affect the interaction energy of the two dipoles. The monopole contribution is not important as it is cancelled by the zero monopole term on C$_{60}$ (see Eq. 4.38).

We also plotted $P_l^0/R^l$ for $(\theta_D, \phi_D) = (\pi/2, 0)$, i.e. with displacement in the $x$ direction (Fig. 4.8). These plots suggest that the only significant contribution to $V_D$ and thus to $\Gamma(D)$ (Eq. 4.1) is the dipole term with $l = 1$, which remains constant no matter what the location of neon is inside the cage. This also means that the giant dipole resonance is the only mode of the plasmon oscillation that gets excited following ICD in (2s$^1$)Ne$^+@C_{60}$, and its value remains constant regardless of the location of the confined neon. These results are of course only valid when there is no overlap between neon and C$_{60}$. But at some radius $r < R$ overlap will start to play a role. Just at which radius this overlap becomes important and how it affects the ICD rate is what we will investigate in the next section using a numerical technique that implements the Wigner-Weisskopf approximation.

### 4.2.2 Numerical Evaluation of the ICD Width in (2s$^1$)Ne$^+@C_{60}$: Dependence of $\Gamma_{ICD}$ on Neon’s Position Inside the Cage

Our semi-analytic approach relied on the assumption that there is zero overlap between neon and the cage, which allowed us to ignore the exchange contribution to the total ICD width. But in order to evaluate accurate values for $\Gamma_{ICD}$ we must also take into account the exchange term. We do this by using a numerical approach based on the Wigner-Weisskopf (WW) method and the Stieltjes Imaging technique (chapter 3). Here we evaluate the ICD width using a code $^5$ that implements this numerical

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$^5$ Code developed by Vitali Averbukh
method by using as input the Coulomb integrals in the molecular orbital basis \(^6\).

Fig. 4.9 shows the ICD widths and energies calculated at the MP2 level for Ne@C\(_{60}\), plotted against displacement D of neon from the centre of C\(_{60}\) for \(D = 0 - 2.5 \ a_0\). The MP2 energies (the red curve) are given with respect to the centrally symmetric Ne@C\(_{60}\) whose energy defines zero in this case. The basis set used is cc-pVQZ \([81]\) augmented by 3s3p2d Kaufmann-Baumeister-Jungen (KBJ) \([82]\) diffuse functions for neon, and is 6–31\(G\) \([83]\) for carbon. The plot shows that the energy remains constant and equal to that of the centrally symmetric case up to a displacement of about \(1 \ a_0\) where the energy starts to rise. The ICD width (the black curve) also experiences the same plateau region (within the errors of the Stieltjes Imaging technique) with a constant ICD width around 0.4 eV spanning a range \(D < 1 \ a_0\). The ICD width then starts to rise so that at \(D = 2.5 \ a_0\) it reaches a value of 0.9 eV.

The steep rise in \(\Gamma_{\text{ICD}}\) is due to the onset of neon overlapping with the wall of C\(_{60}\). The steep rise in energy is due to the increasing Coulomb repulsion between the electrons of neon and those of C\(_{60}\) as neon approaches the wall of the cage.

### 4.3 Summary and Conclusions

In this chapter we have derived analytical expressions that relate the rate of ICD in the at-centre and off-centre \((2s^1)\)Ne\(^+\)@C\(_{60}\) to the C\(_{60}\) plasmon oscillations starting from the Wigner-Weisskopf expression for \(\Gamma_{\text{ICD}}\) in terms of the Coulomb potential matrix elements. The much smaller size of neon compared to the diameter of C\(_{60}\) and also the weak van der Waals interaction between neon and the cage allowed us to ignore the exchange contribution to \(V\): The weak van der Waals interaction means that neon spends most of its time near the centre of the cage, although it experiences vibrations about the centre with a turning point of approximately \(1 \ a_0\) at room temperature \([72]\). The smallness of neon implies that it can freely roam about the centre.

\(^6\) We use MOLCAS for all our numerical quantum chemistry calculations.
Figure 4.9: Plot of ICD widths and MP2 energies for Ne@C\textsubscript{60} versus displacement D of neon from the centre of C\textsubscript{60}. The ICD width is calculated numerically within the WW approximation. The basis set used is cc-pVQZ \cite{81} augmented by 3s3p2d Kaufmann-Baumeister-Jungen (KBJ) \cite{82} diffuse functions for neon and 6-31G \cite{83} for carbon. The MP2 energies (the red curve) are given with respect to the energy of the centrally symmetric Ne@C\textsubscript{60} which in this case defines the zero of energy. The plot shows that the energy remains constant and equal to that of the centrally symmetric case up to a displacement of about 1 \textit{a}_{0} where the energy starts to rise. The ICD width (the black curve) also experiences the same plateau region (within the errors of the Stieltjes Imaging technique) with a constant ICD width around 0.4 eV spanning a range \textit{D} < 1 \textit{a}_{0}, where it starts to rise. The steep rise in \Gamma_{ICD} is due to the onset of neon overlapping the wall of C\textsubscript{60}. The steep rise in energy is due to the increasing Coulomb repulsion between the electrons of neon and those of C\textsubscript{60} as neon approaches the wall of the cage.
up to a radius of about 1 \( a_0 \) before it overlaps with the wall of \( C_{60} \). It also allows us to express the Coulomb operator \( 1/|\mathbf{r} - \mathbf{r}_{C_{60}}| \) in a multipole expansion, which makes it possible for us to analytically separate the recombination on neon and the ionisation on \( C_{60} \).

For the off-centre case we employed an analytical technique developed by Silverstone [79] in order to redefine the orbitals of the off-centre neon relative to the centre of \( C_{60} \). This led to an equation involving a sum over functions of the form \( r^l Y_l^m(\theta, \phi) \) for both neon and \( C_{60} \). The correlation between these functions helped us understand the relation between ICD in \( (2s^1)Ne^+ \oplus C_{60} \) and the different modes of fullerene plasmon oscillations.

Numerical evaluation of the contribution from neon, which acted as coefficients to \( C_{60} \)'s ionisation matrix element, helped us understand which modes of \( C_{60} \) plasmon oscillation get excited as a result of ICD, and also how the ICD rate changes as a function of location of neon inside \( C_{60} \). Our results as shown in Fig. 4.7 and Fig. 4.8 predict that the only significant contribution to the total ICD width comes from the dipole \( l = 1 \) term which remains constant with the displacement of neon from the centre of \( C_{60} \). This suggests that it is a valid assumption to consider the decay width of 2s-ionised Ne inside \( C_{60} \) to be constant throughout the cage, with the dipole contribution corresponding to the interaction energy of two dipole charge distributions, one inside the other.

We also evaluated \( \Gamma_{ICD} \) numerically as a function of displacement of neon from the centre of \( C_{60} \), this time including the exchange contribution which makes the numerical approach a more accurate one. Our results showed an initial plateau up to neon’s vibrational turning point at room temperature (1 \( a_0 \)) followed by a rise that is indicative of the onset of neon’s overlap with the cage. The plateau that we found numerically confirms our analytical findings.
4.4 Outlook

Further investigation of other noble gas endohedral fullerenes is required in order to provide a better picture for the dependence of the ICD rate on the location of the confined atom. These studies could only be carried out numerically using the Wigner-Weisskopf approximation. This is because any noble gas with larger atomic number than neon would be larger than neon, and we have already seen in Fig. 4.2 that argon already shows a large overlap with the $C_{60}$ cage. Therefore we can no longer ignore the exchange contribution to ICD and thus would not be able to proceed analytically as we did with Ne@$C_{60}$. So a sensible next step would be to investigate ICD in Ar@$C_{60}$, and how the location of Ar inside the cage would affect the ICD width, $\Gamma_{ICD}$.

To the author’s best knowledge there has been no experimental evidence for ICD in Ne@$C_{60}$ to this date. Here we briefly suggest two methods of detecting ICD in the said system: 1) one way would be to detect the ICD electrons that are released into the continuum following ICD, using current available low-energy electron spectroscopic techniques [12], or 2) by comparing a sample of Ne@$C_{60}$ to one of pure $C_{60}$ and detecting the fragments that may be released, if any, following photoionisation of a Ne 2s orbital inside the $C_{60}$ cage.

In this thesis we have only looked at ICD in endohedral fullerenes. ICD could also take place in exohedral fullerenes where the atom is attached to the $C_{60}$ cage from the outside rather than confined inside the cage. It would also be interesting to investigate the fate of a noble gas endohedral fullerene after ICD has taken place by taking the motion of the $C_{60}$ nuclei into account - will the doubly ionised structure remain stable, or will it disintegrate in a Coulomb explosion?
Chapter 5

Single Photon Laser-enabled Interatomic Coulombic Decay

5.1 Introduction

So far we have introduced Interatomic Coulombic Decay, and investigated it thoroughly in endohedral fullerenes where the ICD rate is ultrafast. ICD can take place in any hydrogen-bonded or van der Waals cluster with an inner-valence vacancy on one monomer unit provided that the energy of this vacancy is above the double ionisation threshold of the cluster. In chapter 1 we looked at the fate of a 2s vacancy on one of the monomers in the neon dimer, which decays via ICD. The situation would be different in a weakly bound heterocluster such as NeAr, where the location of the initial inner-valence vacancy becomes an important factor: ICD could proceed only if the initial iv-hole has enough energy to ionise the neighbouring monomer. Energetically only neon has the capacity to host an iv-vacancy that decays via the ICD channel in NeAr. An initial 3s-vacancy on argon is not energetic enough to initiate ICD, based on the above-mentioned energy criteria. In this case the NeAr cluster would be ICD-inactive, and left to its own devices, would decay via the slow (nanoseconds) process of photoemission. There is however the possibility of inducing ICD by injecting the cluster with a single external photon that carries the additional energy required for the double ionisation of the cluster. We refer to this mechanism
Figure 5.1: Schematic representation of $sp$LEICD in NeAr+: a $3p$ electron on Ar recombines into the $3s$ vacancy. The resulting energy is transferred onto Ne where a $2p$ electron escapes into the continuum with the help of a single external photon.

as single-photon Laser Enabled Interatomic Coulombic Decay, $sp$LEICD for short. Fig. 5.1 is a schematic of this process in NeAr: a $3s$ vacancy on argon is filled by an argon $3p$ electron. The energy of this transition is not enough to induce outer-valence ionisation on the neighbouring neon atom. NeAr is therefore ICD-inactive. However a single external photon of the right energy could enable this ionisation in the process of $sp$LEICD.

A process similar to $sp$LEICD can take place in isolated atoms or molecules with an inner-valence vacancy that is energetically below the double ionisation threshold (DIP). These excited ionic states of isolated atoms or molecules can therefore not decay through the Auger process and instead decay via the slow process of photo-emission. In such cases, shining a single [84] or multiple [85–87] external photons on the system can activate the Auger process. These mechanisms are referred to as single photon Laser-Enabled Auger Decay ($sp$LEAD) and Laser-Enabled Auger Decay (LEAD) respectively.
Since \( sp \)LEICD is an interatomic process mediated by the Coulomb interaction between two or more monomer units, it naturally has a high sensitivity to the distance between monomer units. \( sp \)LEICD therefore offers the capacity to be developed into a spatially-resolved spectroscopic technique for studying inner-valence ionised states, complementary to the recently theoretically-developed \( sp \)LEAD spectroscopy technique [84] which is currently undergoing experimental investigation.

In this chapter we will study \( sp \)LEICD by building upon the theoretical and numerical methods developed and used by Ref. [84] for \( sp \)LEAD. The following section 5.2 will give a detailed analysis of the energy criteria for the \( sp \)LEICD using NeAr as an example. The quantity we use in order to characterise \( sp \)LEICD is the photoionisation cross section and in section 5.3 we will develop the tools necessary for the calculation of this quantity. Using these tools we calculate the \( sp \)LEICD cross section the NeAr dimer. As previously mentioned we expect the \( sp \)LEICD cross section to depend on the internuclear distance. We investigate this thoroughly both numerically and analytically in section 5.4. In section 5.5 we investigate the larger ArNe\(_5\) cluster as well as the hydrogen-bonded protonated ammonia dimer in section 5.6 Our investigations will pave the way towards future research into \( sp \)LEICD spectroscopy as a potential time-resolved technique for the study of inner-valence ionised states in weakly bound clusters.

### 5.2 \( sp \)LEICD in NeAr\(^+(3s^{-1})\)

The NeAr hetero-dimer is held together by the weak van der Waals force, thus making it a suitable platform for studying \( sp \)LEICD (Fig. 5.1). It has an equilibrium bond length of 3.5 Å [88]. The criteria for choosing a weakly bound cluster where \( sp \)LEICD could proceed are three-fold: 1. the energy released as a result of \((np \rightarrow ns)\) transition following the initial photoionisation must be lower than the double ionisation potential (DIP) of the atom that hosts the initial vacancy (i.e. Auger-inactive)
or of the cluster (i.e. ICD-inactive), 2. the energy of the single external photon must be lower than the single ionisation potentials of the ionised cluster and of each of its constituent units (i.e. no direct ionisation) and, 3. the energy of the single external photon must be low enough so as to block the \( sp\)LEAD channel. \( sp\)LEICD will only take place if the photon arrives before the process of radiative decay which is expected on a nanosecond time scale.

For NeAr\(^+\)(3s\(^-\)) cluster we take a closer look at the energetic requirements for \( sp\)LEICD. Firstly we use the NIST atomic energy levels database to estimate the energy of the initial state with a (3s) vacancy on argon,

\[
E(\text{Ar}[3s3p^6]) = 29.24\text{eV} \quad (5.1)
\]

where this energy and all that follow are expressed relative to the ground state of the neutral NeAr cluster where we have neglected any effects from polarisation.

The double ionisation threshold for the cluster corresponds to the state Ne\(^+\)(2p\(^5\))Ar\(^+\)(3p\(^5\)). This is expressed as [88]

\[
\text{(DIP)}_{\text{NeAr}} = \text{IP(Ne)} + \text{IP(Ar)} + \frac{14.40 \text{eV.Å}}{R} \quad (5.2)
\]

where the last term refers to the Coulomb repulsion that arises from having a charge on each atom with the interatomic distance represented by \( R \) in Å. At the equilibrium distance this is 41.43 eV. This means that in order to open the \( sp\)LEICD channel we require a photon with an energy given by

\[
\hbar \omega = \text{IP(Ne)} + \text{IP(Ar)} + \frac{14.40 \text{eV.Å}}{R} - E(\text{Ar}[3s3p^6]) \quad (5.3)
\]

found to be 12.2 eV at the equilibrium bond length.

The double ionisation threshold argon is 43.39 eV, and therefore the minimum
photon energy required for an Auger process occurring on the argon centre with a spectator neutral neon from our initial state is given by

\[ \hbar \omega = (\text{DIP})_{\text{Ar}} - E(\text{Ar}[3s3p^6]), \tag{5.4} \]

which yields 14.2 eV. For the calculation of the spLEAD threshold we do not need the Coulomb term because neon plays the role of a spectator and so remains neutral throughout the process.

The final state for an ETMD channel leaves two outer-valence holes on the neon and a neutral argon i.e. Ne^{++}(2p^4)Ar. As with the final products of ICD and spLEICD, Ne^{++}(2p^4)Ar may also be prone to disintegration in which case it would be a suitable candidate for coincidence measurement techniques. The minimum energy required from a photon to open up an ETMD channel is calculated using

\[ \hbar \omega = (\text{DIP})_{\text{Ne}} - E(\text{Ar}[3s3p^6]) \tag{5.5} \]

and is found to be 33.28 eV.

Given the spLEICD and spLEAD thresholds are 12.2 and 14.2 respectively, we are left with a photon energy window of 2 eV where spLEICD will be the only process of decay. Since the threshold for ETMD is much higher than spLEAD we do not need to consider these channels any further.

### 5.3 The spLEICD Cross Section

The quantity we use in order to characterize spLEICD is the photoionisation cross section, \( \sigma \), a measure of the likelihood for spLEICD to take place as a function of photon energy. The cross section in the length gauge and within the dipole approximation
can be written as
\[
\sigma_n(\omega) = \frac{4}{3} \pi^2 \alpha \omega \left| \sum_{j=1}^{N-1} \vec{r}_j | \Psi_{E_n+\omega}^{(N-1)} \right|^2
\] (5.6)

where \( \sum_j^{N-1} r_j \) is the dipole operator, and \( \omega \geq \text{DIP} - E_n \) is the frequency of the single external photon, and \( E_n \) is the energy of the one-hole (1h) state \( \Psi_{n}^{(N-1)} \) (\( \text{IP}<E_n<\text{DIP} \)). \( \Psi_{E_n+\omega}^{(N-1)} \) represents the final continuum state \( (E_f = E_n + \omega) \) that has a two-hole-one-particle (2h1p) character, and is normalized to a delta function in energy:
\[
\langle \Psi_{E_f} | \Psi_{E_f} \rangle = \delta(E_f - E'_f)
\] (5.7)

For the case of the NeAr cluster we can express the initial wavefunction \( \Psi_{n}^{(N-1)} \) as \( iv \text{Ar} \) and the final wavefunction \( \Psi_{E_n+\omega}^{(N-1)} \) as \( ov \text{Ar} ov \text{Ne} k \), where \( iv \) stands for the inner-valence hole, \( ov \) the outer-valence hole, and \( k \) represents a continuum electron.

In chapter 4 we approximated the wavefunctions by single Slater determinants. But we cannot adopt the same approximation here since neither of the two holes in the final state corresponds to the hole in the initial state, and because we are using the dipole approximation, which is a one-particle operator, the matrix elements would vanish as a consequence of the Slater–Condon rules (chapter 2); spLEICD is essentially a second-order process. We must therefore resort to more accurate theoretical techniques that explicitly include electron correlation in the initial and final cationic wavefunctions. In order to do this we use the many-body Green’s function technique called the Algebraic Diagrammatic Construction (ADC) method (chapter 3), specifically ADC(2)x which is truncated up to second-order perturbation theory. Within the ADC(2)x scheme the cationic wavefunctions in the Intermediate State Representation (ISR) can be expressed as
\[
\Psi^{(N-1)} = \sum_i c_i \phi_i + \sum_{ij} c_{ij}^a \phi_{ij}^a
\] (5.8)
Figure 5.2: Schematic diagram of NeAr on Cartesian coordinate axes: with neon at the origin, argon lies 3.5 Å away from neon along the x-direction. In this figure, the single incident photon that enables ICD is polarised along the z axis.

where $\phi_i$ and $\phi^a_{ij}$ are the so-called intermediate states of $1h$ (one-hole) and $2h1p$ (two-hole-one-particle) types respectively, with indices $i$ and $j$ representing hole states, and $a$ a particle state.

We carefully select $2h1p$ (two-hole-one-particle) configurations for the final state that corresponds to the ICD transition and remove configurations that relate to an Auger or ETMD channel.

The ADC(2)$\times$ method is implemented in a code that requires as input the SCF energy and Coulomb matrix elements that we calculate using the quantum chemistry software MOLCAS [40]. These ADC calculations are performed using $\mathcal{L}^2$ GTO basis for both the initial and final states of the process. This results in discrete pseudo states in the continuum for the final electronic states corresponding to $sp$LEICD. We therefore need to renormalise them to a delta function in energy using the Stieltjes Imaging technique described in chapter 3.
Figure 5.3: Photoionisation cross section for spLEICD in NeAr$^+$ at the equilibrium distance R=3.5 Å for three polarisations, x, y, and z of the incident photon as indicated on the bottom left hand side of each panel. The cross section is maximum when the polarisation of the incident photon is directed along the x axis, which in this case coincides with the molecular axis. The “y and z cross sections” are both the same due to the symmetry of the molecule, and smaller than the “x cross section” by an order of magnitude. The total cross section (the bottom right hand panel) has a maximum value of about 0.011 at the spLEICD threshold, and gets most of its contribution from the “x cross section”. The legend shows the Stieltjes Imaging orders where convergence has been achieved (see text). The basis set used for both neon and argon is cc-pV5Z [81] with 5s5p5d added Kaufmann Baumeister Jungen (KBJ) [82] diffuse functions.
The spLEICD Cross Section for NeAr

The single external photon that enables spLEICD is assumed to be linearly polarised. Fig. 5.2 shows the geometry of NeAr and the polarisation of the incident photon relative to the molecular axis. In order to calculate the total spLEICD cross section, we average over the partial contributions from three perpendicular $x$, $y$, and $z$ polarisations of the incident photon.

Fig. 5.3 shows the spLEICD cross section for NeAr for the $x$, $y$, and $z$ polarisations of the incident photon, and also the average cross section over all polarisation contributions, as presented in the bottom right hand panel of the said figure. These calculations were performed in the cc-pV5Z basis set [81] with 5s5p5d added Kaufmann Baumeister Jungen (KBJ) [82] diffuse functions using the equilibrium bond length of 3.5 Å. The calculated cross section is shown in the energy window for which spLEICD is the only possible laser-enabled decay mechanism, i.e. between 12.2 and 14.2 eV. The legend shows the Stieltjes Imaging orders at which the spectral moments, used in the evaluation of approximate values for the photoionisation cross section, have converged (see chapter 3).

As Fig. 5.3 shows, the spLEICD cross section for NeAr$^+$ is relatively small overall. The top left hand panel shows the spLEICD cross section when the polarisation of the incident photon is along the $x$ axis, which in this case is coincident with the molecular axis. Here the cross section has a maximum value of about 0.0093 Mb at the spLEICD threshold (12.2 eV), but falls steeply onto a plateau where it experiences a minimum value of about 0.0048 Mb at the spLEAD threshold (14.2 eV). The cross sections from the $y$ and the $z$ polarisations i.e. when the polarisation of the incident photon is transverse to the molecular axis, were found to be identical which is due to the symmetry of the system. They are however very small, with a maximum value that is roughly an order of magnitude less than the peak cross-section from the $x$-polarisation. Therefore most of the contribution to the total cross section
(the bottom right hand panel) comes from the “x cross section”. Plot of the total cross section indicates that the maximum \( sp \)LEICD cross section when NeAr is at its equilibrium bond length (3.5 Å) occurs at a photon energy of 12.2 eV and has a value of about 0.011 Mb. This is a relatively small cross section which makes the \( sp \)LEICD cross section in NeAr a challenge to measure experimentally.

We expect that the presence of a maximum in the total cross section of NeAr is due to a resonance. In section 5.4 we will derive a mechanism for \( sp \)LEICD that could help explain the presence of this resonance. We will first make use of the said mechanism in order to explain the features in the cross section for ArNe\(_5\) in section 5.5, but similar arguments will also hold for NeAr.

### 5.4 Dependence of the \( sp \)LEICD cross section on the internuclear distance

As we mentioned earlier ICD (and therefore \( sp \)LEICD) is mediated by the Coulomb interaction which has a strong dependence on the internuclear distance. Previous work has found that the ICD rate has an \( R^{-6} \) dependence on the separation between cluster sub-units \([45,89]\). As we have shown in the previous chapters the ICD rate is proportional to the square of the Coulomb matrix element. Below we investigate whether the \( sp \)LEICD cross section which depends on the square of the dipole matrix element will have the same \( R \)-dependence as has been found previously for ICD. We will investigate this both analytically and numerically.

**The analytical dependence**

In order to arrive at an analytical formula for the dependence of the \( sp \)LEICD cross section on the internuclear distance \( R \), we express the general equation for the photoionisation cross section (Eq. 5.6) in terms of the transition dipole matrix elements between 1\( h \) (one-hole) and 2\( h1p \) (two-hole-one-particle) states \( \tilde{D}_{i,a'j'} \) as de-
fined within the framework of the ADC(2)\(x\) scheme (chapter 3), in the following way

\[
\sigma_{spLEICD}(\omega) = \frac{4}{3} \pi^2 \alpha \omega |\tilde{D}_{i,\alpha',i',j'}|^2, \tag{5.9}
\]

where the transition dipole matrix element, \(\tilde{D}_{i,\alpha',i',j'}\), between a \(1h\) (one-hole) and a \(2h1p\) (two-hole-one-particle) state is generally defined within the ADC(2)\(x\) scheme [55] as

\[
\tilde{D}_{i,\alpha',i',j'} = \delta_{ij'}d_{\alpha'\alpha'} - \delta_{ii'}d_{j'a'} + \delta_{ii'}\sum_{c,k} \nu^*_{\alpha'k,j'd_{ck}} - \delta_{ij'}\sum_{c,k} \nu^*_{\alpha'i',j'd_{ci}}. \tag{5.10}
\]

The subscripts \(i, j\) and \(a, c\) correspond to occupied (hole) and unoccupied (particle) orbitals, respectively. \(d\) stands for the dipole operator and \(d_{pq}\) (where \(p, q\) can represent either occupied or unoccupied orbitals) denote the dipole matrix elements. For example for the case of \(spLEICD\) in NeAr\(^+\) we are interested in the transition dipole matrix elements between \(1h\) (one-hole) and \(2h1p\) (two-hole-one-particle) states; our initial \(1h\) state is made up of a single inner-valence orbital vacancy on argon (\(iv_{Ar}\)) corresponding to the index \(i\) in the above equation, and our final state of one hole on the argon \(3p\) (\(ov_{Ar}\)) orbital, another hole on the neon \(2p\) (\(ov_{Ne}\)) orbital, and a particle in the continuum, represented by \(i', j',\) and \(k\) respectively. The Kronecker delta functions are between the initial hole and each of the final two holes. The terms \(\nu_{pqrs}\) – where the indices correspond to general (occupied or unoccupied) orbitals – represent the antisymmetrised Coulomb matrix elements, \(V\) through the following relation:

\[
\nu_{pqrs} = \frac{V_{pqrs} - V_{pqsr}}{\epsilon(pqrs)}, \tag{5.11}
\]

where \(\epsilon(pqrs) = \epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s\) is a combination of HF orbital energies.

As the two holes in the final state are different from the one hole in the initial
state Eq. 5.10 reduces to

\[
\hat{D}_{iv_{Ar},k ov_{Ar} ov_{Ne}} = - \sum_c \nu_{c,k ov_{Ar} ov_{Ne}}^* d_{c iv_{Ar}}
\]  

(5.12)

as a consequence of the Slater–Condon rules (see chapter 2). The sum is over all unoccupied orbitals \(c\). Substituting this transition dipole matrix element into the formula for the \(sp\)LEICD cross section (Eq. 5.11) this becomes

\[
\sigma_{sp\text{LEICD}}(\omega) \approx \frac{4}{3} \pi^2 \alpha \omega |\hat{D}_{iv_{Ar},k ov_{Ar} ov_{Ne}}|^2 
\]

\[
\approx \frac{4}{3} \pi^2 \alpha \omega \left| - \sum_c \frac{1}{\epsilon_{c,k ov_{Ar} ov_{Ne}}} \left( \langle ov_{Ar}(1) ov_{Ne}(2) | \frac{1}{r_{12}} | c(1) k(2) \rangle - \langle ov_{Ar}(2) ov_{Ne}(1) | \frac{1}{r_{12}} | c(2) k(1) \rangle \right) \cdot \langle c(1) | d| iv_{Ar}(1) \rangle \right|^2
\]

(5.13)

The Coulomb operator \(1/r_{12} = 1/|r_1 - r_2|\) corresponds to inter-electronic interaction where \(r_1\) and \(r_2\) are positions of electrons 1 and 2 with respect to the centre of their corresponding monomers. In order to obtain the dependence of the \(sp\)LEICD cross section on the internuclear distance we must express the inter-electronic Coulomb interaction in terms of coordinates that allow us to access \(R\) as a variable. Fig. 5.4 is a schematic of NeAr showing how this coordinate transformation could be carried out by defining \(r_i = x_i - R_i\), where \(R_i\) \((i = 1, 2)\) and \(x_i\) share the same origin and define the position vectors of the centre of mass of the monomer and electron \(i\) respectively. We can therefore express Coulomb operator as a multipole expansion \([45]\) in term of \(R\)

\[
\frac{1}{|x_1 - x_2|} = \frac{1}{R} - \frac{\textbf{u}_R \cdot (r_1 - r_2)}{R^2} + \frac{3}{2} \frac{[\textbf{u}_R \cdot (r_1 - r_2)]^2 - (r_1 - r_2)^2}{R^3} + O(\frac{1}{R^4})
\]

(5.14)

where \(\textbf{u}_R := \frac{R_1 - R_2}{R}\) is a unit vector along the direction of \(R_1 - R_2\).
Figure 5.4: Schematic diagram of NeAr$^+$. $\mathbf{r}_i (i = 1, 2)$ is the position vector of electron $i$ with respect to the centre of mass $\mathbf{R}_i (i = 1, 2)$ of its corresponding monomer unit. $\mathbf{x}_i$ defines the position of electron $i$ where $\mathbf{r}_i = \mathbf{x}_i - \mathbf{R}_i$. The internuclear distance is defined by $R = |\mathbf{R}_1 - \mathbf{R}_2|$. 
The above multipole expansion is based on the assumption that there is no overlap between the orbitals of the two monomers and is therefore valid for sufficiently large $R$. We can substitute the expansion into Eq. 5.13 where we ignore the exchange Coulomb matrix element because we assume zero overlap between the orbitals of neon and argon that are involved in $sp$LEICD. The direct Coulomb matrix element takes the following form after the substitution

$$
\langle ov_{Ar}(1) \ ov_{Ne}(2) | \frac{1}{x_{12}} | c(1) k(2) \rangle = \frac{1}{R^3} \left( \langle ov_{Ar}(1) | \mathbf{r}_1 | c(1) \rangle \cdot \langle ov_{Ne}(2) | \mathbf{r}_2 | k(2) \rangle \\
-3\langle ov_{Ar}(1) | \mathbf{r}_1 \cdot \mathbf{u}_R | c(1) \rangle \langle ov_{Ne}(2) | \mathbf{r}_2 \cdot \mathbf{u}_R | k(2) \rangle \right) + O\left(\frac{1}{R^4}\right),
$$

(5.15)

where we have made use of the fact that $\langle ov_{Ar}(1) | c(1) \rangle = 0 = \langle ov_{Ne}(2) | k(2) \rangle$. We substitute the direct Coulomb matrix element Eq. 5.15 back into the equation for the $sp$LEICD cross section (Eq. 5.13):
\[ \sigma_{\text{spLEICD}}(\omega) \approx \frac{4\pi^2\alpha \omega}{3} \left| \frac{1}{R^3} \sum_c \frac{1}{\epsilon_{\text{ivAr},k} \text{ovAr} \text{ovNe}} \right| \]

\[ \left( \langle \text{ovAr}(1)|r_1|c(1)\rangle \cdot \langle \text{ovNe}(2)|r_2|k(2)\rangle \right) \]

\[ -3\langle \text{ovAr}(1)|r_1 \cdot u_R|c(1)\rangle \langle \text{ovNe}(2)|r_2 \cdot u_R|k(2)\rangle \]

\[ \cdot \langle c(1)|d|\text{ivAr}(1)\rangle \left| \frac{2}{2} \right| \]

\[ = \frac{4\pi^2\alpha \omega}{3R^6} \left| \sum_c \frac{1}{\epsilon_{\text{ivAr},k} \text{ovAr} \text{ovNe}} \right| \]

\[ \left( \langle \text{ovAr}(1)|r_1|c(1)\rangle \cdot \langle \text{ovNe}(2)|r_2|k(2)\rangle \right) \]

\[ -3\langle \text{ovAr}(1)|r_1 \cdot u_R|c(1)\rangle \langle \text{ovNe}(2)|r_2 \cdot u_R|k(2)\rangle \]

\[ \cdot \langle c(1)|d|\text{ivAr}(1)\rangle \left| \frac{2}{2} \right| \]

Eq. 5.12 limits the role played by the dipole operator – which represents an external photon – to facilitating transition from an unoccupied orbital to the initial orbital vacancy only, which in the case of spLEICD in NeAr$^+$ is an inner-valence vacancy on argon (ivAr). This already narrows down the possible mechanisms for spLEICD. Eq. 5.13 then provides us with a step by step mechanism that describes the process of spLEICD. According to this equation, the spLEICD mechanism is divided into two separate steps as indicated by matrix elements of the Coulomb (step 1) and dipole (step 2) operators. We start from an (N-1)-electron state with an inner-valence (3s) vacancy on argon. Initially electron correlation between neon and argon causes an outer valence (ov) electron on argon to be excited onto an unoccupied (virtual) or-
bital, $c$, while an ov-electron on neon escapes into the continuum, $k$. This creates an ov-hole on both neon and argon, $ov_{Ne}$ and $ov_{Ar}$ respectively. We now have a $2h1p$ (two-hole-one-particle) state. Therefore step 1 involves the Coulomb interaction $\frac{1}{r_{12}}$ sending electrons from $ov_{Ne}$ and $ov_{Ar}$ out into $k$ and $c$ respectively. Both the direct and exchange terms play a role here. In step 2, a photon of light interacts with the electron in $c$ and de-excites it into the iv-hole on argon, $iv_{Ar}$. This step is illustrated by the matrix element of the dipole operator, $d$. Since the virtual orbitals do not belong to any particular atom, this last term is independent of the internuclear distance, $R$. A schematic diagram of the mechanism that we inferred from Eq. 5.13 is shown in Fig. 5.5.

![Figure 5.5: Schematic representation of spLEICD in NeAr$^+$: possible two-step mechanism inferred from ADC(2)$x$. In step 1 of the process as indicated on top of the figure, electron correlation between outer-valence electrons on Ne and Ar$^+$ causes excitation of an Ar 3$p$ and ionisation of a Ne 2$p$ electron. In step 2, an external photon interacts with the excited electron on Ar and de-excites it into the initial Ar 3$s$ vacancy.](image)

We therefore conclude from the above analysis that spLEICD depends on the internuclear distance through an $R^{-6}$ relationship. This is the same distance dependence as has been seen previously for ICD [45].

The Numerically evaluated dependence

Complementary to our analytical approach in the previous section are our numerical calculations of the dependence of spLEICD cross section on the internuclear distance
Fig. 5.6 is a plot of the $sp$LEICD cross section versus the internuclear distance $R$ for $R = 2.8 - 8.0$ Å. It was obtained by integrating the $sp$LEICD cross section in the $sp$LEICD only energy window for each value of internuclear distance $R$. We used a basis set cc-pV5Z with 5s5p5d added KBJ diffuse functions for both neon and argon [81,90].

The color-coded linear fits to the data correspond to $R^{-12}$ (the blue line) and $R^{-6}$ (the red line) dependences on the internuclear distance. The $R^{-12}$ dependence ends at $R \approx 5$ Å where it is then immediately followed by the $R^{-6}$ dependence.
The $R^{-6}$ dependence of the \textit{sp}LEICD cross section on $R$ agrees with our previous analytical derivation in the limit of sufficiently large internuclear distances, in this case $R > 5$ Å.

Fig. 5.6 does not take into account the spread on the ground state nuclear wavefunction of NeAr$^+$. More accurate results could be obtained by overlapping the cross section at each internuclear distance with the nuclear wavefunction at that distance and integrating in order to arrive at a weighted average cross section. This would allow our results to be compared with possible future experimental observations because in a real sample of NeAr at a given time each molecule would be at a different vibrational state. From Fig. 5.6 we can see that smaller internuclear separations lead to larger cross sections, and thus when we calculate the cross section without taking the spread on the nuclear wavefunction into account we arrive at larger cross sections that are to be expected experimentally. That said, it must be noted that the overall cross section in NeAr is very small anyway and therefore not experimentally feasible to detect. Hence there would be not much point in going into such detail when calculating the cross section at each internuclear separation in NeAr. Fig. 5.6 serves its purpose by providing us with a “feel” as to the distance–dependent profile of \textit{sp}LEICD cross section in a weakly bound system. However if in future such a distance–dependent investigation of \textit{sp}LEICD cross section were to be carried out in a larger system with experimentally observable cross sections, then the effect of different vibrational states and the spread of the nuclear wavefunction must be taken into account.

5.5 \textit{sp}LEICD in Ar$^+(3s^{-1})$Ne$_5$

The previous calculations we performed on NeAr dimer yielded small \textit{sp}LEICD cross sections on the order of 0.01 Mb. Experimentally this would be a challenge to measure. One way we could increase the size of the expected cross section would be to
look at a system with more available ICD channels, for example by adding more neon atoms to the NeAr cluster. We investigate this by looking at the ArNe$_5$ cluster.

Fig. 5.7 shows the geometrical arrangement of ArNe$_5$ [91]. The atoms are in an octahedral arrangement distorted because of the larger radius of argon compared to the neon atoms. We choose to define the $x$ direction to be coincident with the line connecting argon and the neon furthest away. There are potentially two different argon-neon interatomic Coulomb interactions: when the neon is ionised from one of the four equivalent neon atoms that sit in the plane intercepting the $x$ axis, or when it is ionised from the neon furthest away in the $x$ direction. In the optimised geometry for the cluster these two distances are 3.4 Å and 4.7 Å respectively. The neon that is directly opposite argon is more likely to host the positive charge as it would be further away from Ar$^+$, thus lowering the total energy of cluster [45]. However one might expect that as the four neon atoms that form the plane in between the “far” neon and argon are closer to the initial Ar(3s) vacancy they are more likely to take part in the process of spLEICD.
Using similar energetic considerations as described previously for the case of NeAr we discuss the $sp$LEICD only energy window for the ArNe$_5$ cluster. The $sp$LEAD threshold is exactly the same as the one for NeAr given by Eq. 5.4 and is 14.2 eV. For the $sp$LEICD threshold when we use Eq. 5.3 we must consider the two different distances between the two types of neon environments. For the “near” neon atoms at a distance of 3.4 Å from the argon the $sp$LEICD threshold is 12.3 eV. This lies above the $sp$LEAD threshold. For the neon atom that is 4.7 Å away from argon the $sp$LEICD threshold is estimated to be 11.1 eV. These thresholds indicate that there is a 3.1 eV window where $sp$LEICD is the only decay channel opened by a photon.

The $sp$LEICD cross section plots for ArNe$_5$ are presented in Fig. 5.8 for three polarisations, $x$, $y$, and $z$ of the incident single photon. These were calculated in the cc-pVQZ basis set with 5s5p5d added KBJ diffuse functions. As with NeAr the maximum cross section is achieved when the photon is polarised along the $x$ axis, i.e., along the axis on which argon and the “far” neon lie (Fig. 5.7). For the incident photon polarised along the $y$ and $z$ directions, the $sp$LEICD cross sections are both lower than the “$x$ cross section”, and are similar to each other. The small difference between the two is due to the main molecular axis being slightly tilted relative to the $yz$ plane. The “$x$ cross section” experiences a maximum of about 0.02 Mb which is almost twice as large as that experienced by the “$x$ cross section” for NeAr. The total cross section, i.e., the average cross section over the $x$, $y$, and $z$ polarisations of the incident photon, is mainly due to the “$x$ cross section”, and reaches a maximum of about 0.033 Mb, which is about 3 times the $sp$LEICD cross section for NeAr. The larger $sp$LEICD cross section in ArNe$_5$ compared to NeAr points to the presence of more open channels that are available for $sp$LEICD in ArNe$_5$ due to the presence of more atoms (Fig. 5.8).

We believe that the rather broad feature in the total cross section for ArNe$_5$ (Fig. 5.8) is representative of a resonance. We may explain the presence of this resonance by using step 2 of the $sp$LEICD mechanism that we inferred from Eq. 5.13, derived
Figure 5.8: *sp*LEICD cross section for Ar$^+(3s^{-1})$Ne$_5$; the top two and bottom left panels are the partial cross sections for the incident photon polarisation along the $x$, $y$, and $z$ directions as indicated on the panels. The bottom right panel bears the profile of the three partial cross sections as well as the total cross section which is averaged over the three partial contributions from each polarisation (see legend). The total cross section experiences a maximum value of about 0.033 Mb, almost 3 times that of NeAr. As with NeAr the main contribution to the total cross section comes from the $x$-polarisation of the incident photon.

In section 5.4. The said mechanism was described using NeAr dimer as an example, but it should be valid for any other weakly bound system. In the case of ArNe$_5$ with an initial 3s vacancy on argon, step 1 of the mechanism involves excitation of an Ar 3$p$ electron into an unoccupied orbital and ionisation of a 2$p$ electron from one of the neon atoms as a result of electron correlation. In step 2 an external photon helps de-excite the excited electron into the initial inner valence vacancy on argon. When the energy of this transition is the same as the energy of the incident photon within the *sp*LEICD-only photon energy window, maximum *sp*LEICD cross section is achieved and a resonance occurs which appears in Fig. 5.8 as a broad feature.
5.6 \textit{spLEICD} in Protonated Ammonia Dimer

So far our attention has been mainly focused on the van der Waals clusters. As pointed out in chapter 1 ICD can also proceed in hydrogen-bonded clusters \cite{3}. Does the same apply to \textit{spLEICD}, and will the stronger hydrogen bond lead to larger \textit{spLEICD} cross sections that we have seen previously? This is what we will investigate in this section.

Ammonia dimer is an example of a hydrogen-bonded cluster. A hydrogen bond \cite{92} involves a proton donor and a proton acceptor. In the case of ammonia dimer, one of the hydrogen atoms on one monomer (the proton donor) interacts with the lone pair of electrons on the nitrogen in the other monomer (the proton acceptor) to form a hydrogen bond. Ammonia dimer is not a suitable system for the investigation of \textit{spLEICD} as it is ICD-active: the energy of an inner-valence vacancy on one of the monomers lies above the double ionisation threshold of (NH$_3$)$_2$ \cite{93}. This is however not the case for the protonated ammonia dimer NH$_3$ \cdots NH$_4^+$ where an extra proton is attached to one of the ammonia monomers, and “\cdots” represents the
hydrogen bond. This species is ICD-inactive regardless of which monomer hosts the initial inner-valence (iv) vacancy. The proton donor in this case will always be the cation, NH$_4^+$. 

In the following calculations we use the equilibrium geometry for the protonated ammonia dimer as shown in Fig. 5.9. The hydrogen bond of length 1.5 Å is between a lone pair on ammonia and a hydrogen on ammonium ion with N-H-N bond angle that is distorted relative to linear by 6°. If one were to look down the N-N axis, the hydrogens from the ammonium ion would be staggered relative to the ammonia.

5.6.1 Breakdown of the Molecular Orbital Picture

In this section we discuss the breakdown of Molecular Orbital picture of ionisation [94,95] which can arise following ionisation out of an inner-valence orbital. According to Koopmans’ theorem the ionisation energy is equivalent to the electron binding energy (the HF energy of the orbital). This is valid for outer-valence electrons within the single-configuration approximation. However Koopmans’ picture of ionisation breaks down when ionising from an inner-valence shell of a relatively large molecule. In this case the resulting inner-valence ionised state is a complex superposition of many electronic configurations.

Here we return to the concept of intermediate states for the representation of the singly-ionised wavefunction (Eq. 5.8). The coefficients $\sum_i |c_i|^2$ in Eq. 5.8 refer to the spectral intensity, which is a measure of the 1h (one-hole) character of an ionised state. Fig. 5.10 is a plot of these spectral intensities for the protonated ammonia dimer. We calculate these spectra using ADC(2)x in cc-pVQZ [81] with 5s5p5d added Kaufmann Baumeister Jungen diffuse functions. These spectra show the 1h (one-hole) contribution of each (N-1)-eigenstate plotted against the energy of each of these states.

The spectral lines that lie below 25 eV all correspond to outer-valence ionisation and are mostly of 1h (one-hole) character with spectral intensities around 0.9, with
very little (< 10%) of the eigenstates having a 2h1p (two-hole-one-particle) character. These lines are consistent with Koopmans’ picture of ionisation, and thus the ionisation energy can be quite accurately approximated to the binding energy of the orbital from which the electron has been removed.

The lines corresponding to the removal of an electron from the 2s orbital of NH₃ are shown in blue in Fig. 5.10 and for the 2s orbital of NH₄⁺ are shown in red. Firstly, if we remove a single electron from the 2s orbital of NH₃ we do not end up in a single eigenstate of the ion, but a superposition of eigenstates with an energy range between 31 eV and 35 eV. This means the Koopmans’ picture of ionisation no longer holds. If we look at any one of the eigenstates in this range the largest spectral intensity is 0.6 and can be as low as 0.04. This indicates a significant contribution to each of these eigenstates comes from 2h1p (two-hole-one-particle) configurations.

The configuration interaction between 1h (one-hole) and 2h1p (two-hole-one-particle) configurations of the inner-valence ionised state is what gives rise to the breakdown of Koopmans’ picture of ionisation. The 2h1p states are similar in energy to the 1h states because in the 2h1p configurations the two holes can sit on different atomic centres thus reducing the repulsion between the positive charges. Therefore the 2h1p configurations lie lower in energy than they would in an isolated atom or a diatomic molecule.

We expect that the presence of the 2h1p (two-hole-one-particle) configurations would enhance the spLEICD cross section. The reason for this is that, as we have discussed in section 5.3, spLEICD is a second order process that relies on electron correlation or configuration mixing. This is why we consider spLEICD in a cluster such as the protonated ammonia dimer.
Figure 5.10: Plot of spectral intensity versus energy, for the singly ionised protonated ammonia dimer, calculated using ADC(2)x in cc-pVQZ [81] with 5s5p5d added Kaufmann Baumeister Jungen diffuse functions. The red lines are the MO contribution when iv-hole is on the proton donor (NH$_4^+$), and the blue lines the MO contribution when the proton acceptor (NH$_3$) hosts the iv-hole. Black indicates the 1h (one-hole) content of these lines. The double ionisation potential of the cluster is 44 eV.
5.6.2 Energetic Considerations

The $sp$LEICD cross section will vary depending on the location of the initial inner-valence vacancy. The iv-hole could either be on the proton donor, i.e. $\text{NH}_3 \cdots (2s^1)\text{NH}_4^{++}$, or on the proton acceptor, i.e., $(2s^1)\text{NH}_3^+ \cdots \text{NH}_4^+$. As with the previous two systems we must first calculate the photon energy threshold for $sp$LEICD, $sp$LEAD, and the laser-enabled ETMD processes before we proceed with the numerical evaluation of the cross section.

Firstly we consider the energies of our two different initial states. We take these from the spectral intensity plot shown in Fig. 5.10. We consider the eigenstate which has the largest $1h$ (one-hole) contribution. The energy of $(2s^1)\text{NH}_4^{++}$ is found to be 35.5 eV with a spectral intensity of 0.61. The energy $(2s^1)\text{NH}_3^+ \cdots \text{NH}_4^+$ is 32.3 eV with a spectral intensity of 0.59. The DIP of $\text{NH}_3 \cdots \text{NH}_4^+$ is 43.8 eV\(^1\). This corresponds to $(2p^5)\text{NH}_3^+ \cdots (2p^3)\text{NH}_4^{++}$. The minimum energy photon required to enable $sp$LEICD for the case of the proton donor can be calculated using

$$h\omega = DIP(\text{NH}_3 \cdots \text{NH}_4^+) - E(\text{NH}_3 \cdots (2s^1)\text{NH}_4^{++})$$ \hspace{1cm} (5.17)

and is found to be 8.3 eV. Similarly we find the minimum photon energy to be 11.5 eV for the $(2s^1)\text{NH}_3^+ \cdots \text{NH}_4^+$ initial state.

The double ionisation threshold corresponding to two electrons being removed from the $\text{NH}_3$ site in $\text{NH}_3 \cdots \text{NH}_4^+$ is found to be 53.6 eV. If the initial state is $(2s^1)\text{NH}_3^+ \cdots \text{NH}_4^+$ the $sp$LEAD threshold will be 21.3 eV. If however the site was $\text{NH}_3 \cdots (2s^1)\text{NH}_4^{++}$, this double ionisation threshold would correspond to the ETMD threshold which in this case would be 18.1 eV. The double ionisation threshold corresponding to removing two electrons from the $\text{NH}_4^+$ site is found to be 57.0 eV. If

\(^1\)This energy and subsequent one-site double ionisation energies were provided by a collaborator Dr. Premysl Kolorenc. They were calculated using ADC(2)$x$ using the same molecular geometry and basis set as our calculations in the protonated ammonia dimer.
the initial site was \( (2s^1)\text{NH}_2^+ \cdots \text{NH}_4^+ \), this corresponds to ETMD threshold which is 24.7 eV. If the initial state was \( \text{NH}_3 \cdots (2s^1)\text{NH}_4^{++} \) this double ionisation threshold would correspond to \( sp\text{LEAD} \) and is found to be 21.5 eV. These thresholds mean that in the case of the initial state being \( (2s^1)\text{NH}_3^+ \cdots \text{NH}_4^+ \) \( sp\text{LEAD} \) will be the first competing process and the energy window is therefore 9.8 eV \([21.3 - 11.5] \) eV. If the initial state is \( \text{NH}_3 \cdots (2s^1)\text{NH}_4^{++} \) laser enabled ETMD would provide the upper bound to our energy window which again spans 9.8 eV \([18.1 - 8.3] \) eV. This gives us a much larger energy window where \( sp\text{LEICD} \) is the only laser enabled decay channel compared to the NeAr clusters.

5.6.3 The \( sp\text{LEICD} \) cross section

We calculated the \( sp\text{LEICD} \) cross sections for the protonated ammonia dimer with the initial vacancy on the acceptor and on the donor separately using the same technique as before, making use of a \( cc\text{-pVQZ} \) [81] basis set on the nitrogen and hydrogen atoms, with 5s5p5d KBJ added diffuse functions on the nitrogen. Figures 5.11 and 5.12 show the \( sp\text{LEICD} \) cross section plotted against the photon energy within the \( sp\text{LEICD} \) only window, for the proton acceptor and the proton donor hosting the initial vacancy respectively. In each figure average cross sections are plotted for three polarisations of the incident light \( x \), \( y \), and \( z \), and for the total average cross section over all three polarisations.

For the case of the initial orbital vacancy on the proton donor, when the incident photon is polarised along the \( z \) direction, the corresponding panel in Fig. 5.11 experiences a resonance (see below) which peaks at around 0.96 Mb. The cross section when the photon polarisation is along the \( x \) direction also experiences a resonance with a peak that is an order of magnitude smaller than the “\( z \) cross section”. The “\( y \) cross section” is negligible.

For the initial vacancy on the proton donor, the average cross sections for all
Figure 5.11: \( spLEICD \) cross-section for \((2s^1)NH_3^+\ldots NH_4^+;\) the top two and bottom left panels are the partial cross sections corresponding to the \( x, y, \) and \( z \) polarisations of the incident photon as indicated on the panels. The bottom right panel bears the profile of the three partial cross sections as well as the total cross section (see legend). The energy window available for \( spLEICD \) is 9.5 eV, the upper limit of which marks the start of the \( spLEAD \) process.

The polarisations as shown in Fig. 5.12 are overall larger than those in Fig. 5.11. In both figures the “\( x, y, \) and \( z \) cross sections” all bear features that could correspond to resonances, and that is as far as we can comment on these features at this point based on Eq. 5.13 derived in section 5.4. The reader is referred to the end of section 5.5 for further explanation as to why such resonance features may exist.

In both figures 5.11 and 5.12 the \( spLEICD \) cross section is largest when the incident light is polarised along the \( z \) axis, which has the largest component of the molecular axis, although in Fig. 5.12 the maximum cross section corresponding to the \( x \) polarisation of the incident photon is very similar in magnitude to that of the “\( z \) cross section”, and the “\( y \) cross section” is also only half the “\( z \) cross section” as opposed to being negligible as is the case with the “\( y \) cross section” in Fig. 5.11.
Figure 5.12: spLEICD cross-section for NH$_3$...($2s^1$)NH$_4^{++}$; the top two and bottom left panels are the partial cross sections corresponding to the $x$, $y$, and $z$ polarisations of the incident photon as indicated on the panels. The bottom right panel bears the profile of the three partial cross section and the total cross section (see the legend). The energy window available for spLEICD is 9.6 eV, the upper limit of which marks the start of the laser-enabled ETMD process.
This could be due to the extra positive charge on the NH$_4^+$ when it accommodates the initial inner-valence vacancy as opposed to the singly positive NH$_3^+$ with the initial inner-valence vacancy. However we can not be sure how this fact may result such a noticeable difference in cross sections between the donor and the acceptor cases. This calls for further investigation in future.

The total cross section for the proton acceptor has a maximum value of about 1.1 Mb, which is almost 110 times larger than that of NeAr, and about 33 times larger than the total cross section for ArNe$_5$. For the case of the proton donor, the total cross section has a maximum value of about 2.1 Mb, about 210 times larger than that for NeAr and almost 64 times that of ArNe$_5$. This indicates that the strength of the hydrogen bond in protonated ammonia dimer must play a major role in enhancing the spLEICD cross section as compared to the weaker van der Waals interaction in either of NeAr and ArNe$_5$. The other contribution to the comparatively larger cross section in protonated ammonia dimer could be due to more configuration mixing because of the breakdown of the molecular orbital picture of ionisation.

Our previous calculations on NeAr dimer and ArNe$_5$ also showed that the direction of the incident photon affected the resulting spLEICD cross section strongly (although this is not exactly the case with the donor (NH$_4^+$) hosting the inner-valence vacancy in protonated ammonia dimer). It may thus be safe at this point to generalise with the following conclusion: the maximum cross section is achieved when the linearly polarised incident photon is directed along the molecular axis.

5.7 Summary and Conclusions

In this chapter we investigated the process of single photon Laser Enabled Interatomic Coulombic Decay (spLEICD) in the van der Waals systems NeAr and ArNe$_5$, and the hydrogen-bonded protonated ammonia dimer. We characterised spLEICD by the photoionisation cross section, which we calculated numerically using the ADC(2)
scheme for the three clusters. The cross-sections were plotted within the incident photon energy window where \( sp \)LEICD activity takes place, and whose upper limit in almost all cases marked the threshold for single photon Laser Enabled Auger Decay (\( sp \)LEAD). The energy window within which \( sp \)LEICD activity takes place was found to be 2.0 eV for NeAr, 3.1 eV for ArNe\(_5\), and about 9.5 eV for the protonated ammonia dimer. With regards to the latter we considered two separate cases; one with the initial inner-valence hole on the proton donor (NH\(_4^+\)), and one with that on the proton acceptor (NH\(_3\)). The energy windows were found to be the same for both cases, although for the proton donor ETMD threshold preceded \( sp \)LEAD.

Our results in the majority of cases indicated that the direction of the linearly polarised incident photon has a significant impact on the magnitude of the \( sp \)LEICD cross section: the cross section is maximum when the linearly polarised incident photon is directed along the molecular axis. Also, the much larger \( sp \)LEICD cross section found in protonated ammonia dimer as compared to NeAr and ArNe\(_5\) could be due to the presence of a hydrogen bond as well as MO breakdown.

For NeAr we also looked into the dependence of \( sp \)LEICD cross section on the internuclear distance by both analytical and numerical means. Analytically we made use of formulae within the framework of the ADC(2)\( x \) scheme in order to express the dipole matrix element that appears in the representation of the cross section in terms of a sum over products of Coulomb and dipole matrix elements with respect to the two holes and one particle involved in the process. The resulting expression allowed us to infer a two-step mechanism for the \( sp \)LEICD: first electron correlation between the electrons on neighbouring monomers leads to ionisation of the neutral monomer and to excitation of an outer-valence electron on the monomer with the initial iv-hole into an unoccupied orbital. The second step involves an external photon de-exciting the electron into the iv-hole. Since the second step is independent of the internuclear distance, the only distance-dependence of the cross section stems from the interatomic Coulomb matrix element which follows \( R^{-6} \). This was in agreement
with our numerical calculations.

5.8 Outlook

The high sensitivity of the $sp$LEICD cross section on the internuclear distance makes it a suitable candidate for or space-resolved measurements. Future research is required to shed more light on the possibility of developing $sp$LEICD into a time-resolved spectroscopic technique. The strong dependence of $sp$LEICD on the internuclear distance could potentially allow us to investigate the rearrangement of hydrogen bonding in clusters such as in a water droplet following initial ionisation.
Chapter 6

Summary and Conclusions

This thesis studies the non-radiative process of Interatomic/Intermolecular Coulombic Decay (ICD) in selected Van der Waals and hydrogen-bonded clusters. ICD in a weakly bound cluster takes place when an orbital vacancy in the inner sub-shell of the valence shell (inner-valence vacancy) decays by causing valence ionisation on a neighbouring cluster sub-unit. This process is mediated by the Coulomb interaction between electrons. We devote chapter 4 to the study of ICD in noble gas endohedral fullerenes where the confined atom weakly interacts with the $C_{60}$ cage, focusing on how ICD in such a system may excite various modes of $C_{60}$ plasmon oscillations.

In chapter 5 we consider van der Waals and hydrogen bonded clusters where one cluster sub-unit has an inner-valence vacancy whose energy is lower than the double ionisation threshold of the cluster. In such cases ICD would be inactive, however a single external photon could provide the additional energy required for double ionisation of the cluster. This process is referred to as single photon Laser Enabled ICD (spLEICD) and is investigated here for the first time.

In chapter 4 we investigate ICD in the endohedral fullerene Ne@C$_{60}$ both by analytical and numerical means. Specifically we derive analytical expressions for the ICD rate ignoring the exchange contribution based on the assumption that neon has zero-overlap with the wall of $C_{60}$. Our analytical expressions relate the ICD rate in the at-centre and off-centre ($2s^1$)Ne$^+@C_{60}$ to the $C_{60}$ plasmon oscillations which help
us find out if the displacement of neon from its equilibrium position at the centre of cage will excite any multipole C\textsubscript{60} plasmon oscillations.

For the off-centre case we employ an analytical technique developed by Silverstone [79] in order to redefine the orbitals of the off-centre neon relative to the centre of C\textsubscript{60}. This leads to an expression in terms of C\textsubscript{60}'s ionisation matrix elements. We calculate the coefficients of the said matrix elements numerically and plot them against the displacement of neon from the centre of C\textsubscript{60} (Figures 4.7 and 4.8). Our results reveal the modes of C\textsubscript{60} plasmon oscillation that get excited as a result of ICD, and also how the ICD rate changes as a function of the location of neon inside C\textsubscript{60}. Based on these results we predict that the only significant contribution to the total ICD width comes from the dipole $l = 1$ term which remains constant with the displacement of neon from the centre of C\textsubscript{60}. This suggests that it is a valid assumption to consider the decay width of 2s-ionised Ne inside C\textsubscript{60} to be constant throughout the cage, with the dipole contribution corresponding to the interaction energy of two dipole charge distributions, one inside the other.

Numerically, we use the Wigner-Weisskopf method in order to evaluate $\Gamma_{\text{ICD}}$ as a function of neon’s displacement from the centre of the cage. The resulting plot (Fig.4.9) shows an initial plateau up to neon’s vibrational turning point at room temperature (1 $a_0$) which, confirming our results from the analytical approach, shows that $\Gamma_{\text{ICD}}$ remains constant as long as there is no overlap with the cage. After a neon displacement of about 1 $a_0$ the $\Gamma_{\text{ICD}}$ experiences a rise that is indicative of the onset of neon’s overlap with the cage.

Comparing the plot of $\Gamma_{\text{ICD}}$ to that of the potential energy of Ne@C\textsubscript{60} evaluated at the MP2 level with respect to the energy of the centrally symmetric Ne@C\textsubscript{60}, we see that the MP2 curve also remains constant up to a radius of about 1 $a_0$ and then steeply rises with a similar profile to that of $\Gamma_{\text{ICD}}$. 

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In chapter 5 we study, for the first time, the process of single photon Laser Enabled Interatomic Coulombic Decay (spLEICD). We consider spLEICD in the van der Waals systems NeAr and ArNe₅, and the hydrogen-bonded protonated ammonia dimer. The process of spLEICD is characterised via the photoionisation cross section, which we calculated numerically using the ADC(2)x scheme.

Plots of the cross-sections versus the incident photon energy window where spLEICD activity takes place are obtained for three different polarisations of the incident photon (perpendicular to or along the molecular axis). The upper limit of the spLEICD photon energy window in almost all cases marks the threshold for single photon Laser Enabled Auger Decay (spLEAD). For NeAr and ArNe₅, spLEICD activity only spans a window of about 2 eV and 3 eV respectively, while for the protonated ammonia dimer we find a window of 9.5 eV.

For NeAr we also investigate the dependence of spLEICD cross section on the internuclear distance \( R \) by both analytical and numerical means. Analytically we use the ADC(2)x scheme in order to express the dipole transition matrix element that appears in the definition of the spLEICD cross section as a sum over products of Coulomb and dipole matrix elements with respect to the \( 2h1p \) (two-hole-one-particle) final state of the decay process. The resulting expression yields an \( R^{-6} \) dependence of the spLEICD cross section, same as what has been previously found for the dependence of the ICD width on internuclear distance \([45]\).

The above analytical expression for the cross section allows us to infer a two-step mechanism for spLEICD: starting from NeAr⁺ with an inner-valence (iv) vacancy on argon, the neutral neon is ionised and an outer-valence electron on argon gets excited into an unoccupied orbital as a result of electron correlation between the valence electrons on the neighbouring monomers. The second step involves an external photon de-exciting the electron into the iv-hole on argon. Since the second step is independent of the internuclear distance, the only distance-dependence of the cross
section comes from the Coulomb matrix element with a $R^{-6}$ dependence. We also calculate the $sp$LEICD cross section as a function of $R$ numerically, and obtain results in agreement with our analytical derivations.

In the case of the protonated ammonia dimer we consider two separate initial configurations that would lead to $sp$LEICD; one with the initial inner-valence hole on the proton donor ($NH_4^+$), and one with that on the proton acceptor ($NH_3$). We found the photon energy windows where $sp$LEICD is active to be the same for both cases, although in the case of the proton donor ETMD threshold precedes the $sp$LEAD threshold.

On the whole, our results indicate that $sp$LEICD is more efficient in polyatomic clusters than in a diatom due to the availability of more decay channels. Also $sp$LEICD in hydrogen-bonded clusters is more pronounced than in van der Waals clusters because of the orbital overlap due to the hydrogen bond and also as a result of the partial breakdown of the MO picture of ionisation. The polarisation of the linearly-polarised incident photon also has a significant impact on the magnitude of the $sp$LEICD cross section: the cross section is maximum when the linearly polarised incident photon is directed along the molecular axis. As mentioned in chapter 5 $sp$LEAD can be used as a probe in time-resolved spectroscopy. Analogously $sp$LEICD may potentially be used as a spectroscopic technique due to its strong distance-dependence, and may allow us to distinguish processes occurring in different spatial regions of a molecule or a cluster.
Bibliography


Appendix

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