

Coherent Electron Dynamics in Atoms and Small Molecules Following Attosecond Photoionisation

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March 21, 2025

Submitted in partial fulfilment of the requirements for the degree of Doctor of
Philosophy to the Department of Physics of Imperial College London

Statement of Originality

I declare that the results presented in this thesis are my own, and that all other contributing work has been appropriately acknowledged and referenced.

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Abstract

This work seeks to predict and understand novel ultrafast dynamics induced and measured by the action of a laser pulse. For this purpose we develop new theory and we make use of several ab-initio numerical methods. In particular, we apply the recently developed technique of restricted correlation space B-spline ADC, which uses B-spline functions to represent both bound and continuum-like electronic states and thereby model dynamics following ionisation.

This work has three major components. The first is the development of a new interferometric approach for detecting revivals of an initially-decaying molecular state through the use of an $\omega/2\omega$ pulse scheme with carefully controlled relative phase. We develop and solve analytically a model system containing a state coupled to a Bixon-Jortner quasi-continuum, obtaining an interferometric signature of revival which is easily generalised to realistic systems. Moreover, we analyse how this revival signature is influenced by the system parameters, and we suggest optimal conditions for its observation.

The second and most significant component is the application of ab-initio numerical methods to study the dynamics which follow coherent population of ionisation satellites created by the removal of an inner-valence electron in atoms by an attosecond duration laser pulse. Our calculations show that this kind of system exhibits radial electron density oscillations and, for the specific case of the Argon atom, we study the precise nature of these predicted oscillations. We further illustrate several schemes by which this behaviour might be probed, and we provide initial numerical evidence that the probe is sensitive to the electron dynamics.

The final part of the work is a numerical study of Auger decay in a system where the molecular orbital picture of ionisation breaks down, leading to coherent population of a series of decaying states which we predict will exhibit non-exponential decay character.

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This work makes use of atomic units (a.u.) except where noted otherwise. Within this unit system, the electron mass m_e , the electron charge e , the Planck constant $\hbar$, and the permittivity of free space $4\pi\epsilon_0$ are defined as equal to 1. This in particular leads to the following units for energy, length, time, electric field strength and intensity, where a_0 is the Bohr radius:

quantity	formula	S.I. value
Length	$\frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0$	$5.29177 \times 10^{-11}\text{m}$
Energy	$\frac{\hbar^2}{m_e a_0^2}$	$4.35975 \times 10^{-18} \text{ J}$
Time	$\frac{m_e a_0^2}{\hbar}$	$24.1888 \times 10^{-18} \text{ s}$
Electric Field	$\frac{e}{a_0^2} = E_0$	$5.1422 \times 10^{11} \text{ V/m}$
Field Intensity	$\frac{1}{2}\epsilon_0 c E_0^2$	$3.5094 \times 10^{16} \text{ W/cm}^2$

Introduction

In the physics of atomic and molecular systems, the motion of electrons subsequent to excitation or ionisation can be considered one of the most fundamental processes from which much of the later dynamics ultimately flows. Electron motion has a typical timescale ranging from tens of attoseconds (10^{-18} s) up to tens of femtoseconds (10^{-15} s), at the upper end of this range coupling to nuclear dynamics. The relevance of such ultrafast processes thereby extends into a range of other fields such as chemistry and even molecular biology, for instance in the understanding of the mechanics of radiation damage and subsequent ionisation-induced fragmentation of bio-molecules.

At a basic level, the structure of the electronic wavefunction in such systems can be analysed in terms of the molecular orbital picture: each orbital describes the wavefunction of one electron, and the overall wavefunction can be considered as a combination of such orbitals with the correct antisymmetrisation. Ionisation from the outermost orbitals of an atom or molecule is well-described within this framework, typically producing ionic states which can be well-described by a single configuration in which an electron has been removed from one orbital of the neutral, known as a one-hole (1h) configuration. As increasingly tightly bound orbitals are considered, however, configuration mixing starts to be observed. One typical realisation of this is the formation of shake-up states, wherein the 1h-dominated main state is accompanied by a series of primarily two-hole, one-particle (2h1p) satellites. These can be associated with the simultaneous ionisation of one electron and excitation of a second, and are a fundamental manifestation of electron correlation. As the double ionisation potential is approached, even this structure is lost, and in place of any one-hole state in this region is instead a band of many 2h1p-dominated states, in a regime characterised by the complete breakdown of the molecular orbital picture of ionisation [1].

Moving above the double ionisation potential, it is possible for such an initially singly-ionised system to decay non-radiatively through the emission of an electron. This is a form of Auger - or Auger-Meitner - decay [2, 3], a process by which an outer-shell electron recombining with an inner-shell vacancy provides sufficient energy for a second electron to exit the system entirely. For the case of small molecules consisting of light atoms, this is the dominant mechanism of decay, occurring on a typical timescale on the order of femtoseconds [4], as compared to the nanosecond to picosecond timescale of relaxation

via photon emission.

The interaction with light is a primary way in which electron dynamics can be initiated in this class of systems, as the absorption of one or many photons can promote electronic systems into a range of excited states, or with sufficient photon energy or intensity even induce ionisation. Further to this, if the energy width of the laser pulse is sufficient then it can often populate a range of states coherently, introducing dynamics which depend fundamentally on this coherence. This is naturally the case for ionisation by attosecond-duration laser pulses, as the Fourier relation between pulse duration and energy width ensures that such a pulse will have sufficient width to span the gap of several eV which separates, for example, a typical satellite spectrum.

This kind of attosecond pulse has become increasingly widely available over the past couple of decades. Such pulses have historically been provided by high-harmonic generation (HHG) methods [5], which utilise a high-intensity IR pulse to induce ionisation and subsequent recollision of an electron with its parent system, producing harmonics of the initial driving IR frequency. Rapid advances in HHG pulse generation techniques [6, 7, 8] have made it possible to produce pulse lengths of fewer than 100 attoseconds at frequencies in the range of the extreme ultraviolet (XUV) to soft X-ray rays [9]. Due to their relative accessibility, HHG-based schemes have been used to measure a wide variety of dynamics, including time-resolved measurements of the decay of inner-shell holes [4] and other autoionising states [10], the motion of valence electrons [11], and photoionisation [12]. Typically, HHG XUV pulses have usually been used to initiate the system dynamics with the role of the probe performed by a near-infra-red (NIR) pulse [13, 14] due to the limitations on the achievable XUV intensity, but in the past few years this restriction has been overcome and the use of HHG pulses in XUV pump-XUV probe experiments has also been demonstrated [15].

In parallel to these advances, developments within the area of free-electron lasers (FELs) have provided another avenue for accessing the attosecond domain, which in particular allows the creation of comparatively intense pulses in the soft X-ray range. This technique makes use of stimulated emission from free electrons accelerating in a magnetic field, and can produce pulses as short as hundreds of attoseconds in duration at soft X-ray frequencies with tunable photon energy and potentially also controllable pulse delay for a pump-probe setup [16], making them highly useful in X-ray pump, X-ray probe experiments [17, 18]. FELs additionally have the ability to produce a pulse tuned to target transitions involving core orbitals on specific atomic sites within a molecule, allowing the creation or detection of an electron hole on a particular site [19]. With these advances in pulse generation has therefore come a much increased ability to both induce coherent electron motion and subsequently probe the dynamics on the attosecond timescale. As a result, the study of these dynamics has increasingly become a focus of research in atomic and molecular physics.

One fundamentally important manifestation of coherent electronic behaviour which has attracted substantial interest in the past decade is the process of charge migration across molecular systems. This was first experimentally detected via an indirect approach [20], and it was only very recently that a direct observation of charge migration was achieved [17] through the use of an X-ray pump, X-ray probe scheme, utilising a few-femtosecond duration probe tuned to the resonance between a core orbital and a transiently occupied state in the isopropanol molecule. A similar approach has since also been used to probe charge migration in glycine [21]. Charge migration processes tend to fall into one of two distinct categories: the first involves oscillations between several states with charge localised at different points within a molecule [20, 21]; the second is characterised by an initial state containing an inner sub-shell vacancy which is coupled into a large array of bound, delocalised states [17]. This latter behaviour can be often understood as a ‘frustrated Auger’ [22] effect in which the vacancy is filled by exciting a second electron with insufficient energy for it to fully depart the system, and is characterised by the localised hole state initially decaying before experiencing revivals in its population.

Coherent electron motion in molecular systems is typically fairly short lived, with coherence generally being lost over timescales from a few femtoseconds [17, 23, 24] to a few tens of femtoseconds [21]. The major driver of such decoherence is the zero-point vibrational motion of the nuclei in the molecule, which prevents the frequency of coherent oscillations from being assigned a single well-defined value as this would vary depending on the specific geometry. This decoherence leads to the electronic wavepacket ceasing to oscillate, instead becoming localised on particular atomic centres. Also present as a cause of decoherence, albeit generally slower to take effect, is the nuclear motion subsequent to ionisation and the association of particular electronic states with particular evolution of the system geometry. This connects the purely electronic charge migration to the process of charge transfer, in which the localisation of charge within a molecule both drives and is driven by nuclear dynamics [25].

There has also been a drive to theorise and develop novel techniques for measurement of such coherent systems. For instance, the process of single-photon laser-enabled Auger decay [26] suggests a method for investigating the degree and nature of electron correlation in an ionic state through the use of a probe which can induce ionisation via a one-photon two-electron transition - something which is possible only once configuration mixing is taken into account. This technique has since been experimentally demonstrated in ionised neon atoms [27, 28].

For the purposes of predicting new dynamics and gaining insight into the mechanisms behind experimentally-known behaviours in the systems described above, it is important to also have access to theoretical and numerical techniques specialised for modelling highly correlated attosecond-timescale electron dynamics. Within non-relativistic quantum me-

chanics, the equation which governs the evolution of the wave function $|\Psi(t)\rangle$ of a general system is the time-dependent Schrödinger equation (TDSE)

$$\hat{H}|\Psi(t)\rangle = i\frac{\partial}{\partial t}|\Psi(t)\rangle \quad (1.1)$$

where $\hat{H}$ is the system Hamiltonian. For the vast majority of realistic systems, an exact analytical solution of the Schrödinger equation is impossible. Instead, it is common to use the TDSE as a basis for a set of approximations which result in a numerically tractable system. One common starting point for such approximations is the Hartree-Fock (HF) method within the Born-Oppenheimer approximation [29], whereby the nuclei are assumed to be static with respect to electron motion and the wave function is constructed as a single Slater determinant. The Hartree-Fock method alone is computationally inexpensive and does fully capture electron exchange-correlation, but is insensitive to correlation arising from instantaneous coulomb repulsion between electrons. Building on top of this are a series of what are termed ‘post-HF’ methods, which incorporate a greater degree of this missing correlation.

The conceptually simplest of the post-HF techniques is the method of time-dependent configuration interaction (TDCI), in which the system is modelled as a linear combination of HF Slater determinants [29] with time-varying coefficients. In the case of full CI, in which all possible Slater determinants are considered, this is numerically exact but generally impractical for non-trivial systems unless the space of active electrons and accessible orbitals is heavily restricted. Limiting the included set of excited Slater determinants to those containing at most one excitation above the HF ground state produces instead the technique of CI singles (CIS), and this can be systematically extended by including up to double excitations (CISD), triple excitations, and so on. An approach conceptually related to CI which will be the focus of much of this work is that of algebraic diagrammatic construction (ADC) [30], in which excited states are constructed through the action of a excitation operator not on the HF ground state as in the CI case, but instead on the perturbation theoretically corrected ground state. This technique intrinsically includes ground state correlation resulting in a compact representation, can be systematically extended to approach the exact (full CI) limit, and can be modified in an ad-hoc manner to improve the description of particular types of states [31]. One final member of this family of post-HF techniques is the coupled cluster method [32, 33], which includes electron correlation effects by working in a basis constructed through the operation of the exponential of the cluster operator on the HF ground and excited states.

An alternative extension of the HF approach is to allow the Slater determinant basis functions themselves to vary in time. Taking a linear combination of such time-dependent determinants where the coefficients of each are likewise allowed to be time-varying pro-

duced the method of multiconfigurational time-dependent Hartree-Fock (MCTDHF) [34], which constructs an equation of motion for the state coefficients and basis functions via a variational principle formulation. Yet another approach is given by the time-dependent density matrix renormalisation group (TD-DMRG) method, which approximates the full CI solution as a truncated matrix product state and can systematically approach this full CI limit [35, 36].

In general, there is a clear trade-off between the accuracy with which any given approach treats the effects of electron correlation and the corresponding computational cost [37, 38]. For larger molecular systems, it is therefore usually necessary to retreat somewhat from attempting to capture the fine details of electron correlation. The most commonly used approach in such cases is the method of time-dependent density functional theory (TD-DFT) [39, 40]. Rather than working in terms of the wavefunction directly, DFT makes use of the one-particle electron density and models the dynamics as those of a system of non-interacting particles moving in an effective single-particle potential, where the potential is constructed from the density in a self-consistent manner. This approach nonetheless captures some level of correlation through an appropriate choice of exchange-correlation functional which appears in the effective potential. Such a construction allows a reasonably accurate treatment of systems containing more than a few tens of atoms [41] - in some cases as many as thousands [42] - which are often well out of reach of the higher-precision techniques mentioned previously. Conversely, DFT is not generally capable of an accurate description of systems in which electron correlation plays a crucial role, such as those containing auto-ionising states or significant shake-up satellites, which require the use of more computationally expensive techniques such as higher-order ADC or CI to treat the correlation accurately.

In cases where the effects of electron correlation can be ignored almost entirely, it is even possible to make use of a fully single-particle approach, such as in the single active electron (SAE) approximation, which models one electron moving in a static potential arising from the remaining frozen electrons. This is often used, for instance, in the description of strong-field ionisation [43, 44].

Within this work, we make use of several numerical schemes based on the ADC technique. In particular, the main numerical calculations are carried out utilising the recently-developed approach of time-dependent (TD) restricted correlation space (RCS) B-spline ADC [45, 46, 47]. This scheme uses the ADC construction of the Hamiltonian built within a B-spline basis set, permitting accurate representation of both bound and continuum-like states within the same basis, and therefore allowing the modelling of ionisation dynamics. We use this method to model the coherent population and subsequent dynamics of ionic shake-up states in atomic Argon; and to model the coherent population and decay of Auger-active states in the N_2O molecule. For the former part, we additionally incorporate the ADC(2,2) [48] scheme to improve the perturbation theory accuracy of the description

of the resulting ionic states, thus obtaining results which better reflect the reality of this highly-correlated system.

1.1 Outline

The structure of the remainder of this thesis will be as follows:

Chapter 2 will discuss the pre-existing numerical theory behind this work.

In section 2.1, I will outline how the Hartree-Fock method is used to produce an initial approximate solution to the Schrödinger equation, and how this can then be used as a basis for higher-level approximations.

Section 2.2 will introduce the algebraic diagrammatic construction (ADC) numerical scheme. I will outline the two independent but equivalent formulations of ADC: either as a method for obtaining the electron or polarisation propagator; or alternatively as a technique for constructing the electronic Hamiltonian in what is known as the Intermediate State Representation (ISR). I will highlight the key properties of the ADC scheme - and the ISR-ADC construction in particular - which make it an effective tool for high-accuracy *ab initio* computation.

In section 2.3, I will narrow the focus to the specific implementation of restricted correlation space (RCS) B-spline ADC as a method for performing time-dependent simulations of ionisation dynamics. This section will detail the individual building blocks of this approach, including the assembly of the B-spline basis set for modelling both bound and continuum states, the introduction of the RCS construction to reduce the size of the resulting ADC matrices, and the numerical propagation of the system via the Arnoldi-Lanczos algorithm.

Section 2.4 will discuss the alternative ADC(2,2) scheme for constructing the ADC Hamiltonian, which is designed to improve the accuracy with which states consisting primarily of two-hole, one-particle configurations can be calculated beyond that which can be achieved in the more typical ADC(n) hierarchy without rendering the system computationally intractable.

In Chapter 3, I will review the concepts governing the decay dynamics of both unbound and bound atomic or molecular states from an analytical perspective, including in the latter case the subsequent possibility of revivals in the initially decaying state population as represented in the idealised Bixon-Jortner model.

Chapter 4 will present an analytical model of a new interferometric scheme for the measurement of such revivals, before discussing the applicability of the results to realistic systems once various of the model assumptions are dropped.

Finally, in chapter 5 I will discuss a pair of systems for which I have applied the B-spline ADC technique to numerically model the coherent electronic behaviour resulting from ionisation by an attosecond pulse.

Section 5.1 will cover the case of coherent population of a bound atomic shake-up series, illustrating the resulting long-lasting oscillatory dynamics of the electron density and exploring how this behaviour might be detected by a subsequent attosecond probe.

Lastly, in section 5.2 I will examine the contrasting situation of the coherent population of a series of Auger-active states with the goal of observing how this coherence might lead to non-exponential decay dynamics.

Numerical Theory

2.1 Hartree-Fock Approximation and Post-Hartree-Fock Techniques

The starting point of most numerical techniques is the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

This equation is, in general, a function of the positions of all particles in the system - both electrons and nuclei. As the mass of an electron is several orders of magnitude less than that of an atomic nucleus, the typical timescale of electron motion can be expected to be faster than nuclear motion by a similar factor. This is the root of the Born-Oppenheimer approximation, in which the nuclear positions are assumed to be fixed, and the electrons move in the potential created by the static nuclei. This leads to an equation for the electronic Hamiltonian for N electrons and M nuclei

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (2.2)$$

where Z_A and $\vec{R}_A$ are the charge and position of the A^{th} nucleus, and $\vec{r}_i$ is the position of the i^{th} electron. In addition to nuclear motion, relativistic effects have also been neglected. This latter assumption is generally valid for the lighter atoms which make up most organic molecules. It is important to note that in the above expression, as with every subsequent equation which appears in this work, atomic units are used and constants with a value of 1 are left implicit. A general solution to the Schrödinger equation will depend on the coordinates of the electrons as

$$\Psi = \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \quad (2.3)$$

Electrons are spin-half particles, so the coordinate $\vec{x}$ must account for the two possible orthonormal spin states, written as $\alpha(\omega)$ and $\beta(\omega)$, alongside the radial coordinate:

$$\vec{x} = \{\omega, \vec{r}\} \quad (2.4)$$

A single-electron state, or spin-orbital, $\chi(\vec{x})$ is then expressed as $\chi(\vec{x}) = \psi(\vec{r})\sigma(\omega)$, where $\sigma(\omega) = \alpha(\omega), \beta(\omega)$. For a many-electron state, the simplest conceivable form would be in the form of the so-called Hartree product

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \chi_i(\vec{x}_1)\chi_j(\vec{x}_2)\dots\chi_k(\vec{x}_N) \quad (2.5)$$

It is clear that the electrons in such a product are uncorrelated - that is, the state of each electron is independent of the state of all of the others. As fermions, however, electrons must obey the Pauli exclusion principle, expressed mathematically as

$$\Psi(\vec{x}_1, \dots, \vec{x}_i, \dots, \vec{x}_j, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \dots, \vec{x}_j, \dots, \vec{x}_i, \dots, \vec{x}_N) \quad (2.6)$$

for all i, j . It is clear that the Hartree product does not obey this relation, as the effect of interchanging two electron indices is not well defined. A solution which does have the correct behaviour can be obtained by antisymmetrising the Hartree product, expressed simply in terms of the Slater determinant

$$\Phi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \chi_i(\vec{x}_1) & \chi_j(\vec{x}_1) & \dots & \chi_k(\vec{x}_1) \\ \chi_i(\vec{x}_2) & \chi_j(\vec{x}_2) & \dots & \chi_k(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\vec{x}_N) & \chi_j(\vec{x}_N) & \dots & \chi_k(\vec{x}_N) \end{pmatrix} \quad (2.7)$$

As interchanging any two rows or columns of a matrix inverts the sign of its determinant, this must have the required antisymmetry property. The factor of $1/\sqrt{N!}$ is a normalisation factor, accounting for the $N!$ permutations of the spin orbitals which appear in the determinant. A number of well-known properties of the electron wavefunction arise immediately from this expression. In particular, it is clear that it is impossible for two electrons to occupy the same state, as this would cause the determinant to be zero everywhere. By the same reasoning, the wavefunction must go to zero if any two electrons have the same coordinate $\vec{x}$. The typical notation for a single Slater determinant has the form

$$\Phi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = |\chi_i \chi_j \dots \chi_k\rangle \quad (2.8)$$

where the indices $\vec{x}$ have been dropped for brevity, but are still implicit.

A single Slater determinant is the simplest possible form that an electronic wavefunction can take. Restricting only to states of this form, an approximation to the ground state of the system $|\Phi_0\rangle = |\chi_i \chi_j \dots \chi_k\rangle$ can be derived via the variational principle by minimising the energy of this state with respect to changes in the component spin-orbitals

$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \quad (2.9)$$

This approach leads to the well-known Hartree-Fock (HF) approximation [29], with $|\Phi_0\rangle$ being the Hartree-Fock ground state and the resulting χ_i being the Hartree-Fock spin orbitals. Taking such a variational approach leads to the Hartree-Fock equation for the spin orbitals, now expressed in terms of an effective single-electron operator

$$\hat{f}(\vec{x}_1) \chi_i(\vec{x}_1) = \varepsilon_i \chi_i(\vec{x}_1) \quad (2.10)$$

where the Fock operator $\hat{f}$ is defined by

$$\begin{aligned} \hat{f}(\vec{x}_1) \chi_i(\vec{x}_1) = & -\frac{1}{2} \nabla_{\vec{r}_1}^2 \chi_i(\vec{x}_1) - \sum_{A=1}^M \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|} \chi_i(\vec{x}_1) + \sum_{j=1}^N \int d\vec{x}_2 \frac{|\chi_j(\vec{x}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \chi_i(\vec{x}_1) \\ & - \sum_{j=1}^N \int d\vec{x}_2 \frac{\chi_j^*(\vec{x}_2) \chi_i(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} \chi_j(\vec{x}_1) \end{aligned} \quad (2.11)$$

The unphysical $j = i$ terms in the final two summations are not explicitly excluded here as the resulting terms cancel with each other. In this equation, the first two terms correspond simply to the single-particle part of the electronic Hamiltonian. The third term has a simple classical explanation as the contribution to the energy from the interaction of an electron in the orbital χ_i with the electric field due to the remaining electrons, and it is therefore referred to as the ‘Coulomb’ or ‘direct’ term. The fourth term, however, has no such classical explanation. This ‘exchange’ term appears due to the exchange correlation arising from the Pauli exclusion principle, and is purely quantum in nature. In fact, in the closed shell case, the spin element of the Hartree-Fock equations can be integrated out, allowing the equation to be written as

$$\begin{aligned} \hat{f}(\vec{r}_1)\psi_i(\vec{r}_1) = & -\frac{1}{2}\nabla_{\vec{r}_1}^2\chi_i(\vec{r}_1) - \sum_{A=1}^M \frac{Z_A}{|\vec{r}_1 - \vec{R}_A|}\psi_i(\vec{r}_1) + 2\sum_{j=1}^{N/2} \int d\vec{r}_2 \frac{|\psi_j(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}\psi_i(\vec{r}_1) \\ & - \sum_{j=1}^{N/2} \int d\vec{r}_2 \frac{\psi_j^*(\vec{r}_2)\psi_i(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\psi_j(\vec{r}_1) \end{aligned} \quad (2.12)$$

It is clear that the Fock operator itself has non-trivial dependence on its own solutions $\{\psi_i\}$, so the solution proceeds by an iterative method: an initial guess is made for the density matrix of the system, which is used to calculate an initial form for the Fock operator. Having fixed the Fock operator, the orbitals which would solve the Hartree-Fock equation for this static choice of Fock operator are then calculated. The resulting orbitals are used to generate a new, improved density matrix, which is used as a new guess for the density matrix of the system from which the Fock operator can be recalculated. This procedure repeats until the set of orbitals is converged, leading to this process sometimes being termed the ‘self-consistent field’ method.

In order to approach this numerically, the orbitals $\{\psi_i\}$ must be expressed in terms of a basis set

$$\psi_i(\vec{r}) = \sum_{\alpha} c_{\alpha}^i \phi_{\alpha}(\vec{r}) \quad (2.13)$$

As the completeness of the basis is increased, the solution of the HF equation will approach an limiting value known as the Hartree-Fock limit. While only $N/2$ spatial orbitals are needed for the ground state, for any adequate basis the Hartree-Fock equation also produces a substantial number of higher-energy unoccupied ‘virtual’ orbitals. Excited states can therefore also be described in this scheme by constructing a Slater determinant which replaces some of the ground-state occupied orbitals with virtual orbitals. Koopman’s theorem states that the eigenvalue ε_i corresponds to the (negative) ionisation potential for the occupied orbital ψ_i assuming the other orbitals are all left static; and the equivalent is true for the electron affinity if ψ_i is unoccupied.

The Hartree-Fock scheme is computationally inexpensive, and for small molecules it is not unreasonable to get very close to the HF limit. Unfortunately, the single Slater determinant approximation has severe limitations on its accuracy even with arbitrarily large basis sets. In some cases, it can produce qualitatively incorrect results even for very small molecules. As one illustrative example, the symmetry of the HF HOMO in the nitrogen molecule N_2 implies the incorrect symmetry for the singly ionised state [29, 49].

Nonetheless, the molecular orbitals which arise from the HF equation not only provide a very useful perspective for understanding electronic behaviour, but they also serve as

a starting point for a number of more accurate approximations. Probably the most obvious extension is to allow the wavefunction to consist of a linear combination of Slater determinants

$$|\Psi\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \frac{1}{(2!)^2} \sum_{ij,ab} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \frac{1}{(3!)^2} \sum_{ijk,abc} C_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots \quad (2.14)$$

Here the excited Slater determinants are expressed in terms of their differences to the ground state, with the lower indices corresponding to spin orbitals from which an electron has been removed, and the upper indices corresponding to a now-populated virtual orbital. For instance, the term $|\Phi_{ij}^{ab}\rangle$ differs from the ground state by the replacement of the orbitals χ_i and χ_j with the orbitals χ_a and χ_b . It will be useful to introduce the notation of creation and annihilation operators, which act on a Slater determinant as

$$c_a^\dagger |\chi_1 \dots \chi_N\rangle = |\chi_a \chi_1 \dots \chi_N\rangle; \quad (2.15)$$

$$c_i |\chi_i \chi_1 \dots \chi_N\rangle = |\chi_1 \dots \chi_N\rangle; \quad (2.16)$$

$$c_i |\chi_1 \dots \chi_N\rangle = 0 \text{ if } i \text{ is not in } \{1, \dots, N\} \quad (2.17)$$

where it is important to note that in equation (2.15), $|\chi_a \chi_1 \dots \chi_N\rangle$ is zero by definition if a is in $\{1, \dots, N\}$. These operators obey the anticommutation relations

$$\{c_i, c_j^\dagger\} = c_i c_j^\dagger + c_j^\dagger c_i = \delta_{ij}; \quad (2.18)$$

$$\{c_i, c_j\} = \{c_i^\dagger, c_j^\dagger\} = 0 \quad (2.19)$$

The state $|\Phi_{ij}^{ab}\rangle$, for example, can then be expressed as $c_a^\dagger c_b^\dagger c_j c_i |\Phi_0\rangle$. For a system with N electrons, the summation in equation (2.14) above can include up to N -tuply excited determinants. Constructing and diagonalising the Hamiltonian in this set of determinants leads to the approach known as configuration interaction (CI). If all possible determinants are included, this is referred to as full CI. Within a given basis $\{\phi_i(\vec{r})\}$, the states and energies obtained via the full CI approach are as accurate as it is possible to get, however the dimension of this Hamiltonian grows incredibly rapidly with basis size, with the total number of determinants required for n -tuple excitations scaling as

$$\dim_n = \frac{N_{occ}! N_{virt}!}{(n!)^2 (N_{occ} - n)! (N_{virt} - n)!} \quad (2.20)$$

This restricts the relevance of full CI to only the smallest systems. It is possible to extend the applicability of this technique somewhat by forcing some orbitals to remain

occupied and optimising the virtual orbital space to allow the number of virtual orbitals to be sharply restricted [50], but even here systems with around 20 electrons form the upper practical limit.

An alternative common approach is to truncate the CI expansion by including only up to a specific class of excited determinant; the method of configuration interaction singles and doubles (CISD), for instance, adds only the sets of singly and doubly excited Slater determinants to the HF ground state. Truncated CI has one particularly notable flaw, however: it lacks size-consistency. If a system is extended by adding a set of n identical, non-interacting copies of itself, it should be expected that the energy of the new system is simply n times that of the original. Truncated CI fails this test, with the failure becoming increasingly bad as n increases. This can be understood by observing that in, for example, CISD, it is possible to have a single molecule with a double excitation on it. When considering a pair of molecules, however, a double excitation on both would constitute a forbidden quadruple excitation of the full system. Thus, the larger system cannot contain the entirety of both component systems at once, so these systems of different sizes are not treated consistently within this procedure [29]. An alternative method for building on the HF approximation, which forms the basis of all of the heavy numerical calculation performed in this work, is the method of algebraic diagrammatic construction (ADC) [30, 51].

2.2 Algebraic Diagrammatic Construction

In its original form [30], ADC provides a method of deriving approximations to the electron propagator or polarisation propagator which can be extended in a systematic manner to produce an approximation complete through any chosen order of n perturbation theory, $\text{ADC}(n)$. The propagator contains information about a number of quantities such as transition amplitudes and ionisation or excitation energies which can then be retrieved from this calculation. A brief outline of the original derivation will be given in the first section; and the later sections will contain a more in-depth discussion of an alternative formulation of the same theory through a wavefunction approach which extends its applicability to quantities beyond those described by the propagator, in particular allowing the description of general operators within this formalism.

2.2.1 Propagator Approach to ADC

For the ionic system, the ADC procedure arises from the electron propagator, which takes the form in the energy representation [51]

$$\begin{aligned}
G_{pq}(\omega) &= G_{pq}^+(\omega) + G_{pq}^-(\omega) \\
&= \langle \Psi_0 | c_p (\omega - \hat{H} + E_0 + i\eta)^{-1} c_q^\dagger | \Psi_0 \rangle + \langle \Psi_0 | c_q^\dagger (\omega + \hat{H} - E_0 - i\eta)^{-1} c_p | \Psi_0 \rangle \quad (2.21)
\end{aligned}$$

where $c_p, c_q^\dagger$ are the annihilation and creation operators, $\hat{H}$ is the Hamiltonian, E_0 is the exact ground state energy, η is a positive infinitesimal and $|\Psi_0\rangle$ is the exact ground state wave function. The propagator divides into two parts, G^+ and G^- , respectively corresponding to electron attachment and removal. Within the framework of direct ADC, the two parts are treated separately but in the exact same way, so we can restrict to the (N-1)-electron part, G^- , corresponding to ionisation. By inserting the resolution of the identity, it is possible to introduce the spectral representation

$$G_{pq}^-(\omega) = \sum_n \frac{\langle \Psi_0 | c_q^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | c_p | \Psi_0 \rangle}{\omega + E_n^{N-1} - E_0 - i\eta} \quad (2.22)$$

where the sum runs over a complete set of (N-1)-particle states. The electron propagator can thus be expressed as a sum over simple poles. It turns out that a finite perturbation expansion of the propagator is not able to reproduce this correct analytical form, whereas ADC does succeed in this regard through incorporating an infinite partial sum over particular classes of Feynman diagrams [51]. Defining the spectroscopic factors

$$x_p^{(n)} = x_{pn} = \langle \Psi_n^{N-1} | c_p | \Psi_0 \rangle \quad (2.23)$$

and the negative ionisation energies

$$\omega_n = -I_n = E_0 - E_n^{N-1} \quad (2.24)$$

the (transposed) electron propagator matrix can be written

$$\tilde{\mathbf{G}}(\omega) = \mathbf{G}^-(\omega)^T = \tilde{\mathbf{x}}(\omega \mathbf{1} - \mathbf{\Omega})^{-1} \tilde{\mathbf{x}}^\dagger \quad (2.25)$$

where $\tilde{\mathbf{x}}$ is the transpose of the matrix of spectroscopic factors x_{pn} , $\mathbf{\Omega}$ is a diagonal matrix of negative ionisation energies, and the infinitesimal η has been dropped. Inserting an as-yet undetermined unitary transformation $\mathbf{X}$ allows the propagator to be expressed in the ADC representation:

$$\tilde{\mathbf{G}}(\omega) = \mathbf{f}^\dagger (\omega \mathbf{I} - \mathbf{K} - \mathbf{C})^{-1} \mathbf{f} \quad (2.26)$$

making the definitions

$$(\mathbf{K} + \mathbf{C})\mathbf{X} = \mathbf{X}\mathbf{\Omega} \quad \mathbf{X}\mathbf{X}^\dagger = 1 \quad (2.27)$$

and

$$\tilde{\mathbf{x}} = \mathbf{X}^\dagger \mathbf{f} \quad (2.28)$$

The goal of the ADC method is to determine the matrices $\mathbf{K} + \mathbf{C}$ and $\mathbf{f}$, after which the unitary transformation matrix $\mathbf{X}$ can be recovered as the matrix of eigenvectors of $\mathbf{K} + \mathbf{C}$, as expressed in the ADC secular equations (2.27) and the spectroscopic factors can likewise be obtained from (2.28).

The unitary transformation $\mathbf{X}$ can be seen as a rotation between the basis of (N-1)-electron energy eigenstates $|\Psi_n^{N-1}\rangle$ and an alternative basis of intermediate states $|\tilde{\Psi}_I\rangle$, where the index I corresponds to an (N-1)-electron Hartree-Fock configuration. The alternative approach to deriving ADC in which these intermediate states are fundamental will be discussed in the following section. The ADC secular matrix $\mathbf{K} + \mathbf{C}$ can be written as a perturbation expansion:

$$\mathbf{K} + \mathbf{C} = \mathbf{K} + \mathbf{C}^{(1)} + \mathbf{C}^{(2)} + \dots \quad (2.29)$$

where the zeroth order component $\mathbf{K}$, a diagonal matrix of Hartree-Fock ionisation energies, is explicitly separated from the higher order components $\mathbf{C}$, and the difference between the full Hamiltonian than the Hartree-Fock Hamiltonian is treated as a perturbation. The matrices $\mathbf{f}$ can likewise be expanded:

$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \mathbf{f}^{(2)} + \dots \quad (2.30)$$

Finally, expanding the matrix $(\omega \mathbf{I} - \mathbf{K} - \mathbf{C})^{-1}$ as a geometric series in $\mathbf{C}$ allows the propagator $\tilde{\mathbf{G}}(\omega)$ to be separated out into contributions at each order.

$$\tilde{\mathbf{G}}(\omega) = \mathbf{f}^\dagger (\omega \mathbf{I} - \mathbf{K})^{-1} \sum_{\nu=0}^{\infty} (\mathbf{C}(\omega \mathbf{I} - \mathbf{K})^{-1})^\nu \mathbf{f} \quad (2.31)$$

and inserting the expansions of $\mathbf{C}$ and $\mathbf{f}$ allows each term in this expression for $\tilde{\mathbf{G}}(\omega)$ to have a well-defined order. The nature of the $\mathbf{K}$ matrix gives rise to a block structure of the secular matrix, as the elements of $\mathbf{K}$ can be labelled as one hole (1h), two holes, one particle (2h1p), and so on, depending on the number of positive and negative HF energies appearing in each element. The elements $K_{a,a} = \varepsilon_a$ correspond to 1h states, for instance, while the elements $K_{jab,jab} = \varepsilon_a + \varepsilon_b - \varepsilon_j$ are 2h1p. The full secular matrix therefore divides into blocks labelled by excitation order. Now it is possible to proceed through each order of contribution to the propagator, comparing the perturbation expansion of $\tilde{\mathbf{G}}(\omega)$ to the contributions arising from Feynman diagrams of the same order. By matching diagrams to corresponding terms in the ADC perturbation expansion and comparing the mathematical expressions which arise, the values of the matrices $\mathbf{C}$ and $\mathbf{f}$ can be obtained such that the expansion (2.31) reproduces the form of the electron propagator obtained from the Feynman diagrams at this order.

2.2.2 Intermediate State Representation (ISR)

While the ADC method was originally obtained via the propagator approach [30], it was later demonstrated that it was possible to reinterpret and rederive the same set of equations via a more traditional wavefunction approach [51, 52]. This formulation of ADC is known as the intermediate state representation (ISR). As a wavefunction approach, ISR-ADC also allows the construction of general operators between different states, enabling the calculation of transition matrix elements. The ISR approach begins by considering the so-called correlated excited states

$$|\Psi_J^0\rangle = \hat{C}_J |\Psi_0\rangle \quad (2.32)$$

Again considering the (N-1)-electron system, the $\hat{C}_J$ refer to sets of creation and annihilation operators corresponding to Hartree-Fock states of the form 1h, 2h1p, 3h2p, and so on:

$$\{\hat{C}_J\} = \{c_j; c_a^\dagger c_j c_k, j < k; c_a^\dagger c_b^\dagger c_j c_k c_l, a < b, j < k < l; \dots\} \quad (2.33)$$

where the indices $j, k, l, \dots$ refer to occupied orbitals and $a, b, \dots$ refer to unoccupied ones. $|\Psi_0\rangle$ is the perturbation theoretically corrected ground state. This latter point is the

key distinction between ISR-ADC and configuration interaction, where the same operators act on the HF ground state. The inclusion of these corrections within $|\Psi_0\rangle$ ensures that the ground state correlation is incorporated into the entire basis automatically. The set of correlated excited states form a complete basis for the $(N - 1)$ -electron system [53]. These states can be split into excitation classes $[J]$, where $[J]=\mu$ corresponds to the set of $\mu h - (\mu - 1)p$ states. As the operators are no longer acting on the Hartree-Fock ground state, commuting the creation and annihilation operators will not destroy the ground state and thus the states $|\Psi_J^0\rangle$ are not orthonormal:

$$\langle \Psi_I^0 | \Psi_J^0 \rangle = S_{IJ} \neq \delta_{I,J} \quad (2.34)$$

S_{IJ} here are the elements of the overlap matrix. In order to obtain a useful basis, the correlated excited states must be orthonormalized. The procedure chosen for this is known as excitation class orthogonalization (ECO). This process consists of two steps for each excitation class: first, all states within the class are made orthogonal to all lower excitation classes via Gram-Schmidt orthogonalization; and second, symmetric orthonormalization is applied to the states within the excitation class. The first step therefore involves building the precursor states $|\Psi_J^\# \rangle$ which are orthogonalised with respect to the lower excitation classes. Assuming that the intermediate states $|\tilde{\Psi}_K \rangle$ for the classes $[K] < \nu$ have already been constructed, the precursor states for class ν can be expressed as

$$|\Psi_J^\# \rangle = |\Psi_J^0 \rangle - \sum_{[K] < \nu} |\tilde{\Psi}_K \rangle \langle \tilde{\Psi}_K | \Psi_J^0 \rangle, \quad [J] = \nu \quad (2.35)$$

This expression necessarily requires that the excitation classes are built in ascending sequence. Once constructed, the set of precursor states for class ν is then symmetrically orthonormalized within itself:

$$|\tilde{\Psi}_J \rangle = \sum_{[I]=\nu} |\Psi_I^\# \rangle (\mathbf{S}_\nu^{-\frac{1}{2}})_{IJ} \quad (2.36)$$

with $\mathbf{S}_\nu$ the overlap matrix of precursor states of class ν

$$(\mathbf{S}_\nu)_{IJ} = \langle \Psi_I^\# | \Psi_J^\# \rangle, \quad [I] = [J] = \nu \quad (2.37)$$

The choice of symmetric orthonormalization within each excitation class is not strictly necessary for the procedure to work – other orthonormalization methods could in principle be used. A notable property of symmetric orthonormalization, however, is that it

preserves as closely as possible the link between the initial non-orthogonal states and the corresponding orthonormalized states. This choice of orthonormalization procedure therefore means that the final states can typically each be meaningfully associated with a particular HF configuration J . The ground state $|\Psi_0\rangle$ follows the typical perturbation expansion within Møller-Plesset (MP) Rayleigh-Schrödinger perturbation theory, written using intermediate normalisation $\langle\Psi_0|\Phi_0\rangle = 1$ with $|\Phi_0\rangle$ the Hartree-Fock ground state:

$$|\Psi_0\rangle = |\Phi_0\rangle + |\Psi_0^{(1)}\rangle + |\Psi_0^{(2)}\rangle + \dots \quad (2.38)$$

from which it follows that the intermediate states can be similarly expressed as

$$|\tilde{\Psi}_J\rangle = |\Phi_J\rangle + |\Psi_J^{(1)}\rangle + |\Psi_J^{(2)}\rangle + \dots \quad (2.39)$$

Where it has been made explicit that the zeroth order contribution to the intermediate states is just the HF state $|\Phi_J\rangle = \hat{C}_J|\Phi_0\rangle$. Within this perturbation theory, the first order correction to the ground state is a sum over double excitations $|\Phi_{jk}^{ab}\rangle$ of the HF ground state, while the second order correction includes single, double, triple, and quadruple excitations. An explicit expression for the first order correction is given by

$$|\Psi_0^{(1)}\rangle = \sum_{abjk} \frac{\langle ab||jk\rangle}{\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b} |\Phi_{jk}^{ab}\rangle \quad (2.40)$$

Here, the values ε_i are the HF energies of the states i , and

$$\langle ab||jk\rangle = \langle ab|jk\rangle - \langle ab|kj\rangle \quad (2.41)$$

is defined in terms of the the two-electron integrals between spin-orbitals

$$\langle ij|kl\rangle = (ik, jl) = \int \int d\vec{x}_1 d\vec{x}_2 \frac{\chi_i^*(\vec{x}_1) \chi_j^*(\vec{x}_2) \chi_k(\vec{x}_1) \chi_l(\vec{x}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (2.42)$$

Defining the ISR secular matrix $\mathbf{M}$ as the representation of the shifted Hamiltonian in terms of intermediate states

$$M_{IJ} = \langle \tilde{\Psi}_I | \hat{H} - E_0 | \tilde{\Psi}_J \rangle \quad (2.43)$$

and noting that both $\hat{H}$ and E_0 are also split into terms of different order in the

perturbation

$$\hat{H} = \hat{H}_0 + \hat{H}_I \quad (2.44)$$

where $\hat{H}_0$ is the one-particle Hartee-Fock Hamiltonian, and $\vec{H}_I$ is the perturbation; and

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \dots \quad (2.45)$$

it is clear that $\mathbf{M}$ also splits into contributions from different perturbation orders

$$M_{IJ} = M_{IJ}^{(0)} + M_{IJ}^{(1)} + M_{IJ}^{(2)} + \dots \quad (2.46)$$

The matrix $\mathbf{M}$ can be diagonalised, having eigenvectors and corresponding eigenvalues

$$|\Psi_n^{N-1}\rangle = \sum_I X_{In} |\tilde{\Psi}_I\rangle \quad (2.47)$$

$$\omega_n = E_n^{N-1} - E_0 \quad (2.48)$$

which can be expressed in the form of the ISR secular equations

$$\mathbf{M}\mathbf{X} = \mathbf{X}\mathbf{\Omega} \quad \mathbf{X}^\dagger \mathbf{X} = 1 \quad (2.49)$$

At this point, it is possible to draw the connection to the propagator method. It can be more directly observed that the matrix $\mathbf{M}$ can be identified with the propagator method ADC secular matrix $\mathbf{K} + \mathbf{C}$ by inserting the resolution of the identity in terms of intermediate states into the definition (2.21) of the electron propagator [51]. This returns

$$G_{pq}^-(\omega) = \sum_{I,J} \langle \Psi_0 | c_q^\dagger | \tilde{\Psi}_I \rangle \langle \tilde{\Psi}_I | (\omega + \hat{H} - E_0 - i\eta)^{-1} | \tilde{\Psi}_J \rangle \langle \tilde{\Psi}_J | c_p | \Psi_0 \rangle \quad (2.50)$$

Dropping the infinitesimal and comparing to equation (2.26), it can be seen that after making the assignments for the secular matrix

$$(\mathbf{K} + \mathbf{C})_{IJ} = \langle \tilde{\Psi}_I | -\hat{H} + E_0 | \tilde{\Psi}_J \rangle = -M_{IJ} \quad (2.51)$$

and the transition amplitudes

$$\mathbf{f} = \langle \tilde{\Psi}_J | c_p | \Psi_0 \rangle \quad (2.52)$$

the two equations become identical. The spectroscopic factors can again be recovered in the same manner as equation (2.28). The true proof of the equivalence of the two approaches, however, comes in the form of a pair of shared properties: the separability of the system with respect to non-interacting subsystems, and the so-called ‘canonical order relations’ which dictate the lowest perturbation order at which matrix elements between states of different excitation order begin to appear. Both of these will be discussed at greater length in section 2.2.4.

Having obtained a perturbation expansion for the elements of the ADC secular matrix, it is necessary to establish a coherent way to truncate these expansions to obtain a scheme which can be numerically evaluated. The ADC(n) hierarchy of approximations provides one such scheme, including the set of elements of the ADC secular matrix necessary to treat the 1h states consistently through n^{th} order of perturbation theory. Considering now the ADC(2) scheme, the matrix elements can be divided into three blocks. For the 1h-1h coupling block, the elements must be included through second order

$$M_{j,j'} = M_{j,j'}^{(0)} + M_{j,j'}^{(1)} + M_{j,j'}^{(2)} \quad (2.53)$$

The 1h-2h1p block must be expanded through first order

$$M_{j,a'j'k'} = M_{j,a'j'k'}^{(0)} + M_{j,a'j'k'}^{(1)} \quad (2.54)$$

and the 2h1p-2h1p block is only required to zeroth order

$$M_{ajk,a'j'k'} = M_{ajk,a'j'k'}^{(0)} \quad (2.55)$$

The 3h2p block turns out not to be required, as its perturbation theory expansion has no components below second order. To calculate each contribution, it is necessary to expand the matrix elements from (2.43) in terms of the perturbation expansions for the wavefunction (2.39), the Hamiltonian (2.44), and the energy (2.45). It is trivial to

see that the zeroth order contributions are nonzero only between identical intermediate states

$$M_{J,K} = \langle \Phi_J | (\hat{H}_0 - E_0^{(0)}) | \Phi_K \rangle = (E_J - E_0) \delta_{J,K} \quad (2.56)$$

So the zeroth order contribution to the 1h-2h1p block vanishes entirely. So too, it turns out, does the first order contribution to the 1h-1h block. After gathering together all of the contributions at each order, the final matrix elements can be calculated as [51]

$$M_{j,j'} = -\epsilon_j \delta_{jj'} + \sum_{a < b, k} \frac{\langle ab || jk \rangle}{\epsilon_a + \epsilon_b - \epsilon_j - \epsilon_k} \frac{\langle ba || kj' \rangle}{\epsilon_a + \epsilon_b - \epsilon_{j'} - \epsilon_k} (\epsilon_a + \epsilon_b - \epsilon_k - \frac{1}{2}\epsilon_j - \frac{1}{2}\epsilon_{j'}) \quad (2.57)$$

$$M_{j,a'j'k'} = \langle j'k' || ja' \rangle \quad (2.58)$$

$$M_{ajk,a'j'k'} = (\epsilon_a - \epsilon_j - \epsilon_k) \delta_{aa'} \delta_{jj'} \delta_{kk'} \quad (2.59)$$

While this ISR approach to ADC is in many ways easier to interpret than propagator ADC, it turns out to be the case that the actual process of obtaining the expressions for the matrix elements is somewhat lengthy. The expressions tend to be easier to derive in the propagator scheme, and this difference is especially pronounced at ADC(3) and above. Where the crucial advantage of the ISR formulation lies is that, as a wavefunction approach, it also has the ability to express general operators within the same formalism. This is a crucial advantage over the propagator approach, which is limited to quantities derivable from the propagator itself. An operator in the intermediate state representation will have elements

$$\tilde{D}_{IJ} = \langle \tilde{\Psi}_I | \hat{D} | \tilde{\Psi}_J \rangle \quad (2.60)$$

The expectation value of the operator in a given ionic state, D_n , and transition matrix elements between a pair of ionic states, D_{nm} , can be calculated in the standard manner

$$D_n = \langle \Psi_n^{N-1} | \hat{D} | \Psi_n^{N-1} \rangle = \mathbf{X}_n^\dagger \tilde{\mathbf{D}} \mathbf{X}_n \quad (2.61)$$

$$D_{nm} = \langle \Psi_n^{N-1} | \hat{D} | \Psi_m^{N-1} \rangle = \mathbf{X}_n^\dagger \tilde{\mathbf{D}} \mathbf{X}_m \quad (2.62)$$

where $\tilde{\mathbf{D}}$ is the matrix representation of $\hat{D}$ in the basis of intermediate states, and $\mathbf{X}_n$ is the eigenvector from equation (2.47). Another important property is the ability to

modify the Hamiltonian by the addition of a general perturbation operator $\hat{D}$, producing a modified secular matrix equation

$$(M + \tilde{D})X = X\Omega^D \quad X^\dagger X = 1 \quad (2.63)$$

which can later be used for time propagation. In order to do this, the operator must be expressed in the basis of intermediate states. Just like the Hamiltonian, it will have a perturbation theory expansion

$$\tilde{D}_{IJ} = \tilde{D}_{IJ}^{(0)} + \tilde{D}_{IJ}^{(1)} + \tilde{D}_{IJ}^{(2)} + \dots \quad (2.64)$$

which should be truncated at an order consistent with the Hamiltonian for the chosen level of ADC. In the case of ADC(2), this gives

$$\begin{aligned} \tilde{D}_{j,j'} &= \tilde{D}_{j,j'}^{(0)} + \tilde{D}_{j,j'}^{(1)} + \tilde{D}_{j,j'}^{(2)} \\ \tilde{D}_{j,a'j'k'} &= \tilde{D}_{j,a'j'k'}^{(0)} + \tilde{D}_{j,a'j'k'}^{(1)} \\ \tilde{D}_{ajk,a'j'k'} &= \tilde{D}_{ajk,a'j'k'}^{(0)} \end{aligned} \quad (2.65)$$

A generic one-particle operator can be written as

$$\hat{D} = \sum_{pq} d_{pq} c_p^\dagger c_q \quad (2.66)$$

The expressions for the matrix elements of such an operator are somewhat more complex than in the case of the Hamiltonian, and are given in full in reference [54], but it is worth noting here that unlike in the Hamiltonian case the zeroth order contribution $\tilde{D}_{j,a'j'k'}$ can no longer be expected to vanish.

2.2.3 ADC for the Neutral System

The previous discussion of ADC concerned only the $(N - 1)$ -electron system. The exact same analysis transfers essentially unchanged to the N -electron system from both the propagator and ISR perspectives [51, 30], although the resulting matrix elements are somewhat more complicated. In the N -electron case, the relevant states of the system are $\mu h \mu p$ excitations of the neutral - although, for a suitable basis, these excitations can also involve the continuum-like orbitals of ionised electron states.

In the ISR, the first step is again the construction of the correlated excited states $|\Psi_J^0\rangle = \hat{C}_J|\Psi_0\rangle$, but here the excitation operators correspond to the $\mu h\mu p$ excitations

$$\{\hat{C}_J\} = \{c_a^\dagger c_j; c_a^\dagger c_b^\dagger c_j c_k, a < b, j < k; c_a^\dagger c_b^\dagger c_c^\dagger c_j c_k c_l, a < b < c, j < k < l; \dots\} \quad (2.67)$$

and the excitation order $[J] = \mu$ is now defined to correspond to $\mu h\mu p$ states. Proceeding to the ECO procedure, it is important to note that the zero-excitation ground state $|\Psi_0\rangle$ is also a possible state of the N -electron system, forming what is effectively a zeroth excitation class. All of the excitation classes, including the first order, must therefore also be orthogonalised with respect to the ground state during the Gram-Schmidt procedure. Otherwise, the exact same steps are followed: The precursor states are constructed according to (2.35), where the sum over lower excitation classes now includes the ground state. The symmetric orthonormalisation of the precursor states then proceeds exactly as in equation (2.36). Once again, the secular matrix is built in the basis of intermediate states as $M_{IJ} = \langle \tilde{\Psi}_I | (\hat{H} - E_0) | \tilde{\Psi}_J \rangle$, and the generic expressions for the perturbation expansions of the wavefunction (2.39), the Hamiltonian (2.44), the ground state energy (2.45), and the matrix elements (2.46) are identical to the $(N - 1)$ -electron case, albeit with indices I now running over the $\mu h\mu p$ excitations.

For the N -electron system, the ADC(n) heirarchy is again defined such that the first-order excitations are correct through to n^{th} order of perturbation theory, where the first-order excitations are now 1h1p rather than just 1h states. As the ground state is by definition already an eigenstate of the system, it can be left out of the Hamiltonian construction for now. Considering again the ADC(2) case, the required basis is again spanned by the first and second excitation orders - here, the 1h1p and 2h2p states. The non-zero contributions to the matrix elements of each block of the secular matrix take the form [51]

$$M_{aj,a'j'} = M_{aj,a'j'}^{(0)} + M_{aj,a'j'}^{(1)} + M_{aj,a'j'}^{(2)} \quad (2.68)$$

$$M_{aj,a'b'j'k'} = M_{aj,a'b'j'k'}^{(1)} \quad (2.69)$$

$$M_{abjk,a'b'j'k'} = M_{abjk,a'b'j'k'}^{(0)} \quad (2.70)$$

For the 1h1p-1h1p block the full expressions for each contribution are

$$M_{aj,a'j'}^{(0)} = (\epsilon_a - \epsilon_j)\delta_{aa'}\delta_{jj'} \quad (2.71)$$

$$M_{aj,a'j'}^{(1)} = -\langle aj' || a'j \rangle \quad (2.72)$$

$$\begin{aligned} M_{aj,a'j'}^{(2)} = & \frac{1}{2}\delta_{jj'} \sum_{clm} v_{aclm} v_{lma'c} (\epsilon_l + \epsilon_m - \epsilon_c - \frac{1}{2}\epsilon_a - \frac{1}{2}\epsilon_{a'}) \\ & + \frac{1}{2}\delta_{aa'} \sum_{cdl} v_{cdjl} v_{j'lcd} (\epsilon_l - \epsilon_c - \epsilon_d + \frac{1}{2}\epsilon_j + \frac{1}{2}\epsilon_{j'}) \\ & + \frac{1}{2} \sum_{cl} v_{j'la'c} v_{aclj} (\epsilon_l - \epsilon_c + \frac{1}{2}(\epsilon_j + \epsilon_{j'} - \epsilon_a - \epsilon_{a'})) \end{aligned} \quad (2.73)$$

For the 1h1p-2h2p block the expression is

$$M_{aj,a'b'j'k'}^{(1)} = \delta_{aa'}\langle j'k' || jb' \rangle - \delta_{ab'}\langle j'k' || ja' \rangle - \delta_{jj'}\langle ak' || a'b' \rangle + \delta_{jk'}\langle aj' || a'b' \rangle \quad (2.74)$$

and the 2h2p-2h2p block is given by

$$M_{abjk,a'b'j'k'}^{(0)} = (\epsilon_a + \epsilon_b - \epsilon_j - \epsilon_k)\delta_{aa'}\delta_{bb'}\delta_{jj'}\delta_{kk'} \quad (2.75)$$

The shorthand v_{abij} in the above expressions is defined as

$$v_{abij} = \frac{\langle ab || ij \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (2.76)$$

Due to both the larger dimension of the Hamiltonian for a given basis set and the greater number of virtual orbital summation terms required for each matrix element, the computational cost of the ADC(n) approach is substantially higher in this N -electron case than it was for the $(N - 1)$ -electron system, assuming all other parameters of the basis are held constant.

The representation of a general operator is likewise possible in the N -electron ISR, and the general form of its representation in the intermediate state basis $D_{IJ} = \langle \Psi_I | \hat{D} | \Psi_J \rangle$ again matches exactly that from the $(N - 1)$ -electron case, replacing the excitations I with those of the $\mu h \mu p$ type. If such an operator is being treated as a perturbation to the Hamiltonian, it does become necessary to include the ground state explicitly in the Hamiltonian as the perturbation may couple the ground state to the excited intermediate states.

$$D_{00} = \langle \Psi_0 | \hat{D} | \Psi_0 \rangle; \quad D_{0J} = \langle \Psi_0 | \hat{D} | \tilde{\Psi}_J \rangle \quad (2.77)$$

The perturbation order of the blocks required at a given ADC level is also unchanged from the previous discussion. At the ADC(2) level, for a general single-electron operator, the explicit expansions of the matrix elements D_{IJ} are calculable. The full expressions for the matrix elements are fairly lengthy, but can be found at reference [55].

For completeness, it is also worth briefly mentioning the equivalent propagator construction in the N -electron case, which is based on constructing approximations to the polarisation propagator [30, 51]. Unlike the electron propagator, which deals with ionisation, the major quantities of interest given by the polarisation propagator are excitation energies $E_n - E_0$ and transition amplitudes $\langle \Psi_n | c_r^\dagger c_s | \Psi_0 \rangle$ for excited states $|\Psi_n\rangle$. In the spectral representation, the polarisation propagator takes the form

$$\Pi_{pq,rs}(\omega) = \Pi_{pq,rs}^+(\omega) + \Pi_{pq,rs}^-(\omega); \quad (2.78)$$

$$\Pi_{pq,rs}^+(\omega) = \sum_{n \neq 0} \frac{\langle \Psi_0 | c_q^\dagger c_p | \Psi_n \rangle \langle \Psi_n | c_r^\dagger c_s | \Psi_0 \rangle}{\omega - E_n + E_0 + i\eta}, \quad \Pi_{pq,rs}^-(\omega) = \Pi_{sr,qp}^+(-\omega) \quad (2.79)$$

with the excitation energies and transition amplitudes taking the place of the negative ionisation energies and spectral moments in the electron propagator. This directly parallels equation 2.22, and the secular matrix $\mathbf{M} = \mathbf{K} + \mathbf{C}$ can be similarly retrieved by comparing the contributions to

$$\mathbf{\Pi}^+(\omega) = \mathbf{f}^\dagger (\omega - \mathbf{K} - \mathbf{C})^{-1} \mathbf{f} \quad (2.80)$$

to the polarisation propagator Feynman diagrams. Similarly to the $(N - 1)$ -electron case, this provides a more manageable approach to actually obtaining the formulae for the ADC matrix elements at higher levels of approximation.

2.2.4 Properties of ADC

Viewed through the lens of the ISR, ADC provides a method for constructing the Hamiltonian of a system and thus deriving the electronic eigenstates. In the form of the ADC(n) schemes, it provides a systematically improvable approximation to the exact Hamiltonian. In this regard, it is similar to the configuration interaction (CI) approach. Where ADC practically differs from CI is in the form of two useful properties: the separability of the

secular matrix with respect to non-interacting fragments, and the canonical order relations which dictate the lowest order of perturbation theory contributions between matrix elements of particular excitation classes. It is in fact this pair of properties which, due to being shared between the ISR and propagator formulations, also provide a rigorous way of demonstrating the equivalence of the two approaches to ADC in spite of their unrelated derivations [51].

The property of separability with respect to non-interacting fragments relates to the size consistency question which proved to be a major flaw in CI. When considering a system with two non-interacting fragments, the ground state of the composite system can be expressed in the ISR as the product of the ground states of the individual systems

$$|\Psi_0\rangle = |\Psi_0^A\rangle|\Psi_0^B\rangle \quad (2.81)$$

The factorisation theorem states that the intermediate states of the composite system can similarly be expressed as such a product [56]

$$|\tilde{\Psi}_{J_{AB}}\rangle = |\tilde{\Psi}_{J_A}^A\rangle|\tilde{\Psi}_{J_B}^B\rangle \quad (2.82)$$

where J_{AB} labels a general set of Hartree-Fock states and corresponding creation and annihilation operators across both fragments, while J_A and J_B are the corresponding sets of states on each separate fragment. From this, it follows that the ADC secular matrix of such a system has a block structure such that excitations local to one fragment are not coupled to either excitations local to the other fragment, or to non-local excitations across both parts of the composite system. The full matrix is therefore separable into uncoupled blocks, and the blocks corresponding to the individual fragments are identical to the secular matrices of the isolated systems. This property means that unlike truncated CI, ADC can be considered to be a true many-body approach, as it can be extended to arbitrarily large systems without incurring systematic error.

In the previous discussion of the ADC matrix elements, it was noted that the 3h2p excitation class was not required at the ADC(2) level as the coupling between the first and third excitation classes had no contributions below the second order of perturbation theory. This is in fact a specific case of a much more general property of the ADC construction. For any given pair of intermediate states with indices I and J , the lowest order contribution to the corresponding matrix element depends on the corresponding excitation classes $[I]$ and $[J]$ according to the canonical order relations [57]

$$M_{IJ} \sim O(|[I] - [J]|) \quad (2.83)$$

The order relations take an identical form for both the N -electron and the $(N - 1)$ -electron cases. In the ISR approach, this property is a direct consequence of the Gram-Schmidt orthogonalization of excitation classes. The primary consequence of the canonical order relations is that they determine the perturbation order of the error in state energies which results from neglecting particular excitation classes, thus dictating which classes must be included to ensure that states are treated consistently up to a particular order. In general, if a particular eigenstate $|\Psi_n^{N-1}\rangle$ is composed predominantly of states of excitation class μ , the contributions to the corresponding ionisation energy will be linear in the elements of the diagonal block $\mathbf{M}_{\mu\mu}$, and quadratic in elements of the off-diagonal blocks $\mathbf{M}_{\mu\nu}$, $\mu \neq \nu$. This means that the truncation error order caused by neglecting configurations above class ν for the energy of a state $|\Psi_n^{N-1}\rangle$, $[n]=\mu$, is given by

$$O_{TE}^{[n]}(\nu) = 2(\nu - [n] + 1), \quad \nu \geq [n] \quad (2.84)$$

From this follows the ‘compactness’ property of ADC: as ADC(n) represents the class of 1h or 1h1p configurations consistently through the n th order of perturbation theory, additional configurations of excitation class $[\mu]$ (i.e. μ h- $(\mu-1)$ p or μ h- μ p configurations in the $(N - 1)$ - and N -electron cases respectively) must enter the picture at every second order of ADC. The excitation class μ therefore first appears in the calculation at ADC(n) where $n=2(\mu-1)$. This contrasts favourably with CI, in which both second and third excitation classes contribute to the first excitation class energies at second order, with a further two classes being required at each of 4th order, 6th order, and so on for every other order of approximation [51].

Similar expression can be formed for the canonical order relations for the eigenvector coefficients

$$\langle \tilde{\Psi}_I | \Psi_n \rangle \sim O(|[I] - [n]|) \quad (2.85)$$

for the transition amplitudes in the $(N - 1)$ - and N -particle cases

$$\langle \tilde{\Psi}_I | c_p | \Psi_0 \rangle \sim O([I] - 1) \quad \text{for } I \text{ an } (N - 1)\text{-particle configuration;} \quad (2.86)$$

$$\langle \tilde{\Psi}_I | c_q^\dagger c_p | \Psi_0 \rangle \sim O([I] - 1) \quad \text{for } I \text{ an } N\text{-particle configuration} \quad (2.87)$$

and for the matrix elements of a general one-particle operator $\hat{D}$

$$\tilde{D}_{IJ} \sim \begin{cases} O(0), & [I] = [J] \\ O(|[I] - [J]| - 1), & [I] \neq [J] \end{cases} \quad (2.88)$$

Notably, the lowest PT order to arise in each off-diagonal block of such a one-particle operator is one order lower than the corresponding secular matrix block.

Another useful property of ADC is that it can be modified in a somewhat ad-hoc manner to improve the descriptions of particular states beyond the standard ADC(n) scheme without involving the full complexity of a higher ADC(n) order. The most common such modification is made to improve the description of the 2h2p or 2h1p states at the ADC(2) level. While the energies of states in the first excitation class are represented through second order in ADC(2), the corresponding states in the second excitation class are only represented at zeroth order. This means that the treatment of double excitations in the N -electron system, or of ionisation plus excitation in the $(N - 1)$ -electron case, is often rather inaccurate. Following equation (2.84), the missing contribution to the state energies in the second excitation class from the neglected configurations in the third class begins only at second order, so adding just the first order components of the 2h2p-2h2p diagonal block (N -electron case) or 2h1p-2h1p diagonal block ($(N - 1)$ -electron case) is enough to gain an extra PT order of accuracy in these state energies. This first order contribution contains the lowest level of Hamiltonian coupling between different intermediate states in this excitation class, which would otherwise arise only at the ADC(3) level. The method which supplements ADC(2) with this additional contribution is known as ADC(2)x.

2.3 B-spline ADC

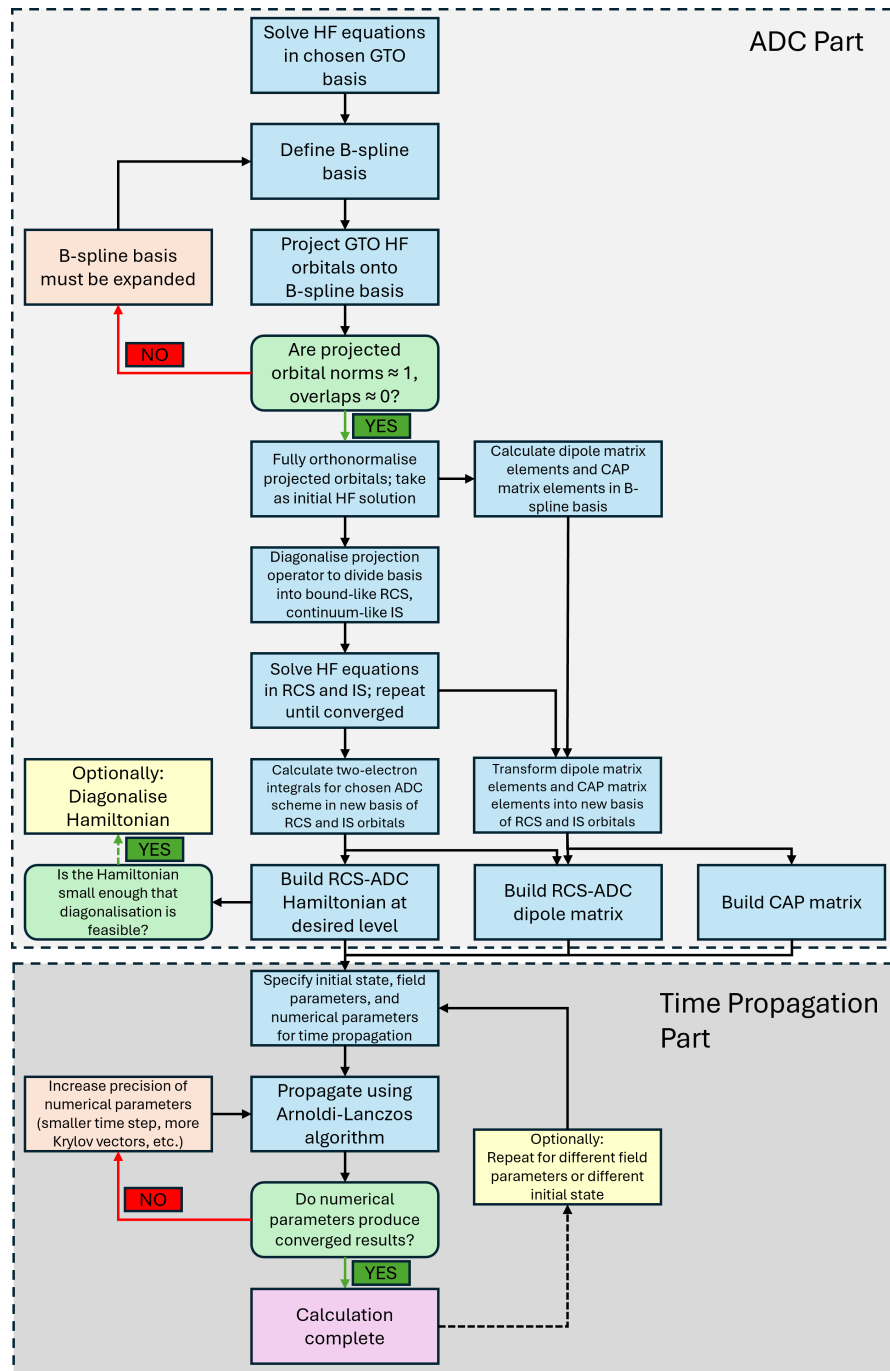


Figure 2.1: An schematic overview of the process of carrying out a calculation using the restricted correlation space B-spline ADC technique.

2.3.1 B-spline Basis

In order to actually carry out the calculation, it is necessary to define the basis set of functions from which the wavefunction can be constructed. Traditional formulations of post-Hartree-Fock approaches such as ADC use square-integrable ($\mathcal{L}^2$) basis functions closely centred on particular atoms within a molecule, most commonly Gaussian type orbitals (GTOs) or Slater type orbitals (STOs), which both exhibit exponential decrease in amplitude at large radii. These functions provide a good representation of the bound states of a molecule however they represent the continuum states poorly, being unable to effectively capture the oscillatory behaviour of the continuum wavefunction up to large distances from the molecule centre. This makes them of only limited use in describing phenomena such as ionisation [58]. Simply expanding the basis set fails to solve the problem, as this leads to the rapid onset of linear dependence issues - each additional basis function beyond a certain basis size can be very nearly expressed as a linear sum of the remaining functions, leading to numerical instability whereby minimal changes in the described state can produce large variation in the basis coefficients. Various methods do exist for getting around this issue, however, typically by replacing or supplementing the typical Gaussian type basis with another more well-suited to describing the continuum states. B-spline ADC [45, 46, 47] is one such method, in which the radial component of the basis functions is composed entirely of B-splines.

B-splines are an incredibly versatile class of $\mathcal{L}^2$ functions designed to closely approximate arbitrary curves [59], making them suitable for representing both the exponentially-decreasing bound states and the oscillatory continuum states. More specifically, B-splines are single-variable piecewise-polynomial functions of polynomial order k , defined over a non-decreasing sequence of points, or ‘knots’, which taken together span a finite interval $[0 : R_{max}]$. These functions have a number of useful properties:

- B-splines produce curves which change smoothly and have well-defined, continuous derivatives everywhere
- The precision of the approximation is dictated by the grid of points which can be made arbitrarily finely spaced, allowing arbitrarily close approximation of any function
- The maximum number of other B-splines that a given B-spline can overlap with is strictly set by the order k , so there is no possibility of running into the problem of linear dependence even with extremely dense basis sets
- The limited overlap also simplifies the numerical calculations, as integrals involving non-overlapping pairs of B-splines can be immediately set to zero

- Coefficients usually change slowly between adjacent B-splines, minimising the likelihood of errors arising from cancellation between different basis functions evaluated at the same point

For the purposes of basis set construction, B-splines were first applied in the atomic case in the 1970s [60], and have since been used in a wide variety of applications including atomic and molecular electronic structure, excitation, and photoionisation [61].

A set of B-splines is uniquely defined over a variable t by its polynomial order k and its knot sequence $\{t_i\}$, where each of the t_i denotes a value of t at which a knot is located. While the knot sequence is non-decreasing, it is possible for multiple knots to be placed at the same value, so the knot sequence can be alternatively defined by a series of unique breakpoints of increasing value $\{\xi_j\}$ with corresponding multiplicities $\{\mu_j\}$, such that μ_j knots lie at breakpoint ξ_j . Each adjacent pair of breakpoints ξ_j and ξ_{j+1} therefore defines an interval I_j .

Given the knot sequence, the first order B-splines are defined simply as

$$B_i^1(t) = \begin{cases} 1, & t_i \leq t < t_{i+1} \\ 0, & \text{otherwise} \end{cases} \quad (2.89)$$

with the higher orders, k , then following from the Cox-de Boor recursion relation [62]:

$$B_i^k(t) = \frac{t - t_i}{t_{i+k-1} - t_i} B_i^{k-1}(t) + \frac{t_{i+k} - t}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(t) \quad (2.90)$$

On each interval, the B-spline is therefore defined by a polynomial of order k , but at the breakpoints there is some level of discontinuity. The degree of continuity at breakpoint ξ_j is described by the continuity class $C^{k-\mu_j-1} = C^{\nu_j-1}$, where ν_j denotes the first level of derivative at which a discontinuity arises. That is, for $\nu_j = 0$ the function is discontinuous at ξ_j ; for $\nu_j = 1$ the first derivative is discontinuous; and so on. No breakpoints may have multiplicity greater than k , as this would result only in additional B-spline functions with a value of zero at all t without changing any of the other B-splines from the multiplicity k case.

From the definitions 2.89 and 2.90, a number of features become apparent. Firstly, the B-spline $B_i^k(t)$ is non-zero only in the range $t_i \leq t < t_i + k$. This is referred to as the basis having ‘minimal support’, and means that the product of two B-splines $B_i^k(t)B_j^k(t) \neq 0$ if and only if $|i - j| < k$. Additionally, this associates each B-spline $B_i^k(t)$ with the corresponding knot t_i which marks the start of its support. A further property is that within the range of its support, each B-spline is always positive. From these properties, it follows that

$$\int B_i^k(t) B_j^k(t) dt = 0, \quad |i - j| \geq k; \quad (2.91)$$

$$\int B_i^k(t) B_j^k(t) dt > 0, \quad |i - j| < k \quad (2.92)$$

and the normalisation is such that

$$\int (B_i^k(t))^2 dt = 1 \quad (2.93)$$

Any function can be approximated as a linear combination of b splines on the interval $[0 : R_{max}]$:

$$f(t) = \sum_{i=1}^n C_i B_i^k(t) \quad (2.94)$$

where n is the total number of B-splines defined on the interval. Notably, at any given t , only a total of k of the B-splines in this expansion are non-zero, which substantially simplifies the evaluation of the function at each point. When approximating a function in this way, another useful feature which arises from the above properties is that since the B-splines are non-negative everywhere and have minimal support, the value of the coefficients for each B-spline tend to be close to the value of the function at the corresponding knots. This ensures that - so long as the B-spline basis is adequate - the coefficients will not oscillate sharply between nearby basis functions. This in turn leads to good numerical stability of the approximation.

The derivative of each B-spline can be simply expressed in terms of B-splines of one order lower as

$$\frac{dB_i^k(t)}{dt} = \frac{k-1}{t_{i+k-1} - t_i} B_i^{k-1}(t) - \frac{k-1}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1} \quad (2.95)$$

And the derivatives of the representation of a function in the B-spline basis can therefore likewise be evaluated.

The maximum errors in the approximation of a function can be quantified as [61]

$$\varepsilon = \frac{h_j^k}{k!} \left| \frac{d^k f(t)}{dt^k} \right|, \quad t_j \leq t < t_{j+1} \quad (2.96)$$

where h_j is the width of the interval $[t_j : t_{j+1}]$. It is therefore possible in principle to

to reduce the error to an arbitrary degree simply by controlling the step size. This is a key advantage of using the local B-spline basis over global basis methods. An alternative way of characterising this feature is that the B-spline basis is complete - in the sense that a given B-spline basis can reproduce any function to within a maximum error ε - so long as the function is sufficiently smooth that the derivatives satisfy a certain upper bound. This re-emphasises the ability of such a basis to replicate both the highly localised bound orbitals along with the oscillatory continuum orbitals present in ionisation calculations. One intuitive limitation on the latter is that the B-spline basis must have sufficient knot density to allow for at least two changes of sign within the wavelength of a continuum electron. This wavelength is given in terms of the electron energy E by $\lambda = 2\pi/\sqrt{2E}$, imposing a restriction on the maximum knot spacing as $\Delta t \leq \lambda/2$. In practice, it has been found that a stricter criterion $\Delta t \leq \lambda/3$ for $k = 9 - 10$, and stricter still for lower k , is preferable to keep the error in the wavefunction phase everywhere below 0.1 radians [61].

For the purposes of our numerical calculations, the knot multiplicity is taken at k at the beginning and end of the interval $[0 : R_{max}]$, with multiplicity 1 at the intermediate breakpoints to preserve maximum continuity. This means that the first and last B-splines on the set can differ from zero at the endpoints of the interval. The boundary condition $\psi(0) = 0$ can be achieved simply by removing the first B-spline from the set. This choice of multiplicity then means that the total number of B-splines in the basis $n = l + k - 1$ where l is the number of intervals. For the approximation of analytic functions, it is typically preferable to use B-splines of order $k = 7 - 10$. In all of the calculations performed in this work, the B-spline order $k = 10$.

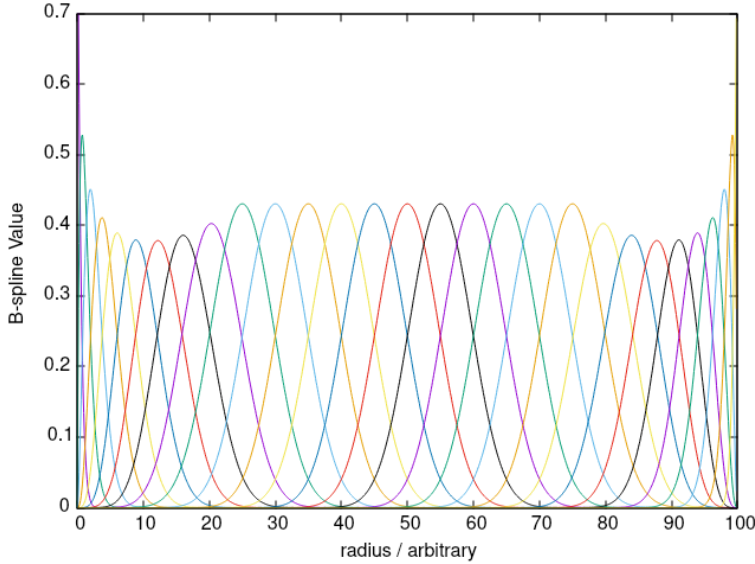


Figure 2.2: An illustration of a series of B-splines of order 10. The B-splines are generated using an breakpoint sequence with a constant spacing of 5 units, with the first and last breakpoint multiplicity set at 10, and the intermediate breakpoint multiplicity set to 1.

The large-radius knot spacing in the numerical calculations in this work is typically constant, dictated by the maximum energy of outgoing electron that needs to be measured. Closer to the centre of the expansion, the bound orbitals tend to vary more rapidly, so a denser knot sequence is required. This is especially true near the atomic centres, where

the more tightly bound s orbitals can increase sharply. One systematic way of generating a breakpoint sequence which combines the even spacing of knots at large radius with an increasing density towards the centre of the expansion is the linear-parabolic sequence, which is defined by the breakpoint sequence

$$\xi_i = ai^2, \quad i = 0, \dots, i_0 - 1; \quad \xi_i = bi + c, \quad i = i_0, \dots, l \quad (2.97)$$

for l intervals, where the parameters a , b , and c are chosen such that the breakpoint value and its first derivative match between the two forms at the crossover point i_0 . In practice, in the calculations performed in this work, the locations of the knots of the inner knots are instead defined manually. The adequacy or otherwise of the inner part of the basis is then determined by the accuracy with which it is possible to represent a set of bound-like Hartree-Fock orbitals generated in a Gaussian basis by an external program, and the knot sequence is adjusted as required.

For the angular part of the basis, spherical harmonics are used. The spherical harmonics are defined as

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos(\theta)) e^{im\phi} \quad (2.98)$$

$P_l^m(x)$ is the generalised Legendre polynomial, and the index m runs from $-l$ to l . This definition produces the normalisation relation

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) \sin(\theta) = \delta_{l,l'} \delta_{m,m'} \quad (2.99)$$

so the set of spherical harmonics is orthonormal. A maximum value of l is chosen for the calculation, and all spherical harmonics with $l \leq l_{max}$ are included in the angular part of the basis.

Many small molecules are highly symmetric, so a large fraction of the integrals between basis functions will be identically zero by symmetry. To prevent wasting computation time and memory in calculating and storing these integrals, for symmetric systems the basis is separated into irreducible representations (irreps) of the overall symmetry group which describe how the functions transform under symmetry operations. Within this implementation, the symmetry separation is restricted to Abelian symmetry groups with real irreps. Such groups consist of the identity operation alongside some or all of the symmetry operations corresponding, for some choice of orthogonal axes, to rotation by π about the x , y , or z axes; reflection in the corresponding xy , yz , and xz planes; and inversion about the symmetry centre. The symmetry group for any given molecule is

that containing the set of operations under which the molecule is left unchanged. The number of distinct irreps therefore depends on the exact symmetry of the molecule, but is never more than the 8 present for the highest-symmetry Abelian point group, D_{2h} , corresponding to molecules which are unaltered under any of the above operations. The one-centre basis set used in B-spline ADC therefore takes the form

$$\xi_{nlh\lambda} = \frac{1}{r} B_n(r) \sum_m b_{mlh\lambda} Y_{lm}(\theta, \varphi) \quad (2.100)$$

where λ indexes the irreps, and h runs over the set of linearly independent angular functions for a given l and λ . The symmetry-adaption coefficients $b_{mlh\lambda}$ produce this set of linearly independent angular functions within the irrep λ .

In molecular systems, it has been found that the augmentation of the primary one-centre expansion with a set of much smaller expansions centred on each off-centre atom dramatically improves the convergence of the approach [63]. This is highly intuitive: all but the lightest atoms will have highly localised orbitals which will require a potentially prohibitively large number of radial and angular functions to describe if the atom is far from the basis centre. For the purposes of the B-spline basis set, these off-centre expansions take an equivalent form to the one-centre expansion, albeit with significantly reduced numbers of b-spines and angular functions. This provides a further set of basis functions [46]

$$\xi_{nlh\lambda}^i = \sum_j \frac{1}{r_j} B_n^i(r_j) \sum_m b_{mlh\lambda j} Y_{lm}(\theta_j, \varphi_j) \quad (2.101)$$

where the index i runs over all symmetrically-inequivalent off-centre atoms, while the index j runs over all each of the atoms in the equivalent set specified by i . The indices r_j , θ_j , and φ_j are the angular coordinates with respect to the atom j . $\{B_n^i\}$ is the set of off-centre B-spline functions for equivalent atom i , which are of the same polynomial order as the main expansion but are otherwise a distinct set of functions to $\{B_n\}$. To prevent linear dependence issues, the off-centre expansions may not overlap with each other. This means that the radius of each off-centre expansion is highly restricted, and they do not contribute in a significant manner to the continuum description. The form of the multicentre expansion is illustrated schematically in figure 2.3.

The representation of states within this basis then takes the form for each symmetry irrep λ

$$\psi_p^\lambda = \sum_{nlh} C_{nlh\lambda}^p \xi_{nlh\lambda} + \sum_i \sum_{nlh} C_{i,nlh\lambda}^p \xi_{nlh\lambda}^i \quad (2.102)$$

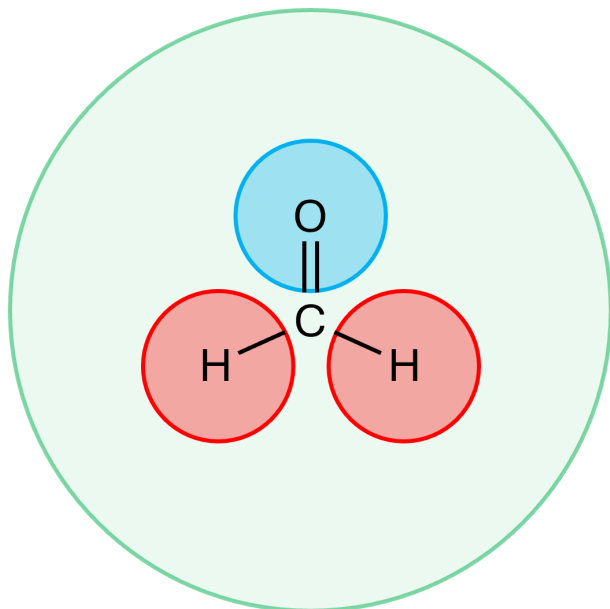


Figure 2.3: A schematic diagram of the structure of the multicentre basis set for the illustrative case of formaldehyde, CH_2O . This molecule is clearly symmetric, and after defining the z axis as the CO bond axis and taking the y axis to lie in the molecular plane, the molecule is unchanged under three non-trivial symmetry operations: reflection in the xz and yz planes, and rotation by π about the z axis, overall corresponding to the C_{2v} symmetry group. The two hydrogen atoms here are considered *equivalent* as they can be interchanged by at least one of these symmetry operations. Thus, the b-spline basis set here contains three groups of terms, each bounded by spheres as represented by the coloured circles in the diagram: the one-centre expansion $\{\xi_{nlh\lambda}\}$ (green) extends from the centre of the basis to a large radius, far outside the molecule (not shown to scale). This is supplemented by two sets of off-centre functions: one, $\{\xi_{nlh\lambda}^1\}$ (blue), within a sphere centred on the oxygen atom; and one, $\{\xi_{nlh\lambda}^2\}$ (red), contained within the pair of spheres centred on each symmetrically-equivalent hydrogen. Just like the one-centre expansion, each of the off-centre functions $\xi_{nlh\lambda}^i$ must be unaltered up to a change of sign following the application of any of the above symmetry transformations to the molecule. As the carbon atom is close to the molecular centre, a typical choice is to place it at the origin of the one-centre expansion, avoiding the need for a further off-centre set.

For the evaluation of the B-spline functions at a given value of r , an implementation exists in the form of the subroutine BSPLVB [62]. This takes as input the spline order k , the value of r , the knot sequence, and the index i of the knot t_i at the start of the relevant interval. The values of all nonzero B-splines on the interval are then calculated through the recursion relation. The derivatives can likewise be calculated from their expression in terms of order $k - 1$ B-splines by the subroutine BSPLVD [62]. For numerical evaluation of the integrals involving the B-spline functions, the Gauss-Legendre quadrature [64] is used. This approach, which approximates the integral of a given function through a weighted sum of its values at a series of n points along its range, has the useful property that the solutions it produces are exact for polynomials up to order $2n$. This means that the integrals of products of B-spline functions are essentially exact. The integration is

performed separately on each interval I_j , over which the basis functions are described by a single polynomial.

In order to proceed with the ADC calculation, it is necessary to first generate the Hartree-Fock states in the B-spline basis which themselves are to be used as a basis for the generation of the ADC intermediate states. This requires solving the closed-shell Hartree-Fock equation (2.12) in the typical self-consistent manner. In order to produce an initial guess for the wavefunction, the Hartree-Fock equation is first solved in a GTO basis using the MOLCAS quantum chemistry package [65], and the resulting orbitals are projected onto the B-spline basis. As the B-spline basis is different from the GTO basis even in the case where it is sufficient to replicate the GTO orbitals near-exactly, the imported orbitals cannot in general be assumed to be exact solutions of the SCF equations in the B-spline basis. A small number of further Hartree-Fock iterations are therefore performed within the B-spline basis to produce the final set of canonical Hartree-Fock orbitals.

For both the Hartree-Fock and the subsequent ADC calculations, it is necessary to calculate two-electron integrals between the Hartree-Fock orbitals of the form

$$(pq|rs) = \int \int d\vec{r}_1 d\vec{r}_2 \psi_p(\vec{r}_1) \psi_q^*(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_r(\vec{r}_2) \psi_s^*(\vec{r}_2) \quad (2.103)$$

For the current multicentre B-spline basis, a numerical library has been developed by Toffoli and Decleva of the University of Trieste [66] which enables the calculation of the two-electron integrals in an efficient manner. This method begins with the calculation of the two-electron integrals involving two B-spline primitives and two Hartree-Fock orbitals, i.e. those of the form $(\psi_i \xi_p | \psi_j \xi_q)$ and $(\psi_i \psi_j | \xi_p \xi_q)$, where the set of basis functions ξ_p runs over all of the one centre and off-centre symmetry-adapted functions $\xi_{nlh\lambda}$, $\xi_{nlh\lambda}^k$. Considering initially the first of these terms

$$(\psi_i \xi_p | \psi_j \xi_q) = \int \int d\vec{r}_1 d\vec{r}_2 \psi_i(\vec{r}_1) \xi_p(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{r}_2) \xi_q(\vec{r}_2) \quad (2.104)$$

and defining the one-particle density

$$\rho_{jq}(\vec{r}_2) = \psi_j(\vec{r}_2) \xi_q(\vec{r}_2) \quad (2.105)$$

it can be noted that such a term arises as a solution to Poisson's equation

$$\nabla^2 V_{jq}(\vec{r}_2) = -4\pi \rho_{jq}(\vec{r}_2) \quad (2.106)$$

for the potential

$$V_{jq}(\vec{r}_2) = \int d\vec{r}_1 \frac{\rho_{jq}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (2.107)$$

This allows equation 2.104 to be re-written as

$$(\psi_i \xi_p | \psi_j \xi_q) = \int d\vec{r}_1 \psi_i(\vec{r}_1) \xi_p(\vec{r}_1) V_{jq}(\vec{r}_1) \quad (2.108)$$

This can be further rearranged by expressing both the potential $V_{jq}(\vec{r})$ and the density $\rho_{jq}(\vec{r})$ in terms of B-spline functions. This involves introducing the definitions

$$V_{jq}(\vec{r}) = \sum_{\alpha} a_{\alpha jq} \xi_{\alpha}(\vec{r}) \quad \langle \xi_{\beta} | \rho_{jq}(\vec{r}) \rangle = b_{\beta qj} \quad (2.109)$$

It is worth observing here that as the density matrix is composed of pairs of B-spline functions multiplied together, it will in general have twice the polynomial order of the standard B-spline basis set, as well as a higher l_{max} . This can lead to truncation errors in the representation in terms of B-splines. To resolve this, it is possible to use a higher-order auxiliary basis for the representation of the density and the potential. The Poisson equation can then be rewritten

$$\sum_{\alpha} \nabla_{\beta\alpha}^2 a_{\alpha jq} = -4\pi b_{\beta qj} \quad (2.110)$$

and the two-electron integrals equation (2.104) is now

$$(\psi_i \xi_p | \psi_j \xi_q) = \sum_{\alpha} a_{\alpha jq} b_{\alpha pi} \quad (2.111)$$

In the same manner, the integrals $(\psi_i \psi_j | \xi_p \xi_q)$ can be evaluated by defining

$$\rho_{ij}(\vec{r}_2) = \psi_i(\vec{r}_2) \psi_j(\vec{r}_2) \quad (2.112)$$

and obtaining the potential $V_{ij}(\vec{r})$ in the same manner as before, leading to the expression for the integral

$$(\psi_i \psi_j | \xi_p \xi_q) = \sum_{\alpha} a_{\alpha ij} b_{\alpha qp} \quad (2.113)$$

where the definitions of $a_{\alpha ij}$ and $b_{\alpha qp}$ are analogous to 2.109. This reduces the problem to the calculation of the two-electron integral into one of calculating the matrix elements $b_{\alpha pi}$, $b_{\alpha qp}$, and the solution of Poisson's equation for the elements $a_{\alpha jq}$, $a_{\alpha ij}$.

The matrix elements $b_{\alpha pi}$, $b_{\alpha qp}$ involve integrals between groups of three basis functions, e.g. as

$$b_{\alpha pi} = \int d\vec{r}_1 \xi_{\alpha}(\vec{r}_1) \psi_i(\vec{r}_1) \xi_p(\vec{r}_1) \quad (2.114)$$

And the HF orbitals ψ_i can of course also be expanded in terms of the primitives ξ_q as necessary. As the basis set is a multi-centre one, some of the primitives $\xi_q = \xi_{i,nlh\lambda}^k$ will correspond to off-centre expansions, so the angular integration may not simply be decomposed through spherical harmonic identities. The computation is simplified somewhat by the stipulation that the off-centre expansions cannot overlap with each other, so only terms corresponding to a single off-centre atom may arise in any given integral. The complexity of these contributions can be reduced further by rotating the coordinate system such that the z axis passes through the coordinate centre of the off-centre expansion, and by performing such a calculation only once for each symmetrically-equivalent atom, obtaining the remaining integrals via symmetry transformations. Nonetheless, the algorithm is somewhat lengthy, and full details are provided in reference [66].

As each B-spline primitive and each Hartree-Fock orbital corresponds to a specific irrep of the overall symmetry group, symmetry considerations are taken into account to restrict the set of b integrals which must be calculated: for a set of functions of irreps λ_1 , λ_2 , and λ_3 , the integral is only nonzero if $\lambda_1 \otimes \lambda_2 = \lambda_3$. Likewise, the equivalence of two-electron integrals under the exchange of certain pairs of indices means that it is only required to calculate, for example, the integral $(\psi_i \xi_p | \psi_j \xi_q)$ for $i \geq j$.

To obtain two-electron integrals involving four Hartree-Fock orbitals as is required, it is necessary to apply a rotation to these expressions as, for example

$$(\psi_i \psi_j | \psi_k \psi_l) = \sum_{p=1}^N C_p^j \left(\sum_{q=1}^N C_q^l (\psi_i \xi_p | \psi_j \xi_q) \right) \quad (2.115)$$

where N is the number of HF orbitals, and the indices are transformed one at a time.

Once the full set of matrix elements and one- and two-electron integrals have been obtained in the canonical Hartree-Fock basis, there is no need to retain the B-spline

primitive basis during the construction of the ADC matrix. The ADC matrix is similarly blocked by symmetry irrep, so only those symmetry blocks of the ADC matrix which correspond to the states of interest in a particular calculation need be calculated. Within the standard ADC procedure, the ADC secular matrix would at this stage be constructed according to section 2.2. The approach taken in this work, however, uses an alternative construction of the ADC Hamiltonian, making use of what is referred to as a restricted correlation space in order to significantly reduce the size of the numerical calculation.

2.3.2 Restricted Correlation Space

The B-spline ADC technique, in its original formulation, was used successfully to describe numerous electronic processes, including photoionisation cross sections [45], high-harmonic generation processes [45, 67], and molecular pump-probe calculations [68]; the latter two involving a full time-dependent calculation. Nonetheless, this approach had clear limitations. The primary drawback of utilising this B-spline basis construction within traditional ADC schemes is that the size of the required basis tends to be very large compared to other *ab initio* techniques. This in particular imposes severe limitations on the application of the approach either for larger molecular systems, or at levels of the ADC hierarchy above the minimal ADC(1) scheme. In such cases, the number of Hamiltonian elements can easily rise into the millions. The issue is exacerbated by the fact that the summations over the virtual orbitals within the ADC formulas worsen the scaling with basis size beyond that arising simply from the Hamiltonian dimension. For n basis functions, the computational cost of the construction of the 1h1p-1h1p block for the N -electron system at the ADC(2) level of approximation scales as n^4 for the construction of the Hamiltonian, and as n^5 for the dipole matrix. This extremely unfavourable scaling is not desirable especially when the required basis size is so large.

A major contribution to this adverse scaling is the presence of the perturbation theoretically corrected ground state in the ISR-ADC formulation. This ground state contains contributions from all of the large number of virtual orbitals, however it can be observed that in practice the highly diffuse continuum-like states which are responsible for the large bulk of the basis will not be expected to form a significant part of this ground state. This insight leads to the introduction of the restricted correlation space (RCS) [46, 47]. Within this approach, the set of basis functions is divided into two orthogonal spaces: the restricted correlation space, which accounts for all of the corrections to the ground state; and the ionisation space (IS), which does not participate in the ground state at all. Formally, this can be expressed as

$$c_\alpha |\Psi_0^{RCS}\rangle \neq 0, \quad c_\mu |\Psi_0^{RCS}\rangle = 0 \quad (2.116)$$

where $|\Psi_0^{RCS}\rangle$ is the correlated ground state which takes the place of the ground state $|\Psi_0\rangle$ and its perturbation theory expansion, and the set of $c_k^\dagger, c_k$ are the standard creation and annihilation operators. Here, $k = \alpha, \beta, \dots$ corresponds to the RCS, while $k = \mu, \nu, \dots$ corresponds to the IS. These operators obey the typical anticommutation relations, noting that the anticommutator involving orbitals in different spaces will always be zero. Denoting the corresponding RCS and IS orbitals as the sets of χ_α and ψ_μ respectively, these orbitals can be expressed in terms of linear combinations of the canonical HF orbitals ζ_k

$$\chi_\alpha = \sum_k C_k^\alpha \zeta_k, \quad \psi_\mu = \sum_k C_k^\mu \zeta_k \quad (2.117)$$

The Fock operator is diagonalised on the two spaces separately, such that the RCS-RCS and IS-IS blocks of the Fock operator are diagonal; however the RCS-IS block of the operator is no longer zero. In the present calculations, the RCS is chosen to correspond to the space of Hartree-Fock orbitals generated in a prior GTO calculation as approximated within the space of B-splines. Denoting these states as $|\tilde{\chi}_\alpha\rangle$, the projection operator

$$\hat{P}^{RCS} = \sum_\alpha |\tilde{\chi}_\alpha\rangle \langle \tilde{\chi}_\alpha| \quad (2.118)$$

is built and diagonalised within the full virtual space. The eigenstates with an eigenvalue close to 1 are taken to define the RCS, while the remaining states have eigenvalues near zero, and define the IS. The RCS and IS states themselves are then constructed through the previously mentioned diagonalisation of the Fock operator within the separate spaces.

The normalised correlated ground state takes an equivalent form to that for the standard ADC approach, but all corrections now only include contributions from the RCS. Through second order, this is

$$\begin{aligned} |\Psi_0^{RCS}\rangle &= |\Phi_0\rangle + |\Psi_0^{[1]RCS}\rangle + |\Psi_0^{[2]RCS}\rangle - \frac{1}{2}|\Phi_0\rangle(\langle\Psi_0'^{RCS}|\Psi_0'^{RCS}\rangle)^{[2]} + \dots; \\ |\Psi_0'^{RCS}\rangle &= |\Phi_0\rangle + |\Psi_0^{[1]RCS}\rangle + |\Psi_0^{[2]RCS}\rangle + \dots \end{aligned} \quad (2.119)$$

where the square brackets indicate the order of the contribution from each term.

The construction of the ISR ADC states then proceeds by the standard excitation class orthonormalisation approach. States with different numbers of particles in the IS will not be mixed during this orthonormalisation procedure as in any matrix element between the correlated excited states $\langle\Psi_0^{RSC}|\hat{C}_I^\dagger\hat{C}_J|\Psi_0^{RCS}\rangle$ it will always be possible to anticommute an

operator $c_\mu^\dagger$ through to annihilate the correlated ground state unless the number of such operators is the same in $\hat{C}_I$ and $\hat{C}_J$. As a result of this, the ISR states can also be assigned to either the RCS or the IS. The ISR states for excitations purely in the RCS therefore take an identical form to those calculated via the standard ADC approach with a basis restricted only to the RCS. For states containing particles in the IS, the case is different. For an N -electron system, it is possible to express the intermediate states containing a single IS orbital in the form in the form

$$|\tilde{\Psi}_{\mu, I_{RCS}}\rangle = c_\mu^\dagger |\tilde{\Psi}_{I_{RCS}}^{N-1}\rangle \quad (2.120)$$

where I_{RCS} is a $nh(n-1)p$ set of configuration indices, $c_\mu^\dagger$ is a creation operator corresponding to the IS orbital, and $|\tilde{\Psi}_{I_{RCS}}^{N-1}\rangle$ is an ISR intermediate state of the $(N-1)$ -electron system within the RCS formulation. A further advantage of the RCS approach over traditional ADC schemes now becomes apparent: here, it is possible to disentangle the final outgoing electron state and the state of the remaining ionic system. Further insight can be obtained by diagonalising the $(N-1)$ -electron Hamiltonian within the RCS space, producing an expression for the ionic eigenstates in terms of ionic intermediate states

$$|\Psi_n^{N-1}\rangle = \sum_I b_I^{n, N-1} |\tilde{\Psi}_I^{N-1}\rangle \quad (2.121)$$

At the ADC(2)x level the index $I = \{i, \alpha i j\}$ runs over 1h, 2h1p RCS excitations. This allows the rotation of the $(N-1)$ -electron intermediate states onto the ionic eigenstates, and therefore a general state of the system can be written as

$$|\Psi\rangle = a_0 |\Psi_0^{RCS}\rangle + \sum_{I_{RCS}} a_{I_{RCS}} |\tilde{\Psi}_{I_{RCS}}^N\rangle + \sum_{\mu, n} a_{\mu n} c_\mu^\dagger |\Psi_n^{N-1}\rangle + \{\geq 2 \text{ IS excitations}\} \quad (2.122)$$

In this expression, the separation into specific ionic decay channels is clear. In principle, intermediate states containing two electrons in the IS can be expressed in the same manner in terms of a pair of creation operators acting on an intermediate state of the $(N-2)$ -electron system. In fact, this property generalises to any number m of electrons in the IS for higher ADC(n) orders which include mh - mp configurations. In the current implementation, however, only a maximum of one IS electron is permitted in order to restrict the Hamiltonian dimension. This does come at the cost of sacrificing the ability to model a system with two electrons in the continuum at one time, but it is necessary to achieve a reasonable calculation size.

The final expression for the Hamiltonian in the RCS-ADC formulation therefore takes

the form at ADC(n)

$$H^{RCS-ADC} = \begin{pmatrix} H_{ADC(n)}^{RCS} & \langle \tilde{\Psi}_{I_{RCS}}^N | (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \Psi_n^{N-1} \rangle \\ \langle \Psi_n^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) | \tilde{\Psi}_{I_{RCS}}^N \rangle & \langle \Psi_m^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \Psi_n^{N-1} \rangle \end{pmatrix} \quad (2.123)$$

Here it is necessary to note that unlike the typical N-electron ADC case, the ground state $|\Psi_0^{RCS}\rangle$ must also be included in the Hamiltonian since its coupling to the IS states is non-zero. The RCS-RCS block of the Hamiltonian is exactly the ADC(n) Hamiltonian constructed in a basis consisting only of the RCS intermediate states. The remaining terms are constructed using the ADC(n) $(N - 1)$ -electron RCS eigenstates, and must subsequently be truncated at a perturbation order consistent with the desired order of ADC. As the $(N - 1)$ -electron eigenstates contain both 1h and 2h1p components, this will typically require the truncation of particular contributions to a given matrix element at different orders. As an illustrative example, consider an element of the IS-IS block of the Hamiltonian at ADC(2)x, expanding in terms of $(N - 1)$ -electron intermediate states using 2.120

$$\begin{aligned} H_{\mu n, \nu m} &= \langle \Psi_m^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \Psi_n^{N-1} \rangle \\ &= \sum_{i,k} b_i^n b_k^m \langle \tilde{\Psi}_k^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \tilde{\Psi}_i^{N-1} \rangle^{[2]} \\ &\quad + \sum_{\alpha ij, k} b_{ij\alpha}^n b_k^m \langle \tilde{\Psi}_k^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \tilde{\Psi}_{\alpha ij}^{N-1} \rangle^{[1]} \\ &\quad + \sum_{i, \beta kl} b_i^n b_{\beta kl}^m \langle \tilde{\Psi}_{\beta kl}^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \tilde{\Psi}_i^{N-1} \rangle^{[1]} \\ &\quad + \sum_{\alpha ij, \beta kl} b_{\alpha ij}^n b_{\beta kl}^m \langle \tilde{\Psi}_{\beta kl}^{N-1} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \tilde{\Psi}_{\alpha ij}^{N-1} \rangle^{[1]} \end{aligned} \quad (2.124)$$

In this full expansion the terms in the first summation correspond to 1h1p-1h1p contributions and are evaluated through second order; the terms in the second and third summations are 1h1p-2h2p terms, which are evaluated up to first order; and the final summation contains 2h2p-2h2p matrix elements which are also evaluated to first order at the ADC(2)x level. The RCS-IS blocks of the Hamiltonian likewise have to be expanded in terms of intermediate states and truncated to the correct order.

In a similar manner to the above, the matrix for the dipole operator $\hat{D} = \sum_{pq} d_{pq} c_p^\dagger c_q$ can be constructed in the same basis

$$D^{RCS-ADC} = \begin{pmatrix} D_{ADC(n)}^{RCS} & \langle \tilde{\Psi}_{IRCS}^N | \hat{D} c_\mu^\dagger | \Psi_n^{N-1} \rangle \\ \langle \Psi_n^{N-1} | c_\nu \hat{D} | \tilde{\Psi}_{IRCS}^N \rangle & \langle \Psi_m^{N-1} | c_\nu \hat{D} c_\mu^\dagger | \Psi_n^{N-1} \rangle \end{pmatrix} \quad (2.125)$$

where the RCS-RCS block is again identical to the standard ADC scheme with the virtual orbital summations restricted to the RCS states. As in the case of the Hamiltonian, the ionic eigenstates are expanded in terms of intermediate states and the matrix elements are truncated to the appropriate order. In the ADC(2)x case, this is second order for the 1h1p-1h1p elements, first order for 1h1p-2h2p and zeroth for 2h2p-2h2p. The dipole matrix elements in the RCS-IS and IS-IS blocks take on a significantly simpler form than in the standard ADC(n) scheme. In particular, in another example of the way in which intuitive results emerge from the RCS formalism, the dipole matrix elements between the ground state and the IS states are just sums over the spectroscopic amplitudes

$$\langle \tilde{\Psi}_0^N | \hat{D} c_\mu^\dagger | \Psi_n^{N-1} \rangle = \sum_{a \in RCS} d_{a\mu} \langle \tilde{\Psi}_0^N | c_a^\dagger | \Psi_n^{N-1} \rangle = \sum_{a \in RCS} d_{a\mu} x_{an} \quad (2.126)$$

As the $(N-1)$ -electron eigenstates are formed entirely in the RCS, it is evident that the IS states do not appear in any of the virtual orbital summations for the matrix elements. It is this difference that is critical in making the RCS ADC approach computationally tractable in the higher-order ADC schemes. The computational cost of generating the RCS-RCS Hamiltonian and dipole matrix blocks retains the original scaling as n_{RCS}^4 and n_{RCS}^5 respectively at ADC(2), however the RCS dimension is only a small fraction of the total so the impact of this scaling is much reduced from the typical ADC case. The bulk of the computational work, especially for atomic and smaller molecular systems, is typically in calculating the matrix elements for the IS-IS block as the dimensions of the IS can stretch up to a few thousand per irrep. The total number of elements in this block scales as $n_{IS}^2 n_{channels}^2$, while the computational cost per matrix element is n_{IRCS}^2 where n_{IRCS} represents the typical number of intermediate states in the expansions of $|\Psi_m^{N-1}\rangle$. The number of available ionisation channels can be restricted by excluding those ionic states which can be expected to have negligible impact on the dynamics.

For the calculation of the matrix elements, the two-electron integrals of the form $(pq|rs)$ given in equation 2.103 are required. These integrals can be calculated in the same manner as described in section 2.3.1, but in this RCS-ADC construction only those integrals involving at most two IS states are required. This provides a substantial reduction in the time required to calculate the two-electron integrals, since the IS dimension is much larger than the RCS. Additionally, as the basis set is symmetry-adapted, the Hamiltonian will be built only in those irreps which are desired for the calculation. In

the case of an laser ionisation calculation, this would be the ground state and those irreps coupled to it by the dipole operator of the electric field of the chosen pulse or pulses.

The RCS B-spline ADC approach can be extended to the description of ionic systems, with the Hamiltonian being constructed in an exactly analogous manner to equation (2.123). Replacing the N -electron RCS intermediate states and N -electron RCS Hamiltonian with their $(N - 1)$ -electron equivalents $|\tilde{\Psi}_{I_{RCS}}^{N-1}\rangle$ and $H_{ADC(n)}^{(N-1),RCS}$, and replacing the ionic RCS eigenstates with the dicationic RCS eigenstates $|\Psi_n^{N-2}\rangle$, gives the general RCS-ADC expression for the ionic Hamiltonian

$$H^{(N-1),RCS-ADC} = \begin{pmatrix} H_{ADC(n)}^{(N-1),RCS} & \langle \tilde{\Psi}_{I_{RCS}}^{N-1} | (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \Psi_n^{N-2} \rangle \\ \langle \Psi_n^{N-2} | c_\nu (\hat{H} - E_0^{RCS}) | \tilde{\Psi}_{I_{RCS}}^{N-1} \rangle & \langle \Psi_m^{N-2} | c_\nu (\hat{H} - E_0^{RCS}) c_\mu^\dagger | \Psi_n^{N-2} \rangle \end{pmatrix} \quad (2.127)$$

If the set of configurations used in the construction of the ADC Hamiltonian includes only 1h and 2h1p configurations, however, an alternative rotation of the Hamiltonian basis becomes possible. In this case, it is possible to rotate the entire 2h1p part of the basis to express it in terms of functions of the form $c_p^\dagger |\Psi_n^{N-2}\rangle$, where p now includes both RCS and IS configurations, as opposed to the general case above in which the equivalent decomposition was only possible if the particle was in the IS. Thus, the wavefunction can be generally expressed in the form

$$|\Psi\rangle = \sum_i a_i |\tilde{\Psi}_i^{N-1}\rangle + \sum_{p,n} a_{pn} c_p^\dagger |\Psi_n^{N-2}\rangle \quad (2.128)$$

with $|\tilde{\Psi}_i^{N-1}\rangle$ the 1h intermediate states, and the sum in the second term running over all dicationic states n and all unoccupied (RCS and IS) states p . The $(N - 1)$ -electron Hamiltonian then becomes

$$H^{(N-1),RCS-ADC} = \begin{pmatrix} \langle \tilde{\Psi}_j^{N-1} | (\hat{H} - E_0^{RCS}) | \tilde{\Psi}_i^{N-1} \rangle & \langle \tilde{\Psi}_j^{N-1} | (\hat{H} - E_0^{RCS}) c_p^\dagger | \Psi_n^{N-2} \rangle \\ \langle \Psi_n^{N-2} | c_q (\hat{H} - E_0^{RCS}) | \tilde{\Psi}_i^{N-1} \rangle & \langle \Psi_m^{N-2} | c_q (\hat{H} - E_0^{RCS}) c_p^\dagger | \Psi_n^{N-2} \rangle \end{pmatrix} \quad (2.129)$$

The RCS dicationic states $|\Psi_n^{N-2}\rangle$ used in the construction of the basis can be expressed as a sum over intermediate states corresponding to 2h configurations only, and they therefore correspond to the eigenstates of the RCS dicationic Hamiltonian calculated at the ADC(1) level of theory. As the indices p and q on the creation and annihilation operators in equation (2.129) now run over both the RCS and IS spaces, the precise

expressions for the corresponding matrix elements will depend on which of these spaces p and q belong to. The dipole matrix can be similarly constructed in the same basis as

$$D^{(N-1), RCS-ADC} = \begin{pmatrix} \langle \tilde{\Psi}_j^{N-1} | \hat{D} | \tilde{\Psi}_i^{N-1} \rangle & \langle \tilde{\Psi}_j^{N-1} | \hat{D} c_p^\dagger | \Psi_n^{N-2} \rangle \\ \langle \Psi_n^{N-2} | c_q \hat{D} | \tilde{\Psi}_i^{N-1} \rangle & \langle \Psi_m^{N-2} | c_q \hat{D} c_p^\dagger | \Psi_n^{N-2} \rangle \end{pmatrix} \quad (2.130)$$

The current implementation of the B-spline ADC calculation makes use of this construction of the ionic Hamiltonian and dipole matrices, which is valid within the standard ADC(n) hierarchy up to ADC(3). The inclusion of 3h2p configurations within the basis would require reverting to the more general form of the ionic RCS-ADC construction given in equation (2.127), however such a scheme would in any case be unrealistic to use for calculations within the B-spline basis due to the large associated increase in the computational cost.

2.3.3 Time Propagation via Arnoldi-Lanczos Iterative Diagonalisation

In this work, the primary purpose of the numerical approach is to simulate the excitation, evolution, and measurement of electron dynamics induced by a laser pulse. This requires the ability to numerically propagate an initial state in time under the influence of a time-varying Hamiltonian

$$\hat{H}(t) = \hat{H}_{static} + \hat{H}_{laser}(t) \quad (2.131)$$

where $\hat{H}_{static}$ is the field-free Hamiltonian, and $\hat{H}_{laser}$ is the coupling induced by the laser field. Using the dipole approximation within the length gauge, the laser-induced Hamiltonian contribution can be written simply as

$$\hat{H}_{laser}(t) = \hat{D} \cdot \vec{E}(t) \quad (2.132)$$

where $\vec{E}(t)$ is the laser field due to the pulse, and $\hat{D}$ is the dipole operator

$$\hat{D} = \sum_i \vec{r}_i \quad (2.133)$$

The field-free Hamiltonian and the dipole matrix will be constructed in the RCS-ADC basis as described in section 2.3.2. This basis is ultimately derived from the primitive

basis of B-spline functions of section 2.3.1, which means that it will necessarily have a finite radial extent. The ionised electrons will therefore travel out to the maximum radius R_{max} , at which point they can travel no further as the functions to describe the more distant states will no longer exist. In the absence of any further modification, the edge of the basis will act as a hard barrier from which the outgoing electrons will reflect, redirecting them back towards the system centre. Such unphysical reflections will induce entirely spurious dynamics, so they must be avoided. One trivial way to achieve this would be to extend the maximum radial extent of the basis sufficiently that the highest-energy outgoing electrons would not have time to reach the edge before the end of the time propagation calculation. This, however, has the obvious drawback that it would in many cases require substantially increasing the basis size, which would result in vastly larger computation time and memory requirements.

An alternative approach is to damp the outgoing wavefunction before it reaches the boundary, reducing the amplitude of the reflected wave to zero. This is most easily achieved through the introduction of a complex absorbing potential (CAP) [69, 70]. The CAP adds a negative imaginary component to the Hamiltonian above a fixed radius, r_{CAP} , which damps the wavefunction within this region. r_{CAP} should be large enough that all bound states have negligible amplitude above that radius and all outgoing electron states which reach the CAP would otherwise proceed to infinity without further interaction with the bound system. In this work, the CAP is chosen to increase quadratically above r_{CAP}

$$\hat{W} = \begin{cases} 0, & r \leq r_{CAP} \\ \eta(r - r_{CAP})^2, & r > r_{CAP} \end{cases} \quad (2.134)$$

The magnitude of the damping coefficient η must be sufficiently large that the outgoing wavefunction is damped to zero before it can reflect, while also being sufficiently small that the CAP itself does not induce significant reflections. The optimal value of the CAP parameter depends on the length of the damping region and on the energy of the typical outgoing electrons [71].

The modified Hamiltonian now reads

$$\hat{H}(t) = \hat{H}_{static} + \hat{D} \cdot \vec{E}(t) - i\hat{W} \quad (2.135)$$

The CAP contribution to the Hamiltonian is complex symmetric, which breaks the hermiticity of the Hamiltonian and causes the norm of the wavefunction to decay over time.

It is well-established that a solution to the time-dependent Schrödinger equation can be expressed as

$$|\Psi(t)\rangle = \hat{U}(t, 0)|\Psi(0)\rangle \quad (2.136)$$

Where the time propagation operator $\hat{U}(t, 0)$ is defined as

$$\hat{U}(t, 0) = \hat{T} \exp\left(\int_0^t -i\hat{H}(t')dt'\right) \quad (2.137)$$

The time-ordering operator $\hat{T}$ can be understood as ensuring that the operators $\hat{H}(t)$ always appear in ascending order of the corresponding t in the series expansion of the exponential. In the case where the Hamiltonian is time-independent, the time-propagation operator simplifies dramatically:

$$\hat{U}(\Delta t) = \hat{U}(t, t + \Delta t) = \exp(-i\hat{H}\Delta t) \quad (2.138)$$

While the Hamiltonian of, for instance, a molecule in a laser field is clearly time-dependent, it is nonetheless possible to approximately apply the time-independent operator if the relevant time step Δt is sufficiently small that the variation in the Hamiltonian is minimal. Furthermore, it is possible to use this approximation to propagate the system over a longer period of time by sequentially applying a series of time-independent operators, each with the Hamiltonian calculated at that particular time step. This approximation will be accurate so long as the Hamiltonian at no point changes significantly over a single time step.

In order to apply the operator $\hat{U}(t, t + \Delta t) = \exp(-i\hat{H}\Delta t)$, the Hamiltonian must be constructed and diagonalised. Once the state is projected onto the resulting eigenvectors $|\Psi_n\rangle$, the time propagation would then proceed simply using

$$|\Psi(t + \Delta t)\rangle = \hat{U}(t, t + \Delta t)|\Psi(t)\rangle \quad (2.139)$$

$$= \exp(-i\hat{H}\Delta t) \sum_n c_n |\Psi_n\rangle \quad (2.140)$$

$$= \sum_n \exp(-iE_n\Delta t) c_n |\Psi_n\rangle \quad (2.141)$$

where, in the time-dependent case, the Hamiltonian and the resulting eigenvalues and eigenvectors are all specific to the time t . The complication here from a numerical perspective is that this rebuilding and diagonalisation of the time-dependent Hamiltonian must be performed at every time step. While this might be plausible for very small systems or at low levels of approximation, the systems of interest in this work are highly

correlated many-electron systems which require high levels of approximation to produce accurate results. This leads to large Hamiltonian matrices with numbers of elements often running into the millions for the B-spline basis sets used in this work. For such systems, this full diagonalisation process can take days or weeks even with significant parallelisation on modern high-performance computational hardware, so performing the repeated diagonalisation required here with the full Hamiltonian would be entirely unfeasible.

To circumvent this problem, the Arnoldi-Lanczos algorithm [72, 73] is used for time propagation. This is a variant on the Lanczos time propagation algorithm adapted to work with non-Hermitian Hamiltonians such as the one produced by the introduction of the CAP. The essence of this approach is to replace the full Hamiltonian in the time propagation with a reduced Hamiltonian built in a subspace of Krylov vectors for which diagonalisation at each step is numerically feasible.

A Krylov subspace of a matrix - in this case the Hamiltonian H - is the m -dimensional space spanned by the vectors $\{V_0, HV_0, H^2V_0, \dots, H^{m-1}V_0\}$, where m is typically much smaller than the full H matrix dimension n . The first Krylov vector V_0 is in this case chosen as the initial wavefunction $\psi(t)$, which ensures that all of the eigenstates of H relevant to the time propagation will be present in the vector subspace. In their initial construction, the Krylov vectors are neither normalised nor orthogonal, so they are not yet sufficient to provide a useful basis. In the case of a Hermitian H , a simple Gram-Schmidt orthonormalisation scheme produces the basis of Lanczos states [74], which form a tridiagonal reduced matrix representation of the Hamiltonian. The use of this scheme for numerical propagation of the time-dependent Schrödinger equation is well-established [75, 76, 77].

To understand why this particular form of reduced subspace is useful, it is possible to consider the polynomial expansion of the full time propagation operator acting on the ground state, terminated at order $m - 1$:

$$\exp(-iH\Delta t)\psi(0) \approx \sum_{j=0}^{m-1} \frac{(-i\Delta t)^j}{j!} H^j \psi(0) \quad (2.142)$$

which reproduces the set of m Krylov vectors with varying prefactors. This approach can therefore be understood as analogous to replacing the time propagation operator $\hat{U}(t)$ with its $m - 1$ -th order approximation.

In the case of a non-Hermitian Hamiltonian, a modified Gram-Schmidt orthonormalisation procedure is used. The initial vector V_0 must first be normalised, as the initial choice $\psi(0)$ may have a norm less than 1 due to the action of the CAP. The remaining vectors V_j are then constructed recursively as follows:

Assuming the first j vectors have already been constructed, the vector V_{j+1} is built by first applying the Hamiltonian to the previous vector V_j

$$|\tilde{V}_{j+1}^{(1)}\rangle = \hat{H}|V_j\rangle \quad (2.143)$$

and then orthogonalising the resulting vector with respect to each of the preceding vectors V_i , $i = 1, \dots, j$

$$|\tilde{V}_{j+1}^{(i+1)}\rangle = |\tilde{V}_{j+1}^{(i)}\rangle - \beta_{ij}|V_i\rangle, \quad \beta_{ij} = \langle V_i | \tilde{V}_{j+1}^{(i)} \rangle; \quad i = 1, \dots, j \quad (2.144)$$

The final vector is then normalised to give the vector V_{j+1}

$$|V_{j+1}\rangle = \frac{|\tilde{V}_{j+1}^{(j+1)}\rangle}{\beta_{j+1,j}}, \quad \beta_{j+1,j} = \sqrt{\langle \tilde{V}_{j+1}^{(j+1)} | \tilde{V}_{j+1}^{(j+1)} \rangle} \quad (2.145)$$

While in principle the orthonormalisation is exact, in a real calculation there is a tendency for numerical imprecision to lead to some overlap between the resulting vectors. To avoid this issue, once each of the vectors $|\tilde{V}_{j+1}^{(j+1)}\rangle$ has been calculated but before proceeding to the next step, it is re-orthogonalised with respect to the j preceding vectors following the Kahan-Parlett ‘twice is enough’ algorithm [78], which can be expected to succeed so long as the norm of the orthogonal part of the vector to be orthonormalised, $\tilde{V}_{j+1}^{(1)}$, is not so small that it becomes of a comparable magnitude to the numerical precision of the preceding vectors V_i . This proceeds exactly as before:

$$|\tilde{V}_{j+1}^{twice(1)}\rangle = |\tilde{V}_{j+1}^{(j+1)}\rangle,$$

$$|\tilde{V}_{j+1}^{twice(i+1)}\rangle = |\tilde{V}_{j+1}^{twice(i)}\rangle - \beta_{ij}^{second}|V_i\rangle, \quad \beta_{ij}^{second} = \langle V_i | \tilde{V}_{j+1}^{twice(i)} \rangle; \quad i = 1, \dots, j \quad (2.146)$$

$$|V_{j+1}\rangle = \frac{|\tilde{V}_{j+1}^{twice(j+1)}\rangle}{\beta_{j+1,j}^{final}}, \quad \beta_{j+1,j}^{final} = \sqrt{\langle \tilde{V}_{j+1}^{twice(j+1)} | \tilde{V}_{j+1}^{twice(j+1)} \rangle}$$

where the total matrix element β_{ij}^{final} is given by

$$\beta_{ij}^{final} = \beta_{ij}^{first} + \beta_{ij}^{second} \quad (2.147)$$

and β_{ij}^{first} is the value β_{ij} calculated in the first orthonormalisation procedure. It can be intuitively seen with each application of H , the Krylov vectors will approach

the eigenvector of H with the largest eigenvalue, and as such will become increasingly parallel. As a result, as the number of Krylov vectors is increased the norm of the newly-orthogonalised state will become increasingly small. Due to the propensity for this to lead to numerical inaccuracy, if the norm falls below a certain threshold value then the recursion is terminated early; otherwise, it will continue until the pre-determined number m of orthonormal vectors have been generated.

The reduced Hamiltonian is subsequently built by projecting the full Hamiltonian onto the Arnoldi-Lanczos vector subspace, and can be seen to have elements $H_{ij}^A = \beta_{i-1,j-1}$ for $i \leq j + 1$, such that

$$H^A = \begin{pmatrix} \beta_{0,0} & \beta_{0,1} & \beta_{0,2} & \dots & \beta_{0,m-3} & \beta_{0,m-2} & \beta_{0,m-1} \\ \beta_{1,0} & \beta_{1,1} & \beta_{1,2} & \dots & \beta_{1,m-3} & \beta_{1,m-2} & \beta_{1,m-1} \\ 0 & \beta_{2,1} & \beta_{2,2} & \dots & \beta_{2,m-3} & \beta_{2,m-2} & \beta_{2,m-1} \\ 0 & 0 & \beta_{3,2} & \dots & \beta_{3,m-3} & \beta_{3,m-1} & \beta_{3,m-1} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \beta_{m-2,m-3} & \beta_{m-2,m-2} & \beta_{m-2,m-1} \\ 0 & 0 & 0 & \dots & 0 & \beta_{m-1,m-2} & \beta_{m-1,m-1} \end{pmatrix} \quad (2.148)$$

where the ‘final’ superscript of the β_{ij} terms has been dropped. The matrix H^A is an upper Hessenberg matrix: all elements of below the first subdiagonal are zero. In the case where H is hermitian, the matrix H^A must reduce to a tridiagonal form, which reproduces the case of the previously-discussed Lanczos algorithm.

Having constructed the Arnoldi-Lanczos approximation to the Hamiltonian H^A , it is now possible to approximate the time propagation operator by its representation in the Krylov subspace:

$$\hat{U}(\Delta t) \approx \hat{U}^A(\Delta t) = \exp(-iH^A\Delta t) \quad (2.149)$$

and therefore

$$|\Psi(t + \Delta t)\rangle \approx \exp(-iH^A\Delta t)|\Psi(t)\rangle \quad (2.150)$$

The dimension m of H^A is typically in the range of 15-25 - a number orders of magnitude less than that of the full Hamiltonian - so the diagonalisation of this matrix at each step is now entirely feasible. Following this diagonalisation, it is now possible to express the time propagation operator in terms of a rotation onto the eigenvector basis of H^A , a scaling of each eigenvector, and a rotation back onto the original basis

$$\hat{U}^A(\Delta t) = Z^{-1} \exp(-iD^A \Delta t) Z \quad (2.151)$$

Here, D^A is the diagonal matrix of eigenvalues λ_n of H^A , and Z is a matrix of the corresponding eigenvectors. Remembering that the initial vector $\Psi(t)$ was chosen as the first Krylov vector V_0 , the propagated vector can then be expressed in the basis of orthonormalised Krylov vectors $\{V_j\}$ as

$$\Psi(t + \Delta t) = \hat{U}^A(\Delta t) \Psi(t) = \sum_{j=0}^{m-1} a_j V_j \quad (2.152)$$

where the coefficients a_j take the form

$$a_j = \sum_{k=0}^{m-1} (Z^{-1})_{jk} \exp(-i\lambda_j \Delta t) Z_{k0} \quad (2.153)$$

In the current case of a non-Hermitian Hamiltonian, the inverse of the matrix Z must be calculated explicitly as $Z^{-1} \neq Z^\dagger$. This adds extra computational cost relative to the simpler Lanczos case, but the full Arnoldi-Lanczos approach nonetheless achieves good computational efficiency. The error induced by the approximation of H with H^A can be understood by considering the polynomial expansion in equation (2.142). If the approximation is adequate then the coefficient on the final basis vector V_{m-1} should be small. If this coefficient exceeds some threshold value, either the size of the Krylov space should be increased, or otherwise the time step should be reduced to ensure convergence.

The presence of excessively high-energy orbitals in the calculation can hinder the convergence of the Arnoldi-Lanczos propagation scheme due to its dependence on the spectral radius of the Hamiltonian. Such orbitals are in any case often entirely unphysical, existing only as a result of the limitations of any finite numerical basis, so a threshold energy is imposed above which all further orbitals are discarded. Such a threshold should be set sufficiently high that no physical orbitals relevant to the calculation are excluded. For the calculations in this work, all Hartree-Fock orbitals of energy greater than 40 au were removed. This value is sufficient to ensure convergence of the time propagation algorithm without altering the predicted dynamics of the systems of interest.

2.3.4 Ionic Density Matrix

During an ionisation process, the initial state of the electronic system is described in its entirety by the many-electron wavefunction $|\Psi^N\rangle$. This remains the case following the interaction with the ionising pulse, but now the departing electron travels increasingly far

from the system centre. If we are solely interested in the behaviour of the remaining ionic system and the outgoing electron ceases to be observed then, while in principle the full N -electron wavefunction still describes the system state, we no longer have access to this full wavefunction and instead we are restricted to describing the $(N - 1)$ -electron states. The state of the system does still have some relationship to the now-lost information about the outgoing electron, however, which means it is now impossible to form a single wavefunction which describes the full $(N - 1)$ -electron state. In the case of a system interacting with a long-duration pulse, the remaining coherence can often be very small and it may be sensible to consider each of the states of the ion as fully independent. In the case of attosecond ionisation, however, not only can the coherence not be assumed to be small, but it is often the root of the precise behaviours that we are interested in.

In order to describe such ‘mixed states’ we must use the density matrix formalism [79], which allows the description of a partially-coherent ensemble of states. An implementation of this exists within the B-spline ADC computational code [47, 68]. Here, the density matrix for the full N -electron system is first formed

$$\hat{\rho}^N(t) = |\Psi^N(t)\rangle\langle\Psi^N(t)| \quad (2.154)$$

This describes the pure state of the N -electron system. To obtain the resulting reduced density matrix for the ionic system, it is necessary to take the trace over the unobserved subspace. In this case this involves tracing over the ionised photoelectron states $|\psi_\mu\rangle$.

$$\hat{\rho}_{red}^{N-1}(t) = \text{Tr}_\mu\{\hat{\rho}^N(t)\} \quad (2.155)$$

In the RCS-ADC construction, the index μ can be taken to correspond to the ionisation space states. Dropping the subscript from the reduced density matrix for brevity and expressing the wavefunction in the basis given in equation 2.122, the matrix elements are therefore given by

$$\begin{aligned} \rho_{m,n}^{N-1}(t) &= \sum_{\mu} \langle\Psi_m^{N-1}|c_\mu|\Psi^N(t)\rangle\langle\Psi^N(t)|c_\mu^\dagger|\Psi_n^{N-1}\rangle \\ &= \sum_{\mu} a_{n\mu}(t)a_{m\mu}^*(t) \end{aligned} \quad (2.156)$$

and the full ionic density matrix in the basis of ionic states is

$$\hat{\rho}^{N-1}(t) = \sum_{m,n=1}^N \rho_{m,n}(t) |\Psi_n^{N-1}\rangle \langle \Psi_m^{N-1}| \quad (2.157)$$

This construction by its nature does not include contributions from the bound excited states of the neutral, as the ionic states $c_\mu^\dagger |\Psi_m^{N-1}\rangle$ are orthogonal to the bound part of the wavefunction. It is important to note again here that the trace is taken over the unobserved subspace. The density matrix construction supposed here assumes that all information about the outgoing electron has been lost, so it is not applicable in cases where the outgoing electron is detected. In those cases, the trace would have to run over only those states which were not distinguishable by the measurement of the electron.

For the time propagation calculation, the complex absorbing potential was introduced to prevent unphysical reflections from the grid boundary by damping the outgoing electron wavefunction. This becomes an issue when summing over precisely these outgoing electronic states, so it must be accounted for here. This is done by calculating the lost contribution to the density matrix at each point in time, propagating it analytically up to the current time, and adding it back to recover the un-damped matrix [47]

$$\rho_{m,n}^{N-1}(t) = \sum_{\mu} a_{n\mu}(t) a_{m\mu}^*(t) + 2 \int_{-\infty}^t dt' \sum_{\mu\nu} a_{n\nu}(t') a_{m\mu}^*(t') w_{\nu,\mu} e^{i(I_n - I_m)(t-t')} \quad (2.158)$$

where the I_m are the ionisation potentials, and $w_{\nu,\mu}$ is the CAP matrix element between the IS orbitals ν and μ .

Several key quantities can be easily calculated from the density matrix. The occupation probability of each ionic state are given by the diagonal matrix elements $\rho_{n,n}^{N-1}(t)$, and the total ionisation probability is therefore given by the trace of the density matrix. The off-diagonal matrix elements are the coherences between the corresponding ionic states. For the purposes of comparison, it is useful to express these as a fraction of the maximum possible coherence

$$T_{mn}(t) = \frac{|\rho_{m,n}^{N-1}(t)|}{\sqrt{\rho_{m,m}^{N-1}(t) \rho_{n,n}^{N-1}(t)}} \quad (2.159)$$

$T_{mn}(t) = 0$ corresponds to a fully incoherent statistical mixture of the two states, while $T_{mn}(t) = 1$ is the maximum possible coherence, and the value that would be obtained in the case of a pure single-wavefunction state. In a typical ionisation calculation, the density matrix will fluctuate not just during the pulse, but also for the period of time that it takes for the ionised electrons to fully depart the bound system. This occurs because

the continuum electrons close to the bound region can still mediate interactions between the bound states. Once the ionised electrons have fully departed the system, it is possible to propagate the density matrix analytically. The time evolution of the density matrix is governed by the von Neumann equation:

$$\frac{d}{dt}\hat{\rho}^{N-1}(t) = -i \left[\hat{H}^{N-1}(t), \hat{\rho}^{N-1}(t) \right] \quad (2.160)$$

where $\hat{H}^{N-1}(t)$ is the ionic Hamiltonian and the commutator $[\hat{a}, \hat{b}] = \hat{a}\hat{b} - \hat{b}\hat{a}$. In the time-independent case that is considered in this work, this can be solved as

$$\hat{\rho}^{N-1}(t) = e^{-i\hat{H}^{N-1}(t-t_0)}\hat{\rho}^{N-1}(t_0)e^{i\hat{H}^{N-1}(t-t_0)} \quad (2.161)$$

which, in the basis of ionic eigenstates, is simple expressed as

$$\rho_{m,n}^{N-1}(t) = e^{-i(E_m^{N-1} - E_n^{N-1})(t-t_0)}\rho_{m,n}^{N-1}(t_0) \quad (2.162)$$

It is important to mention here that if the ionised electron wavepacket retains significant amplitude in the vicinity of the bound system then this propagation will not capture its interactions with the bound system as the continuum electron here has been traced out. This residual interaction, if treated properly, causes changes in the ionic state populations and coherences over time. Once these values have stabilised, this indicates that the remaining interaction between the bound system and the departing electron is no longer significant, and thus no significant error will be incurred by switching from wavefunction to density matrix propagation after this point.

It is possible to diagonalise the density matrix to produce an orthonormal set of states which are by definition all mutually incoherent, as all of the off-diagonal density matrix elements are zero. The corresponding eigenvalues represent the occupation probabilities of these states. Within the RCS-ADC formulation, this diagonalisation enables a two-stage time propagation calculation to model double ionisation resulting, for example, from autoionisation or from a delayed probe pulse. Since the density matrix eigenstates have no coherence with each other, each one describes a separate fully coherent wavefunction and each eigenstate can therefore be taken individually as an input to the ionic time propagation calculation.

One way to numerically analyse the dynamics of the ionised system is through the calculation of the 1h density at each time step [80, 81]. defining the hole density operator $Q(\vec{r}, t)$ as the difference between the densities in the neutral ground state and the ionic system

$$\begin{aligned}
Q(\vec{r}, t) &= \langle \Psi_0 | \hat{R}(\vec{r}) | \Psi_0 \rangle - \langle \hat{R}(\vec{r}) \rangle_{ion} \\
&= \langle \Psi_0 | \hat{R}(r) | \Psi_0 \rangle - \text{Tr} \left(\hat{R}(\vec{r}) \hat{\rho}^{N-1}(t) \right)
\end{aligned} \tag{2.163}$$

where

$$\hat{R} = \sum_{pq} \varphi_p^*(\vec{r}) \varphi_q(\vec{r}) c_p^\dagger c_q \tag{2.164}$$

is the typical local density operator represented in terms of RCS orbitals $\varphi_p(\vec{r})$, and $\langle \hat{R} \rangle_{ion}$ refers to the expectation value of the density operator within the ionic system. On the second line of (2.163), the formula $\langle \hat{M} \rangle = \text{Tr}(\hat{M} \hat{\rho})$ for the expectation value within the density matrix formalism has been used, making use of the normalised density matrix defined as

$$\hat{\rho}^{N-1} = \frac{\hat{\rho}^{N-1}}{\text{Tr}(\hat{\rho}^{N-1})} \tag{2.165}$$

Expanding $\hat{R}(\vec{r})$ in terms of the explicit sum in equation (2.164) and collecting terms with the same spatial functions together, the hole density operator can be written as

$$Q(\vec{r}, t) = \sum_{pq} \varphi_p(\vec{r})^* \varphi_q(\vec{r}) N_{pq}(t) \tag{2.166}$$

where

$$N_{pq}(t) = \sum_{mn} \tilde{\rho}_{mn}^{N-1} \left(\delta_{mn} \langle \Psi_0 | c_p^\dagger c_q | \Psi_0 \rangle - \langle \Psi_n^{N-1} | c_p^\dagger c_q | \Psi_m^{N-1} \rangle \right) \tag{2.167}$$

Diagonalising the hole-density matrix $N_{pq}(t)$ allows the operator $Q(\vec{r}, t)$ to be expressed as

$$Q(\vec{r}, t) = \sum_p |\tilde{\varphi}_p(\vec{r}, t)|^2 \tilde{n}_p(t) \tag{2.168}$$

where the eigenfunctions $\tilde{\varphi}_p(\vec{r}, t)$ are known as 'natural charge orbitals', and their respective eigenfunctions, $\tilde{n}_p(t)$, are the 'hole occupation numbers'. The occupation num-

bers indicate how much charge is located within the corresponding charge orbital. Taken together, they describe how the charge is spread across the ionic system. Both the natural charge orbitals and their eigenfunctions are now time-dependent, so both must be recalculated at each time step. As the ionic density matrix used to calculate $Q(\vec{r}, t)$ is normalised, so is the hole density $Q(\vec{r}, t)$ itself, and therefore the hole occupation numbers must sum to 1.

One final quantity that can be extracted from the density matrix is its purity, a measure of how much coherence is present in the system overall. The purity is the trace of the square of the density matrix, and is equal to one for a fully coherent system. For a system of M linearly independent states, the minimum value of the purity is $1/M^2$, which occurs in the case of a totally incoherent statistical mixture with equal populations in each state.

2.4 ADC(2,2)

As discussed in section 2.2.4, the energies of states belonging to different excitation classes will not in general be calculated to the same perturbation order. In particular, within the standard ADC(2)x scheme, the energies of states in the 1h excitation class will be accurate to the second order of perturbation theory, whereas the state energies for the 2h1p class are calculated only to first order. The latter part is true even for the full ADC(3) scheme, and is in fact as good as it is possible to get for these 2h1p energies without including the 3h2p excitation class in the calculation.

While the inclusion of the first order perturbation correction to the 2h1p energies makes ADC(2)x a substantial improvement over the simpler ADC(2) scheme, there are nonetheless numerous systems where it is desirable or even necessary to go further. An example of a common process in which improved representation of the 2h1p states can be useful is that of Auger decay, which involves transitions from 1h to 2h1p-type states meaning that any imbalance in the treatment of the two can introduce some inaccuracy into the calculations. Likewise, satellite states are by definition 2h1p-dominated, and first order perturbation theory is not always sufficient to correctly capture the correlation in these states [82]. This means that ADC(2)x will not always be adequate in cases where such satellites contribute significantly. It is therefore desirable to be able to represent the energies of the 2h1p states correctly through the second order of perturbation theory, placing them on a level with the 1h states. This is the essence of the ADC(2,2) formulation [48].

As was already suggested with the earlier introduction of the ADC(2)x scheme, the ADC approach is not at all rigid, and it is possible to include additional blocks within the ADC secular matrix in an ad-hoc manner to improve the representation of particular states. Denoting as $M_{\mu,\nu}^{(j)}$ the j^{th} order contribution to the block of the ADC matrix coupling excitation classes μ and ν , where excitation class μ here refers to $\mu h(\mu - 1)p$ states, it is possible to enumerate the contributions which must be added to the ADC(2) scheme to represent the 2h1p states through second order.

It is immediately obvious that the direct contributions to the 2h1p block $M_{2,2}^{(1)}$ and $M_{2,2}^{(2)}$ must be included in this scheme. Beyond this, it becomes apparent that the ADC(2,2) scheme must include 3h2p configurations, as the elements $M_{2,3}^{(1)}$ also contribute at second order to the 2h1p energies

$$E_{2h1p} \propto (M_{2,3}^{(1)})^2 \quad (2.169)$$

The zeroth-order 3h2p-3h2p block $M_{3,3}^{(0)}$ likewise contributes through terms of the form

$$E_{2h1p} \propto (M_{2,3}^{(1)})^2 M_{3,3}^{(0)} \quad (2.170)$$

These four additional contributions comprise all of the second-order contributions to the 2h1p energies, and therefore make up the required additions to ADC(2) to produce the minimal ADC(2,2) scheme. In practice, several other contributions are useful to significantly improve the numerical results. Including also the first order contribution to the 3h2p-3h2p block $M_{3,3}^{(1)}$ adds a third-order correction to the 2h1p energies as

$$E_{2h1p} \propto (M_{2,3}^{(1)})^2 M_{3,3}^{(1)} \quad (2.171)$$

which improves consistency with the treatment of the 1h states by balancing the equivalent third-order contribution to the 1h energies from the addition of the $M_{2,2}^{(1)}$ block. The final contribution which has been seen to be useful is the second order contribution to the 1h-2h1p coupling block, which contributes at third order to both the 1h and 2h1p energies and is required to obtain accurate Auger decay widths

$$E_{1h}, E_{2h1p} \propto M_{1,2}^{(1)} M_{1,2}^{(2)} \quad (2.172)$$

This constitutes the full ADC(2,2) scheme, which is the version that we use in section 5.1. In total the block structure of this scheme is

	1h	2h1p	3h2p
1h	$M_{1,1}^{(0)} + M_{1,1}^{(2)}$	$M_{1,2}^{(1)} + M_{1,2}^{(2)}$	...
2h1p	$M_{2,1}^{(1)} + M_{2,1}^{(2)}$	$M_{2,2}^{(0)} + M_{2,2}^{(1)} + M_{2,2}^{(2)}$	$M_{2,3}^{(1)}$
3h2p	...	$M_{3,2}^{(1)}$	$M_{3,3}^{(0)} + M_{3,3}^{(1)}$

Within this scheme, the corresponding error in the eigenvector coefficients begins at second order for states of both 1h and 2h1p character. This is again one order better for the 2h1p states than is possible in ADC(2)x. Further improving the 1h coefficient accuracy would in principle be possible by accounting for the neglected second-order coupling from the 1h to the 3h2p configurations; however the corresponding correction to the 2h1p coefficient would require the inclusion of the 4h3p configuration space, which would render the calculation impractical in the overwhelming majority of systems. This scheme is therefore essentially as good as it is possible to get within current computational limits.

The trade-off for this increase in accuracy is worsened scaling with basis size, primarily due to the required inclusion of the 3h2p excitation class. The full ADC(2,2) approach scales as $N_{occ}^3 N_{virt}^4$, with N_{occ} and N_{virt} the number of occupied and virtual orbitals respectively, compared to the $N_{occ}^3 N_{virt}^2$ scaling of standard ADC(2)x for the ionic Hamiltonian. N_{virt} tends to be the substantially larger of the two numbers, and is the one which increases if a larger basis is chosen for a given molecule, so this increase in computational cost can be significant. In particular, this means that the ADC(2,2) technique has no possibility of being used to model the distant continuum states in the way that was possible with ADC(2)x in the B-spline construction. In the implementation used in this work, the basis for the ADC(2,2) Hamiltonian is instead constructed from localised Gaussian-type orbitals, as is standard for the ADC approach.

Analytical Theory

3.1 Decay of Bound and Unbound States

3.1.1 Decay of Unbound States

An atomic or molecular quantum system in an excited state which does not undergo immediate fragmentation will typically fall to a lower energy state either through the emission of a photon or an electron carrying away the excess energy. These decay processes are important as they provide a timescale for the relevant excitations. Decay by electron emission, known as Auger (or Auger-Meitner) decay [2, 3], occurs in systems with an inner-shell hole of sufficient energy. If the presence of this hole elevates the system above its ionisation potential, it is possible for an outer-valence electron to recombine with this vacancy, providing the energy to eject a second outer-shell electron into the continuum. As a purely electronic process, Auger decay has a typical timescale on the order of femtoseconds [4] and, especially in light atoms, is often the dominant form of decay; although for core vacancies in heavier atoms, decay by photon emission at hard X-ray frequencies is more competitive due to the ω^3 scaling of the spontaneous emission rate. Inner-shell vacancies are commonly created during the interaction of atoms or molecules with high-frequency or high-intensity radiation, and Auger decay is therefore of particular interest within ultrafast laser physics.

A system of a bound state $|\psi_0\rangle$ coupled to a continuum $|\psi_E\rangle$ can be described in terms of its wavefunction

$$|\Psi(t)\rangle = c_0(t)e^{-iE_0t}|\psi_0\rangle + \int dE \rho(E) c_E(t) e^{-iEt} |\psi_E\rangle \quad (3.1)$$

and the system Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad (3.2)$$

where $\hat{H}_0$ gives the state energies in the absence of coupling: $\hat{H}_0|\psi_0\rangle = E_0|\psi_0\rangle$,

$\hat{H}_0|\psi_E\rangle = E|\psi_E\rangle$; and $\hat{H}_1$ contains the coupling between the bound and continuum states. $\rho(E)$ represents the density of continuum states as a function of energy. Applying the Schrödinger equation, the decay of the bound system can be expressed precisely in terms of the coupled differential equations

$$\dot{c}_0(t) = -i \int dE e^{-i(E-E_0)t} \langle \psi_0 | \hat{H}_1 | \psi_E \rangle \rho(E) c_E(t); \quad (3.3)$$

$$\dot{c}_E(t) = -ie^{i(E-E_0)t} \langle \psi_E | \hat{H}_1 | \psi_0 \rangle c_0(t) \quad (3.4)$$

A very common and widely applicable approximation is to take the bound state probability as exponentially decaying [83]:

$$|c_0(t)|^2 = e^{-\Gamma t} \quad (3.5)$$

with decay rate [84]

$$\Gamma = 2\pi |\langle \psi_0 | \hat{H}_1 | \psi_{E=E_0} \rangle|^2 \rho(E_0) \quad (3.6)$$

Where the density of states and the transition matrix element have been replaced by their values at the bound state energy E_0 . At short times, this expression for Γ is just a statement of the Fermi golden rule for transition rates, but the extension of its validity to longer times is an application of the Wigner-Weisskopf approximation [85] as follows: by explicitly integrating 3.4 and substituting back into 3.3, the variation of the bound coefficient can be re-expressed as [84]

$$\dot{c}_0(t) = - \int_0^t dt' F(t') c_0(t-t') \quad (3.7)$$

where

$$F(t') = \int dE e^{-i(E-E_0)t'} |\langle \psi_0 | \hat{H}_1 | \psi_E \rangle|^2 \rho(E) \quad (3.8)$$

Noting that $\rho(E)$ and $|\langle \psi_0 | \hat{H}_1 | \psi_E \rangle|^2$ are typically slowly varying functions of E , $F(t')$ must be non-negligible only for very small t' where the exponential in the integral is not fast-oscillating with energy. So long as $c_0(t)$ does not vary much over this interval, it can be pulled out of the integral (3.7) to give

$$\dot{c}_0(t) = -c_0(t) \int_0^t dt' F(t') \quad (3.9)$$

where the upper limit of the integral is then taken to be infinity, and explicit evaluation returns

$$\int_0^\infty dt' F(t') = -\left(\frac{\Gamma}{2} + i\delta E_0\right) \quad (3.10)$$

reproducing the Fermi golden rule rate, and introducing an energy shift δE_0 of the bound state due to the interaction with the continuum. The energy distribution derived from 3.4 then takes the form

$$|c_E(t = \infty)|^2 = \frac{|\langle \psi_0 | \hat{H}_1 | \psi_E \rangle|^2}{(E - (E_0 + \delta E_0))^2 + (\Gamma/2)^2} \quad (3.11)$$

Which is a Lorentzian-like function so long as $\langle \psi_0 | \hat{H}_1 | \psi_E \rangle$ is slowly varying compared to the decay width $\Gamma/2$.

3.1.2 Decay and Revivals of Bound States: the Bixon-Jortner Model

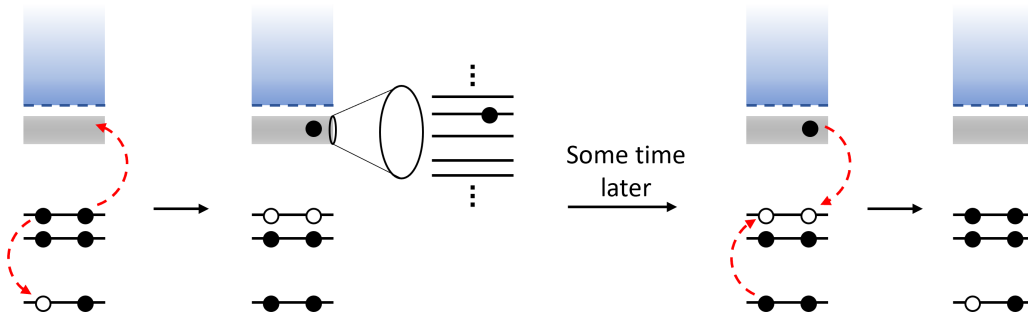


Figure 3.1: A schematic representation of the process of frustrated Auger decay. Left: An outer shell electron fills an inner shell vacancy, promoting a second electron into a closely-spaced quasicontinuum of discrete states slightly short of ionisation. Right: after some period of time, the initial inner-shell vacancy is spontaneously recreated.

In many inner-valence ionised molecular systems [86, 87], as well as in multiply-ionised systems with a core vacancy [88], Auger decay is energetically forbidden. Nonetheless, it is often still possible for an outer-shell electron to recombine with the hole and impart the resulting energy to a second electron. Here, however, the electron is excited into a series of diffuse orbitals close to but short of ionisation in a process referred to as ‘frustrated

Auger decay' [22]. The initial vacancy does therefore initially decay in an approximately exponential manner, however the electron remains bound and in some systems it is possible that after some length of time the initial inner-shell vacancy experiences partial quantum revivals [17, 89]. This is illustrated schematically in figure 3.1. Classically, this can be interpreted as the departing electron failing to overcome the attraction to the leftover ion and falling back towards the system, re-exciting the remaining bound electrons as it does so.

The orbitals nearest to the ionisation threshold are often very narrowly spaced, forming what is referred to as a quasicontinuum. The precise nature of this quasicontinuum is system-dependent, but the archetype for these dynamics is provided by the Bixon-Jortner model [90]. This is an idealised model consisting of a single initially-populated main state coupled to an infinite quasicontinuum with a small, constant state spacing δ , identical coupling α between the main state and every quasicontinuum state, and zero coupling between separate quasicontinuum states. All states are defined to be orthonormal. Denoting the main state as $|\psi\rangle$ and the quasicontinuum states as $|\phi_m\rangle$, the Bixon-Jortner Hamiltonian is therefore given by

$$\hat{H}_{BJ} = E_\psi |\psi\rangle\langle\psi| + \sum_{m=-\infty}^{\infty} E_m |\phi_m\rangle\langle\phi_m| + \sum_{m=-\infty}^{\infty} \alpha \left(|\psi\rangle\langle\phi_m| + |\phi_m\rangle\langle\psi| \right) \quad (3.12)$$

Where E_ψ is the main state energy, and $E_m = m\delta$ is the energy of quasicontinuum state $|\phi_m\rangle$. This is illustrated in figure 3.2

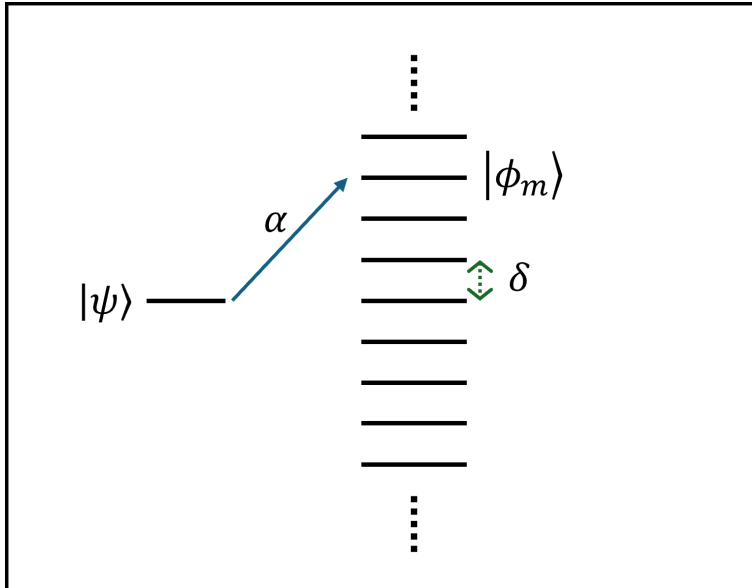


Figure 3.2: The level scheme for the Bixon-Jortner model. The main state $|\psi\rangle$ is coupled to an infinite quasicontinuum of states $|\phi_m\rangle$. The spacing between adjacent quasicontinuum states is a constant value δ , and the coupling coefficient is the same value α between the main state and each quasicontinuum state.

The critical advantage of this model is that it has an exact analytical solution, which can be calculated either by a Laplace transform-based approach [91] or a memory function-based approach [92]. A sketch of the former is as follows:

The system wavefunction is expressed as

$$|\Psi\rangle = c_\psi(t)e^{-iE_\psi t}|\psi\rangle + \sum_{m=-\infty}^{\infty} c_m(t)e^{-iE_m t}|\phi_m\rangle \quad (3.13)$$

with initial conditions $c_\psi(0) = 1$, $c_m(0) = 0$. Using the Schrödinger equation, the rate of change of the coefficients is given by

$$i\dot{c}_\psi(t) = \alpha \sum_{m=-\infty}^{\infty} c_m(t)e^{-i(m\delta - E_\psi)t}; \quad (3.14)$$

$$i\dot{c}_m(t) = \alpha c_\psi(t)e^{i(m\delta - E_\psi)t} \quad (3.15)$$

The Laplace transform $\mathcal{L}(f(t)) = \tilde{f}(s)$ is defined as

$$\tilde{f}(s) = \int_0^\infty dt e^{-st} f(t) \quad (3.16)$$

where s is complex. Using the identity $\mathcal{L}\left(\frac{df}{dt}\right) = s\tilde{f}(s) - f(0)$ to obtain the Laplace transformed equations, substituting the second into the first and rearranging gives

$$\begin{aligned} \tilde{c}_\psi(s) &= \left[s + \sum_{m=-\infty}^{\infty} \alpha^2 (s + i(m\delta - E_\psi))^{-1} \right]^{-1} \\ &= \left[s + \frac{\pi\alpha^2}{\delta} \coth\left(\frac{\pi(s - iE_\psi)}{\delta}\right) \right]^{-1} \end{aligned} \quad (3.17)$$

where in the second line an identity for $\coth(x)$ has been used. Defining $\gamma_\alpha = \pi\alpha^2/\delta$, applying the inverse Laplace transform and redefining the integration variable gives

$$c_\psi(t) = \frac{e^{iE_\psi t}}{2\pi i} \int_{-\infty i + \lambda}^{\infty i + \lambda} ds e^{st} \left[s + iE_\psi + \gamma_\alpha \coth\left(\frac{\pi s}{\delta}\right) \right]^{-1} \quad (3.18)$$

where the integral is taken along a vertical contour in the imaginary plane defined by λ such that all poles of the integrated function lie to its left. Explicitly expanding the hyperbolic cotangent in terms of exponentials and rearranging gives

$$c_\psi(t) = \frac{e^{iE_\psi t}}{2\pi i} \int_{-\infty i + \lambda}^{\infty i + \lambda} ds e^{st} \frac{1 - e^{-2\pi s/\delta}}{s + iE_\psi + \gamma_\alpha} \left[1 - \frac{s + iE_\psi - \gamma_\alpha}{s + iE_\psi + \gamma_\alpha} e^{-2\pi s/\delta} \right]^{-1} \quad (3.19)$$

Noting that λ can be taken to be arbitrarily positive, a contour can be chosen such

that the series expansion for the square bracketed term will converge everywhere, and therefore the integral can be rewritten in terms of a sum over poles

$$c_\psi(t) = \frac{e^{iE_\psi t}}{2\pi i} \int_{-\infty i + \lambda}^{\infty i + \lambda} ds e^{st} \left[\frac{1}{s + iE_\psi + \gamma_\alpha} - 2\gamma_\alpha \sum_{n=1}^{\infty} \frac{(s + iE_\psi - \gamma_\alpha)^{n-1}}{(s + iE_\psi + \gamma_\alpha)^{n+1}} e^{-2\pi n s / \delta} \right] \quad (3.20)$$

This can finally be evaluated term by term through standard contour integration, choosing to close each contour at $s = -\infty$ or $s = \infty$ to ensure that $e^{s(t-2\pi n/\delta)}$ goes to zero on the arc - and thus respectively including or excluding the corresponding poles at time t . This leads to the final expression for the main state coefficient

$$c_\psi(t) = e^{-\gamma_\alpha t} + \sum_{n=1}^{\infty} \sum_{m=0}^{n-1} \binom{n-1}{m} \frac{(-2\gamma_\alpha(t - nt_r))^{n-m}}{(n-m)!} e^{-\gamma_\alpha(t-nt_r)} e^{inE_\psi t_r} \Theta(t - nt_r) \quad (3.21)$$

where $\Theta(x)$ is the Heaviside step function; the revival time $t_r = 2\pi/\delta$; and $2\gamma_\alpha = \Gamma_\alpha$ can now be identified with the Fermi golden rule decay rate. What is notable about this result is that the initial decay of the main state is exactly exponential and it remains this way until t_r , at which point the initial state experiences a sharp revival in its occupation probability. Further revivals follow at each interval of t_r . The main state therefore resembles a state decaying into a continuum for small times, and it is only after t_r that the quasicontinuum nature of the system becomes apparent. An illustrative plot of this behaviour is shown in figure 3.3.

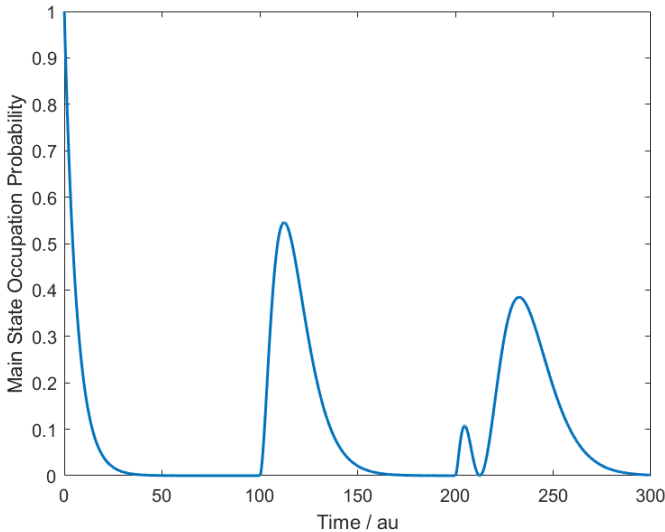


Figure 3.3: The initial pure-exponential decay and the first two revivals of the main state in a Bixon-Jortner model system with initial decay rate $\Gamma_\alpha = 0.16$ au and revival time $t_r = 100$ au. The parameters here are chosen for illustrative purposes.

While the exact structure of the Bixon-Jortner quasicontinuum is not particularly realistic, the feature of initial exponential-like decay of an inner-shell hole followed by spontaneous revivals at some later time is a feature of real systems [17], and corresponds to a type of charge migration where an initially localised charge diffuses across the system

before re-localising on its initial site. This model therefore provides a useful way to approach such dynamics analytically.

Analytical Results

4.1 Detection of Quantum State Revivals Through an Interferometric Approach

4.1.1 Overview

Most typical measurements of ultrafast electronic processes make use of attosecond duration laser pulses. This usually takes the form of an attosecond pump pulse to initialise the dynamics, with the later behaviour being probed either by a second attosecond pulse with a controlled delay, or by a near-infra-red probe. Recently, it has been shown analytically that it is possible to measure the decay rate of an Auger-active state via an interferometric method [93] using an $\omega/2\omega$ coherent scheme in which the relative phases of the two pulses are carefully controlled and the pulse durations are long. In that approach, termed ‘molecular Auger interferometry’ (MAI), the decay rate can be simply derived from the modulation of the final ionisation yield as the relative phase of the two pulses is varied. Here, we investigated from an analytical perspective the possibility of using a technique similar to that used in MAI to detect revivals in an initially-decaying state of the ‘frustrated Auger’ type [94], thus providing an avenue to observe these ultrafast dynamics without using any attosecond pulse, instead observing the dynamics through very precise control of the relative phase of a pair of longer-duration pulses. Similarly to the MAI approach, we consider two simultaneous laser pulses of frequencies ω and 2ω with a carefully controlled phase offset. While MAI concerns an exponentially decaying Auger-active state, for the ‘frustrated Auger’ systems of interest here the relevant idealised representation is the Bixon-Jortner model [90] described in section 3.1.2. In our modified system, the Bixon-Jortner main state directly replaces the Auger-decaying state from the MAI case. The exact analytical solution of the Bixon-Jortner model [91, 92] can in fact be extended to more general systems incorporating such a quasicontinuum [95]. We are able to use this feature of the model to obtain analytically an interferometric signature of the revival which can be generalised to systems incorporating a non-idealised quasicontinuum.

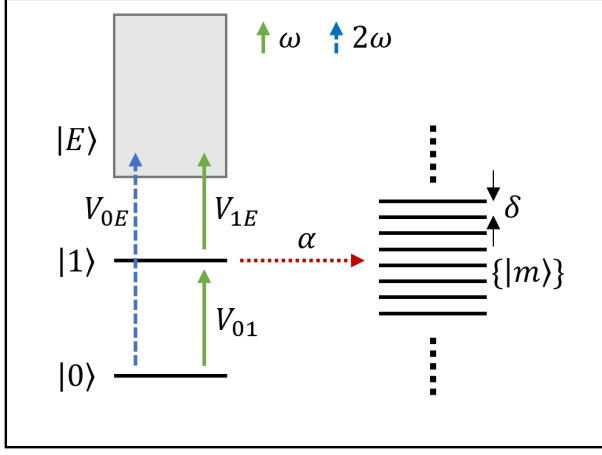


Figure 4.1: The level scheme for quantum revival interferometry with a Bixon-Jortner quasicontinuum. The system contains a bound ground state $|0\rangle$ which is ionised via two pathways: either directly by a photon with energy 2ω or in a two-step process via an intermediate, where each transition is caused by a photon of frequency ω . The intermediate state in this case is a Bixon-Jortner main state $|1\rangle$, so it is coupled to an infinite, evenly spaced quasicontinuum $|m\rangle$ with coupling α between the main state and all quasicontinuum states, and quasicontinuum energy spacing δ .

4.1.2 Analytical Approach

The system we consider is depicted in figure 4.1. Similarly to the Auger interferometry system [93], the bound ground state $|0\rangle$ is ionised either directly through the absorption of a single photon of energy 2ω , or through the absorption of two photons of energy ω , where the system passes through the intermediate $|1\rangle$. So long as the symmetry conditions for Auger interferometry are fulfilled, these two paths can interfere, and this interference can be controlled by the phase offset ϕ between the two laser pulses. For two lasers with linear, parallel polarisation, this symmetry condition is that the direct product of the representation of the dipole operator D_{dip} with itself, contains itself [93]: $D_{\text{dip}} \otimes D_{\text{dip}} \supset D_{\text{dip}}$. This is possible, for instance, for molecules of the groups C_s , C_n , C_{nv} , and $C_{\infty v}$ with the ground state and intermediate state both in the fully symmetric irreducible representation; and can also be achieved for certain states of molecules in the D_3 , D_{3h} , and T_d point groups. Where this system differs from that used in Auger interferometry is that rather than decaying into a continuum, the intermediate takes the form of a Bixon-Jortner main state and is coupled to an infinite quasicontinuum with constant spacing δ , where the main state has identical coupling α to all quasicontinuum states $|m\rangle$.

We therefore start with the ansatz for the wavefunction

$$\begin{aligned} \Psi(t) = & c_0(t)e^{-iE_0t}\psi_0 + c_1(t)e^{-i(E_0+\omega)t}\psi_1 \\ & + \sum_m c_m(t)e^{-iE_mt}\phi_m + \int dE c_E(t)e^{-iEt}\psi_E \end{aligned} \quad (4.1)$$

and the Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) + \hat{H}_{\text{BJ}}, \quad (4.2)$$

$\hat{H}_0$ is the diagonal matrix of state energies, $\hat{V}(t) = -\hat{d}\mathcal{E}_1 \cos(\omega t) - \hat{d}\mathcal{E}_2 \cos(2\omega t + \phi)$ is the

coupling due to the laser fields, and $\hat{H}_{\text{BJ}}$ is the matrix giving the coupling between the Bixon-Jortner main state $|1\rangle$ and the quasicontinuum states $|m\rangle$. In this model, $\hat{V}$ does not couple the quasicontinuum states, and the field amplitudes $\mathcal{E}_1$ and $\mathcal{E}_2$ are assumed to be constant in time. The non-zero terms of $\hat{H}_{\text{BJ}}$ are $\langle 1|\hat{H}_{\text{BJ}}|m\rangle = \langle m|\hat{H}_{\text{BJ}}|1\rangle = \alpha$, for all quasicontinuum states $|m\rangle$; while the energy of quasicontinuum state $|m\rangle$ is $\epsilon_m = E_1 + m\delta + \tilde{\delta}$, where $\tilde{\delta}$ is the offset of the quasicontinuum from the Bixon-Jortner main state. E_0 and E_1 are the energies of the ground state and main state respectively. After applying the time-dependent Schrödinger equation $\hat{H}(t)\Psi(t) = i\frac{\partial}{\partial t}\Psi(t)$, with $\hat{H}(t)$ and $\Psi(t)$ defined as above, this returns the system of equations for the complex amplitudes of the states

$$\begin{aligned} i\dot{c}_0 &= \langle \psi_0|\hat{V}(t)|\Psi\rangle e^{iE_0t} \\ i\dot{c}_1 &= \langle \psi_1|\hat{V}(t)|\Psi\rangle e^{i(E_0+\omega)t} + \Delta_{01}c_1 + \alpha \sum_m e^{-i(m\delta+\delta_0)t} c_m \\ i\dot{c}_E &= \langle \psi_E|\hat{V}(t)|\Psi\rangle e^{iEt} \\ i\dot{c}_m &= \alpha e^{i(m\delta+\delta_0)t} c_1. \end{aligned} \tag{4.3}$$

Subsequently using the rotating wave approximation to simplify the $\langle \psi_j|\hat{V}(t)|\Psi(t)\rangle$ terms and then applying the technique of the adiabatic elimination of the continuum [96], the equations for the bound state coefficients are obtained:

$$\begin{aligned} i\dot{c}_0 &= (V_{01} - \frac{i}{2}e^{i\phi}\Gamma_{01})c_1 - \frac{i}{2}\Gamma_0^i c_0 \\ i\dot{c}_1 &= (V_{10} - \frac{i}{2}e^{-i\phi}\Gamma_{10})c_0 - \frac{i}{2}\Gamma_1^i c_1 + \Delta_{01}c_1 \\ &\quad + \alpha \sum_m e^{-i(m\delta+\delta_0)t} c_m \\ i\dot{c}_m &= \alpha e^{i(m\delta+\delta_0)t} c_1, \end{aligned} \tag{4.4}$$

where $\Gamma_0^i = 2\pi|V_{0E}|^2$, $\Gamma_1^i = 2\pi|V_{1E}|^2$, and $\Gamma_{01} = 2\pi V_{0E}V_{E1}$; and the matrix elements $V_{0E} = -d_{0E}\mathcal{E}_2/2$, $V_{01} = -d_{01}\mathcal{E}_1/2$, and $V_{1E} = -d_{1E}\mathcal{E}_1/2$. Δ_{01} is the detuning of the photon energy from the energy difference between the ground state and the Bixon-Jortner main state, $\Delta_{01} = E_1 - E_0 - \omega$; and δ_0 is the energy offset of the quasicontinuum from the main state shifted by the detuning, $\delta_0 = \tilde{\delta} + \Delta_{01}$. The continuum occupation is given by the integral

$$c_E = -i \int_0^t dt' e^{-i(E_0-E+2\omega)t'} (V_{E0}c_0 e^{-i\phi} + V_{E1}c_1). \tag{4.5}$$

The system of equations (4.4) obtained at this point is similar to one solved via a Laplace transform method by Kyrölä and Eberly [95], which is in turn a generalisation of the approach developed by Stey and Gibberd for the solution of the Bixon-Jortner model

described in section 3.1.2. We therefore take an equivalent approach to obtaining the time variation of the ground and intermediate state coefficients. After redefining the quasicon-
tinuum coefficients c_m to eliminate the exponentials through $a_m(t) = e^{-i(m\delta+\delta_0)t}c_m(t)$,
taking the Laplace transform of equations (4.4) with the initial condition $c_0(0) = 1$ gives

$$\begin{aligned} sc_0(s) - 1 &= -i\beta_{01}c_1(s) - \frac{1}{2}\Gamma_0^i c_0(s) \\ sc_1(s) &= -i\beta_{10}c_0(s) - \frac{1}{2}\Gamma_1^i c_1(s) - i\Delta_{01}c_1(s) - i\alpha \sum_m a_m(s) \\ sa_m(s) &= -i\alpha c_1(s) - i(m\delta + \delta_0)a_m(s), \end{aligned} \quad (4.6)$$

where we define

$$\begin{aligned} \beta_{01} &= V_{01} - \frac{1}{2}ie^{i\phi}\Gamma_{01} \\ \beta_{10} &= V_{10} - \frac{1}{2}ie^{-i\phi}\Gamma_{10} \end{aligned} \quad (4.7)$$

leading finally to expressions for $c_0(s)$ and $c_1(s)$ in the form:

$$\begin{aligned} c_0(s) &= (s + \frac{1}{2}\Gamma_0^i + \beta_{01}\beta_{10}(s + \frac{1}{2}\Gamma_1^i + i\Delta_{01} + \alpha^2 K)^{-1})^{-1} \\ c_1(s) &= -i\beta_{01}c_0(s)(s + \frac{1}{2}\Gamma_1^i + i\Delta_{01} + \alpha^2 K)^{-1}, \end{aligned} \quad (4.8)$$

where

$$K = \sum_m \frac{1}{s + i(m\delta + \delta_0)} = \frac{\pi}{\delta} \coth\left(\frac{\pi(s + i\delta_0)}{\delta}\right) \quad (4.9)$$

and we subsequently define the Bixon-Jortner main state initial decay rate $\Gamma_\alpha = 2\pi\alpha^2/\delta$.
Expressing the hyperbolic cotangent part explicitly in terms of exponentials and rear-
ranging, the series expansion of $(1-x)^{-1}$ can be used to rewrite both c_0 and c_1 terms
as sums over powers of $e^{-2\pi(s+\delta_0)/\delta}$. This finally allows the inverse Laplace transform
 $f(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds f(s) e^{st}$ to be expressed as:

$$c_j(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds e^{st} \left(\frac{A^j(s)}{(s-s_+)(s-s_-)} + \sum_{n=1}^{\infty} e^{-i\delta_0 n t_r} e^{-n t_r s} B^j(s) \frac{[(s-s'_+)(s-s'_-)]^{n-1}}{[(s-s_+)(s-s_-)]^{n+1}} \right) \quad (4.10)$$

with $j = 0, 1$ and the revival time $t_r = 2\pi/\delta$. The parameters $s_\pm$, A^j , and B^j are defined

in this case as:

$$\begin{aligned}
s_{\pm} &= \frac{1}{2} \left[-\left(\frac{1}{2}\Gamma_{\alpha} + i\Delta_{01} + \frac{1}{2}\Gamma_1^i + \frac{1}{2}\Gamma_0^i\right) \pm \sqrt{\left(\frac{1}{2}\Gamma_{\alpha} + i\Delta_{01} + \frac{1}{2}\Gamma_1^i - \frac{1}{2}\Gamma_0^i\right)^2 - 4\beta_{10}\beta_{01}} \right] \\
s'_{\pm} &= \frac{1}{2} \left[-\left(-\frac{1}{2}\Gamma_{\alpha} + i\Delta_{01} + \frac{1}{2}\Gamma_1^i + \frac{1}{2}\Gamma_0^i\right) \pm \sqrt{\left(-\frac{1}{2}\Gamma_{\alpha} + i\Delta_{01} + \frac{1}{2}\Gamma_1^i - \frac{1}{2}\Gamma_0^i\right)^2 - 4\beta_{10}\beta_{01}} \right]
\end{aligned} \tag{4.11}$$

and

$$\begin{aligned}
A^0(s) &= s + \frac{1}{2}\Gamma_{\alpha} + i\Delta_{01} + \frac{1}{2}\Gamma_1^i \\
B^0(s) &= \Gamma_{\alpha}\beta_{01}\beta_{10} \\
A^1(s) &= -i\beta_{10} \\
B^1(s) &= i\left(s + \frac{1}{2}\Gamma_0^i\right)\Gamma_{\alpha}\beta_{10}.
\end{aligned} \tag{4.12}$$

The integral now takes an analogous form to that obtained by Kyrölä and Eberly [95], and the corresponding solution via contour integration can be followed. Using the above definitions for the various parameters, this leads to the expressions for the state coefficients:

$$\begin{aligned}
c_j(t) &= \sum_{\pm} \frac{A^j(s_{\pm})e^{s_{\pm}t}}{s_{\pm} - s_{\mp}} + \sum_{\pm} \sum_{n=1}^{\infty} \sum_{p=0}^n \sum_{m=0}^p e^{-i\delta_0 n t_r} e^{s_{\pm}(t - n t_r)} L_{n-p}^{p-1}(-(s_{\pm} - s'_{\pm})(t - n t_r)) \\
&\quad \times (-1)^m \binom{n+m}{n} (s_{\pm} - s'_{\pm})^{p-1} (s_{\pm} - s'_{\mp})^{n+m-p-1} (s_{\pm} - s_{\mp})^{-n-m-1} \\
&\quad \times \left[B^j(s_{\pm}) \binom{n-1}{p-m} + \frac{dB^j}{ds}(s_{\pm})(s_{\pm} - s'_{\mp}) \binom{n-1}{p-m-1} \right] \Theta(t - n t_r), \tag{4.13}
\end{aligned}$$

where $L_m^n(x)$ are the associated Laguerre polynomials, and the definitions $\binom{a}{b} = 0$ for $b < 0$ or $b > a$ and $L_n^{-1}(x) = -\frac{x}{n}L_{n-1}^1(x)$ have been used [95]. $\Theta(t)$ is the Heaviside step function.

In the case where $t < t_r$, only the first sum in (4.13) contributes, and after inserting the explicit expressions for A^j , $j = 0, 1$, it can be shown that the coefficients of the ground and intermediate states are identical to those obtained by Khokhlova *et al.* for an Auger-decaying intermediate state with decay rate Γ_{α} [93], noting here that the convention we have chosen for Γ_{α} makes it equivalent to twice the decay rate Γ_1 used in their work. Thus, in exactly the same manner as the original unmodified Bixon-Jortner model, the quasicontinuum features of the decay only become apparent after the revival time t_r and this system does approach the case of coupling to a true continuum as t_r is taken to infinity. A significant consequence of this is that the simple modulation behaviour of the

ionisation yield obtained in the Auger interferometry case also holds here immediately prior to the first revival, so long as t_r can be considered to lie in the large-time limit. This limit is given by the conditions $|Re(s_-)|t \gg 1$ and $|s_-|t \gg A^0(s_-)/A^0(s_+)$, where the second condition is simply a broader case of the first so long as $|s_-| \gg \Gamma_0^i$.

In order to obtain the effect of revivals on this ionisation yield behaviour, we now proceed by inserting the expressions (4.13) for $c_0(t)$ and $c_1(t)$ into the integral (4.5) for c_E . In order to make progress here, we restrict to times $t < 2t_r$, where revivals after the first do not contribute. This means that only the $n = 1$ term of the second sum in (4.13) is non-zero, and we can express the remaining Laguerre polynomials explicitly. This gives the expression for c_E

$$c_E = -i \sum_{j=0}^1 \sum_{\pm} V_{Ej} e^{-i\xi_j} \left(\int_0^t dt' e^{i\tilde{E}t'} e^{s_{\pm}t'} A^j(s_{\pm})(s_{\pm} - s_{\mp})^{-1} \right. \\ \left. + \theta(t - t_r) \frac{e^{-i\delta_0 t_r}}{(s_{\pm} - s_{\mp})^2} \int_{t_r}^t dt' e^{i\tilde{E}t'} e^{s_{\pm}(t'-t_r)} \left[(t' - t_r) B^j(s_{\pm}) - 2B^j(s_{\pm})(s_{\pm} - s_{\mp})^{-1} + \frac{dB^j}{ds}(s_{\pm}) \right] \right), \quad (4.14)$$

where $\xi_0 = \phi$, $\xi_1 = 0$, and $\tilde{E} = E - E_0 - 2\omega$. Evaluating this integral over time returns

$$c_E = -i \sum_{j=0}^1 \sum_{\pm} V_{Ej} e^{-i\xi_j} \left[\frac{e^{(i\tilde{E}+s_{\pm})t} - 1}{i\tilde{E} + s_{\pm}} A^j(s_{\pm})(s_{\pm} - s_{\mp})^{-1} \right. \\ \left. + \theta(t - t_r) \frac{e^{-i\delta_0 t_r}}{(s_{\pm} - s_{\mp})^2} \left(\frac{e^{i\tilde{E}t_r} (e^{(i\tilde{E}+s_{\pm})(t-t_r)} - 1)}{i\tilde{E} + s_{\pm}} (-2B^j(s_{\pm})(s_{\pm} - s_{\mp})^{-1} + \frac{dB^j}{ds}(s_{\pm})) \right) \right. \\ \left. + \frac{e^{i\tilde{E}t_r} e^{(i\tilde{E}+s_{\pm})(t-t_r)}}{i\tilde{E} + s_{\pm}} B^j(s_{\pm})(t - t_r) - \frac{e^{i\tilde{E}t_r} (e^{(i\tilde{E}+s_{\pm})(t-t_r)} - 1)}{(i\tilde{E} + s_{\pm})^2} B^j(s_{\pm}) \right]. \quad (4.15)$$

4.1.3 Conditions for interferometric observation of revivals

In order to see how the revival impacts the modulation behaviour, the simple Auger system modulation obtained by Khokhlova *et al.* [93] must hold in the absence of revivals so that the deviation from this well-described system can be observed. The A^j term of equation (4.15) describes the behaviour of the Auger system, and from this equation a couple of conditions can be derived for the simple behaviour to apply in the Auger case. The first requirement is that the modulation behaviour of the system without revivals would approach the large-time limiting case. This will be true if the condition $|Re(s_-)|\tau \gg 1$ is satisfied, where τ is the total length of the applied laser pulse. The simple formula provided for the modulation behaviour in this case is also conditional on the modulation of the total ionisation yield being well represented by its resonant part. Defining $G = \frac{1}{2}\Gamma_{\alpha} + \frac{1}{2}\Gamma_0^i + \frac{1}{2}\Gamma_1^i + i\Delta_{01}$ and assuming $\Delta_{01} \ll G$, we can show that this can

be guaranteed only if

$$|G|^2 \gg |\Gamma_0^i \Gamma_\alpha + 4|V_{01}|^2| \quad \text{and} \quad |G|^2 \gg 4|V_{01}\Gamma_{01}|.$$

Provided that these conditions are met, along with the further requirement for sinusoidal modulation of the ionisation yield with ϕ [93] which is satisfied if either

$$\Gamma_\alpha \gg \frac{4|V_{01}V_{1E}|}{|V_{0E}|} \quad \text{or} \quad 1 \gg \frac{2\pi|V_{0E}V_{1E}|}{|V_{01}|},$$

the modulation depth of the ionisation yield immediately prior to revivals should approach a constant value given by the formula

$$\mathcal{M} = 2 \left(\frac{2|V_{01}V_{1E}|}{|V_{0E}\Gamma_\alpha|} + \frac{|V_{0E}\Gamma_\alpha|}{2|V_{01}V_{1E}|} \right)^{-1}. \quad (4.16)$$

The modulation depth $\mathcal{M}$ is defined such that the resonant yield $|c_{E,res}|^2$ is given by

$$|c_{E,res}(t, \phi)|^2 = F(t)(1 + \mathcal{M}(t)\sin(\phi + \phi')), \quad (4.17)$$

where $\phi' = \phi_{01} = \arg(V_{0E}) - \arg(V_{1E})$ in the Auger-like case, but may take on a different value after revivals take effect; and $F(t)$ is the ionisation yield when $\phi + \phi' = 0$. This modulation behaviour extends to the total yield $\int |c_E|^2 dE$ so long as the above conditions for the resonant part being representative are met. The laser parameters can therefore be chosen to set the modulation depth such that it would approach a maximal value of 1 in the absence of revivals. If it is additionally true that $|Re(s_-)|t_r \gg 1$, then the system will reach this constant modulation depth before revivals take effect.

If the revivals are to be detected by an interferometric approach, it is also necessary that the effect of the revival part in equation (4.15) for c_E is both significant in comparison to the Auger-type contribution, and also that it is dependent on the 2ω laser phase offset ϕ . The $\Theta(t - t_r)$ term in this equation describes the contribution to c_E due to the first revival. Assuming that the above conditions on the Auger system are met, and that $|Re(s_-)|(t - t_r) \gg 1$ and $\Gamma_0^i \ll G$, we can determine the ratio of the revival contribution to the $j = 1$ part of (4.15) to the Auger contribution in two opposite limiting cases: for times such that $|Re(s_+)|t \ll 1$, this ratio becomes approximately $\Gamma_\alpha(t - t_r)/(Gt)$; and for the other limit $|Re(s_+)|(t - t_r) \gg 1$ the ratio approaches $\frac{1}{2}\Gamma_\alpha\Gamma_0^i(2(s_+ - s_-)^{-2} + (s_+ - s_-)^{-1}(s_+^{-1} + s_-^{-1}))$. If it is the case that $s_- \approx -G \approx -\frac{1}{2}\Gamma_\alpha$ then the revival contribution to this $j = 1$ part of (4.15) will always be significant at least in the $|Re(s_+)|t \ll 1$ case; and under these conditions the contribution of the revival term to the $j = 0$ part will be small, leading to phase-dependence of the revival contribution. Furthermore, laser parameters can always be chosen such that the condition

$\Gamma_\alpha \gg \Gamma_0^i, \Gamma_1^i, 2\Delta_{01}, 2|V_{01}|$ is met, and therefore $s_- \approx -G \approx -\frac{1}{2}\Gamma_\alpha$, while also meeting all of the previously described conditions on the Auger system. This leads to an optimal set of conditions under which an interferometric measurement of revivals can be performed:

$$\frac{\mathcal{E}_1^2}{\mathcal{E}_2} \approx \frac{\Gamma_\alpha |d_{0E}|}{|d_{01}d_{1E}|} \quad (4.18a)$$

$$\Gamma_\alpha \gg 2|d_{01}|\mathcal{E}_1 \quad (4.18b)$$

$$\Gamma_\alpha \gg 2\Delta_{01} \quad (4.18c)$$

$$\mathcal{E}_2 \ll \frac{|d_{01}|}{\pi|d_{0E}d_{1E}|} \quad (4.18d)$$

$$\Gamma_\alpha \gg \frac{1}{4}\mathcal{E}_2^2|d_{0E}|^2 + \frac{1}{4}\mathcal{E}_1^2|d_{1E}|^2 \quad (4.18e)$$

$$\frac{1}{2}\Gamma_\alpha(\tau - t_r) \gg 1. \quad (4.18f)$$

These conditions can all be satisfied with sufficiently small $\mathcal{E}_1$, $\mathcal{E}_2$, and Δ_{01} , and sufficiently large τ . While these conditions are derived for the system with the non-physical Bixon-Jortner quasicontinuum, we argue that they should generalise at least approximately to systems with more realistic quasicontinua. Conditions (4.18a-4.18d) relate to the pre-revival system, the solution to which is mathematically identical to the already-realistic case of Auger decay. Condition (4.18e) states that the rate of decay into the quasicontinuum should be large compared to the rate of decay of the ground and intermediate states into the continuum — a sensible condition if the subsequent revivals from the quasicontinuum are to significantly affect the continuum population. Lastly, condition (4.18f) is simply a requirement that sufficient time has passed after the revival begins at t_r for it to substantially alter the population of the intermediate state. It is therefore reasonable to expect that interferometric measurement of revivals in realistic systems should also be subject to roughly the same conditions. While these conditions are derived from equation (4.15), and are therefore only strictly valid for the Bixon-Jortner system for total pulse lengths $\tau < 2t_r$, in most realistic systems any revivals which occur on timescales greater than a few femtoseconds will be damped out by atomic motion [17, 23], so no more than one revival is likely to be seen, and the range of validity of these equations can be extended past $2t_r$.

We now seek to understand how the Bixon-Jortner system would behave with realistic choices for the initial decay rate Γ_α and revival time t_r . In order to do this, we take the values of the initial decay rate and revival time calculated for the $3a_g$ hole state in the molecule trans-1,3 butadiene calculated by Craigie *et al.* [89] at the ADC(2)x level of approximation [31]. In atomic units, these values are $\Gamma_\alpha = 0.19$ and $t_r = 75$. This is a fairly rough exercise, so it is sufficient for our purposes to take an order of magnitude

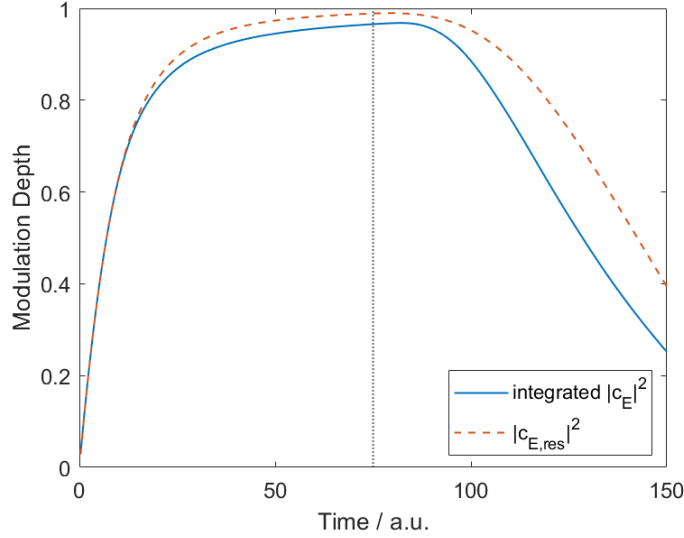


Figure 4.2: The modulation depth of the ionisation yield plotted versus time. The orange dashed line is obtained from the resonant part of (4.15), while the solid blue line is the modulation of the total yield obtained by numerically integrating the expression for $|c_E|^2$ over energy. The vertical black dotted line marks the revival time t_r . The parameters for the Bixon-Jortner main state are chosen to match the initial decay rate and the revival time of 1,3 trans-butadiene: $\Gamma_\alpha = 0.19$ and $t_r = 75$. The dipole transition matrix elements d_{01} , d_{0E} , and d_{1E} are all approximated as being equal to 1, and field parameters are $\mathcal{E}_1 = 0.01$, $\mathcal{E}_2 = 5.3 \times 10^{-4}$ and a total pulse duration $\tau = 150$; with all values given in atomic units

estimate of 1 for the matrix elements d_{01} , d_{0E} , and d_{1E} . We can choose the field strength $\mathcal{E}_1$ of the ω laser freely, ensuring that the fields remain within the weak field limit, and we then choose the field strength $\mathcal{E}_2$ of the 2ω beam to maximise the modulation depth of the system in the absence of revivals. At a total pulse length of $\tau = 150$ a.u. (≈ 10 laser cycles for the ω laser), this system obeys all of the conditions (4.18). The behaviour of the system is illustrated in figure 4.2. Prior to t_r , the modulation depth approaches the Auger-type large time limit of 1, and a steady and substantial decrease in the modulation depth beginning shortly after t_r therefore provides a clear signature of the revival. The slight delay following t_r before the effect on the modulation becomes clear is due to the fact that the revival does not instantaneously change the intermediate state coefficient. Its effect on c_1 instead grows to saturation over a timescale $2\Gamma_\alpha^{-1}$, and it is over this same timescale that the gradient of $\mathcal{M}$ changes. It is also apparent from this figure that the resonant part of $|c_E|^2$ adequately represents the total yield behaviour in this case. It is worth noting at this stage that an initial decrease of the modulation depth is only guaranteed if its value prior to revivals is maximal — if the modulation depth is substantially below 1 at t_r then it is possible that it initially increases instead, depending on the value of the revival phase factor $e^{-i\delta_0 t_r}$, which determines the phase of the revival contributions in equations (4.13 - 4.15).

Figure 4.3 provides a further illustration of the way in which the values of $\Gamma_\alpha t_r$ and

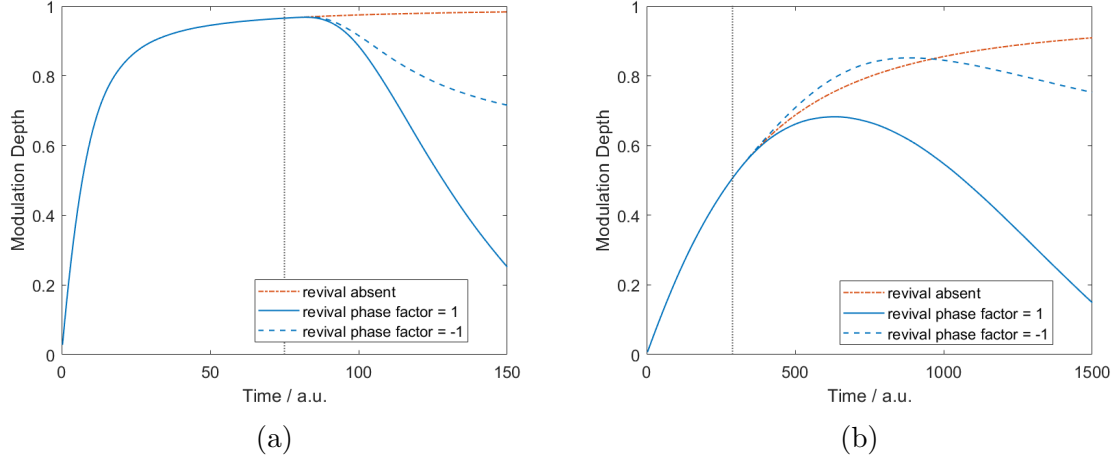


Figure 4.3: An illustration of how revivals affect the modulation depth with Bixon-Jortner quasicontinuum parameters derived from (a) $3a_g$ -ionised transbutadiene [89] and (b) $6a$ -ionised isopropanol [17] molecules. The values of Γ_α , t_r and $\frac{1}{2}\Gamma_\alpha t_r$ are respectively: (a) 0.19, 75 and $7.1 \gg 1$; (b) 4.8×10^{-3} , 290 and $0.70 < 1$. The dipole transition matrix elements in both cases are all taken to be 1, and in case (b) only one revival is assumed to occur. The laser fields are chosen separately for these two cases to ensure that the conditions (4.18) are fulfilled for both and the large-time limit modulation depth would approach 1 in the absence of revivals: (a) $\mathcal{E}_1 = 0.01$ and $\mathcal{E}_2 = 5.3 \times 10^{-4}$, and (b) $\mathcal{E}_1 = 0.001$ and $\mathcal{E}_2 = 2.1 \times 10^{-4}$. t_r is marked on both plots by a vertical black dotted line.

the revival phase factor influence how revivals are reflected in the modulation depth. It can be seen that for $\frac{1}{2}\Gamma_\alpha t_r \gg 1$, the modulation depth is close to the large-time limit value of the Auger-type system at t_r , and begins to decline shortly afterwards; whereas in the case where $\frac{1}{2}\Gamma_\alpha t_r < 1$, the effect of revivals only clearly manifests when the time t is several times greater than t_r . In the latter case, revivals after the first have again been neglected.

It is also clear that the phase factor influences the strength of revivals, especially in the case where $\frac{1}{2}\Gamma_\alpha t_r < 1$. While the revivals do cause the modulation to fall below the Auger-type system large-time limit value of 1 in all these cases, this effect is comparatively weak if $\frac{1}{2}\Gamma_\alpha t_r < 1$ for certain values of the revival phase factor. With this Bixon-Jortner quasicontinuum, the phase factor being 1 corresponds to the case where the revival contribution to c_1 is approximately π out of phase with the Auger-type contribution, while a value of -1 means that the two contributions have approximately the same phase.

4.1.4 Mechanism for Revival Interferometry

A qualitative understanding of the behaviour of equation (4.15) can be gained from considering equation (4.5) from which it is derived. This can be re-written as

$$c_E = \left[-i \int_0^t dt' e^{-i(E_0 - E + 2\omega)t'} V_{E0} c_0(t') \right] e^{-i\phi} + \left[-i \int_0^t dt' e^{-i(E_0 - E + 2\omega)t'} V_{E1} c_1(t') \right] \quad (4.19)$$

$$= c_E^0 e^{-i\phi} + c_E^1. \quad (4.20)$$

If we consider sinusoidal modulation of c_E in the Auger case, where either $\Gamma_\alpha \gg 4|V_{01}V_{1E}|/|V_{0E}|$ or $1 \gg 2\pi|V_{0E}V_{1E}|/|V_{01}|$, then the dependence of $s_\pm$ on ϕ is weak. This means that c_0 also has only weak dependence on ϕ , while c_1 varies with ϕ approximately as β_{10} . The modulation of β_{10} with ϕ is simply sinusoidal, and the modulation depth is maximal where $V_{10} = \Gamma_{10}/2$. This modulation behaviour has the exact same form as the Auger-type modulation behaviour for c_E in equation (4.16) if the initial decay rate Γ_α in that expression is replaced by Γ_1^i . If $\Gamma_\alpha \gg \Gamma_1^i$ then the parameters for which modulation of c_E is large prior to revivals will not coincide with those for which the modulation of c_1 is significant, so the variation of c_1 with ϕ can also be assumed to be weak.

Neglecting this weak ϕ dependence of c_0 and c_1 , it can be seen that the modulation of c_E arises in a very simple way from the interference between the part of c_E corresponding to the transition from the ground state $|0\rangle$ and the part corresponding to the transition from the Bixon-Jortner main state $|1\rangle$, with the relative phase of the contributions controlled by ϕ . It can be shown that for $\frac{1}{2}\Gamma_\alpha\tau \gg 1$, in the absence of revivals, the modulation depth at τ is approximately the same as in the large-time limit and the relative amplitudes of the c_E^0 and c_E^1 parts of equation (4.20) are therefore constant. This can be understood by considering the value of c_1 as being controlled by the balance between excitation from state $|0\rangle$ into state $|1\rangle$, and transitions from state $|1\rangle$ into the continuum $|E\rangle$ and quasicontinuum $|m\rangle$. c_1/c_0 will therefore approach a constant value for which these two rates are equal; this is given by $c_1 \approx c_0\beta_{10}/(\Gamma_1^i/2 + \Gamma_\alpha/2)$. As c_0 and c_1 determine the rate of change of the integrals c_E^0 and c_E^1 respectively, these two integrals will also approach proportionality, and the modulation of $|c_E|^2$ will be determined by the ratio of their absolute values. When the first revival occurs at t_r , the coefficient c_1 is rapidly changed, altering the ratio of c_1 to c_0 . This will in turn cause the ratio of c_E^0 and c_E^1 to shift. As this ratio determines the modulation of $|c_E|^2$, the revival will initially lead to a steady change in the modulation depth. Figure 4.4 illustrates this behaviour: at t_r , c_1 changes rapidly and, in this case, approaches approximately -1 times its previous value. This significantly alters the rate of change of $|c_E^1|$, while $|c_E^0|$ continues to increase at essentially the same rate as prior to the revival. The ratio of these two contributions therefore shifts,

leading to the change in modulation depth shown in figure 4.2.

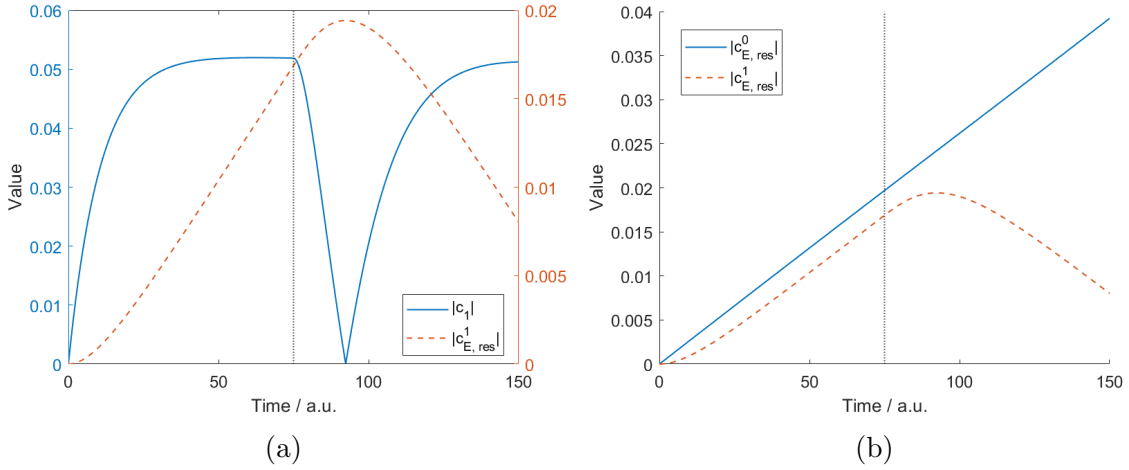


Figure 4.4: (a) Illustrative example of how the changes in the value of c_1 (solid blue) impact the behaviour of c_E^1 (dashed orange). The plot shows the absolute values of both quantities. The value of c_1 very nearly passes through zero at a time of 92 a.u., and its phase subsequently changes by approximately π . (b) Comparison of the behaviour of the c_E^0 (solid blue) and c_E^1 (dashed orange) contributions to the resonant part of c_E in equation (4.19). These plots correspond to the system shown in figure 4.2, and the revival time is marked by the vertical black dotted line at 75 a.u.

The full qualitative explanation of the quantum revival interferometry behaviour is therefore as follows: the two ionisation paths shown in diagram 4.1 interfere with each other, and the relative phase of the two contributions ranges from 0 to 2π as the phase offset ϕ of the 2ω beam is varied. In the Auger-type system (that is, one in which the intermediate decays into a continuum), the relative contribution to the continuum occupation from the two pathways reaches a steady value, and the modulation depth is determined by this relative amplitude. In the Bixon-Jortner case, however, this is disrupted after t_r by the revival of the Bixon-Jortner main state which affects primarily the two-photon ionisation pathway, and the change in relative amplitude of the contributions from the two pathways leads to a change in modulation depth. We have therefore shown and explained the existence of an interferometric signature of the revival in the form of an abrupt change in the behaviour of the modulation depth.

In a real system, the precise and analytically solvable behaviour seen here would not occur, however equation (4.19) applies generally for any form of intermediate state, making no reference to the specific form of the quasicontinuum or revivals. Any revival behaviour of the intermediate state $|1\rangle$ would manifest as a sharp change in the coefficient c_1 , changing the contribution to the integral c_E^1 and therefore altering the modulation depth from the case in which revivals were absent. In order for this change to be detected, however, it must be the case that the behaviour of the system prior to revivals is well-understood so that a deviation from expected modulation behaviour can be observed. This will be the case if the intermediate state initially displays exponential decay with

an at least approximately constant decay rate Γ prior to t_r . In this case, so long as the conditions (4.18) are met with Γ_α replaced by Γ , the revivals should be able to be observed through the deviation from the projected Auger-type behaviour after t_r . If it is additionally the case that $\frac{1}{2}\Gamma t_r \gg 1$, the modulation prior to t_r should approach an approximately constant value before rapidly deviating from this value after t_r , providing the clearest possible signature of revivals. It should be noted that while a change in the modulation depth under these circumstances will definitely be observed if and when a revival takes place, it is not in itself sufficient to prove that such a revival has occurred — for instance, if the intermediate state ceased to decay after some period of time but without any substantial repopulation then this could also impact the modulation depth.

A group of systems of broad significance which can display this sort of revival behaviour is the set of molecules which have undergone inner-valence ionisation and are left in a state just below the double ionisation potential. Examples of molecules which display revivals include the previously mentioned $3a_g$ -ionised trans-butadiene [89] and $6a$ -ionised isopropanol [17]. These types of systems typically show signs of breakdown of the molecular orbital picture [1], and the state produced by removing an electron from an inner valence orbital is therefore not a molecular eigenstate, but is instead coupled into an array of states nearby in energy. The system lacks the energy required to undergo further ionisation, however, and as a result it is possible that after some amount of time has passed there is again a substantial likelihood of finding the system in its original state. The technique described in this paper provides a potential avenue for observing such revivals.

4.1.5 Measurement Scheme

The analytical discussion up to this point has assumed a pulse which rises instantaneously to a constant value at time zero and subsequently remains constant at this level. It is useful to observe that as the system being modelled contains no autoionising states, further ionisation will stop immediately once the pulse is turned off. This therefore indicates the ideal experimental implementation which would retrieve exactly the form presented in figure 4.3: the system interacts with a pair of $\omega/2\omega$ pulses with fixed relative phase ϕ which both follow the same rectangular envelope of length t , and the final ionisation yield is measured. This process is repeated for a series of values of ϕ in the range $0 - 2\pi$, and the modulation depth of the ionisation yield with ϕ at pulse length t is thus obtained. Assuming that the pulse contains sufficiently many field cycles that carrier envelope phase effects can be neglected, this corresponds exactly to the modulation depth at time t in figure 4.3. To retrieve the full modulation behaviour as a function of time, all that would then be needed would be to repeat the process with a series of rectangular pulses of varying lengths.

The ideal of a rectangular pulse is in practice not currently achievable on the few-

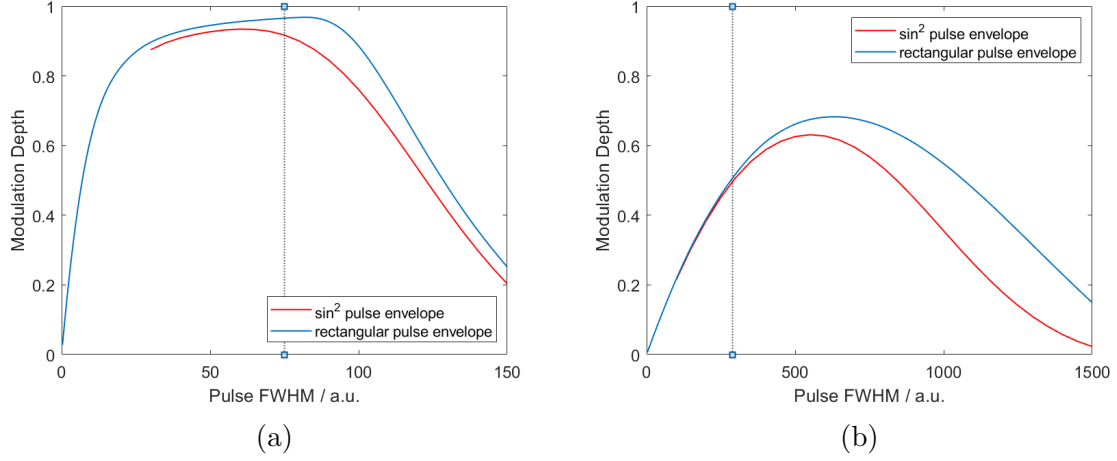


Figure 4.5: An illustration of how the modulation depth behaviour differs between the cases of a pulse with a rectangular envelope and a pulse with a sine squared envelope revivals for systems with Bixon-Jortner quasicontinuum parameters derived from (a) $3a_g$ -ionised transbutadiene and (b) $6a$ -ionised isopropanol molecules, as in figure 4.3. All other system parameters are identical to this previous case, and the rectangular pulse is modelled analytically as before and presented again here for ease of comparison.

femtosecond timescale that we suppose here. Nonetheless, our numerical calculations suggest that this approach is moderately robust to the use of a non-rectangular pulse. We numerically obtain the modulation behaviour of the transbutadiene and isopropanol model systems previously presented in figure 4.3, now under the action of an attosecond pulse with a more realistic sine squared envelope function at various pulse lengths. The outcome of this calculation is presented in Figure 4.5, and the new results can be seen to be very similar in both systems to the analytically-modelled rectangular pulse case. The decline of the modulation depth starts to take effect for a sine squared pulse of FWHM slightly less than the corresponding length value of the rectangular pulse, perhaps due to revival effects associated with the leading pulse tail; however, the pulse length at which the modulation depth deviates from its approach to a constant value can nonetheless be clearly associated with the revival timescale. As was the case for the rectangular pulse, for the transbutadiene system with $\frac{1}{2}\Gamma_\alpha t_r \gg 1$ the effect on the modulation depth becomes clear when the pulse FWHM exceeds the revival timescale even slightly, whereas for the isopropanol case where $\frac{1}{2}\Gamma_\alpha t_r < 1$ the pulse FWHM must be significantly larger than the revival timescale before the revival effects become apparent. It is worth noting that in the isopropanol model case, our numerical simulations do not neglect revivals after the first as was done for the analytical model, however this appears to have little impact on the resulting modulation behaviour. The robustness of our results to variation in the pulse shape reinforces the viability of this technique as a practical measurement method.

4.1.6 Conclusions

To conclude, we have extended the theory of Auger interferometry to include systems with a bound intermediate state which decays into a quasicontinuum. We have shown that if the intermediate subsequently experiences revivals in its population then this will impact the observed modulation of the ionisation yield, and the signature of such revivals is a steady shift in this modulation beginning shortly after the revival time t_r . We have described the field parameters which should be used to generate a clear revival signature, and we have also illustrated that for realistic revival times and decay rates of the initial state, the effect of the revival is clearly visible. The ‘frustrated Auger’ systems for which the approach that we describe is most clearly applicable have been a topic of substantial recent experimental interest [17], and this work may provide a new avenue for experimental observation of the revivals that are expected to be present in such systems. Modern free electron laser facilities such as FERMI@Elettra are capable of the precision control of the relative phase ϕ of the two lasers required [97] for this approach.

Numerical Results

5.1 Breathing Ions

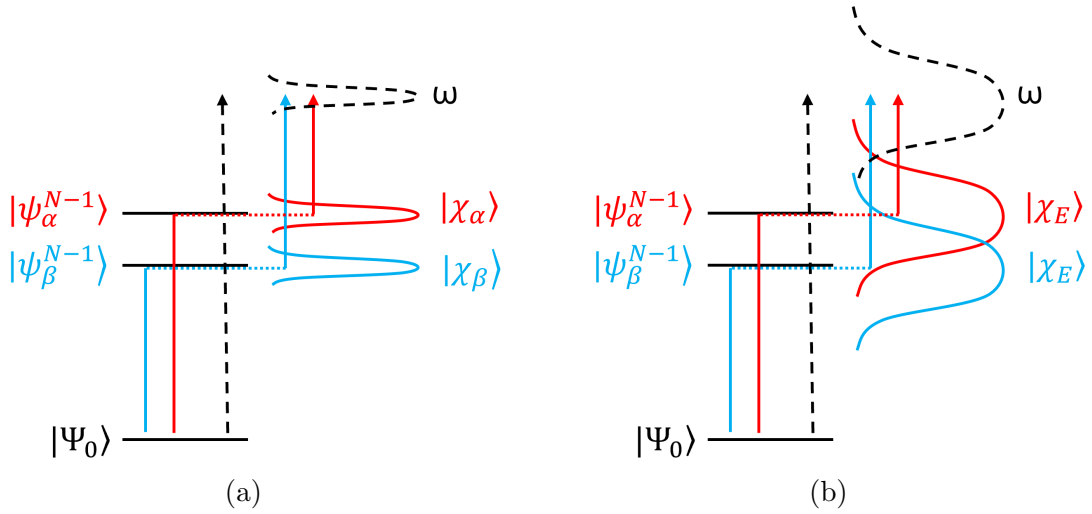


Figure 5.1: A photon of energy ω ionises the neutral system $|\Psi_0\rangle$, with the energy of the continuum electron determined by energy conservation. In the case of a narrow-bandwidth pulse, (a), the continuum electrons $|\chi\rangle$ associated with each ionic state $|\Psi_{\alpha,\beta}^{N-1}\rangle$ have narrowly defined energy ranges which do not overlap. In the case of a broad pulse, (b), both ionic states can be associated with an overlapping range of continuum states, allowing ionic coherence.

The ionisation of an atomic or molecular system by a laser pulse in the XUV frequency range will typically produce a series of ionic states. Each ionic state will be associated with certain states of the outgoing ionised electron, with the range of these states dictated by both symmetry considerations and the conservation of energy. In particular, if the pulse has a long duration - and by extension, a narrow bandwidth - then the energy range of the associated ionised electron states will be small. This leads to ionic states which are populated incoherently after the ionised electron is lost from the system. In a simplified illustrative example of two ionic states, the wavefunction decomposes as

$$|\Psi^N\rangle = C_\alpha |\Psi_\alpha^{N-1}\rangle |\chi_\alpha\rangle + C_\beta |\Psi_\beta^{N-1}\rangle |\chi_\beta\rangle \quad (5.1)$$

where the states $|\chi_{\alpha,\beta}\rangle$ represent continuum electron states and $|\Psi_{\alpha,\beta}^{N-1}\rangle$ are the ionic states. In contrast, if the pulse is sufficiently short and the energy width correspondingly large compared to the ionic state spacing then the range of outgoing electron energies with which the separate ionic states can be associated with will overlap.

$$|\Psi^N\rangle = \int dE \left(C_{\alpha}^E |\Psi_{\alpha}^{N-1}\rangle + C_{\beta}^E |\Psi_{\beta}^{N-1}\rangle \right) |\chi_E\rangle \quad (5.2)$$

This is shown schematically in figure 5.1. As it is possible for different ionic states in this second case to be associated with the same outgoing electron, some coherence will remain between the ionic states even after the ionised electron departs the system. This second scheme requires the pulse width to be at least on a similar order to the ionic state separation. Ionic coherence is therefore most easily observed in systems with multiple closely-spaced ionic states which can be accessed by a laser pulse.

The process of electronic shake-up [98] produces an often fairly densely clustered series of satellites of partial one-hole character, thus forming exactly the type of system in which ionic coherence can be induced. In the case of atomic ionisation by an attosecond pulse, the dynamics resulting from the coherent population of the shake-up state series are predicted to be dramatically different to the case of ionisation by a monochromatic pulse. The main state is of primarily one-hole character, and the electron density is therefore highly localised near the atomic centre; however the states in the shake-up series can correspond to excited configurations which are much more diffuse. We predict that the electron wavepacket created by coherent population of such a series of states will therefore exhibit attosecond oscillations characterised by a radial expansion and contraction of the electron density. We term these dynamics ‘breathing ions’. Similarly to the case of hole migration in molecules via the frustrated Auger process [22], this can be interpreted as an Auger transition which is energy-forbidden, forcing the departing electron to return to the system. A crucial difference, however, is that in molecular systems any coherences are rapidly damped by nuclear motion over a period of at most a few tens of femtoseconds [17, 21, 23]. This is of course not a factor in the atomic case, and this oscillatory quantum beating can therefore be expected to persist until the system relaxes via photon emission - a process with a typical timescale on the order of nanoseconds for the relevant excitations [99, 100]. This makes these oscillations extremely long-lived by comparison to the typical timescales of electron motion.

As an ideal candidate system for the measurement of such oscillations, we choose the argon atom. This system is known to have a strong satellite spectrum for the 3s hole, with only a little over 50% of the intensity in the main 3s line, and with numerous discernible satellites with strength of as high as 20% of that of the main line [101, 102]. The satellite spectrum covers an energy range of 14.1 eV from the 3s main state at 29.2eV up to the double ionisation potential [103]. A pulse of duration 300-400 attoseconds is sufficient to

span most of this range, and this is well within the limits of practically accessible laser pulses at XUV and soft X-ray frequencies [15, 19, 18]. Furthermore, as a relatively light atom, argon is reasonably tractable to numerical calculation.

The main numerical calculation is to be performed via the B-spline ADC method [45, 46, 47], however this approach only has the capacity to represent the ionic states at the ADC(2)x level of approximation. This is sufficient to accurately represent states of primarily one-hole character, but here the two-hole one-particle-dominated satellites are precisely the states which drive the dynamics of interest, and these are only represented through the first order of perturbation theory. In order to overcome this problem, the ionic states are first calculated at the ADC(2,2) level of approximation [48], allowing consistent representation of the satellite states through the second order of perturbation theory and placing them on the same level as the 1h-dominated main state.

In order to facilitate the translation of the ionic states from the ADC(2,2) representation to the B-spline ADC representation, the same basis of Hartree-Fock orbitals is used as a starting point for the construction of the ADC Hamiltonian in both schemes. This basis is constructed using the MOLCAS [65] software package, which solves the Hartree-Fock equations for a basis of Gaussian-type orbitals (GTOs). For the ADC(2,2) calculation, the GTO basis is imported directly, whereas for the B-spline calculation the basis is projected onto the basis of B-splines as described in section 2.3.2 in order to form the restricted correlation space. The necessity of using an equivalent basis between the two ADC formulations means that the standard step of performing further Hartree-Fock iterations within the B-spline basis is no longer possible. Any further iterations can allow arbitrary rotation of the Hartree-Fock states within degenerate subspaces, thus breaking the link to the projected basis and making translation between the ADC(2,2) and B-spline ADC representations substantially more complicated. The change in the Hartree-Fock states during such iterations is minimal especially in the atomic case so long as the B-spline basis is sufficient to closely represent the projected orbitals, so this restriction does not pose a serious problem.

During the construction of the RCS-ADC Hamiltonian, the states containing a particle in the ionisation space are represented as a combination of an ionic state and a particle in an IS orbital. In the typical RCS B-spline ADC construction, these ionic states are built by diagonalising the ionic ADC secular matrix built within the space of RCS orbitals. Here, the states are instead imported from the preceding ADC(2,2) calculation. This is possible because the ADC(2,2) calculation is performed in the basis of Hartree-Fock orbitals from which the RCS is constructed. The ADC(2,2) states contain some 3h2p component which is lost upon importing them into the B-spline ADC representation, since this only includes 1h and 2h1p configurations. The ADC(2,2) ionic states which are retained within the calculation are restricted to those with at most 50% 3h2p contribution, and in practice the 3h2p fraction is substantially smaller than this after the states with negligible 1h

character are also removed. Nonetheless, the retained ADC(2,2) states typically have around 10% 3h2p character which is lost upon the reduction of the configuration basis, so they are no longer orthonormal. A symmetric orthonormalisation process is therefore applied to restore this property while ensuring minimal changes in the states themselves.

Within the numerical calculation, the symmetry is treated explicitly only within the D_{2h} symmetry group, as the numerical codes do not implement the full continuous spherical symmetry of the atomic system. Nonetheless, the ionic states are selected based on their pole strength, and the satellites must share the same symmetry as the main state, so the symmetry of the ionic systems can be assigned an atomic symmetry label in the standard way. The orientation of the laser pulse dictates one of the axes of the D_{2h} symmetry system, but the axis directions orthogonal to the pulse are arbitrary.

5.1.1 Preliminary Calculations

As the characteristic ‘breathing’ behaviour is expected to be associated with the transfer of an electron into a nearly-ionised diffuse orbital, it is necessary for the ionic states within the numerical calculation to be able to extend to large radii. Previous experimental measurement of the valence excitation spectrum of Argon, in combination with numerical modelling, means that the satellites of the main 3s and 3p lines are known along with their assignment to particular electronic configurations [101, 102]. Such an analysis suggests that the strongest satellites of the 3s line take the form of a series of configurations $\{\text{Ne}\}3s^23p^4nd$ with $n = 3, 4, 5$, but continuing with diminishing intensity through increasing n . There is an additional weaker satellite of the form $\{\text{Ne}\}3s^23p^44s$. The primary satellite lines of the 3p orbital are weaker, but correspond to configurations of the form $\{\text{Ne}\}3s^23p^44p$.

The configurations involving higher-lying orbitals can be expected to be increasingly Rydberg-like and increasingly diffuse. As a rough estimate, consideration of the 4s, 4p, and 5d hydrogenic orbitals for a central charge $Z = 2$ indicates that the orbital amplitude might be expected to be non-negligible up to a radius of 30-35 au, requiring a basis that likewise extends to at least this distance. For the modelling of such diffuse orbitals in a Gaussian basis with radial component $r^l \exp(-\alpha r^2)$, we use the form of the Gaussian exponents α optimised for modelling Rydberg-like orbitals by Kaufmann *et al.* [104]. The exponents here take the form

$$\alpha = \left(\frac{Z}{2n}\right)^2 \left(\frac{1}{a_l k + b_l}\right)^2 \quad (5.3)$$

where l is the angular momentum of the orbital to be modelled, Z is the effective charge, the index n corresponds to the principal quantum number of the Rydberg orbital and runs from $l + 1$ to infinity, and for each n the value of k runs over $k = n - 1, n$. The

parameters a_l and b_l are optimised values for each l .

The basis we choose therefore consists of a core part plus the Rydberg-like augmentation. For the core basis, we choose the ANO-RCC-VQZP Gaussian set [105], which is the smallest basis set to achieve essentially converged energies and pole strengths when compared to other non-diffuse bases and therefore leaves the greatest room for further augmentation. For the Rydberg-like diffuse basis part, we consider bases with some number of Gaussians defined by equation (5.3) with increasing α . We use an effective charge $Z = 1.5$ for the construction of this part of the basis. This choice is somewhat arbitrary, although it can be thought to correspond to partial shielding of the outermost electrons. In practice, this is chosen because it allows a smaller number of basis functions to extend to a larger radius as compared to $Z = 2$, while providing a better representation of higher-lying states than the still more diffuse $Z = 1$ case. We considered augmentations of the form 12s12p12d10f3g and 15s15p15d13f5g, where this notation indicates the number of radial Gaussians in the set defined by equation (5.3) used for each angular momentum value.

The Hartree-Fock equation is solved within this full basis consisting of the ANO-RCC-VQZP GTO set augmented with the Rydberg-like continuum augmentation using the MOLCAS [65] software package. The resulting HF orbitals are then used as a basis for the ADC(2,2) calculation. Within this calculation, the 1s and 2s orbitals are frozen, and the ADC(2,2) secular matrix is constructed and diagonalised using a filter diagonalisation method.

Separately, the dicationic ADC secular matrix is also constructed and diagonalised at the ADC(2)x level of approximation in a manner consistent with the ADC(2,2) calculation [106, 107], and this is used to determine the value of the double ionisation potential.

A comparison of the 12s... and 15s... augmentations is seen in figure 5.2.

It can be seen that the 12s... augmentation is already fairly well converged, with the exception of a small region just above 1.6 au where multiples of lines in the 15s... basis are collapsed together into single lines in the smaller set. The difference between the 15s... and the 12s... augmentation can be associated with the series of $\{\text{Ne}\}3s^23p^4nd$ satellites, which converge on a threshold at approximately 1.64 au [101]. This series involves increasingly diffuse Rydberg-like orbitals, which require a correspondingly diffuse basis to model them. Such a series can in principle become arbitrarily diffuse, so perfection is never going to be achieved here, and we judge that the 12s... basis is sufficient as it captures all lines of significant strength and correctly represents the states below the DIP, while having almost half the computational memory requirements as compared to the 15s... basis.

By comparing to previous experimentally and numerically observed lines [101, 103], the first three 3s satellite lines in figure 5.2 can be assigned to $\{\text{Ne}\}3s^23p^44s$, $\{\text{Ne}\}3s^23p^43d$, and $\{\text{Ne}\}3s^23p^44d$ configurations. Above this, making a clear assignment becomes more difficult, although it can be expected that the $\{\text{Ne}\}3s^23p^45d$ configuration contributes

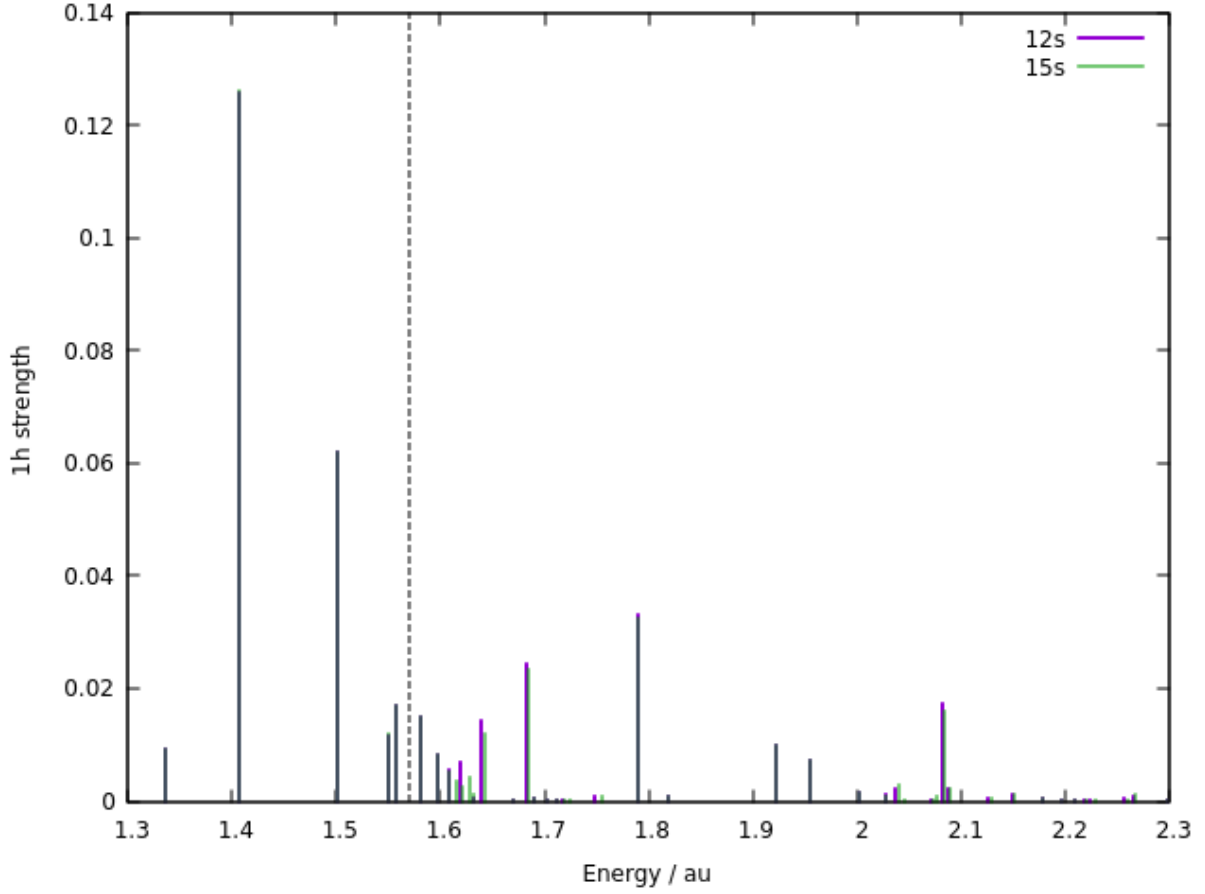


Figure 5.2: the 3s satellite spectrum (excluding the main line with strength 0.59 at 1.07 au) of singly-ionised Ar calculated at the ADC(2,2) level. The purple lines shows the states calculated after building the ADC Hamiltonian starting from an ANO-RCC-VQZP gaussian basis set with 12s12p12d10f2g Rydberg-like augmentation [104], while the green lines use a larger 15s15p15d13f5g Rydberg-like augmentation. The overlap of the two lines is grey, and it can be seen that these two bases are very similar with the exception of a small region just above the DIP (dashed line at 1.572 au).

somewhat to the pair of lines just below the DIP

5.1.2 Neutral Argon Calculation

In order to carry out the full numerical calculation, the chosen set of GTO Hartree-Fock orbitals must be translated to the B-spline basis. The B-spline basis used has a knot spacing of 0.25 au in the inner region up to 2 au, rising to a 0.5 au spacing between 2 au and 8 au, and rising again to a spacing of 1.1 au stretching out to a maximum radius R_{max} of 122 au. The maximum angular momentum $l_{max} = 5$. This basis was found to be sufficient to represent the 12s... set of GTO-based HF orbitals very accurately, with a maximum error of 0.0003 in the projection norms, and with most such errors on the order of 10^{-7} - 10^{-8} . The maximum continuum electron energy representable to good accuracy within this basis is determined from the maximum knot spacing as 1.8 au. The complex absorbing potential is taken to begin at a radius of 91 au, which is significantly outside

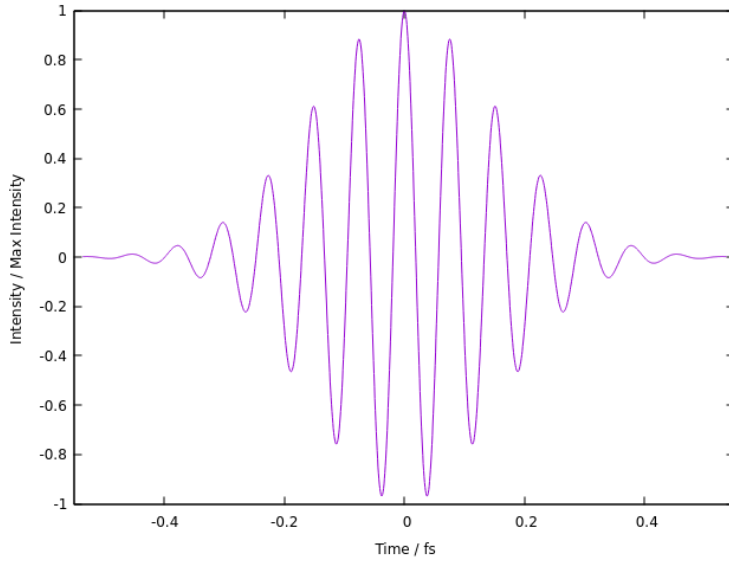


Figure 5.3: The pulse considered for exciting the breathing dynamics. This pulse has a central energy of 2 au and a gaussian envelope of FWHM 0.358 fs, giving a corresponding energy FWHM of 0.375 au

the expected maximum radius of even the most diffuse part of the bound system, and the CAP has a scaling parameter of 0.004.

Following the projection of the GTO orbitals onto the B-spline basis set, the generation of the ionisation space and the calculation of the one- and two-electron integrals proceeds by the usual method, with the exception that no further HF iterations are performed in order to preserve the link between the RCS orbitals and the initial GTO set. During the ADC calculation, the 1s and 2s orbitals are frozen. A cutoff is imposed on the imported ADC(2,2) ionic states such that only those states with 1h character greater than 1% are used in the construction of the IS block of the Hamiltonian. This retains 98% of the 3s 1h strength while ensuring that the final RCS-ADC Hamiltonian and dipole matrices do not significantly exceed 1TB in size and therefore remain within the capability of the available high-performance computing resources.

The primary system of interest is the 3s main state and its satellite states. To coherently excite this series, we considered initially two different pulses: a pulse of central energy 2 au and duration FWHM 0.358 fs in the field amplitude (energy FWHM 0.375 au), and a pulse of central energy 1.5 au and duration FWHM 0.340 fs (energy FWHM 0.394 au). These pulses are well within the experimentally accessible range [108, 15]. These are sufficient to span the range between the 3s main state and the lower satellites, and to span the 3s and 3p satellite spectra. The gap between the 3s main line and the DIP falls within the 20%-20% range of the pulse energy spectrum, so some coherence would be expected here as well. The carrier envelope phase (CEP) of the pulse considered here is such that the pulse peak aligns with the envelope maximum. The CEP may have some influence on the results, but the pulse contains sufficiently many cycles that this impact is expected to be comparatively small. The pulse peak intensity was chosen as $10^{13}\text{W}/\text{cm}^2$, which is expected to be well within the weak-field regime insofar as that the contribution of multiphoton and non-resonant transitions is small. This matches the intensity recently

achieved for attosecond pulses of comparable duration in a laboratory setting [15]. The weak-field case is required as the B-spline ADC method is only able to model one continuum electron at a time. The system was propagated until the final state populations and the final purity of the density matrix reached a steady value. During the numerical propagation, the number of Krylov vectors used was 20, and the time step was 0.031 au during the action of the pulse, and 0.062 au during the field-free propagation - parameters for which the final results for the ionic density matrix were found to be converged with respect to further reduction of the time step or increase of the Krylov space dimension.

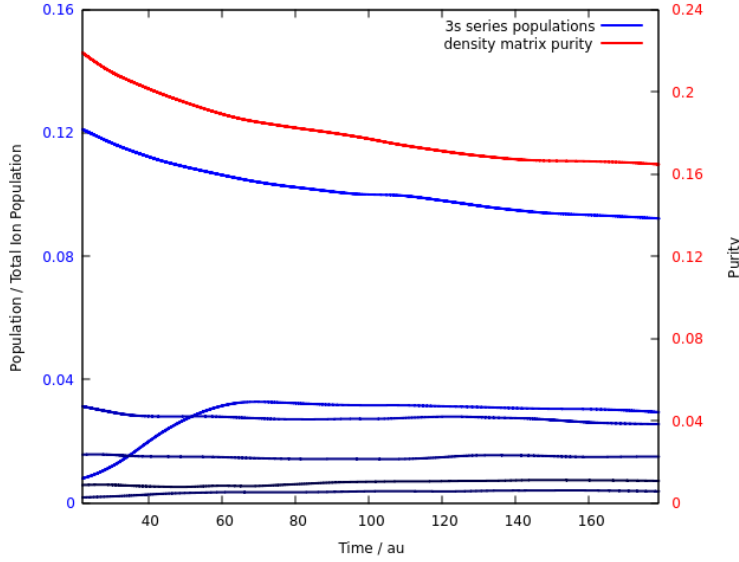


Figure 5.4: Blue: the variation of the calculated populations of the 3s main state and bound satellites with time. Red: the variation of the density matrix purity with time. The x axis gives the time relative to the pulse peak, and the figure shows the time region following the end of the pulse.

Figure 5.4 shows how the density matrix purity and the 3s bound state populations vary with time for the 2 au pulse. The purity declines steadily with time, only reaching a stable value approximately 160 au (3.9 fs) after the pulse peak. This decline is expected as the ionised electrons steadily cease interacting with the system and carry some of the coherence with them. The overall purity is fairly low primarily because of the lack of coherence between ionic states of different symmetries, and does not indicate a low level of coherence within the individual satellite spectra. The state populations mostly reach a stable value at around 60-100 au, although there are still some slight variations and the 3s main line population in particular continues to decline somewhat, only beginning to level out at 140 au. The variation in the populations can likewise be attributed to transitions due to interaction with the bath of ionised electrons which are yet to depart the system. At the end of the numerical propagation, the total probability of ionisation is calculated as 0.164%, and the probability of double ionisation which cannot be fully modelled by the numerical code is therefore negligible.

Comparing the two pulses, figure 5.5 shows the relative populations of the satellite series for the two pulses. It can be seen that the 2 au pulse has much greater populations in all satellites compared to the 1.5 au pulse. The following discussion will therefore focus on the results obtained for the 2 au pulse, as the coherent electron motion will be much

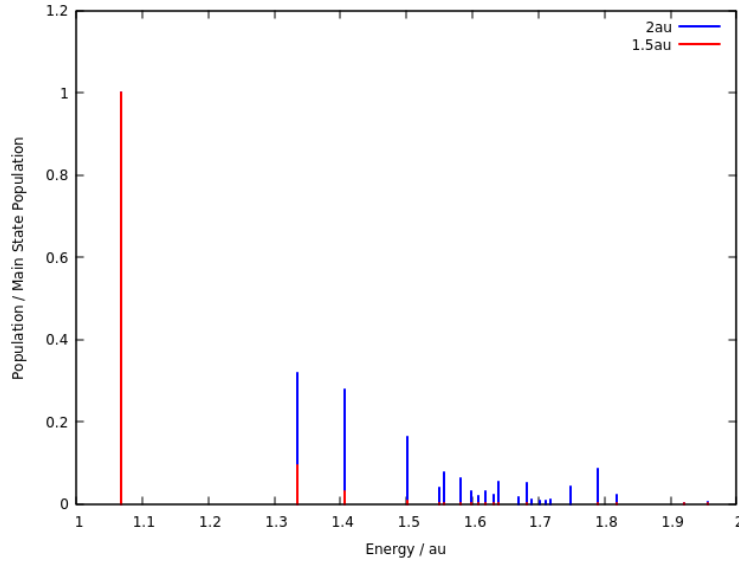


Figure 5.5: A comparison of the populations of the 3s satellite series for the 2 au pulse (blue) and the 1.5 au pulse (red), normalised such that the main state population is 1

stronger in this case.

As the expected oscillatory behaviour persists for timescales much larger than that of the initial ionising pulse, it is highly impractical to numerically propagate the system for the full duration. Once all populations and coherences have reached a stationary value, I switch to an analytical propagation of the density matrix of the ionic system [47] which can be easily extended to tens of femtoseconds beyond the end of the pulse at negligible computational cost. Within this analysis I neglect the contributions from ionic states above the DIP as these will undergo Auger decay on a comparatively fast timescale (on the order of femtoseconds [4]) and will therefore not contribute to the long-duration oscillations which otherwise characterise this type of system.

5.1.3 Results and Discussion

Ionic State Populations

Figure 5.6 shows the populations calculated for the 3s and 3p satellite spectra which are expected to be coherently populated by the pulse, running from the 3s main line at 1.07 au to just above the double ionisation potential where the $\{\text{Ne}\}3s^23p^4nd$ series of 3s satellites would be expected to converge. The 3p spectrum which is shown corresponds to the 3p state oriented along the pulse polarisation direction. The populations of the 3p states orthogonal to the polarisation axis (not shown) look similar, but with populations skewed slightly further towards the lower-energy satellites.

The system of primary interest is the 3s state and its satellites, which will all be populated with some level of coherence. When summed together, the 3s bound satellite series has a population almost 90% of that of the main line. The population is greater in the more tightly bound states, but the states close to the DIP still have not-insignificant occupation on the order of 5-10% of the main line.

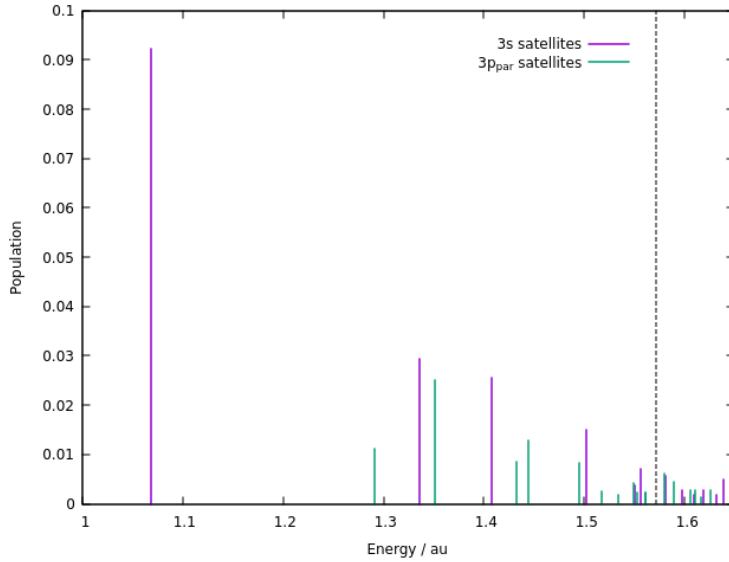


Figure 5.6: The populations of the coherently populated 3s main line and satellites (purple), and the 3p satellites along the polarisation axis of the pulse (green). The 3p main line at 0.58 au is not shown, however this state does not contribute to coherent oscillations. The black dashed line indicates the double ionisation potential.

The majority of the population of the modelled ionic system is in the 3p main state, which accounts for approximately 55% of the ionic population. Due to the energy gap between the 3p main state and its satellites, this state is not expected to participate in the coherent oscillations. Nonetheless, the 3p state does have significant population in its satellite series - summed together, the population in the bound part of the 3p satellite series is calculated to be almost 40% of the strength of the main line, and these satellites will be populated coherently. Therefore, this state series will be expected to participate in the radial breathing behaviour in some manner.

The large populations in the satellite series are ideal as this increases the part of the wavefunction at large radius, and with it the amplitude of the radial oscillations. These populations are a fairly strong function of the pulse energy: In the sudden ionisation limit of large pulse energies, the relative populations of the satellites will be expected to approach the corresponding 1h strengths [26, 109, 110], which are substantially more concentrated on the main state. For the 3s spectrum, this limiting case would have 59% of the 3s satellite series population in the main line, and for the 3p spectrum the corresponding number would be 94%. On the other hand, a preliminary calculation with a pulse central energy at 1.5 au also yielded much lower satellite populations, with 95.5% of the ionic population in the 3p main line and 3.4% in the 3s main line, with the remaining 1% almost entirely in the 3s satellites. The current pulse central energy of 2 au provides much better satellite populations than either of these two previous cases, however more testing could be done to further optimise this.

Ionic State Coherences

The calculated coherence strengths $T_{ij} = |\rho_{ij}|/\sqrt{\rho_{ii}\rho_{jj}}$ between the different states are shown in figure 5.7 for the 3s and 3p satellite spectrum up to and around the DIP. It can be seen that for the 3s spectrum the coherence is fairly strong within this region, with

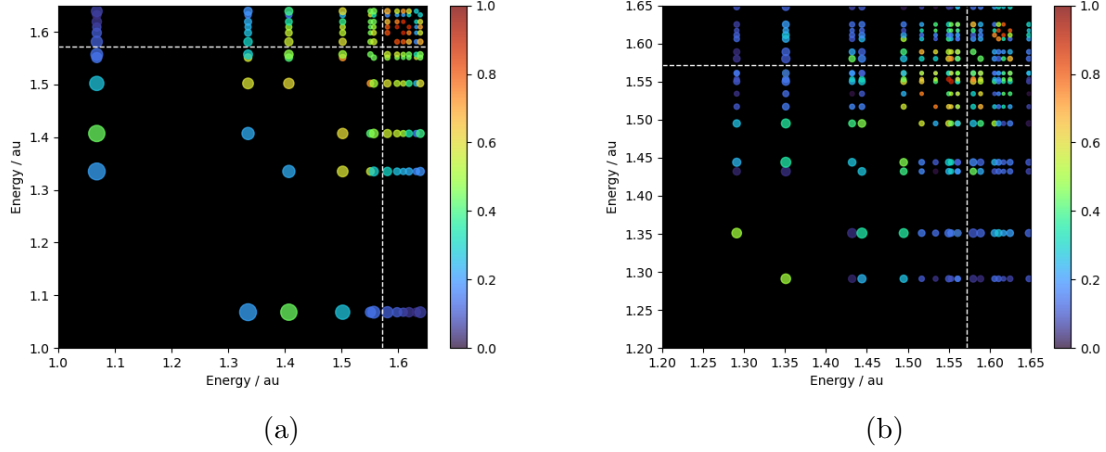


Figure 5.7: The coherence strength of the ionic states up to 1.65 au after the pulse of central energy 2 au for (a) the 3s satellite spectrum, and (b) the 3p satellite spectrum along the pulse axis. The 3p main line at 0.59 au with negligible coherence to any of the satellites is excluded from plot (b). The dashed line indicates the double ionisation potential. The coherence is given as a proportion of its maximum possible value. The size of each point on the plot is proportional to the geometric mean of the populations of the pair of ionic states $\sqrt{\rho_{ii}\rho_{jj}}$, indicating how significant that state pair is in terms of the overall coherence of the system.

most pairs of states having coherence strength in the range of 0.4 to 0.8, although the coherences with the main line are typically weaker. For the 3p satellites, the coherence to the main line (not shown) is negligible, and the values of the other coherences are more varied, although there is still substantial coherence within the spectrum overall. In both cases, the span of the band of satellites up to the DIP falls easily within the FWHM energy width of the pulse of 0.37 au, so it is likely that the coherences observed are close to their maximum possible values, with the potential exception of those involving the 3s main line. A preliminary calculation with a pulse of FWHM 1.05 au indicates that this is indeed the case, with the coherence strength between the main line and the satellites up to the DIP increasing to values in the range of 0.4-0.6, with the other coherences remaining largely unchanged. This however came at the cost of a factor of 3-4 reduction in satellite populations relative to the main line.

Coherences between the satellites of different symmetry are all either zero or negligible. For the 3p satellites oriented orthogonal to the laser field, the coherences to other spectra are all identically zero by symmetry. The coherences between the 3s spectrum and that for the 3p satellites parallel to the pulse polarisation axis is non-zero only once multiple transitions are allowed for. As the pulse considered is well within the weak-field case this means all coherences between the different symmetries are less than 0.01 and can also be neglected.

Radial Density Oscillations

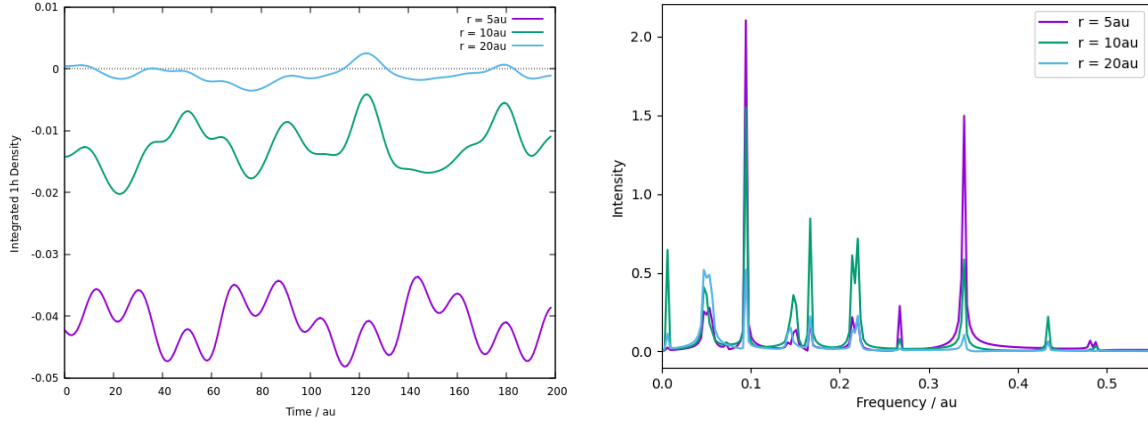


Figure 5.8: Left: the time variation of the total integrated 1h density above various radial thresholds r for the 3s state and its satellites. Right: The corresponding oscillation frequencies associated with the density above the given radial thresholds

The density matrix can be used to obtain the 1h density in terms of the natural charge orbitals as in equation (2.168). These are expressed in terms of the ADC intermediate states, however the composition of the intermediate states in terms of Hartree-Fock orbitals is stored and can be used to expand these natural charge orbitals instead in terms of HF orbitals where the wavefunction is known as a function of radial and angular coordinates. This therefore expresses the 1h density in terms of a set of orbitals with known populations and shapes, providing a full picture of where there is excess electron or hole density at any given time.

In particular, the quantity of interest in this work is the electron density at large radius. By integrating the hole density over all points above a certain radius, it is possible to quantify the variation with time of the diffuse part of the wavefunction. Furthermore, considering several different radial cutoffs gives insight into the different types of radial oscillations. This is illustrated in figure 5.8: the left panel shows the oscillations in time of the 1h density for the 3s satellite system above three different radii, while the right panel indicated the corresponding oscillation frequencies. The 1h density is given relative to the neutral: negative 1h density indicates that the probability of finding an electron in the region is increased following ionisation, and can therefore be associated with 2h1p states.

The first cutoff at a radius of 5 au lies slightly outside the region containing most of the electron density of the neutral, but still corresponds to relatively localised states. The third cutoff at 20 au, on the other hand, corresponds to highly diffuse oscillations. The integrated hole density above 5 au is consistently negative, indicating that the electron density in the region outside of the radius of the neutral system sees a clear increase in electron density following ionisation with this pulse. The 5 au radius line consists mostly

of two superimposed oscillations with well-defined frequencies of 0.34 au and 0.095 au, corresponding to oscillation periods of 18 au (0.45 fs) and 66 au (1.60 fs). The oscillation frequencies are respectively very close to the energy gaps between the main line and second ($\{\text{Ne}\}3s^23p^43d$) satellite, and the second and third ($\{\text{Ne}\}3s^23p^44d$) satellites in the 3s satellite spectrum (figure 5.6). Both of these correspond to relatively strong coherences in figure 5.7. At low radii, the density oscillations can therefore be understood to be dominated by regular oscillations involving only a small number of states. At larger radii, the behaviour is more complicated - the same frequencies corresponding to the motion of the electron in the inner region also contribute here, but in addition there are contributions involving yet more diffuse satellites, including the pair of states near the DIP which likely have $\{\text{Ne}\}3s^23p^45d$ character. Above 20 au, there is minimal excess electron density in comparison to the neutral, although there are still some weak oscillations.

The time offset of the beginning of the plots from the pulse is essentially arbitrary. It must be sufficient for the ionised electrons to have fully departed the vicinity of the bound system - a delay found to be on the order of 4 fs - but otherwise the nature of the oscillations is not expected to change for hundreds of femtoseconds following the pulse.

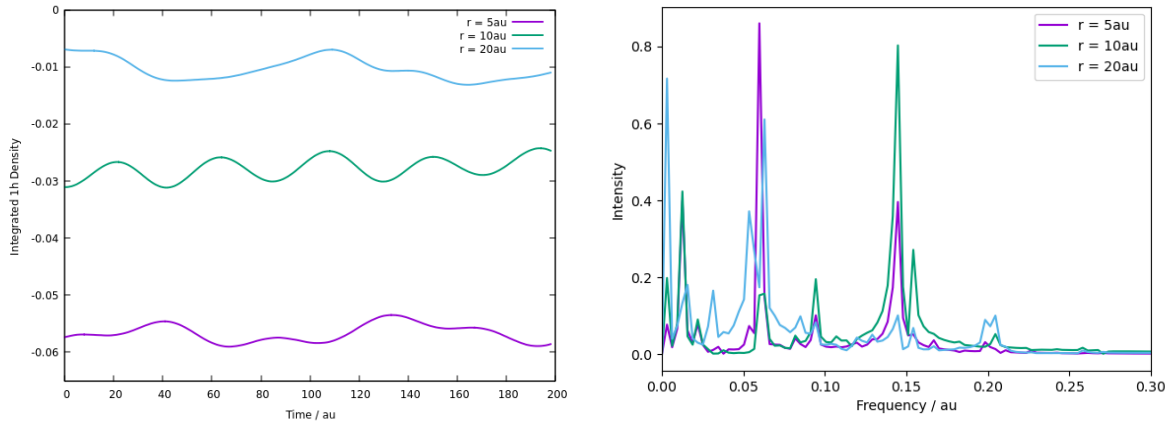


Figure 5.9: Left: the time variation of the total integrated 1h density above various radial thresholds r for the 3p state oriented along the polarisation axis of the pulse and its satellites. Right: The corresponding oscillation frequencies associated with each line in the plot on the left

Figure 5.9 shows the corresponding oscillations for the 3p satellite system. Unlike the 3s system, the oscillations of the 3p satellites are entirely decoupled from the 3p-hole main state, as the large energy gap to the main state prevents any coherence between it and the satellite spectrum. Despite the only very limited MO breakdown of the 3p hole state, the populations of the 3p satellites are calculated to be comparable to those of the 3s satellites for the pulse considered here. The oscillations here are comparatively weak, but they are clearly present: at small radii, the primary contribution is a slow-moving oscillation of period 100 au which likely corresponds to the oscillation between the first two satellites corresponding to configurations $\{\text{Ne}\}3s^23p^4(^3P)4p$ and $\{\text{Ne}\}3s^23p^4(^1D)4p$. The 10 au

radius line has one primary component of 0.14 au frequency, which can be assigned to the coherence between the first satellite and the third with configuration $\{\text{Ne}\}3s^23p^4(^3P)5p$. Above radii of 20 au, it is notable that the 3p 1h density retains significant magnitude, suggesting that the most diffuse oscillations are likely to result from the 3p satellite system and not the 3s.

For both the 3s and 3p spectra, it should be noted that the loss of the 3h2p component of the ADC(2,2) ionic states in the translation to the B-spline basis likely somewhat reduces the total probability to find the electron at large radius. This will not influence the oscillation frequencies, which are determined by the state energies, but might have significant influence the amplitude of the most diffuse oscillations.

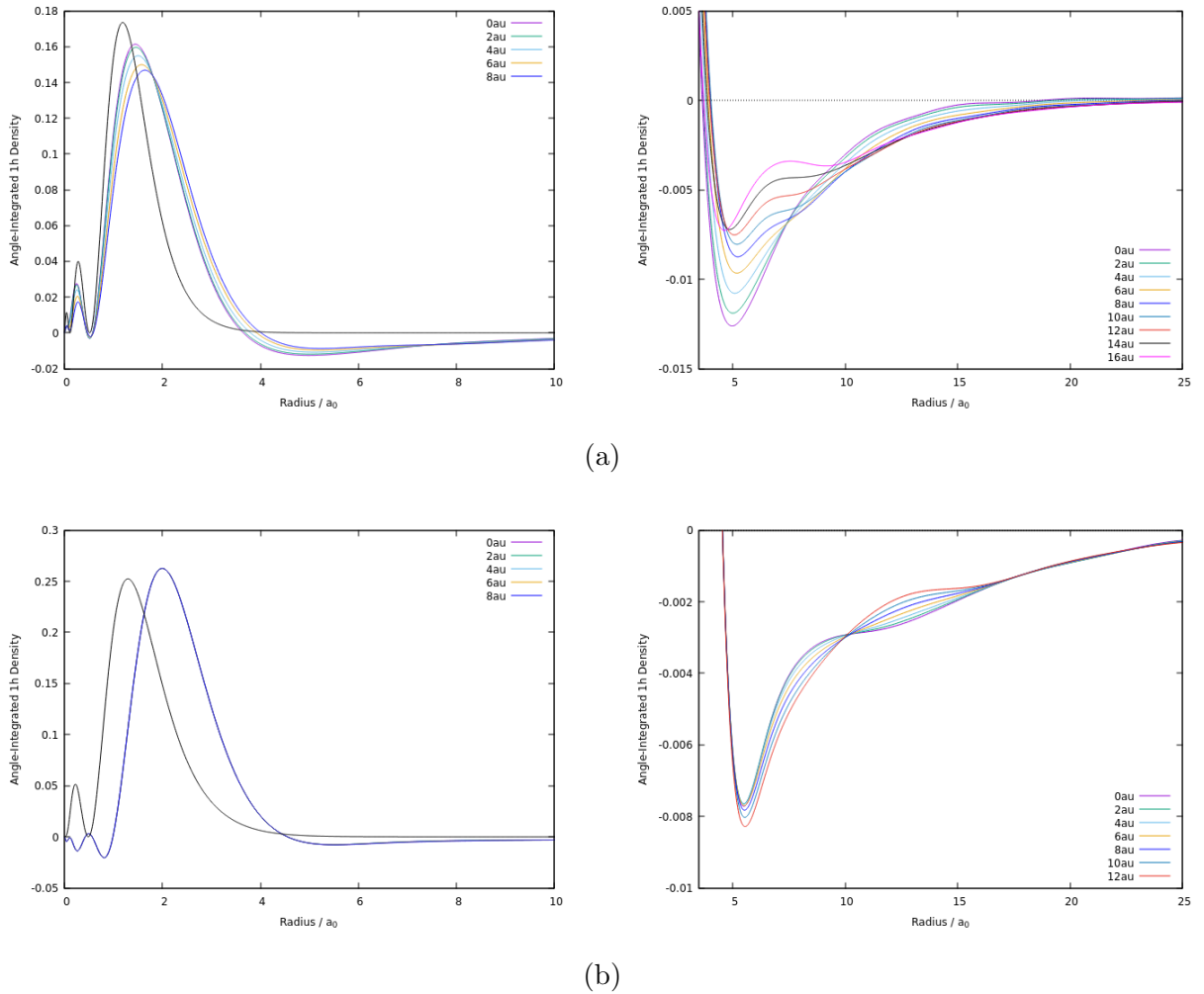


Figure 5.10: The variation of the angle-integrated hole density with radius for (a) the 3s main state and its satellites, and (b) the 3p main state oriented along the direction of the pulse and its satellites. The left plots show the variation in the region closer to the nucleus up to 10 au radius; while the plots on the right show the variation in the region excluding the atomic core, from 3.5 au to 25 au radius, with a much reduced y axis. The separate lines show how the hole density evolves between several different times (relative to an arbitrary starting point). The unlabelled grey lines in the left plots show the Hartree-Fock 3s (a) and 3p (b) orbital for reference. The plots are normalised such that the integrated 1h probability is 1 when summed over all symmetries.

Figure 5.10 provides a more direct illustration of the predicted radial motion of the electron density over a short period. Considering first the plot corresponding to the 3s satellite spectrum, figure 5.10a, it can be seen that the radial hole density structure is in general characterised by a region of large positive hole density centred around a radius of 2 au corresponding to the removal of an electron from the outer region of the atom; however there is also a small region of negative hole density peaking near 5 au and trailing off towards larger radii. This indicates an increased probability of finding an electron in this region as compared to the neutral, corresponding to the 2h1p satellites.

Focusing first on the inner region, the figure illustrates over the time period presented the region of positive hole density broadening and the peak moving outwards to higher radius, indicating a greater contribution from 2h1p configurations with two 3p-type holes rather than one 1s hole. Half an oscillation is shown in the figure, with the 1h density peak afterwards returning to its original shape before the process repeats. The full period is around 16 au, which aligns with the fast inner-region oscillation discussed previously. This also reinforces the association of this fast oscillation with the coherence between the 1h-dominated main state and the 2h1p-dominated first satellite. The association with the fast oscillation of figure 5.8 can be deepened by noting that the regions where the density distribution is most 2h1p-like correspond exactly to the regions where the fast-oscillating part of the hole density above 5 au in figure 5.8 is most negative.

The behaviour of the large-radius part illustrated in the right panel of figure 5.10a is more complicated as it can be associated with multiple coherences, but over the time span of the plot it can be seen that the relatively localised electron density near 5 au steadily shifts towards large radii. Again, the density will later contract, although in a less regular manner than the inner-region oscillations.

In the case of the 3p satellites shown in figure 5.10b, there is essentially zero movement of the main peak. This expected since the coherence between the main state and the satellite spectrum is essentially zero. The lack of coherence therefore means that there is no oscillation between states of 1h and 2h1p character. Within the diffuse region, however, the oscillation between the $\{\text{Ne}\}3s^23p^4(^3P)4p$ and the $\{\text{Ne}\}3s^23p^4(^3P)5p$ satellites is apparent. The oscillations at even larger radii are not visible on the timescale shown in this plot.

It is noticeable for both the 3s and 3p satellites in figure 5.10 that the hole density peak lies at a slightly larger radius than the corresponding Hartree-Fock orbital. This can be attributed to a few factors: first, the general contraction of the electron density towards lower radius in the ionic system as compared to the neutral would tend to decrease the hole density at low radius while raising it at higher distance. On top of this, in the 3s case the filling of the 3s hole in the 2h1p satellites also shifts the peak 1h density outwards. This cannot fully explain the location of the 3p peak, however, so it must also be assumed that the additional electron correlation accounted for in the ADC calculation also shifts

the neutral 3p state to higher radii than the HF case.

Testing the Assignment of Bound States

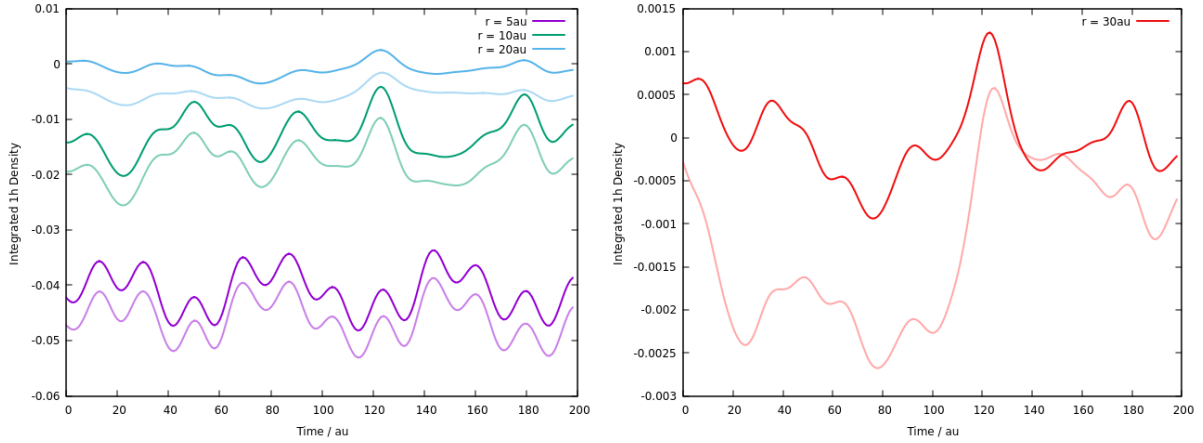


Figure 5.11: Left: A comparison of the time variation of the integrated 1h density above various radial thresholds r if ionic states up to 1.572 au are considered non-autoionising (dark lines), and if ionic states up to 1.595 au are considered non-autoionising (pale lines). This increases the 1h density above large radii, but does not alter the oscillations. Right: The same plot for a radial threshold r of 30 au. Above this threshold, the oscillation dynamics change significantly.

One risk in a numerical calculation such as this is the potential for the results to vary depending on the numerical choices made rather than any real phenomena. In this case, it is worth noting that due to the significant number of ionic states in the range of the double ionisation potential, the calculation here could plausibly have some sensitivity to the exact choice of numerical basis and how this affects which states are considered bound and therefore included in the ionic calculation. For instance, if the experimental DIP of 1.595 au [111] is used in this calculation instead of the numerically calculated DIP of 1.572 au, this leads to the inclusion of one additional 3s satellite state. As seen in figures 5.11 and 5.12, while this does shift more electron density away from the atomic centre, it does not substantially affect the nature of the oscillations up to a radius of 20 au. While a few more oscillation frequencies appear in the lower-radius frequency plots, the amplitudes are small and they do not significantly change the overall dynamics. It is only when looking at the very large radius part above 30 au at which the amplitude was previously negligible where significant differences now emerge.

The states near the DIP correspond to diffuse configurations of the series $\{\text{Ne}\}3s^23p^4(^1D)nd$ [101]. The higher-energy states in this series therefore have an electron in a very diffuse rydberg orbital, so these states are important in determining the oscillations of the very large radius part of the system, but their populations are small in comparison to the more tightly bound states and they have only minimal significance to the moderately diffuse region at a radius of 5-10 au where the strongest electron density

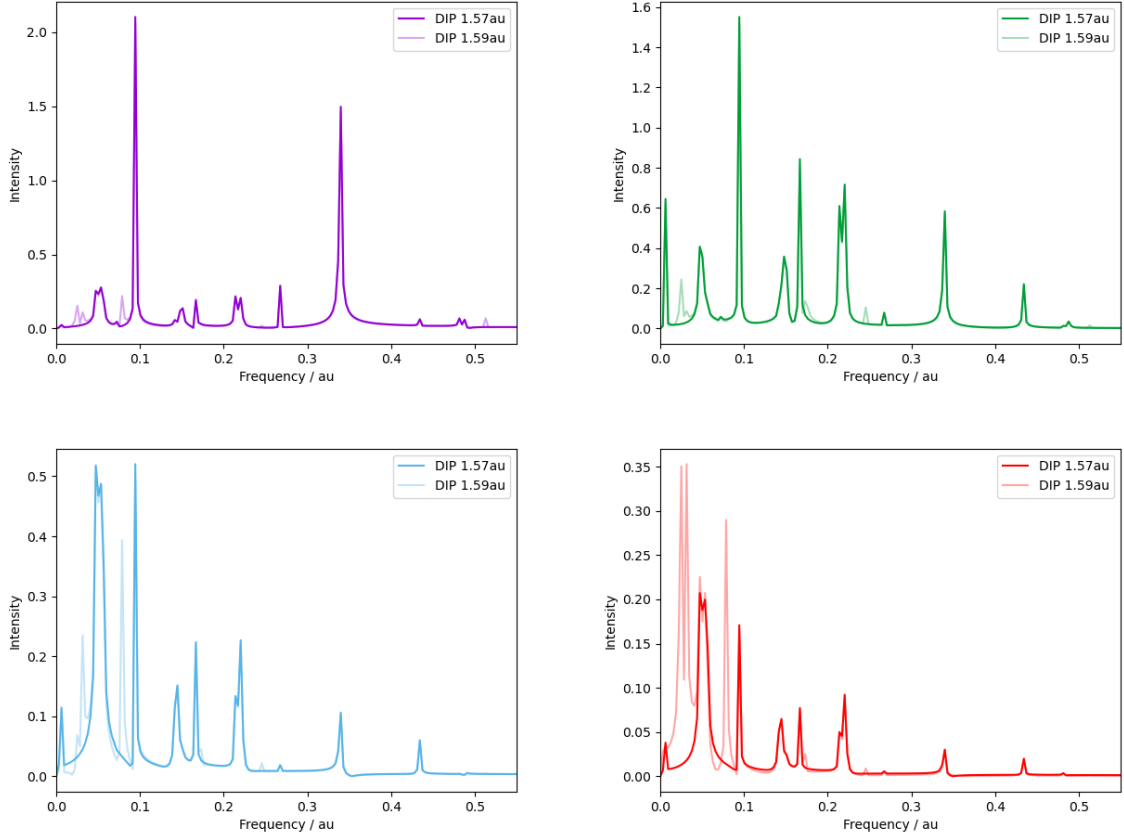


Figure 5.12: The frequency spectra for oscillations in density above 5 au (purple), 10 au (green), 20 au (blue) and 30 au (red), comparing which frequencies are present in the oscillations if the double ionisation potential is assumed to be 1.572 au (dark lines) or 1.595 au (pale lines).

oscillations take place. Thus, the effect of the choice of numerical basis on the precise details of the included states around the DIP would not be expected to have significant influence on the results of the calculation outside of the extremely diffuse region.

The effect of considering slight variation of the DIP on the oscillations of the 3p satellites is essentially identical, causing significant shifts only in the most diffuse part of the oscillations.

5.1.4 Simulation of Probes of the Ionic System

The analysis of the density matrix gives a prediction of the actual electron motion within the system, however it does not in itself indicate what should be expected to be observed during any practical measurement of the oscillations. The attosecond timescale oscillations suggest that such a system could be effectively measured by an attosecond pump-attosecond probe experiment of the kind that has become increasingly accessible over the past few years [15, 16, 17, 18]. We therefore numerically simulate such a setup with a probe pulse of variable delay relative to the pump, and observe the resulting

variation in the predicted rate of further ionisation.

The full numerical approach proceeds from the prior calculation on the neutral system as follows: First, the density matrix is diagonalised to obtain a set of mutually incoherent states which can each individually be expressed in terms of a fully coherent wavefunction. As there is no coherence between these states, they can each be treated separately and only recombined at the end. For each state the ionic system is propagated analytically up to the start of the pulse: $|\Psi^{N-1}(t)\rangle = \sum_m c_m e^{-iE_m t} |\Psi_m^{N-1}\rangle$, where the index m runs over the ADC(2,2) ionic eigenstates with energies E_m and coefficients c_m obtained at the end of the previous numerical propagation.

Separately, the B-spline ADC secular and dipole matrices for the ionic system are constructed in the same basis as for the neutral calculation, and the ionic secular matrix is diagonalised. During this process, the dicationic secular matrix is also obtained and diagonalised within the RCS. The ionic secular matrix here differs from the ionic secular matrix used in the neutral system as it includes 2h1p configurations with the particle in the ionisation space, thus allowing a second ionisation process. The analytically-propagated ionic states derived from the previous diagonalisation of the density matrix are then re-expressed in the ionic B-spline ADC basis and numerically propagated under the action of a laser pulse. At the end of the pulse, the final wavefunction of the system is projected onto the eigenstates of the B-spline ADC secular matrix. The ionisation fraction is then taken as the sum of the probabilities of all eigenstates below the lowest-energy calculated dicationic eigenstate. Finally, the total ionisation rate is then obtained by summing the results for the separate coherent states weighted based on their populations. This process is repeated for a range of time delays t to establish how the ionisation rate depends on the probe delay.

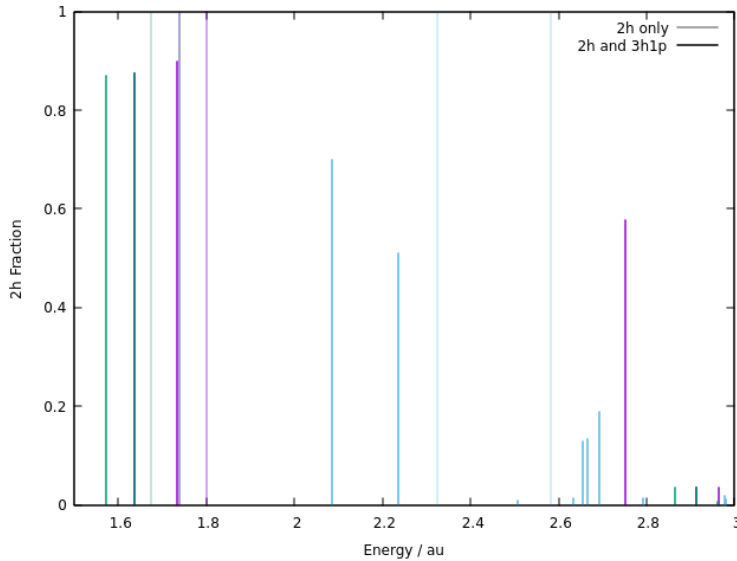


Figure 5.13: The dicationic spectrum calculated at ADC(1) with 2h configurations only (pale lines), and at ADC(2)x with 2h and 3h1p configurations (dark lines). The different colours indicated different D_{2h} symmetries.

In the current numerical propagation calculation, the ADC matrix for the dicationic system is constructed only in terms of 2h configurations. For consistent treatment with

the ADC(2,2) ionic states, the contributions from 3h1p configurations would also need to be included and the dicationic states treated at the ADC(2)x level. The capacity for constructing the ADC dicationic Hamiltonian in a manner consistent with the ADC(2,2) approach does exist [106, 107], however this has not yet been combined with the B-spline ADC code for the ionic system. Implementing this is therefore an obvious step for improving the description of the ionic propagation. Figure 5.13 illustrates the difference between the two calculations: for the first three dicationic levels, corresponding to $\{\text{Ne}\}3s^23p^4$ configurations of varying total angular momentum [112], the dicationic states are shifted slightly lower in energy once 3h1p configurations are included in the calculation - the first two by about 0.1 au, and the third by 0.07 au - but they are still mostly pure 2h states and can be clearly identified across both levels of calculation. The higher-energy dicationic states, however, differ much more substantially. One manifestation of this inconsistency is that the eigenstates of the ADC(2,2) ionic Hamiltonian are not quite eigenstates when constructed in the B-spline ADC ionic code and in fact have some small level of unbound character. To account for this fact in the numerical propagation of the ionic system, the calculated 'unbound' fraction in the absence of the pulse is subtracted to obtain the true ionisation probability due to the pulse for each pulse delay. Nonetheless, a more rigorous treatment in which the ionic and dicationic states are treated at consistent levels is desirable, and is planned for future work.

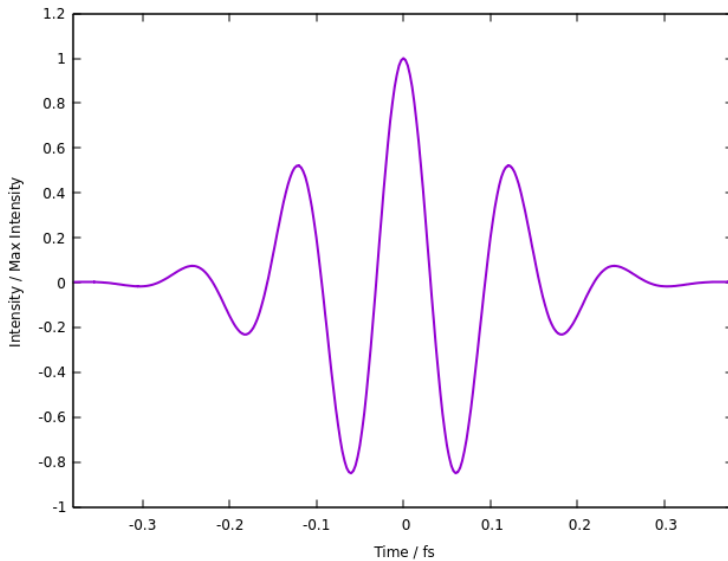


Figure 5.14: The shape of the probe pulse. This pulse has a central frequency of 1.2127 au and a Gaussian envelope with time FWHM of 10.5 fs

The probe considered here is modelled on that used in a recent demonstration of attosecond pump-attosecond probe spectroscopy (APAPS) using exclusively HHG sources [15]. The pulse has a central energy of 1.21 au and a Gaussian envelope with a time FWHM of 10.5 au (253 as), and is oriented parallel to the pump pulse. The pulse energy is sufficient to directly ionise the entire ionic state spectrum. The pulse duration is slightly over half the period of the fast oscillation between the 3s main state and second satellite, so it is plausible at the outset that this fast oscillation would be detected, while

all other significant oscillations would occur on a slow enough timescale that any effects would definitely be observed. The pulse intensity is again taken as 10^{13} W/cm², so still within the weak-field regime. This pulse is very short, containing only two full field cycles within the FWHM. This means that the carrier envelope phase (CEP) could plausibly have a substantial impact on the observed results. In the current case, the CEP is chosen such that the peak of the field oscillation aligns with the maximum of the envelope. In a real experimental APAPS implementation it is often the case that the pulse is not CEP-stabilised, however [15, 113], so it may be useful in the future to investigate whether shifting the CEP materially changes the results. During the numerical propagation, the number of Krylov vectors used was 25, and the time step was 0.1 au, for which the final wavefunction was found to be converged with respect to changes in these parameters.

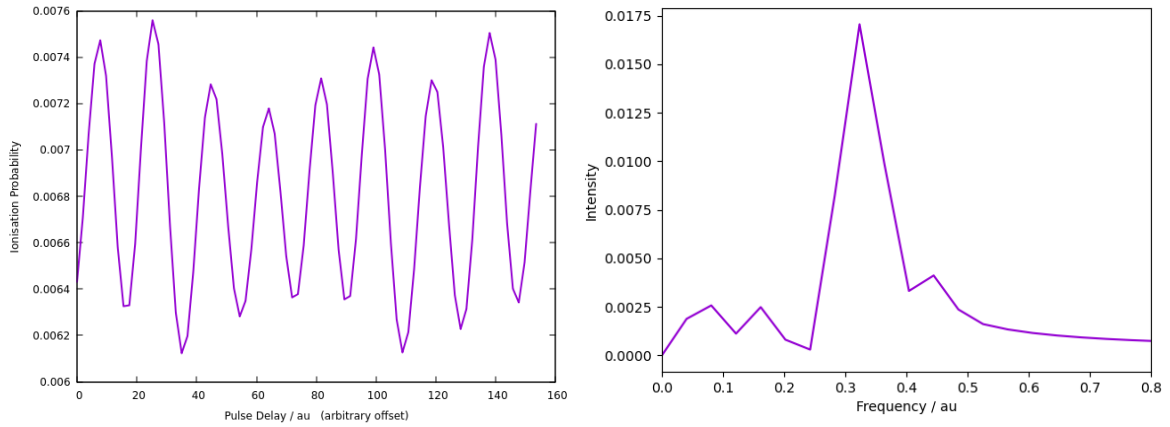


Figure 5.15: Left: the calculated time variation of the ionisation probability with pulse delay (relative to an arbitrary offset). Right: The oscillation frequencies present in the ionisation rate.

Restricting the focus initially to the 3s system, the diagonalisation of the density matrix produces three significant 3s-character coherent states, respectively containing 62.3%, 22.6%, and 11.7% of the total 3s series population. Each of these states is propagated analytically for a range of probe delays ranging from 0 au to 154 au in steps of 1.94 au preceding the numerical propagation of the ionic system. The probe delay is given relative to an essentially arbitrary 179 au offset from the centre of the probe pulse corresponding to the total numerical propagation time of the neutral system in the prior calculation. The variation of the resulting ionisation probability with probe delay and the frequency spectrum of these oscillations are shown in figure 5.15. The oscillations here have one primary component at approximately 0.33 au which leads to a 15-20% variation in the predicted ionisation rate. This matches the frequency of the oscillations between the 3s hole main state and the {Ne}3s²3p⁴3d satellite. While there are a few other weak frequency contributions, the resolution of the current numerical calculation is insufficient to assign them. Nonetheless, the indications here are that this probe is sensitive to oscil-

lations from the 1h state to the 2h1p spectrum, but has little sensitivity to oscillations within the diffuse part of the wavefunction. This indicates that the 3p satellite oscillations would likely also not have a significant impact on the ionisation rate, although numerical calculations on this system would be required to establish this definitively.

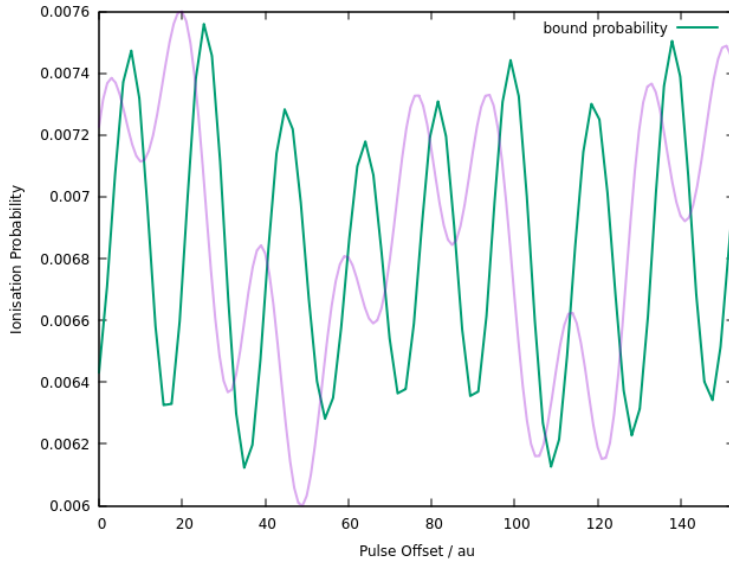


Figure 5.16: The variation in ionisation probability with probe delay (green), with the 5 au radius density oscillation plot (purple, see figure 5.8) overlaid and aligned with the peak of the pulse.

The pulse has its maximum intensity 15 au after the beginning of the numerical propagation, and it is informative to consider the state of the ionic system at this peak. Comparing the ionisation probability to the 5 au oscillations plotted previously, it appears that there is an association between the ionisation rate and the fast oscillations in this line. The ionisation rate is almost exactly $\pi/2$ out of phase with the fast oscillating contribution, taking its maximal value at the points at which the fast-oscillating term in the hole density above 5 au is decreasing most rapidly (or, equivalently, where the electron density above 5 au is most rapidly increasing). This can be associated with the period at which the system is shifting from 1h to 2h1p character and a formerly 3p-orbital electron is moving outward to larger radius. This is a somewhat unexpected result - the expectation would have been that the peaks in the 2h1p probability and the ionisation rate would align, rather than being offset by a phase of $\pi/2$.

Unfortunately, the inconsistency in treatment between the dicationic and ionic systems does leave open the possibility that the effects seen in the current probe calculation are still influenced by numerical artefacts in spite of the implemented corrections. As a next step in this work, it is therefore vital to implement the consistent ADC(2)x treatment of the dicationic states within the ionic B-spline calculation.

There are several other forms the probe pulse could take, which we also plan to investigate. One possible probe would target the 2p-3s transition energy. This would induce a transition with a rate proportional to the probability of the 3s hole being present at the time of the pulse. The resulting state would rapidly undergo Auger decay, and the resulting variation in double ionisation probability would be a direct measure of the oscillations

between 1h and 2h1p configurations. As this would be a direct probe of the 3s hole, it would not be expected to provide information about the diffuse part of the wavepacket. The 2p-3s transition energy is calculated at approximately 8.5 au. Pulses at this energy of sufficient intensity and sufficiently short duration for a probe of the oscillations in this system can be easily achieved by modern free-electron lasers [16, 17, 18].

An alternative choice of probe which might be more likely to capture some of the diffuse oscillations would be one chosen to measure the process of single-photon laser-induced Auger decay (spLEAD) [26]. The requirement for such a pulse is that it has energy sufficient to excite a state above the double ionisation potential, but not sufficient to remove a single electron without simultaneous rearrangement of the remaining electron configuration. In the case of the 3s main state, this requires a pulse energy sufficient to reach the lowest-energy $\{\text{Ne}\}3s^23p^4$ configuration, but insufficient to reach the lowest-energy $\{\text{Ne}\}3s3p^5$ configuration. Within the ADC(2,2) consistent treatment, these energies are 1.57 au and 2.08 au respectively. Combined with the 3s-hole main state at 1.07 au, this requires a pulse with energy between 0.50 and 1.01 au. In the current numerical implementation, however, the same dicationic energies are calculated less accurately at 1.67 au and 2.32 au, which would imply a required pulse energy between 0.6 au and 1.25 au for the numerical calculation. In fact, to ensure a pure spLEAD process, it is also necessary to account for the pulse width, which lowers the maximum pulse energy somewhat further. For instance, while the pulse used in the preceding numerical calculation has a central energy on 1.21 au, it also has an energy standard deviation of 0.23 au so nearly half of the pulse lies above the 1.25 au threshold and ionisation without Auger character is therefore possible.

The advantage of this setup is that spLEAD is a direct measure of the 2h1p part of the system, since the single-photon two-electron transition required for this process is impossible within the dipole approximation for a purely 1h state. This may therefore provide a better likelihood of observing the oscillations in the diffuse region of the wavepacket. The drawback here is that the upper limit on pulse energy makes it more difficult to achieve a pulse short enough to effectively detect the fast oscillating contributions such as the low-radius oscillations with period 18 au. A probe such as this which is sensitive to the dynamics of the diffuse part of the wavepacket would likely observe a combination of oscillations from the 3s and 3p satellite spectra, since both have comparable populations in the diffuse satellites; so a numerical calculation of the probe pulse would need to also treat the 3p satellite system.

5.1.5 Conclusions and Next Steps

By combining the methods of RCS B-spline ADC and ADC(2,2), we have been able to simulate numerically the ionisation of an atomic system by an attosecond pulse with an energy width sufficient to coherently populate the satellite spectrum from the 3s main state

up to the double ionisation potential with a high-accuracy description of the electronic correlation. We provide clear numerical evidence to support the initial expectation that an experimentally realisable attosecond duration laser pulse is capable of inducing long-lasting radial oscillation of the electron density in such systems. We predict numerically that for the specific case of the Argon atom, a pulse of central frequency 2 au and duration 0.358 fs - well within the range of experimentally accessible pulses - is capable of inducing this type of diffuse oscillations. We predict that oscillations in this case correspond to a movement of around 3% of the overall hole density, and that the total 3s electron density above a radius of 10 au varies by around a factor of two over a timescale of around 20 au while the corresponding 3p diffuse hole density varies by around 15%.

Furthermore, we find an initial indication that at the oscillations corresponding to the transition from 1h to 2h1p-type states may be able to be detected by a practically implementable probe pulse, although this needs further confirmation from a more rigorous and consistent treatment of the ionic and dicationic systems. Thus, we plan to incorporate the ADC(2)x treatment of the dicationic states into the ionic B-spline ADC calculation in an exactly equivalent manner to the inclusion of the ADC(2,2) ionic states in the B-spline ADC calculation for the neutral system. Additionally, we plan to numerically simulate other possible forms of the probe pulse, including an spLEAD-type probe and a higher-frequency probe targeting the 2p-3s transition, in order to establish which approaches will be most suitable for observing different aspects of these oscillations.

5.2 Auger-Active State Wave Packets

5.2.1 Overview

In the previous section, we considered the dynamics arising from coherent population of a series of bound states, which was seen to lead to oscillatory behaviour. Alternatively, it is possible to create coherence between excitations which are not bound, but instead undergo Auger decay. In such a system, it can be expected that some sort of oscillatory dynamics will still be present; however here they are strictly time-limited by the rapid Auger decay of the excitation. Furthermore, it can often be expected that the dynamics of the system are encoded in the decay itself due to variation in the local electronic environment of the hole.

There are several circumstances under which such a coherent decaying system can be created. The first is a system with multiple Auger-active hole states sufficiently close in energy that they can all be accessed by a single broad pulse. This can occur for core holes of the same type on atoms with different chemical shifts within the same molecule, or it can occur for inner-valence holes which undergo MO breakdown to produce a band of closely spaced states with partial 1h character. In addition to this, an electric field can be used to create or influence coherence by coupling two distinct states. This happens naturally in the case of sufficiently strong fields, for which the non-resonant dipole transition between ionic states begins to drive transitions once the product of the dipole matrix element and the electric field exceeds the state energy splitting.

Nitrous oxide (N_2O) has two inner-valence hole states close to its experimental DIP of ~ 1.31 au [114, 115] which both show near complete MO breakdown character. Of these, the 4σ satellite spectrum is expected to be mostly above the DIP, while the 5σ spectrum is expected to be mostly below [116, 117]. This nonetheless provides a band of Auger-active states which can be coherently populated. N_2O is also a relatively small molecule, which makes tackling it with the B-spline ADC code a relatively feasible task - although with three non-hydrogenic atoms and many significant ionic states it is at the upper end of what is manageable. Initially, we consider the case of ionisation of the 4σ and 5σ satellites by a broad low-intensity pulse with a bandwidth large enough to span the main part of the 4σ and 5σ satellite spectrum.

In such a system, the hole created will not be static, but will instead move within the molecule in a similar manner to the process of hole migration. The broad band of states with individually weak 1h character, were it below the DIP, would again be indicative of ‘frustrated Auger’ type dynamics where the hole delocalises before experiencing revivals; however, here, decay *is* possible. As a result, it might be expected that rather than a single exponential decay, or several independent exponential decay terms as could be expected for incoherent population of multiple ionic states with different decay rates,

the probability to find the system in an undecayed state might have some more complex variation in time. In particular, it might be expected that the Auger decay rate would vary in time as some electronic configurations might be more favourable to decay than others. We also aim to show revivals of the initial state which will decline as the system undergoes Auger decay.

Recently, the existence and feasibility of measurement of Auger-active state wavepackets has been demonstrated experimentally for the related case of resonant Auger decay of core-excited nitric oxide (NO) [118], including the observation of a coherence-dependent 'quantum beat' in the ionisation rate. Here, we are instead considering normal (i.e. non-resonant) Auger, with an inner valence hole which may display hole migration features prior to decay, however this recent work does demonstrate that it is possible to detect in a practical context the kinds of features that we are hoping to understand numerically.

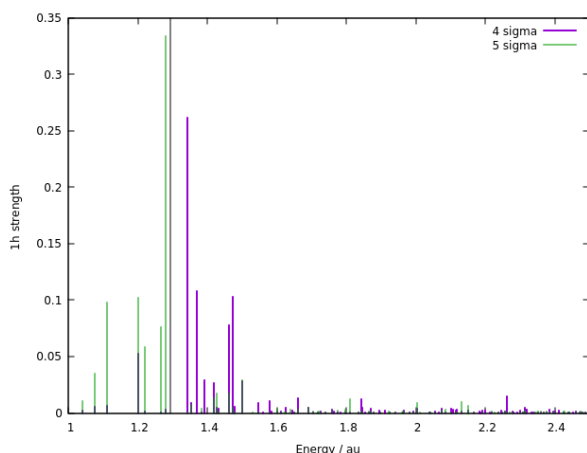


Figure 5.17: the the 4σ (purple) and 5σ (green) hole satellite spectrum for N_2O calculated using ADC(2)x starting from a pVTZ gaussian basis. The DIP calculated in the same basis is marked with a grey line at 1.294 au. MO breakdown is clear in both spectra. The 4σ spectrum lies mostly above the DIP, while the 5σ spectrum is mostly below.

5.2.2 Numerical Details

This work again makes use of the B-spline ADC code. Central to the B-spline ADC implementation is the division of the ADC Hamiltonian into the restricted correlation space (RCS) and the ionisation space (IS). As the RCS is a representation of a set of molecular orbitals constructed from a basis of Gaussian-type orbitals, it is therefore localised close to the molecular centre, while the IS is approximately continuum-like. We take advantage of this division by assuming that the initial state of the Auger-decaying system can be constructed purely within the RCS - built here using a pVTZ GTO basis - and it will then decay once coupling to the IS is included. It is expected that for an initial ionising photon of sufficient frequency, within the approximation of sudden ionisation, the populations of the ionic states following the initial photoionisation will be proportional to their one-hole strengths [109]. As an initial approximation, we therefore diagonalise the smaller RCS Hamiltonian and assume that populations of the resulting eigenstates can simply be taken as their one-hole fraction. The resulting ionic system is numerically propagated in time, and the calculated wavefunction can be used to determine the survival probability of the

initial state.

Here, we use a knot spacing starting at 0.25 au up to a radius of 4 au, above which the knot spacing steadily rises, reaching a maximum spacing of 1 au above a radius of 8 au. the knot basis runs up to a maximum radius of 117 au. The maximum angular momentum value used is 10. The primary B-spline expansion is centred on the central nitrogen atom in the molecule, and the off-centre expansions centred on the other two atoms have a radius of 1 au and a maximum angular momentum of 2 au. The CAP begins at 50 au and has a scaling parameter of 0.004.

Simultaneously, to verify the applicability of the ionisation model, we run a parallel calculation for the neutral system. As this code is more computationally intensive, we use a smaller RCS built starting from a pVDZ gaussian basis, and a correspondingly smaller B-spline basis; however the qualitative features of the system remain similar to the full basis used for the ionic calculation. The propagation of the neutral system produces a density matrix for the ionic system. In order to proceed, we diagonalise this density matrix, producing a set of fully coherent states which are mutually incoherent with each other. We can then numerically propagate these in time again using the B-spline ADC code.

For the smaller basis, the basis is altered by reducing the maximum radius to 60 au and reducing the maximum angular momentum value to 7. In order for the CAP to have enough time to properly damp the wavefunction, the CAP radius is reduced to 30 au.

5.2.3 Results and Discussion

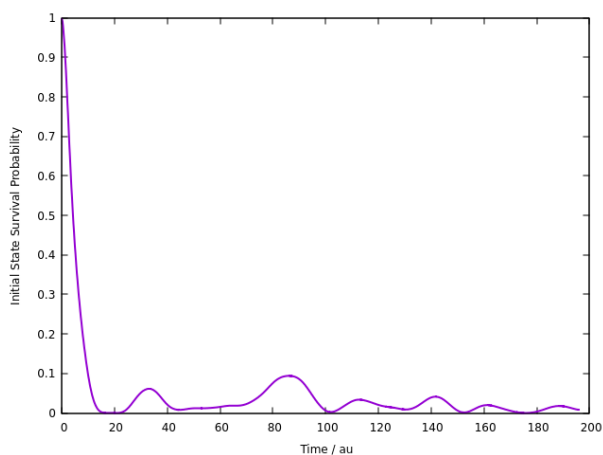


Figure 5.18: The time-variation of the initial state survival probability for the N_2O ionic system in a pVTZ basis using the simple model for initial state coefficients. The initial decay is rapid, and there is a weak revival at 85 au

After numerical propagation of the model ionic system, it can be observed that the survival probability of the initial state rapidly falls to zero over a timescale of roughly 10 au, and remains close to zero for the full propagation period, shown in figure 5.18. The rapid decline in survival probability can be compared to the survival probability of a non-decaying system - in that case, the survival probability would be given simply by

$$S(t) = |\langle \Psi(0) | \Psi(t) \rangle|^2 = \left| \sum_j |c_j|^2 e^{-iE_j t} \right|^2 \quad (5.4)$$

A rough estimate for the expected timescale for the survival probability to decay simply due to the phases becoming unaligned might be obtained by looking at the energy span of the populated ionic states, here given by the 1h strengths in plot 5.17. The energy envelope is very approximately gaussian with a full width of around 0.4 au (or a standard deviation of 0.17). As a very rough exercise, writing

$$S(t) \approx \left| \int dE A e^{-E^2/2\sigma^2} \sum_j \delta(E - E_j) e^{-iE_j t} \right|^2 \quad (5.5)$$

and applying the convolution theorem for Fourier transforms leads to a very approximate timescale of ~ 5 au for the survival probability to halve, which is consistent with that observed in figure 5.18, and which suggests that the primary driver of the initial loss of survival probability of the initial state is due to accumulation of phase difference between the coherent states, rather than Auger decay. This indicates that the coherent wavepacket motion in this system occurs on a faster timescale than the Auger decay.

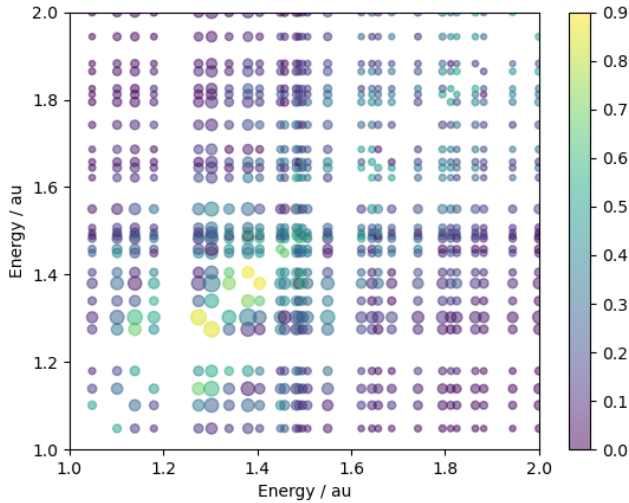


Figure 5.19: The coherences of the N_2O 4σ and 5σ satellites for a pulse of width 0.25 au and central frequency 5 au with the field oriented along the molecular axis. The size of the points is proportional to the geometric mean of the populations of the two states. Only states with populations over 0.3% of the total ionic population are shown.

For the numerical propagation of the neutral system, we considered several different sets of parameters, using a central frequency of 4 au or 5 au and a pulse width of 0.25 au or 0.5 au. The results of these calculations were all qualitatively similar, so here we focus only on the 5 au-frequency, 0.25 au-width pulse. After numerical propagation of the neutral system, we find that the population is distributed across a wide band of partially coherent states. This is the case for all sets of pulse parameters that we considered, with the coherences shown in figure 5.19 being representative. These coherences seem to be

almost as good as can be achieved for this system, as doubling the pulse energy width from 0.25 to 0.5 au made minimal difference to the coherence. The diagonalisation of the density matrix for the ionic system showed that the population is distributed across a large number of mutually incoherent states, with the single highest population being under 20% of the total. We therefore proceeded by numerically propagating in time several of the most populated σ -symmetry ionic states.

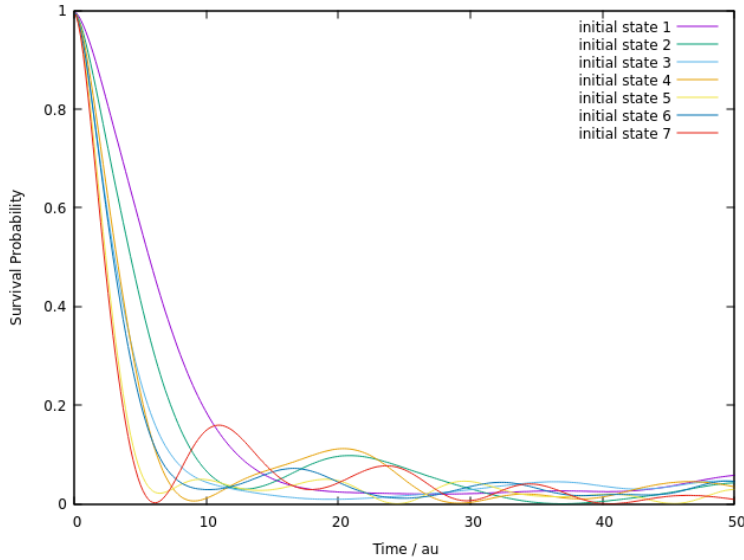


Figure 5.20: the initial decay of the survival probability for the initial state for each of the most populated coherent states of σ symmetry following ionisation by a pulse of energy width 0.25 au and central frequency 5 au oriented along the molecular axis.

Figure 5.20 shows how the survival probability of the initial state varies in time for these fully-coherent σ -symmetry states. It can be seen that, similarly to the model system, the survival probability rapidly falls to zero. At this stage, it would be desirable to calculate the total probability for the electron to remain localised on the atom as a measure of overall decay rate, however this proves to be difficult: one approach which was considered was the projection of the electron state at each time onto the bound-like RCS space, however this was found to exhibit heavy numerical artefacts. Further calculations showed that the bound eigenstates - defined here as states which lie below the DIP - in fact have some non-negligible component in the IS. This is likely due to the fact that with the correct linear combination of IS states, a state of localised character may be formed, so it is not possible to assume that transitions into the ionisation space necessarily represent an electron departing the bound system.

One limitation of the numerical code that I am using is that it is unable to treat single and double ionisation simultaneously. Instead, it is necessary to run a first calculation for the initial ionisation step, and then take the resulting ionic states and run a second calculation for the decay. The total length of time propagation for the initial ionising pulse (from pulse amplitude zero to zero) is ~ 28 au, which corresponds to a timescale over which the decaying state would lose 40-60% of its amplitude - although the region with significant field amplitude (e.g. 10% to 10%) is roughly half this. Nonetheless, this is something cannot be fully accounted for in this calculation, which introduces a possible

source of numerical inaccuracy.

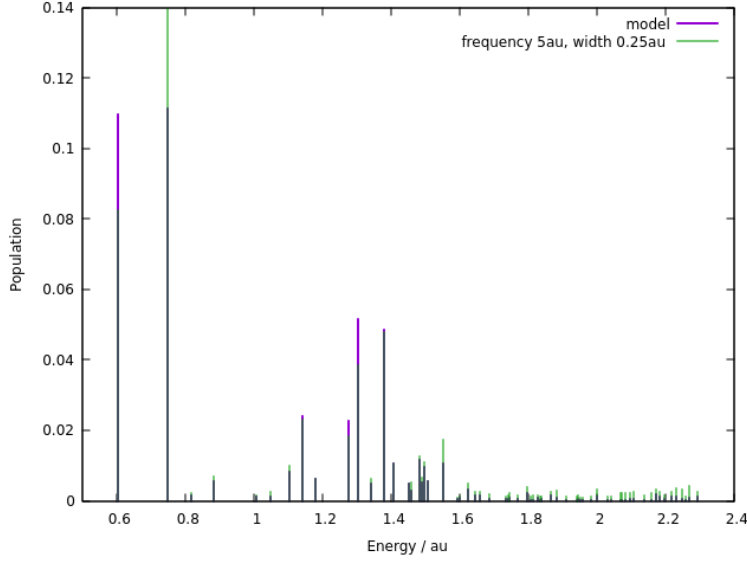


Figure 5.21: The populations of the ionic states obtained in the sudden ionisation model plotted alongside the populations obtained numerically and averaged over molecular orientations. the purple bars show where the model populations are higher, and the green bars show where the calculated populations are higher.

In order to verify the range of applicability of the model system, it is necessary to find at what energy the approximation of sudden ionisation became valid. It is expected that for sufficiently high ionising photon energies the departing electron should exit the system sufficiently fast that the approximation of sudden ionisation [109] should hold, and the populations of the ionic states should approach proportionality to the one-hole strengths. It was not possible to reach such a regime with the current basis, however. The highest ionising pulse frequency that was possible to consider while still being able to represent the outgoing electron wavefunction was at 5 au, almost 4 times the DIP with minimum outgoing electron energies of 3 au, however this still had significant deviations from the model in the ionic state populations. Notably, the populations of the weaker 1h, higher energy states systematically exceed the model populations, although there is no such consistency in the lower-energy region. Writing $E = v^2/2$ (in atomic units), the outgoing electron energies of 3-4 au correspond to velocities of around 2.5 au, meaning that they leave the system within a few au of time. This is only moderately faster than the ~ 5 au timescale of electron motion in the system, and so it may be plausible that this is the explanation for why the sudden ionisation regime could not be reached.

Conclusions

One of the core aims of this work was to predict and model new ultrafast dynamics through the application of recently-developed numerical techniques. For this purpose, we made use of the method of RCS B-spline ADC [45, 46, 47], which has provided us with the ability to study coherent ionisation in substantial detail.

Within our numerical calculations, we have provided clear evidence that strong coherence between ionisation satellites in atoms can be induced by a laser pulse a few hundred attoseconds in duration. We show that this leads to radial oscillation of the electron wavepacket, and for the specific example of argon we further illustrate the complex series of dynamics underlying the overall oscillation. We show how the oscillations consist of relatively rapid motion of the electron density just outside the main region of electron density of the neutral, combined with much lower frequency oscillation extending to large radii where the probability of finding the electron in the neutral would have long since fallen to zero. In addition to this, we provide initial evidence that at least the fast oscillating part of the wavefunction can be detected through an probe pulse accessible through high-harmonic generation techniques.

We have been careful to match both the pump and probe laser pulses that we considered closely to those which can be achieved in a realistic experimental setup [15]. We believe that this work can therefore provide impetus and guidance for a practical experimental measurement of this process in the near future. To further this aim, we intend to both study further which pump pulse parameters maximise the oscillatory dynamics, and to simulate with greater rigour a series of further probes including probes of the spLEAD type [26] and probes which aim to measure core-valence transitions. The former is suitable for experiments using HHG sources, while the significantly higher pulse energies in the latter case suggest an experiment which would be conducted through the use of a free-electron laser.

We have also sought to demonstrate non-exponential decay rates arising from coherent population of Auger-active states, however here there remains significant work to do. Even within the multi-centre RCS B-spline ADC approach, the fragmentation of the 1h strength across a large series of states in the MO breakdown region requires the inclusion of many ionic states in the full calculation, increasing the calculation time substantially and straining the computational practicality of this approach to its limit. Beyond this, we

have not at this stage implemented the capability to precisely assign in a time-dependent manner the fraction of the electronic wavefunction which still remains in an undecayed state, so direct modelling of the decay rate variation is not possible. Nonetheless, there is still work that can be done here within our current approach: restricting the initial state of the system to exclusively decaying states above the DIP and observing the survival probability, for instance, would provide insight into the damping of oscillations of the unbound system as it undergoes Auger decay.

The second core aim of the work was to develop new theory to model new kinds of dynamics. This is the aim served by the work on revival interferometry. Here, we have extended the method of Auger interferometry, built for the calculation of Auger decay rates, to the measurement of systems where decay is not constant in time, but is instead sharply interrupted by repopulation of the initial state. Such systems are of great interest in the context of charge migration. We indicate that it is possible through this interferometric technique to obtain both the initial decay rate and the timescale at which the subsequent revival occurs. We provide a highly illustrative model for this behaviour which not only allows us to generalise the result beyond the idealised case, but also gives good insight into the underlying causes of the final dynamics that we observe. This method can be contextualised within the broader category of coherent control-based techniques [93], extending the application of such approaches to the measurement of highly dynamical quantities which fluctuate on an attosecond timescale. Once again, this is not just in the realm of abstract theory, but is a technique which could be put into practice using currently available laser systems at modern FEL facilities.

Overall, the work in this thesis, as is the aim of all theory, seeks to advance the field by both providing an explanation for measurable behaviours and by producing predictions which we hope will invite further experimental investigation.

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