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Time Resolving Electron Dynamics in Atomic and Molecular Systems Using High-Harmonic Spectroscopy

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Time resolving electron dynamics in atomic and molecular systems using high-harmonic spectroscopy

by

M. R. Miller

B.A., Northwestern University, 2011

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Time resolving electron dynamics in atomic and molecular systems using high-harmonic spectroscopy
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has been approved for the Department of Physics

Prof. Andreas Becker

Prof. Agnieszka Jaron-Becker

Date ________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Miller, M. R. (Ph.D., Physics)

Time resolving electron dynamics in atomic and molecular systems using high-harmonic spectroscopy

Thesis directed by Prof. Andreas Becker

The generation of intense, femtosecond-duration laser pulses using near-IR to IR wavelengths of light opened a new frontier of highly nonlinear physics characterized by the resolution of electronic dynamics on their natural time scale through the application of attosecond-duration coherent light. These developments were made possible through the strong-field induced phenomenon of high-order harmonic generation (HHG), which results from the tunnel ionization, propagation, and recombination of an electron wavepacket with an atomic or molecular system. By emitting a broad spectrum of coherent radiation, this process enabled the development of attosecond-duration light. Due to its fundamental dependence upon electronic dynamics ongoing within the generative system, high-order harmonic generation has promise as a spectroscopic tool capable of resolving structural and dynamical processes within molecules. In this thesis, we apply numerical methods to study the time-resolution afforded by HHG in atomic and molecular systems. We also develop and validate new methods for simulating the single-electron response of multi-electron systems in the presence of intense laser fields.

To begin, we demonstrate the capacity for high-order harmonic generation to function as a signal of the dynamics of a propagating electron wavepacket. Through the use of an isolated attosecond pulse we gate the moment of ionization, selecting for or against electron trajectories that revisit the parent ion multiple times. With this control, we identify spectral and temporal signals which conclusively demonstrate the presence of these multiple revisitations.

In addition to imaging electron dynamics during propagation, we also show that high-order harmonic generation can be used to resolve electron dynamics inside of molecules. As driving field sources become available with increasingly long wavelength, electron dynamics in large and
conjugated systems show evidence of a highly nonadiabatic response. Using the model system of $H_2^+$, we demonstrate that the frequency-dependent amplitude and phase of emitted high-order harmonic generation is highly demonstrative of these dynamics. The intrinsic frequency chirp of the emitted radiation enables the translation of these spectral alterations into a time-resolved picture of the counterintuitive transient localization of the electron on alternating sides of the molecular system.
Dedication

To my family.
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how to effectively present my work to all types of audiences.

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Chapter 1

Introduction

During the last thirty years, the introduction of infrared pulsed laser technologies with femtosecond ($10^{-15}$ s) duration and focal intensities exceeding $10^{15}$ Wcm$^{-2}$ has advanced our capacity to control and image atomic and molecular systems [1]. The interaction of this laser light with matter yields a method to produce coherent light on the attosecond time scale ($10^{-18}$ s), sufficient to initiate and control transitions within bound electronic states on the natural time scale of the ongoing dynamics [2]. In this chapter, we introduce fundamental physics concepts describing the interaction of strong laser fields with atomic and molecular systems, explore the production of attosecond duration light pulses, and consider the control advanced by conducting studies on molecular systems driven by intense laser fields.

1.1 Strong-field ionization

The interaction of an atom with an applied electric field can be expressed through the Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_{\text{int}}(t),$$

separating the field-free Coulombic interaction $\hat{H}_0$ from a time-dependent electric field interaction term $\hat{H}_{\text{int}}(t)$. At weak field strengths, the addition of an electric field acts as a perturbation to the field-free term, and is consequently well described by perturbation theory. Successes of this theoretical treatment include predictions of $n$-photon induced electronic transition rates with the
Figure 1.1: The presence of an intense laser field (red dashed line) distorts the Coulombic barrier binding the electron to the atomic system. When this laser field is sufficiently intense, the barrier is suppressed, permitting tunnel ionization. The conceptual framework is the first step leading to many strong field processes.

A general finding that transition probabilities decay rapidly with an increasing number of requisite photons to complete a given transition [3].

As the intensity of the electric field is increased, and in particular as the intensities achievable by modern pulsed femtosecond-duration lasers are considered, this perturbative approximation fails. In particular, intensities of $10^{12}$ W cm$^{-2}$ are sufficient to produce nonperturbative behavior [4]; at intensities of $10^{15}$ W cm$^{-2}$, the applied electric field strength to rivals the Coulomb interaction in the 1s shell of the hydrogen atom. The potential surface under this condition is displayed in Fig. 1.1. Modeling physics within the parameter regime where the perturbative approximation fails requires, in general, the application of computational and numerical techniques.

Strong-field ionization can be broadly classified into three different categories: multiphoton ionization, tunneling ionization, and over the barrier ionization. The first of these ionization varieties is distinguished from the final two through the Keldysh parameter [5],

$$\gamma = \sqrt{\frac{I_P}{2U_P}}$$

(1.2)

where $I_P$ is the ionization potential of the system. The ponderomotive energy, or the cycle-averaged quiver energy of the oscillating electron, is given in atomic units, $(\hbar = m_e = e = 1)$ as

$$U_P = \frac{E_0^2}{4\omega^2}.$$  

(1.3)
The quantity $\gamma$ differentiates between a conceptual framework in which the large incident number of photons and large photon energy favors $n$-photon ionization events ($\gamma > 1$) and one for which the magnitude of the field deforms the Coulomb binding potential to favor a tunneling process ($\gamma < 1$). When the incident field strength grows excessively large, the field-free bound state energy exceeds the height of the potential barrier that restricts ionization. In this case, the electron can enter the continuum without tunneling and rapidly ionizes.

Figures such as Fig. 1.1 portray the potential structure of the field-matter interaction when the electric field is at its peak amplitude. Understanding strong-field ionization processes through such figures assumes a quasi-static model of ionization, in which the majority of the electron ionization takes place during a time window that is much less than the electric field cycle duration. This model is often justified due to the exponential reduction in the tunneling ionization rate with respect to the barrier height, and has been accurately implemented in studies of strong-field induced physics in atomic systems [6].

1.2 High-order harmonic generation

Following tunnel ionization, the departing electron wavepacket is accelerated by the laser field. The time difference between the ionization event and local electric field maximum dictates whether the electron will propagate away from the parent ion without returning, or, alternatively, whether the electric field may reverse direction and steer the electron to recollide with the parent ion. In some cases, this recollision is a recombination event: the electron wavepacket emits energy absorbed from the incident electric field in the form of a high energy photon and returns to the ground state. The electron dynamics leading to the photoemission can be conceptualized in this three-step description (ionization, propagation, and recombination) [7, 8], which is visually represented in Fig. 1.2(a).

Due to the strength of the electric field driving the photoemission, the release of radiation is a highly nonlinear event characterized by a nearly constant emission amplitude into odd multiples of the driving laser frequency spanning a broad energy range. An example of such a spectrum is shown in Fig. 1.2(b) for a hydrogen atom driven by an intense, linearly polarized electric field with a
wavelength of 800 nm and an intensity of $3 \times 10^{14} \text{ W cm}^{-2}$. The structure of the radiation spectrum possesses the following typical characteristics: strong emission at the photon energy of the laser field, followed by a steep drop off of radiative efficiency due exponential decay of perturbative $n$-photon events at low orders; subsequent constant-efficiency generation through a plateau of photon energies; and a dramatic decrease of radiation efficiency at a cut-off energy, signaling the termination of the plateau. Energies are conventionally measured as multiples of the fundamental laser frequency. This is a consequence of the symmetry properties of the system: the atom considered possesses inversion symmetry through the plane orthogonal to the laser polarization direction, while the oscillating direction of the field imparts a constructive interference condition to the emitted radiation that preserves only odd harmonics of the driving laser field frequency \cite{9}. Due to the extended plateau of energies emitted, this process in total is known as high-order harmonic generation (HHG).

The cut-off energy of the harmonic plateau is determined by the ionization potential of the system and the ponderomotive energy of the electron in the laser field as \cite{10}

$$E_{\text{cut-off}} = I_P + 3.17U_P.$$  \hspace{1cm} (1.4)

The ionization potential of the system enters into the equation through the recombination step, wherein the electron recombines to the ground state from the continuum; the magnitude of the contribution from the ponderomotive energy can be well predicted through classical analysis of the possible electron trajectories contributing to HHG, neglecting the Coulombic force due to the parent ion. These classical predictions are demonstrated in Fig. 12(c), where the kinetic energy of an electron released into an electric field at different points in time is plotted according to the simulated instant of ionization and predicted moment of recombination. These predictions follow from solving Newton’s equations for propagation in the oscillating electric field,

$$\ddot{x}(t) = -E(t)\dot{x},$$  \hspace{1cm} (1.5)

$$\dot{x}(t = 0) = 0,$$  \hspace{1cm} (1.6)

$$x(t = 0) = 0.$$  \hspace{1cm} (1.7)
Figure 1.2: (a) HHG can be conceptualized through a three-step mechanism involving tunnel ionization of an electric wavepacket, propagation driven by the incident laser field, and recombination of the electron with the parent core. Upon recombination, energy absorbed from the electric field is released as a high-energy photon (from [11]). (b) An exemplary HHG spectrum features radiation with consistent efficiency throughout an extended interval of frequencies. (c) The photon energies contributing to the HHG spectrum can be predicted through use of a classical model, indicating a time-dependent relationship between ionization, recombination, and the energy released. Each color corresponds to the same classical trajectory, indicated in (d); gray lines indicate ionization events that do not recombine, and hence do not contribute to HHG.
Solutions to this system of equations function well to interpret electron dynamics contributing to HHG when the electric field is linearly polarized and the wavelength and intensity of the electric field drive the electron far from the parent ion, where the Coulombic interaction is small. Figs. 1.2(c) and (d) demonstrate the solutions of the classical trajectories emerging during a center cycle of the field used to generate the HHG spectrum shown in Fig. 1.2(b). Each color corresponds to a different ionization time and represents the same trajectory in panels (c) and (d). Several conclusions can be drawn through this analysis: for every energy except for the cut-off frequency, two different electron trajectories contribute to each photon energy, following short and long excursion distances, respectively. Only the electrons ionized during the quarter field cycle preceding each zero of the electric field will recombine. And the excursion distance of the greatest-energy trajectory can be predicted by evaluating the quiver radius of the electron,

$$\alpha_0 = \frac{U_p}{\omega^2}. \quad (1.8)$$

The long excursion trajectories travel further than this quiver radius, requiring that simulations of HHG processes consider roughly twice this distance to fully capture all contributing dynamics.

In Fig. 1.2, the classical analysis considered ionization throughout a single time interval. However, the driving laser field will induce ionization throughout each half cycle of the driving laser field, resulting in several periodic bursts of radiation. This scenario is shown in Fig. 1.3 (upper panel), in which the energy distribution resulting from ionization throughout the duration of electric field is shown. Separate recombination events form a train of high-energy pulses of light, which is reproduced in Fig. 1.3(b) by considering energies greater than 35 harmonic orders. The spectral width the generated pulse cannot be more narrow than the Fourier limit, based on the Fourier relationship between time and energy. However, the inherent frequency chirp imparted by the relationship between time and recombination energy increases the temporal duration beyond the Fourier limit. Nevertheless, the pulse train of light produced can be generated with time scales on the order of attoseconds, providing a method of producing coherent pulses of light on the same time scale as electronic processes inside of atoms and molecules.
Figure 1.3: (Upper panel) Recombination of the electron wavepacket occurs at each half-field cycle of the driving laser with energies determined by the shape of the electric field throughout the contributing cycle. The recombination of different wavepackets is represented by different colors. (Lower panel) The release of radiation forms a train of attosecond-duration pulses.
To this point, it has been implicitly assumed that the dipole approximation holds for the motion of the electron in the linearly polarized laser field. In this approximation, the electron motion is restricted to the polarization direction of the laser source, and the electric field is assumed to possess constant magnitude over the spatial extent encountered by the electron. However, it is also evident that increasing the maximum energy produced efficiently within the HHG spectrum results in increases in the excursion distance traveled by the electron, requiring multipole moments of the electron to be considered \[\text{[12]}\]. These multipole effects introduce additional forces in the direction of the wave vector of the electric field, diverting the electron from the location of the parent ion and reducing the efficiency of HHG. Several studies have been performed to estimate the scaling of HHG production with regard to increases in the wavelength or intensity of the driving field \[\text{[13, 14]}\]; the parameter space in which these effects become important is, however, at much greater wavelength or intensity than the conditions explored within this thesis.

1.3 Generation of attosecond pulses

HHG supplies a method for producing a train of high-energy, attosecond-duration (1 as = $10^{-18}$ s) pulses of coherent light. Individually, these light pulses possess ideal properties for use as a tool to probe electronic structure in atomic or molecular systems. These pulses are separated with fixed time duration set by the period of the driving field; additionally, the spectral content of each pulse is different. A greater flexibility is gained through the production of isolated attosecond pulses, which can be used to more precisely manipulate electron dynamics. In this section, we briefly describe several techniques that have been proposed and used to generate these attosecond-duration pulses.

Careful consideration of Fig. 1.3(a) reveals that most energies within the HHG spectrum are generated at several time instants throughout the interaction of the incident laser field with the system. In contrast, the highest energies are selectively emitted near the peak of the electric field. One method for generating single pulses applies this realization by selecting photon energies near the cutoff that are only emitted through one recombination event, and using a filter to absorb
Figure 1.4: Several methods have been developed to isolate attosecond pulses from HHG, including: (a) filtering cutoff frequencies (from [15]); (b) varying the polarization of the electric field (from [16]); (c) rotating the spatial wavefront of the driving field (from [17]); (d) manipulating the phase-matching conditions of emitted radiation (from [18]).
photons emitted with lower energies. Such a strategy is shown in Fig. 1.4(a). This technique is sensitive to the carrier-envelope phase of the laser field: selection of a pulse with two equivalent maximal energies produces all energies twice; a carrier envelope phase which results in a single global maximum favors the production of the isolated pulse. Additionally, a few-cycle driving pulse increases the number of harmonic frequencies emitted exclusively at the central recombination event, augmenting the spectral content and intensity of the isolated light pulse [15, 19–21].

A second method for attosecond pulse production introduces a non-linear polarization to the electric field and rotates the polarization direction as a function of time. Through this polarization gating technique, shown in Fig. 1.4(b), near-linear polarization is achieved only near the center of the laser pulse. During this narrow window, the electron can recombine efficiently with the parent ion to release an attosecond pulse. All other electron wave packets released at different ionization times are steered away from the position of the parent ion, preventing recombination from taking place [16, 22, 23]. Consequently, an isolated pulse is emitted.

Alternatively, introducing a time-dependent rotation of the wavefront direction of an intense, few-cycle laser field provides a method for separating the attosecond pulses produced in a pulse train [17, 24]. As shown in Fig. 1.4, emitted light acquires a time-dependent propagation direction according to the moment of production from the rotated intense field. The spatial position of each pulse in the train is distinct and well defined, enabling the directional extraction of individual pulses. Additionally, this scheme suggests a method for studying time-dependent system dynamics. The spectral structure of each attosecond pulse can be studied independently; dynamics encoded within these pulses can be used to reconstruct time-dependent behavior.

Finally, isolated attosecond pulse generation has been recorded in systems featuring high intensities and midinfrared light sources, such as the scenario shown in Fig. 1.4(d) [18, 25]. The production of coherent light from HHG relies upon the satisfaction of phase-matching conditions for emitted radiation. The phase of different emitted photon energies depends upon both the inherent chirp of the microscopic radiative process and by macroscopic properties such as the index of refraction of the medium and geometry of the laser pulse used. Increasing the pulse duration and
gas pressure allows the index of refraction of the gas to change during the course of the light pulse, so that emission near the peak of the laser field can be favored and isolated from light emission at different times.

1.4 Imaging and controlling electron dynamics

The interaction of laser light with atomic systems, and in particular with rare gas atoms, has been studied comprehensively. Several *ab-initio* theoretical techniques as well as systematic approximation methods have been developed to achieve qualitative agreement with experimental observations. The strong-field ionization of rare gas atoms has been successfully modeled predominantly through two theoretical strategies: use of the strong-field approximation (SFA, or Keldysh-Faisal-Reiss theory [3, 5, 26]), or by quasi-static tunneling models [5, 6, 27]. Both models of atom-field interaction make two fundamental assumptions: (a) only one of the bound electrons in the atoms responds to the external field to become dynamically active and, (b) the response of this electron is to follow oscillations of the electric field adiabatically. Consequently, much of strong field atomic physics relies on a quasi-static interpretation of the interaction of the strong electric field with the atomic potential, assuming, for example, that ionization depends straightforwardly upon a potential barrier strength modulated by a well-characterized electric field.

The assumption of an adiabatic electron response in atoms, and specifically in rare gas atoms, is justified in view of the large spacing between electronic energy levels. In general, however, the energy levels of molecules are much closer, slowing electron dynamics beyond that of atomic systems. Furthermore, it has been argued that as the molecular size increases, the time it takes for an electron to traverse a molecule can rival the period of the laser field. These characteristics of electron dynamics in molecules favor a nonadiabatic response to an oscillating electric field, invalidating assumptions of the quasi-static model of tunnel ionization [28, 30].

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9 The discussion presented in this section is also published in the review article, M.R. Miller, Y. Xia, A. Becker and A. Jaron-Becker, "Laser driven nonadiabatic electron dynamics in molecules," Optica 3, 259-269 (2016).
Figure 1.5: Ionization and fragmentation patterns represented by the mass spectra of hexatriene, decatetraene and β-carotene for the interaction with laser pulses at 800 nm and 1450 nm. From [28].
1.4.1 Nonadiabatic effects in large conjugated molecules

The transition from adiabatic to nonadiabatic electron dynamics in large molecules is particularly evinced by highly conjugated systems, as examined by Lezius et al. [28, 29] for cases of linear conjugated systems, and Markevitch et al. [31, 32] for aromatic molecules. In Fig. 1.5, experimental evidence for a nonadiabatic response is present in the mass spectra of three linearly, fully conjugated all trans hydrocarbons of increasing length following the interaction with laser pulses at different wavelength are shown [28].

Two peaks occur in the mass spectrum of the smallest molecule (hexatriene), indicating the stable production of the first two charge states of the parent ion accompanied with little fragmentation. These results are in agreement with the qualitative predictions of the quasi-static ionization picture and, hence, the assumption of an adiabatic electron response to the oscillating electric field of the laser, independent of its period. In contrast, the largest molecule (β-carotene) shows a mass spectrum indicative of persistent nonadiabatic electron dynamics through extensive fragmentation of the molecule at both wavelengths considered. Most interesting in the present context is the strong wavelength-dependent variation of the mass spectrum of decatetraene, which exhibits population of the singly, doubly and triply charged parent ion at 1450 nm, but demonstrates strong fragmentation at the shorter wavelength of 800 nm. It was pointed out by Lezius et al. that this observation suggests a transition from the adiabatic single-active electron picture to a nonadiabatic multi-electron ionization dynamic. At 800 nm, the duration of the field oscillation was argued insufficient for the electron to traverse the large molecule adiabatically. In contrast, the longer field cycle of 1450 nm did afford the electron wavepacket sufficient response time, resulting in the stable production of a few charge states. Similar strong variations in the ionization and fragmentation patterns have been observed for aromatic molecules at a given wavelength for rather small variations of the laser intensity [31, 32].

Following qualitative considerations about the role of Landau-Zener type transitions [28, 29], a model was introduced to describe the onset of the transition from adiabatic single-active electron
to nonadiabatic multi-electron dynamics through a coupling of the ground state and the low-lying excited states in molecules \[31, 32\]. According to this model, the strongest of these transitions involves a charge-transfer state as a doorway state. Further elements of the theory take into account the multi-electron nature of the polyatomic molecules used in related experiments.

### 1.4.2 Charge resonance enhanced ionization

Signatures of nonadiabatic dynamics similar to those seen in multielectron systems arise in single electron molecules as well. As first identified by Mulliken \[33\], symmetric molecular ions such as \( \text{H}_2^+ \) possess pairs of charge-resonant states which, at large internuclear distance \((R_0)\), become nearly degenerate and couple strongly to electromagnetic fields. Further investigations using \( \text{H}_2^+ \) as a model system have elucidated the important role these states play in the process of laser induced ionization \[34, 35\], with similar effects observed in experiments involving the higher charge states of \( \text{CO}_2 \) \[36\]. In particular, theoretical predictions show the charge-resonant states can amplify the rate of ionization of \( \text{H}_2^+ \) by one to three orders of magnitude in models including both electronic and nuclear motion \[37\]. Throughout an interval of internuclear distances preceding dissociation, the \( |g\rangle \) and \( |u\rangle \) states of \( \text{H}_2^+ \), which possess opposite parity, act as a charge-resonant pair.

The relevancy of this coupling is obvious in the quasi-static picture of ionization at the peak of the electric field. Near its equilibrium internuclear distance, \( \text{H}_2^+ \) ionizes predominantly from the downhill well through a mechanism analogous to adiabatic single-active electron atomic ionization. However, as the internuclear distance increases, the electric field alters the shape of the barrier between nuclear wells. The shifted energy level of the uphill state enables shorter tunneling times or promotes population immediately into the continuum. This scenario is portrayed in Fig. 1.6 in the case of a static electric field. When \( R_0 = 6.0 \) in panel (a), the intramolecular potential barrier is suppressed beneath the energy of the uphill state, resulting in the dramatically increased ionization rate shown in Fig. 1.6(d) \[35\]. As \( R_0 \) continues to increase, the barrier reasserts itself (b) until ionization from the uphill well is ultimately again suppressed (c). This situation results in the charge-resonance enhanced ionization (CREI) effect \[34, 35\] throughout a critical region of
internuclear distances shown in Fig. 1.6(d). The prominent double-peak structure in the ionization rate as a function of internuclear distance has recently been observed experimentally [38].

The strong enhancement of the ionization signal due to CREI suggests that most strong-field induced signals will be dominated by dynamics occurring throughout the CREI regime. This is particularly important in the context of resolving nonadiabatic behavior, as in addition to an obvious enhancement of ionization, CREI coincides with a modification of the localization behavior of the electron between the two nuclei. Early predictions of this effect suggested that the near degeneracy of the relevant energy levels enabled population to be preferentially trapped in the uphill well [34]. More recently, it has been proposed that additional ionization channels involving excitation followed by ionization from either site of the molecule may contribute to this quasi-static picture [39]. In addition, numerical results showed evidence that the inversion symmetry of the electron density was broken during laser propagation, potentially enabling the production of even harmonics in HHG spectra [35].

The importance of nonadiabatic electron behavior has become increasingly obvious with time-resolved examination of electron dynamics occurring in the CREI regime, where the quasi-static description of electron behavior has proven incomplete [40]. In fact, time-resolved studies of ionization in H$_2^+$ and electron behavior therein demonstrated that ionization was not only enhanced but that the timing of peak ionization could be changed as well: at laser parameters supporting nonadiabatic behavior, ionization no longer occurred with maximum amplitude near the electric field peak. Instead, several discrete bursts of ionization occurred throughout each half cycle of the driving laser field [41]. Analysis of the time-dependent electron density distribution in H$_2^+$ illustrates that bursts of ionization are accompanied by a transient electron localization upon alternating nuclear centers several times per half field cycle of the driving laser field [40–43]. This dynamic drives population toward the uphill potential well, from which it can be efficiently and rapidly ionized. This dynamic is highly sensitive to the strength and frequency of the electric field used. Different wavelengths or field strengths result in different numbers of localizations during each half laser cycle, so that selection of the appropriate wavelength enables the localization of the
Figure 1.6: Charge-resonance-enhanced ionization in $\text{H}_2^+$ is attributable to the energy level structure of the two lowest states of $\text{H}_2^+$ are pictured at a peak field strength of $10^{14}$ W cm$^{-2}$ when (a) $R_0 = 6.0$, (b) $R_0 = 10.0$, and (c) $R_0 = 14.0$ a.u. along the laser polarization axis $z$. In (d), theoretical predictions for the ionization rate for a $10^{14}$ W cm$^{-2}$, 1064 nm laser source spanning an interval of internuclear distances. Adapted from [35].
wavefunction counterintuitively and predominantly on the uphill well, reminiscent of the modulated charge distribution described in [44].

1.5 Outline of this thesis

High harmonic generation provides a natural framework from which to extract time-resolved information regarding the dynamics of electrons in atomic and molecular systems. Using HHG, we can produce intense coherent light on the time scale of bound electronic motion, making accessible the targeted manipulation of electronic population on a controlled temporal scale. Additionally, HHG is encoded with information regarding the state of the system driven by the intense laser source at both the time of ionization and recombination. Accessing and interpreting the phase and amplitude of different harmonics conveys the response of the system under exposure to intense laser fields. In the case of induced nonadiabatic electron dynamics, HHG is a resource for capturing counterintuitive electronic response to inform efforts to control quantum mechanical electron behavior. This thesis addresses these themes in the following structure.

In Chapter 2, we introduce numerical and computational methods used to solve the time-dependent Schrödinger equation (TDSE) for an atom or molecule in the presence of an intense laser field. These calculations are necessary to fully capture the nonperturbative nature of the combined laser field and Coulombic interactions. We address in particular the efficient time propagation of solution wavefunctions to the TDSE, how to accurately and efficiently construct field-free states prior to propagation in the laser field, and which parameters are needed to confer sensitivity to small-magnitude effects. We summarize methods for calculating time-dependent observables relevant to the study of HHG and discuss theoretical tools used to simultaneously extract time and frequency-dependent information from the radiation spectrum.

In Chapter 3, we consider the construction of accurate single-electron models of multielectron systems. Using density functional theory, we account for electron exchange and correlation effects in the calculation of field-free bound states of a multielectron noble gas atom. Using these states, we introduce a self-consistent method for calculating effective potential energy surfaces which can
be further used to compute single-electron response to laser fields. We fit simple and physically-grounded analytic expressions to these computed expressions, and evaluate their accuracy through the calculation of photoionization cross sections and HHG spectra, identifying in particular the Cooper minimum in the 2p shell of Argon.

Chapter 4 applies an attosecond pulse tuned to an internal atomic electronic transition to gate the moment of electron ionization in the process of HHG. Using this strategy, we demonstrate and characterize the emergence of different subsequent electron dynamics. Among these electron behaviors is the ionization of an electron wavepacket that reencounters the parent ion multiple times: we explore the capacity of isolated attosecond-duration pulses to selectively produce these multiple rescattering events and consider the capacity of these events to produce trains of pulses with extremely short temporal duration, implicated in the new construction of zeptosecond (10⁻²¹ sec) duration events.

The nonadiabatic response of the electron in H₂⁺ is studied in Chapter 5 using HHG as a spectroscopic tool. We identify moments of suppressed ionization due to the ongoing nonadiabatic dynamic. This suppressed ionization alters the structure of the HHG plateau, suppressing radiation into an interval of energies. The spectral position of this minimum structure can be used to identify the timing of the ionization suppression event, and hence can be used to identify the moment when the electron predominantly populates the uphill side of the molecule exposed to the laser field. Application of the attosecond lighthouse technique can be used to trace the evolution of this nonadiabatic dynamic by identifying the shifting energetic position of the minimum. We additionally explore the elimination of the odd-harmonic generation condition due to the evolving and symmetry-breaking nonadiabatic dynamic. The disappearance of odd-harmonic generation corresponds to the efficient emission of energies at times when electron dynamics during recombination changes rapidly. Despite the absence of odd-harmonics in the spectrum, we show the likely efficient phase-matching of these plateau energies in a simulated Gaussian laser spatial profile. In total, HHG is demonstrated an ideal means for identifying the presence of these nonadiabatic dynamics and directly resolving the time-dependent electronic behavior.
Finally, in Chapter 6, we conclude with a summary of the topics discussed within this thesis and consider future directions of the field supported by this work.
Chapter 2

Numerical Methods

In this chapter, we review the numerical methods we use to conduct simulations for results reported in this thesis. In each study presented, we seek to solve the time-dependent Schrödinger equation (TDSE) in the context of intense laser field interaction with atomic and molecular systems of interest. We thus begin by introducing a general strategy through which this solution can be achieved. By discretizing the solution to the TDSE in both time and space, we present a finite-difference technique for propagating a time-dependent wavefunction. Using this solution method, we begin by discussing how to compute the eigenstates of the system Hamiltonian and demonstrate how to ensure that the states possess accurate short and long-range behavior. We next focus upon the use of these eigenstates as an initial state of the system, which can be propagated forward in time to solve the TDSE. The convergence properties of this real-time propagation step are discussed, addressing strategies to reduce numerical noise in the final solution.

With this propagation method in place, we consider the calculation of observables relevant to this thesis. In particular, we review the calculation of high-order harmonic generation (HHG) spectra. Using this observable, we demonstrate computational performance relevant to gauge and dipole form selection to optimize the accuracy of the calculations. We also introduce theoretical tools that can be used to provide additional time-resolved information concerning dynamics contributing to the HHG process, which we implement frequently throughout this thesis to better understand the relevancy of dynamical events to the structure of the HHG spectrum.
2.1 Solution of the TDSE

In the regime of strong-field induced laser physics, the strength of the electron interaction with the laser field occurs with comparable magnitude to the Coulomb interaction binding the electron within the atomic or molecular system. Consequently, it is difficult to consider either interaction as a perturbation upon dynamics mediated by the other, limiting the applicability of strictly analytic treatments of the ongoing dynamics. To confront this problem, studies regarding strong-field physics are often conducted computationally. In the following section, we describe an algorithm implemented to solve a discretized form of the TDSE, elaborate upon the need to impose effective absorbers along the boundary of the spatial domain allotted for electron wavefunction propagation, consider strategies for calculating field-free wavefunctions to serve as initial states for our systems, and conclude by assessing the convergence properties of solutions to the TDSE in different systems.

2.1.1 Discretization and propagation of the TDSE

Within this thesis, numerical simulations are a central tool used to solve the time-dependent Schrödinger equation for a single-electron wavefunction $\Psi(r,t)$. Formally, the objective of these calculations is to solve the TDSE,

$$i \frac{\partial}{\partial t} \Psi(r,t) = \hat{H}_{\text{tot}} \Psi(r,t).$$

(2.1)

In the current context, we are interested in $\hat{H}_{\text{tot}}$ representing the light-matter interaction of an electron exposed to a laser field. Separating this interaction into time-dependent and time-independent components, we write $\hat{H}_{\text{tot}} = \hat{H}_0 + \hat{H}_I$, where

$$\hat{H}_0(r) = -\frac{\nabla^2}{2} + V(r)$$

(2.2)

is the field-free part of $\hat{H}_{\text{tot}}$. The potential, $V(r)$, represents the Coulombic interaction: in the case of single-electron systems, this term takes the form $-Z/|r|$, where $Z$ is the nuclear charge; in the
case of more complex systems, this term can be complicated considerably to take into account, for example, the mean-field influence of other electrons within the system.

The laser interaction is introduced with the term $\hat{H}_I$, which in the length gauge acquires the form

$$\hat{H}_I(\mathbf{r}, t) = \mathbf{E}(t) \cdot \mathbf{r}. \tag{2.3}$$

Throughout the course of this thesis, $\mathbf{E}(t)$ is frequently assumed to be linearly polarized. The use of light with linear polarization is common in the generation of high-order harmonic generation to maximize radiative efficiency. The selection of an electric field of the form $E(t) = E_0 \cos(\omega t) \sin^2(\pi t / N \tau)$ is made to mimic the shape of Gaussian laser profiles frequently encountered experimentally throughout the peak of the laser field strength, and omits the problematic long tails that would introduce step-like discontinuities to the shape of $\hat{H}_I$ or demand long propagation times.

In total, then, the solution of Eq. (2.1) requires use of an algorithm suitable to propagate second order partial differential equations. A straightforward means of implementing this solution is to discretize the wavefunction on a spatial grid (involving points $\{N_1, N_2, ..., N_M\}$ with separation $\Delta x_i$ in each modeled dimension) and to advance the solution forward in time by finite intervals $\Delta t$. For each small time step taken, it is known that

$$\Psi(\mathbf{r}, t + \Delta t) \approx e^{-i\hat{H}(t)\Delta t}\Psi(\mathbf{r}, t) \tag{2.4}$$

2.1.1.1 Split-operator method

To further simplify the solution of this problem, the Hamiltonian can be decomposed along each of the $N_{\text{dim}}$ spatial dimensions considered as

$$H_{Tot} = H_{x_1} + H_{x_2} + \cdots + H_{x_{N_{\text{dim}}}}, \text{ where} \tag{2.5}$$

$$H_{x_1} = -\frac{\nabla^2_{x_1}}{2} + \mathbf{E} \cdot \mathbf{x}_1 + \frac{V(\mathbf{r})}{N_{\text{dim}}}, \tag{2.6}$$

$$H_{x_2} = -\frac{\nabla^2_{x_2}}{2} + \mathbf{E} \cdot \mathbf{x}_2 + \frac{V(\mathbf{r})}{N_{\text{dim}}} \cdots \tag{2.7}$$
and so on for each of the dimensions. This decomposition allows us to rewrite Eq. (2.4) in the split-operator form

\[ \Psi(r, t + \Delta t) \approx e^{-iH_{x_1}(t)\frac{\Delta t}{2}} e^{-iH_{x_2}(t)\frac{\Delta t}{2}} \cdots e^{-iH_{x_Ndim}(t)\frac{\Delta t}{2}} \cdots e^{-iH_{x_2}(t)\frac{\Delta t}{2}} e^{-iH_{x_1}(t)\frac{\Delta t}{2}} \Psi(r, t) \]  

(2.8)

which follows from the Baker-Campbell-Hausdorff formula, and can be shown to have accuracy \( O(\Delta t^3) \) \cite{45}. In general, the problems discussed within this thesis will have \( N_{\text{dim}} = 2 \) or 3, but the solution strategy shown generalizes easily to any number of dimensions and does not restrict the selection of coordinate geometry. Through this method, the propagation of the wavefunction reduces to updating along one dimension at a time. In the subsequent subsection, we demonstrate this propagation procedure restricted to a single dimension for the purposes of clarity.

### 2.1.1.2 Crank-Nicholson method

The Crank-Nicholson method is a unitary, energy conservative, and stable method for the solution of the TDSE to second order accuracy in time and space \cite{46}. To begin, the time evolution is rewritten in Cayley form through a Taylor expansion as \cite{47}

\[ e^{-iH(t)\Delta t} \approx 1 - i\frac{\Delta t}{2} H + i\frac{\Delta t}{2} H, \]  

(2.9)

which is accurate to second order in time. From this, and with Eq. (2.4),

\[ \left( 1 + i\frac{\Delta t}{2} H \right) \Phi(t + \Delta t) = \left( 1 - i\frac{\Delta t}{2} H \right) \Phi(t). \]  

(2.10)

Along one dimension (arbitrarily denoted \( x \)), the Hamiltonian can be written as

\[ H = A(x, y) \frac{\partial^2}{\partial x^2} + B(x, y) \frac{\partial}{\partial x} + V(x, y), \]  

(2.11)

where the variable \( y \) represents all other coordinates within the system. \( A(x, y) \) and \( B(x, y) \) represent the functional coefficients appropriate to the geometry of the system. The Crank-Nicholson
method for the coordinate $x$ reads

\[
\Phi_n(t + \Delta t) + i \frac{\Delta t}{2} \left( A_n(y) \frac{\Phi_{n+1}(t + \Delta t) - 2\Phi_n(t + \Delta t) + \Phi_{n-1}(t + \Delta t)}{(\Delta x)^2} + B_n(y) \frac{\Phi_{n+1}(t + \Delta t) - \Phi_{n-1}(t + \Delta t)}{2\Delta x} + V_n(y) \Phi_n(t + \Delta t) \right)
\]

\[
= \Phi_n(t) - i \frac{\Delta t}{2} \left( A_n(y) \frac{\Phi_{n+1}(t) - 2\Phi_n(t) + \Phi_{n-1}(t)}{(\Delta x)^2} + B_n(y) \frac{\Phi_{n+1}(t) - \Phi_{n-1}(t)}{2\Delta x} + V_n(y) \Phi_n(t) \right)
\]  

(2.12)

Here $n$ represents the respective grid point in the $x$ direction. Equation (2.12) leads to the following system of linear equations:

\[
\begin{pmatrix}
2X_1 & 3X_1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
1X_2 & 2X_2 & 3X_2 & 0 & \cdots & 0 & 0 & 0 \\
0 & 1X_3 & 2X_3 & 3X_3 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & 1X_{N-1} & 2X_{N-1} & 3X_{N-1} \\
0 & 0 & 0 & 0 & \cdots & 0 & 1X_N & 2X_N
\end{pmatrix}
\begin{pmatrix}
\Psi_1(t + \Delta t) \\
\Psi_2(t + \Delta t) \\
\Psi_3(t + \Delta t) \\
\vdots \\
\Psi_{N-1}(t + \Delta t) \\
\Psi_N(t + \Delta t)
\end{pmatrix}
\]

\[
= \begin{pmatrix}
2Y_1 & 3Y_1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
1Y_2 & 2Y_2 & 3Y_2 & 0 & \cdots & 0 & 0 & 0 \\
0 & 1Y_3 & 2Y_3 & 3Y_3 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & 1Y_{N-1} & 2Y_{N-1} & 3Y_{N-1} \\
0 & 0 & 0 & 0 & \cdots & 0 & 1Y_N & 2Y_N
\end{pmatrix}
\begin{pmatrix}
\Psi_1(t) \\
\Psi_2(t) \\
\Psi_3(t) \\
\vdots \\
\Psi_{N-1}(t) \\
\Psi_N(t)
\end{pmatrix}
\]  

(2.13)
where $N$ is the total number of grid points in the $x$ direction, and

\begin{align*}
1X_n &= \frac{i\Delta t}{2(\Delta x)^2} A_n(y) - \frac{i\Delta t}{4\Delta x} B_n(y), \quad (2.14) \\
2X_n &= 1 - \frac{i\Delta t}{(\Delta x)^2} A_n(y) + \frac{i\Delta t}{2} V_n(y), \quad (2.15) \\
3X_n &= \frac{i\Delta t}{2(\Delta x)^2} A_n(y) + \frac{i\Delta t}{4\Delta x} B_n(y), \quad (2.16) \\
1Y_n &= -\frac{i\Delta t}{2(\Delta x)^2} A_n(y) + \frac{i\Delta t}{4\Delta x} B_n(y), \quad (2.17) \\
2Y_n &= 1 + \frac{i\Delta t}{(\Delta x)^2} A_n(y) - \frac{i\Delta t}{2} V_n(y), \quad (2.18) \\
3Y_n &= -\frac{i\Delta t}{2(\Delta x)^2} A_n(y) - \frac{i\Delta t}{4\Delta x} B_n(y). \quad (2.19)
\end{align*}

The tridiagonal solver required for this set of linear equations is completed through LU decomposition \[48\]. Symmetries in the Hamiltonian can be accommodated through modification of the boundary points along the grid in the relevant spatial dimension: for example, cylindrical coordinates consider $\rho \in [0, R_{\text{max}}]$, requiring adaptation of the boundary condition at $\rho = 0$ to accommodate the geometry of the coordinate system. To ensure that spurious oscillations do not enter the solution during propagation, the spatial and time steps must maintain the following relationship \[49\]:

\[ \frac{\Delta t}{\Delta x^2} \leq \frac{1}{2}. \quad (2.20) \]

\subsection{Initial state calculation}

In the implementation of this propagation scheme, we immediately encounter a need to select an initial state for our system. As all studies considered in this thesis propose an atom or molecule exposed to an electric field that gradually ramps from zero intensity, a natural selection for the initial state considers the ground state of the system in a field free environment. In this subsection, we explore methods to accurately calculate an initial state.
2.1.2.1 Imaginary time propagation

Several methods exist to solve such eigenstate problems, such as matrix diagonalization [48], the random shooting method [50], or the spectral method [51]. Here, we consider implementation of imaginary time propagation (ITP) to solve for states possessing eigenenergies of successively smaller magnitudes [52]. In this process, we write an arbitrary wavefunction as a superposition of the eigenstates of the system

$$\psi(t = 0) = \sum_n c_n \psi_n(t = 0).$$  \hspace{1cm} (2.21)

We note that we can advance $\psi(t = 0)$ one step forward in time under the field free Hamiltonian as

$$\psi(t = \Delta t) = \sum_n c_n \psi_n(0)e^{-iE_n t}. \hspace{1cm} (2.22)$$

Under the ITP scheme, we consider time imaginary:

$$\psi(t = -i\Delta t) = \sum_n c_n \psi_n(0)e^{-E_n t}. \hspace{1cm} (2.23)$$

Critically, we expect ground states to be bound, and hence carry $E_n < 0$. As we continue to propagate forward in imaginary time, the expansion term with the largest $|E_n|$ will exponentially dominate the series, converging to the ground state of the system. To find the next excited state, we repeat the process, but at every time step, project out the ground state from the wavefunction using Gram-Schmidt orthogonalization:

$$\psi(t = -iN\Delta t) = \psi(t = -iN\Delta t) - \frac{\langle \psi(t = -iN\Delta t) | \psi_0 \rangle}{|\psi(t = -iN\Delta t)|^2}. \hspace{1cm} (2.24)$$

All higher-lying excited state sates can similarly be obtained through ITP and projection of lower states from the evolving wavefunction, so long as they are part of the basis of the initial expansion of $\psi(0)$ ($c_n \neq 0, \forall n$). In principle, ITP would fail to distinguish degenerate states; however, discretization of $V(r)$ on the spatial grid is often sufficient to break degeneracies. In particular, energies of $l = 0$ states are often lifted due to the softened representation of the potential: $\frac{\Delta x^2}{x}$ is the nearest point to the center of the grid considered, which removes the full character of the Coulomb singularity.
In practice, ITP is continued until $\psi(t)$ converges to threshold values of $\langle E \rangle$ and $\langle x_i \rangle$, demanding that two iterations diverge by no more than $10^{-16}$ in either quantity. This leads to excellent convergence of the wavefunction in the spatial regions for which $|\Psi|^2$ is greatest. In regions for which $|\Psi|^2$ is small, we observe that the selection of initial guess may begin to alter the final shape of the results. This behavior is examined in Fig. 2.1 for a model argon atom, which usefully possess several populated states with eigenenergies spanning two orders of magnitude. The radial wavefunction is computed in 1D, with spherically symmetry assumed. To examine the convergence dependence on time step selection or $\Delta(r)$, we consider $\Delta t = 0.0001$ and $\Delta t = 0.0003$ (both of which suit the convergence criterion of Eq. (2.20)) and demand $\Delta(r) \leq 10^{-12}$ or $10^{-16}$: this is sufficient to constrain $\langle E \rangle$ to a greater or equivalent value, as $\langle r \rangle$ will weight more strongly the contributions of the wavefunction far from the nucleus, which we expect to be the portion most difficult to converge.

In Fig. 2.1 each column shows the states yielded when different initial guesses are used. Regardless of the guess function selected, we note that the short-range structure of the wavefunctions converges in each case. In contrast, the long-range behavior does continue to exhibit non-converged behavior, particularly in the $1s$, $2s$, and $2p$ states. For example, initial selection of a flat spatial distribution, as made in the first column, preserves a spuriously flat spatial character. Even more troubling, highly nonphysical behavior can result from a non-fortuitous initial guess selection such as the one made in column 2 calculations, where $\psi(t = 0) \propto e^{-r}$ was assumed. In these cases, the wavefunction is seen to increase in magnitude for large values of $r$. To improve ITP to produce more robust solutions, we address these problems through two strategies. For an arbitrary potential, we first calculate the eigenenergies $E_n$ using an arbitrary selection of guess through ITP. In a second step, we reintroduce these eigenenergies as a new initial guess of the form $\psi(t = 0) \propto e^{E_n r}$. We also record the number of iterations used to calculate each state in the initial step, and demand that the most tightly bound state iterate over a comparable number of steps to higher-lying states. Through these strategies, we achieve the state solutions shown in the third column of Fig. 2.1. These states are shown to possess the exponential decay tails expected of atomic state solutions.
Figure 2.1: Bound states of an argon atom are calculated through imaginary time propagation with varying initial guess; the functional form of the guess is seen to substantially alter the long-range behavior of the calculated state. In the first column, the initial guess assumes a flat spatial distribution. In the second, wavefunctions are assumed to exponentially decay. In the third column, strategies are implemented to correct for the long range behavior by setting $\psi_n(t = 0) \propto e^{E_n r}$ and calculating tightly bound states for additional iterative steps. These strategies are seen to reproduce solutions that are physically well-behaved at large $r$. 

---

Radial convergence: 1e-16; dt: 0.0001
---

Radial convergence: 1e-12; dt: 0.0001

Radial convergence: 1e-12; dt: 0.0003

Radial convergence: 1e-16; dt: 0.0003
with little qualitative dependence on the values of $\langle E \rangle$ or $\langle x_i \rangle$.

### 2.1.2.2 Real time propagation

Despite the careful solution through ITP presented in the preceding section, implementation of these solutions in a real-time propagation scheme reintroduces a small quantity of numerical error associated with the transition from imaginary to real time. As shown in Fig. 2.2 for a model neon atom, this numerical error exhibits as a burst of wavefunction population departing from the grid as a function of time. The fraction of population departing is seen to vary with the time step applied, suggesting that a smaller time step could be used to control this behavior if it becomes a substantial source of computational noise. The energy of the evolving state is also seen to amplify this behavior, with deeper states contributing more departing population. In all cases, however, the magnitude of population departure is seen to decrease as a function of time, suggesting that this source of error can be well controlled by real-time propagation for a period of time prior to introduction of the laser source. The duration for which the state must be propagated depends on the magnitude of the ionization signal expected to be induced by the laser, with weaker signals demanding longer prior propagation.

Figure 2.2: Propagation of the $|2s\rangle$ state of a neon atom demonstrates the relationship between the initial loss of wavefunction from the grid and the magnitude of the time step used. ITP calculations were performed with $dt = 0.0025$.
2.1.3 Absorption methods

With propagation of the wavefunction established, and a strategy to calculate an initial state in place, one must next confront the treatment of departing portions of the wavefunctions from the spatial grid. Ionization is often a desired consequence of laser-induced electron physics: accurate record of the momentum or timing of a departing wavefunction can reveal a great deal about the underlying physics of the interaction, and interaction of a propagated wavefunction with the parent core is responsible for the useful and physically insightful phenomenon of high-order harmonic generation. One method to treat the spatial breadth of the departing wavepacket is to simply utilize a grid sized large enough to capture the entirety of the wavefunction throughout the full time propagation. However, maintaining a grid of this size can rapidly become computationally prohibitive for the long-duration and wavelength fields often used in strong-field physics scenarios. Additionally, some signals, such as HHG, consider predominantly the portion of the electron wavepacket that remains near the atomic core, motivating the consideration of only the space that is needed to converge the signal.

Propagation of the electron wavepacket on a truncated spatial grid can result in unphysical reflections of the outgoing wavepacket back toward the center of the grid, as the edge of the grid behaves effectively as an infinite potential barrier. To prevent these reflections from contributing to the signal of interest, a typical strategy is to implement a region through which a propagating wavefunction is damped, as demonstrated schematically in Fig. 2.3. This absorbing region is sized so that only an infinitesimal fraction of the departing wavefunction encounters the final edge of the grid, eliminating the problematic reflections. Care must be taken when implementing such a scheme to ensure that the absorbing strategy does not introduce additional reflections. One method which successfully accomplishes this task is exterior complex scaling (ECS), which operates by rotating the coordinate axes into complex space \[53\,55\]. This procedure converts the oscillatory behavior of continuum states into an exponentially damped function, resulting in the decay of wavefunction population in this region. We demonstrate the implementation of this procedure for the case of
Figure 2.3: A diagram of the absorbing barrier scheme is shown. A wavefunction with outgoing momentum is damped by coordinate rotation into the complex plane by angle $\eta$, reducing computational noise from barrier reflections.
cylindrical coordinates, and noting that it can be implemented straightforwardly in any coordinate geometry. To begin, we redefine the axes as

\[
  z = \begin{cases} 
    z_1 + (z - z_1)e^{i\eta}, & \text{if } z < z_1 \\
    z_2 + (z - z_2)e^{i\eta}, & \text{if } z > z_2 \\
    z & \text{otherwise}
  \end{cases}
\]  

(2.25)

where the absorbing boundaries are positioned at \( z = z_{1,2} \) and \( \eta \) is the angle of rotation with value \( 0 < \eta < \pi/2 \). In practice, so long as \( \eta \) falls within this range, the functionality of the absorber is not strongly altered; for all applications in this thesis, we consider \( \eta = \pi/3 \). In the \( \rho \) direction, we proceed similarly with

\[
  \rho = \begin{cases} 
    \rho + (\rho - \rho_1)e^{i\eta}, & \text{if } \rho < \rho_1 \\
    \rho & \text{otherwise}
  \end{cases}
\]  

(2.26)

where the behavior of the wavefunction near \( \rho = 0 \) is already constrained by the boundary conditions of the propagator, and \( \rho_1 \) sets the boundary approaching \( \rho_{\text{max}} \). Within this redefined coordinate system, we can rewrite Eq. (2.4) along either coordinate by first expressing the field-free Hamiltonian and potential terms in the complex rotated region as

\[
  \Psi(t + \Delta t) \sim e^{-\frac{i}{2} \cos(2\eta) \hat{p}_z^2} e^{-\frac{i \sin(2\eta)}{2} \hat{p}_z^2} e^{-i \text{Re}(V) \Delta t} e^{\text{Im}(V) \Delta t} \Psi(t).
\]  

(2.27)

By requiring that \( 0 < \eta < \pi/2 \), the second exponential term functions to damp the wavefunction in the boundary region, so long as \( \text{Im}(V) \geq 0 \), which is true for all real atomic and molecular potentials considered in this thesis. In the presence of a laser field, the laser interaction contributes an additional term to the time propagation operator, which we show in the \( z \) direction in the length-gauge representation as

\[
  e^{-iE(t)z\Delta t} = e^{-iE(t)(z_{1,2}+(z-z_{1,2})\exp(i\eta))\Delta t}
\]  

(2.28)

in the absorbing boundary region. Depending on the time instant considered, \( E(t) \) can take positive or negative values, and can thus act either as the damping term desired, or as a source term to amplify the magnitude of the wavefunction in the absorbing region. As the latter scenario introduces
sufficient noise into the wavefunction to overwhelm the signal of interest, it is recommended that the ECS method be implemented without rotating the electric field interaction term into the complex plane \[54, 55\]. While this step is difficult to justify formally, it is observed in numerical simulations to provide the behavior desired: absorption of the departing wavefunction using the pseudo-ECS method achieves noise levels beneath that of the popular masking function method, and is thus used in this thesis to address the departing wavefunction.

2.2 Calculation and analysis of observables

In this section, we consider the implementation of the numerical methods described in the preceding section toward the performance of numerical experiments to understand the effects of exposing atomic and molecular systems to intense laser fields. Among the signals that can be produced though interaction with intense laser fields, high-order harmonic generation is an excellent demonstration of probing system dynamics, as information regarding the state of the system can be captured during both the ionization and recombination of the electron wavepacket. In this section, we present information regarding the calculation of observables needed to compute the total HHG signal both to demonstrate the synthesis of the topics outlined in the previous section and as a foundation for further discussion of HHG in several contexts throughout the following chapters. We additionally explore theoretical tools to further analyze HHG emission that lack analogs in existing experimental technologies, acknowledging the capacity for such numerical experiments to confer additional insight into light-induced dynamics.

2.2.1 Calculation of HHG Spectra

According to the Larmor formula \[56\], which states that

\[
P = \frac{2}{3} \frac{a^2}{e^3},
\]

the power spectrum of the radiation emitted by an accelerating charge is proportional to the square of the magnitude of the acceleration. In HHG, the charge considered is dipole created by the electron
wavepacket and the parent ion \[10\]. Assuming a propagating electron wave function \(\Psi(r, t)\), the dipole moment of the electron \(d(t)\) can be recorded numerically by computing
\[
d(t) = \langle \Psi(r, t) | r | \Psi(r, t) \rangle
\] (2.30)
at each time step of the calculation. The dipole acceleration can then be computed as the second time derivative of this quantity. Alternatively, through the Ehrenfest theorem, the dipole acceleration can be conveniently obtained directly as
\[
a(t) = \langle \Psi(r, t) | -\nabla V(r) + E(t) | \Psi(r, t) \rangle.
\] (2.31)
The HHG signal is the Fourier transform of this quantity, and particularly concerns the presence of high-frequency oscillations in the dipole acceleration signal. In some cases, the contribution of \(E(t)\) is omitted from the calculation of \(a(t)\), as it would only contribute to the amplitude of the fundamental frequency in the signal.

In all calculations within this thesis, we consider a linearly-polarized electric field which is conventionally polarized in the \(z\) direction. This polarization represents the laser sources most frequently available from experiment, and also often simplifies the symmetry of the problem to a 2D cylindrical representation. With this polarization assumed, we extract the total HHG signal as the portion emitted in the \(z\) direction as
\[
P(\omega) = \left| \frac{1}{\sqrt{2\pi}} \int_0^T a_z(t)e^{-i\omega t}dt \right|^2.
\] (2.32)
Examination of this transform through integration by parts would show that \(P(\omega)\) could also be obtained by calculating the dipole or dipole velocity of the electron so long as \(P(\omega)\) is appropriately scaled by a power of \(\omega\) \[57\]. Numerical implementation of these strategies is less evidently equivalent on the discrete spatial grid, as we show in Fig. 2.4. The noise threshold of the transformed dipole is significantly greater than the dipole acceleration form, obscuring part of the high-energy structure of the signal. This noise is caused by residual population of the spatial grid through the trailing end of the laser field, which is given more weight through the factor of \(z\) in the dipole expression in comparison with the Ehrenfest dipole acceleration form. As HHG emerges
Figure 2.4: Comparing the HHG signals calculated from the dipole (red) and windowed dipole (black) forms of the transformed observable show that, on a spatial grid, the dipole moment transfers substantial noise to the computed spectrum. This noise can be remitted by adding a windowing function to the transform to damp post-field oscillations residually populating the grid, as demonstrated for two intensity cases in the case of atomic hydrogen: $3 \times 10^{14}$ Wcm$^{-2}$ (top) and $5 \times 10^{14}$ Wcm$^{-2}$ (bottom).
through the recombination of the electron wavepacket with the nuclear core at small values of $z$, this long-range weighting serves largely to obscure the signal of interest. This problem can be reduced by applying a windowing function to the dipole moment before computing the Fourier transform. However, when possible, we select to calculate the HHG spectrum through the Ehrenfest theorem to circumvent these additional steps.

Similar reasoning also applies when deciding between length and velocity gauge formulations of the problem to treat the laser interaction with the system. In this thesis, we treat propagation largely in the length gauge, which offers better convergence for problems dominated by physics occurring near the nuclear center at small values of $z$ [58]. In comparison, the velocity gauge Hamiltonian takes the form

$$\hat{H}_v(r, t) = \frac{(p - A(t))^2}{2} + V(r)$$

which provides the greatest accuracy far from the nucleus, where the electron momentum possess moderate values. This formulation is appropriate for studies focusing on electron ionization, but risks sacrificing the accuracy afforded by the length-gauge formulation in spatial regions near the nuclear center.

2.2.2 Time-frequency analysis

Experimental observations of HHG generally focus exclusively upon time-domain information (accessible through the intensity profile of attosecond pulses produced) or through the frequency-domain structures of HHG. However, gaining information about both domains simultaneously also provides useful information, as it permits the association of harmonic emission into different energy regimes with radiation at different times. Accessing this information experimentally is challenging, but analysis of numerical results allows the extraction of this information through different strategies.

The most conceptually straightforward method to obtain the frequency composition of different time intervals is to apply a windowing function to $a_z(t)$ prior to the Fourier transform. Gaussian filters are a popular choice in this context, as they suppress the signal outside of the time window
Figure 2.5: An example of a wavelet transform is shown, demonstrating the simultaneous time and frequency resolution obtained. In the top panel, schematic wavelet transforms are shown: shorter envelopes are used to transform higher frequencies. Applying this window along the duration of the signal leads to the colormap representation of harmonic emission in the lower panel. Integration across the x or y directions retrieves experimentally-measurable harmonic spectra or time-resolved intensity profiles of the emitted radiation.
of interest without introducing additional structure to the spectral signal structure. Application of a windowing function to a Fourier transform is known as short-time Fourier transform (STFT) \[59\], and modifies the conventional Fourier transform as

\[
SF(\tau, \omega) = \int_{0}^{T} a_z(t)w(t - \tau)e^{-i\omega t}dt.
\] (2.34)

The windowing function, \(w(t)\), is shifted across the signal according to the parameter \(\tau\), which specifies the width of the transform. In the case of HHG, however, the spectral composition of the \(a_z(t)\) can extend through several hundred harmonic orders of a fundamental frequency, complicating analysis using this straightforward windowing technique. Resolution of the fundamental component would require a long-duration window in comparison with frequencies in the high-energy plateau, so that any value of \(\tau\) would sacrifice resolution of potentially interesting sections of the HHG signal.

A natural correction to the windowing approach is to adjust the size of the window according to the frequency transformed, introducing a scaling proportional to the period of the signal. This is known as a continuous wavelet transform (CWT) \[60\], and is used throughout this thesis to resolve the time-dependence of frequency emergence in the HHG signal. Formally, the CWT can be obtained as

\[
C(t_0, \omega) = \frac{1}{\sqrt{2\pi}} \int_{0}^{T} a_z(t)W\left(\frac{\omega(t - t_0)}{2\pi}\right)dt,
\] (2.35)

where \(W(x) = \frac{1}{\sqrt{\pi}}\exp(2\pi ix)\exp(-x^2)\), the windowing function, is the so-called complex Morlet wavelet \[60\]. While several functional forms for the wavelet exist, the Morlet wavelet is commonly selected in the analysis of HHG as it mimics the shape of the generated radiation. An example of the wavelet transform is shown in Fig. 2.5. We additionally demonstrate the convergence of the wavelet transform to the experimentally recognizable signals of the HHG spectrum and the attosecond pulse train by integrating over the time and frequency domains, respectively.
Chapter 3

Single active electron models

Numerical studies of strong-field physics necessarily require a great deal of computational effort due to the large difference in the relevant time scales that must be modeled in the system. These studies are driven by femtosecond-duration laser pulses, but the electronic physics of interest evolves on attosecond-duration time scales. The discretization of time is thus limited by the electron dynamic time scale, but must be rendered under the full laser pulse to simulate a realistic scenario. This preexisting limitation makes it difficult to conduct simulations over a large number of spatial dimensions. For all systems larger than hydrogen, one encounters the problem of simulating the simultaneous interaction of several electrons with an external laser source. Each electron requires three dimensions of simulated motion, rapidly rendering the simulation size too large for any modern supercomputer. This is problematic not only for studies relevant to strong laser field interaction, but also to many problems in solid state physics or chemistry, where problems scale to exceedingly large numbers of electrons, and hence, dimensions.

One method to overcome this problem is limit full computational treatment to a single electron within the calculation, treating all other electrons as frozen spectators to the evolving physics [61]. When tunnel ionization dominates the physics of interest, this is a credible assumption, as only the least-bound electron is expected to respond to the laser field [62]. Consequently, the use of single active electron models has been shown to place theoretical studies of strong field induced physics in agreement with experiment, for example when studying ATI spectra of argon [63] or in the multiphoton ionization of xenon [64].
The construction of a pseudo-potential to model the single active electron behavior has been pursued through several different strategies. Among the more exact procedures is the use of density functional theory (DFT) to fully account for electronic interactions in a field-free environment [65, 66]. Using DFT, a numerical pseudo-potential is calculated through a self-consistent procedure involving the simultaneous solution of the potential and the orbital states. For convenience, single active electron models are frequently developed using analytic functions with free parameters that are fit to accurately simulate experimental behavior in the scenario of interest [67–69]. In this chapter, we pursue this strategy and develop a method to obtain analytic pseudopotential models based on physical reasoning regarding the electronic structure of an atomic system. We use these models to calculate both HHG spectra and photoionization cross-section distributions to validate the models we develop.

3.1 Single-active-electron potentials: Modeling atomic species

In this section, we discuss the development of single-active-electron (SAE) pseudopotentials for a variety of atomic systems, and examine strategies to converge these calculations.

3.1.0.1 DFT-formalism

In the Kohn-Sham DFT formulation of multielectron systems [70], one solves for each orbital involved in the ground state of the spin-polarized ($\sigma$) N-electron system by solving the following set of Schrödinger-like eigenvalue equations (in a.u.),

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff},\sigma}(r)\right]\psi_{i\sigma}^{KS}(r) = E_{i\sigma}^{KS}\psi_{i\sigma}^{KS}(r), \quad (3.1)$$

where $V_{\text{eff},\sigma}$ is the effective Kohn-Sham potential and is the sum of three contributions,

$$V_{\text{eff},\sigma}(r) = V_{\text{ext}}(r) + V_{H}(r) + V_{xc,\sigma}(r). \quad (3.2)$$

In these representations, $\rho$ is the electron density, equivalent to

$$\rho(r) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\psi_{\sigma,i}|^2. \quad (3.3)$$
\( V_{\text{ext}}(r) \) is the external potential, representing the interaction of the electron with the nuclear center possessing charge \( Z \),

\[
V_{\text{ext}}(r) = -\frac{Z}{|r|},
\]

the second term in the sum, \( V_H(r) \), is the Hartree potential term, accounting for electron-electron repulsions as

\[
V_H(r) = \int \frac{\rho(r')}{|r - r'|},
\]

and \( V_{xc,\sigma}(r) \) is the exchange-correlation potential term, found by minimizing

\[
V_{xc,\sigma} = \frac{\delta E_{xc}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma(r)}. \tag{3.6}
\]

Referring to Eq. (3.6), we note that the form of \( E_{xc} \) is not known, requiring approximation. Several popular approximations to this quantity exist. One of the most straightforward and popular approximations is the local spin-density approximation (LSDA) (or local density approximation (LDA), if spin is not relevant to the problem) \[71\]. Use of these approximations inevitably introduces spurious self-interaction contributions \[72\]. This can be seen clearly when considering a one-electron system, as \( V_{xc} \) and \( V_H \) do not cancel each other out exactly. This spurious behavior causes \( V_{xc} \) to decay exponentially with incorrect long-range behavior, leading to a \( V_{\text{eff}} \) that produces incorrect orbitals and ionization behavior.

Two methods have been proposed to correct this problem: the so-called self-interaction correction method (SIC) \[72\] and the optimized effective potential method (OEP) \[73\]. In the following, we present each and show how they can be used together to construct accurate potentials.

In SIC, the value of \( E_{xc} \) is adjusted to explicitly remove self-interactions for each orbital, proposing a new \( E_{xc}^{\text{SIC}} \) of the form

\[
E_{xc}^{\text{SIC}}[\rho_\uparrow, \rho_\downarrow] = E_{xc} - \sum_\sigma \sum_{i=1}^{N_\sigma} J[\rho_i, \sigma] + E_{xc}[\rho_i, \sigma, 0] \tag{3.7}
\]

where \( \rho_i \) is the single-particle density of each orbital. This correction is constructed to remove the single-particle exchange error, but requires different correction terms for each orbitals. The introduction of an orbital-dependent term to \( V_{\text{eff}} \) leads to orbitals which are not orthogonal,
compromising the accuracy of the solution or requiring additional work to orthogonalize these solutions.

An alternate strategy is the OEP method. As the name suggests, this technique proceeds by optimizing the form of the potential to minimize a quantity - namely, the expectation value of the total Hamiltonian, \( E[\{\psi_{i,\sigma}\}] \). This condition can be expressed as

\[
\frac{\delta E[\psi_{i,\sigma}]}{\delta V^0_\sigma(\mathbf{r})} = \sum_{i,\sigma'} \int d\mathbf{r'} \frac{\delta E}{\delta \psi^0_{i',\sigma'}(\mathbf{r'})} \frac{\delta \psi^0_{i',\sigma'}(\mathbf{r'})}{\delta V^0_\sigma(\mathbf{r})} + \text{c.c.} = 0, \tag{3.8}
\]

where \( \psi^0_{i',\sigma'}(\mathbf{r'}) \) are the eigenstates of a set of equations analogous to Eq. (3.1), in which the modified OEP potential is implemented. The OEP formalism, as initially presented, requires the inversion of Eq. (3.8) which is prohibitively computationally expensive. However, Krieger, Li, and Iafrate proposed a strategy to construct an effective potential which approximates the results of the OEP method with excellent accuracy, and requires much less computational effort (KLI) \([65]\). The reasoning behind the construction was presented both analytically and through insightful physical arguments; the latter reasoning we repeat here. We define the approximative effective potential proposed by KLI as \( V^{KLI}_{xc\sigma} \), and following the derivation of \([65]\), note that it can be represented as

\[
V^{KLI}_{xc\sigma}(\mathbf{r}) = \sum_i \frac{\rho_i(\mathbf{r})}{\rho_\sigma(\mathbf{r})} v_{xc\sigma}(\mathbf{r}) + \sum_{i \neq m} \frac{\rho_i(\mathbf{r})}{\rho_\sigma(\mathbf{r})} (\bar{V}^{KLI}_{xc\sigma} - \bar{v}_{xc\sigma}), \tag{3.9}
\]

where

\[
v_{xc\sigma}(\mathbf{r}) = \frac{\delta E_{xc}[\psi_{i\sigma}]}{\psi_{i\sigma} \delta \psi^*_\sigma}, \tag{3.10}
\]

\[
\bar{V}^{KLI}_{xc\sigma} = \langle \psi_{i\sigma} | V^{KLI}_{xc\sigma} | \psi_{i\sigma} \rangle, \tag{3.11}
\]

\[
\bar{v}_{xc\sigma} = \langle \psi_{i\sigma} | v_{xc\sigma}(\mathbf{r}) | \psi_{i\sigma} \rangle \tag{3.12}
\]

The sum over the final term in Eq. (3.9) does not extend over the highest-order orbital \((m)\), as the contribution from that orbital is expected to dominate the form of \( v_{xc\sigma} \), which will cancel with \( V^{KLI}_{xc\sigma}(\mathbf{r}) \). To solve for the difference term between Eqs. (3.11) and (3.12), a set of linear equations was proposed, taking the form

\[
\sum_{i=1}^{N_\sigma-1} (\delta_{ji} - (M_\sigma)_{ji})(V^{KLI}_{xc\sigma} - \bar{v}_{xc\sigma}) = \bar{V}^S_{xc\sigma} - \bar{v}_{xc\sigma}, \tag{3.13}
\]
where
\[(M_\sigma)_{ji} = \int \frac{\rho_j \sigma(r) \rho_i \sigma(r)}{\rho_\sigma(r)} \, dr, \tag{3.14}\]
and
\[V^{S}_{xcj\sigma} = \langle \psi_{j\sigma} | \sum_{i=1}^{N_\sigma} \frac{\rho_{i\sigma}(r) v_{xc\sigma}}{\rho_\sigma(r)} | \psi_{j\sigma} \rangle. \tag{3.15}\]

Within this formulation, as indicated in Ref. [66], we can apply OEP to select a form for the exchange-correlation term, which can be expressed as
\[v_{xc\sigma}(r) = \left( \frac{6}{\pi} \right)^{1/3} - [\rho_\sigma(r)]^{1/3} + [\rho_{i\sigma}(r)]^{1/3} - \int \frac{\rho_{i\sigma}(r')}{|r - r'|} \, dr'. \tag{3.16}\]
After solving Eq. (3.16) for a given electron density \(\rho\), the linear equations of Eq. (3.13) can be efficiently solved, ultimately yielding a solution for \(V^{KLI}_{xc\sigma}\). However, at the start of this procedure, the correct form of \(\rho_{i\sigma}(r)\) is not known. To solve for all quantities, a self-consistent procedure is needed, in which an effective potential is guessed and is used to calculate a set of eigenstate orbitals, which are then used to update the form of the effective potential. Both the orbitals and the potential are thus solved for simultaneously until a convergence criterion is met. In the case of this work, we demand that the eigenvalue of the highest occupied energy level converge to a precision of \(\Delta \langle E \rangle = 10^{-12}\). We note that the correct solution of the long-range behavior of the potential demands careful consideration regarding the orbital solution method, as detailed in Sec. 2.1.2.1. While imaginary time propagation can remain a useful and efficient method for obtaining accurate eigenstates if appropriate guesses and iteration procedures are used, the shape of the potential tail can be spuriously influenced by the behavior of the electron wavefunctions throughout the low-density regions far from the nuclear core. This is a particular danger as atomic size increases and the magnitude of \(E_{1s}\) grows, as the energy and radial expectation values will converge much more rapidly than the long-range wave function behavior. Happily, as discussed in Sec. 2.1.2.1, these problems are not insurmountable when proper care is taken.

One detail omitted from this implementation description is how to treat degeneracies between orbital levels. In this thesis, it is generally assumed that all atoms considered possess spherical symmetry, which is a reasonable approximation for smaller, closed-shell atoms. Consequently, all \(m\)
levels are treated as degenerate within the atom. To include this degeneracy within the presented formalism, one simply includes a multiplicative factor $n_{i\sigma}$ within Eq. (3.9) to accommodate the repeated expression of the $\psi_{\sigma i}$, as

$$V_{xci}^{KLI}(\mathbf{r}) = \sum_i n_{i\sigma} \rho_{i\sigma}(\mathbf{r}) v_{xci}(\mathbf{r}) + \sum_{i \neq \bar{n}} n_{i\sigma} \rho_{i\sigma}(\mathbf{r}) (\bar{V}_{xci}^{KLI} - \bar{v}_{xci}),$$

(3.17)

where $n_{|1s,\uparrow|} = 1$, $n_{|2p,\uparrow|} = 3$, and so forth.

A final consideration is how to best ensure the convergence of the self-consistent calculation. As the number of electrons in the system grows, instabilities within the system become more likely, resulting in the possible divergence of the solution. And example of such an instability when one set of orbital solutions $\psi_{n,1}$ supplies the effective potential $V_1(\mathbf{r})$; however, the eigenstates of $V_1(\mathbf{r})$ are a different set of states, $\psi_{n,2}$, which construct $V_2(\mathbf{r})$, whose own eigenstates are the original $\psi_{n,1}$. Several strategies have been considered to resolve this problem [74]. Among these, even the simplest strategy is sufficient to converge atomic systems through Kr.

We damp undesirable charge oscillations during the iterative process by mixing the set of new states with a fraction of the results of the previous iterative step. For example, if $\psi_{\text{new}}$ corresponds to the most recent $(m + 1)$ iteration of the calculation, then the next set of orbitals are constructed as

$$|\psi_{m+1,i\sigma}\rangle = (1 - \alpha) |\psi_{\text{new},i\sigma}\rangle + \alpha |\psi_{m,i\sigma}\rangle.$$

(3.18)

The value of $\alpha$ can be varied to optimize the convergence speed of the calculation. We typically find that $\alpha = 0.3$ functions well to ensure speedy solution.

### 3.2 Analytic fits to single active electron potentials

The procedure outlined in the previous section successfully produces a potential that approximates the contributions of multielectron effects in a field free environment. Such solutions have a wide range of applicability, including the many problems in strong field physics for which the response of the outermost electron to the laser field dominates the physics of interest, and
the innermost electrons can be assumed to behave as a frozen core. In practice, it is often convenient to possess an analytic approximation to the full numerical solution for the field-free potential. Such analytic fits can often succeed in reproducing experimental studies by possessing the correct long-range potential structure, which is necessary to correctly model ionization behavior [75, 76]. On the other hand, many analytic models present in the literature are not grounded in a physical representation of the short-range atomic structure. In this section, we present a new method for constructing analytic fits that is grounded in a physical understanding of the potential substructures that contribute to atomic orbital structure.

3.2.1 Proposed fitting strategy

Our motivation in the construction of physically transparent analytic fits arises from the structure of the exchange-correlation component of the full field-free potential, $V_{xc}$. As shown in Fig. 3.1 for the case of an argon atom, the slope of $V_{xc}$ varies considerably throughout the radial extent of the atom. Logarithmic scaling of the radial axis enables this subtle substructure to become more apparent. Comparison with the scaled orbital densities of the different ground-state levels of argon makes the connection between $V_{xc}$ and the location of orbital peaks increasingly transparent, as demonstrated by dashed lines connecting steeply sloped structures to the location of peaks in the wavefunction densities. Ideally, we wish to construct an analytic expression that favors the inclusion of this substructure in the functional form of the total potential.

In the past, two different elemental functions have been used to construct accurate analytic fits of noble gas atoms. Yukawa potential terms of the form

$$f(x) = \frac{a_1 \exp(-a_2 x)}{r},$$

possess a $1/r$ dependence that is damped for increasing values of $r$ through the multiplied exponential decay, and are natural physical representations for Coulombic behavior. Often, exponential decay terms ($g(x) = b_1 \exp(-b_2 r)$) are also added to analytic fit potentials to model step-like decreases in the magnitude of $V_{xc}$, such as those observed in Fig. 3.1. These functions are plotted in
Figure 3.1: The exchange-correlation term contribution to the total field-free potential (bottom) possesses a substructure that closely aligns with the density of the atomic orbitals (top).
Fig. 3.2 and will be used to design our analytic fits.

To proceed, we use the following algorithm to construct physically accurate analytic fits. We first ensure the correct long-range behavior by including one term of the form $-C_0/r$; in the case of a neutral atomic system, $C_0 = 1$; for ionic systems, this coefficient would be increased accordingly. To this term, we add one Yukawa term with the form $f(r) = -(Z - 1) \exp(-ar)/r$, where $Z$ is the value of the nuclear charge of the system. This term creates the correct short-range Coulombic behavior near the nucleus, exponentially modified to mimic shielding effects due to the inclusion of a greater number of inner orbitals with increasing radial distance. We finally add $N$ exponential decaying terms, where $N$ is the principle quantum number of the system of interest. The inclusion of these final terms permits better structural matching to $V_{xc}$. In total, the suggested analytic model has the form

$$V(r) = -\frac{1 - a_1e^{-a_2r} + a_3re^{-a_4r} + \ldots + a_{2N+1}re^{-a_{2N+2}r}}{r}.$$ (3.20)

All coefficients in this expression are determined empirically through a least-squares regression using the numerical pseudopotential as a reference. Physically insightful initial guesses can be made for the exponential decay coefficients by considering the step-like structure of $V_{xc}$. Tests of smaller atomic systems where the number of free parameters ($a_n$) is small have shown that the values of the exponentiated coefficients match the location of large changes of the slope of $V_{xc}$. Our strategy proposes the use of a function that possesses an increasing number of free parameters with increasing atomic size, which potentially complicates the construction of an accurate approximation through the least squares regression procedure. However, since the expression of this model is grounded in physical intuition for the shape of the correct potential structure, we can overcome this problem by starting the fitting algorithm in an ideal parameter space location.

Through this strategy, we have successfully constructed analytic fits for helium, neon, argon, and krypton, with coefficients tabulated in Tab. 3.1. As a first assessment of the accuracy of the analytic fits, we consider the ionization energy from each orbital of argon in Tab. 3.2. We compare the numerical value of the approximated ionization energies to those calculated from the initial
Figure 3.2: Two different functional terms are commonly used to model the electronic structure of atomic systems: the exponential decay function (orange) and the Yukawa function (blue).

Figure 3.3: A least-squares linear regression algorithm is used to fit the converged potential from a self-consistent DFT calculation to a proposed analytic function. The error accumulated through this approximation is displayed for neon and argon as a function of radial distance. The black curve represents the error from the analytic fit used in [67]; the red curve demonstrates error between the calculated potential and the fit proposed in this chapter.
Table 3.1: The tabulated coefficients used in the analytic fit described in Eq. (3.20)

<table>
<thead>
<tr>
<th></th>
<th>((Z - 1))</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(a_4)</th>
<th>(a_5)</th>
<th>(a_6)</th>
<th>(a_7)</th>
<th>(a_8)</th>
<th>(a_9)</th>
<th>(a_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.0</td>
<td>2.392</td>
<td>0.667</td>
<td>3.840</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ne</td>
<td>9.0</td>
<td>2.088</td>
<td>-5.408</td>
<td>4.158</td>
<td>1.026</td>
<td>66.33</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ar</td>
<td>17.0</td>
<td>0.8482</td>
<td>-15.372</td>
<td>1.250</td>
<td>-27.744</td>
<td>4.395</td>
<td>2.194</td>
<td>90.046</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Kr</td>
<td>35.0</td>
<td>0.791</td>
<td>-28.65</td>
<td>1.121</td>
<td>-64.83</td>
<td>3.07</td>
<td>-40.62</td>
<td>12.17</td>
<td>7.176</td>
<td>85.0</td>
</tr>
</tbody>
</table>

DFT potential. In each case the analytic fit does the best job of fitting the innermost energy levels of the atomic system. As the orbital level increases, the fit loses some accuracy due to the increasing number of approximative terms needed to model this region of the atom. We can better understand the origin of error in this model through examination of the least-squares error between analytic fits and the initial DFT potential, which we plot as a function of \(r\) in Fig. 3.3. In general, the fitting error is greatest between 0.1 – 1.0 a.u. However, in comparison with other literature fits [67] our method reduces error even in this region while converging well in the long-range regime necessary to reproduce correct ionization behavior.

3.3 Application of the analytic model

In this section, we evaluate the accuracy of the proposed analytic fits. To examine the behavior of the outermost subshell calculations under the effects of a strong-field ionization process, we begin by studying evidence of the Cooper minimum in the HHG spectrum of argon. We next evaluate the accuracy of the calculated inner-shell states by calculating the photoionization cross-section distribution for several of energy levels of neon and argon.

3.3.1 Cooper minimum

As first proposed by Cooper [77], the nodal structure of the energy-dependent dipole transitions from bound to continuum wave states allows, for certain angular momentum values, the inversion of the sign of the matrix element. This is notably the case when considering transitions
Table 3.2: The eigenenergies calculated according to the proposed analytic fit are calculated using ITP. Error is assessed by comparing the eigenenergies to those of the original DFT potential to ascertain which orbitals express the greatest degree of deviance due to the fitting used.

<table>
<thead>
<tr>
<th>Level</th>
<th>Energy (au)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-114.78</td>
<td>-1.74e-4</td>
</tr>
<tr>
<td>2s</td>
<td>-11.410</td>
<td>-4.38e-4</td>
</tr>
<tr>
<td>2p</td>
<td>-9.046</td>
<td>3.98e-4</td>
</tr>
<tr>
<td>3s</td>
<td>-1.097</td>
<td>1.09e-2</td>
</tr>
<tr>
<td>3p</td>
<td>-0.5824</td>
<td>1.08e-2</td>
</tr>
</tbody>
</table>

between $|p⟩$ bound to continuum states. For argon in particular, it was shown that the matrix element representing transitions from the $3p$ to $d$-wave states were generally several times greater than transitions to $s$-wave states, and consequently more influential in physical signatures of ionization events. Consequently, zeros in the energy-dependent transition matrix element involving the $d$-wave states result in a considerable reduction in observable signals such as photoionization.

The Cooper minimum is also evident in HHG spectra. The behavior of the recombination event mimics the photoionization behaviors of atomic systems [78]; consequently, the same suppression evident in the photoionization cross section from the $3p$ shell of Ar is visible in the HHG spectrum from the atom [79]. Through this reasoning, HHG provides a tool sensitive to internal atomic structure [80]. The incidence of suppressed photoemission also supplies a method for shaping the time profile of emitted attosecond-duration pulses [81].

As seen in Fig. 3.4, our model for argon reproduces the position of the Cooper minimum, predicted by the dashed line to occur near 47 eV [79]. We calculated this HHG spectrum considering a driving laser field of 800 nm and intensity $3 \times 10^{14}$ W cm$^{-2}$. The success of this model in the reproduction of the minimum from the HHG spectrum indicates that our proposed potential functions well to produce interesting physical phenomena in the context of strong-field numerical studies.
Figure 3.4: The HHG spectrum generated from argon using a driving field with intensity $3 \times 10^{14}$ and a wavelength of 800 nm demonstrates a minimum at 32 harmonic orders, corresponding to the predicted energetic position of the Cooper minimum of the 3p shell of argon.
3.3.2 Photoionization cross section

An alternate method to evaluate the performance of the analytic fits computed is to implement these solutions in the evaluation of photoionization cross-section distributions for atomic systems. This quantity measures the probability of observing the release of an electron after exposure to photons of different energies. The ionization probability depends sensitively on the potential structure of the system considered; consequently, evaluation of this energy-dependent quantity in comparison with established models gives a metric for the evaluation of performance.

In this section, we replicate the method of [83] to calculate the probability of ionization in each calculation. Through this method, we are capable of testing both the success of our numerical simulations and the fitting strategy to correctly reproduce ionization distributions. We calculate an effective ionization rate $\Gamma$ by propagating a wavefunction prepared in the atomic shell of interest in the presence of a laser field and for an extended duration afterward, until the quantity of wavefunction remaining on the grid converges. We define the survival probability $P_0$ as the likelihood that an electron remains in its initial state, and use this quantity to evaluate the ionization rate as

$$\Gamma = \frac{1}{T} \ln P_0(T),$$

where $T$ is the duration of the incident laser field. In practice, we calculate the value of $P_0$ as the proportion of the wavefunction that remains on our grid after numerical propagation. The photoionization cross section is related to the ionization rate through the relationship

$$\sigma = \frac{I}{\omega^2} \Gamma.$$

We verify this relationship by comparing numerical results with an analytical model for ionization from the $1s$ state of hydrogen, shown in Fig. 3.5. Very good agreement is achieved throughout the model. We do note that the high-energy tail of the distribution, throughout which little ionization occurs, is much more sensitive to numerical error than the low energy structure, which is more sensitive to the quality of the numerical fit and the duration of the post-laser propagation time.
Figure 3.5: The calculated photoionization cross-section from the 1s shell of hydrogen demonstrates the accuracy of the grid-based method for photoionization calculation used in this thesis (blue line). Results are compared to central-model calculations from [82] (red dots).
Figure 3.6: The photoionization cross-section from several subshells of single-atom neon and argon (blue line) is compared to literature values [82] (red dots).
However, as we are most interested in the fidelity of the analytic fit structure, this method remains an excellent way of testing our model.

In Fig. 3.6, we present the ionization cross sections for the $2s$ and $2p$ shells of neon, and the $2p$, $3s$, and $3p$ shells of argon. Due to the degeneracy of the $p$-state orbitals under the central potential model we use [84], we must also adjust the photoionization cross section by a geometric factor of $NC_k/N$, where $N = 6$ and $k = 2$ for $l = 1$ states [85]. Small deviations from the literature comparison data are observed at small energies; however, in each case, examination of values $> 4$ a.u. generally demonstrates very good reproduction of known data. This suggests that the analytic fit does not overly distort the structure of the exchange-correlation potential and validates these models for use in other contexts.
Detecting multiple rescatterings in high-order harmonic generation through VUV gating

In this chapter, we examine methods for detecting the involvement of multiple electron wavepacket rescatterings in the process of HHG. This phenomenon refers to the participation of an ionized electron wavepacket which revisits the parent ion multiple times, emitting radiation throughout several rescattering events. The contributions of these events to the HHG process provide an avenue to generate light pulses with sub-attosecond duration. However, their involvement within the total HHG signal is often obscured by the higher-energy recombination event of the first rescattering of the wavepacket. In the following, we implement a scheme to disentangle and control the emergence of multiple rescattering events by introducing a second laser pulse tuned to a transition within the target atom.

Within the framework of this process, the relative delay between the principal driving electric field and the ionization-gating VUV-frequency pulse can be controlled. Altering the time delay between the pulses reveals signatures of the variant presence and absence of multiple rescattering events in both the spectral and time-domain signals.

By gating the moment of ionization through the application of the additional light, we demonstrate the selective release of electrons into trajectories which revisit the parent nucleus several times and examine the single-atom signatures of multiple rescatterings in both the temporal and

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\(^{0}\) Results presented in this chapter are also published in M.R. Miller, C. Hernandez-Garcia, A. Jaron-Becker and A. Becker, "Targeting multiple rescatterings through VUV-controlled high-harmonic generation," Physical Review A 90, 053409 (2014).
frequency domains of the generated radiation. We additionally analyze a way of employing this technique to advance the frontier of ultrashort light pulse production through the use of two VUV pulses.

4.1 Introduction

Recent experiments have investigated driving HHG with midinfrared light, and thus extending the harmonic plateau to keV energies [25]. At these longer wavelengths, it has been proposed that electrons which rescatter multiple times from a parent ion play an important role [86], and furthermore may open a way of producing zeptosecond waveforms [87]. However, detection and resolution of light on the zeptosecond time scale as a route to confirm the presence of these multiple rescattering events poses a challenge to current experimental techniques.

As shown previously, interrogation of the process of HHG production can be achieved through the application of a second color of light to the traditional three-step model of HHG [7, 8] (c.f., Fig. 4.1a)). Through use of an attosecond pulse train, the excursion distance of an electron wave packet (whether it follows a long or short trajectory to recombine with a specific energy) may be controlled [88, 89]. In the form of an isolated pulse or as an attosecond pulse train, this additional light has been theorized [90, 91] and experimentally demonstrated [92, 93] to enhance the HHG signal. Attosecond pulse trains have been used to replace tunnel ionization entirely as a mechanism for electron release, inducing HHG even when the driving laser field strength is insufficient to allow tunnel ionization [94]. And isolated pulses have been studied as a means to filter for and to resolve short and long trajectories on a single-atom scale [95, 96].

We build upon these schemes to present a method for verifying the existence of multiple rescatterings through the control afforded by using an isolated pulse of VUV light. We proceed by first outlining the scheme used to obtain this control. Through classical analysis of the electron behavior following ionization, we show our capacity to selectively release electrons into trajectories which revisit the parent nucleus multiple times. Comparison of the predictions of this simple model to the full numerical calculation validates the control mechanism used. We next proceed
to demonstrate single-atom signatures of the multiple rescatterings in both the spectral and time-
domain signals produced by our calculations by manipulating the electron wavepacket behavior
through modifications in the time-delay between the two laser fields. We conclude by applying this
technique to gate the release of two separate rescattering wavepackets to explore a way of using
this technique to advance the frontier of ultrashort light pulse production.

4.2 VUV-controlled HHG scheme

In this section we discuss the application of a control scheme based on the gating of electron
emission to induce single versus multiple rescattering events. In addition, we present the methods
used for the implementation of the scheme in numerical calculations.

4.2.1 Concept

Based on proposals in previous works [88–96], we assert control over the HHG yielded from
our system by adding a VUV pulse to modify the traditional HHG process (Fig. 4.1(a)). The target
atom, prepared in its ground state, is exposed to an intense infrared (IR) driving laser field. The
intensity of this field is tuned to be insufficient for depletion of population from the ground state.
An isolated ultrashort VUV light pulse is introduced at a controlled delay time with respect to the
IR field, transferring population into excited states that can be depleted by the driving laser. Thus,
the transferred population rapidly transitions into the continuum and is propagated in the laser
field until recombining with the parent ion and emitting the HHG. In this framework, the time of
ionization is gated by the application of the VUV field, so that the time of ionization becomes an
accessible and controllable quantity.

The importance of the time of ionization to the multiple rescattering process is readily un-
derstood by considering the classical propagation of an electron in a driving laser field [7]. In Fig.
4.1(b), we consider ionization times throughout one half cycle of the driving field. For each ioniza-
tion time considered, we then calculate all times of subsequent crossings of zero position. Three
separate regimes are evident: (i) an interval of time delays for which no rescattering trajectories are
Figure 4.1: (a) Schematic of the VUV-controlled HHG scheme, in which the moment of ionization is induced by transferring population into excited states using a VUV pulse. Mapping classical predictions of the electron ionization time to return times (b) suggests that multiple rescattering trajectories can be selectively produced in this way.
evident, (ii) a second interval generating electrons that rescatter multiple times, and (iii) a third interval of trajectories that will only revisit the parent ion once. Thus, the mediation of ionization via the VUV pulse should lead to control over the production of multiple rescattering trajectories.

4.2.2 Calculation methods

To verify the predictions of the simple classical model, we solve the time-dependent Schrödinger equation (TDSE) for the interaction between a single atom with an external electric field, expressed in Hartree atomic units \((e = \hbar = m = 1)\) as

\[
i \frac{\partial \Psi(z, \rho; t)}{\partial t} = [H_0(z, \rho) + V_L(t)]\Psi(z, \rho; t),
\]

where \(H_0\) is the field-free Hamiltonian with an effective potential for the helium atom \([67]\) and \(V(t) = z[E_{IR}(t) + E_{VUV}(t + t_d)]\), where \(E(t) = E_0 \cos(\omega t) \cos^2(\pi t/\tau)\) for both the IR and VUV fields. In order to retain 2D cylindrical symmetry, we have chosen the linear polarization directions of both the IR and the VUV fields to be parallel. The results of this chapter consider a ten-cycle (full temporal duration, \(\tau_{IR}\)) IR driving field with peak intensity \(I_{IR,0} = |E_{IR,0}|^2 = 1 \times 10^{14} \text{ W cm}^{-2}\) and \(\omega_{IR} = 0.0253\) (wavelength: 1800 nm). At a delay \(t_d\), a five-cycle VUV field of intensity \(I_{VUV,0} = 1 \times 10^{12} \text{ W cm}^{-2}\) is applied. The frequency is chosen to match the energy gap between the ground and the lowest excited state and, hence, would depend on the target atom: for the model He atom explored here, we choose the 33rd harmonic of the 1800 nm driving field. Throughout the following discussion, time will be considered in units of field cycles of the driving field, with \(t = 0\) defined at 4.75 field cycles to coincide with a local driving field maximum. We have chosen this reference point in time as we will apply the gating VUV pulse either immediately before or after this field maximum to produce an effectively rescattering wavepacket with different trajectory components.

We have solved the TDSE numerically by using the Crank-Nicholson method on a grid for which \(z\) spans from -200 to 200 au and \(\rho\) from 0 to 100 au. An absorbing boundary was placed at \(z = \pm 180\) au and at \(\rho = 90\) au using the exterior complex scaling method \([53, 55, 97]\) as described.
in Sec. 2.1.3. The size of this grid, in comparison with the maximum quiver radius of the electron wavepacket in the IR field of 83.4 au, is sufficient to achieve convergence of results. The points were spaced evenly with \( \Delta z = 0.1, \Delta \rho = 0.2, \) and \( dt = 0.01 \text{ a.u.} \)

At each time step, we use the updated wavefunction to obtain the dipole acceleration \( d_{\alpha_z}(t) \) of the electron. We can analyze the frequency composition of this observable through calculation of the total HHG radiation spectrum as discussed in Sec. 2.2

\[
P(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^T d_{\alpha_z}(t) e^{-i\omega t} dt^2.
\] (4.2)

Alternatively, we can perform a time-frequency analysis to access time-dependent frequency emission by transforming the dipole acceleration using the continuous wavelet analysis

\[
C(t_0, \omega) = \frac{1}{\sqrt{2\pi}} \int_0^T d_{\alpha_z}(t) W \left( \frac{\omega(t - t_0)}{2\pi} \right) dt,
\] (4.3)

where \( W(x) = \frac{1}{\sqrt{\pi}} \exp(2\pi i x) \exp(-x^2) \) is the complex Morlet wavelet.

To extract the time-domain profile of the emitted radiation consisting of customized frequency components, we use the inverse Fourier transform over the desired range of frequencies. This method is used to approximate the attosecond pulse profile resulting from HHG.

### 4.2.3 Validation of control scheme

To establish our capacity to observe and control multiple rescattering events in HHG we have solved the TDSE for delay times positioning the VUV field throughout one representative half-cycle of the driving laser field. In Fig. 4.2 we show a colormap image of all yielded HHG spectra. Within this figure, a transition between two distinct regimes of behavior can be observed. Zooming in on a small region of times in the lower panel demonstrates a transition between two regimes of behavior. Placing the VUV field before the driving field cycle maximum, the high-energy plateau structure features a deep interference structure. As the VUV field is placed after the maximum at progressively more positive delay values, this interference structure disappears, and the highest energy emitted decreases rapidly. The evolution of the plateau cut-off energy is readily explained
Figure 4.2: The transitioning behavior in HHG spectra prior to and following a maximum of the IR field suggests ionization gating as means of manipulating electron trajectory selection. The top panel demonstrates a sample IR field, with a highlight blue region corresponding to calculations reported in the bottom panel. Two separate types of spectra are induced by VUV placement at the black dashed lines, marked in both the top and bottom panels for reference.
by the positioning of the VUV field and serves as an initial numerical validation of our control scheme: maximum HHG energies are generated near the field maximum. Excluding the contributing ionization times by introducing the VUV field 0.03 field cycles following the electric field peak forbids the efficient production of these energies in the total spectrum. To better understand the modulation of the plateau interference structure and its relation to multiple rescattering events, we can examine the time-frequency analysis of the dipole acceleration for representative cases from each behavioral regime.

4.2.4 Wavelet analysis

In Fig. 4.3(a), the VUV pulse is applied prior to the local maximum of the driving field, at \( t_d = -0.065 \) field cycles. The wavelet analysis demonstrates a clear signature of multiple reencounters of the wavepacket via the emission of harmonics at every half field cycle subsequent to the initial rescattering. Note that the multiple rescatterings occur despite the application of the VUV pulse at a time preceding the corresponding interval in our classical analysis (Fig. 4.1(b)). This is due to the finite width of the VUV pulse and the dispersion of the wavepacket during propagation. The results show that the harmonic emission occurs with similar efficiency at each event. The classically predicted energies of each rescattering event, calculated using ionization times spanning the peak of the VUV field to the subsequent zero of the IR field, are superimposed (black circles) and match well with the results of the quantum mechanical calculation.

These results are contrasted to those in Fig. 4.3(b), in which the peak of the VUV field is placed at \( t_d = 0.129 \) field cycles, i.e. after the local field maximum. The dominant contribution to the harmonic emission is observed at the first rescattering event, near \( t = 0.5 \) optical cycles, without any further significant emission at later times. This is again in agreement with expectations inferred from the classical model, associating this single rescattering event to the recombination of short trajectory electrons. We note as well the participation of these short trajectory events in the previous case of multiple rescatterings: no matter the choice of \( t_d \), sufficient population remains excited through the peak of the driving laser field to generate short trajectory events. This shows
Figure 4.3: Wavelet analysis of the electron dipole acceleration for application of the VUV pulse at $t_d = -0.065$ (a) and $t_d = 0.129$ (b) field cycles (see inset). Superimposed black circles represent the results of a classical simulation which considers ionization times beginning at the peak of the VUV field and ending at the subsequent zero of the driving field. The presence of several rescattering events in (a) as compared to the single event in (b) shows the desired control. Recombination energies in (b) exceeding the classically predicted energy are attributed to ionization preceding the VUV field maximum.
that the present scheme allows the isolation of short trajectory events, but not long trajectory events, by choosing an appropriate value of $t_d$. Nonetheless, our numerical results clearly confirm that selective control over the appearance of multiple rescatterings can be achieved through the excitation of the atom via an ultrashort VUV pulse.

4.3 Spectral signatures of multiple rescatterings

In this section, we apply the validated control scheme to characterize the role of multiple rescatterings in structuring the emitted HHG spectrum and the attosecond pulse train. We proceed by analyzing these observables for the two cases presented in the time-frequency analysis in the previous section to disentangle the influence of one rescattering event from the involvement of many rescatterings by the same electron wavepacket.

4.3.1 High-order harmonic generation

Evidence of the multiple rescatterings is present both in the frequency and time domains of the radiated signal (Fig. 4.4). The HHG spectrum in Fig. 4.4(a) ($t_d = -0.065$ field cycles) shows a plateau step structure characteristic of multiple rescattering events. The highest harmonic orders (> 110th) are generated in the first rescattering event only ($0.5 < t < 1.0$ field cycles in Fig. 4.3(a)). The structure in this part of the spectrum results from interference between the so-called short- and long-trajectory contributions. At lower harmonic orders, the HHG spectrum grows in magnitude due to the yields from additional rescattering events and also in complexity due to interferences between events. Both the first and third reencounters of the wavepacket increase yield into energies between 95 – 110 harmonic orders. Between 70 – 95 harmonic orders, emission from the first, second, and third rescattering events is present, and so, again, the overall yield is seen to increase, comprising another subplateau. Emission of harmonics below the 70th harmonic order occurs throughout all rescattering events, and thus constitutes another final increase in the overall harmonic yield.

In contrast, for a single rescattering event the resultant HHG plateau shows little interference
Figure 4.4: Harmonic spectra for $t_d = -0.065$ (left) and $t_d = 0.1$ (right). Dashed lines in (a) mark the classically predicted maximum rescattering energies of the first, second, and third events, between which individual subplateaus appear (depicted on linear scale in subpanels). In contrast, (b) lacks subplateaus due to the dominant contribution of an isolated rescattering event. Subpanels, presented on a linear scale, are given in the same arbitrary units as the main panels, scaled by $10^{-6}$ to match those of panels (a) and (b).
structure (Fig. 4.4(b)), as photons at each harmonic order are emitted at only one time instant (see Fig. 4.3(b)). Furthermore, there is no evidence of subplateaus throughout the plateau. From this, we conclude that the appearance of subplateaus within the HHG plateau may be used to experimentally identify the presence or absence of multiple rescattering events as the VUV delay time is changed.

4.3.2 Attosecond pulse generation

The existence of multiple rescattering events is further evidenced by examining harmonic emission in the time domain. In Fig. 4.5, we consider the temporal signature of multiple rescatterings induced by placing the VUV field at $t_d = -0.065$. By considering each of the subplateaus identified in Fig. 4.4, we connect the appearance of individual pulses within the full pulse train (Fig. 4.5(d)) to separate rescattering events. Beginning in Fig. 4.5(a), we select energies contributing only to the highest-energy subplateau. As indicated by Fig. 4.3(a), these energies contribute exclusively to the first rescattering of the electron wavepacket, and thus lead to the formation of an isolated attosecond pulse located between $0.5 - 1.0$ field cycles in Fig. 4.5(a). Similar examination of the next subplateau with energies spanning 100-115 harmonic orders leads to the appearance of a new pulse between $1.5 - 2.0$ field cycles, representing the participation of the third rescattering event. Likewise, transformation of energies between $75 - 100$ harmonic orders constructs an additional pulse between $1.0 - 1.5$ field cycles due to yield from the second rescattering event. The full temporal picture of the HHG spectrum, considered in Fig. 4.5(d), thus forms an attosecond pulse train which can be used as a clear signature of multiple rescatterings in the temporal domain.

In Fig. 4.6, we consider instead the temporal signature of an electron wavepacket which rescatters by centering the VUV field at $t_d = 0.1$ field cycles. Considering the same energy ranges as in the previous analysis in Figs. 4.6(a)-(c), we construct in each case an isolated attosecond pulse occurring between $0.5 - 1.0$ field cycles. The suppression of radiation outside of this time interval is caused by the elimination of high-order rescattering events, so that each energy regime receives yield only during the first rescattering. The temporal width and position of the pulse is related
Figure 4.5: Attosecond pulse formation for $t_d = -0.065$, constructed by transforming energies corresponding to each of the subplateaus distinguished in Fig. 4.4: in (a), 115 – 180 harmonic orders; in (b), 100 – 115 harmonic orders; in (c), 75 – 100 harmonic orders; and in (d), 75 – 180 harmonic orders, comprising the full HHG plateau. The inset figure is reproduced from Fig. 4.4(a), with shaded regions corresponding to the energies considered.
Figure 4.6: Attosecond pulse formation for $t_d = 0.1$, with subpanels considering transformations of the same energy values as Fig. 4.5. Each subpanel reproduces an isolated attosecond pulse corresponding to the single emission event allowed by the placement of the VUV field. The inset figure is reproduced from Fig. 4.4(b).
to, and thus varies with, the time of emission of the energies it contains. Consequently, the pulse containing the largest bandwidth (corresponding to the longest time interval of emission) has the greatest temporal width. This feature is most evident in Fig. 4.6(d), for which transformation of the complete HHG temporal signal shown in Fig. 4.6(d) is an isolated attosecond pulse.

### 4.4 Dependence on driving laser wavelength

We now examine how the control strategy generalizes for the resolution of multiple rescattering events using different driving field wavelengths. In Fig. 4.7 we consider driving HHG using wavelengths of 0.8, 1.2, and 2 $\mu$m. In each case, the VUV field is centered at $t_d = -0.08$ field cycles, before the local field maxima and consequently gating for multiple rescattering events. The duration of this pulse is scaled to persist for the same fraction of a field cycle for each driving wavelength to liberate electrons that follow similar trajectories in each case. We also consider an increased field intensity of $2.5 \times 10^{14}$ W/cm$^2$, which remains weak enough to suppress significant ionization from the ground state relative to the population transferred by the VUV field.

The time-frequency analyses performed in Fig. 4.7 demonstrates that multiple rescattering events are generated similarly in each case. In the conventional generation of HHG, including the release of electron wavepackets at every half field cycle, short driving wavelengths pose a particular challenge for multiple rescattering resolution due to the decreased energy separation between coincident rescattering events. As the present control scheme enables the isolated release of a single electron wavepacket, it is possible to resolve each rescattering event in the wavelet analysis (upper row), even at the shortest driving wavelength. This clearly corresponds to the separation of each rescattering event in the temporal domain, as seen in the second row of Fig. 4.7. Here, for each wavelength, we observe the formation of well-defined attosecond pulse trains, where each pulse within the train again corresponds to a different rescattering order.
Figure 4.7: In the first column, the time-frequency analysis of the HHG spectrum driven by the combination of an IR laser pulse (intensity $2.5 \times 10^{14}$ W/cm$^2$) and a VUV field: in the first row, 0.8 $\mu$m (9.6 fs FWHM) IR and 6 cycles full width (392 as FWHM) VUV; in the second row, 1.2 $\mu$m (14.4 fs FWHM) IR and 9 cycles (589 as FWHM) VUV; in the third row, 2 $\mu$m (24 fs FWHM) IR and 15 cycles (981 as FWHM) VUV. In each case, the VUV field is centered at -0.08 field cycles. In the second column, the temporal profile of harmonics with energies exceeding 2.2 au is shown for each driving wavelength.
Figure 4.8: (a) Time evolution of the frequency emission due to the application of two VUV pulses at $t_d = -0.53$ and $t_d = -0.03$ field cycles. Superimposed are classical predictions induced by the first (black circles) and the second (white circles) VUV pulse. The harmonic spectrum (b) is structurally similar to the case of multiple rescatterings shown in Fig. 4.4 (a), but exhibits additional interference. The intensity profile of the radiation is shown in (c), in which every element of the attosecond pulse train with the exception of the first demonstrates a substructure beating; (d) examines this substructure between 0.5 and 1.0 field cycles.
4.5 Production of ultrashort light pulses with two VUV fields

Finally, we examine the possibility of applying more than one VUV pulse to yield ultrashort light pulses. To investigate this scenario, we apply two isolated VUV pulses of same peak intensity and wavelength at delay times spaced one half cycle of the driving 1.8 µm IR field apart in time, at $t_d = -0.53$ and $t_d = -0.03$ field cycles. The wavelet analysis of the resulting dipole acceleration in Fig. 4.8(a) demonstrates two separate sets of multiple rescattering events in agreement with the classical predictions for ionization induced at each of these delay times. Reencounters of the wavepackets with the parent ion occur simultaneously for times following 0.5 field cycles. However, the energies emitted by the respective wavepackets are distinct at each event. Evidence of two multiple rescattering wavepackets is contained within the resulting harmonic signal of Fig. 4.8(b). Subplateaus are evident, substantiating multiple revisitations; however, we further note another signature of the presence of two rescattering wavepackets, namely that even harmonic orders are now emitted even throughout the highest energies of the plateau. Instances of coincident rescatterings are apparent in the temporal structure of the emitted radiation as well, shown in Fig. 4.8(c) for harmonics in excess of the 75th order. The pulse train profile, characteristic of multiple rescatterings, is now modulated by a rapidly beating substructure for all but the first pulse of the train. In the second pulse, shown in Fig. 4.8(d), this beating occurs with a period of $\tau \approx 3.0$ au, corresponding to an energy of 80 harmonic orders of the driving field which matches the classically predicted energy difference between photons emitted by simultaneously rescattering wavepackets. This difference is proportional to the ponderomotive energy, $U_p$, so that increasing either the wavelength or intensity of the driving field will decrease $\tau$.

4.6 Summary

We have demonstrated the use of isolated attosecond VUV pulses to target the formation and detection of multiple rescattering trajectories on the single atom level. Informed by a classical intuition for HHG, we anticipated that an ionized electron wavepacket to exhibit at least one of the
following behaviors: propagation away from an atomic (or molecular) source without subsequent return or radiation yield; propagation followed by a single revisitation; or multiple (two or more) rescattering events. Numerical solution of the TDSE using a VUV laser field to control the moment of ionization validated this understanding and enabled us to select preferentially for an electron wavepacket that revisited the target atom multiple times.

Gating the moment of ionization with this VUV pulse has thus been shown to provide conclusive signatures of multiple rescatterings both in the frequency and time domains through structural modifications of these respective signals. The capacity for VUV laser pulse gating to yield these distinguishing features was shown to generalize to a wide range of driving field wavelengths, enabling detection of multiple rescatterings in contexts where the energy separation between coincident rescattering events from different electron wavepackets is ordinarily challengingly small. Furthermore, the capacity to target multiple wavepacket rescatterings in the HHG process may allow for their further use as experimental tools; for example, in the production of ultrashort laser pulses.
As discussed in Sec. 1.4, the response of molecules to a strong electric field is complicated beyond the atomic picture by the addition of rotational and vibrational degrees of freedom, a multi-center nuclear frame, and a more complex electronic energy level structure. In particular, strong field ionization and fragmentation from molecular targets can be significantly altered from expectations informed by quasi-static or cycle-averaged formulations of electron dynamics. The proximity of energetic states and the large dipole moments induced by the greater spatial extent of the system can result in an enhancement of multi-electron effects and induce nonadiabatic electron motion in response to the external field [28, 34, 35].

In this chapter, we focus on one example of electronic response beyond the conventional quasi-static model: the transition from an adiabatic to a nonadiabatic electron dynamic in the presence of an oscillating external field. This nonadiabatic motion frequently consists either of electron flux in opposition of the induced gradient of the electric field accompanied by enhanced ionization, or represents induced localization of the electron density. While these behaviors are frequently encountered in multi-electron systems, similar signatures of nonadiabatic dynamics arise in single electron molecules as well. We consequently explore nonadiabatic enhanced ionization and transient electron localization behaviors in the hydrogen molecular ion (H$_2^+$) as a simple and representative model. The reduced number of spatial dimensions needed to represent this system makes it highly amenable to theoretical treatment in contrast to larger molecular targets. Numerically, H$_2^+$ is fully treatable from \textit{ab-initio} principles; in addition, the predominant participation of the ground
(|g⟩) and first excited state (|u⟩) when driven by strong near- and mid-infrared (IR) laser pulses permits rigorous theoretical treatment. As we review, previous numerical and theoretical studies have indicated that transient electron localization modifies fragmentation patterns in dissociating molecules and photoelectron momentum distributions. Motivated by these studies and by our understanding regarding the importance of tunnel ionization to the generation of HHG, we complete in this chapter a comprehensive study of the methods in which transient localization modifies the amplitude and phase of radiation emitted from \(H_2^+\). We show that these findings are robust under experimental conditions, and explore how such nonadiabatic dynamics contributes to the shaping and spectral content of attosecond pulses. Understanding the intramolecular electron dynamics induced by strong laser fields is necessary to further use strong laser fields as a probe of electronic structure; simultaneously, knowledge of ongoing electron dynamics can be used to shape or customize the attosecond pulses that emerge from HHG.

### 5.1 Transient electron localization

Studying the simplest molecule \(H_2^+\) offers the opportunity to focus upon the spectroscopic signatures of nonadiabatic dynamics, disentangled from multi-electron effects. In this system, nonadiabatic dynamics occurs due to the near degeneracy of the \(|g⟩\) and \(|u⟩\) states of \(H_2^+\) at extended internuclear distances.

Instants of maximal spatial localization are predicted to satisfy \[^{41}\]

\[
t_{\text{loc}} = \frac{1}{2\pi} \arccos \left( -\frac{\omega (m\pi + \chi)}{2E_0 \langle g | z | u \rangle} \right) - \phi, \tag{5.1}
\]

where \(\chi\) is a mixing angle between Floquet states reducing to \(|g⟩\) and \(|u⟩\) at zero field intensity (for a system prepared initially in its ground state, \(\chi = 0\)), \(m\) is an integer satisfying \(m \in \mathbb{Z}\), and assuming a driving electric field \(E(t) = E_0 \sin(\omega t + \phi)\). Eq. (5.1) shows that the number of incidences of localization per laser cycle can be increased by using a laser source with higher intensity or longer wavelength. To begin, we focus upon controlling the nonadiabatic dynamic induced by modifying the wavelength of the driving field used. This progression is demonstrated in Fig. 5.1.
Figure 5.1: The wavelength dependence of nonadiabatic electron dynamics is demonstrated by considering the distribution of electron density and the intranuclear electron wavefunction phase difference.
In the top row of Fig. 5.1, the \( \rho \)-integrated electron density is shown on a logarithmic scale for three different wavelengths, each of which incites a different number of localizations per half cycle of the driving laser field. The electron dynamics throughout one cycle of the laser field are shown during the center of the pulse, when the induced nonadiabatic electron dynamics are most pronounced. On a logarithmic scale, intermittent interruptions of electron wavepacket ionization are evident when examining the distribution of the electron wavepacket near \( z = 10 \) for ionization in the positive direction, and then \( z = -10 \) for ionization departing toward the negative direction.

In the second row, electron density is plotted on a linear scale to show increasing numbers of transient localization events with increasing wavelength. This behavior is evident when studying the population localized near the nuclear centers at \( z = \pm 3.5 \) which becomes increasingly modulated at longer wavelengths. Integrating along the \( z \) axis and considering the electron population of the \( z > 0 \) portion of the spatial grid in the third row further clarifies the evolving dynamic: increasing the driving wavelength also augments the nonadiabatic character of the electron dynamic by adding additional localization events.

The nonadiabatic dynamics is closely related to the evolving phase difference between the electron wavefunction centered upon each of the two protons in \( \text{H}_2^+ \)

\[
\alpha = \arg(\Psi_+) - \arg(\Psi_-),
\]

where \( \arg(\Psi_i) \) represents the phase of the wavefunction at the grid point located nearest to the proton on the positive or negative sides of the grid, respectively. As shown in the fourth row of Fig. 5.1(c), at instants when \( \alpha = 0 \), the electron is localized upon the upper potential well within the molecule, opposite the direction of ionization. Identifying \( \alpha(t) = 0 \) thus reveals the moments when the ionization of the electron is suppressed. As shown in the fourth row of Fig. 5.1, the number of these instances increases rapidly with wavelength.

5.2 Observations of nonadiabatic electron dynamics in \( \text{H}_2^+ \)

---

A variety of studies have focused upon identifying and quantifying signatures of transient electron localization in experimental observables by inducing a nonadiabatic response in \( \text{H}_2^+ \). In addition to characterizing the nonadiabatic behavior of the electron, we note that studies performed regarding the physically simple system of \( \text{H}_2^+ \) are a useful method to distinguish signatures of electron localization from different forms of nonadiabaticity arising from many-body mechanisms. In addition, these studies provide a foundation to observe dynamics occurring on the attosecond scale, positioning such methods at the forefront of attosecond science. In the following subsections, we review several of these techniques.

5.2.1 Photoelectron momentum distributions

Ionization of atomic and molecular systems using circularly or elliptically polarized light can be used to extract timing information regarding the ionization event [99]. According to a quasi-static picture of ionization, ionization is expected to peak when the electric field is strongest. When using elliptically polarized light to investigate atomic targets, this affords maximal ionization along major polarization axis. For diatomic molecular systems, circularly polarized light similarly ionizes most efficiently along the molecular symmetry axis. In each case, the photoelectron momentum distribution (PMD) can be collected and analyzed to reconstruct the momentum with which photoelectrons were released, indicative of the electric field present during ionization. Coincidence measurements of the times of flight and positions of both the electron and protons enable the reconstruction of the internuclear distance at the time of ionization as well. In the particular case of \( \text{H}_2^+ \), for which the nonadiabatic electron dynamics expected are sensitive to the internuclear distance of the molecule, this enables an analysis that connects the transient electron localization to modifications of the ionization signal.

This procedure has been theoretically and experimentally studied as a means to image the bursts of ionization that emerge during transient electron localization. As these ionization events no longer coincide directly with the peak of the interacting electric field, the PMD is expected to rotate in momentum space, corresponding to a delay in the timing of peak ionization. This effect
Figure 5.2: Rotation of the PMD due to nonadiabatic dynamics that shift the timing of ionization. In (a), the experimental PMD from H$_2^+$ is shown integrated over the internuclear coordinate and $p_z$ directions. In (b), experimental results (blue circles) and TDSE predictions (red squares) for the angular displacement of the PMD is shown in comparison with the quasi-static ionization prediction (dashed line). The results of further theoretical studies in (c) indicate that the angular displacement of the PMD of H$_2^+$ (solid black line) is sensitive to the wavelength of the driving field used due to transient electron localization, in contrast to adiabatically responsive atomic hydrogen (red dashed line). Panels (a), (b) from [100]; panel (c) from [101].
was measured in [100], and is shown in Fig. 5.2. Additional comparisons to simulations using the 2D time-dependent Schrödinger equation (TDSE) and predictions from quasi-static ionization were performed in this study. The dependence of the experimental results and respective theoretical predictions upon internuclear distance is compared in Fig. 5.2(b). The simple formulation of quasi-static ionization of a molecular target by a circularly polarized field yields a constant angular distribution, in contrast to the internuclear distance-dependent experimental results and numerical calculations. The numerical prediction approximates the response of H$_2^+$ in the experimental system, suggesting that the inclusion of nonadiabatic electron behavior is critical to accurately reproduce photoionization behavior in H$_2^+$.

Further theoretical studies investigated the departure of PMDs from the quasi-static tunnel ionization model and found that the long-range Coulomb interaction plays an essential role in determining the angular distribution of both atomic and molecular PMDs. In [101], numerical calculations were completed using a screened Coulomb potential, with a cut-off implemented at different radial distances. Extending the interaction range of the Coulomb potential introduced a drift angle $\theta$ into the final distribution of H$_2^+$ ionized by circularly polarized light and atomic hydrogen ionized by elliptically polarized light. The behavior of this feature when the wavelength of the ionizing field varied was also investigated for a laser with intensity $6 \times 10^{13}$ W cm$^{-2}$, the results for which are reproduced in Fig. 5.2(c). In these results, hydrogen (red dashed line) serves as a reference of adiabatic behavior: as wavelength is increased, the drift angle monotonically decreases due to an increasing excursion distance from the parent ion. In contrast, the drift angle accumulated in the PMD of H$_2^+$ is nonmonotonic, which is connected to fluctuations in the timing of peak ionization depending on the wavelength of the laser source used. Transient electron localization determines the moment at which the electron is most localized upon the uphill well of the H$_2^+$, from which ionization occurs, influencing the appearance of the resultant PMD.
5.2.2 Control over fragmentation

The formation and breakage of molecular bonds during chemical reactions is mediated by the correlated motion of electrons and nuclei: controlling electron motion can thus be seen as a means to control chemical reactions. The development of strong field lasers with subfemtosecond duration made it feasible to image a variety of fundamental processes relevant to the electronic dynamics exhibited by a system undergoing a chemical reaction, such as dissociation. Dissociating molecules undergo complex electronic behavior rendering a full understanding of the process difficult to obtain. Consequently, theoretical studies regarding \( \text{H}_2^+ \) serve as an important prototype for the complex dynamics expected by incorporating additional bodies or degrees of freedom to the system.

Even in the relatively simple case of \( \text{H}_2^+ \), however, the final dissociation probability is complicated considerably by ongoing transient localization of the electron wavefunction in response to driving the dissociation by a strong laser field. In Fig. 5.3 the modification of the final electron distribution can be seen to be influenced strongly by laser intensity, and correspondingly by the induced nonadiabatic electron dynamics. Based on numerical calculations involving 2D electron motion and an additional nuclear degree of freedom \[102\], driving \( \text{H}_2^+ \) with the same laser profile (wavelength, envelope, and number of cycles) while changing the intensity of the field afforded control over the relative population of the two dissociated nuclei. In this study, an initial UV field was introduced to populate the dissociating \( 2p\sigma_u \) state from the molecular ion prepared in the non-dissociating \( 1s\sigma_g \) state; the total dissociating wavepacket was extracted through projection onto \( 2p\sigma_u \), and subsequently integrated over positive and negative space in the laser polarization direction to evaluate the relative probabilities of occupying either nucleus during and following interaction with an 800 nm laser field.

For the pulse profile depicted in Fig. 5.3(a), the results of driving with three different intensities are shown in Fig. 5.3(b-d). Transitioning from a field intensity of \( 3 \times 10^{12} \) W cm\(^{-2} \) (b) to the moderately more intense case of \( 2 \times 10^{13} \) W cm\(^{-2} \) (c) reverses the ultimate direction favored by the electron, while further increase to \( 10^{14} \) W cm\(^{-2} \) favors each nucleus evenly. This surprising
Figure 5.3: Subsequent to UV-laser induced population of the dissociating $2p\sigma_u$ state, H$_2^+$ is driven with an IR laser source with a profile as shown in (a). The electron density occupying the positive (red dashed line) and negative (black solid line) spatial regions is shown during and following interaction with a laser field of intensity (b) $3 \times 10^{12}$ W cm$^{-2}$, (c) $2 \times 10^{13}$ W cm$^{-2}$ and (d) $10^{14}$ W cm$^{-2}$. Comparison of results following field interaction (e.g., at 10 fs) show that the dissociation product distribution is highly influenced by the laser intensity selected due to the participation of transient electron localization. Adapted from [102].
dynamics is a direct result of the nonadiabatic intramolecular electronic response induced by the electric field. As $\text{H}_2^+$ fragments, the electron is initially free to traverse between nuclei. However, the potential barrier between the centers increases with nuclear separation, ultimately confining the electron to occupy one of the two centers. In a system for which the electron followed the laser field adiabatically, the final distribution of the electron would be expected to consistently reflect the laser profile selected; in the present case, within which transient localization plays an important role, the electron may be driven to favorably occupy one side of the molecule. As this particular case shows, inducing nonadiabatic transient localization thus allows laser intensity to be potentially used as a tunable means for producing a desired dissociation product.

5.3 Structural modulation of the HHG plateau

Previous experimental and theoretical studies have focused upon signatures that are modified by the nonadiabatic ionization behavior of the system. The demonstrated relevance of transient electron localization to such a variety of signals motivates the use of HHG to look for signatures of this behavior. Harmonic radiation with photon energies extending from the VUV to the soft-X-ray region \cite{25} is generated upon recombination of the electron with the parent ion and serves as a natural probe of the nuclear and electronic structure or dynamics of molecular targets \cite{103}. Each of the three steps, namely emission, propagation and recombination of the electron wavepacket, occurs on a femto- or sub-femtosecond time span. HHG is therefore a spectroscopic tool and has been used to time resolve vibrational wave packet dynamics \cite{104,107}, adiabatic electron wave packet motion in bound states of a molecule \cite{108,110}, and the dynamics in excited electronic states during photodissociation \cite{111,113}.

Dynamical or structural effects during any step of the process leading to harmonic emission in molecules may significantly influence the spectra, in particular to imprint minima at specific harmonic orders. Structural interference minima have been theoretically \cite{114,116} and experimen-

\footnote{Results presented in this chapter are also published in M.R. Miller, A. Jaron-Becker, and A. Becker, "High-harmonic spectroscopy of laser-driven nonadiabatic electron dynamics in the hydrogen molecular ion," Physical Review A 93, 013406 (2016).}
tally studied as a means of probing molecular structures and nuclear dynamics by defining a destructive interference criterion relating the deBroglie wavelength of the returning electron to the internuclear distance of the molecule analogous to two-center interference.

In contrast, dynamical minima result when the temporal evolution of the system results in a phase difference between electron wavepackets. This is, for example, the case when multiple molecular orbitals are energetically close to the continuum and are thus allowed to tunnel through the potential barrier in the first step of harmonic generation. The residual molecular ion remains in a coherent superposition of the ground and excited states which accumulate a destructive phase difference with the returning wavepacket for suitable electron excursion times.

Ionization is a critical first step to the production of the spectrum. Intermittently interrupting the flow of ionization from the molecule could result in a reduction of emitted radiation at relevant frequencies. Additionally, as we reviewed in Sec. 1.2, radiation through HHG possess an intrinsic chirp which enables the connection of dynamical events occurring during ionization and recombination to the modification of specific energies in the total spectrum.

Consideration of the HHG emanating from a system undergoing transient electron localization indeed demonstrates a minimum in the structure of the spectral plateau which is distinct from previously explored mechanisms. An example is shown in Fig. 5.4(a) for H$_2^+$ prepared in its ground state with internuclear distance $R_0 = 7$ a.u., driven by a 20 cycle full-width mid-infrared (IR) laser pulse with wavelength $\lambda = 1.8 \, \mu m$ and peak intensity $6 \times 10^{13} \, Wcm^{-2}$. The spectral structure is noticeably modulated in comparison with HHG driven using a shorter $\lambda = 0.8 \, \mu m$ wavelength, shown in Fig. 5.4(b). The location of the minimum in the $\lambda = 1.8 \, \mu m$ spectrum around the 87th harmonic order cannot be explained as a structural two-center interference minimum, which would predict minima at the energies indicated by the dashed lines in Fig. 5.4(a) [114, 115]. Since H$_2^+$ is a single-electron system, this minimum must also be distinct from dynamical minima arising from multi-electron effects [109]. And as we discuss in the following, its presence is predicated on the selection of appropriate laser parameters, and so has not been identified in previous theoretical examinations of the role of laser-coupled orbitals in the HHG of H$_2^+$ [123, 124]. To proceed, we seek
Figure 5.4: The HHG spectrum generated by a driving laser field with $\lambda = 1.8 \, \mu m$ (a) demonstrates a spectral minimum not observed for shorter wavelengths ($\lambda = 0.8 \, \mu m$, b). The spectral location of HHG suppression does not match the predictions of previously studied mechanisms, such as two-center interference (noted by dashed lines).

to connect the sub-cycle transient localization of the electron with the emission of radiation from the system. As discussed in Sec. 5.1, nonadiabatic transient localization results in several distinct bursts of ionization throughout each half-cycle of the driving field, predicted theoretically [41] and corroborated by indirect measurement of the ionization time delay probed by circularly polarized light [100]. These bursts of ionization are notably separated by instants of suppressed wavepacket emission, corresponding to solutions of Eq. (5.1) for even $m$. This provides a likely cause for the observed harmonic minimum: since the first step of harmonic generation relates to the emission of the wavepacket, analysis of the origin of the spectral minima in the HHG spectrum of Fig. 5.4 provides a route to directly observe the highly nonadiabatic electron dynamics within $H_2^+$.  

As the full HHG spectrum provides no temporal resolution to inform this comparison, we employ the continuous wavelet analysis

$$C(t_0, \omega) = \frac{1}{\sqrt{2\pi}} \int_0^T da_+(t) W \left( \frac{\omega(t - t_0)}{2\pi} \right) dt,$$  

where $W(x) = \frac{1}{\sqrt{\pi}} \exp(2\pi ix) \exp(-x^2)$ is the complex Morlet wavelet. In Fig. 5.5 we demonstrate the use of the wavelet transform to resolve harmonic emission throughout a single rescattering event near the peak of the driving field using wavelengths of 1.4 $\mu m$ (a) and 0.8 $\mu m$ (b). In each case,
Figure 5.5: Wavelet analyses of the electron dipole acceleration throughout recombination spanning 10.0 – 10.75 field cycles driven by a 1.4 μm (a) reveals intervals of reduced harmonic emission, in contrast to driving using a 0.8 μm (b) laser source. Electron behavior is represented using $\alpha$ during the classically reconstructed time of ionization (c,d) and during recombination (e,f). (g) Relation via a classical model [7] between ionization and recombination times.
the wavelet picture provides HHG emission throughout 10.0 – 10.75 field cycles, corresponding to ionization events between 9.75 – 10.0 field cycles. For the 1.4 µm case, we note with a dashed line a period of suppressed harmonic emission, matching a spectral interval of suppressed emission from the full HHG spectrum. Consequently, to understand the source of the minimum, we can examine the evolution of the electron wavepacket during ionization and recombination time intervals contributing to the HHG to reveal the mechanism which transiently suppresses harmonic radiation.

Harmonic emission occurs at the time of electron recombination, so a comparison of the electron dynamics and harmonic emission throughout the recombination interval is straightforward. Addressing dynamics during ionization is more complicated, as the timing of ionization is inherently ill-defined for a quantum mechanical system. For the purpose of this study, we find the classical model of electron behavior in the driving field used in HHG to be a sufficient approximation [7]. Using this picture, and as discussed in greater depth in Sec. 1.2, we assume that the electron acts as a point negative charge and is released from the molecule with \( z = \dot{z} = 0 \) throughout a series of ionization times spanning 9.75 – 10.0 field cycles. Assuming recombination to occur at the first instance when \( z = 0 \), each classical trajectory specifies a unique pair of ionization and recombination times, as shown in Fig. 5.5(g). We then use the set of ionization times associated with recombination during the time interval of interest to analyze the electron dynamics during ionization. To characterize the nonadiabatic intramolecular electron dynamics, we consider the variation of the phase difference \( \alpha \) which is presented at instants of ionization in Fig. 5.5(c,d) and of recombination in Fig. 5.5(e,f), respectively.

In the long wavelength case depicted in Fig. 5.5(a), we observe that the spectral minimum coincides with \( \alpha = 0 \) at the time of ionization, but is not influenced by the behavior of \( \alpha \) during electron recombination. This relationship is further tested by applying a shorter wavelength laser source, as in Fig. 5.5(b): in this case, the phase difference \( \alpha \) is not equal to zero throughout the ionization window and consequently suppressed harmonic generation is no longer observed. On the other hand, the short wavelength results let us conclude that the occurrence of \( \alpha = 0 \) at the time of recombination does not lead to a suppression of harmonic emission. Thus, we can conclude that
the present minima in the harmonic spectra are a spectroscopic signature of nonadiabatic electron dynamics at the time of ionization while it is not characteristic for the dynamics at the time of recombination.

This analysis does admit some ambiguity regarding the best approximation for the ionization and recombination positions. In Fig. 5.6, the extent to which the analysis response to different selections of these boundary conditions is considered: the purple dotted line corresponds to ionization from \( z = 3.5 \) and recombination to \( z = -3.5 \), corresponding to the positions of the nuclear centers; the red dotted line assumes \( z = 0 \) for both ionization and recombination; and the yellow dotted line admits the opposite of purple, assuming \( z = -3.5 \) at ionization and \( z = -3.5 \) at recombination. The variance between these conditions is seen to be sufficiently small to preserve a connection between ionization dynamics and the intervals of HHG suppression. Especially in the case of high-energy features, the large excursion distance traveled by the classical electron reduces the difference between ionization timings in the three cases to a nearly negligible variance.

### 5.3.1 Intensity dependence

We have validated the use of HHG as a spectroscopic tool to record nonadiabatic dynamics induced by a mid-IR intense laser field. As suggested by Eq. (5.1), we may also consider the variance of the nonadiabatic dynamic with increases in laser intensity. Toward the specific goal of identifying more than one localization event in HHG spectra, increasing intensity affords a computational advantage over increasing wavelength, as the quiver radius of the electron increases linearly with intensity but quadratically with wavelength. Therefore, much smaller grids can be used to drive dramatic increases in the nonadiabaticity of the electron response.

To capture the evolving electron dynamic, the localization of the electron on the \( z > 0 \) half of the spatial grid is shown in Fig. 5.7 for increasing intensity when \( \lambda = 1.4 \mu \text{m} \). These figures display both the evolution of nonadiabaticity as a function of time in response to the ramping intensity of the electric field and the overall increase in nonadiabaticity displayed as the peak intensity is increased. In each intensity case, the number and timing of the localization events remains nearly
Figure 5.6: Classical approximation of the returning electron enables the connection of ionization suppression during ionization to minima in harmonic generation. The predictions of classical analyses considering different initial and final position criteria for the propagating point electron are shown as an estimation of the uncertainty involved in this calculation.
Figure 5.7: Electron dynamics are shown throughout one 20 cycle, 1.4 µm laser pulse with varying intensities. Dynamics in each case transition from adiabatic to nonadiabatic behavior; the dynamics during the central cycles of the highest intensity case (last row) exhibit the strongest nonadiabatic character.
constant throughout the peak of the driving laser pulse where the intensity of the field remains relatively constant. In the driving field parameter regime considered so far, the behavior of the electron during the center of the laser pulse is the dominant contributor to the structure of the emitted HHG; studying electron dynamics in this interval has thus been sufficient to explain the structure of the entire HHG spectrum.

However, the electron behavior can vary tremendously from the onset of the laser field to the moment when the field is strongest. This is best demonstrated by the highest intensity case shown, with $2.0 \times 10^{14}$ Wcm$^{-2}$, where the electron behavior is seen to transition through several different numbers of localizations per field cycle. The central cycle of the nonadiabatic dynamics induced by the $2.0 \times 10^{14}$ Wcm$^{-2}$ driving laser field shows numerous incidences of transient electron localization, while electron dynamics near the beginning and end of the pulse are essentially adiabatic. We next consider the capacity for HHG to additionally capture this evolving dynamic.

To address this question, we perform windowed Fourier transforms of individual recombin- nation events. This strategy mimics the experimental use of the attosecond lighthouse technique [17, 24] which imposes a temporal rotation of the instantaneous driving field wavefront, imparting angular separation to attosecond pulses emitted at different times. Through this technique, HHG generated from gases has been used to track the evolution of plasma formation and nonadiabatic dynamics in the generating medium [125], and similarly would be expected to provide an avenue to image the time-dependent electron dynamics ongoing within $\text{H}_2^+$. Using a driving field strength of $2.0 \times 10^{14}$ Wcm$^{-2}$, we present a case where the transient localization of the electron dramatically modifies the spectral signal from one attosecond pulse to the next. At the peak of the driving field, we anticipate that the system will localize on the counterintuitive nucleus twice during the ionization window of HHG, resulting in two spectral minima. However, as the field ramps up throughout the first half of the laser pulse, we expose the electron to a changing effective intensity. The increasing magnitude of the electric field transitions the electron from an adiabatic regime to the nonadiabatic behavior of interest, and in particular provides the opportunity to image a changing number of localizations.
Figure 5.8: (left) Fourier transform of individual recombination events between 7.0-9.25 field cycles illustrates evolving electron dynamics (green, top: 7.0-7.75, teal: 7.5 - 8.25, blue: 8.0-8.75, purple, bottom: 8.5-9.25 field cycles; each spectrum shifted downward from predecessor by one order of magnitude). Using a $2.0 \times 10^{14}$ W cm$^{-2}$ driving laser, electron dynamics transitions between satisfying $\alpha = 0$ once (top right) to twice (bottom right), resulting in the addition of a second minimum to the harmonic spectrum.
To resolve this progression, we show the spectral structure of several distinct rescattering events in Fig. 5.8(a). We begin in a regime in which $\alpha = 0$ once at the time of ionization (green) as seen in Fig. 5.8(b) and depict the transition toward satisfying $\alpha = 0$ twice during ionization (purple) shown in Fig. 5.8(c). Initially, we note only one spectral minimum, occurring at 83 harmonic orders. As the peak intensity at each cycle increases, this minimum shifts to higher energies in subsequent spectra. However, we also observe the formation of a second minimum beginning at 29 harmonic orders corresponding to recombination between 7.5 – 8.25 field cycles (teal). Initially, the second minimum corresponds to fulfilling $\alpha = 0$ near the beginning of the recombination event at 7.5 field cycles. As intensity increases, $\alpha = 0$ progressively later with respect to the beginning of the recombination event, leading to a spectral minimum at greater energies. We envision this time-dependent behavior could be revealed through the use of the attosecond lighthouse technique of imaging, which would enable the separation of these rescattering events.

5.4 Generation of radiation at non-integer harmonic frequencies

In addition to a modulated amplitude of radiation emission, HHG signals generated by an electron demonstrating highly nonadiabatic behavior also possess a modified interference structure throughout the spectral plateau. An example of such a modification is shown in Fig. 5.4(a). Peaks spanning the energy interval between the plateau minimum and the HHG cutoff energy no longer occur only at odd-harmonic values; instead, the spectral structure in this interval is highly irregular. This behavior departs from the consistent odd-harmonic generation at lower energies in the 1.4 $\mu$m case or at any energy in the 0.8 $\mu$m case (Fig. 5.4(b)). The coincidence of the spectral minimum with the interruption of odd-harmonic generation suggests that the two phenomena may share a common cause, implicating the induced nonadiabatic behavior of the electron in the creation of the complex high-energy interference structure.

When analyzing the cause of the spectral minimum, we begin by separating different rescattering events and comparing the contributing behavior of the electron at times critical to the formation of the HHG. We find that the structure of the interferences are sensitive to variations
Figure 5.9: The interference structure of different sets of recombination events demonstrates the variant interference structure of the HHG. In (a), recombination events occurring near the center of the driving laser (9.5-11.25 field cycles) result exclusively in odd harmonic generation. In contrast, recombination events considered between 12.0-13.75 field cycles (b) exhibit peaks at non-integer or even harmonics. Both spectra result from driving with a 1.4 μm, 20 cycle, $6 \times 10^{13}$ W cm$^{-2}$ laser field. The position of odd (even) harmonics along the x-axis is indicated by yellow dashed (purple solid) lines.
in the behavior of the electron. As seen in Fig. 5.9, isolating the harmonic signal from sequential recombination events occurring during different dynamical behaviors of the electron shifts the position of peaks within the signal; in contrast, a stable electron behavior returns the anticipated odd-harmonic generation. In Fig. 5.9(a), the harmonic signal generated during the central cycles (9.5 - 11.25 field cycles) of the laser field is shown to result in peaks along odd harmonic values, despite the ongoing nonadiabaticity of the electron throughout this temporal window. Critically, within this time interval, the electron demonstrates a consistent nonadiabatic behavior from one half-cycle to the next. On the other hand, selecting the same number of recombination events from an interval when the intramolecular electron dynamics varies produces a harmonic signal that no longer peaks exclusively along the odd harmonics. Instead, particularly at high energies, the peaks are produced at non-integer or even harmonics.

It is additionally notable that the non-odd harmonic generation in Fig. 5.9(b) occurs with equal efficiency to the signal generated during the center cycles of the laser field. While the interval shown in Fig. 5.9(a) would ordinarily dominate the total signal, the suppression of harmonic generation due to the transient localization of the electron on the non-ionizing side of the molecular ion reduces the efficiency of harmonic production. The matching amplitudes of harmonic production near the 50th harmonic order in Fig. 5.9(a) and (b) result in the highly-structured interference structure from this portion of the harmonic signal in Fig. 5.4(a).

The connection between the nonadiabatic behavior and the interruption of the odd-harmonic interference condition is explored further in Fig. 5.10. Here, the dynamics of the electron during the relevant ionization and recombination events corresponding with the signals produced in Fig. 5.9 are shown. Subpanels (a), (c), and (e) correspond to the scenario in which odd-harmonics are conventionally produced. In this case, the three sequential contributing events (colored in purple, blue, and teal according to their temporal ordering - the middle event is inverted along the y-axis to assist visual comparison) represent similar ongoing dynamics. Correspondingly, odd harmonics are generated due to the preservation of inversion symmetry within the system from one event to the next.
Figure 5.10: Interference structure of the harmonic spectrum is modified by changing electron dynamics at the time of recombination. The time frequency analyses (a, b) correspond to representative recombination events contributing to Fig. 5.9 (a, b) respectively. Dynamics at the time of recombination (c) and ionization (e) remain relatively unchanged throughout three sequential recombination events during the peak of the driving field. Recombination events occurring between 12.0-13.75 field cycles (d) notably diverge at times corresponding to energies exhibiting non-odd harmonic generation in Fig. 5.9 (b), while ionization behavior remains consistent throughout this interval. Times along x-axis represent recombination times of second recombination event from the set of three considered; second event is inverted along the y-axis to assist comparison of dynamics with other recombination events.
This scenario is modified by considering a subsequent time interval of recombination events. A black dashed line in Fig. 5.10(b) indicates the energy at which odd harmonics are no longer observed in Fig. 5.9(b). This energetic position in the time-frequency analysis of radiation emission corresponds to the time indicated by the vertical dashed line descending through panels (d) and (f). Throughout the energies at which odd-harmonics are no longer observed, we note that the electron behavior at the time of recombination is highly modified from one interval to the next. Ionization behavior throughout this interval remains constant, implicating recombination dynamics as the dominant descriptive mechanism in the destruction of inversion symmetry needed to prevent the formation of odd-harmonics. The electron behavior at the time of ionization and at the time of recombination both exhibit dynamical differences within the first 0.2 field cycles of the recombination event. While the difference between events is nearly as large as those following the black dashed lines, early events yield into low harmonic orders with contributions that are easily masked by the greater amplitude of radiative yield occurring during preceding harmonic events. As shown previously in Fig. 5.9(b), the modified interference structure exhibited near the black dashed line contributes obviously to the full harmonic spectrum due to the earlier suppression of radiation at these energies. Augmenting the nonadiabaticity demonstrated by the system by increasing the laser field intensity also increases the degree to which recombination behavior varies from one cycle to the next; this results in the complex peak structure observed at high energies in Fig. 5.4(a).

5.5 Attosecond pulse train

The effects of transient localization upon the structure of the HHG spectrum are profound, modifying both the amplitude and interference structure of the plateau if a suitable selection of driving field wavelength and intensity is made. It is natural to question what form these structural changes take when the emitted radiation is considered instead in the time domain of the process. Physically, this time-domain information represents the intensity profile of the emitted radiation pulse, which is considered in the following for an H\textsuperscript{+}\textsubscript{2} ion driven by 1.8 µm light with intensity $6 \times 10^{13}$ Wcm\textsuperscript{-2}.
Figure 5.11: The onset of nonadiabaticity modulates the structure of the attosecond pulses generated. For the same laser field parameters as shown in Fig. 5.4(a), individual pulses within the are reduced in amplitude and acquire a double-peak structure near the center of the field. These features follow from the same mechanism inducing a minimum in the HHG spectrum.
The effect of nonadiabaticity upon the generation of attosecond pulses is also pronounced, as demonstrated in Fig. 5.11. In this figure, we transform the energy region spanning 80 – 120 harmonic orders, capturing the spectral minimum and the extent of the spectrum efficiently producing non-odd harmonics. Throughout the central cycles of the driving laser field, when the nonadiabatic character of the intramolecular electron dynamic is strongest, the reconstructed attosecond pulse train shows deep amplitude modulations. This results in a double-peak structure, and an overall reduction of pulse amplitude. The source of this amplitude modulation is the same mechanism modulating the HHG spectrum amplitude: portions of the returning electron wavepacket are transiently reduced by suppressed ionization. The overall width of each pulse is, however, unchanged due to the modification of interference structure due to the intrinsic chirp of the harmonic generation process.

5.6 Experimental signatures

In the preceding sections, we have explored several manifestations of nonadiabatic electron dynamics in the molecular HHG signal. For the sake of transparency when establishing the link between modifications of the HHG spectrum and the presences of nonadiabatic dynamics, these theoretical demonstrations have relied upon assumptions of fixed laser intensity and internuclear distance. In this section, we relax these conditions to estimate the stability of these features in experimental scenarios.

5.6.1 Robustness of the HHG spectral minimum

Our capacity to observe the HHG structural minimum under experimental conditions requires that the minimum remains robust under variations of laser intensity, molecular internuclear distance $R_0$, and carrier envelope phase. We begin by considering the stability of the spectral minimum over a range of internuclear distances in Fig. 5.12(a). Near equilibrium, and for increasingly extended internuclear values (> 9.0 au) the HHG plateau remains flat; consequently, the addition of these spectra to the final signal increases the signal at all harmonic orders similarly. Other
Figure 5.12: (a) The integrated HHG signal calculated for fixed internuclear distances spanning 5.0–10.0 au maintains the spectral minimum for $\lambda = 1.4 \, \mu\text{m}$, intensity $6 \times 10^{13} \, \text{Wcm}^{-2}$. (b) Fitting a distribution of laser intensities to a Gaussian beam profile, with maximum intensity $7.0 \times 10^{13} \, \text{Wcm}^{-2}$, similarly maintains the minimum structure.
internuclear distances (for example, $R_0 = 5.0$) contribute spectral minimum at a similar frequency. Consequently, integration over internuclear distances spanning $5.0 - 10.0$ a.u. in Fig. 5.12(a) does not eliminate the spectral minimum.

In Fig. 5.12(b), we examine the effect of moderate laser intensity variation by simulating an integrated HHG signal due to a Gaussian pulse profile. At low intensities, we note that the transient localization of the electron does not take place. Consequently, spectra emitted by the system are flat throughout the plateau region, and contribute evenly to the total harmonic structure. As laser intensity increases, the spectral minimum appears and increases linearly with the laser intensity, as seen for intensity values between $5.0 - 7.0 \times 10^{13}$ Wcm$^{-2}$ in the inset of Fig. 5.12(b). This linear behavior is due to the relatively invariant time for which $\alpha = 0$ at the time of ionization, which corresponds to an electron recombining with energy that increases with the driving laser intensity. Thus, upon addition of harmonic spectra across this range with $\Delta I = 0.2 \times 10^{13}$ Wcm$^{-2}$ in Fig. 5.12(b), the minimum remains apparent. Additional calculations have shown that the position of the minimum remains stable under variations of the carrier-envelope phase, which we expect: the temporal position of $\alpha = 0$ events will shift with $\phi$ according to Eq. (5.1); simultaneously, however, we shift the peak of the electric field by the same phase, and the duration of our laser field is sufficient so that the presence and location of the minimum will overall be unchanged.

### 5.6.2 Phase-matching effects in HHG

Having established the capacity for transient electron localization to significantly modify both the structure and amplitude of the generated harmonic spectrum, it remains to consider the extent to which these features will remain detectable in a macroscopic environment such as a gas. In particular, a realistic experimental scenario for the detection of HHG introduces different generating molecular ions to different effective intensities due to the transverse and longitudinal spatial intensity distributions of the driving laser. For a HHG signal to be detected, harmonics emitted at the same energy from different sources must not interfere destructively. This requirement establishes a criterion for phase matching that has been productively explored toward the generation
of isolated attosecond pulses \cite{25}. In the context of detecting nonadiabatic dynamics, the question of phase matching is particularly relevant due to the modified interference structure of the plateau harmonic energies evident in, for instance, Fig. 5.4(a). In the following, we seek to establish how the modified interference structure additionally alters the phase matching conditions of the emitted radiation.

To estimate this effect, we assume that a Gaussian beam is used to drive a gas jet sample. We wish to estimate both the transverse and longitudinal coherence lengths of radiation emitted by the samples, which we evaluate through the phase mismatch accumulated as $L_{\text{coh}}^\parallel = \pi/\Delta k_\parallel$ and $L_{\text{coh}}^\perp = \pi/\Delta k_\perp$. Following \cite{87}, the respective phase mismatches of any order $q$ can be estimated as

$$\Delta k_q^\parallel \approx (q - 1) \frac{\partial \zeta(z)}{\partial z} + \frac{\partial \phi_q I}{\partial I} \frac{\partial I}{\partial z}$$ (5.4)

where $\zeta(z)$ is the Gouy phase and $\phi_q$ is the phase of the emitted harmonic of interest, and the density of the gas has been assumed to be low enough so that dephasing due to the presence of free charges and neutrals in the sample can be neglected. The intensity of the field is represented by $I(z, \rho)$. In the transverse direction,

$$\Delta k_q^\perp \approx -q \frac{\omega}{c} n(\omega) \frac{\rho}{R(z)} + \frac{\partial \phi_q I}{\partial I} \frac{\partial I}{\partial \rho},$$ (5.5)

where $n(\omega)$ is the index of refraction of the sample and $R(z)$ is the radius of curvature of the Gaussian beam.

Within these representations of the phase mismatch, the influence of the nonadiabatic electron dynamic is expressed in the quantity $\phi_q$, as all other terms result from the beam parameters and estimations of the index of refraction of the sample. To approximate $\partial \phi_q / \partial I$, we calculate discrete harmonic spectra at separate fixed peak intensities spanning $5.0 \times 10^{13}$ to $7.0 \times 10^{13}$ Wcm$^{-2}$ with $\Delta I = 2 \times 10^{12}$ Wcm$^{-2}$. The lower bound of these intensities is selected to include all contributions with sufficient radiation amplitude to modify the composite spectrum. Using these calculations, the harmonic phase dependence upon intensity can be approximated. We note that this discrete intensity approximation introduces variation in the coherence lengths predicted by the model.
In the following figures, we present the median value of the predicted coherence lengths, which accurately follow the aggregate behavior of the phase matching predictions. In calculations of $\Delta k_{\perp}$, we estimate that $n(\omega) \approx 1.5$ as a reasonable value for the wavelengths presented, noting that any value spanning $1 \leq n(\omega) \leq 2$ produces the same result in the following analysis.

In Fig. 5.13(a,b), and (c,d) we present the respective transverse and longitudinal phase matching behavior of harmonics generated throughout the plateau energies using a driving wavelength of $1.4 \mu\text{m}$. The Gaussian laser beam is assumed to have peak intensity $7.0 \times 10^{13} \text{ Wcm}^{-2}$ with a beam waist of $W_0 = 100 \mu\text{m}$. In Fig. 5.13(a) and (c), the placement of the gas jet is modeled at 10 mm preceding the focus; in Fig. 5.13(b) and (d), the jet is placed 10 mm after the focus. In each case, the dashed line demarcates the boundary between the energy regime in which conventional odd harmonics are emitted and that in which the interference structure becomes more complex.

The two instances of transverse phase matching demonstrate similar qualitative differences between the two energy regimes. In Fig. 5.13(a), the region of odd-harmonic generation demonstrates clear variations in the coherence length between odd-harmonic values and emission into all other photon energies. Odd harmonics maintain coherence over greater distances than any other value. In contrast, the coherence lengths of photon energies emitted throughout the second regime of the complex HHG interference structure demonstrate greater consistency. Non-odd harmonic values are emitted with equivalent coherence lengths to odd-harmonic values, with an average magnitude comparable to that of odd harmonics emitted in the first region. In Fig. 5.13(b), the positioning of the gas jet following the laser focus generally reduces the coherence length of all emitted harmonics. Nevertheless, similar trends are found: odd-harmonic detection is strongly favored in the first region, while all energy values in the second region are emitted with less variable coherence lengths. In each case, the coherence lengths of radiation emitted at energies signaling nonadiabatic electron dynamics are sufficiently long to permit detection.

The longitudinal phase matching is examined in Fig. 5.13(c) and (d). In this case, positioning the gas jet prior to the focus is seen to reduce the coherence lengths of emitted photons in comparison with placement after the focus. In Fig. 5.13(d), similar behavior to transverse phase matching is
Figure 5.13: The transverse (a, b) and longitudinal (c, d) coherence lengths of the high-energy HHG plateau indicate qualitative differences between variation and magnitudes of coherences induced by transient electron localization. In (a) and (c), the gas jet is positioned 10 mm preceding the laser focus; in (b) and (d), the gas jet is set 10 mm after the focus. The driving laser is assumed a Gaussian beam with waist $W_0 = 100 \, \mu m$, peak intensity $7.0 \times 10^{13} \, Wcm^{-2}$, and wavelength $1.4 \, \mu m$. The dashed lines mark the position in the HHG spectrum of the transition from pronounced odd-harmonic generation to a more complex interference structure.
clearly observed: odd harmonics initially present with longer coherence lengths, but all values throughout the highest energy section of the plateau demonstrate nearly constant efficiency with greater magnitude that the preceding non-odd harmonics. The pre-focus gas jet positioning of Fig. 5.13(c) ultimately reduces the coherence lengths of the highest-energy values due to the dominance of the Gouy phase term in determining the magnitude of the phase mismatch. However, comparison of proximal energy intervals exhibiting difference interference behaviors in the HHG spectrum show similar features described in the analysis of Fig. 5.13(d). In each case, the coherence lengths are again sufficient to enable the detection of the transient localization signatures.

5.7 Conclusion

In this chapter, we have demonstrated the capacity for transient electron localization to strongly modify and modulate the generated HHG signal. We have studied this behavior in the context of a fixed-internuclear distance model, for which the nonadiabatic behavior of interest is well-understood. In addition to developing our understanding for the conditions which enable transient electron localization to suppress harmonic emission at critical energy intervals, we have also explored the mechanism causing the highly-structured interference pattern at the highest plateau energies of molecules undergoing nonadiabatic electron behavior.

Strong laser field induced transient electron localization is accompanied with instants of suppression of ionization, corresponding to localizations of the electron on the uphill side of the molecule. Through classical analysis of the emitted electron trajectories, it is possible to associate the timing of these ionization suppressions to the energetic location of the HHG spectrum minimum. Consequently, the minimum can be used to trace the ongoing electron dynamics. This capacity is extended to image changing dynamics by isolating different recombination events and studying the emergence and movement of spectral minima within separated attosecond pulses.

Additionally, the breaking of the inversion symmetry of the electron distribution at the time of recombination during sequential half-cycles of the laser field is seen to interrupt the conditions conventionally producing distinct odd-harmonics. Expression of this modified interference structure
within the total HHG spectrum relies upon the modulation of the HHG signal, which equalizes the amplitude of harmonic emission during the middle field cycles and along the rising and trailing ends of the field. In combination, these two effects result in a complex high-energy structure.

In addition to efficiently yielding non-odd harmonics, transient electron localization alters the accumulated phase mismatch of radiation throughout the highest energies of the HHG plateau. Non-odd harmonic energy values acquire coherence lengths of comparable value to odd-harmonic values in this regime along both the transverse and longitudinal planes of the modeled Gaussian beam. This property assists the detection of the HHG signal in this regime. Transient electron localization is seen to modify the time-domain structure of the emitted radiation through the same mechanism that modulates the HHG amplitude. Individual peaks within the yielded pulse train are seen to acquire a two-peak feature due intervals of suppressed emission during electron wavepacket recombination.

In total, these findings show that HHG is a sensitive tool for the detection of nonadiabatic intramolecular electron dynamics. Both the amplitude and phase of each harmonic encode events ongoing during ionization and recombination of the electron wavepacket. In turn, the capacity for nonadiabatic electron dynamics to strongly modify the spectral content of the emitted radiation offers a potential method for further customizing attosecond pulses and for further imaging the laser-driven behavior of electrons inside of molecules.
This thesis reprised theoretical efforts to resolve electron dynamics on attosecond timescales through the use of high-order harmonic spectroscopy. To this end, we began in Chapter 1 with a description of concepts fundamental to intense laser electronic physics. Strong-field ionization introduces a highly non-perturbative ionization mechanism. When a system is introduced to an intense, long wavelength laser field, deformation of the Coulomb barrier allows part of the electron wavepacket to tunnel away from the parent ion. Subsequent to this ionization event, several electron dynamics may result; the most relevant to this thesis concerned acceleration of the electron in the laser field and recombination with the parent ion. Should a recombination event occur, the electron wavepacket emits energy gained from the laser field as a single high-energy photon. This radiation results in the composite yield of a broad spectrum of energy extending to soft X-ray regime; this spectrum, known as high-order harmonic generation, emitted with constant frequency-dependent amplitude. This radiation can be converted into isolated attosecond pulses through several experimental strategies. HHG is also encoded with information regarding the participation of different electron trajectories and the status of the evolving electron wavepacket remaining within the parent ion. This makes HHG a promising tool to advance investigations of counter-intuitive electron dynamics initiated by strong laser fields in molecular systems. As we discussed, existing studies of fragmentation patterns suggest large and conjugated molecules are particularly susceptible to a nonadiabatic laser field response. These behaviors are mimicked by transient electron localization behaviors in $H_2^+$, which has been studied extensively as a model of single-
electron nonadiabatic behavior. All of these studies benefitted from the use of the numerical methods discussed in Chapter 2, which enabled the exact treatment of the system response to the strong laser field. Discretization of space and time enabled the solution of field-free eigenfunctions of a system of interest and the subsequent propagation of a time-dependent wavefunction. During propagation, time-dependent observables were calculated and subsequently used for the calculation of HHG spectra and the theoretical analysis of radiation emission.

The numerical methods discussed in Chapter 2 outlined a successful method to solve a single-electron problem. In Chapter 3, we added to this discussion by considering problems for which more than one electron are present. In the regime of strong-field physics, we reviewed the common usage of a single-active-electron approximation to a multielectron system. Under this treatment, the reasoning of tunnel ionization was applied to argue that only the least-bound electron in an arbitrary system would respond to an incident electric field. While this framework did not follow from ab-initio theoretical principles, it had, in the past, achieved agreement with experimental results of ionization studies. We reviewed an algorithm that used density functional theory to fully compute electronic interactions of a field-free system: this potential was applied to study laser-induced effects. We also considered, developed, and tested the output of a strategy for fitting numerical pseudopotentials to a concise analytic expression which was physically grounded in structure of the exchange-correlation component of the full potential. Our models successfully reproduced the Cooper minimum in the HHG spectrum of argon, which is known to be highly sensitive to the electronic structure of the generating system. We also calculated the photoionization cross section distributions of both argon and neon to demonstrate the quantitative accuracy afforded by our model.

In Chapter 4, we used a single-active-electron approximation and our knowledge of the contributions of electron trajectories to HHG to propose a method to optimize the production of an ionized electron wavepacket that rescatters multiple times from the parent core, emitting a train of attosecond pulses in the process. We used a second VUV laser pulse to gate the ionization step of this process and exert control over the distribution of electron trajectories that emanated from the
parent core. Identification of conditions which favored multiple rescatterings and single attosecond pulse production enabled a comprehensive study of the spectral and temporal signatures that differentiate these two behaviors. In particular, we noted the interference structure of the plateau region of the HHG spectrum strongly varied between cases. Evidence of multiple rescatterings was evident through differences in the amplitude of different sections of the plateau which received radiative contributions from different numbers of rescattering events. We considered the importance of controlling for these multiple rescattering events in view of the capacity to selectively interfere the radiation from two separate rescattering wavepackets, which has been implicated as a potential future source of zepto-second duration light pulses.

Finally, in Chapter 5, we assessed the capacity of HHG to resolve nonadiabatic electron dynamics in $H_2^+$. This system is known to demonstrate a single-electron nonadiabatic laser response due to the strong induced coupling of the ground and first excited states. Under these conditions, ionization is dramatically enhanced; simultaneously, the electron begins to oscillate across the molecule to transiently localize on the counterintuitive side of the molecule several times per half field cycle. The depletion of the ionizing side of the molecule intermittently interrupts the ionization of the electron wavepacket from the system. We demonstrated that HHG is responsive to this effect. When a sufficient number of transient localizations occur per half field cycle, a minimum develops in the HHG plateau. The energetic position of this minimum was shown to coincide with the time at which ionization had been transiently suppressed. HHG suppression was demonstrated to be robust under approximative experimental positions, and was also suggested as a tool to follow changes in the electron nonadiabatic dynamic followed as the driving field ramps or decreases in intensity. Notably, this minimum structure was attributed exclusively to ionization behavior within the system, whereas recombination events are usually implicated in minimum structures identified in HHG.

In addition, the alteration of the interference structure of the highest plateau energies was shown to possess structure due to changing recombination dynamics in the system. The elimination of inversion symmetry across the plane orthogonal to the linearly polarized laser field altered the
phase demonstrated in the HHG plateau; notably, odd harmonics are no longer visible in the spectrum, in favor of a highly complex peak structure. This feature was contingent upon the manifestation of the spectral minimum. Consideration of the phase mismatch encountered under experimental conditions demonstrated that this feature was sufficiently robust for observation. Additionally, the novel spectral structure of this region of the HHG plateau may further enable efforts to customize the spectral content or shape of attosecond pulses.
Bibliography


