

Using parametric theories to understand carrier-envelope phase and multi-color
processes

by

Dustin Ursrey

B.S., University of the Cumberland, 2009

M.A., Western Kentucky University, 2014

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

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Abstract

The interaction between intense laser pulses and matter can drive a wide range of processes: for example, atoms or molecules can undergo breakup to create new systems, excitation can occur to create products with different properties and reactivities, and chemical reactions can be affected in ways that enhance/dehance the probability of specific outcomes. Changing the incident light can alter all of these aforementioned processes, giving rise to the possibility of coherent control in an experimental setting. In order to understand the control provided over a specific observable, it is necessary to develop a theory that allows us to understand the physical mechanisms that contribute to this control, as well as how these mechanisms depend on the parameters of the incident light. This thesis will focus on our group's parametric formalism for carrier-envelope phase (CEP) and multi-color control. Our formalism, outlined in Chap. 2, allows any observable to be expressed in terms of the interference between different photon pathways, and explicitly shows how changing the CEP or the relative phase between different colors controls this interference. Application of our formalism to understand control over dissociation is demonstrated in Chap. 3 and Chap. 6. Here, knowledge of system allows us to predict the most likely pathways taken during breakup, and the construction of observables in terms of these pathways allows for quantitative, *a priori* predictions about control. In Chap. 4 and Chap. 5, it will be shown that our formalism can also allow for the extraction of important physical information from a known result. Chapter 4 will focus specifically on the problem of characterizing the CEP of a pulse, showing that our formalism provides not only a deeper understanding of currently used experimental techniques, but can also offer a slight improvement in the precision of the extracted phase. Chapter 5 will focus on directly extracting photon pathways from a measured spectrum, allowing us to identify the exact physical mechanisms that must have been present to create a given feature in a measured spectrum.

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Approved by:

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Abstract

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Chapter 1

Introduction

1.1 Opening Remarks and Thesis Structure

Much of our knowledge about atoms and molecules comes from studies involving the interaction between light and matter. From early measurements in spectroscopy, to modern studies using ultrafast lasers to probe atomic/molecular processes on their characteristic timescale, results describing light-matter interactions have long elucidated the properties of both the matter and light being studied. In this thesis, I will continue this line of work by presenting and applying our group's parametric formalism for understanding the interaction between intense, ultrashort laser pulses and atoms/molecules. This formalism provides a simple theoretical framework for understanding the features of an observable in terms of the different physical pathways that the system can take to a given final state, and allows us to make quantitative, *a priori* predictions about the control that can be provided over the observable by altering certain parameters of the laser. Furthermore, our formalism allows us to extract information about these pathways (and the light itself) from a given spectrum, providing a deeper understanding of the physical mechanisms involved in the process of laser excitation..

This chapter will serve to introduce many of the ideas that will be encountered throughout the remainder of the thesis. We will outline some key historical findings that put modern work in context, provide a review of relevant results in intense, ultrashort physics, and discuss other approaches used to understand these results. The limitations of current methods and the need for new methods will be discussed — specifically when it comes to understanding certain aspects

of strong-field, coherent control.

1.2 The Nature of Matter

1.2.1 Discovery of Atoms and Molecules

One of the most fundamental questions science aims to answer is “What is the nature of matter?”. Inquiries into this question far predate scientific modernity, with writings from over 2000 years ago already weighing in on the subject. Famously, the Greek philosopher Democritus argued that matter was composed of tiny, indivisible particles known as atoms. In this view, matter could only be split into pieces a finite number of times before you were left with a fundamental building block that could no longer be broken into constituent parts. By contrast, Aristotle and others suggested that matter was continuous, and that no such smallest building block of matter existed. For over two millennia, this question remained mostly in the realm of philosophy — with no way to examine such small things directly, scientific inquiry into the subject was quite difficult.

One of the first attempts to think about the composition of matter in a scientific fashion came from Daniel Bernoulli in 1738 [8,9]. Bernoulli, who wanted to understand experimentally determined gas laws seen in chemistry, was able to mathematically derive Boyle’s Law (which states that pressure and volume are inversely proportional for an ideal gas) by assuming gases were made of discrete particles that interacted with each other and their container through the well-understood principles of classical mechanics. However, this idea gained very little traction in the scientific community until nearly a half-century later when John Dalton proposed his atomic theory to explain a number of additional laws observed in chemistry [10].

Dalton’s atomic theory can be summarized by three ideas: all elements are made up of discrete atoms that cannot be further broken down by chemical means, atoms of an individual element are indistinguishable while the atoms of any two distinct elements are fundamentally different, and a given compound is formed by atoms of different elements joining together in a fixed ratio [11]. In this view, chemical reactions are merely a rearrangement of atoms. Because atoms cannot be destroyed via chemical means, his atomic theory explains the (then) recently discovered law of conservation of mass [12], which was observed in comparisons of product and reactant masses

in chemical reactions. Similarly, the idea that a given compound is composed of a fixed ratio of atoms readily explains why compounds always have a fixed mass ratio of their constituent elements — the law of definite proportions [13]. The theory also provides explanation for why elements that can combine to create multiple, distinct compounds always create compounds where the mass ratio of a given element is the ratio of two integers (e.g., FeO and Fe₂O₃ were both observed by Dalton and shown to have an oxygen mass ratio of 2 : 3 for a fixed amount of iron) —the law of multiple proportions [10, 13].

Although the atomic theory had many prominent doubters in its early years, its continued, successful application for explaining observed phenomena would build evidence for the theory throughout the mid- to late-nineteenth century. Bernoulli's idea of treating gases as a collection of discrete particles was developed into to a much more rigorous kinetic theory of gases that allowed for concepts such temperature and heat transfer to be understood in terms of the kinetic energy of atoms/molecules in a gas [14–16]. Eventually, in 1907, Einstein would develop a kinetic theory of his own that could quantitatively explain the observation that small particles undergo erratic motion when suspended in water (Brownian motion). In Einstein's theory, Brownian motion was viewed as the result of collisions between the suspended particle and water molecules [17]. The experimental verification of Einstein's theory [18] is generally viewed as a turning point where atomic theory became almost universally accepted among scientists [19].

During the period of time that atomic theory was still debated, experiments demonstrated that neutral elements could be forced to eject negatively charged particles and that the mass-to-charge ratio of these particles was independent of the matter from which it came [20]. This led to the realization that negatively charged particles (electrons) must exist inside of all atoms. Because of the neutrality of elemental atoms, it was implied that positive charges must also exist. While various models for the distribution of positive and negative charges inside of the atom were proposed, a series of famous scattering experiments in the early twentieth century led by Ernest Rutherford showed that the positive charge of an atom was entirely focused in one small region (the nucleus) [21]. By 1920, Rutherford would show that a hydrogen nucleus could be extracted from a nitrogen nucleus through atom-atom collisions [22] — leading to the understanding that all nuclei are composed of some number of hydrogen nuclei, eventually named the “proton”.

Although scientists would add details to our understanding of atomic composition over the years, the general idea of atoms being composed of a positive nucleus with bound negative electrons has been the same for over a century. While these early experiments gave us amazing insight into the composition of matter, they didn't tell us much about the properties of individual atoms or molecules. A thorough understanding of the internal structure of atoms/molecules, and how it leads to their individual properties, would require a number of studies aimed at probing atoms and molecules on a deeper level. Many of the studies that would eventually provide this understanding have been carried out by examining the intricate relationship between light and matter. In many ways, these studies serve as a precursor for the probing of matter by intense, ultrashort pulses that will be examined in this thesis.

1.2.2 Early Experiments Probing Matter with Light

Some of the first experimental insight into the strange internal structure of atoms and molecules came before Dalton's atomic theory was proposed, let alone accepted. In the early nineteenth century, both William Wollaston and Joseph Von Fraunhofer independently discovered that when sunlight reaching the earth's surface is split into its constituent colors, a number of dark lines appear in the spectrum [23, 24]. Later experiments throughout the century would show that similar dark lines appeared in light that was passed through gaseous samples; additionally, it was found that these samples could be forced to emit light at specific, discrete frequencies through the addition of heat or electricity [25]. In the eighteen sixties, Kirchhoff and Bunsen showed that (for a given gaseous sample) the dark lines of an absorption spectrum are at the same frequencies as the bright lines of an emission spectrum, and that these special frequencies differed for gaseous samples of different chemical compositions. These findings led them to propose that elements only emit/absorb light at specific, discrete frequencies, and that these frequencies are unique to each element [26]. Eventually this idea would allow for the identification of specific elements in the sun's atmosphere, and would be applied by Kirchhoff and Bunsen to discover various new elements [25].

As atomic theory was slowly accepted by scientists, it became clear that the discrete absorption/emission spectra of given elements was related to the properties and internal structure of

the atoms that composed them. Patterns in the absorption spectrum of hydrogen were identified by Balmer, who was able to find a mathematical formula that not only fit all previously observed lines in the hydrogen spectrum, but that predicted additional lines in the ultraviolet and infrared regions that would later be found. This clearly demonstrated that some mathematical laws must exist to govern how atoms absorb/emit light, even if the physical reasons behind these laws was not at all understood [27].

The next piece to the puzzle came from a series of studies in the late nineteenth and early twentieth centuries on the photoelectric effect. Hertz first discovered that ultraviolet light incident upon a metal plate can result in the emission of electrons. Lenard expanded these studies to show, among other things, that there exists a cutoff frequency below which no electrons are ionized. These findings were puzzling, as classical electromagnetism predicted that the energy of the incident light depended only on intensity and not frequency [28]. Einstein would eventually provide a solution to this problem by proposing that light is composed of particles called photons, each carrying energy $E = \omega$. Within this description, electrons would be emitted with a maximum energy of $E = \omega - W$, where W was the “work function” describing the amount of energy binding the electron to the metal. The cutoff frequency for ionization would occur when $\omega < W$ [29]. It is interesting to note that while Einstein’s theory of light quantization accurately described the results seen in the photoelectric effect and was ultimately correct, the eventual development of quantum mechanics would show that the photoelectric effect can be fully understood without taking the quantum nature of light into account.

Niels Bohr was the first to put the pieces together; by combining conservation of energy, Einstein’s idea of photons, and the observation that atoms could only absorb/emit light at specific frequencies, Bohr suggested that the electrons within an atom have quantized energy levels. Within this picture, atoms can only absorb a photon at a particular frequency if the energy of that photon is resonant with the energy difference between the atom’s discrete energy levels. Just as atoms could absorb these resonant photons to “jump” to higher energy levels, they could also emit photons when falling back into the lower levels — explaining why atoms emit and absorb at the same frequency [30].

These early experiments on how light interacts with gas-phase elements and metallic sur-

faces led directly to our current theoretical understanding of the internal structure of atoms and molecules. Bohr eventually developed a simple theory of quantization that succeeded in predicting Balmer’s formula for the absorption lines in hydrogen. Louis de Broglie would also attempt to explain the quantization of atomic energy levels with his conjecture that electrons have wave-like properties, in addition to the particle-like properties that had been previously observed [31]. While neither of these theories turned out to give the correct quantitative results for complicated atoms, they did lead to the eventual development of quantum mechanics and the time-dependent Schrödinger equation (TDSE) — a theory that provides our best current understanding of atomic and molecular properties, and that predicts both energy-level quantization and wave-like properties of matter [32].

1.2.3 Early Laser Experiments

While early experiments on light-matter interactions led to the development of quantum mechanics, the theory of quantum mechanics would in turn create many predictions that led to experimental advances in the light sources used for probing systems — most importantly, the laser. The TDSE predicts that not only can atoms and molecules be excited to higher energy states by a resonant source of light, but that these systems can be driven down from excited states to lower energy states by a resonant light source as well. Due to conservation of energy, this process causes the emission of a photon at the resonant frequency. This process, known as stimulated emission, was first described by Einstein [33]. It was quickly realized that this process could serve to produce many photons of the same frequency, thus providing a method for creating a coherent, nearly monochromatic beam of light. Within 43 years of Einstein’s work, such devices were constructed to produce light in the microwave [34] and visible regions [35] of the spectrum.

The years following the invention of the laser led to a revolution in the ability to accurately study atomic and molecular processes. The near monochromaticity of laser light allowed for far greater resolution in measurements of atomic/molecular energy levels, resulting in highly accurate measurements of hyperfine structure in atoms and molecules — small splittings in energy levels that arise from the interaction between the nuclear and electron magnetic dipoles, *i.e.*, spin-spin interaction — and resolution of molecular rotational and vibrational structure [36–41].

Additionally, the much larger intensity of lasers provided a much larger numbers of photons to drive transitions in a system. This opened up the possibility of studying systems that were not responsive enough to measure with weaker, traditional light sources [42].

The high intensity of lasers also provided a means for measuring processes where multiple photons are absorbed or emitted simultaneously. The ability to drive two-photon processes led to the creation of Doppler-free two-photon spectroscopy — a method that allowed for measurements of the $1s$ to $2s$ transition in atomic hydrogen [43], and for accurate resolution of the energy associated with a number of two-photon hyperfine transitions [44–48]. Two-photon spectroscopy is still being applied to make increasingly accurate measurements of the $1s$ to $2s$ transition in hydrogen [49–51], with measurements of the same transition in anti-hydrogen being made recently as well [52, 53]. The high accuracy of these measurements provides a means for probing physical phenomena beyond those predicted by the TDSE, allowing for tests of quantum electrodynamics and the standard model — see, for example, Refs. [54–57] and the references therein.

As lasers with increasingly high intensities became available, the observation of processes that require the absorption of far more than two photons became possible. Such multiphoton processes were observed in transitions between bound states [58], and in ionization/dissociation where a system that has already experienced breakup absorbs additional photons in the field [59–62]. This second phenomenon, known as above threshold ionization/dissociation (ATI/ATD), was first observed by Agostini *et al* in the photoelectron spectrum of xenon [59]. The spectrum clearly showed not only a peak in the photoelectron spectrum at the energy predicted by ionization of the system by six photons (the minimum number required to overcome the atoms binding energy), but also showed a less probable, subsequent peak spaced by one photon in energy that was associated with absorption of an additional photon by the already ionized electron. With modern lasers, an entire series featuring more than a hundred of these peaks, separated by the energy of a single photon, can be observed [63].

1.2.4 Pulsed Laser Experiments and Dynamics

While the list of individual techniques in spectroscopy and the important measurements that came from them is far beyond the scope of this thesis, it suffices to say that laser spectroscopy has

provided our most accurate and complete idea of the internal structure of atoms and molecules. In addition to these structural insights, lasers also allowed for the first measurements of atomic and molecular dynamics on their intrinsic timescales. While early laser experiments made use of nearly monochromatic light with very long pulses (infinite in the purely theoretical case of a perfectly monochromatic light), modern laser technology allows for the creation of pulsed lasers that exist only for a very small duration of time (but have a correspondingly larger bandwidth in frequency). It is standard convention to refer to the nearly monochromatic lasers as continuous-wave, while referring to lasers with short duration as pulsed lasers — with “nearly monochromatic” typically being defined by the relative size of the bandwidth in frequency and the energy levels of the system being studied.

Pulsed lasers can be thought of as akin to cameras; if you wish to photograph an object that is moving, it is important to have a shutter speed fast enough that the camera only receives light during a time period where the object’s motion is negligible. A shutter speed that is too slow will allow the camera to receive light from the object while it is at multiple positions throughout its trajectory and, thus, create a blurry image. Similarly, measuring an observable produced by the interaction of a pulsed laser with an atom/molecule provides information about the state of the system at some time during the duration of the pulse. In order to get a clear, time-resolved picture of how the state of the system changes, the laser pulse must be short enough that any changes to the system are negligible during the pulse’s duration. Because nuclear processes in molecules typically occur on the picosecond or femtosecond timescale, while electronic processes tend to occur on the attosecond timescale, laser pulses with durations on these timescales are necessary for studies of nuclear and electronic dynamics.

With the advent of laser pulses in this picosecond/femtosecond regime, probing the temporal dynamics of molecular processes became possible for first time [64–69]. Early picosecond studies allowed for time-resolved measurements of changes in excited state populations, providing orientational relaxation times for molecules that had previously been aligned with a laser pulse [70], vibrational relaxation times in excited molecules [71], and decay times for cis-trans isomerization processes [72]. Studies of changes in vibrational population over time were able to show clear quantum interference effects for heavy nuclei where such effects were not expected — with

studies on anthracene showing revivals of excited vibrational-state populations with well-defined periods, as opposed to the anticipated exponential decay [73, 74]. Similarly, early femtosecond pulses provided the means to resolve the dynamics of bond breaking and formation that occur during chemical reactions. The first of these experiments focused on molecular breakup, showing how the triatomic system ICN split apart to form I+CN and monitoring the rise and decay of intermediate transition states throughout the process [75, 76]. Soon thereafter, time-resolved studies were carried out on the bond formation $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$ [77], and on the effects of solvents on dissociation in I_2 [78].

Since the production of the first attosecond pulse in 2001 [79], there has been considerable interest in studying the fast electronic motion in atoms and molecules in a manner similar to the way nuclear motion was studied with pico- and femtochemistry [80]. While meaningful results have come at a much slower pace (compared to the first twenty years of pico- and femtochemistry), some initial progress has been made. For example, attosecond experiments have studied the role of electron correlation in the autoionization of atoms, diatomics, and small polyatomic systems [81–84]. Additionally, studies have claimed to answer questions about the time it takes for ionization to occur by using attosecond streaking measurements to infer relative ionization times between electrons in different orbitals [85, 86]. However, the interpretation that the differences seen in these measurements were caused by photoemission delays has been debated; additionally, attempts to extract such delays from calculations have failed to produce agreement with the experiment (see discussion in Ref. [87] and the references within).

More recently, the use of free-electron lasers to generate attosecond pulses in the x-ray regime has been achieved [88–90]. Such pulses have photon energies high enough to ionize tightly bound, inner-shell electrons, and provide the temporal resolution necessary for studying how the remaining electrons adjust to the “hole” left behind by the ionized electron. Studies of this nature have probed the dynamics of the remaining electrons and examined Auger decay — the process where an excited electron drops into the lower-energy hole and redistributes its excess energy to other electrons in such a way that ionization occurs [91–95]. Some believe that promising early work with x-ray attosecond pulses suggests that the use of free-electron sources could provide a breakthrough in attoscience, although others remain skeptical about whether attoscience will ever

be able to provide the level of understanding for electron dynamics that pico- and femtochemistry did for nuclear dynamics [96]. Regardless, attosecond science remains a popular research topic and a candidate for furthering our understanding of atomic and molecular processes.

1.3 Carrier-Envelope and Multi-Color Control

Section 1.2 illustrates how integral the role of laser-matter interactions has been for furthering our understanding of both the internal structure of atoms/molecules and the dynamics that occurs in these systems as they undergo chemical processes. We now turn our attention to the specific type of laser-matter interaction studies that this thesis will focus on: the use of pulsed, ultrashort lasers to control atomic and molecular processes. The ability to produce pulses that have temporal durations on the order of (or smaller than) electronic and nuclear motions not only allowed for time resolution of atomic and molecular dynamics, it also opened up the possibility of using lasers to actively alter these processes as they occur to produce a favorable outcome (coherent control). While there are numerous laser parameters that can be varied to obtain control, we will restrict ourselves to control via the carrier-envelope phase (CEP) of a single pulse and the relative phase between individual components of multi-color pulses. The CEP of a laser is given by the offset between the envelope of the pulse’s electric field, $\mathcal{E}_0(t)$, and its oscillating carrier wave — denoted by φ in the field $\mathcal{E}(t) = \mathcal{E}_0(t) \cos(\omega t + \varphi)$. Similarly, the relative phase between two colors ω_1 and ω_2 in a multi-color pulse is defined as the difference between the phases φ_1 and φ_2 in the field $\mathcal{E}(t) = \mathcal{E}_1(t) \cos(\omega_1 t + \varphi_1) + \mathcal{E}_2(t) \cos(\omega_2 t + \varphi_2)$

Changing the CEP of a pulse will alter the electric field experienced by the system and, therefore, can produce changes in a measured observable. These changes in observables are negligible for long pulses approaching the continuous-wave limit — where the number of cycles is much larger than one — but become pronounced for the few-cycle pulses common in ultrashort physics. The ability to alter the CEP of an incident pulse to change the outcome of an experiment has led to interest in using the CEP as a means for coherent control. The first experimental observation of the CEP dependence of physical observables came from studies on photoionization in noble gases, which showed that the direction of the emitted electron is sensitive to the CEP of

the pulse [97]. Later experiments would directly measure this effect as a function of the CEP [98, 99], discover that double-ionization of atomic systems can be controlled by the CEP [100], and show that the direction of electron emission could also be controlled in molecular ionization [101].

Carrier-envelope phase effects can also be observed in nuclear dynamics, where studies show that the emission direction of nuclear fragments can be controlled by varying the CEP. Such effects were first predicted for H_2^+ and its isotopologues D_2^+ and HD^+ , where it was proposed that the momentum distribution, kinetic energy release spectrum, and total dissociation probability could all be controlled by the CEP [102]. These predictions were realized experimentally for a number of diatomic systems including H_2^+ [103, 104], H_2 [105], D_2 [106], HD [107], CO [108, 109], and DCI [110]. Eventually it was shown that the CEP can also be used to control branching ratios in the isomerization and fragmentation of polyatomic molecules [111], or between the resultant ionic states in LiH dissociation [112].

Multi-color control originated before the use of CEP control, as unlike CEP control it does not require ultrashort pulses to be employed effectively. A general scheme for this type of control was proposed by Brumer and Shapiro, where they demonstrated that control over physical observables could be obtained using two pulses with central frequencies $\omega_1 = \omega$ and $\omega_2 = 3\omega$ (and, in later work, with $\omega_2 = 2\omega$) [113–115]. Because the absorption of three ω_1 photons will leave the system in a state with the same energy as the absorption of a single ω_2 photon, these two pathways will interfere to produce the observable. Simple calculations from perturbation theory show that this interference can be controlled by varying the relative phase between the two pulses, with early calculations predicting this control in IBr dissociation [113, 116].

The first experimental observation of ω - 3ω , two-color control came from studies on the total ionization yield of Hg [117]. Soon thereafter, similar studies demonstrated coherent control of HCl [118, 119], H_2S [120], and CO [119]. Later studies would demonstrate that some observables can also be controlled by the relative phase of pulses with $\omega_1 = \omega$ and $\omega_2 = 2\omega$ [114, 121–125]. It is worth noting that control over the total dissociation yield is not seen in this control scheme. A number of works have also shown the branching ratios of dissociating molecules into different product states can be controlled by both ω - 2ω and ω - 3ω schemes [121, 122, 126].

More recently, experiments that employ multi-color control on the attosecond level have

become of interest — specifically, in the form of using attosecond pulse trains. Attosecond pulse trains are simply a series of laser pulses, each separated by — and having a duration on the timescale of — attoseconds. Such pulse trains are generated by combining a series of laser pulses with commensurate frequencies, typically created through the process of high harmonic generation. Varying the relative phase between the different colors used to construct the pulse train provides a means for a multi-color control scheme using attosecond pulses. Pulse trains provide a convenient means for attosecond control because they are more easily generated than isolated attosecond pulses (which presents a number of technical challenges) [127–130].

1.4 Understanding CEP and Two-Color Control

Both experiment and theory have conclusively shown that it is possible to control a number of physical observables for a variety of different systems by varying the CEP of a single pulse or relative phase between multiple pulses. In order to go beyond simply demonstrating control, it is ideal to have an *ab initio* theory that allows for predictions about the type of control that will be available for a particular system and provides insight into how to increase the degree to which control is possible over a given observable. In Chap. 2, we will introduce our group’s formalism for understanding coherent control — which explicitly shows how different pathways interfere to create a given observable, and shows how altering the CEP or delay provides control over this interference. This formalism has been successfully applied to understand strong-field control over a number of systems previously [7] [103, 104, 131–133], and the extension and application of this formalism will be the focus of this thesis. In this section, we will review some other commonly used methods for understanding intense, ultrashort physics in order to provide context and illustrate the differences between our approach.

1.4.1 Numerical Solutions of the TDSE

The most obvious starting point for a theoretical understanding of CEP and multi-color control is the TDSE. However, there are issues with directly solving the TDSE in order to understand control. One such problem is that exact solutions cannot be obtained analytically for even the

simplest atom or molecule in a pulsed laser field. It is, of course, possible to numerically solve the TDSE in order to study how an observable depends that laser parameter. Unfortunately, without an analytic expression for the observable, the information gained from such a method is somewhat limited. For example, CEP control can be easily be observed in calculations of the photoelectron spectrum of hydrogen; it can be seen that the spectrum oscillates with the CEP at certain energies, and both the magnitude and periodicity of these changes can be observed. However, such results cannot provide information about how the magnitude and periods of these oscillations depend on other laser parameters (pulse length, intensity, wavelength, etc.) without additional calculations that span a representative sample of the entire parameter space. Moreover, they do not provide insight into the physical mechanisms that are responsible for this control — information that is needed to extrapolate these findings to other systems where the contributing mechanisms might be larger or smaller, or where new mechanisms might arise altogether.

In many ways, the limitations of understanding coherent control through direct solution of the TDSE are similar to the limitations in understanding coherent control through studies of experimental spectra. In both cases control can be observed, and, if calculations/experiments are carried out for a large number of systems and laser parameters, patterns will begin to emerge. Still, much is left to be desired in this understanding and an approach that provides an analytic expression, especially one that can be understood in terms of physical mechanisms, can provide additional information. The TDSE does provide some advantage over experiment in the sense that solutions of the TDSE allow for more detailed studies where certain physical mechanisms can be excluded from a solution in order to determine their effect on control. A calculation can, for example, exclude permanent-dipole transitions and only include electronic transitions to study the role of each in control.

Conversely, solving the TDSE also has some limitations that are more strict than in experimental studies — specifically with regard to studying more complicated atoms or molecules. For a simple system like atomic hydrogen with center-of-mass motion removed, a wavefunction must be stored at all points on a grid of size $N_r N_\theta N_\phi$ (where N_i is the number of points required for a converged result for the radius, polar angle, and azimuthal angle, respectively). For a three-particle system, this product has six terms, and it is apparent that as the number of particles

increases the total number of data points will increase exponentially. Although basis expansions and clever coordinate choices can be used to decrease the amount of information needed for each new coordinate, this scaling still quickly causes issues with storing all of the relevant data points in a computer's memory. Because of this limitation, TDSE studies tend to focus on atoms and molecules with a small number of constituent particles, or focus on calculations that artificially reduce the degrees of freedom included in the calculation.

1.4.2 Perturbation Theory

One common approach to laser-matter interaction problems that does provide some physical interpretation is lowest-order perturbation theory (LOPT). In general, perturbation theory allows for the approximate calculation of the wavefunction to an order k that corresponds to the total number of photons exchanged with the field; it also describes observables in terms of matrix elements that represent transitions between different states. These two ideas allow us to interpret the perturbative approximation of an observable in terms of the interference between different total-photon pathways to a given final state. A simple example outlining the four lowest-order pathways to the first peak in a photoelectron spectrum is shown in Fig. 1.1. In LOPT, only the pathway associated with the smallest number of total photons expected to contribute at a given energy is included in the calculation. For example, a LOPT calculation of the first peak in the photoelectron spectrum corresponding to Fig. 1.1 would include only the pathway involving the

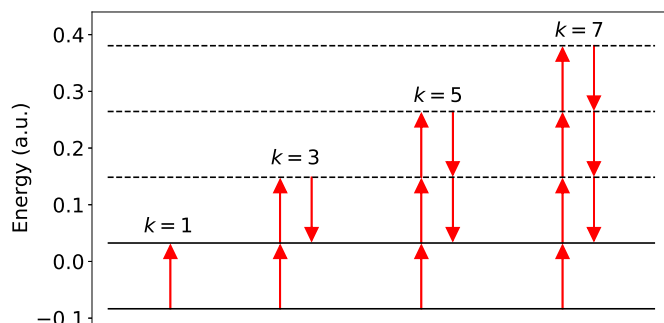


Figure 1.1: Illustration of the total-photon pathways of order k (in the wavefunction) that contribute to the first peak in a photoelectron spectrum. The arrows represent absorption/emission of photons at the central frequency, the solid lines represent the initial and final energies of the system, and the dashed lines represent intermediate state energies.

absorption of a single photon.

Because of its interpretive power and its ability to provide an analytic expression that clearly separates the more system-dependent quantities (matrix elements), LOPT is an important tool in our theoretical understanding of how atoms and molecules behave in a laser field. Unfortunately, due to the large number of photons exchanged, LOPT often breaks down for interactions involving intense laser pulses [134]. For example, when the intensity is high enough that the higher-order pathways in Fig. 1.1 occur with a large enough probability, the LOPT approximation of the first peak in the photoelectron spectrum will fail to reproduce the peak given by the TDSE. When LOPT breaks down, it is still possible to calculate an accurate spectrum through perturbation theory if enough orders are included. However, many orders are often needed for a converged calculation and there is no *a priori* way to know how many orders to include for a given field/intensity. This complicates the process of applying perturbation theory to make simple predictions about two-color and CEP control in intense fields.

1.4.3 Floquet Theory

The shortcomings of LOPT for describing intense, ultrashort physics necessitates the use of alternative approaches to understand physics in this regime. One common theory for understanding intense-field physics is Floquet theory. Floquet theory originated as a mathematical theorem for linear differential equation of the form $\dot{x} = A(t)x$ with a periodic coefficients $A(t + T) = A(t)$. The theorem states that such problems are not required to have a periodic solution $x(t) = x(t + T)$, but are required to have a solution that can be separated into the product $x(t) = e^{i\epsilon t}\Phi(t)$ where $\Phi(t) = \Phi(t + T)$ is a periodic function [135].

Floquet theory was first used in quantum mechanics for time-independent Hamiltonians with spatial periodicity, such as an electron moving through a uniform solid where it sees the same repeating interaction as it travels from one atom to the next. In this context, Floquet theory is often referred to as Bloch's theorem [136] — as it was rediscovered by Bloch in his treatment of these spatially periodic systems. Floquet theory was eventually applied to atoms and molecules in intense, purely monochromatic laser fields by taking advantage of the $T = 2\pi/\omega$ periodicity of the laser's electric field, $\mathcal{E} = \mathcal{E}_0 \cos \omega t$ [137]. In applications of Floquet theory it is very

common, though not necessary, to also expand the periodic portion Φ of the wavefunction in a Fourier series to write $\Psi(t) = e^{i\epsilon t} \sum_n \Phi_n e^{in\omega t}$ [20, 137].

The equations produced for Φ_n in this Fourier-Floquet representation have the advantage of being time-independent and tri-diagonal, and solutions of the equations have been carried out for a variety of systems [138]. One of its most important features, however, is in its contribution to understanding multiphoton processes on a conceptual level. Comparison of the Fourier-Floquet equations to a more formal treatment that quantizes the electromagnetic field reveals that (within the dipole approximation) the summation index n can be interpreted as the net number of photons exchanged with the field [137]. The functions Φ_n therefore provide an amplitude that corresponds to the probability of exchanging a net number of n photons with the field, and, thus, allow us to interpret physical observables in terms of photon pathways associated with these exchanges.

The main limitation of Floquet theory is that it cannot be applied to ultrafast pulses where the field is no longer periodic in time. Two-time formalisms [139, 140] and adiabatic Floquet theories [141–143] that circumvent this issue have been developed and applied, allowing for the treatment of systems interacting with pulsed lasers. However, while these extensions of Floquet theory can provide an intuitive method for understanding a spectrum in terms of the interference between different net-photon pathways, they do not provide a method for understanding how these interferences change as a function of the CEP or relative phase. Without the ability to understand the role of these phases in interference, straightforward application of Floquet theories to understand control is somewhat limited without explicitly doing calculations for a given system.

1.4.4 The Three-Step Model and Strong-Field Approximation

The three-step model is another method that is commonly used for a conceptual understanding of the physical mechanisms that contribute to ionization [144]. This *ad hoc* model breaks the dynamics of an ionized electron in three steps. In the first step, ionization occurs as the electron escapes the atom through the process of tunneling. Second, the ionized electron propagates away from the resulting ion in the laser’s electric field (neglecting the effect of the Coulomb interaction). Finally, the electron is, potentially, driven back towards the ion as the field oscillates to change direction. This third step is essential in using the three-step model to understand high-harmonic

generation [144, 145], above threshold ionization [59–62], and non-sequential double ionization (see Ref. [146] and the references within).

While the three-step model is often used only for qualitative descriptions, it is possible to model each of the individual steps using a combination of quantum and classical mechanics in order to make quantitative approximations. In such approaches, tunneling ionization rates in the first step are approximated to determine the distribution of ionization times — often using the quasistatic Ammosov-Delone-Krainov (ADK) tunneling rate [147]. The electron propagation in the second and third steps can be modeled classically by solving Newton’s equations for the electron trajectories corresponding to ionization at the different times found in step one. Some electrons do not return to the parent ion, the so-called “direct electrons”, and will simply leave — for these electrons, the above steps are all that is needed to model the electron’s trajectory.

In contrast, some electrons will be driven back toward the parent ion, causing an interaction between the two particles. This interaction can lead to two processes — rescattering and recombination. Rescattering can cause a change in the energy of the electron, or — if the return energy is larger than the ionization energy of the ion — a second ionization. Recombination can also occur, where the electron becomes bound to the ion once more and emits a photon to account for its lost energy. Both the rescattering and recombination that occur in the third step can be modeled using a variety of methods — more details of calculations based on this model can be found in Ref. [60] and the references within.

Results from these types of quantitative implementations of the three-step model can predict a number of features in the photoelectron and high-harmonic spectra that have been observed experimentally. However, these implementations cannot give quantitative agreement with spectra nor can they predict all relevant features [60]. The theory is mainly used today due to its simple ability to attribute certain observed phenomena to the types of (easily understood) classical electron trajectories required to create them. Quantitative improvements can be made to the various approximations used in each step of the model, however it is an *ad hoc* model and is inherently limited by that fact. Unlike LOPT or Floquet theory, which come directly from the TDSE and will always approach the exact result when high enough orders are included, there is no way to systematically improve the three-step model in a way that is guaranteed to converge

to the correct answer.

Although it can be viewed as a separate theory, in many ways the strong-field approximation (SFA) is a fully quantum mechanical extension of the three-step model. In the SFA, the quantum mechanical probability of ionizing with a given momentum $\mathbf{p}$ is approximated by using Volkov states — exact solutions to the TDSE for a free electron in an electromagnetic field — in place of the exact electron state that includes the effects of both the electromagnetic field and the Coulomb potential. This approximation is somewhat analogous to the classical propagation in the three-step model, which also ignores the Coulomb interaction. The resulting integrals are carried out using the Born series, with only the first two terms of the Born series typically included. These terms can be shown to correspond to direct electrons that do not rescatter from the parent system and electrons that do undergo rescattering/recombination, further connecting to the ideas of the three-step model.

The SFA was originally formulated for studying ionization by Reiss [148], although it is often grouped with earlier, less exact theories formulated by Keldysh [149] and Faisal [150] — which require tunneling or high frequency approximations, respectively [151]. This grouping is often referred to as KFR theory for the initials of the contributing authors. Strong-field approximations were later extended to describe high-harmonic generation [152]. Calculations based on the SFA can provide good qualitative (and, sometimes, quantitative) agreement for a number of experimentally observed phenomena. Results are most accurate when applied to single ionization from negative ions, where the Coulomb interaction experienced by the ionized electron is zero to first order (neglecting polarization of the parent ion) [153, 154]. It also has been successfully applied to understand ionization from neutral targets on a qualitative level, although the degree of agreement with experiment and TDSE calculations is worse when interaction with the parent ion becomes more important — with results sometimes being off by orders of magnitude [155, 156].

Modern versions of both SFA and tunneling theories have attempted to improve the agreement of the theory with experiment and TDSE solutions. Tunneling theories have now been expanded to include the effects of the dipole that were neglected in earlier works [157, 158]. Improvements of SFA are based on the idea of reducing the relevant matrix elements into a factorized form, with each of the factors corresponding to an individual step in the three-step model. By using intu-

ition about the physical processes that occur during the individual steps, it is possible to improve these factors in order to increase the overall accuracy of the complete matrix elements [159–162]. One common method of achieving this factorization applies the Feynman path integral formulation of quantum mechanics — which allows for the expression of the relevant matrix elements in terms of a sum over all possible trajectories the system can take between the initial and final time. Such methods further connect the SFA to the three-step model, which is viewed in terms of electron trajectories, and allow for the possibility of seeing exactly which trajectories are required to reproduce an experimental result. This second feature provides useful information for understanding the physical phenomena that contribute specific features in a spectrum [159–161].

Strong-field approximations, in any form, suffer from a few issues that limit their applicability to understanding control. First, SFAs make use of Volkov states that neglect the Coulomb interaction; this approximation fails to correctly reproduce the observed physics for some systems. Improvements upon SFA can be made by replacing Volkov states with Coulomb-Volkov states — which approximately include the effect of the Coulomb interaction [163–165]. However, while the use of Coulomb-Volkov states can improve agreement with experiment [166], discrepancies still exist between Coulomb-Volkov theories and direct calculations from the TDSE [164]. Second, the theory depends on the choice of gauge; for example, calculations carried out using velocity and length gauge can give different answers [167, 168]. Finally, the strong-field approximation does not provide a simple analytic description of how the transition amplitudes calculated within SFA depend on the CEP or delay of a pulse — much like the TDSE it requires solving numerically for every individual phase in order to see the effects of changing those laser parameters.

1.5 Closing Remarks

As evidenced throughout this chapter, using light to better understand atomic/molecular structure and processes has a long and rich history. In more recent years, it has become possible to use lasers to control the dynamics of these systems on their intrinsic time scale. The potential applications of controlling chemical reactions is of great interest and, as such, it is important to develop theories that allow us to understand the type of control possible for a given system.

While many theories for ultrashort, intense laser physics exist, they are limited in their ability to provide quantitative predictions about specific control mechanisms. They also tend to rely on approximations that neglect some of the physics necessary to explain experimentally observed phenomena.

The goal of this thesis will be to introduce and apply an essentially exact formalism that allows for certain quantitative predictions about the types of control that can be obtained in CEP and multi-color experiments. This picture will allow for the interpretation of observables in terms of photon-pathways, much like perturbation theory and Floquet, that provide an intuitive understanding of the processes that contribute to control. In Chap. 2 our group's formalism will be introduced, while in Chap. 3 and Chap. 6 we will apply our formalism to understand CEP and multi-color control. Chapters 4 and 5 will demonstrate the ability to use our formalism to extract information about both the pulse and system from experimental data sets; allowing for us to better understand methods of pulse characterization, and to extract information about the physical mechanisms that contribute to a given feature in a spectrum.

Chapter 2

Parametric Formalism

As stated in Section 1.5, the goal of this thesis is two-fold. First, we will outline and apply our group’s parametric formalism in order to make predictions about, and understand the physical processes that contribute to, the control that is obtained over a given observable by varying the the carrier-envelope phase or relative phases between colors. Second, we will address the inverse problem and use our parametric theory to extract information about the system or laser from data showing clear multi-color control or CEP effects. In this chapter, we will develop the parametric theory for CEP and multi-color control upon which the remainder of the thesis will be based. Similar derivations of our theory for single-color CEP control have been outlined and applied in previous work [7] [103, 104, 131–133], while generalization to two- and three-color pulses exist in unpublished work from our group [2, 3]. We begin by examining the general assumptions that are required for the results derived within our parametric formalism to hold.

2.1 Starting Points, Limitations, and Assumptions

The derivation of our formalism begins from the TDSE within the dipole approximation, and, as such, the results derived are limited to systems with dynamics that can be accurately described by this equation. Because the TDSE is a non-relativistic equation, it does inherently fail for heavy atoms where bound electrons can reach relativistic speeds, for systems interacting with lasers that produce breakup with particle speeds that approach the speed of light, or for laser intensities large enough that pair-production of additional particles becomes relevant [169–175]. “Simpler”

relativistic effects such as spin can be included in our theory by adding the spin portion of the wavefunction as a direct product in the usual manner.

Additional constraints are applied on our formalism by making the dipole approximation. In the dipole approximation, the vector potential associated with the laser's electromagnetic field is approximated as constant in space. Mathematically, this is equivalent to keeping only the first term in the Taylor expansion of the spatial portion for the carrier wave of the vector potential — $e^{i2\pi\hat{\mathbf{k}}\cdot\mathbf{x}/\lambda} \approx 1 + \mathcal{O}(x/\lambda)$, where λ is the wavelength of the light and $\mathbf{x}$ is the vector describing the position of the charged particles in the vector potential. This approximation can be justified for lower intensities, where ATI/ATD is negligible and ionization/dissociation occurs mainly through bound-free transitions, by appealing to LOPT. In this case, the relevant limits of integration are determined by the size of the bound system, implying that the dipole approximation is valid as long as the wavelength of the light is much larger than the bound system.

While this justification of the dipole approximation is less applicable for higher intensities where free-free transitions become important, the dipole approximation still typically holds for intense field physics [176]; non-dipole effects are mostly observed when the wavelength of light becomes smaller than to the size of the system being studied [177–183]. There are, however, two exceptions worth noting: ponderomotive shifts and effects due to the magnetic field associated with the pulse. Both of these effects have been observed even outside of the large system or short wavelength limit.

2.1.1 Pondermotive Effects

Pondermotive effects occur in short pulses and result in a shift in energy of the fragments produced during break-up, producing a spectrum with peaks at energies lower than would be predicted for the absorption of a given number of photons from the initial state [185,186]. Classical calculations have explained this shift in terms of the energy gained by charged particles as they traverse the spatial gradient of the laser's electric field [186,187]. In these descriptions, the energy absorbed from photons during break-up is distributed among the various degrees of freedom of the system, with some of the energy being associated with the charged particles oscillating along with the field — the pondermotive energy. As the oscillating particles experience the field's gradient and

are pushed away from the spatial center of the pulse, this ponderomotive energy will decrease to match the lessened field strength in these regions. This lost ponderomotive energy is equal to the translational/rotational energy gained through interaction with the field's spatial gradient; *i.e.*, the ponderomotive energy is converted to the forms of energy that are detected in experiment.

These classical calculations predict that for long enough pulses, particles created during breakup will have time to traverse the full spatial profile of the pulse and convert the entirety of their ponderomotive energy into translational/rotational energy. In contrast, when shorter pulses are used, particles will not have time to move a considerable distance through the spatial profile of the field and only a portion of the ponderomotive energy will be converted — resulting in ponderomotive shifts for short pulses. For calculations carried out within the dipole approximation, none of the ponderomotive energy can be regained because the vector potential and associated electric field are constant in space. As such, discrepancies between the energies of particles observed in experiment and calculation can occur for long pulses.

2.1.2 Effects of the Magnetic Field

By approximating the vector potential as constant in space, all magnetic forces are neglected in the dipole approximation. Because the Lorentz force is proportional to the speed of the charged particles, this is typically a small effect for non-relativistic particles traveling in short pulses. However, previous theoretical work has found an intensity regime in which ionized electrons have non-relativistic speeds, but still are considerably altered by the presence of a magnetic field [184, 188, 189]. Such effects were found to be important when the value of the intensity I approaches $I = 8c\omega^3$, where c is the speed of light in a vacuum — for the commonly used Ti:sapphire laser systems producing roughly 800-nm light, this corresponds to $I = 5 \times 10^{15} \text{ W/cm}^2$. These effects can result in the failure of the dipole approximation even when the wavelength is much larger than the system, provided the intensity is large enough.

2.1.3 Choice of Electric Field

Within the dipole approximation, and using the length gauge, the TDSE becomes

$$i\frac{\partial}{\partial t}\psi(t) = [H_0 - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{d}] \psi(t), \quad (2.1)$$

where H_0 is the field-free Hamiltonian for the system being probed by the laser, $\boldsymbol{\mathcal{E}}$ is the electric field associated with the laser, and $\boldsymbol{d} = \sum q_i \boldsymbol{r}_i$ is the dipole for the system (with q_i and $\boldsymbol{r}_i$ being the charges and coordinates, respectively, of the system's constituent particles). Atomic units [190] have been used in Eq. (2.1) and will be used throughout this thesis unless explicitly noted¹. The choice of gauge is not important, as our theory can be equivalently derived with other gauge choices.

Our theory is derived by exploiting certain properties of the electric field, and, therefore, will only apply to interactions involving lasers with these properties. All results that follow will hold for any field with the form

$$\boldsymbol{\mathcal{E}}(t) = \sum_{s=1} \boldsymbol{\mathcal{E}}_s(t) \cos(\omega_s t + \varphi_s). \quad (2.2)$$

Equation (2.2) allows for pulses of multiple colors to be combined, with $\boldsymbol{\mathcal{E}}_s(t)$ being the envelope (including polarization) of an individual pulse with phase φ_s and central frequency ω_s . Setting $\omega_s = s\omega$ will allow for a straightforward application of our theory to the multi-color control involving a fundamental pulse $\boldsymbol{\mathcal{E}}_1(t)$ and its harmonics $\boldsymbol{\mathcal{E}}_s(t)$. Similarly, setting $\boldsymbol{\mathcal{E}}_{s>1}(t) = 0$ allows us to study how varying the CEP, φ_1 , of a single-color pulse provides control for a given observable. This thesis will only be concerned with classical, non-quantized electric fields. It is possible, however, to derive our theory using a quantized field for interactions where the quantum nature of light becomes relevant — *i.e.*, for problems where the photon densities of the incident pulses are not large enough to neglect the effect of the creation and annihilation of individual photons.

It is worth noting that all dependence of the electric field on the parameters φ_s is explicitly written in Eq. (2.2); the envelopes are not dependent upon these phases. Our formalism describes

¹Atomic units set $m = \hbar = e = 1$, where m and e are the mass and charge of an electron, respectively, and $\hbar$ is the reduced Planck constant.

the types of control that can be obtained by varying these relative phases, and, as such, will not apply to control obtained by varying the envelopes of the individual pulses relative to one another. This does impose some limitations; for example, our formalism will not directly apply to two-color pump-probe experiments where a pump pulse interacts with the system to facilitate a reaction, and a subsequent probe pulse is introduced at various delays to study the resulting dynamics. However, varying the phases in a multi-color harmonic pulse train can create a similar temporal delay between the fundamental pulse and pulse train, and our formalism can be applied to this form of pump-probe experiment.

Overall, the limitations imposed by starting our theory from Eq. (2.1) and Eq.(2.2) do restrict us to a certain subset of experiments involving laser-matter interactions, however this subset comprises a large portion of the intense, ultrafast physics being done in experiment. For ultrashort laser pulses with intensities small enough to avoid relativistic and magnetic effects, the dipole approximation can produce results that explain phenomena seen in experiment quite accurately for most atomic and molecular systems. Similarly, with the notable exception of certain pump-probe experiments, our theory will allow us to study a wide range of CEP and multi-color control schemes.

2.2 Parametric Formalism Development

2.2.1 Derivation of Formalism

We begin by noting that the electric field in Eq (2.2) — and, thus the Hamiltonian in Eq. (2.1) — are unchanged by the transformations $\varphi_s \rightarrow \varphi_s + 2\pi$. Unlike the case of Floquet theory (Sec. 1.4.3), where the periodicity in the equations of motion is with respect to the dependent variable of time, the periodicity we take advantage of is with respect to independent parameters. As such, our solution $\psi(t)$ will feature the same periodicity in φ_s as the field itself — differing from the Floquet formalism where solutions do not have the same periodicity in time as the field, but instead require an additional phase $e^{i\epsilon t}$. Therefore, we may express $\psi(t)$ exactly as the

discrete Fourier series

$$\psi(t) = \sum_{\mathbf{n}} \psi_{\mathbf{n}}(t) e^{-i\mathbf{n} \cdot \boldsymbol{\varphi}}. \quad (2.3)$$

In Eq. (2.3), $\mathbf{n} = (n_1, n_2, n_3 \dots)$ is the vector that includes the Fourier summation index n_s for each pulse included in the field; similarly, $\boldsymbol{\varphi}$ is the vector containing the phase of each pulse. For example, if a two-color field with frequencies $\omega_1 = \omega$ and $\omega_2 = 2\omega$ is used in Eq. (2.2), then the sum will be over all integer values of n_1 and n_2 — a Fourier expansion in the two phases φ_1 and φ_2 . The convention of using negative or positive arguments in the imaginary exponential terms is irrelevant mathematically because the sum is over both positive and negative values of $\mathbf{n}$; our choice is made specifically so that positive n_s will be associated with photon absorption rather than emission (see Sec. 2.2.2).

In order to make the physical meaning of $\psi_{\mathbf{n}}$ and $\mathbf{n}$ more apparent, we can include the additional factorization $\psi_{\mathbf{n}} = \Phi_{\mathbf{n}} e^{-i\mathbf{n} \cdot \boldsymbol{\omega} t}$ — where $\boldsymbol{\omega}$ is the vector containing the frequency of each pulse. Substituting the resulting expression into Eq. (2.1) and using the linear independence of the basis functions to equate like terms gives

$$i \frac{\partial \Phi_{\mathbf{n}}}{\partial t} = [H_0 - \mathbf{n} \cdot \boldsymbol{\omega}] \Phi_{\mathbf{n}} - \frac{1}{2} \mathbf{d} \cdot \sum_s \boldsymbol{\mathcal{E}}_s [\Phi_{\mathbf{n} + \boldsymbol{\delta}_s} + \Phi_{\mathbf{n} - \boldsymbol{\delta}_s}]. \quad (2.4)$$

In Eq. (2.4), the summation over s is understood to be over all pulses and $\boldsymbol{\delta}_s$ is the unit vector with element i given by $\delta_{i,s}$; the pulse $\boldsymbol{\mathcal{E}}_s$ couples the state with n_s to the states with $n_s \pm 1$ while leaving all other n_i unchanged. For clarity, the equations for the two-color field used above would be:

$$\begin{aligned} i \frac{\partial \Phi_{n_1 n_2}}{\partial t} &= [H_0 - n_1 \omega - 2n_2 \omega] \Phi_{n_1 n_2} - \frac{\mathbf{d} \cdot \boldsymbol{\mathcal{E}}_1}{2} [\Phi_{(n_1+1)n_2} + \Phi_{(n_1-1)n_2}] \\ &\quad - \frac{\mathbf{d} \cdot \boldsymbol{\mathcal{E}}_2}{2} [\Phi_{n_1(n_2+1)} + \Phi_{n_1(n_2-1)}]. \end{aligned} \quad (2.5)$$

2.2.2 Interpretation and Physical Meaning

As a direct consequence of Eq. (2.4), we can gain insight into the physical interpretation of the summation indices $\mathbf{n}$ and $\Phi_{\mathbf{n}}$. At a time before the pulse is turned on, Eq. (2.4) clearly describes states $\Phi_{\mathbf{n}}$ that have energies shifted by $E = E_0 + (n_1 \omega_1 + n_2 \omega_2 + n_3 \omega_3 + \dots)$ from

the unperturbed energies E_0 of the system (or, equivalently, as states existing in potentials that are shifted down, or “dressed”, in energy by the same amount). As such, we can think of $\Phi_{\mathbf{n}}$ as describing states associated with the absorption of a total energy $n_1\omega_1 + n_2\omega_2 + n_3\omega_3 + \dots$ — which is equivalent to stating that n_s counts the net number of ω_s photons absorbed to get into a channel $\Phi_{\mathbf{n}}$ from the initial state with $\mathbf{n} = 0$. This interpretation of $\mathbf{n}$ as counting the net number of photons is also apparent when comparing Eq. (2.4) with Floquet theory, as our theory is equivalent to the Fourier-Floquet representation in the continuous-wave limit. While the interpretation of our formalism in terms of photons becomes more apparent with the additional factorization $\psi_{\mathbf{n}} = \Phi_{\mathbf{n}}e^{-i\mathbf{n}\cdot\boldsymbol{\omega}t}$, the interpretation is also true for $\psi_{\mathbf{n}}$ — which can be understood as a state associated with the exchange of $\mathbf{n}$ photons with the field. As such, we will mainly work with $\psi_{\mathbf{n}}$ in this thesis, except for cases where we wish to generate dressed potentials like those discussed in Sec. 2.3.1 and Sec. 2.3.2.

A specific example illustrating how $\mathbf{n}$ can be determined for various pathways involved in the ionization of hydrogen by the aforementioned two-color field is shown in Fig. 2.1 for clarity. The initial state of the system clearly begins with $n_1 = 0$ and $n_2 = 0$, as the interaction with the field has yet to occur and no energy has been absorbed. Every absorption/emission of a fundamental photon takes the system from $\mathbf{n} = (n_1, n_2) \rightarrow (n_1 \pm 1, n_2)$. Similarly, the absorption/emission of a second harmonic photon takes the system from $(n_1, n_2) \rightarrow (n_1, n_2 \pm 1)$. Because the order in which photons are exchanged has no effect on the final values of $\mathbf{n}$, permutations of pathways are not shown in Fig. 2.1. For example, the pathway involving the absorption of ω_2 followed by the emission of ω_1 is shown, but the pathway involving the emission of ω_1 followed by the absorption of ω_2 is omitted. With the exception of these permutations, all pathways to the first peak in the photoelectron spectrum involving the exchange of up to four total photons at the central frequencies are shown.

2.2.3 Observables in Parametric Formalism

With the physical interpretation of $\mathbf{n}$ from Sec. 2.2.2, we can quantify what exactly is meant by our goal of using information about physical pathways to make predictions for a given observable. The probability associated with measuring a particular value λ for any observable with an associated

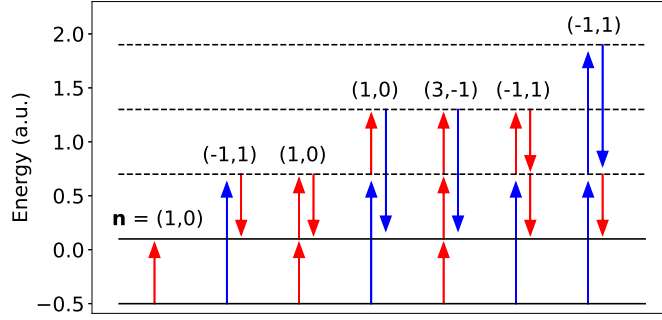


Figure 2.1: Diagram illustrating photon pathways for the ionization of hydrogen from the $n = 1$ initial state ($E = -0.5$ a.u.) in a field with $\omega_1 = 0.6$ a.u. (red arrow) and $\omega_2 = 2\omega_1$ (blue arrow). These photon sizes were chosen to simplify the diagram by allowing for single-photon ionization via ω_1 absorption. Final and initial energies are shown by solid-black, horizontal lines; intermediate state energies are shown with dashed-black, horizontal lines. Each arrow represents the absorption/emission of a single photon.

operator Λ satisfying $\Lambda|\lambda\rangle = \lambda|\lambda\rangle$, can be written explicitly in terms of the wavefunction as:

$$\frac{dP}{d\lambda} = \left| \langle \lambda | \sum_{\mathbf{n}} \psi_{\mathbf{n}} e^{-i\mathbf{n} \cdot \boldsymbol{\varphi}} \rangle \right|^2 = \sum_{\mathbf{n}, \mathbf{n}'} \langle \lambda | \psi_{\mathbf{n}} \rangle \langle \lambda | \psi_{\mathbf{n}'} \rangle^* e^{-i(\mathbf{n} - \mathbf{n}') \cdot \boldsymbol{\varphi}}. \quad (2.6)$$

Equation (2.6) immediately gives information about the pathways that can interfere to create control within a given observable. Because all of the dependence of the observable on the phases $\boldsymbol{\varphi}$ has been explicitly written ($\psi_{\mathbf{n}}$ is independent of $\boldsymbol{\varphi}$), it is apparent that only interference between pathways leading to states with different values of n_s can be controlled by varying the phase φ_s . As such, distinct pathways that end with the same values of $\mathbf{n}$ — such as the multiple pathways shown in Fig. 2.1 that end with $\mathbf{n} = (1, 0)$ — will not contribute to CEP or multi-color control.

As a simple example to illustrate how observables can be determined from pathways in our formalism, we return to previous example from Fig. 2.1 of hydrogen ionization in a two-color field comprised of $\omega_1 = \omega$ and $\omega_2 = 2\omega$. For linearly polarized light, the photoelectron spectrum for hydrogen is given by

$$\frac{dP}{dE} = \sum_{\ell} \frac{dP_{\ell}}{dE} = \sum_{\ell} \sum_{\substack{n_1, n_2 \\ n'_1, n'_2}} A_{n_1 n_2 \ell} A_{n'_1 n'_2 \ell}^* e^{-i(n_1 - n'_1) \varphi_1} e^{-i(n_2 - n'_2) \varphi_2}, \quad (2.7)$$

where $A_{n_1 n_2 \ell} = \langle E \ell | \psi_{n_1 n_2} \rangle$ is the projection of the energy-normalized continuum eigenstate $|E \ell\rangle$

of hydrogen with energy E and angular momentum ℓ onto the component $\psi_{n_1 n_2}$ of the final wavefunction. From Eq. (2.7), we see that only the interference between pathways that end in the same state $|E\ell\rangle$ produce interference that contributes to the photoelectron spectrum.

For the pathways in Fig. 2.1 — which includes all pathways involving the exchange of up to four total photons from an initial state with $\ell = 0$ and $E = -0.5$ a.u. — only two pathways will interfere to provide control in φ over the photoelectron spectrum: the total two-photon pathway to $\mathbf{n} = (-1, 1)$ and the total four-photon pathway to $\mathbf{n} = (3, -1)$. These pathways will create the interference terms $A_{-1,1,\ell} A_{3,-1,\ell}^* e^{i4\varphi_1} e^{-i2\varphi_2}$ (and their complex conjugates) for both $\ell = 0$ and $\ell = 2$. The lowest-order contribution to control will, therefore, involve modulation of the photoelectron spectrum through variation of φ_1 with periodicity of $\pi/2$, or through variation of φ_2 with periodicity π .

Because pathways requiring the fewest number of total photons tend to be the most probable, we can also understand the relative sizes of the different terms that contribute to the photoelectron spectrum in Eq. (2.7). The total four-photon pathway to $A_{3,-1,\ell}$ required for control is expected to be considerably less likely than the total two-photon pathway to $A_{-1,1,\ell}$ with which it interferes. Similarly, both pathways are expected to be less probable than the total one-photon pathway that contributes to $A_{1,0,1}$. As such, we expect the φ -dependent interference term to be much smaller in magnitude than the phase-independent terms $|A_{1,0,1}|^2$, $|A_{-1,1,0}|^2$, and $|A_{-1,1,2}|^2$ — producing only a comparatively small modulation of a larger signal as φ is varied.

2.2.4 CEP Effects for Single-Color Pulses

In Sec. 2.2.2, it was shown that control via the phase φ can only be obtained when two (or more) pathways end at the same energy and with different values of $\mathbf{n}$. In the multi-color case, these pathways were provided by having multiple pulses with different central frequencies (see Fig. 2.1). However, when only a single-color pulse is present, it is not possible for two pathways to end at the same energy if they involve the exchange of different numbers of net photons at the central frequency. As such, in order to see control in the CEP, φ_1 , of a single-color pulse, it is necessary for the pulse to have a large enough bandwidth to drive non-negligible transitions involving photons at frequencies other than the central frequency, ω_1 .

The bandwidth of a pulse is defined as the width of the power spectrum $|\tilde{\mathcal{E}}(\omega')|^2$, typically measured as the full width at half maximum. Here, ω' is used to differentiate from the central frequency of the electric field, and the power spectrum is given by the Fourier transform

$$\tilde{\mathcal{E}}(\omega') = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \mathcal{E}(t) e^{-i\omega' t} dt. \quad (2.8)$$

In general, the frequency bandwidth, $\Delta\omega_{\text{FWHM}}$, will be inversely related to the pulse length, $\Delta\tau_{\text{FWHM}}$, of the intensity envelope — as pulses become shorter, $\Delta\omega_{\text{FWHM}}$ becomes larger and the absorption and emission of photons at frequencies other than the central frequency becomes increasingly likely. In this scenario, diagrams like those shown in Fig. 2.1 will still give an accurate description of pathways associated with absorption/emission at the central frequency; however, pathways involving the exchange of photons with other frequencies within the bandwidth must also be included. The end result is that a given ψ_n will have a width in energy space, as opposed to being sharply peaked.

This broadening in energy of ψ_n is illustrated in Fig. 2.2 for the case of hydrogen ionization discussed in Sec. 2.2.3, with the only change being that a single-color field is used rather than a two-color field. For this case, the photoelectron spectrum in Eq. (2.7) will be given by

$$\frac{dP}{dE} = \sum_{\ell} \sum_{n, n'} A_{n\ell} A_{n'\ell}^* e^{-i(n_1 - n'_1)\varphi}, \quad (2.9)$$

where $A_{n\ell}(E) = \langle E\ell | \psi_{n_1} \rangle$. In order to observe CEP effects in the photoelectron spectrum, Eq. (2.9) says that $A_{n\ell}$ with different n must have amplitudes at the same energy — requiring $A_{n\ell}(E)$ to have a large enough width in energy to create overlap between pathways with different net photon numbers. Taking dipole-selection rules into account, this overlap must occur between pathways with a difference Δn that is an integer multiple of two.

The expected overlap in energy between different amplitudes $A_{n\ell}$ can be estimated from the ratio $\Delta\omega_{\text{FWHM}}/\omega$ of the incident laser pulse; Figure 2.2 gives a schematic illustration of how the overlap changes as a function of this ratio. This figure is based on lowest-order perturbation theory, where an amplitude $A_{n\ell}$ is contributed to only by processes involving a *total* absorption of n photons. The LOPT picture gives peaks with a profile defined by the power spectrum of the

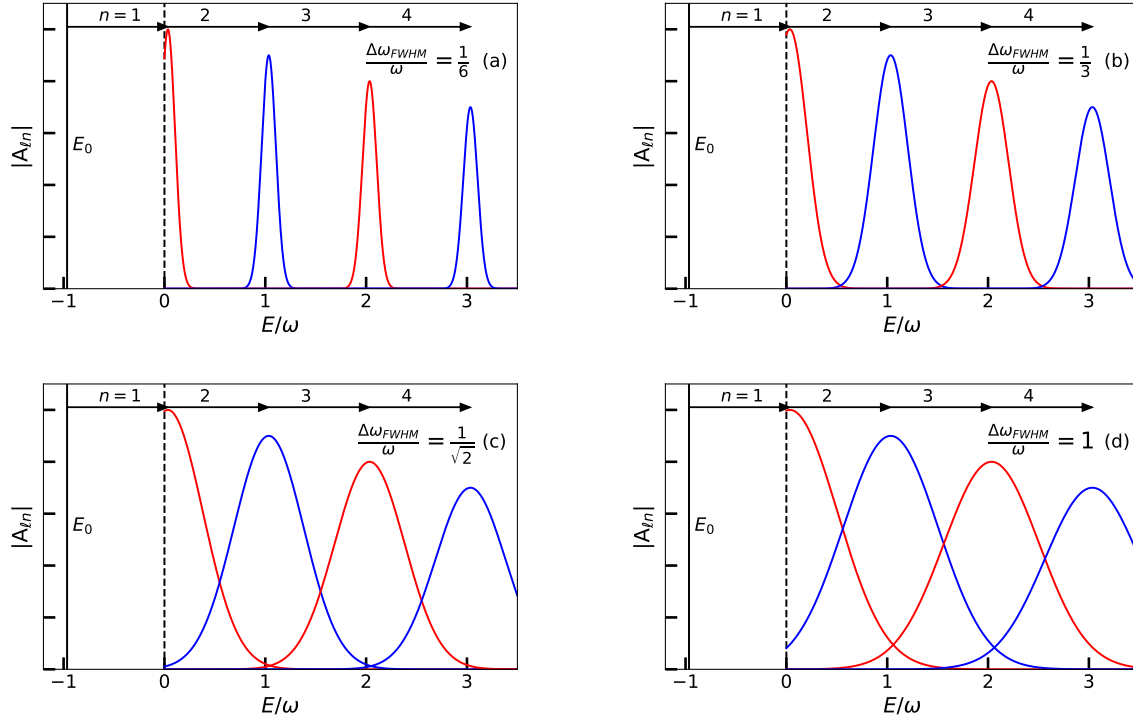


Figure 2.2: Schematic illustration, based on LOPT, of the magnitudes $|A_{n\ell}(E)|$ in Eq. (2.9) for the photoelectron spectrum of hydrogen. The figure shows amplitudes associated with $n=1, 2, 3$, and 4 for (a) $\Delta\omega_{\text{FWHM}}/\omega = 1/6$, (b) $\Delta\omega_{\text{FWHM}}/\omega = 1/2$, (c) $\Delta\omega_{\text{FWHM}}/\omega = 1/\sqrt{3}$, and (d) $\Delta\omega_{\text{FWHM}}/\omega = 1$. The amplitudes are shown in arbitrary units and on a log-scale; in accordance with LOPT, the amplitudes of subsequent peaks decrease linearly.

laser pulse, thus providing a simple way to connect changes in the width of the power spectrum to changes in the width of the amplitudes $A_{n\ell}$. It should be noted that LOPT also predicts a broadening of higher-order amplitudes associated with the free-free transitions that occur in ATI — *i.e.*, all peaks with $n > 1$ in Fig. 2.2. This effect, which is not shown in Fig. 2.2, can increase CEP effects for higher-order peaks provided that the signal is still large enough at the associated energies. A more detailed discussion of the mechanisms that contribute to this peak broadening is provided at the end of this section.

For small values of the ratio $\Delta\omega_{\text{FWHM}}/\omega$, Fig. 2.2(a) shows that no overlap exists between amplitudes with different values of n . In this case, observables will be unaffected by varying the CEP of the pulse. As the ratio approaches a value of roughly $1/3$, Fig. 2.2(b) shows that amplitudes with $\Delta n = 1$ begin to have some overlap in the region between adjacent peaks. While amplitudes differing by $\Delta n = 1$ cannot interfere in the photoelectron spectrum in Eq. (2.9), these amplitudes can interfere in other observables such as the momentum distribution. As such, CEP

effects will first be seen at roughly this ratio, and will occur at energies between peaks in the photoelectron spectrum (where the overlap is largest).

Because nothing about Fig. 2.2 is specific to hydrogen (other than the energy of the initial state), this rough estimate for the minimum value of $\Delta\omega_{\text{FWHM}}/\omega$ at which CEP effects become observable applies to other systems as well — assuming a Gaussian pulse, and, thus, a Gaussian power spectrum. Effects beyond LOPT will obviously alter the width of the amplitudes $A_{n\ell}$ — as will resonances, the structure of the dipole, and the aforementioned broadening of higher-order peaks. However, even with these deviations, our estimate is still in fairly good agreement with experiment. For example, the first measurement of CEP effects in ionization found CEP-dependent electron asymmetries in 800-nm, 5-femtosecond pulses; no CEP-dependence was found in the same experiment with 8-femtosecond pulses [97]. Our estimate of $\Delta\omega_{\text{FWHM}}/\omega = 1/3$ for the laser parameters in that experiment suggest that the cutoff for CEP effects should occur at roughly 3.1 femtoseconds.

When the ratio $\Delta\omega_{\text{FWHM}}/\omega$ approaches $1/\sqrt{2}$, amplitudes differing by $\Delta n = 2$ begin to overlap — providing observable CEP effects in the photoelectron spectrum. As with interference between peaks with $\Delta n = 1$, this ratio will serve as a rough approximation for the value where CEP effects become observable in the photoelectron or kinetic energy release (KER) spectrum of other systems as well. From Fig. 2.2(c) and Fig. 2.2(d), we see that the maximum overlap between peaks differing by $\Delta n = 2$ tends to occur at the peak between $A_{n\ell}$ and $A_{n+2,\ell}$, allowing for modulation of the photoelectron peaks themselves via the CEP. This will, of course, provide only a small modulation on top of a (relatively) large signal.

If the ratio $\Delta\omega_{\text{FWHM}}/\omega$ is further increased, amplitudes associated with pathways differing by $\Delta n \geq 3$ will also begin to interfere. Of course, how large this ratio can become is restricted by how short the pulse can be made. For Gaussian pulses, $\Delta\omega_{\text{FWHM}}/\omega$ is determined solely by the number of optical cycles, N_{cyc} , as

$$\frac{\Delta\omega_{\text{FWHM}}}{\omega} = \frac{2 \ln(2)}{\pi N_{\text{cyc}}}. \quad (2.10)$$

As such, achieving $\Delta\omega_{\text{FWHM}}/\omega = 1$ — the value at which pathways with $\Delta n = 3$ begin to

overlap in Fig. 2.2 — already requires a sub-half-cycle pulse. We will see in Chap. 5, however, that mechanisms not included in our simple schematic can lead to overlap between peaks with $\Delta n \geq 3$ without meeting this requirement on N_{cyc} .

Broadening of Higher-Order Amplitudes

The broadening of higher-order ATI peaks — and, consequently, the associated photon-pathway amplitudes A_{nl} — can be understood through the following picture (see Fig. 2.3). A given n -photon peak in the spectrum has a width due largely to the bandwidth of the laser pulse. Starting from any of the energies in this n -photon peak, an additional photon can be absorbed, giving rise to the $(n + 1)$ -photon peak. This absorbed “photon” itself has a width due to the bandwidth of the laser pulse. The $(n + 1)$ -photon peak finally observed in the photoelectron or KER spectrum is the sum of all transitions originating from every energy in the n -photon peak distribution—including, in reality, interference, resonance effects, effects beyond LOPT, and any energy dependence of the dipole matrix elements (none of which are accounted for in this simple picture). The resultant $(n + 1)$ -photon peak is thus broader than the n -photon peak.

Quantifying this picture, the $(n + 1)$ -photon peak is a convolution of the n -photon peak with the laser’s power spectrum. To see that the energy dependence of the $(n + 1)$ -photon peak can be obtained through this convolution, we convert the sketch in Fig. 2.3 into mathematics. We

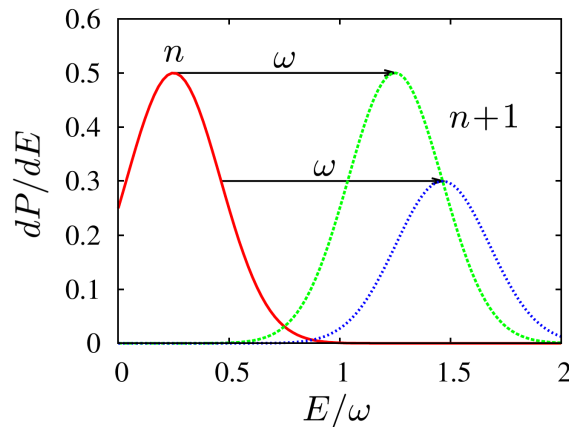


Figure 2.3: Sketch of the photoelectron spectrum, in arbitrary units, showing pathways producing the $(n + 1)$ -photon peak based on the heuristic explanation in the text. The absorption of an additional photon beyond the n -photon peak originates from different energies within the peak, leading to a broadening of the $(n + 1)$ -photon peak relative to the n -photon peak. Figure adapted from Ref. [7].

denote the n -photon peak probability distribution by $P_n(E)$ and the laser's power spectrum as $|\tilde{\mathcal{E}}(E)|^2$. The former peaks at E_n , the latter peaks at ω .

The distribution for both of the new peaks (green dashed and blue dotted lines) depicted in Fig. 2.3 is just the laser's power spectrum, but based on different starting energies E'_i within $P_n(E)$ (red solid line) and weighted by the probability for this energy, $P_n(E'_i)$. Thus, the distribution for each of these new peaks is $P_n(E'_i)|\tilde{\mathcal{E}}(E - E'_i)|^2$. Consequently, $P_{n+1}(E)$ is approximately

$$P_{n+1}(E) \approx P_n(E'_1)|\tilde{\mathcal{E}}(E - E'_1)|^2 + P_n(E'_2)|\tilde{\mathcal{E}}(E - E'_2)|^2 \quad (2.11)$$

when just the two peaks in Fig. 2.3 are taken into account. Since all values of E' within $P_n(E)$ should be used, we take the continuum limit to obtain

$$P_{n+1}(E) = \int dE' P_n(E') |\tilde{\mathcal{E}}(E - E')|^2. \quad (2.12)$$

Thus, in this simple picture, the $(n+1)$ -photon peak distribution is a convolution of the n -photon peak with the laser's power spectrum.

Applying this result iteratively using the fact that the first peak in the spectrum has width $\Delta\omega_{\text{FWHM}}$, one can show that this picture predicts that the width of the n -photon peak for a Gaussian laser spectrum is proportional to $\sqrt{n}\Delta\omega$. Based on the empirical fact that in the ATI photon peaks can be observed to very high orders, this simple picture likely overestimates the growth of the width.

2.3 Dressed Potentials

2.3.1 Diabatic Dressed Potentials

Section 2.2 described how $\psi_{\mathbf{n}}$ can be interpreted as the state of a system that has exchanged a net number of $\mathbf{n}$ photons with the field, changing the system's total energy from E_0 to $E = E_0 + \mathbf{n} \cdot \boldsymbol{\omega}$. This approach was applied in Sec. 2.2.3, where arrows representing photon absorption/emission were used to trace pathways from E_0 to $E = E_0 + \mathbf{n} \cdot \boldsymbol{\omega}$, allowing us to predict interference effects in the spectrum. An alternative, but equivalent, approach involving dressed potentials was also

briefly mentioned in Sec. 2.2.2. In this approach, the term $-\mathbf{n} \cdot \boldsymbol{\omega}$ in Eq. (2.4) is associated with the potential energy V in the unperturbed Hamiltonian $H_0 = T + V$ (with kinetic energy T) to define dressed, diabatic potentials $U_{\mathbf{n}}^D = V - \mathbf{n} \cdot \boldsymbol{\omega}$. Dressed potentials can provide another useful way to trace pathways to a given final state — especially for multi-channel problems where a number of potentials are involved. Both the diabatic, dressed potentials discussed in this section and the adiabatic, dressed potentials discussed in Sec. 2.3.2 have previously been used within Floquet to explain phenomena in molecular processes in CW lasers [191–200].

Examples of diabatic dressed potentials can be seen in Fig. 2.4 for H_2^+ . Here, the potentials are the Born-Oppenheimer $1s\sigma_g$ and $2p\sigma_u$ potentials, dressed by odd and even numbers of photons, respectively, to account for dipole-selection rules (assuming an initial state in the $1s\sigma_g$ potential). Higher-energy Born-Oppenheimer electronic channels are ignored here for simplicity. Figures 2.4(a) and 2.4(b) show dressed potentials for single-color fields with 800- and 400-nm light ($\omega_1 = 0.058$ a.u. and $\omega_1 = 0.116$ a.u.). Figure 2.4(c) shows the potentials in the combined two-color field ($\omega_1 = 0.058$ a.u. and $\omega_2 = 0.116$ a.u.).

Because the photon energy is viewed as shifting the potentials by $-\mathbf{n} \cdot \boldsymbol{\omega}$ in the dressed diabatic representation, the energy of the system is approximately conserved during its interaction with the pulse. This energy is shown by the black, horizontal line in Fig. 2.4. In the CW limit, it can be shown that the system's energy (referred to as the “quasi-energy” in Floquet) is strictly conserved when using dressed potentials. For pulsed lasers, this energy conservation is only approximate within the bandwidth of the laser — as it is possible to absorb/emit photons not at the central frequency.

Arrows are used in Fig. 2.4 to indicate various pathways for dissociation. The likelihood of taking a given pathway is, in large part, determined by the location of the crossing between the system's initial potential (here, $U_{1s\sigma_g} - 0\omega_1$), and the potential that the pathway proceeds along². The top blue arrow in Fig. 2.4(a) represents the one-photon pathway onto the $U_{2p\sigma_u} - 1\omega_1$ potential for $\omega_1 = 0.058$ a.u. It can easily be seen the crossing between the $U_{1s\sigma_g} - 0\omega_1$ and $U_{2p\sigma_u} - 1\omega_1$ potentials occurs near the system's energy — indicating a near-resonant transition.

²The relevance of curve-crossing locations to transition probabilities is most easily seen in the adiabatic picture — see Sec. 2.3.2 for details.

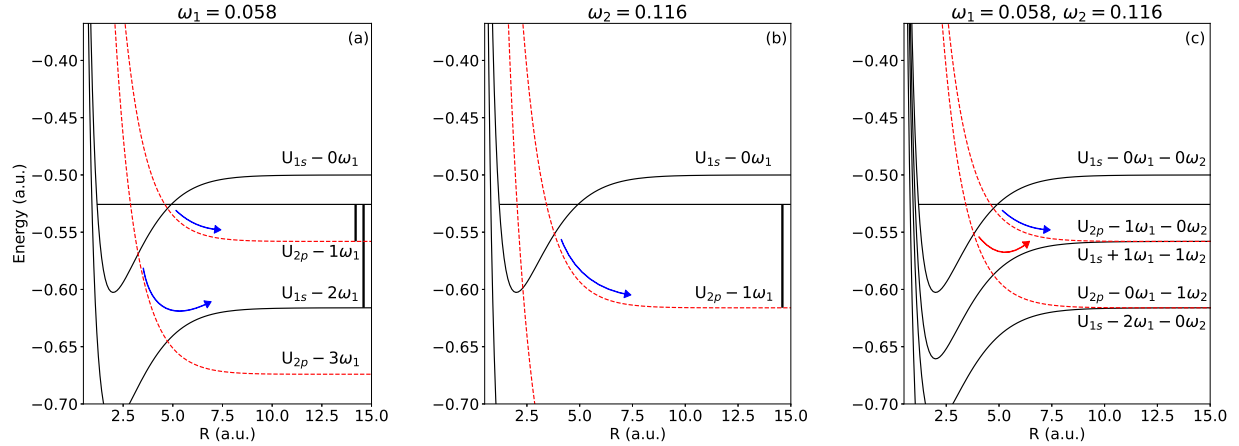


Figure 2.4: Dressed potentials for H_2^+ molecular ion in an 800-nm (a), 400-nm (b), and two-color 800 + 400-nm field (c). $1s_g$ potentials (U_{1s}) are shown in black, $2p\sigma_u$ potentials (U_{2p}) are shown in red. The horizontal line represents the systems energy, and the individual arrows represent different pathways for dissociation — with blue arrows representing pathways involving only a single color, and the red arrow representing a two-color pathway. Vertical black lines from the dressed potentials to the system energy in (a) and (b) illustrate the expected KER produced by the corresponding pathways to these potentials.

The expected KER for this pathway, shown in the figure by a vertical black line, is given by the difference between the system's energy and the asymptotic limit of the $U_{2p\sigma_u} - 1\omega_1$ potential.

The bottom blue arrow in Fig. 2.4(a) shows the net two-photon pathway onto the $U_{1s\sigma_g} - 2\omega_1$ potential, with the KER corresponding to this pathway also illustrated in the figure. This pathway proceeds through the absorption of $3\omega_1$ onto the $U_{2p\sigma_u} - 3\omega_1$ potential, followed by the stimulated emission of ω_1 to end on the $U_{1s\sigma_g} - 2\omega_1$ potential — a process involving the total exchange of four photons. While this pathway is further from resonance than the pathway to $U_{2p\sigma_u} - 1\omega_1$, it is clearly still much closer to resonance than the direct pathway to the $U_{1s\sigma_g} - 2\omega_1$ potential — which does not cross the $U_{1s\sigma_g} - 0\omega_1$ potential at all. As such, this picture predicts an unexpected phenomenon: for a range of intensities large enough to drive total four-photon processes, the dominant pathway to the net two-photon KER peak in H_2^+ will involve four photons rather than two. This total four-photon pathway will be even more likely for lower-lying vibrational states, which will have energies near the crossing between $U_{2p\sigma_u} - 3\omega_1$ and $U_{1s\sigma_g} - 0\omega_1$.

Figure 2.4(b) shows the one-photon pathway onto the $U_{2p\sigma_u} - 1\omega_1$ potential for $\omega_1 = 0.116$ a.u., along with its predicted KER. This pathway is mainly included due to its importance in the two-color pathways in Fig. 2.4(c). The two-color diagram provides an illustration of how the introduction of an additional color opens up new pathways for interference. The blue

arrow in the two-color field represents the pathway where the system absorbs a single 800-nm photon to move onto the $U_{2p\sigma_u} - 1\omega_1 - 0\omega_2$ potential. The red arrow represents the pathway where the system absorbs a single 400-nm photon to transition onto the $U_{2p\sigma_u} - 0\omega_1 - 1\omega_2$ potential, before emitting a single 800-nm photon to end on the $U_{1s\sigma_g} + 1\omega_1 - 1\omega_2$ channel. It is clear from the figure that these pathways end with the same kinetic energy. Although these pathways end in different electronic channels, we will see in later chapters that some observables allow for interference between these pathways. Due to their differing values of n_1 and n_2 , this interference can be controlled by either φ_1 or φ_2 .

The dressed-potentials discussed in this section do not include the coupling between different states ψ_n caused by the electric field in Eq. (2.4) — as such, they are referred to as being diabatic in time (or, equivalently, the electric field). As we will see in this next section (Sec. 2.3.2), it is also possible to include these couplings in order to generate a new set of potentials — such potentials are said to be adiabatic in the electric field. Both the diabatic and adiabatic representation are exact and contain the same physics (assuming all channels and couplings are included), but adiabatic potentials can provide additional insight into certain physical processes.

2.3.2 Adiabatic Dressed Potentials

To illustrate the difference between adiabatic and diabatic potentials, we examine simple adiabatic dressed potentials for single-photon processes using a system with a field-free ground state potential U_1 and an excited potential U_2 . The two channels are coupled through the dipole interaction by a single-color pulse, and the laser polarization is assumed to be aligned with the system's dipole. Equation (2.4) gives the diabatic potential matrix

$$V^D = \begin{pmatrix} U_1 & \mathcal{E}_0(t)d/2 \\ \mathcal{E}_0(t)d/2 & U_2 - \omega \end{pmatrix}, \quad (2.13)$$

where the diagonal elements give the diabatic, dressed potentials $U_1^D = U_1$ and $U_2^D = U_2 - \omega$. The adiabatic representation is obtained by diagonalizing V^D ; the adiabatic potentials are given by the resulting eigenvalues.

For a CW laser, the couplings in Eq. (2.4) will be independent of time — thus creating

adiabatic potentials that are constant in time with non-adiabatic coupling only in R . For a pulsed laser, the envelope in Eq. (2.4) will result in time-dependent couplings — creating adiabatic potentials that are functions of time with non-adiabatic coupling in both R and t . At $t \rightarrow -\infty$, when the envelope of the pulse is zero and no coupling exists, the adiabatic and diabatic potentials have the same shape. As the envelope becomes larger, the avoided crossing between the adiabatic potentials grows to create a gap between the potential energy curves. This gap will follow the envelope of the pulse, reaching its largest size when the envelope is at its peak and then decreasing until the the adiabatic potentials return to their field-free limit. This time-dependent process is illustrated in Fig. 2.5. In Fig. 2.5, U_1 and U_2 are chosen to be Morse potentials, the dipole is given by $d = R(1 + \tanh(2.4 - R))$, and a Gaussian envelope is used. The formation of an avoided crossing is a universal feature that does not depend on these choices.

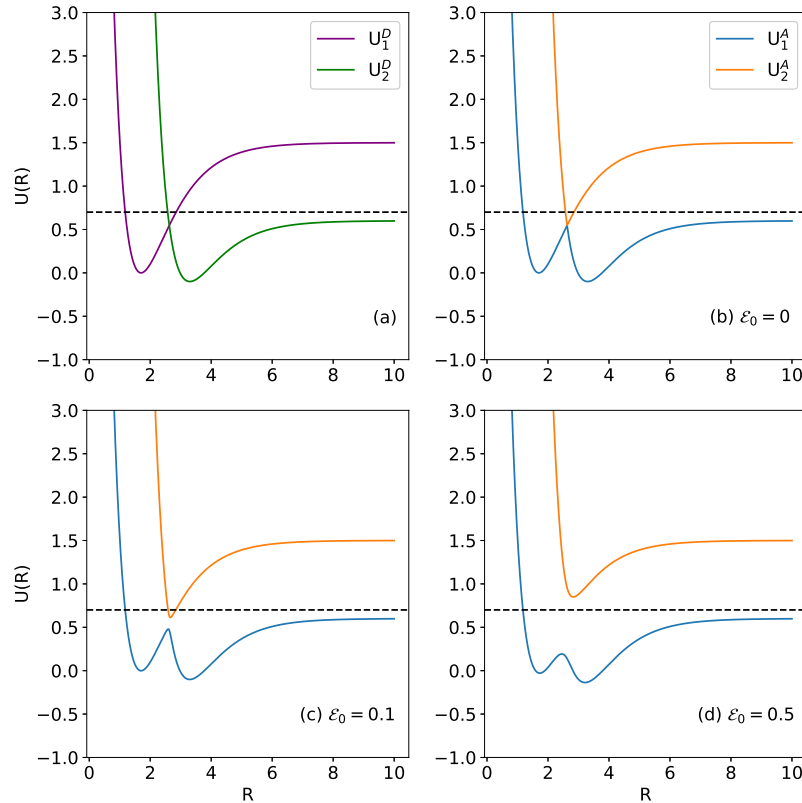


Figure 2.5: (a) Dressed diabatic potentials $U_1^D = U_1$ and $U_2^D = U_2 - \omega$ for our model system. (b-d) Dressed adiabatic potentials at times when the coupling envelope is given by $\mathcal{E}_0(t) = 0$, $\mathcal{E}_0(t) = 0.1$, and $\mathcal{E}_0(t) = 0.5$. The horizontal, black line marks the energy of an initial state near the $\mathcal{E}_0 = 0$ crossing. The figure provides a simple illustration of how the crossing found in the diabatic potentials turns into an increasingly large avoided crossing in the adiabatic representation as the coupling is turned on.

At $t \rightarrow -\infty$, the system will be in a vibrational eigenstate of the field-free U_1 potential. As the pulse envelope grows and the adiabatic potentials begin to separate, the system will no longer be in an eigenstate of the new potentials — causing wavepacket motion at a fixed mean energy. For states with energy near the field-free crossing, such as the state labeled in Fig. 2.5 with a horizontal line, we expect the wavepacket to go over the barrier of the lowest adiabatic potential and through the avoided crossing. It should be clear from the Fig. 2.5 that if the system goes through the crossing, it will end in a final state associated with the potential that goes to $U_2 - \omega$ asymptotically — and, as such, will be observed in a state associated with the field-free U_2 potential after the pulse has gone to zero. For the choices in Fig. 2.5, the wavepacket is at an energy above the breakup threshold and dissociation will occur.

For energies much lower or higher than the crossing energy (not within the gap between adiabatic potentials), transitions will be less probable. For very low energies, the system will likely remain bound in the first well of the U_1^A potential ($R \approx 1.7$ a.u.), resulting in the system remaining in a state associated with the field-free U_1 potential as the envelope decreases back to zero. For slightly higher energies (still below the crossing), a mixture of bound states in the two wells will likely occur — causing bound populations in the states associated with both field-free potentials once the envelope goes to zero. For energies much higher than the crossing, transitions can occur via tunneling out of the U_1^A potential onto the U_2^A potential (above the breakup threshold), but such transitions are still less likely than the resonant case for energies near the crossing. Because the adiabatic and diabatic representations are equivalent, all information from the adiabatic representation about the energies where transitions are most likely to occur can be applied in the diabatic representation as well.

2.4 Closing Remarks

In this chapter we have derived a parametric formalism that allows us to express the wavefunction for a system exactly in terms of net-photon pathways. Although the direct application of the results in this chapter requires certain restrictions on the field and system (Sec. 2.1), the results hold for a large number of intense, ultrashort physics experiments. Using the knowledge that

the summation indices $\mathbf{n}$ in Eq. 2.3 count the net number of photons absorbed from the field, we can identify the most likely pathways of photon absorption/emission and determine which $\psi_{\mathbf{n}}$ will be most relevant in our wavefunction expansion. Dressed potentials can aid in this process, allowing us to identify the resonant energies where transitions are likely to occur. By expressing observables in terms of the relevant pathways, we can predict which pathways will interfere to provide control — allowing us to make quantitative predictions about the energies where control will occur and about the nature of the control itself.

In Chap. 3 and Chap. 6, we will focus on using knowledge of pathways derived from dressed potentials and dipole-matrix elements to make predictions about these types of control, and carry out calculations to show the merits of the theory. In Chap. 4 and Chap. 5, we will shift our focus to extracting information about the laser or the pathways associated with $\psi_{\mathbf{n}}$ themselves from a given spectrum. This will allow us to devise methods for better understanding pulse characterization, and provide an understanding of what pathways are causing a given effect in an observable even in situations where we do not have enough *a priori* knowledge to predict the pathways beforehand.

Chapter 3

Single-Color Carrier-Envelope Phase Effects

In Chap. 2, we laid out our parametric formalism for understanding single-color and multi-color control. In this chapter, we will apply our formalism to the (mathematically) simplest case of carrier-envelope phase control using a single-color pulse, specifically focusing on CEP effects in the dissociation of HeH^+ . Here the electric field in Eq. (2.2) becomes

$$\mathcal{E}(t) = \mathcal{E}_1(t) \cos(\omega t + \varphi), \quad (3.1)$$

and the wavefunction in Eq. (2.3) becomes

$$\psi(t) = \sum_n \psi_n(t) e^{-in\varphi}. \quad (3.2)$$

The subscripts from Eq. (2.2) and Eq. (2.3) are altered in Eq. (3.1) and Eq. (3.2) to give $n_1 = n$ and $\varphi_1 = \varphi$ for simplicity of notation in the single-color case. This chapter will closely follow the previous publication of our work in Ref. [6, 7].

3.1 Calculations for Dissociation of HeH^+ in Intense, Ultrashort Pulses

HeH^+ is the simplest heteronuclear molecule with an electronic asymmetry within the Born-Oppenheimer approximation. Because it has only two electrons, accurate calculations for both the structure and intense-field dynamics of HeH^+ are relatively simple when compared to other heteronuclear diatomics. As such, it is an obvious choice, from a theoretical standpoint, for a benchmark heteronuclear system. Experimentally, HeH^+ has been shown to be a viable target for ion-beams studies. Such experiments have demonstrated the existence of metastable HeH^{2+} [201, 202] and measured the dissociation of HeH^+ via electronic transitions in a free-electron laser [203].

Our work shows that HeH^+ can also dissociate solely through permanent-dipole transitions — producing a large enough yield for experimental observation in intense fields with wavelengths of 2000 nm or longer [6]. The results of this work, presented in Sec. 3.2, have since been verified in strong field experiments [204, 205]. These studies demonstrated the importance of permanent-dipole transitions in the dissociative ionization of HeH^+ [204], and provided the first measurements of the system’s dissociation to $\text{He}(1s)+\text{H}^+$ through solely permanent-dipole transitions [205]. Because its dissociation is dominated by permanent-dipole effects in the long wavelength regime, HeH^+ provides an interesting contrast to other systems we have studied using our parametric formalism — which were dominated by electronic transitions [103, 104, 132, 206]. The application of our formalism to understand CEP effects in HeH^+ is presented in Sec. 3.3.

3.1.1 Schrödinger Equation in the Single-Channel Approximation

We begin by numerically solving the TDSE. The dipole in Eq. (2.1) is given for the system by

$$\mathbf{d} = -\left(\frac{3 + m_A + m_B}{2 + m_A + m_B}\right)(\mathbf{r}_1 + \mathbf{r}_2) + \left(\frac{m_A - 2m_B}{m_A + m_B}\right)\mathbf{R}. \quad (3.3)$$

The definition of coordinates and masses are shown in Fig. 3.1; $\mathbf{r}_1$ and $\mathbf{r}_2$ give the electron coordinates, while $\mathbf{R}$ is the vector from He^{2+} to H^+ . The resultant TDSE is given by

$$i\frac{\partial}{\partial t}\psi = \left[-\frac{1}{2\mu_{AB}}\nabla_R^2 + H_{\text{el}} - \boldsymbol{\mathcal{E}}(t) \cdot \mathbf{d}\right]\psi, \quad (3.4)$$

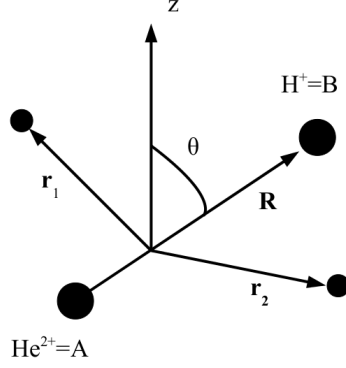


Figure 3.1: The definition of the coordinates used in the Hamiltonian. Figure adapted from Ref. [6]

where the reduced mass μ_{AB} is

$$\frac{1}{\mu_{AB}} = \frac{1}{m_A} + \frac{1}{m_B}. \quad (3.5)$$

In Eq. (3.4), the center-of-mass motion of the system has been separated out and H_{el} contains both the electronic kinetic energy and all potential energy terms.

The electronic degrees of freedom are represented in the Born-Oppenheimer basis functions Φ_α that solve

$$H_{\text{el}}\Phi_\alpha(R;\mathbf{r}_1,\mathbf{r}_2) = U_\alpha(R)\Phi_\alpha(R;\mathbf{r}_1,\mathbf{r}_2). \quad (3.6)$$

From Fig. 3.2, we see that there is a difference of at least 0.40 a.u. in energy between the ground electronic channel $X^1\Sigma^+$ and the first-excited channel $A^1\Sigma^+$. Therefore, a minimum of eight photons is required for electronic excitation at 800 nm, the shortest wavelength that we consider. Moreover, we see from Fig. 3.2 that the magnitudes of the permanent dipole, $\langle\Phi_1|\mathbf{d}|\Phi_1\rangle$, and the $X^1\Sigma^+-A^1\Sigma^+$ transition dipole matrix element, $\langle\Phi_1|\mathbf{d}|\Phi_2\rangle$, have nearly the same value for $1.0 \text{ a.u.} \leq R \leq 2.0 \text{ a.u.}$, and that the permanent dipole is larger for $R > 2.0 \text{ a.u.}$ In the range where the matrix elements are comparable, however, a minimum of thirteen 800-nm photons is required for electronic excitation. Taken together, these considerations suggest that electronic excitation will be negligible for all but very high intensities. Therefore, we will neglect electronic excitation in our calculations and keep only the $X^1\Sigma^+$ state.

Because we consider a Σ state, the nuclear angles can be expanded in spherical harmonics Y_{JM} — where J and M give the total angular momentum of the nuclei and the total angular momentum projection along the laser's polarization, respectively. Within this representation, the

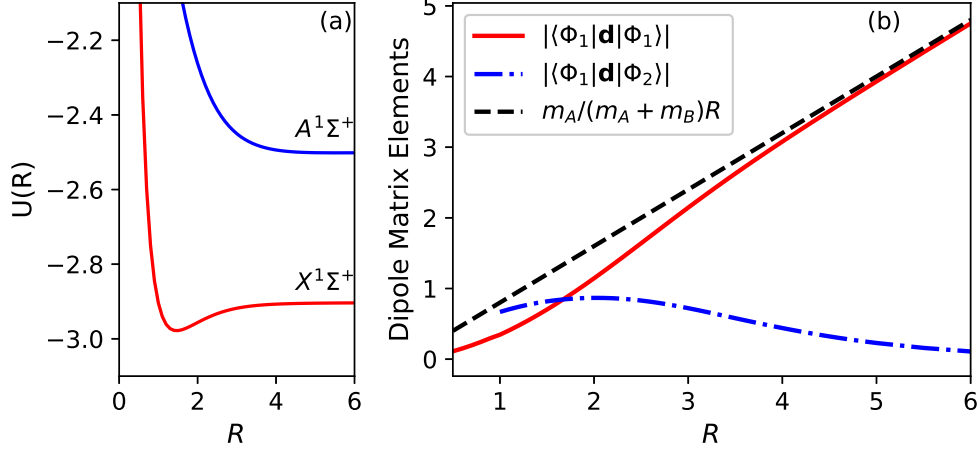


Figure 3.2: (a) The adiabatic potential energy curves [207] for the ground state of HeH^+ , $X^1\Sigma^+$, and the first excited singlet state, $A^1\Sigma^+$. (b) Magnitude of the $X^1\Sigma^+$ permanent dipole, $\langle\Phi_1|\mathbf{d}|\Phi_1\rangle$, and $X^1\Sigma^+-A^1\Sigma^+$ transition dipole, $\langle\Phi_1|\mathbf{d}|\Phi_2\rangle$, from Ref. [207], along with the approximate permanent dipole used in Sec. 3.2.1. Figure adapted from Ref. [6].

full wavefunction is given by

$$\psi = \frac{1}{R} \sum_{J,M} F_{JM}(R,t) Y_{JM}(\theta, \phi) \Phi(R; \mathbf{r}_1, \mathbf{r}_2), \quad (3.7)$$

where $\Phi \equiv \Phi_{X^1\Sigma^+}$ and we have included a factor of $1/R$ to remove first-derivative terms in R in our final equations. In Eq. (3.7), the angles θ and ϕ give the polar and azimuthal angles that describe the orientation of $\mathbf{R}$ relative to the laboratory frame. For this thesis, all calculations are carried out using linearly polarized light — so channels with different M will not be coupled by the laser. We use $M = 0$ states for all calculations and will drop the label M for the remainder of this chapter.

With these considerations, substituting ψ into Eq. (3.4) and projecting out $Y_{J0}\Phi$ gives the coupled differential equations that we must solve:

$$i \frac{\partial}{\partial t} F_J = \left[-\frac{1}{2\mu_{AB}} \frac{\partial^2}{\partial R^2} + \frac{J(J+1)}{2\mu_{AB}R^2} + U \right] F_J - \sum_{J'} \sqrt{\frac{4\pi}{3}} \mathcal{E}(t) D \langle Y_{J0} | Y_{10} | Y_{J'0} \rangle F_{J'}, \quad (3.8)$$

where D is the magnitude of the permanent dipole. In this work, we use ^4He and ^1H with masses $m_A = 7351.67$ a.u. and $m_B = 1836.15$ a.u., respectively. This isotope choice maximizes the magnitude of the permanent dipole [6]. Because it is truncated to only a single channel, there is

no electronic coupling in Eq. (3.8) from either the external field or the field-free Coriolis coupling and non-Born-Oppenheimer effects.

For our calculations in Sec. 3.3, the Born-Oppenheimer potentials and permanent dipole from Ref. [207] are used. The calculations in Sec. 3.2.1 will, however, use the approximate form $D = m_A/(m_A + m_B)R$ — as the data from Ref. [207] was not available to us at the time when those calculations were carried out. This form is exact asymptotically as the system dissociates to $\text{He}(1s^2) + \text{H}^+$. This approximate permanent dipole is seen in Fig 3.2, along with the (more accurate) dipole matrix elements from Ref. [207].

3.1.2 Numerical Methods

The remaining task is to solve Eq. (3.8). Initial states for the system are calculated by finding the eigenfunctions χ_{vJ} and eigenvalues E_{vJ} of Eq. (3.8) for the field-free case ($\mathcal{E}_1 = 0$). This is accomplished by using the generalized finite differencing scheme from Ref. [208] and diagonalizing the resulting tridiagonal Hamiltonian matrix for a given value of J . A non-uniform radial grid is used, with the definition of the grid determined by the parameters of the laser pulse. For two-cycle pulses, the grid is defined by $R_{\min} = 0.5$ a.u., $R_{\max} = 110.0$ a.u., and a grid spacing $\Delta R \approx 0.002$ a.u. for $R \leq 8.0$ a.u. and $\Delta R \approx 0.0094$ a.u. for $R > 8.0$ a.u. For five- and ten-cycle pulses, where we examine shorter wavelengths that produce breakup with higher energies, the grid is defined by $R_{\min} = 0.2$ a.u., $R_{\max} = 200.0$ a.u., and a grid spacing $\Delta R \approx 0.00094$ a.u. for $R \leq 10.0$ a.u. and $\Delta R \approx 0.0085$ a.u. for $R > 10.0$ a.u. is used. Three-point averaging, where each of three adjacent grid points is weighted equally, is applied 20 000 times to the grid in order to smooth the abrupt change in grid spacing at $R = 8.0$ a.u.

Time propagation of a given initial state in the field is accomplished for small time steps δ by using the short-time propagator

$$\mathbf{F}(R, t + \delta) = e^{-i\mathbf{H}(t+\delta/2)\delta} \mathbf{F}(R, t). \quad (3.9)$$

In Eq. (3.9), $\mathbf{F}$ is the column vector whose elements are the F_J in Eq. (3.8). Similarly, $\mathbf{H}(t)$ is the matrix representation of the full Hamiltonian in Eq. (3.8). The action of this short-time

propagator is carried out by applying split-operator techniques and the Crank-Nicolson method outlined in Ref. [209]. A time step of $\delta = 0.008$ a.u. is used in our calculations for two-cycle pulses, while $\delta = 0.03$ a.u. is used for five- and ten-cycle pulses. The number of partial waves J included in our expansion of ψ is dynamically increased [210], with additional partial waves added when the partial wave associated with the maximum J at a given time-step passes a population threshold (typically on the order of 10^{-7}).

We use initial vibrational states with $J = 0$ for all calculations and express the electric field¹ as

$$\mathcal{E} = \mathcal{E}_0 e^{-(t/\tau)^2} \cos(\omega t + \varphi) \hat{\mathbf{z}}, \quad (3.10)$$

where $\tau = \tau_{\text{FWHM}}/\sqrt{2 \ln 2}$. Calculations in Sec. 3.2.1 are carried out for τ_{FWHM} corresponding to both five- and ten-cycle pulses, using wavelengths in the 800 – 2400-nm range and intensities between 10^{12} W/cm² and 10^{14} W/cm². In these calculations, the CEP is set to $\varphi = 0$ — although this specific choice is irrelevant because we expect minimal CEP effects for such long pulses. In Sec. 3.3, calculations will be carried out for shorter, two-cycle pulses in order to examine CEP effects. There, wavelengths of 3200 and 4000 nm are used, with an intensity of 10^{14} W/cm². The initial and final times used in our calculations (t_i and t_f) are chosen such that t_i is the time when the intensity first reaches 10^7 W/cm², and t_f is the time after peak intensity when the intensity falls off to 10^8 W/cm². The initial and final times, along with all other numerical parameters discussed in this section, were chosen to give three digits of accuracy in the KER spectrum for all energies shown in this thesis.

¹The field strength in atomic units is defined as $\mathcal{E} = \sqrt{I/3.5 \times 10^{16} \text{ W/cm}^2}$

3.2 Multiphoton Dissociation of HeH^+

3.2.1 Dissociation Probability

To quickly determine the parameters that produce substantial dissociation, we first consider the total dissociation probability

$$P = 1 - \sum_{vJ} |\langle \chi_{vJ} | F_J(t_f) \rangle|^2, \quad (3.11)$$

for a series of initial vibrational states. In Eq. (3.11), χ_{vJ} are the field-free, ro-vibrational eigenstates, while $F_J(t_f)$ are the components given by Eq. (3.8). The intensity dependence of P for several initial vibrational states is presented in Fig. 3.3. From the figure, we see that $P \propto I^n$ for most initial vibrational states, which is the result expected from LOPT for n -photon absorption. Deviations from I^n do appear in some cases for high intensities, indicating that lowest-order perturbation theory is no longer adequate. For an initial $v = 0$ state — $E_{0,0} = -2.9715$ a.u. — in a potential with $U(R \rightarrow \infty) = -2.9032$ a.u. — two photons are required for dissociation at 800 nm and 1200 nm, three photons are required at 1600 nm and 2000 nm, and four photons are required at 2400 nm. These values of n match the slopes found in Fig. 3.3. This same analysis

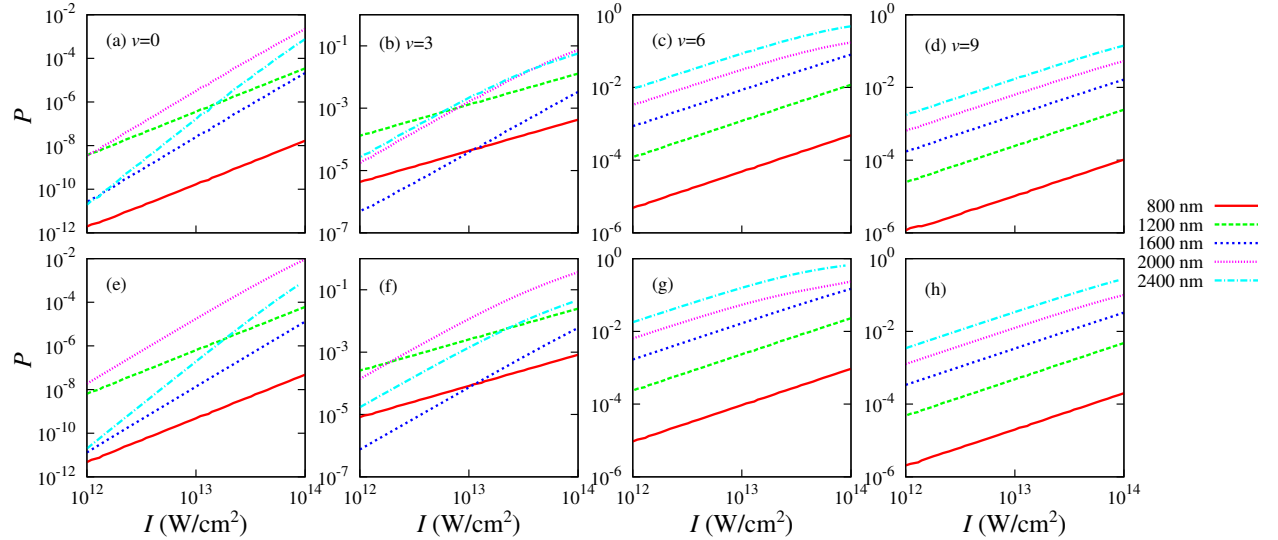


Figure 3.3: Figure shows the total dissociation probability P as a function of intensity for different wavelengths, pulse lengths, and initial vibrational states. The top figures are for five-cycle pulses, while the bottom figures are for ten-cycle pulses. From left to right, the columns correspond to the initial vibrational states $v = 0, 3, 6,$ and 9 . Note that different scales are used for the probabilities in $v = 0$ and 3 , when compared to $v = 6$ and 9 . Figure adapted from Ref. [6].

can be applied to explain the slopes seen for other initial states in the figure.

From Fig. 3.3, we see that there do exist parameters that produce substantial dissociation: up to 8.5% (five cycles) and 16% (ten cycles) for 10^{13} W/cm², and up to 48% and 65% for 10^{14} W/cm², respectively. The experiment in Ref. [205] has since showed that it is possible to detect dissociation for 10^{14} W/cm² pulses with wavelengths from 800 to 2400 nm; dissociation was only detected at 10^{13} W/cm² for wavelengths longer than 3000 nm. Direct comparison with their results is difficult because the molecules started in a distribution of initial states and they did not use a fixed number of cycles for different wavelengths. However, they did observe the same rough increase in dissociation probability for longer wavelengths that we see in Fig. 3.3.

In our results, the maximum P occurred for $v = 6$ at 2400 nm — which was true at all intensities in both five- and ten-cycle pulses. This result is not surprising considering only one photon is required for dissociation from this state. Dissociation from $v = 9$, however, also requires only a single photon, yet its dissociation probability is an order of magnitude smaller than for $v = 6$. The difference in dissociation probability for these two states is explained by the radial part of their bound-free dipole matrix elements,

$$D_{Ev} = \left\langle E, J = 1 \left| \frac{m_A}{m_A + m_B} R \right| \chi_{v0} \right\rangle, \quad (3.12)$$

where $|E, J\rangle$ is the the energy normalized field-free continuum state with energy E and angular momentum J .

Figure 3.4 shows D_{E9} and D_{E6} along with the ranges of KER (denoted as E) expected for the absorption of one photon with wavelengths between 2400 nm and 800 nm. Keeping in mind that the vertical scale in the figure is logarithmic, it is clear that D_{E9} is roughly ten times smaller than D_{E6} at any given wavelength — yielding, in turn, a much smaller dissociation probability. While this argument only strictly applies to relative size of the one-photon dissociation probabilities, multiphoton processes will provide smaller contributions to the total yield. Additionally, multiphoton dissociation requires a bound-free transition prior to the free-free transitions that produce higher-order peaks, and that bound-free transition will involve a matrix element similar to the one in Eq. (3.12).

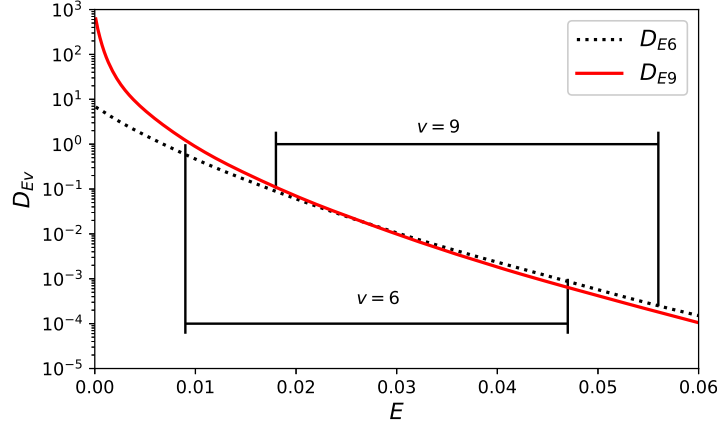


Figure 3.4: Bound-free dipole matrix elements, Eq. (3.12), as a function of KER E (which is measured relative to the threshold $U(R \rightarrow \infty) = -2.9032$ a.u.) for $v = 6$ and $v = 9$. The range of energies expected for one photon absorption at wavelengths between 2400 nm and 800 nm is indicated for both initial ro-vibrational states. Figure adapted from Ref. [6]

The wavelength dependence of P , which is evident in Fig. 3.3, can also be explained by D_{Ev} . In Fig. 3.4, we see that for $v = 6$ and 9 the dipole matrix elements decrease roughly exponentially with increasing KER. In fact, this behavior is a general feature of D_{Ev} for this system. Therefore, assuming the number of photons required is the same, longer wavelengths are expected to give the largest dissociation probability because they produce dissociating fragments with the lowest KER.

3.2.2 Kinetic Energy Release Spectrum and Momentum Distribution

Before moving on to studying CEP control of HeH^+ dissociation, it makes sense to examine the structure of the observables that will be controlled — specifically, the KER spectrum and the momentum distribution. Section 3.2.1 demonstrated that both five- and ten-cycle pulses with $I = 10^{14}$ W/cm² produce dissociation probabilities greater than 1.0% for both $\lambda = 2000$ nm and $\lambda = 2400$ nm in all studied initial vibrational states except $v = 0$. The largest dissociation occurs for intensities between 10^{13} W/cm² and 10^{14} W/cm² and at a wavelength of 2400 nm, therefore, we constrain our studies of the KER and momentum distribution to this region of parameter space.

Because there is only one electronic channel relevant for our laser conditions, the dressed potentials from Sec. 2.3.1 and Sec. 2.3.2 are not as useful in understanding the bound-free

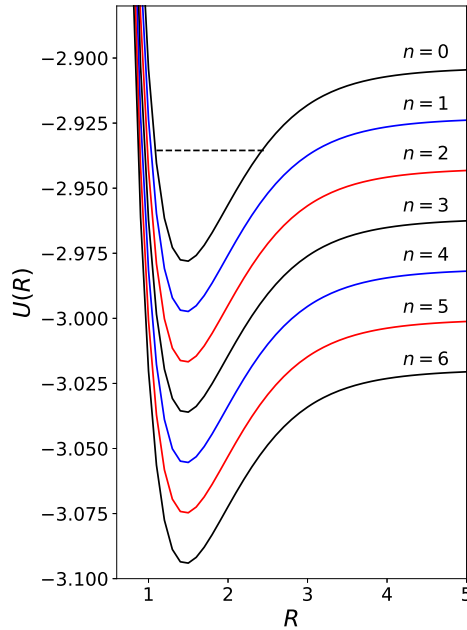


Figure 3.5: Dressed diabatic potentials $U_n = U_{X^1\Sigma^+} - n\omega$ at 2400 nm for transitions involving up to the absorption of $n = 6$ net photons. The dashed horizontal line inside the $U_{X^1\Sigma^+} - 0\omega$ potential shows the energy of the system, given here by a $v = 3$ initial state.

transitions that result in HeH^+ dissociation. Dressed potentials for HeH^+ can be defined and are shown in Fig. 3.5; however, potentials with $n > 1$ do not produce crossings within the well of the $U_{X^1\Sigma^+} - 0\omega$ potential. This lack of crossings is, of course, a general feature of dressed potentials associated with permanent-dipole transitions — such curves will always be parallel to each other up to the centrifugal barrier. Consequently, bound-free transitions for permanent-dipole transitions will always non-resonant. Non-resonant transitions are also possible between the electronic channels shown in Fig. 2.4 for H_2^+ , however resonant transitions will be dominant in that case.

The dressed potentials in Fig. 3.5 do still provide some useful information. The energy of the KER peaks can be predicted from the difference between the system's energy and the threshold of dressed potentials with $n > 1$. Additionally, the dressed potentials can give information about resonant bound-bound transitions. We see from Fig. 3.5 that the energy of the system lies within the well of the $U_{X^1\Sigma^+} - 1\omega$ potential. If the $U_{X^1\Sigma^+} - 1\omega$ potential has a bound state near this energy, then a resonant transition to the bound state will occur. When such a transition occurs as an intermediate step to dissociation, the process is referred to as resonance enhanced multiphoton

dissociation (REMPD) — a molecular analog of the resonance enhanced multiphoton ionization (REMPI) that is commonly observed in photoelectron spectra [20].

In addition to REMPD, it makes sense to look for other similarities between HeH^+ dissociation and atomic ionization. Adopting an atomic ionization picture to understand HeH^+ is particularly appealing when you note that Eq. (3.8) looks very similar to the coupled equation for the radial wavefunction of an electron in a hydrogenic atom. Pursuing this atomic analogy, Eq. (3.8) — with the approximate dipole $D = m_A/(m_A + m_B)R$ — shows that the “electron” in HeH^+ has a charge of $q = m_A/(m_A + m_B)$, a mass of μ_{AB} , and interacts via a short-range, central potential. In atoms, multiphoton ionization occurs when the Keldysh parameter is larger than one [149]. For the laser parameters used in this chapter, our Keldysh parameter will always lie well above this value. Consequently, we expect to see many of the same phenomena that are seen in multiphoton ionization in the strong-field dissociation of HeH^+

In HeH^+ , the KER spectrum is given by

$$\frac{dP}{dE} = \sum_J |\langle EJ|F_J(t_f)\rangle|^2. \quad (3.13)$$

A typical result for the KER spectrum in the parameter space that we are considering is shown in Fig. 3.6. This spectrum clearly shows the characteristic photon-spaced peaks expected for ATD, with peaks given by $E_n = n\omega + E_{v,J} - U_p$ — where $U_p = q^2\mathcal{E}_0^2/4\mu_{AB}\omega^2$ is the ponderomotive energy from Sec. 2.1.1. Because $U_p/\omega \approx 0.040$ for the parameters in Fig. 3.6 (and Fig. 3.7), this result gives $E_n/\omega = E_{v,J}/\omega + n$ to good approximation — as would be predicted from the dressed potentials in Fig. 3.5. For $v = 3$ and $\lambda = 2400$ nm, we expect the first peak to occur for two photon absorption at $E_{n=2}/\omega = 0.26$, which is in good agreement with the result in Fig. 3.6.

It is also important to note the large number of ATD peaks visible in Fig. 3.6. Our result shows more ATD orders than is typically seen in H_2^+ — a consequence of the large energy difference between the $X^1\Sigma^+$ and $A^1\Sigma^+$ potentials, which allows for the absorption of many photons before electronic excitation plays a role and blurs the peaks. Even so, the highest ATD peak shown in Fig. 3.6 lies 0.19 a.u. — more than eleven photons — below the minimum of the $A^1\Sigma^+$ potential.

Pursuing the atomic analogy further, one might expect to see an ATD plateau like those

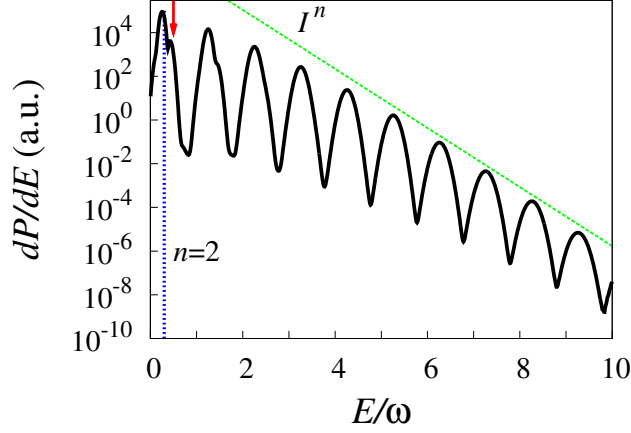


Figure 3.6: The KER spectrum for an initial vibrational state of $v = 3$ in a five-cycle, 2400-nm pulse with intensity $8.9 \times 10^{13} \text{ W/cm}^2$. The vertical dashed line at $E/\omega = 0.26$ corresponds to the expected location of the first peak, and the dashed diagonal, green line shows the $dP/dE \propto I^n$ behavior expected from lowest-order perturbation theory. The red arrow shows the splitting of the $n = 2$ peak caused by REMP. Figure adapted from Ref. [6].

typically seen in ATI spectra for $2U_p < E < 10U_p$ [60]. However, the small ponderomotive energy for our system would put this plateau in the energy range between $E/\omega = 0.08$ and $E/\omega = 0.40$ — *i.e.*, smaller than one of the peaks. Physically, this small interval is due to the fact that the massive nuclei are unable to gain a substantial amount of energy in the field. For a pulse with $I = 8.9 \times 10^{13} \text{ W/cm}^2$, it would require a wavelength of almost $3.7 \mu\text{m}$ to produce a plateau region with a large enough energy range to fit two KER peaks. Further increasing wavelength should eventually create a plateau with many peaks, like those seen in ATI. Similarly increasing the intensity at a fixed wavelength should eventually produce a plateau; for example, at 2400 nm an intensity of 10^{16} W/cm^2 would be needed to produce a plateau region with an energy range large enough to fit two peaks.

In addition to the KER, we also examine the distribution in the energy and angle associated with the relative momentum $\mathbf{k}$, which we will refer to as the “momentum” distribution for convenience, given by

$$\frac{\partial^2 P}{\partial E \partial \theta_k} = 2\pi \left| \sum_J (-i)^J e^{i\delta_J} Y_{J0}(\theta_k) \langle EJ | \Psi(t_f) \rangle \right|^2. \quad (3.14)$$

Here, θ_k is measured with respect to the laser polarization and δ_J is the scattering phase shift for state $|EJ\rangle$. Note that Eq. (3.13) is obtained from Eq. (3.14) by integrating over the angle

θ_k . The momentum distribution for $v = 3$ and $\lambda = 2400$ nm, the same case shown in Fig. 3.6, is shown in Fig. 3.7. We, of course, still see the photon-spaced peaks with decreasing probability. The angular distribution of each ATD peak is consistent with the identification of the number of photons involved. For instance, the peaks at $E/\omega = 0.3, 2.3, \dots$ are nonzero at $\theta_k/\pi = 0.50$ as expected for even-parity final states produced by the absorption of $n = 2, 4, \dots$ photons from the $J = 0$ initial state. Similarly, the peaks at $E/\omega = 1.3, 3.3, \dots$ have a node at $\theta_k/\pi = 0.50$ corresponding to an odd number of photons absorbed.

In both Fig. 3.6 and Fig. 3.7, there is additional structure on the two-photon peak in the form of a peak at $E/\omega = 0.50$ (indicated by arrows in the figures). This peak can be explained by noting that the $v = 3$ to $v = 6$ transition is nearly on resonance for 2400 nm: $\omega_{6,3} = E_{v=6,J=1} - E_{v=3,J=0} = 1.2\omega$. Even though the effective intensity at the resonant frequency $\omega_{6,3} = 1.2\omega$ is reduced by seven orders of magnitude in the power spectrum of our pulse, the resonant enhancement is still sufficient to produce a peak. Moreover, this REMPD mechanism correctly predicts the peak to be at $E/\omega = 0.50$ in agreement with our calculations.

A REMPD peak is noticeable in Fig. 3.6 on the $n = 3$ peak as well. For higher order peaks, however, the REMPD peak grows increasingly broad in energy due to the bandwidth of the laser

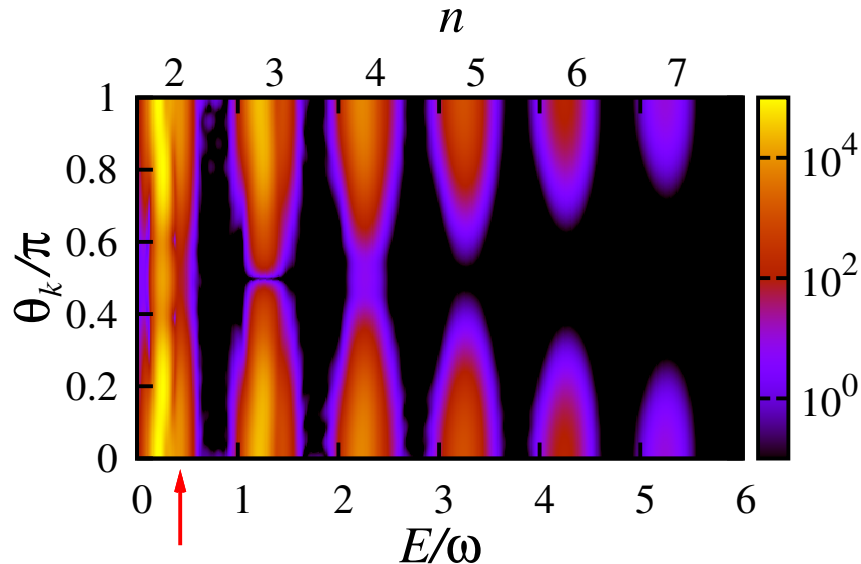


Figure 3.7: “Momentum” distribution from Eq. (3.14) plotted as a function of energy and angle θ_k for an initial ro-vibrational state with $v = 3$ and $J = 0$ in a five-cycle pulse with an intensity of 8.9×10^{13} W/cm² and a wavelength of 2400 nm. The upper-axis label n indicates the net number of photons absorbed. The red arrow shows the splitting of the $n = 2$ peak caused by REMPD. Figure adapted from Ref. [6].

pulse, washing it out as a distinct peak. We expect REMPD to be ubiquitous in long wavelength dissociation of HeH^+ since these wavelengths are more likely to drive a bound-bound resonant transition.

3.3 Parametric Formalism for HeH^+ Observables

We will now extend our calculations to look at CEP effects in HeH^+ dissociation. In order to understand the results, we will apply our parametric formalism in the usual fashion. The total wavefunction in Eq. (3.7), within the single electronic channel approximation for initial states with $M = 0$, is given within our formalism by

$$\Psi = \frac{1}{R} \sum_{J,n} F_{nJ}(R, t) Y_{J0}(\theta, \phi) \Phi(R; \mathbf{r}_1, \mathbf{r}_2) e^{-in\varphi}. \quad (3.15)$$

We will begin our study of CEP effects by looking at the momentum distribution within our formalism, as the other observables that we study (KER, spatial asymmetry, and dissociation probability) can all be defined directly from this distribution. While this section deals specifically with HeH^+ , we stress that all of the results derived here apply equally well to any single-channel problem where J is a good quantum number for the field-free system. Similarly, although we examine observables that are of interest in this specific problem, any observable can be expressed within our formalism.

3.3.1 Momentum Distribution and Spatial Asymmetry

Using the parametric expansion of the final wavefunction in Eq. (3.15) and defining the amplitudes A_{nJ} by

$$A_{nJ}(E) = (-i)^J e^{i\delta_J} \langle EJ | F_{nJ} \rangle, \quad (3.16)$$

the momentum distribution becomes

$$\frac{\partial^2 P}{\partial E \partial \theta_k} = 2\pi \sum_{n,J,J'} \left[A_{nJ} A_{nJ'}^* + \sum_{n' \neq n} A_{nJ} A_{n'J'}^* e^{i(n-n')\varphi} \right] Y_{J0}(\theta_k) Y_{J'0}^*(\theta_k). \quad (3.17)$$

We emphasize once more that all of the CEP dependence is explicit in the exponential factor. Moreover, the energy dependence is entirely contained within the amplitudes A_{nJ} ; the angular dependence is entirely contained in Y_{J0} .

Because n is the net number of photons, $A_{nJ}(E)$ has the standard interpretation from Chap. 2 of being the amplitude associated with exchanging n net photons with the field to end in a state with energy E and angular momentum J . We have explicitly separated interference terms in Eq. (3.17) from those that involve pathways with the same final n — and, thus, do not interfere in a way that can be controlled via the CEP — in order to more easily identify the pathways that we are interested in for CEP control. We see from Eq. (3.17) that CEP effects can be observed in the momentum distribution when there exists an energy E and angle θ_k where the product $A_{nJ}A_{n'J'}^*Y_{J0}Y_{J'0}$ is non-zero — allowing for pathways with different final J to contribute to CEP effects in this observable. Consequently, pathways differing by odd Δn can create CEP effects in the momentum distribution. Because pathways with the smallest $|\Delta n|$ have the largest overlap (see Fig. 2.2), $|\Delta n| = 1$ terms will create the largest contribution to CEP effects in the momentum distribution.

Consequently, CEP effects in the momentum distribution will be considerably larger than in the observables discussed in Chap. 2 — which required interference between pathways with even Δn to produce control. These CEP effects will tend to be largest in the region between adjacent photon peaks, where pathways with $|\Delta n| = 1$ have maximum overlap, and will create oscillations in the signal with a periodicity of 2π in the CEP. Because interfering pathways with any value of Δn can produce CEP control in Eq. (3.17), higher-order interferences will also contribute to CEP effects. These interference terms will typically be much smaller than $|\Delta n| = 1$ terms, and will create oscillations in the signal with periodicities of $2\pi/|\Delta n|$.

Visualizing CEP effects in the complete momentum distribution is difficult — as it is a function of three variables when the dependence on φ is included. It is common, instead, to examine control over a spatial asymmetry — defined as the difference between the integrated momentum distribution in two angular ranges. Using a difference, as opposed to looking at a single angular range, has the advantage of eliminating the CEP-independent portion of the signal — as will be demonstrated below. For HeH^+ , defining the angular ranges as 0 to $\pi/2$ and $\pi/2$ to π provides a

measure of the control over the energy-dependent probability of the H^+ ion traveling up or down (relative to the laser polarization).

Here, we define this spatial asymmetry using a slightly different normalization convention than is standard in experiment as:

$$\mathcal{A}(E) = \left[P_{\text{up}}(E) - P_{\text{down}}(E) \right] \left\langle \frac{dP}{dE} \right\rangle_{\varphi}^{-1}, \quad (3.18)$$

where

$$P_{\text{up}} = \int_0^{\pi/2} \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k \quad (3.19)$$

and

$$P_{\text{down}} = \int_{\pi/2}^{\pi} \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k. \quad (3.20)$$

We note that in using the CEP-averaged KER in the denominator of Eq. (3.18) we have deviated from standard practice of normalizing by the CEP-dependent KER in Eq. (3.23), which is obviously equivalent to $P_{\text{up}} + P_{\text{down}}$. The downside of this choice is that $\mathcal{A}$ no longer strictly lies between -1 and 1 . However, we gain simplicity in interpretation since any CEP dependence in $\mathcal{A}$ can now only come from the numerator — as the KER is, in general, dependent upon the CEP.

It can be shown that the numerator in Eq. (3.18) reduces to

$$P_{\text{up}} - P_{\text{down}} = \frac{\sqrt{\pi}}{2} \sum_{\substack{n, J \text{ even} \\ n', J' \text{ odd}}} C_{JJ'} A_{nJ} A_{n'J'}^* e^{i(n-n')\varphi}. \quad (3.21)$$

The constant $C_{JJ'}$ resulting from the angular integration can be written in terms of Clebsch-Gordan coefficients as

$$C_{JJ'} = \sum_{L=|J-J'|}^{J+J'} \frac{\sqrt{(2J+1)(2J'+1)} \langle JJ'00 | L0 \rangle}{\Gamma(\frac{2-L}{2}) \Gamma(\frac{3+L}{2})}. \quad (3.22)$$

The spatial asymmetry thus extracts the terms in the momentum distribution that are antisymmetric with respect to $\theta_k = \pi/2$ — namely, those with J and J' of opposite parity. The symmetric piece is completely eliminated by the subtraction in Eq. (3.21). This provides a contrast with the KER spectrum discussed in Chap. 2 (and derived for this system in Sec. 3.3.2), where only the

the symmetric piece of the momentum distribution survives integration. This result holds true even if the integration limits in Eq. (3.19) and Eq. (3.20) are defined only over an angular range less than $\pi/2$ — as long as the cuts are symmetric about $\pi/2$. This is significant as it is common for experiments to use only a small range of angles near the polarization vector.

Because we begin in an initial state with definite parity, the fact that only terms with J and J' having different parity contribute to $P_{\text{up}} - P_{\text{down}}$ means that n and n' must also have different parity to contribute². As a result, $\mathcal{A}$ has no CEP-independent terms and oscillates about $\mathcal{A} = 0$ with terms having periodicities 2π , $2\pi/3$, $2\pi/5$, and so on in the CEP. It is expected that the 2π periodicity will dominate for most systems because it results from interference between pathways with $|\Delta n| = 1$, which have a larger overlap than $|\Delta n| = 3, 5, \dots$ pathways. Because photon pathways differing by only a single photon dominate $\mathcal{A}$, we expect to see larger CEP effects for $\mathcal{A}$ than for the KER discussed in Sec. 3.3.2 or total dissociation probability discussed in Sec. 3.3.3.

3.3.2 Kinetic Energy Release

We may calculate the KER spectrum from the momentum distribution by integrating over all angles θ_k to give:

$$\frac{dP}{dE} = \sum_{n,J} \left[|A_{nJ}|^2 + \sum_{\substack{n' \neq n \\ n-n' \text{ even}}} A_{nJ} A_{n'J}^* e^{i(n-n')\varphi} \right]. \quad (3.23)$$

Equation (3.23) is equivalent to the single-color case of the hydrogen photoelectron spectrum in Eq. (2.7) — as expected based on the previously mentioned similarities between the Hamiltonians of the two systems. Unlike Eq. (3.17), Eq. (3.23) only allows for interference of final states with the same angular momentum. Therefore, CEP effects can only occur in the KER spectrum when dissociation pathways $|\Delta n| = 2, 4, \dots$ overlap in energy. As such, the dominant CEP-dependence in the KER spectrum will be a linear combination of $\cos 2\varphi$ and $\sin 2\varphi$, and the CEP effects found in the KER spectrum can generally be expected to be smaller than those found in the momentum distribution.

Moreover, we know from Fig. 2.2 that the CEP effects from the $n + 1$ peak interfering with

²Here, parity refers to whether n is an even or odd number — as opposed to the spatial parity associated with the value of J .

the $n - 1$ peak will generally lie at energies overlapping the n -photon peak — creating a small CEP-dependent variation on a large signal. To quantify the CEP effects in the energy spectrum, we use the normalized yield $\mathcal{Y}$,

$$\mathcal{Y}(E) = \frac{dP}{dE} \left\langle \frac{dP}{dE} \right\rangle_\varphi^{-1}, \quad (3.24)$$

where $\langle dP/dE \rangle_\varphi$ is the CEP-averaged spectrum. Given our analysis above, $\mathcal{Y}(E)$ can thus be parameterized as

$$\mathcal{Y} = 1 + \mathcal{Y}_2 \cos(2\varphi + \beta_2) + \mathcal{Y}_4 \cos(4\varphi + \beta_4) + \dots \quad (3.25)$$

Note that all of the $\mathcal{Y}_n$ and β_n are energy dependent and that the $\mathcal{Y}_n$ give the relative magnitudes of the CEP effects caused by the interference of pathways differing by n .

3.3.3 Total Dissociation Probability

Finally, we obtain the total dissociation probability by integrating the KER spectrum over all energies,

$$P = \int \frac{dP}{dE} dE. \quad (3.26)$$

Like the KER spectrum, the total dissociation probability only allows for interference of final states with the same angular momentum and $|\Delta n|$ even. Therefore, the total dissociation probability will have smaller CEP effects than the momentum distribution. Moreover, we expect that the CEP control over the total dissociation probability will also be smaller than that of the KER spectrum since the differing energy dependence of β_n from Eq. (3.25) will lead to cancellations in the integral over energy.

3.4 Carrier-Envelope Phase Effects — Results and Discussion

Calculations of the CEP-dependence of observables in HeH^+ are carried out using the methods outlined in Sec. 3.1.1 and Sec. 3.1.2 for thirty, uniformly spaced values of the CEP over a range from $\varphi = 0$ to $\varphi = 2\pi$. All calculations that follow will use an initial state with $J = 0$, and will be carried out for two-cycle pulses with intensities of 10^{14} W/cm^2 and wavelengths of either

3200 or 4000 nm. By fixing the number of cycles for the two wavelengths, we keep the value of $\Delta\omega_{\text{FWHM}}/\omega$ constant — therefore, any change in CEP effects will be caused by factors other than the trivial bandwidth broadening outlined in Sec. 2.2.4. While it would be possible to solve for the states $F_{n,J}$ using Eq. (3.15) to derive a system of equations similar to those in Eq. (3.8), we will solve directly for F_J and use the quantities $F_{n,J}$ merely for their interpretive power — as is our typical approach.

3.4.1 Spatial Asymmetry

We begin by examining the spatial asymmetry from, Eq. (3.18), which is shown in Fig. 3.8 for $v = 0$ and $v = 1$ in a 4000-nm pulse. Here, we show results for 4000-nm light because the calculated asymmetry shows considerably larger CEP effects than at 3200 nm. Figure 3.8 shows energy-dependent peaks with 2π periodicity, as predicted by Eq. (3.21) for the interference of pathways with $|\Delta n| = 1$. Comparing the spatial asymmetries to their corresponding CEP-averaged KER — shown in in Fig. 3.8(a) and Fig. 3.8(c) — we see that the largest CEP effects occur between adjacent KER peaks. This is, of course, the expected result for $|\Delta n| = 1$ interference.

As will be seen in Sec. 3.4.2 and Sec. 3.4.3, the CEP dependence of the spatial asymmetry is much more apparent than that of the KER spectrum or total dissociation probability. This is

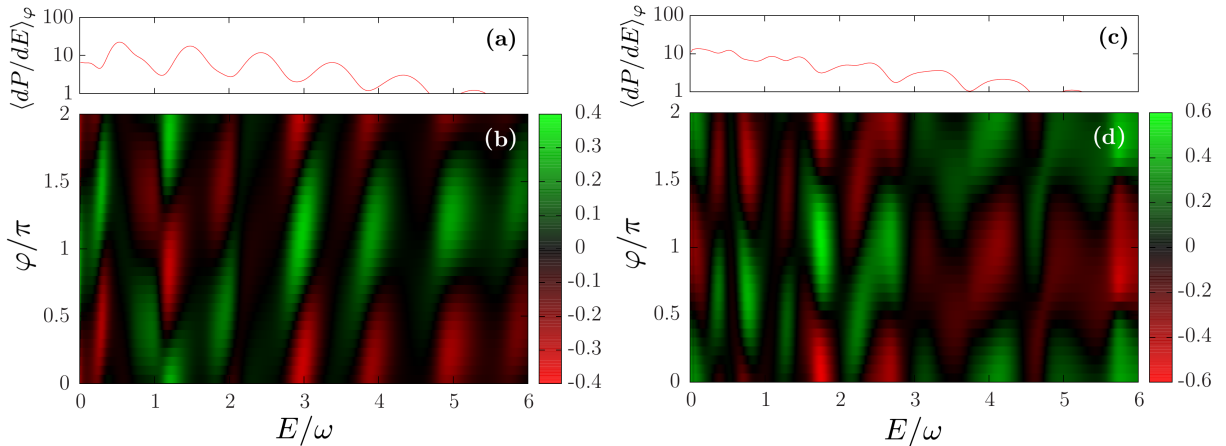


Figure 3.8: (a) and (c): CEP-averaged KER spectrum, $\langle dP/dE \rangle_\varphi$, in atomic units for (b) and (d), respectively. (b) and (d): Normalized spatial asymmetry $\mathcal{A}$ as a function of CEP and KER in a 4000-nm pulse. Panels (a) and (b) are for $v = 0$; and (c) and (d), for $v = 1$. Per the discussion in the text, the areas of largest spatial asymmetry generally occur between KER peaks, where the overlap between adjacent photon pathways is largest. Figure adapted from Ref. [7].

expected, as both of those observables require interference between pathways with $|\Delta n| = 2$. We also note that CEP effects in Fig. 3.8 are larger for $v = 1$ than for $v = 0$. The larger asymmetry for the $v = 1$ initial state can be explained by a broadening of the KER peaks (and associated A_{nJ}) caused by REMP. This peak broadening is also the likely reason that CEP effects are largest in our calculations at 4000 nm. We further discuss peak broadening from REMP in Sec. 3.4.2, where the effect is easily seen in the KER.

The large spatial asymmetry that we see for HeH^+ is particularly interesting considering that CEP control over the spatial asymmetry of molecular dissociation is routinely equated with control over electron localization. Since the dynamics are governed by just the ground-state channel $X^1\Sigma^+$ that dissociates to $\text{He}(1s^2)+\text{H}^+$, however, the electrons *always* localize on the He atom during dissociation, independent of the CEP. Therefore, the CEP-dependent spatial asymmetry seen here has nothing to do with electron localization. Instead, the CEP-controlled spatial asymmetry is actually control over the rotational degrees of freedom of the nuclei. Extension of our formalism to other multi-channel systems — where electron localization on different nuclear centers is possible — shows that control over spatial asymmetry in dissociating nuclear fragments can be understood as control over nuclear degrees of freedom in those cases as well. This can be seen in Sec. 6.1.3, where we express the spatial asymmetry for D_2^+ in our parametric formalism.

Of course, control over electron localization via the CEP does occur for multi-channel problems with distinguishable final states; this effect can be measured via a channel asymmetry between channels. For HeH^+ , this asymmetry (as a function of E and θ_k) between the lowest two electronic channels can be defined as the difference between the two momentum distributions

$$\frac{\partial^2 P_{X^1\Sigma^+}}{\partial E \partial \theta_k} = 2\pi \sum_{n,J,J'} \left[A_{nJ}^{(X^1\Sigma^+)} A_{nJ'}^{*(X^1\Sigma^+)} + \sum_{n' \neq n} A_{nJ}^{(X^1\Sigma^+)} A_{n'J'}^{*(X^1\Sigma^+)} e^{i(n-n')\varphi} \right] Y_{J0}(\theta_k) Y_{J'0}^*(\theta_k), \quad (3.27)$$

and

$$\frac{\partial^2 P_{A^1\Sigma^+}}{\partial E \partial \theta_k} = 2\pi \sum_{n,J,J'} \left[A_{nJ}^{(A^1\Sigma^+)} A_{nJ'}^{*(A^1\Sigma^+)} + \sum_{n' \neq n} A_{nJ}^{(A^1\Sigma^+)} A_{n'J'}^{*(A^1\Sigma^+)} e^{i(n-n')\varphi} \right] Y_{J0}(\theta_k) Y_{J'0}^*(\theta_k). \quad (3.28)$$

Here, the additional index i in $A_{nJ}^{(i)}$ denotes that the pathway ends in electronic channel i —

with the amplitude otherwise having its usual interpretation. The amplitudes will, however, have a slightly different definition because the continuum state used in the projection will itself be a multi-channel wave function. With the exception of the electronic label, Eq. (3.27) and Eq. (3.28) are identical to the single-channel momentum distribution in Eq. (3.17). As can be seen from Eq. (3.27) and Eq. (3.28), varying the CEP will alter the size of the signal in each channel, providing control over whether the electrons localize to form $\text{He}(1s^2)+\text{H}^+$ or $\text{He}^+(1s)+\text{H}(1s)$. Control over channel asymmetries will be discussed further for HD^+ in Sec. 6.1.5.

3.4.2 Kinetic energy release spectrum

The KER spectrum as a function of CEP is shown in Figs. 3.9(b) and 3.9(d) for a wavelength of 4000 nm and initial states with $v = 0$ and $v = 1$, respectively. For a fixed CEP, we clearly see the characteristic photon-spaced peaks of ATD in the KER spectrum; similar peaks were observed in Fig. 3.6 for a 2400-nm pulse. From Fig. 3.9(b) and Fig. 3.9(d), we see that CEP effects in the KER are much smaller than in the spatial asymmetry. The amplitude $\mathcal{Y}_2$ from Eq. (3.25) provides a measure of the size of these CEP effects (to leading order) and is shown in Fig. 3.9(a) and Fig. 3.9(c).

From Fig. 3.9(a), we see that $\mathcal{Y}_2$ does not exceed three percent — except for regions where it is trivially enhanced by small signals. The small size of $\mathcal{Y}_2$ for $v = 0$ is reflected in the lack of

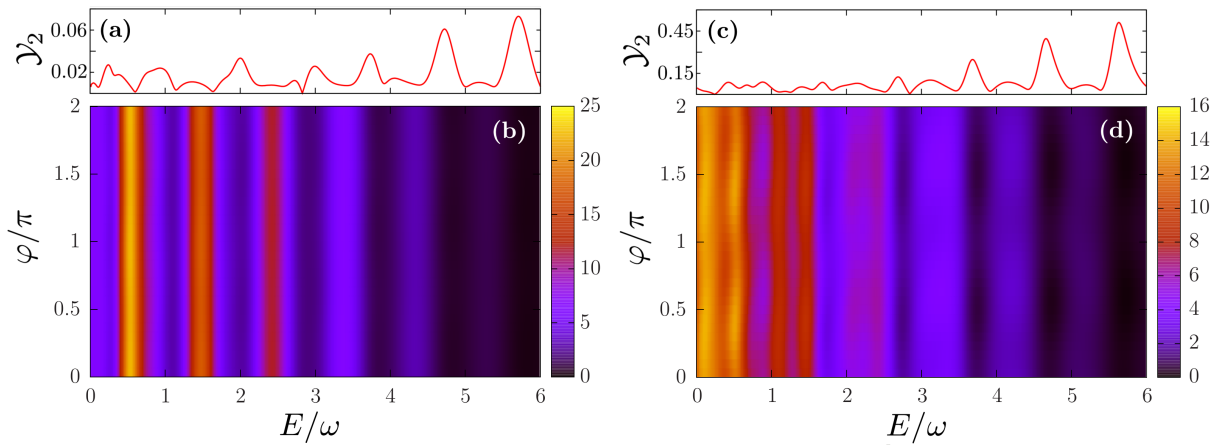


Figure 3.9: (a) and (c): The relative amplitude $\mathcal{Y}_2$ of the CEP-dependent oscillation defined in Eq. (3.25) for (b) and (d), respectively. (b) and (d): KER spectrum dP/dE as a function of CEP in a 4000-nm pulse. Panels (a) and (b) are for $v = 0$; and (c) and (d), for $v = 1$. Figure adapted from Ref. [7].

any visible changes in Fig. 3.9(b) as a function of CEP. As with the spatial asymmetry, we see larger CEP effects in the $v = 1$ case; $\mathcal{J}_2$ is nearly 10% at energies with substantial signal, and CEP effects are visible in Fig. 3.9(d). For both vibrational states, CEP effects were found to be smaller when 3200-nm light was used.

These results imply that going from 3200 nm to 4000 nm, or from $v = 0$ to $v = 1$ at 4000 nm, creates a larger overlap between photon pathways. However, because the number of cycles is fixed for all calculations, mechanisms other than the bandwidth must be responsible for this increased overlap between peaks. As previously mentioned, we believe that this broadening of the KER peaks can be explained by REMP — a phenomenon we identified at shorter wavelengths in Sec. 3.2.2. This conclusion is based on the telltale splitting of the first three KER peaks in Fig. 3.9(d), an effect that can be seen even more clearly in Fig. 3.10.

Comparison of the spectra in Fig. 3.10 at a given wavelength shows that this peak splitting is much larger for $v = 0$ than $v = 1$. Most of the individual photon peaks in the $v = 1$ case have very little structure; the magnitude of each photon peak decreases as a function of energy in a fairly monotonic fashion as you move away from its maximum value. The individual photon peaks for $v = 0$, in contrast, exhibit a clear revival at a second energy near their expected maximum ($E_n = n\omega + E_{vJ}$). We attribute this revival to a nearly-resonant intermediate transition between bound states separated by energy ΔE — which creates an enhancement of the n -photon peak at the slightly shifted energy $E_n = n\omega + E_{vJ} + (\Delta E - \omega)$. The result of this REMP is that

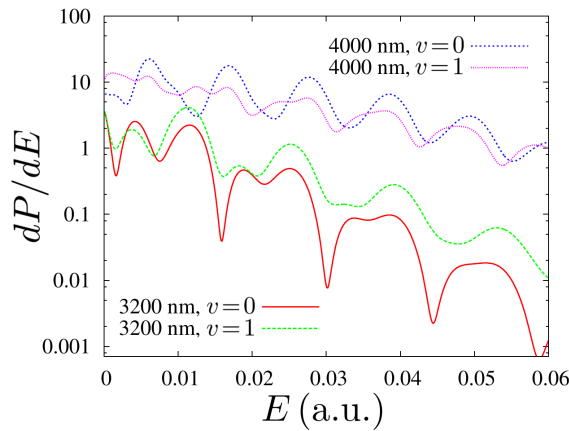


Figure 3.10: KER spectra, dP/dE , in atomic units for $\varphi = \pi$ cuts of Figs. 3.9(b) and 3.9(d) along with the equivalent spectra for 3200 nm. Figure adapted from Ref. [7].

the individual photon peaks become broader in energy — which can be easily seen by comparing the width of the $v = 0$ and $v = 1$ peaks in Fig. 3.10.

From Fig. 3.10, we see that this peak broadening from REMPD occurs for $v = 1$ in both wavelengths. However, the effect is more pronounced in 4000 nm — where the individual peaks are wide enough that no pronounced minimum exists between adjacent peaks at low energies. Based on the size (in energy) of the peak splitting, we believe that the nearly resonant transition in the 4000-nm case occurs between the $v = 1$ initial state and the $v = 2, J = 1$ state. Of course, this increased overlap between adjacent photon peaks in the KER spectrum corresponds to an increased overlap between the associated amplitudes A_{nJ} . This explains that larger CEP effects in the 4000-nm, $v = 1$ case.

3.4.3 Total dissociation probability

The final observable of interest is the total dissociation probability. Our calculations confirm the π periodicity in P expected from Eq. (3.26) that arises from the $|\Delta n|=2$ interference (see Fig. 3.11). We also find that the CEP effects are larger for 4000 nm than for 3200 nm, which is convenient for potential experiments in the sense that the 4000-nm pulse produces the larger total dissociation probability. However, these effects are still small and in no case did we find a modulation of P greater than 1% of the CEP-averaged probability $\langle P \rangle_\varphi$. We again find the largest effects for $v = 1$ in a 4000-nm pulse, caused by broadening of peaks from REMPD.

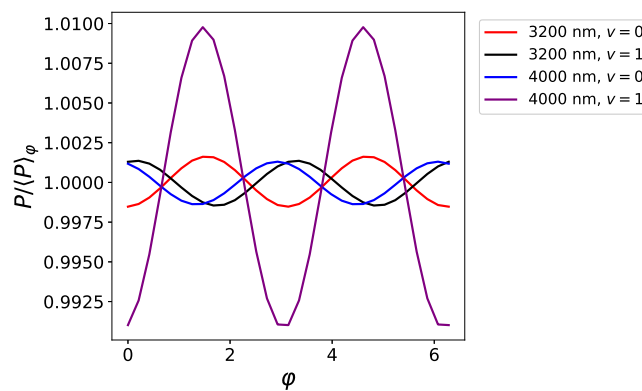


Figure 3.11: CEP-dependence of the dissociation probability (normalized by the CEP-averaged dissociation probability) for HeH^+ from $v = 0$ and $v = 1$ initial states, in 3200- and 4000-nm light.

3.5 Closing Remarks

In this chapter, we have proposed HeH^+ as a simple, heteronuclear benchmark for studying ICEP control. We have shown that long-wavelength dissociation of HeH^+ is dominated by permanent-dipole transitions and demonstrated that an experimentally detectable dissociation yield can be produced in this wavelength regime. Experiments directly measuring this permanent-dipole dissociation have since been achieved [204,205]. Additionally, we have shown that control over the spatial asymmetry can be obtained at experimentally observable magnitudes for long wavelengths (3200 nm or longer) and at intensities approaching 10^{14} W/cm^2 . Using our parametric formalism, we have provided a simple picture that provides a quantitative understanding of the control observed. In the next chapter, we will continue our exploration of CEP effects, but will turn our attention to using our parametric formalism to learn about the CEP of the pulse itself — rather than the observables being controlled through the phase's variation.

Chapter 4

Parametric Asymmetry Plots Within Our Parametric Formalism

In Chap. 3, we showed how carrier-envelope phase effects can be understood for single-color pulses within our parametric formalism. Specifically, we focused on using our theory to explain the CEP control seen in the dissociation of HeH^+ ; while our theory was applied to numerical calculations, it can, of course, be applied in the same manner to understand experimental spectra. However, in order to generate experimental, CEP-dependent spectra like as those seen in Figs. 3.9, 3.11, and 3.8, the CEP for each shot of the laser must be known.

In this chapter, we will continue our exploration of single-color, CEP effects. Here, we will transition from understanding physical observables for known CEPs to extracting the phase itself from the spatial asymmetry of a photoionization spectrum. In Sec. 4.1, we will briefly outline relevant experimental techniques for characterizing the carrier-envelope phase of a pulse. In the sections that follow, we will show how our parametric theory can be applied to understand from first principles how this method of CEP extraction works, and — potentially — how our theory can be used to improve the shot-to-shot characterization of the CEP.

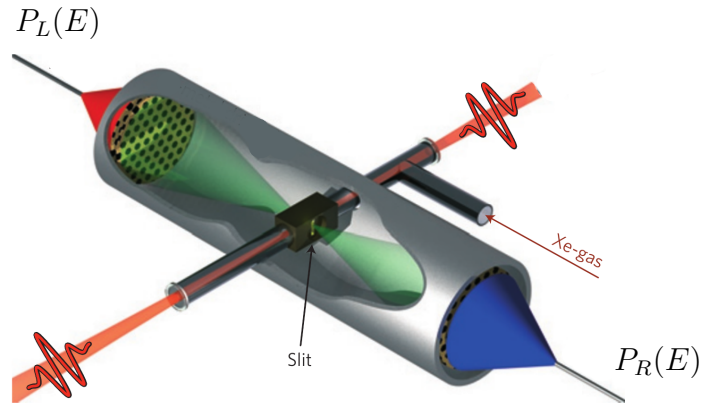


Figure 4.1: Diagram of CEPM. Adapted with permission from Ref. [214].

4.1 Experimental Methods of Carrier-Envelope Phase Extraction

There are two main approaches for determining the CEP in experiment: locking the CEP to a given, known value in order to obtain a spectrum and then repeating for a number of different phases; or, allowing the CEP to vary randomly between shots and explicitly measuring it for each individual shot. The first of these methods can be achieved using optical techniques — such as f - $2f$ interferometry [211]. However, even a pulse with a “locked” CEP will have shot-to-shot variations, especially at the long run-times required to accumulate sufficient counts. For example, shot-to-shot variation in the CEP from f - $2f$ interferometric techniques were found to produce uncertainties of around 300 mrad for run-times on the order of hours in previous studies [212,213].

In f - $2f$ techniques the goal is to limit shot-to-shot variations, keeping the CEP as close to a locked value as possible. In contrast, the second of the aforementioned techniques uses shot-to-shot variation as an advantage — allowing the CEP to randomly vary in order to scan the 2π range of possible phases. Here, the CEP is measured for each individual shot, typically by a CEP-meter (CEPM) that makes use of stereo ATI [214–216]. For each shot, a portion of the linearly-polarized beam is split off and sent to the CEPM; the remaining portion of the beam is used for the intended experiment.

The CEPM itself is comprised of two electron detectors centered on the laser’s polarization axis, with a xenon gas cell centered between the two detectors (Fig. 4.1). The intensity of the split-off portion of the beam is adjusted to put the interaction with xenon predominately in the

single-ionization regime. For each shot, the energy of the ionized electrons are measured on one of the two detectors — producing left and right photoelectron spectra, $P_L(E)$ and $P_R(E)$.

The two measured spectra are then integrated over two energy ranges within the plateau region of the ATI spectrum — a higher energy range, ΔE_H , and a lower energy range, ΔE_L [63, 216]. The normalized difference between the two integrated spectra (evaluated in both energy ranges) produces two spatial asymmetries for each shot — $\mathcal{A}_H$ and $\mathcal{A}_L$. The two asymmetries are then plotted as a parametric asymmetry plot (PAP) of $\mathcal{A}_L$ versus $\mathcal{A}_H$ for each shot (Fig. 4.2).

By carefully controlling experimental conditions and optimizing the selection of high and low energy ranges, it has been found experimentally that it is often possible to create a PAP that approximately takes the shape of a circle [215, 216]. Mathematically, the condition for a circular PAP is that both $\mathcal{A}_L$ and $\mathcal{A}_H$ oscillate sinusoidally in the CEP, ninety degrees out of phase and with the same amplitude. We have already shown in Sec. 3.3.1 that when only pathways with $\Delta n = 1$ interfere, the spatial asymmetries will be exactly sinusoidal in the CEP with energy-dependent phases. However, this was independently observed in experiment during the development of the methods outlined in this section — opening the possibility of choosing energy ranges to generate a circular PAP [216].

A circular PAP is desirable because the CEP can be related to the polar angle θ of the PAP

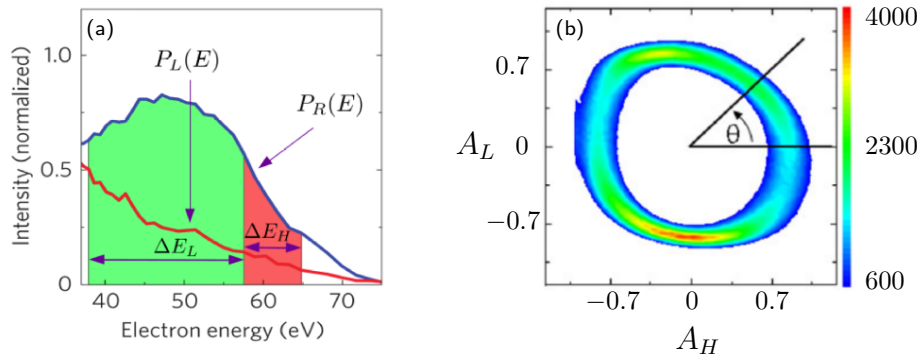


Figure 4.2: (a) Photoelectron spectra $P_{L/R}(E)$ measured by the left and right detectors, respectively, with high and low energy ranges defined. Adapted with permission from Ref. [214]. (b) Parametric asymmetry plot (PAP) for asymmetries $\mathcal{A}_{H/L}$ produced by taking the normalized difference of $P_{L/R}(E)$ as defined by Eq. (4.4), and then integrating over the energy ranges $\Delta E_{H/L}$. Adapted with permission from Ref. [216].

by

$$\tan \theta = \frac{\mathcal{A}_L}{\mathcal{A}_H} = \tan (\varphi + \varphi_0), \quad (4.1)$$

which gives the linear relationship $\varphi = \theta - \varphi_0$ [214, 215]. The absolute phase cannot be retrieved solely through use of a CEP, and its value depends on the definition of the carrier wave of the pulse. Some work has been done to characterize the absolute phase through a combination of theory and CEPs [217–219]; this work will be further discussed in Sec. 4.2.

Generating a circular PAP is not possible for all pulses and is far from the most general case. When the PAP is not circular, other methods must be used to retrieve the CEP for each shot. Most commonly, the CEP is extracted using the fact that the physics of the pulse generation leads to the CEP having a random, uniformly distributed value from shot to shot. In the infinite-shot limit, the same number of shots will occur in any infinitesimal range $d\varphi$ of the CEP. This implies a connection between the infinitesimal range $d\theta$ of the polar angle and $d\varphi$ given by

$$d\varphi = \frac{\rho(\theta)}{\langle \rho \rangle} d\theta, \quad (4.2)$$

where ρ is the density of shots as a function of the polar angle and $\langle \rho \rangle$ is the average number of shots in the range $d\varphi$ [215]. Equation (4.2) can be applied to any shape of PAP, with its accuracy determined by the number of shots and bin size. However, it is still ideal to generate a PAP that is as close to circular as possible in order to minimize the error in the extracted CEP [215, 216].

4.2 Application of the Parametric Formalism

While the experimental methods used to extract the CEP from a PAP are simple to apply and commonly used, there has been little work aimed at providing a theoretical underpinning of the PAP itself. Some theoretical work related to PAPs does exist; for example, previous work compared numerical solutions of the TDSE in a single-active electron potential to experimental results in an attempt to improve CEP extraction [217]. Here, it was found that theory could aid in determining the absolute CEP, something that experiment alone is not capable of doing. Similar studies have compared calculations based on SFA and quantitative rescattering theory (QRS) to

experimental results to determine the absolute phase [218, 219]. The latter of these methods is not only much faster than solving the TDSE, but provides an interpretation of the CEP effects in terms of the CEP-dependent changes in the wavepacket that rescatters from the parent ion to create high-energy ATI.

Although methods based on QRS and SFA have shown promise, they are based on approximations that neglect certain physical processes. Additionally, these methods — and solutions of the TDSE — require numerical solutions at each CEP rather than providing an analytic expressions for left/right photoelectron spectra. With our parametric formalism, we are able to generate an analytic expression for the expected behavior of $\mathcal{A}_H$ and $\mathcal{A}_L$ as a function of CEP from first principles. Our theoretical framework additionally provides insight into the physical mechanisms that determine the shape of a PAP, what processes cause deviations from a circular PAP, and how these deviations can be reduced or eliminated completely. Thus, our formalism allows for the possibility of improving the extraction of the CEP from a PAP.

We begin by expressing the momentum distribution for the electrons detected in the CEP-M within our parametric formalism. In the single-active electron approximation, the TDSE for the system is identical in form to that of Eq. (3.8) for HeH^+ — with the potential and masses changing, along with changes in notation to r and ℓ to represent the electronic coordinate and angular momentum. Because of these similarities, we can forego the derivations and use Eq. (3.17), which for the ionized electron is given by

$$\frac{\partial^2 P}{\partial E \partial \theta_k} = 2\pi \sum_{n, \ell, \ell'} \left[A_{n\ell} A_{n\ell'}^* + \sum_{n' \neq n} A_{n\ell} A_{n'\ell'}^* e^{i(n-n')\varphi} \right] Y_\ell Y_{\ell'}^*. \quad (4.3)$$

In Eq. (4.3), linearly polarized light is used to match experimental conditions — as such, states with different values of m are not coupled.

For a xenon sample, ionized electrons will likely come from $\ell = 1$ orbitals — with $m = 0$ and $m = \pm 1$ all contributing to the ionization spectrum. Electrons from each initial m will have a momentum distribution — all of which have the form of Eq. (4.3). As such, it should be noted that the amplitudes $A_{n\ell}$ and the spherical harmonics depend on m . A more general result could be derived by averaging the momentum distribution for each of these m to better match the

experimental conditions. However, the specific m -value will not affect any of the results derived in this chapter and we will use $m = 0$ to demonstrate how our formalism applies to PAPs.

From the momentum distribution in Eq. (4.3), we can arrive at the relevant quantities $\mathcal{A}_L$ and $\mathcal{A}_H$ needed for the PAP. Following the definition used in experiment [216], these asymmetries are given by:

$$\mathcal{A}_{H/L} = \frac{\int_{\Delta E_{H/L}} (P_L - P_R) dE}{\int_{\Delta E_{H/L}} (P_L + P_R) dE}. \quad (4.4)$$

Here, the energy-dependent probabilities, P_L and P_R , are defined by:

$$\begin{aligned} P_L(E) &= \int_0^\beta \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k \\ P_R(E) &= \int_{\pi-\beta}^\pi \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k. \end{aligned} \quad (4.5)$$

In Eq. (4.5), the acceptance angle β of both detectors is assumed to be the same. Similarly, both detectors are assumed to be exactly centered on the laser's polarization axis. The azimuthal integration has already been carried out in Eq. (4.3).

Carrying out the relevant integrations, the numerator and denominator of $\mathcal{A}^{H/L}$ are given by

$$\begin{aligned} \int_{\Delta E_{H/L}} (P_L - P_R) dE &= \int_{\Delta E_{H/L}} \left(\int_0^\beta \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k - \int_{\pi-\beta}^\pi \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k \right) dE \\ &= \sum_{n > n'}^{\text{odd}} \tilde{B}_{nn'}^{H/L} \cos[(n - n')\varphi] - \tilde{C}_{nn'}^{H/L} \sin[(n - n')\varphi], \end{aligned} \quad (4.6)$$

and

$$\begin{aligned} \int_{\Delta E_{H/L}} (P_L + P_R) dE &= \int_{\Delta E_{H/L}} \left(\int_0^\beta \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k + \int_{\pi-\beta}^\pi \frac{\partial^2 P}{\partial E \partial \theta_k} \sin \theta_k d\theta_k \right) dE \\ &= \sum_{n \geq n'}^{\text{even}} \tilde{B}_{nn'}^{H/L} \cos[(n - n')\varphi] + \tilde{C}_{nn'}^{H/L} \sin[(n - n')\varphi]. \end{aligned} \quad (4.7)$$

The summations in Eq. (4.6) and Eq. (4.7) differ only in that fact that the former is carried out over odd values of $n - n'$, while the latter is carried out over even values. These restrictions come from the angular integration and are the same as those discussed for the spatial asymmetry in Sec. 3.3.1; only odd $\ell - \ell'$ survive the difference in the numerator, while only even $\ell - \ell'$ survive

the sum in the denominator. The restrictions on net photon numbers are, of course, equivalent because we are in the dipole approximation and begin in an eigenstate of angular momentum.

The coefficients $\tilde{B}_{nn'}$ and $\tilde{C}_{nn'}$ in Eq. (4.6) and Eq. (4.7) are given by the expressions

$$\tilde{B}_{nn'}^{H/L} = 2\pi (4 - 2\delta_{nn'}) \int_{\Delta E_{H/L}} \left| \sum_{\ell, \ell'} A_{n\ell} A_{n'\ell'}^* \int_0^\beta Y_\ell Y_{\ell'} \sin \theta_k d\theta_k \right| \cos \alpha_{nn'} dE, \quad (4.8)$$

and

$$\tilde{C}_{nn'}^{H/L} = 8\pi \int_{\Delta E_{H/L}} \left| \sum_{\ell, \ell'} A_{n\ell} A_{n'\ell'}^* \int_0^\beta Y_\ell Y_{\ell'} \sin \theta_k d\theta_k \right| \sin \alpha_{nn'} dE. \quad (4.9)$$

While omitted for simplicity, it is understood that the summations over ℓ and ℓ' within the coefficients $\tilde{B}_{nn'}^{H/L}$ and $\tilde{C}_{nn'}^{H/L}$ have the same parity restrictions as n and n' . Here, the coefficients in $P_L - P_R$ only include terms with ℓ and ℓ' having different parity, while the coefficients in $P_L + P_R$ only include terms with ℓ and ℓ' having the same parity. For all of the above expressions, the phase α is given by the argument

$$\alpha_{n, n' \neq n} = \text{Arg} \left[\sum_{\ell, \ell'} A_{n, \ell} A_{n', \ell'}^* \int_0^\beta Y_\ell Y_{\ell'} \sin \theta_k d\theta_k \right],$$

$$\alpha_{n, n} = 0. \quad (4.10)$$

Finally, we simplify the notation by defining the quantities

$$B_{\Delta n}^{H/L} = \sum_n \tilde{B}_{n+\Delta n, n}^{H/L}, \quad (4.11)$$

and

$$C_{\Delta n}^{H/L} = \sum_n \tilde{C}_{n+\Delta n, n}^{H/L}, \quad (4.12)$$

where $\Delta n = n - n'$ gives the difference in the net number of photons between interfering pathways. This gives the desired asymmetries as the the ratio of discrete Fourier series with even and odd frequencies:

$$\mathcal{A}_{H/L} = \frac{\sum_{\Delta n > 0}^{\text{odd}} B_{\Delta n}^{H/L} \cos(\Delta n \varphi) - C_{\Delta n}^{H/L} \sin(\Delta n \varphi)}{\sum_{\Delta n \geq 0}^{\text{even}} B_{\Delta n}^{H/L} \cos(\Delta n \varphi) + C_{\Delta n}^{H/L} \sin(\Delta n \varphi)}. \quad (4.13)$$

The numerator of Eq. (4.13) sums the interference between all pathways that end at the same energy and differ by an odd number of net photons in the given energy range ($\Delta E_{H/L}$). Similarly, the denominator sums all of the interfering pathways that differ by an even number of net photons in this energy range.

Before ending this section, there are a few properties of Eq. (4.13) worth mentioning. First, the cancellation of even and odd Δn in the numerator and denominator, respectively, hinges upon both detectors being centered on the polarization axis of the laser. If the detectors are misaligned, terms with even Δn will contribute to the numerator, while terms with odd Δn will contribute to the denominator. Second, this cancellation results in $\mathcal{A}_{H/L}$ having half-wave symmetry¹. Consequently, the asymmetries can be re-written as a single Fourier series containing only odd harmonics to give

$$\mathcal{A}_{H/L} = \sum_k^{\text{odd}} b_k^{H/L} \cos(k\varphi) - c_k^{H/L} \sin(k\varphi). \quad (4.14)$$

While pathways differing by $\Delta n = 2$ (or higher-order even terms) will contribute to Eq. (4.13) through their presence in the denominator, no even frequencies will be seen in the observed signal — as shown by Eq. (4.14). Similarly, if we had chosen to use a non-normalized asymmetry in Eq. (4.4), or normalized by a CEP-averaged quantity, terms involving even Δn would not contribute to the CEP-dependence of the spectrum at all.

4.2.1 Effect of Photon Pathways on the Shape of the PAP

By lowering the intensity of the pulse sent into the CEPM — thus, decreasing the magnitude of higher-order pathways $A_{n\ell}$ — it is possible to enter a regime where all higher-order interferences become negligible and only $\Delta n = 1$ terms contribute in Eq. (4.13). Because the width of ATI peaks tends to grow with energy in a LOPT picture (Sec. 2.2.4), our formalism suggests that interference between pathways with $\Delta n \geq 2$ can potentially be further reduced by choosing energy ranges $\Delta E_{H/L}$ at lower energies (that still exhibit clear CEP effects). Of course, our peak-broadening picture neglects higher-order effects and resonances, and, as such, only weakly

¹A periodic function $x(t)$ with period T is said to have half-wave symmetry if $x(t + T/2) = -x(t)$.

applies in the plateau region of the spectrum.

When $\Delta n \geq 2$ is negligible, Eq. (4.13) can be written as

$$\mathcal{A}_{H/L} = \sqrt{\left(\frac{B_1^{H/L}}{B_0^{H/L}}\right)^2 + \left(\frac{C_1^{H/L}}{B_0^{H/L}}\right)^2} \sin(\varphi + \varphi_1^{H/L}), \quad (4.15)$$

where

$$\varphi_1^{H/L} = \tan^{-1}(B_1^{H/L}/C_1^{H/L}). \quad (4.16)$$

This lowest-order result clearly predicts a circular PAP when the magnitudes of the two asymmetries are equal and φ_1^H and φ_1^L are ninety degrees out of phase. It also provides a theoretical framework for understanding why it is often possible to create circular PAP in experiment: for the majority of cases, lowest-order effects will dominate the signal and oscillations with higher frequencies will be negligible or contribute only small perturbations to the sinusoidal behavior.

In its most general case, Eq. (4.15) is the parametric equation for an ellipse. The polar angle of the PAP and the CEP are related here by the transcendental equation

$$\tan \theta = \frac{\sqrt{\left(\frac{B_1^L}{B_0^L}\right)^2 + \left(\frac{C_1^L}{B_0^L}\right)^2}}{\sqrt{\left(\frac{B_1^H}{B_0^H}\right)^2 + \left(\frac{C_1^H}{B_0^H}\right)^2}} \left(\frac{\sin(\varphi + \varphi_0^L)}{\sin(\varphi + \varphi_0^L) \cos \gamma + \cos(\varphi + \varphi_0^L) \sin \gamma} \right), \quad (4.17)$$

where $\gamma = \varphi_0^H - \varphi_0^L$ is the phase difference between the two integrated asymmetries. The magnitudes of the two asymmetries appear in Eq. (4.17) and can be roughly estimated from the maximum values seen in an experimental PAP. However, arbitrary values of γ cannot be easily inferred from the PAP. The values $\gamma = \pi/2$ and $\gamma = \pi$ are exceptions to this rule, as they create distinct shapes — an ellipse with semi-major and semi-minor axes of $\mathcal{A}_{H/L}$ or a line, respectively. As such, Eq. (4.17) is rarely useful in practice.

In the experimental methods outlined in Sec. 4.1, the ranges of integration ΔE_H and ΔE_L are adjusted to produce integrated asymmetries with $\gamma = \pi/2$. As just mentioned, this phase difference creates a distinct shape for the PAP — making it easy to identify in experiment. In

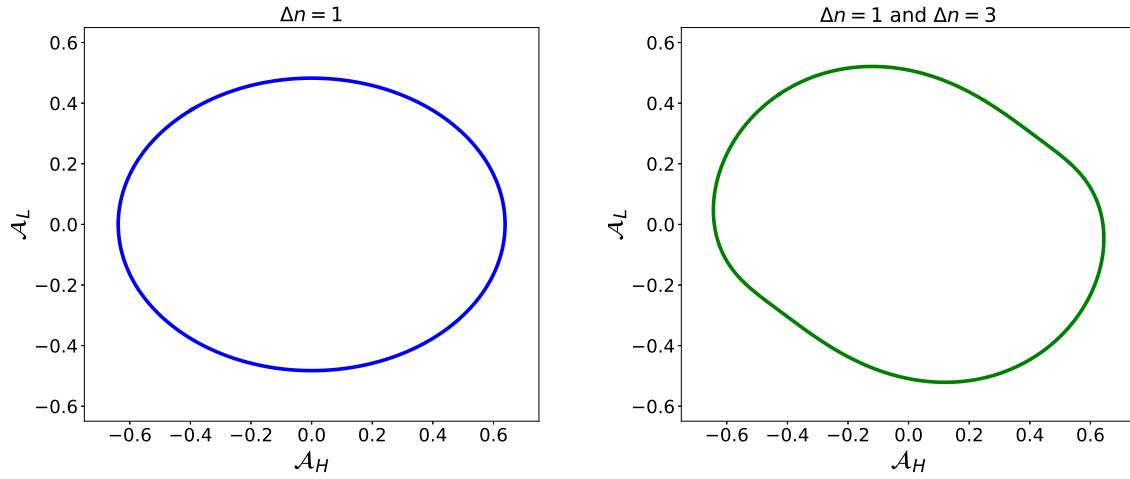


Figure 4.3: Parametric asymmetry plots from Eq. (4.14) showing the emergence of non-elliptical behavior as higher-order terms become relevant. Equation (4.14) is used to avoid $\Delta n = 0$ and $\Delta n = 2$ terms, thus reducing the number of parameters needed. (a) PAP when only $\Delta n = 1$ pathways interfere and Eq. (4.14) and Eq. (4.13) are equivalent; coefficients given by $b_1^L = 0.38$, $c_1^L = 0.30$, $b_1^H = -0.40$, and $c_1^H = 0.50$. (b) PAP with the same first-order coefficients and $b_3^L = 0.05$, $c_3^L = 0.04$, $b_3^H = -0.03$, and $c_3^H = 0.04$.

this case, Eq. (4.17) reduces to

$$\varphi + \varphi_0^L = \tan^{-1} \left(\frac{\sqrt{\left(\frac{B_1^H}{B_0^H}\right)^2 + \left(\frac{C_1^H}{B_0^H}\right)^2} \tan \theta}{\sqrt{\left(\frac{B_1^L}{B_0^L}\right)^2 + \left(\frac{C_1^L}{B_0^L}\right)^2}} \right). \quad (4.18)$$

Care must be taken in solving Eq. (4.18) for φ , as the inverse tangent function will only return values of φ between $-\pi/2$ and $\pi/2$. This can be addressed by keeping the returned value of φ at $\theta = 0$ and then shifting each subsequent φ by the appropriate integer multiple of π to ensure that φ increases monotonically as a function of θ . Because CEPMS only give φ up to a constant, the values of φ can be shifted to set $\varphi = 0$ at $\theta = 0$, thus putting all returned values of φ in the desired range of 0 to $2\pi^2$.

For higher intensity pulses, interference between pathways differing by $\Delta n = 2$ or more photons becomes unavoidable. In this case, Eq. (4.15) no longer applies and the PAP will begin to deviate from an ellipse. As shown in Fig. 4.3, as the interference between photon-pathways with $\Delta n \geq 2$ becomes relevant, the PAP begins to develop corners and take on the so-called “phase-potato” shape that is commonly seen in experiment [215, 216]. Parametric asymmetry

²The problem of phase-jumps can also be addressed using the two-argument arctangent function.

plots generated from Eq. (4.14) show that this “potato-shaped” deviation from circular behavior can be seen even when the higher-order coefficients are an order of magnitude smaller than those for $\Delta n = 1$ pathways.

4.3 Extracting the CEP from General Parametric Asymmetry Plots

When higher-order photon pathways become relevant, $\tan \theta = \mathcal{A}_L/\mathcal{A}_H$ still holds and — using Eq. (4.13) — provides the relationship between θ and the CEP. However, there is no simple method for using the resulting expression to obtain φ from the polar angle when higher-order contributions become relevant; neither an analytic expression, like that for the circular PAP, nor a simple transcendental equation, like that for an elliptical PAP, exists in this regime. Moreover, attempting to directly fit the ratio of asymmetries in Eq. (4.13) or Eq. (4.14) to $\tan \theta$ has issues of non-uniqueness; regardless of the number of shots there will be more unknown parameters than data points. For N shots, including frequencies up to $k_{\max}$ in Eq. (4.14) gives $2(k_{\max} + 1)$ unknown parameters $b_k^{H/L}$ and $c_k^{H/L}$ and N unknown φ — with only N known values of θ .

An alternative method for extracting the CEP from a given PAP is try to improve upon the existing experimental method embodied in Eq. (4.2). To do this, we follow the method outlined in Ref. [215] to obtain the CEP from a non-circular PAP. In this method, the shots are binned in θ and the average value of both integrated asymmetries is calculated in each bin. The total number of shots, combined with the number of shots in each θ -bin, allows for the calculation of both $\rho(\theta)$ and $\langle \rho \rangle$ in Eq. (4.2). This equation is then used to map each θ -bin to a corresponding φ -bin.

The standard method used for determining the CEP stops at this point. We propose taking the additional step of carrying out the sine and cosine Fourier transforms of this data in φ to obtain the coefficients $b_k^{H/L}$ and $c_k^{H/L}$ in Eq. (4.14). Once these coefficients are obtained, Eq. (4.14) can be used to find the CEP for each individual shot — not just the average CEP for the bins — by finding the CEP that solves

$$\frac{\mathcal{A}_L^{\text{data}}}{\mathcal{A}_H^{\text{data}}} = \frac{\mathcal{A}_L(\varphi)}{\mathcal{A}_H(\varphi)}. \quad (4.19)$$

In Eq. (4.19), $\mathcal{A}_{H/L}(\varphi)$ are the analytic expressions in Eq. (4.14) and $\mathcal{A}_{H/L}^{\text{data}}$ are the experimentally determined integrated asymmetries for the shot in question. Simple root-finding techniques can be used to solve Eq. (4.19) for φ .

Because the asymmetries in Eq. (4.13) have the property $\mathcal{A}_{H/L}(\varphi \pm \pi) = -\mathcal{A}_{H/L}(\varphi)$, φ and $\varphi \pm \pi$ will provide equally good solutions to Eq. (4.19). This is, of course, similar to the problem we encountered for Eq. (4.17). We address the problem of phase-jumps using the technique discussed in Sec. 4.2.1. It is worth noting that this property of the spatial asymmetries gives rise to a PAP with the same property in θ , $\mathcal{A}_{H/L}(\theta \pm \pi) = -\mathcal{A}_{H/L}(\theta)$. This mirror symmetry in the PAP will be broken if the detectors are not properly aligned, or if the CEP is not uniformly distributed in 0 to 2π .

4.3.1 Numerical Details

To test our proposed method, we will extract the CEPs from simulated experimental data. The error found in experimental measurements of spatial asymmetries is dominated by statistical errors due to electron counting and by shot-to-shot variations in the pulses [215]. These errors will, of course, create a distribution about our analytic expression in Eq. (4.13) for a given θ . While the uncertainties $\delta\mathcal{A}_{H/L}$ are not typically reported in the literature for the individual shots used to generate a PAP, we can infer the errors from previous experimental work.

The uncertainties $\delta\mathcal{A}_{H/L}$ can be related to the width δr of the PAP at a given θ . Using standard error propagation and the Cauchy–Schwarz inequality, an upper bound for this relationship is given by

$$\delta r^2 = \left| \frac{\mathcal{A}_H}{\sqrt{\mathcal{A}_H^2 + \mathcal{A}_L^2}} \right| \delta \mathcal{A}_H^2 + \left| \frac{\mathcal{A}_L}{\sqrt{\mathcal{A}_H^2 + \mathcal{A}_L^2}} \right| \delta \mathcal{A}_L^2. \quad (4.20)$$

Equation (4.20) holds when the errors in two asymmetries are correlated, which is the expected case. Noting that the fractions in Eq. (4.20) are always less than or equal to one, and approximating the two uncertainties to be equal, this gives a reasonable approximation for the errors as

$$\delta \mathcal{A}_{H/L} = \frac{\delta r}{\sqrt{2}}. \quad (4.21)$$

In contrast to $\delta\mathcal{A}_{H/L}$, single-shot uncertainties in δr have been reported as a function of pulse

length in Ref. [220], where they were found to be on average $\delta r = 0.1$ — with no value larger than $\delta r = 0.125$ reported. Similarly, the width δr can be approximated by visually examining a PAP. Based on reported values of δr , and the examination of several PAPs in the literature, we use $\delta \mathcal{A}_{H/L} = 0.1$ (corresponding to $\delta r \approx 0.14$) as the maximum uncertainty in our calculations. We believe that this should provide a reasonable upper bound for the errors.

For our tests, each shot was assigned a randomly generated carrier-envelope phase for a uniform distribution within the range $0 < \varphi < 2\pi$. Calculations are carried out for 200 000, 100 000, and 50 000 shots. While the number of shots used in experiments varies greatly, sometimes as low as 4500 [214], this range matches the majority of experiments we found. Asymmetries are then calculated from Eq. (4.14) with terms up to $k = 5$ included. The coefficients from the PAP in Fig. 4.3 are used, with $b_5^{H/L} = 0.1b_3^{H/L}$ and $c_5^{H/L} = 0.1c_3^{H/L}$.

For each shot, errors are added to the resulting value of $\mathcal{A}_{H/L}$ by sampling a normal distribution with standard deviation $\delta \mathcal{A}_{H/L}$. As with the number of shots, we carry out calculations for multiple standard deviations to test our method for data that mimics varying experimental conditions. The standard deviations used are $\delta \mathcal{A}_{H/L} = 0.1, 0.07$, and 0.05 . To apply Eq. (4.2), we use 180 bins in θ with a uniform width of two degrees (approximately 0.035 radians) — mimicking the the 200 000-shot experiment in Ref. [215].

4.3.2 Results and Discussion

Figure 4.4 shows the PAP calculated using 200 000 shots for two different uncertainties $\delta \mathcal{A}_{H/L}$. The PAPs in Fig. 4.4 look similar to those found in experiment — both in terms of the radial width and shape. The retrieved single-shot mapping between θ and φ found using our method is also shown for each PAP in Fig. 4.4. Here, the plot is made for a range of $\theta = 0$ to $\theta = \pi$ — taking advantage of the previously described symmetry in the PAP. Visual inspection shows that our method provides a good fit for the relationship between the polar angle and CEP.

By construction, we know the actual CEP φ_i for each shot; therefore, we can calculate an absolute error for each extracted CEP. In order to compare the errors using our method and Eq. (4.2), we calculate the respective RMS errors $\delta \varphi^{\text{Th}}$ and $\delta \varphi^{\text{Ex}}$ for the extracted phases. These

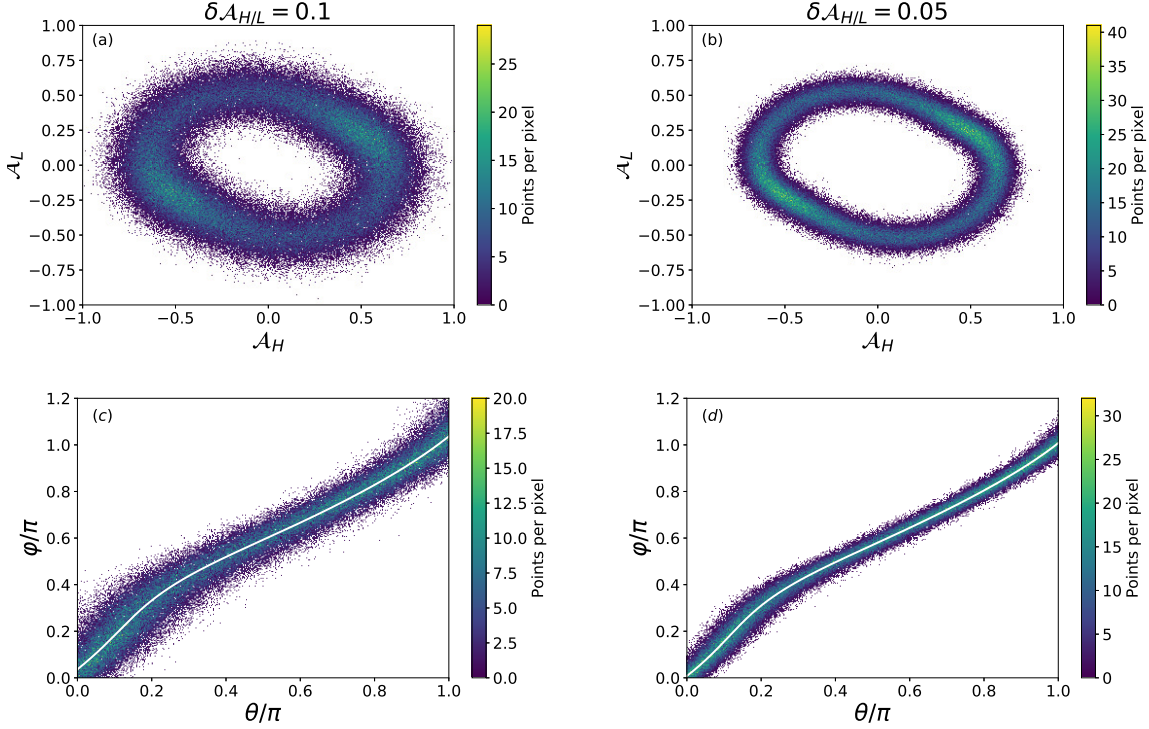


Figure 4.4: PAP generated with 200 000 shots from Eq. (4.14) with (a) $\delta\mathcal{A}_{H/L} = 0.1$ and (b) $\delta\mathcal{A}_{H/L} = 0.05$. (c) and (d) Mapping from the geometric angle θ to the CEP φ for the PAPs in (a) and (b), respectively. For the density plots, the known value φ_i of each shot was used in Eq. (4.14) to find the asymmetries. Error was added to these asymmetries, and their ratio was used to find the polar angle θ_i for each shot. The white line following the center of the distribution shows the retrieved phase φ^{Th} from our method at each θ_i .

errors are given by

$$\delta\varphi^{\text{Ex/Th}} = \frac{1}{\sqrt{N}} \sqrt{\sum_i^N \left(\varphi_i - \varphi_i^{\text{Ex/Th}} \right)^2}, \quad (4.22)$$

where $\varphi_i^{\text{Ex/Th}}$ gives the CEP extracted for each shot using the two methods and N is the total number of shots. For the PAPs in Fig. 4.4, these values are found to be $\delta\varphi^{\text{Ex}} = 229$ mrad and $\delta\varphi^{\text{Th}} = 228$ mrad for $\delta\mathcal{A}_{H/L} = 0.1$; and $\delta\varphi^{\text{Ex}} = 103$ mrad and $\delta\varphi^{\text{Th}} = 101$ mrad for $\delta\mathcal{A}_{H/L} = 0.05$. These values are quite similar to those found in the literature — with values ranging from 113 mrad to 350 mrad being reported [214–216]. This further validates our estimates for $\delta\mathcal{A}_{H/L}$. The CEP extraction using our method for the PAPs shown in Fig. 4.4 provides an improvement of one to two milliradians.

If our method for generating the PAPs in Fig. 4.4 is repeated — using the same number of shots and $\delta\mathcal{A}_{H/L}$ — the values of the RMS errors $\delta\varphi^{\text{Ex/Th}}$ we find will vary across the individual

trials. This is, of course, true in repeated trials of an actual experiment as well. The resulting distribution created by the individual $\delta\varphi^{\text{Ex/Th}}$ will have both an average value $\langle\delta\varphi^{\text{Ex/Th}}\rangle$ and a standard deviation $\sigma^{\text{Ex/Th}}$. This standard deviation addresses the question of how well the estimated errors $\delta\varphi^{\text{Ex/Th}}$ can be expected to agree if an identical experiment is carried out multiple times.

The averaged errors and standard deviations for N_T trials are shown in Table 4.1 for multiple values of $\delta\mathcal{A}_{H/L}$ and numbers of shots N . The number of trials ran for a given set of parameters was chosen such that $\langle\delta\varphi^{\text{Ex/Th}}\rangle$ was converged to 0.1 mrad. Table 4.1 shows that there is almost no difference between the standard deviations found using the two different methods. This is not particularly surprising, as the variance is expected to be mainly tied to the number of shots and the size of the errors $\delta\mathcal{A}^{H/L}$. This relationship is seen in Table 4.1, where $\sigma^{\text{Ex/Th}}$ decreases for larger N and smaller $\delta\mathcal{A}^{H/L}$. We note that for the 200 000-shot case with $\delta\mathcal{A}^{H/L} = 0.1$ (seen in Fig. 4.4), $\sigma^{\text{Ex/Th}}$ is 103.2 mrad — nearly 38% of the averaged error. This value shows that even for high shot numbers, reported errors can have a large variance if δr is large.

Also of interest is the product $N \times N_T$ between the number of shots and the number of trials required for convergence. We see that for a given error $\delta\mathcal{A}^{H/L}$, this product is roughly the same across the number of shots. For example, at $\delta\mathcal{A}^{H/L} = 0.1$ this product is given by 7 400 000, 7 800 000, and 7 900 000 (for $N = 200\,000$, $N = 100\,000$, and $N = 50\,000$, respectively). Because you can imagine combining the trials for a given N , this suggests that a single experiment for this $\delta\mathcal{A}^{H/L}$ would need nearly eight million shots to retrieve the CEP with an accuracy of 0.1 mrad.

Examining the averaged errors, Table 4.1 shows that our method provides a modest improve-

$\delta\mathcal{A}^{H/L}$	$N = 200\,000$					$N = 100\,000$					$N = 50\,000$				
	$\langle\delta\varphi^{\text{Ex}}\rangle$	$\langle\delta\varphi^{\text{Th}}\rangle$	σ^{Ex}	σ^{Th}	N_T	$\langle\delta\varphi^{\text{Ex}}\rangle$	$\langle\delta\varphi^{\text{Th}}\rangle$	σ^{Ex}	σ^{Th}	N_T	$\langle\delta\varphi^{\text{Ex}}\rangle$	$\langle\delta\varphi^{\text{Th}}\rangle$	σ^{Ex}	σ^{Th}	N_T
0.1	265.3	264.7	103.2	103.2	37	312.6	311.7	107.5	107.5	78	337.8	316.7	117.3	117.2	158
0.07	207.1	205.9	31.2	31.3	10	240.1	238.7	33.6	33.4	18	265.1	263.4	38.6	38.6	38
0.05	140.2	138.6	19.3	19.2	7	151.4	149.3	21.3	21.3	13	163.4	160.8	25.1	25.1	27

Table 4.1: Averaged errors and standard deviations (reported in milliradians) in the extracted CEP across N_T trials. The number N_T was chosen to provide 0.1 mrad convergence in the averaged errors for each $\delta\mathcal{A}_{H/L}$ and N shown.

ment over the commonly used experimental method in all cases studied. Moreover, the data suggests that the improvement offered by our method increases for experiments with smaller numbers of shots, or for PAPs with a smaller radial spread δr . It is worth noting that in each of the individual trials ran to create the averaged quantities shown in Table 4.1, our method was slightly better than the purely experimental method. However, it is also worth noting that across all trials, our method never produced an improvement greater than 12 mrad.

Before ending this section, it is worth mentioning an additional benefit of our method. The Fourier coefficients found in our method can also be used to determine how close an experimental PAP is to the lowest-order regime — *i.e.*, it provides a metric for determining the size of interfering pathways with $\Delta n \geq 2$. This information could be used as a diagnostic that allows experimentalists to decrease the intensity of the incident pulse, or adjust the energy ranges used for integration, to a point where interference from higher-order pathways becomes negligible. Reducing the intensity and adjusting the energy ranges to enter this lowest-order regime has the benefit that the error in experimental CEP extraction is decreased for PAPs that are circular/elliptical [214, 216].

4.4 Closing Remarks

In this chapter, we extended the application of our parametric formalism to provide insight into the characterization of the CEP of an experimental pulse. Using our theory, we have shown that the integrated asymmetries plotted in a PAP can be understood as being created by the interference of different photon pathways that end at the same energy. Moreover, we have shown that the ideal case of a circular PAP — where extraction of the CEP is provided up to a constant by the polar angle — can only be achieved when interference between pathways with $\Delta n \geq 2$ is negligible. Our theory provides insight into what changes can be made in experiment to enter this low-order regime, and provides a method for mapping the polar angle θ to the CEP within this regime (even when the PAP is elliptical, rather than circular). Additionally, we have proposed a method for calculating the Fourier coefficients for higher-order pathways, providing a quantitative metric for determining how well an experimental PAP fits into the lowest-order regime.

Finally, in experiments where it is not possible to neglect higher-order terms, we proposed method for improving CEP characterization that provides an actual shot-to-shot measurement of the CEP — as opposed to an average CEP for a bin containing multiple shots. While the improvements offered by our method were modest, it did outperform the commonly used experimental method in every trial we ran. In the next chapter, we will extend this idea of using our parametric formalism to extract information from measured observables. Chapter 5 will focus on directly extracting the amplitudes associated with exchanging n net-photons with the field from a given momentum distribution — allowing for the possibility of seeing exactly which physical processes contribute to a given feature observed in experiment.

Chapter 5

Extraction of Photon-Pathway Amplitudes

In Chap. 4, we began examining the possibility of using our parametric formalism to directly extract physical information from a measured or calculated spectrum — specifically, extracting the CEP of a single-color pulse from a stereo ATI spectrum. In this chapter we will further this idea, focusing on the extraction of photon-pathway amplitudes $A_{nJ}(E)$ directly from a CEP-dependent momentum distribution. This can be considered the inverse of the work done in Chap. 3, where knowledge of the system allowed us to make predictions about which A_{nJ} would be most relevant at a given energy and deduce the control over a specific observable. Here, instead, we will take a given CEP-dependent spectrum and infer which photon-pathways must have interfered to create the features seen at a given energy. In other words, this extraction will allow us to gain valuable information about the specific physical processes that occurred to create the observed spectrum.

We will begin by briefly describing how the A_{nJ} can be calculated from a known wavefunction. This method has been employed previously by our group in Ref. [221] and will provide the comparison for testing the accuracy of the extracted amplitudes. The remainder of the chapter will focus on developing and testing a method for extracting pathways from a momentum distribution. Such a method of extracting amplitudes is clearly advantageous, as it can be applied to experimentally measured spectra where the wavefunction is, of course, unknown — opening up the possibility of studying systems that are too complex to be treated accurately in calculations.

5.1 Extracting Photon-Pathways from the Wavefunction

For systems where numerical solutions of the TDSE can be found, calculation of photon-pathway amplitudes from single-color, CEP-dependent calculations is straightforward. For the field in Eq. (3.1), the inverse transform based on Eq. (3.2) gives the Fourier coefficients ψ_n as

$$\psi_n(t) = \frac{1}{2\pi} \int_0^{2\pi} \psi(\varphi; t) e^{in\varphi} d\varphi, \quad (5.1)$$

where the TDSE solution $\psi(\varphi; t)$ depends parametrically on the CEP. The amplitude associated with an n -photon pathway to a given final state $|EJ\alpha\rangle$ is then determined from

$$A_{nJ}^\alpha(E) = \langle EJ\alpha | \psi_n \rangle. \quad (5.2)$$

Here, $|EJ\alpha\rangle$ is the continuum state with energy E , angular momentum J , and any additional quantum numbers α necessary to uniquely identify the state.

Equation (5.2) allows for the simple extraction of photon pathways from a known wavefunction; this methodology has previously been used by our group to calculate $A_{n\ell}$ for ionization of atomic hydrogen and dissociation of H_2^+ in Ref. [221]. Of course, the overall phase of the wavefunction is arbitrary, as it has no consequence on observables. Therefore, only relative phases between A_{nJ} have physical meaning.

Unfortunately, calculating amplitudes using this method limits us to systems where the TDSE can be solved. One of the highlights of our formalism is that it applies equally well to *any* system exposed to a laser pulse that can be described by Eq. (2.2). The number of systems that can be — or have been — studied in such fields far exceeds the number of systems for which the TDSE can be accurately solved. Development of a method that allows for the extraction of the quantities A_{nJ}^α directly from a spectrum, as opposed to a wavefunction, would greatly expand the number of systems accessible to photon-pathway analysis. To this end, our goal for the remainder of this chapter is to develop a method for extracting A_{nJ}^α directly from a momentum distribution.

5.2 Extracting Photon-Pathways from a Momentum Distribution

5.2.1 Theory

We will use the momentum distribution as a function of the CEP for our test cases, but other observables could also be used. Using the momentum distribution enables the extraction of J -dependent amplitudes at a given energy. Angle-integrated quantities, such as Eq. (3.23), only allow for the retrieval of more limited information — for example, the sums $\sum_J A_{nJ}$. While the exact form of the momentum distribution will depend on the system being studied, single-channel systems will have the form of Eq. (3.17):

$$\frac{\partial^2 P}{\partial E \partial \theta_k} = \sum_{n,J,J'} \left[A_{nJ} A_{nJ'}^* + \sum_{n' \neq n} A_{nJ}(E) A_{n'J'}^*(E) e^{i(n-n')\varphi} \right] Y_J(\theta_k) Y_{J'}^*(\theta_k), \quad (5.3)$$

Equation (5.3) can be extended to multi-channel systems undergoing two-body breakup — provided that the relevant channels produce distinguishable final products (see Sec. 6.1.5). With small adjustments, it can also apply to multi-channel systems with indistinguishable final products, as shown for D_2^+ in Sec. 6.1.4.

In this chapter, we will limit ourselves to the types of systems described by Eq. (5.3). In order to extract A_{nJ} , we first find the Fourier components $c_m(E, \theta_k)$ of the spectrum at each energy and angle:

$$c_m(E, \theta_k) = \frac{1}{2\pi} \int_0^{2\pi} \frac{\partial^2 P}{\partial E \partial \theta_k} e^{-im\varphi} d\varphi. \quad (5.4)$$

These coefficients can be expressed in our parametric formalism as

$$c_m(E, \theta_k) = \sum_{nJJ'} A_{n,J}(E) A_{n-m,J'}^*(E) Y_J(\theta_k) Y_{J'}(\theta_k). \quad (5.5)$$

In terms of the magnitudes $|A_{nJ}|$ and phases β_{nJ} for each amplitude, Eq. (5.5) gives:

$$\begin{aligned}\text{Re}[c_m] - \sum_{nJJ'} |A_{n,J}| |A_{n-m,J'}| \cos(\beta_{n,J} - \beta_{n-m,J'}) Y_J Y_{J'} &= 0, \\ \text{Im}[c_m] - \sum_{nJJ'} |A_{n,J}| |A_{n-m,J'}| \sin(\beta_{n,J} - \beta_{n-m,J'}) Y_J Y_{J'} &= 0.\end{aligned}\quad (5.6)$$

Finding the solutions A_{nJ} of Eq. (5.6) for the c_m with $m \geq 0$ is sufficient since the momentum distribution is real.

5.2.2 Methods

Equation (5.7) provides a set of $q = N(2m_{\max} + 1)$ equations for A_{nJ} at each energy, with N the number of angles for which the c_m are known and $m_{\max}$ the largest m such that $|c_{m_{\max}}|^2$ is above a suitable cutoff. Experimental measurements introduce errors in the momentum distribution that cause deviations of the measured Fourier coefficients from Eq. (5.5). Therefore, exact solutions of Eq. (5.7) cannot be found and we frame the task of solving for A_{nJ} as a non-linear least squares problem.

The problem of extracting the amplitudes is solved by finding the A_{nJ} that minimize the square of the residual vector $\mathbf{R}$, defined at each energy by:

$$\begin{aligned}R_1 &= \text{Re}[c_0(\vartheta_1)] - \sum_{nJJ'} |A_{nJ}| |A_{n,J'}| \cos(\beta_{nJ} - \beta_{n,J'}) Y_{J0}(\vartheta_1) Y_{J'0}(\vartheta_1) \\ R_2 &= \text{Re}[c_1(\vartheta_1)] - \sum_{nJJ'} |A_{nJ}| |A_{n-1,J'}| \cos(\beta_{nJ} - \beta_{n-1,J'}) Y_{J0}(\vartheta_1) Y_{J'0}(\vartheta_1) \\ R_3 &= \text{Im}[c_1(\vartheta_1)] - \sum_{nJJ'} |A_{nJ}| |A_{n-1,J'}| \sin(\beta_{nJ} - \beta_{n-1,J'}) Y_{J0}(\vartheta_1) Y_{J'0}(\vartheta_1) \\ &\vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\ R_q &= \text{Re}[c_{m_{\max}}(\vartheta_N)] - \sum_{nJJ'} |A_{nJ}| |A_{n-m_{\max},J'}| \cos(\beta_{nJ} - \beta_{n-m_{\max},J'}) Y_{J0}(\vartheta_N) Y_{J'0}(\vartheta_N).\end{aligned}\quad (5.7)$$

In Eq. (5.7), ϑ_i denotes the individual angles θ_k . The number of terms A_{nJ} included in the fit is inferred from physics, much of which uses LOPT as a starting point. The largest of the $|A_{nJ}|$ at a given energy can be estimated from energy conservation with the minimum number of photons for the process. For example, A_{5J} will typically have the largest magnitude of any pathway at

energies near the peak associated with net five-photon absorption.

The range of nearby n that also contribute at this energy can be estimated from the values of c_m , which only include interference from terms differing by m photons. If in the net five-photon example $c_{m_{\max}} = 2$, then only amplitudes with $3 \leq n \leq 7$ are interfering in the spectrum. The number of J included can be inferred through similar means. For high intensities, the maximum $|A_{nJ}|$ at a given energy might deviate from our prediction — which is based on LOPT. However, as long as the number of nearby n included in the fit is large enough, no issues will arise¹. All of these choices are, of course, convergence parameters.

Because the fit is independent at each energy, there are two ways one might proceed. All of the A_{nJ} that are expected to contribute over the entire energy-dependent spectrum can be identified, and this same set of A_{nJ} can be used for the fit at every energy. Alternatively, the A_{nJ} expected to contribute at each individual energy can be identified, with the amplitudes included in the fit adjusted at different energies. Because each A_{nJ} will only be non-zero for a subset of the energies in the spectrum, the latter of these methods has the clear advantage of decreasing the dimensionality of our solution vector $\mathbf{A}$ at each energy. However, the former method has advantages as well — which will be discussed at the end of this section.

Once choices are made for the minimum/maximum values of n and J to include at a given energy, a solution vector $\mathbf{A}$ containing all $|A_{nJ}|$ and β_{nJ} is constructed. When dipole selection rules are not accounted for, or parity-unfavored transitions are possible, the dimensionality of $\mathbf{A}$ will be given by $p = 2(n_{\max} - n_{\min} + 1)(J_{\max} - J_{\min} + 1)$. Of course, the dimensions of $\mathbf{A}$ will be reduced if the system begins in a state with well-defined parity and dipole-selection rules require $J \rightarrow J + 1$ for the absorption of a photon. For the fits we do in Sec. 5.3, $p = 64$; for the fit in Sec. 5.4, $p = 124$. To avoid overfitting, it is necessary for $\mathbf{R}$ to have a larger dimensionality than $\mathbf{A}$ ($q > p$). In the scenario with the smallest possible q , where only pathways with $\Delta n = 1$ interfere and, thus, $m_{\max} = 1$, this condition would require $N = 22$ and $N = 44$ angular points for our two values of p — within the confines of what can be resolved in experiment. We used $N = 200$ for all of our calculations, giving values of $1800 \leq q \leq 2600$.

With the composition of $\mathbf{A}$ chosen, the resulting minimization problem is solved using a

¹A different issue results from including too many n in the fit, as discussed in Sec. 5.2.3

modified Levenberg-Marquardt method [222]. We found it to outperform two other methods we tested (Powell’s hybrid method [222] and the Nelder-Mead method [223]) for the problems in Sec. 5.3. Because R^2 has many local minima as a function of A_{nJ} , the vast majority of initial guesses for our problems found local minima rather than the desired global minimum. To overcome this issue, a large number of initial guesses spanning the p -dimensional solution space are used. The values of R^2 for each returned solution are then compared to identify the global minimum.

The initial guesses for β_{nJ} are sampled from a uniform distribution defined from 0 to 2π . Initial guesses for $|A_{nJ}|$ are sampled from a log-uniform distribution defined by the maximum and minimum values that we expect any of the magnitudes to have. The largest expected value used in our log-uniform distribution, $|A_{\max}|$, can be crudely estimated by assuming only a single A_{nJ} contributes to the momentum distribution. In this case, Eq. (5.5) would give the magnitude of the maximum (and only) amplitude as

$$|A_{\max}| \equiv \sqrt{\int_0^\pi c_0(E, \theta_k) \sin(\theta_k) d\theta_k}. \quad (5.8)$$

Because multiple pathways contribute, Eq. (5.8) will always provide an overestimate of $|A_{\max}|$. We were able to find the global minimum in all of our tests by using this estimate, along with a minimum magnitude set as $|A_{\min}| = 10^{-6}|A_{\max}|$. Both of these values can be easily adjusted if necessary.

For the problems discussed in Sec. 5.3 and Sec. 5.4, the local minima never gave a value smaller than $R^2 = 0.1$; the global minima never gave a value larger than $R^2 = 10^{-11}$. The latter can be decreased further by changing the tolerance of the fit. Therefore, global minima were easily identified for our problems. The number of initial guesses required to find the global minimum at least once at a given energy was typically 200 for Sec. 5.3, and 1000 for the larger problem in Sec. 5.4. The average runtimes for a single initial guess at a given energy were approximately 1 minute and 5 minutes, in the respective sections. Therefore, total runtimes (in CPU hours) to find a global minimum at a single energy were roughly 3.5 hours and 83 hours. However, this number is drastically reduced by running initial guesses in parallel across multiple threads — since

the calculation for each initial guess is entirely independent. Running across 56 cores (Intel Xeon Gold 6132 processors), these single-energy calculations took roughly 16 minutes or 7 hours for the respective sections.

For the runtimes above, we used the method of determining all relevant A_{nJ} in the entire spectrum and using the same $\mathbf{A}$ at all energies. This method drastically increases the runtime when sampling the solution space at a single energy, as it produces a higher-dimensional space that includes amplitudes that are approximately zero. However, because A_{nJ} varies smoothly in energy, the solution found using this method at one energy can be used without modification as the initial guess for the neighboring energies. This approach eliminates the need to generate an ensemble of initial guesses for all energies other than one, and provides a solution that is very close to the global minimum of its neighbors. Consequently, fits at subsequent energies had runtimes on the order of seconds — meaning the runtime for the entire energy range was nearly the same as the numbers reported above.

5.2.3 Uniqueness of Solutions

As is typical in multidimensional non-linear least squares problems [224], non-unique global minima can exist in Eq. (5.7). With the obvious exception of the absolute phases β_{nJ} , we only encountered one general type of non-unique solution in our calculations. There may exist other forms of non-unique solutions, but we have seen no evidence of them. In this section, we will address this type of non-unique global minima, along with methods for overcoming it.

The non-unique solutions we found come from including more A_{nJ} than are necessary in the fit at a given energy, resulting in some of the A_{nJ} included being effectively zero. This problem is particularly common when the elements of $\mathbf{A}$ are determined from the entire spectrum — as this choice for $\mathbf{A}$ will inherently include more amplitudes than necessary at every energy. Given the quadratic form of the residual vector in Eq. (5.7), swapping zero and non-zero amplitudes A_{nJ} can leave $\mathbf{R}$ unchanged. As such, certain permutations $A_{nJ} \leftrightarrow A_{n',J}$ involving amplitudes that are zero can produce two solutions that provide equally good fits.

As a simple example, consider a momentum distribution with four peaks measured for a system that ionizes through absorption of a single photon. Pathways with $1 \leq n \leq 4$ are clearly

present in the spectrum and should be included in the fit. Assume that at the first peak, A_{3J} and A_{4J} are negligible. Under the permutations $A_{1J} \leftrightarrow A_{3,J}$ and $A_{2J} \leftrightarrow A_{4,J}$, Eq. (5.5) gives:

$$\begin{aligned}
c_0 - \sum_{JJ'} [A_{1,J}A_{1,J'}^* + A_{2,J}A_{2,J'}^* + A_{3,J}A_{3,J'}^* + A_{4,J}A_{4,J'}^*] Y_{J0}Y_{J'0} &\rightarrow \\
c_0 - \sum_{JJ'} [A_{3,J}A_{3,J'}^* + A_{4,J}A_{4,J'}^* + A_{1,J}A_{1,J'}^* + A_{2,J}A_{2,J'}^*] Y_{J0}Y_{J'0} & \\
c_1 - \sum_{JJ'} [A_{2,J}A_{1,J'}^* + A_{3,J}A_{2,J'}^* + A_{4,J}A_{3,J'}^*] Y_{J0}Y_{J'0} &\rightarrow \\
c_1 - \sum_{JJ'} [A_{4,J}A_{3,J'}^* + A_{1,J}A_{4,J'}^* + A_{2,J}A_{1,J'}^*] Y_{J0}Y_{J'0} & \\
c_2 - \sum_{JJ'} [A_{3,J}A_{1,J'}^* + A_{4,J}A_{2,J'}^*] Y_{J0}Y_{J'0} &\rightarrow \\
c_2 - \sum_{JJ'} [A_{1,J}A_{3,J'}^* + A_{2,J}A_{4,J'}^*] Y_{J0}Y_{J'0} & \\
c_3 - \sum_{JJ'} [A_{4,J}A_{1,J'}^*] Y_{J0}Y_{J'0} &\rightarrow \\
c_3 - \sum_{JJ'} [A_{2,J}A_{3,J'}^*] Y_{J0}Y_{J'0}. & \quad (5.9)
\end{aligned}$$

Equation (5.9) clearly shows that only the c_0 term is generally invariant under this transformation. However, when A_{3J} and A_{4J} are zero, all c_m are invariant under the transformation. As a result, when fitting in an energy range near the one-photon peak, the target solution with $A_{3J} = 0$ and $A_{4J} = 0$ will provide an equally good fit as the transformed solution with $A_{1J} = 0$ and $A_{2J} = 0$. The problem of finding equally good fits for two solutions involving permutations of the elements of $\mathbf{A}$ is quite general when zeroes are involved, and was observed in all of our tests. The exact form of the permutations that leave the residual invariant will depend on the number of amplitudes in the fit — both non-zero and approximately zero. For example, in Sec. 5.3.1 we will encounter cyclic permutations of the form $A_{nJ} \rightarrow A_{n+2,J}$ in our fits.

One possible solution to this problem is partitioning the energy ranges and using a smaller, more appropriate, set of amplitudes in each range. Physical intuition can then be used to remove the $|A_{nJ}|$ that are expected to be the smallest, along with the corresponding β_{nJ} . This process is repeated until no zeroes are present in the fit. Alternatively, the same intuition can be used to infer which amplitudes should be largest and undo the permutations manually — as it is typical

to (qualitatively) know the relative size of amplitudes with different n at a given energy. For example, in the above problem, if a solution is returned with $|A_{1J}| = 0$ at the one-photon energy, it is clear that a permutation has occurred. This approach typically only needs to be applied once if using the same $\mathbf{A}$ for all energies — as the amplitudes are smoothly varying². We use this approach for our calculations in Sec. 5.3 and Sec. 5.4.

5.3 Photon-Pathway Extraction for a Test Case

5.3.1 Extraction at a Single Energy

As a first test for our method, we will follow a similar scheme to the one used for CEP extraction in Chap. 4. We will choose amplitudes A_{nJ} , construct a momentum distribution from them using Eq. (5.3), and then apply our method to extract the amplitudes at a single energy — comparing the results to the input A_{nJ} to check for accuracy. We will first test our method at a single energy to demonstrate the second class of non-unique solutions discussed in the previous section — and outline how we deal with the issue — before moving on to the more general problem of amplitudes that are functions of energy.

The amplitudes $|A_{nJ}|$ and phases β_{nJ} chosen for this test are shown in Table 5.1. We chose these values specifically to have more amplitudes in the fit than is necessary at a given energy. The choices loosely model a system that undergoes breakup through absorption of a single photon, and produces a momentum distribution with seven total peaks. The fitting is done at the energy associated with two-photon absorption, where $|A_{2J}|$ have the largest amplitudes. The phases β_{nJ} are chosen randomly from a uniform distribution on 0 to 2π .

The momentum distribution at this energy is constructed from Eq. (5.3) using sixty values of φ and $N = 200$ points in θ_k — uniformly distributed from 0 to 2π and 0 to π , respectively. The value of $m_{\max}$ was seven by construction, as no pathways with $\Delta n > 7$ were included; numerically an $m_{\max}$ of five was able to provide equivalent convergence. The minimization is carried out using

²It is also possible to combine these two approaches: solutions can be found in a partitioned region using a more appropriately sized $\mathbf{A}$, and this $\mathbf{A}$ can be transferred across the partition boundary to the next region (with the appropriate padding or trimming of elements). While slightly more involved, this could be beneficial for complicated problems where many amplitudes are needed.

$\mathbf{A}$ defined by $n_{\min} = 0$, $n_{\max} = 7$, $J_{\min} = 0$, and $J_{\max} = 7$. The estimate provided by Eq. (5.8) gives $|A_{\max}| = 400$ and $|A_{\min}| = 10^{-6}|A_{\max}|$. Ten thousand initial guesses were used, and ran in parallel across 56 cores. Of the initial guesses, 57 returned a global minimum — with only 6 giving the target result that is free of permutations. The returned global minima had values of R^2 ranging from $R^2 = 10^{-15}$ to 10^{-12} ; no noticeable pattern distinguished the target and transformed solutions based on their values of R^2 . The example shown in Table 5.1 had $R^2 = 10^{-12}$.

It is easily seen from Table 5.1 that the returned solution at the two-photon peak features the cyclic permutations $A_{nJ} \rightarrow A_{n+2,J}$. Even without knowing the actual amplitudes, this can be easily deduced from A_{4J} being larger than A_{2J} — despite the former being two photons away, while the latter is expected to be the largest amplitude. Similarly, it is clearly incorrect that A_{1J} is approximately zero despite being only one photon away, while A_{7J} and A_{6J} are both considerably larger. The corrected values obtained by undoing these permutations are also shown in Table 5.1.

All retrieved amplitudes with $n \leq 5$ have $|A_{nJ}|^2$ that are converged to six digits. This level of convergence is likely unnecessary for any application, especially if extracting from experiment. The performance of our fit can be improved using less strict criteria. The small amplitudes $n = 6$ and $n = 7$ are, of course, not converged to this level. However, we have convergence of all $|A_{nJ}|$ that are within five orders of magnitude of the largest amplitude — corresponding to ten orders of magnitude in $|A_{nJ}|^2$. The relative phases found are also shown in Table 5.1, for $n \leq 5$ they are converged to three digits. As with $|A_{nJ}|$, we do not attempt to converge the phases for $n = 6$ and 7 since they are small. As a general for this chapter, we will only attempt to converge $|A_{nJ}|$ that are within five orders of magnitude of the largest magnitude at a given energy.

5.3.2 Test Case — Photon-Pathway Extraction Across All Energies

In this section, we will extend the method to amplitudes that are functions of energy. We use Gaussian $A_{nJ}(E)$ such that

$$A_{nJ}(E) = A_{nJ}^0 \exp \left\{ - \left[\frac{E - (E_0 + n\omega)}{\sigma} \right]^2 \right\} e^{i\beta_{nJ}}, \quad (5.10)$$

	$ A_{nJ} ^2$			$\Delta\beta_{nJ}$	
	Actual	Corrected Result	Returned Result	Actual	Corrected
A_{00}	6.10×10^{-3}	6.100000×10^{-3}	2.659109×10^{-26}	0	0
A_{02}	4.10×10^{-3}	4.100000×10^{-3}	1.235900×10^{-25}	0.1465	0.1462
A_{04}	2.00×10^{-3}	1.999998×10^{-3}	3.472986×10^{-25}	5.441	5.4407
A_{06}	1.00×10^{-3}	1.000003×10^{-3}	1.212304×10^{-25}	2.285	2.2853
A_{11}	9810.58	9810.581	2.440733×10^{-27}	4.132	4.1316
A_{13}	7030.07	7030.068	1.183377×10^{-27}	0.1514	0.15144
A_{15}	4740.24	4740.242	3.312701×10^{-28}	1.732	1.7318
A_{17}	2532.00	2531.999	7.394890×10^{-28}	2.411	2.4115
A_{20}	65880.34	65880.34	6.100000×10^{-3}	1.701	1.7013
A_{22}	27866.25	27866.25	4.100000×10^{-3}	3.015	3.0149
A_{24}	22868.33	22868.33	1.999998×10^{-3}	3.872	3.8722
A_{26}	10702.43	10702.41	1.000003×10^{-3}	0.1397	0.13970
A_{31}	2784.68	2784.684	9810.581	6.085	6.0853
A_{33}	2020.91	2020.913	7030.068	1.691	1.6906
A_{35}	1495.24	1495.244	4740.242	4.853	4.8534
A_{37}	1038.20	1038.197	2531.999	4.529	4.5291
A_{40}	1.10×10^{-1}	1.099997×10^{-1}	65880.34	4.525	4.5255
A_{42}	2.50×10^{-1}	2.500054×10^{-1}	27866.25	6.069	6.0693
A_{44}	6.3×10^{-1}	6.299996×10^{-1}	22868.33	3.541	3.5406
A_{46}	1.8×10^{-1}	1.799999×10^{-1}	10702.41	2.349	2.3485
A_{51}	2.00×10^{-4}	2.000000×10^{-4}	2784.684	6.084	6.0845
A_{53}	2.50×10^{-3}	2.499996×10^{-3}	2020.913	2.152	2.1522
A_{55}	6.50×10^{-3}	6.499999×10^{-3}	1495.244	1.508	1.5074
A_{57}	1.65×10^{-3}	1.650003×10^{-3}	1038.197	1.238	1.2387
A_{60}	4.23×10^{-14}	2.659109×10^{-26}	1.099997×10^{-1}	4.2710	2.377
A_{62}	2.65×10^{-14}	1.235900×10^{-25}	2.500054×10^{-1}	2.2781	4.900
A_{64}	1.35×10^{-14}	3.472986×10^{-25}	6.299996×10^{-1}	0.9305	3.607
A_{66}	1.18×10^{-14}	1.212304×10^{-25}	1.799999×10^{-1}	3.712	4.062
A_{71}	7.65×10^{-20}	2.440733×10^{-27}	2.000000×10^{-4}	0.1402	1.039
A_{73}	5.28×10^{-20}	1.183377×10^{-27}	2.499996×10^{-3}	2.882	1.356
A_{75}	3.82×10^{-20}	3.312701×10^{-28}	6.499999×10^{-3}	1.401	5.376
A_{77}	1.63×10^{-20}	7.394890×10^{-28}	1.650003×10^{-3}	0.8394	5.978

Table 5.1: Table shows the values of $|A_{nJ}|$ and β_{nJ} for the 32 amplitudes used to construct the momentum distribution for our test case, along with the values returned in our fit. It is clear that the returned amplitudes have undergone a cyclic permutation $A_{nJ} \rightarrow A_{n+2,J}$ (see Sec. 5.2.3). The corrected $|A_{nJ}|$ that undo this permutation are shown next to the actual values for ease of comparison — all returned amplitudes are reported to seven significant digits to illustrate the degree of convergence. All relative phases are reported relative to β_{00} with $\Delta\beta_{nJ} \equiv \beta_{nJ} - \beta_{00}$

where A_{nJ}^0 gives the peak of the magnitude $|A_{nJ}|$ at energy $E = n\omega - E_0$. We use $\omega = 0.2$ a.u. and $E_0 = -0.1$ a.u., although these choices only shift the amplitudes. A width $\sigma = \omega$ is chosen such that $|A_{nJ}(E)|$ falls off by roughly one order of magnitude at an energy $\pm 1.5\omega$ away from its peak. This value gives a full width at half maximum of 0.17 a.u., corresponding roughly to a pulse with 2.5 cycles (see Sec. 2.2.4). Although the width of individual amplitudes will typically vary as a function of n and J (see Sec. 2.2.4), we have chosen to make all widths the same for simplicity.

We again include amplitudes with $n = 0$ and $J = 0$ through $n = 7$ and $J = 7$. The resulting amplitudes $|A_{nJ}(E)|$ for our choices are shown in Fig. 5.1. The A_{nJ}^0 were selected to qualitatively mimic the relative magnitudes of amplitudes expected in an actual spectrum — for example, pathways with larger n are typically smaller, as are amplitudes for higher-order $n < J$ states. As is clear from Fig. 5.1, the width of the amplitudes allows for visible overlap between pathways differing by up to $\Delta n = 3$. Overlap between pathways differing by larger net-photon numbers obviously exists, but it is much smaller.

The phases β_{nJ} are chosen randomly on a uniform distribution from 0 to 2π and are independent of energy. This choice is a simplification, but suffices for our test. Energy-dependent

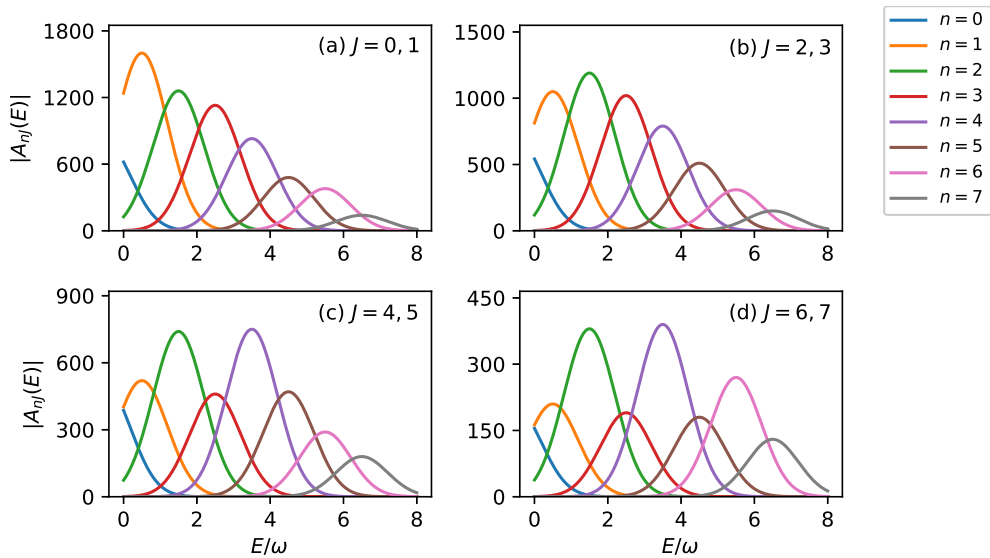


Figure 5.1: Photon-pathway amplitudes $|A_{nJ}(E)|$ used in constructing our momentum distribution for (a) $J = 0$ and $J = 1$, (b) $J = 2$ and $J = 3$, (c) $J = 4$ and $J = 5$, and (d) $J = 6$ and $J = 7$. Net photon numbers $n = 0$ through $n = 7$ are included.

phases are retrieved for HeH^+ in Sec. 5.4 and do not significantly complicate the problem. The fit is first done at the one-photon peak; $|A_{\max}| = 2030$ and $|A_{\min}| = 10^{-6}|A_{\max}|$ were used. As discussed in Sec. 5.2.2, the same $\mathbf{A}$ — which contains all amplitudes that contribute in the entire spectrum — is used at every energy. Once corrected for permutations, our retrieved amplitudes at the one-photon peak agreed to six digits with the known magnitudes and to three digits with the relative phases — provided that our convergence criteria from Sec. 5.3.1 was met.

The corrected solution found at the one-photon peak was used as the initial guess for neighboring energies, with this process repeated for the entire spectrum (see Sec. 5.2.2). The magnitude of each extracted amplitude, $|A_{nJ}|$, was found to be converged to six digits over the entire energy range. Figure 5.2 shows our best-fit $|A_{nJ}|$ alongside the model magnitudes from Eq. (5.10). The phase extraction was carried out at each energy — despite it being a constant in our calculation. The relative phases were converged to three digits at all energies where their corresponding amplitudes were converged.

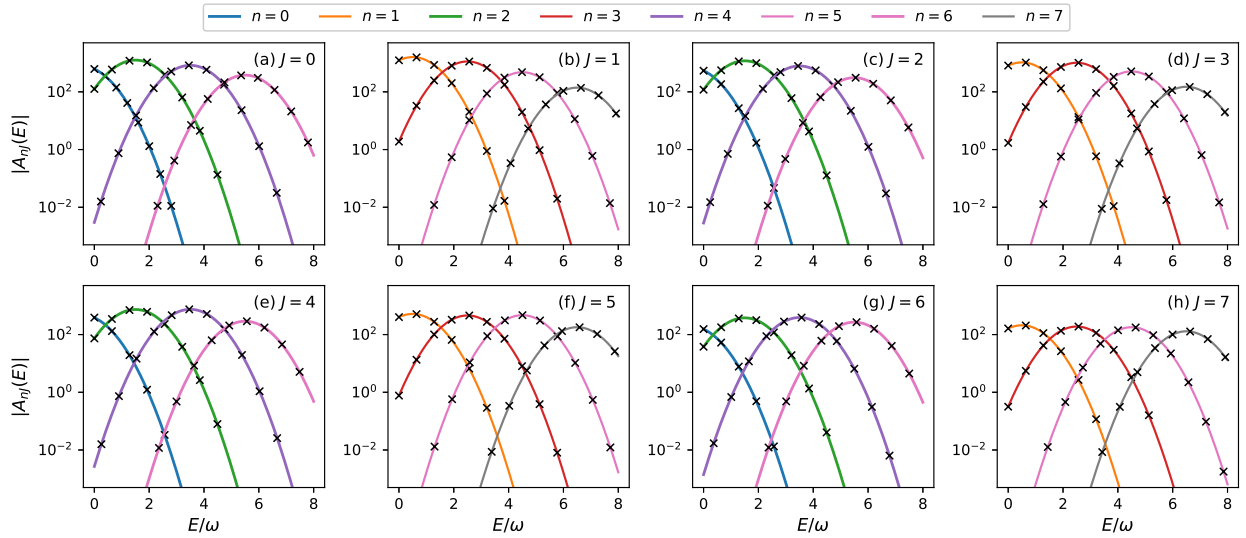


Figure 5.2: (a)-(h) Photon-pathway amplitudes $|A_{nJ}(E)|$ from Eq. (5.10) are shown in solid lines alongside the extracted amplitudes (denoted “x” at selected energies) for $J = 0$ to $J = 7$. Extracted amplitudes are only shown within the energy range where they are within five orders of magnitude of the largest $A_{nJ}(E)$.

5.4 Photon-Pathway Extraction for HeH^+

These test cases show that it is possible to retrieve A_{nJ} for a model system. Additional tests including a larger number of Gaussian amplitudes have also been carried out, with similar levels of accuracy. In this section, we will move to a realistic system and extract pathways for strong-field dissociation of HeH^+ . Calculation of the CEP-dependent momentum distribution from which the pathways are extracted was discussed in Chap. 3; here, we will focus on the calculations from that chapter using the $v = 1$, $J = 0$ initial state in a 4000-nm, two-cycle pulse with intensity 10^{14} W/cm^2 .

We first fit at the energy associated with the lowest-energy peak in the momentum distribution, which corresponds to net five-photon absorption and occurs at an energy of $E = 0.0023 \text{ a.u.}$ The corresponding KER spectrum — shown in Fig. 3.9 — features peaks associated with the net absorption of $n = 5 - 10$ photons. For our fit, we include the possibility of below-threshold dissociation [225, 226] with $n = 4$, along with the possibility of contributions from higher-order pathways $n = 11$ and $n = 12$ that are wide enough to overlap the ten-photon peak, leading us to use $n_{\min} = 4$, $n_{\max} = 12$, $J_{\min} = 0$, and $J_{\max} = 12$ for $\mathbf{A}$ at all energies. Higher-energy solutions are obtained with our usual method, and the retrieved amplitudes are shown in Fig. 5.3. The amplitudes were also calculated directly from the wavefunction using Eq. (5.1) and Eq. (5.2). Comparing the two results shows three digits of agreement at all energies where the magnitudes met our standard criteria. The relative phases were found to be converged to two digits over this range.

The agreement of the results in Fig. 5.3 with those from the wavefunction indicates that our method is capable of accurately extracting photon pathways for HeH^+ — where $\mathbf{A}$ was 124-dimensional. With the additional possibility of extracting amplitudes in partitioned energy ranges (with a different but overlapping $\mathbf{A}$ in each region), such a large number of amplitudes will likely provide an accurate fit for a wide range of problems in strong-field physics. So, while it is a simple system, we believe that HeH^+ serves as a reasonable test of the general applicability of our method to systems with momentum distributions described by Eq. (5.3).

Examining the $|A_{nJ}|$ in Fig. 5.3, we can see the REMPD splitting of the individual photon

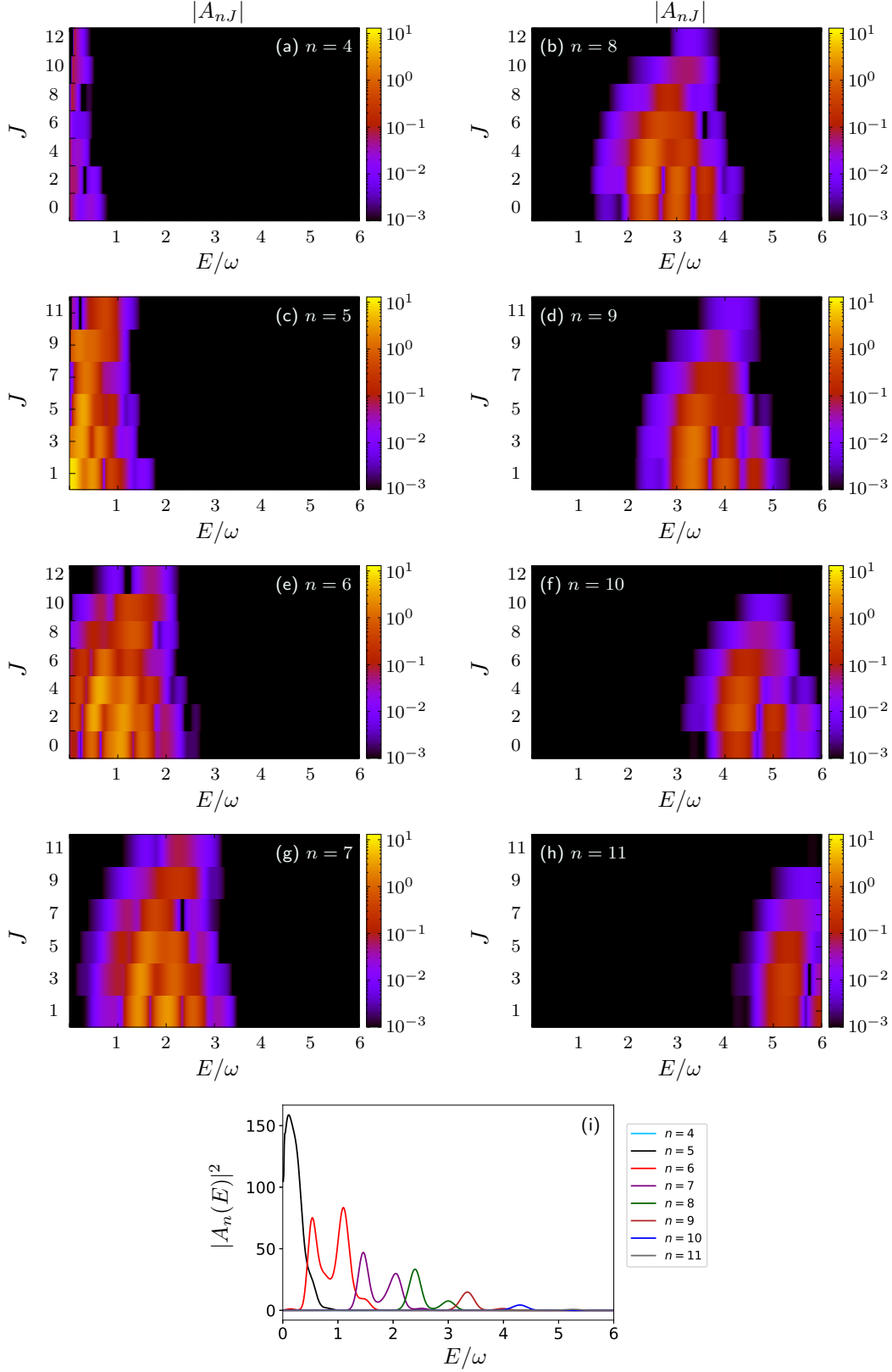


Figure 5.3: (a)–(h) Extracted photon-pathways $|A_{nJ}(E)|$ for HeH^+ dissociation in the $X^1\Sigma^+$ channel ($n = 5$ through $n = 11$). (i) Pathways $|A_n(E)|$ as defined by Eq. (5.11). Pathways with $n = 12$ are approximately zero in this energy range.

pathways that widen the amplitudes. We proposed this mechanism in Sec. 3.4.2 to explain why CEP effects were greater for dissociation from $v = 1$ than $v = 0$. This effect is not only seen for $n = 5$ — the lowest-order pathways expected for dissociation — but propagates to higher-order pathways in the spectrum as well. In fact, the splitting is even more prominent in $n = 6$ and $n = 7$, and multiple peaks can be seen at some J for most n shown in Fig. 5.3.

The CEP-independent portion of the KER spectrum in Eq. (3.23),

$$|A_n(E)|^2 = \sum_J |A_{nJ}(E)|^2, \quad (5.11)$$

is included in Fig. 5.3(i) and provides an illustration of the total overlap between $|A_{nJ}|^2$ with different n . Figure 5.3(i) makes the splitting of the peaks even more apparent. The right-most peak in the $n = 6$ and $n = 7$ cases closely matches the expected ATD peak (without REMPD) from energy conservation, which predicts locations of roughly $E/\omega = 1.2$ and 2.2 . This suggests that the resonant bound-bound transition had an energy splitting smaller than the photon energy, producing a REMPD peak at an energy below the standard ATD peak.

We see from Fig. 5.3(i) that the overlap between pathways with $\Delta n = 1$ is much larger than for $\Delta n = 2$. For example, $|A_6|^2$ and $|A_7|^2$ cross at an energy where they are both still larger than most of the other amplitudes in the spectrum. In fact, the width of $|A_7|^2$ is nearly a photon wide — far exceeding the value of 0.23ω suggested from the arguments in Sec. 2.2.4. Other pathways in Fig. 5.3(i) also have widths exceeding the bandwidth of the pulse. Amplitudes for pathways differing by $\Delta n = 1$ in Fig. 5.3 have maximum overlap in the region between the center of their corresponding $|A_n|$ — validating our assumption from previous chapters that CEP effects in the momentum distribution and spatial asymmetry will tend to be largest between peaks in the spectrum. The REMPD splitting of the peaks does cause the region of overlap to be shifted, however, with the right-most peak in $|A_6|^2$ having very little separation from the left-most peak of $|A_7|^2$. With a slightly larger bandwidth, it might be possible to see significant CEP effects in the momentum distribution or spatial asymmetry on the peaks themselves.

Figure 5.3 also shows that some below-threshold dissociation (BTD) can occur through $n = 4$ pathways. This effect is nearly two orders of magnitude smaller than the $n = 5$ pathways at the

same energy, but it is still interesting to note its presence. The $n = 4$ pathway is due entirely to the bandwidth of the laser pulse — it is the high-end tail of the laser’s power spectrum that produces this BTD. This effect could be made larger by increasing the bandwidth of the pulse, or by preparing the system in a more highly excited initial state. In fact, the $n = 4$ pathway is larger than the $n = 6$ pathway at very low energies, with integration of Eq. (5.11) from $E/\omega = 0$ to $E/\omega = 0.5$ showing the probability of the net absorption of 4 photons to be nearly 1.5 times larger than the net absorption of 6 photons. Because it is the largest even-parity pathway, it is possible that a signature of BTD would exist for low energies in an angular distribution. Indeed, one potentially interesting application of our extracted amplitudes is to reconstruct an observable both with and without the inclusion of specific pathways — allowing us to identify how the presence of a given pathway affects the spectrum.

Figure 5.3 also shows interesting trends in the J -distribution for a given n . We notice in Fig. 5.3 that the peak splitting tends to be washed out for higher J , typically disappearing for values $J > n$. This can be seen more clearly in the plot of the individual $|A_{nJ}|$ in Fig. 5.4. A shift in the center of $|A_{nJ}|$ towards higher energies also tends to occur for larger J . For smaller n , the distribution in J is fairly flat — with all $|A_{nJ}|$ for a given n being roughly the same order of magnitude in Fig. 5.4. This indicates that effects beyond LOPT theory are particularly significant in pathways with smaller n , where absorption of more total photons than n is necessary to populate these $J > n$ states. In contrast, higher n in Fig. 5.3 tend to have very little population for $J > n$.

5.5 Closing Remarks

In this chapter, we have proposed a method for extracting photon-pathways directly from a given momentum distribution and demonstrated its effectiveness. For a model system where the momentum distribution was given to machine precision by Eq. (5.10), we found that all $|A_{nJ}(E)|$ could be converged to six digits — provided that they were within five orders of magnitude of the largest amplitude at that energy. Similarly, relative phases for the system were converged to three digits over this range. For pathway extraction from a calculated HeH^+ spectrum, where

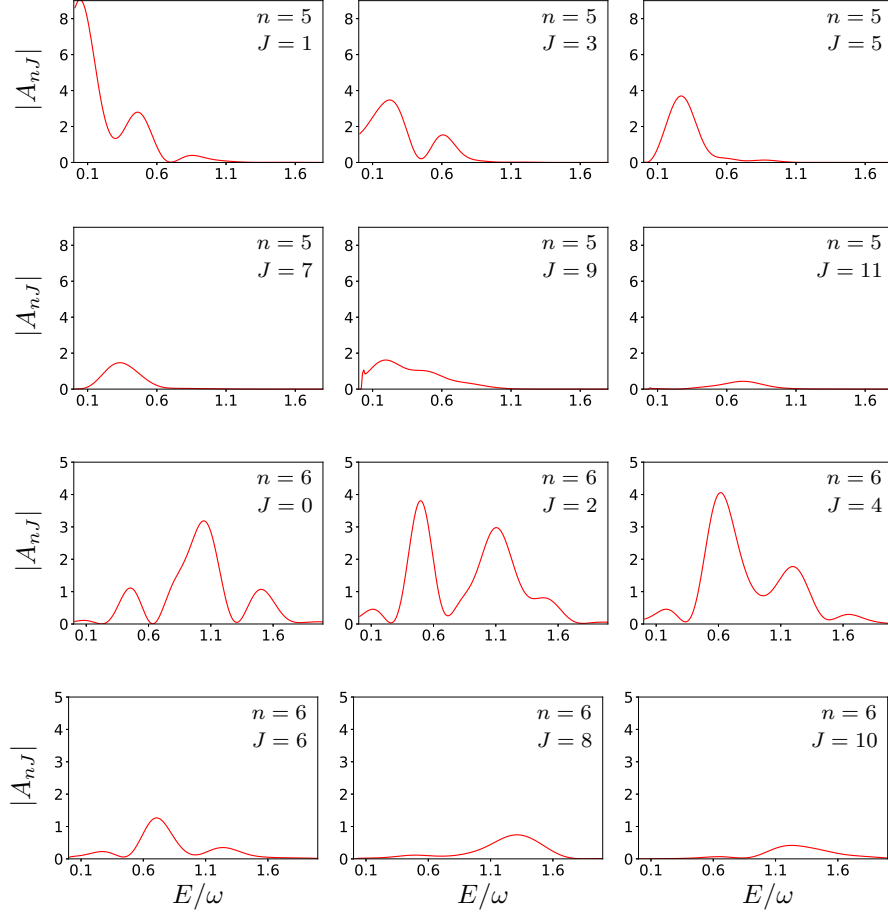


Figure 5.4: Individual photon-pathway amplitudes $|A_{nJ}(E)|$ for $n = 5$ and $n = 6$.

the momentum distribution was converged to four digits, we were still able to accurately extract pathways — with convergence to three digits in the amplitudes and two digits in the relative phases.

The high-dimensionality of the pathway extraction for HeH^+ , coupled with the possibility of partitioning regions of energy so that fewer amplitudes are needed for the fit, makes us optimistic that our method will work for more complicated systems. However, there is still much work to be done. For multi-channel experiments where distinguishable final channels are not resolved, the number of amplitudes needed in our fit will increase roughly linearly with the number of channels. Moreover, systems with less strict selection rules will allow parity-unfavored transitions that do not require n and J to have the same parity — effectively doubling the number of J needed in our fit.

It is also unlikely that a momentum distribution from experiment will be converged to four

digits, and fitting with experimental noise will be an obstacle. While initial tests adding random noise to the Gaussian amplitudes in Sec. 5.3.2 have been successful, this still needs to be extended to more complicated systems with more realistic errors. While potential issues certainly exist for amplitude retrieval from experimental spectra of complicated systems, our method will still certainly apply to a large range of problems. Future work will allow us to more clearly define the limitations of our method.

Chapter 6

Multi-Color Phase Control

The previous three chapters have focused on the application of our parametric formalism to single-color, carrier-envelope phase control. In this chapter, we will return to the more general formulation of our theory in Eq. (2.3) and extend our studies to multi-color control schemes. Multi-color control via relative phases is, of course, described perturbatively in the classic Brumer-Shapiro scheme [113–115] discussed in Sec. 1.3. Here we will extend those ideas beyond perturbation theory and devise a general formalism for treating the problem.

Specifically, we will study the two-color dissociation of D_2^+ . As in Chap. 3, we will use our formalism to express all observables in terms of photon-pathway amplitudes. The most relevant amplitudes for breakup will be identified with the aid of the dressed potential energy curves from Sec. 2.3.1, allowing us to make predictions about the phenomena seen in calculated observables. While we limit ourselves to only D_2^+ in this thesis, application of our theory to understanding observables for other system (whether theoretical or experimental) is straightforward.

6.1 D_2^+ Dissociation in a Two-Color Field

6.1.1 Theoretical Details

We begin by studying the dissociation of D_2^+ in a two-color field. As in Chap. 3 for HeH^+ , we will solve the TDSE directly; the expansion of the wavefunction in our parametric formalism will be used only in predicting and interpreting phenomena in the final results, not in the calculations themselves. Using the Born-Oppenheimer representation, we break the Hamiltonian

into electronic and nuclear parts — once again arriving at Eq. (3.4). Here, the reduced mass is $\mu_{AB} = m_d/2$ — where m_d is the mass of the deuteron — and $\mathbf{d}$ gives the dipole for the system in the center-of-mass frame. The electronic coordinates of the wavefunction are expanded on the basis Φ_α that solves the eigenvalue problem

$$H_{el}\Phi_\alpha(R; \mathbf{r}) = U_\alpha(R)\Phi_\alpha(R; \mathbf{r}). \quad (6.1)$$

In Eq. (6.1), α is the set of quantum numbers necessary to specify an individual electronic state. The potentials, U_α , and electronic wavefunctions, Φ_α , are found using prolate spherical coordinates with the methods outlined for HD^+ in Ref. [227].

The polar and azimuthal angles of the internuclear vector (θ and ϕ , respectively) are expanded using a linear combination $\Omega_{\Lambda M}^{J\pi}$ of Wigner D functions $\tilde{D}_{\Lambda M}^J(\theta, \phi, 0)$. Because we will work only with states that have total nuclear spin $S = 0$, $\Omega_{\Lambda M}^{J\pi}$ is chosen such that the spatial part of the wavefunction is symmetric under the exchange of the identical nuclei. More details of this approach for symmetrization can be found in Ref. [228], where the problem was worked out for the general symmetrization/anti-symmetrization of the wavefunction for H_2^+ using our specific conventions.

Normalization of $\Omega_{\Lambda M}^{J\pi}(\theta, \phi, 0)$ is carried out over two angles rather than three [229]. The indices of $\Omega_{\Lambda M}^{J\pi}$ correspond to the total parity π , the total orbital angular momentum J , its projection onto the lab-frame z -axis M , and the magnitude of its projection onto the internuclear axis Λ (the body-frame z -axis). The index Λ is, of course, one of the quantum numbers in the set α . With these choices, the total wavefunction can be written as

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \frac{1}{R^{5/2}} \sum_{JM\alpha\pi} F_{JM\alpha\pi}(R, t) \Omega_{\Lambda M}^{J\pi}(\theta, \phi, 0) \Phi_\alpha(R; \mathbf{r}). \quad (6.2)$$

Substituting into the TDSE, Eq. (3.4) reduces to the system of coupled equations:

$$i \frac{\partial}{\partial t} F_{JM\alpha\pi} = \left(-\frac{1}{2\mu_{AB}} \frac{\partial^2}{\partial R^2} + \frac{J(J+1) - \Lambda^2}{2\mu_{AB} R^2} + U_\alpha \right) F_{JM\alpha\pi} - \sum_{J'\alpha'\pi'} \langle \Phi_\alpha \Omega_{\Lambda M}^{J\pi} | \mathcal{E}(t) \cdot \mathbf{d} | \Phi_{\alpha'} \Omega_{\Lambda' M'}^{J'\pi'} \rangle F_{J'M\alpha'\pi'}. \quad (6.3)$$

We include only the lowest two electronic channels in Eq. (6.3) — $1s\sigma_g$ and $2p\sigma_u$, both of which have $\Lambda = 0$. Excitation to higher electronic channels, along with ionization, is neglected in our calculations. However, for the laser parameters we consider, this approximation is expected to work well within the length gauge [195]. While off-diagonal non-Born-Oppenheimer couplings and Coriolis couplings between the $1s\sigma_g$ and $2p\sigma_u$ are zero, Eq. (6.3) neglects the diagonal elements of the non-Born-Oppenheimer couplings.

Finally, the two-color electric field used for our calculations is given by

$$\mathcal{E}(t) = \mathcal{E}_1(t) \cos(\omega t + \varphi_1) + \mathcal{E}_2(t) \cos(2[\omega(t - \tau) + \varphi_1]) \quad (6.4)$$

This choice of electric field reflects the case where the field is composed of a fundamental, $\omega_1 = \omega$, and a harmonic, $\omega_2 = 2\omega$, that is generated directly from the fundamental. When the harmonic is generated from the fundamental, the phase φ_2 in Eq. (2.2) will not be independent of φ_1 ; rather, it will be the sum of $2\varphi_1$ and an additional phase (which is independent of φ_1). As such, we express the phase as $\varphi_2 = -2\omega\tau + 2\varphi_1$. The choice makes τ a temporal delay between the carrier-waves of the two pulses.

6.1.2 Numerical Details

The solution of Eq. (6.3) is found using the methods detailed in Ref. [228]. Conceptually, the methods are very similar to those used for solving the nuclear equation for HeH^+ in Eq. (3.8). The initial, bound states for the system are found by solving the eigenvalue problem for the field-free version of Eq. (6.3); numerically, this is accomplished using a generalized finite-differencing method [208]. For this problem, the non-uniform grid in R is determined from the local WKB wavelength associated with nuclear motion in the $1s\sigma_g$ channel at an energy of 0.12 a.u. above the large R threshold. This value corresponds to the largest energy we consider in any of our calculations and allows for the (net) absorption of two fundamental photons or one harmonic photon. We used 130 points per local wavelength. Finally, the resultant Hamiltonian is diagonalized to obtain the ro-vibrational states χ_{vJg} and χ_{vJu} in the $1s\sigma_g$ and $2p\sigma_u$ channels.

Initial states are propagated by applying the short-time propagator using the Crank-Nicolson

and split-operator techniques [209] discussed in Sec. 3.1.2. The number of partial waves included is increased dynamically during the calculations (see Sec. 3.1.2), and the time step is 0.12 a.u. The initial and final times in our calculations are chosen to correspond to the times on both sides of $t = 0$ when the pulse envelope has fallen to an intensity of 10^7 W/cm². All parameters were chosen to give convergence of three digits in the calculated KER spectrum up to our maximum energy of interest, 0.12 a.u. As in Chap. 3, we use a Gaussian pulse envelope for both colors — here, $\tau_{\text{FWHM}}=40$ fs is used for both pulses. Intensities are chosen as 10^{13} and 10^{12} W/cm², respectively, for the fundamental and harmonic pulses with wavelengths of 790 and 395 nm.

6.1.3 Observables in Parametric Formalism

As in previous chapters, all of the observables that we study will be calculated directly from the momentum distribution of the dissociating fragments. In order to construct a scattering state corresponding to the lowest-energy dissociation limit, D(1s)+d, a linear combination of scattering states in the $1s\sigma_g$ and $2p\sigma_u$ channels is required. Taking identical particle symmetry into account (see Ref. [228]) the resulting distribution associated with the deuteron and deuterium atom traveling apart with relative momentum $\mathbf{k}$ is given by

$$\frac{\partial^2 P}{\partial E \partial \theta_k} = 2\pi \left| \sum_{\substack{J \\ \text{even}}} (-i)^J e^{i\delta_{Jg}} Y_J(\theta_k) \langle EJMg | F_{JMg} \rangle + \sum_{\substack{J \\ \text{odd}}} (-i)^J e^{i\delta_{Ju}} Y_J(\theta_k) \langle EJM u | F_{JM u} \rangle \right|^2. \quad (6.5)$$

In Eq. (6.5), $|EJMg\rangle$ and $|EJM u\rangle$ are the field-free continuum states in the $1s\sigma_g$ and $2p\sigma_u$ channels, and δ_{Jg} and δ_{Ju} are the scattering phase shifts. We have dropped the state label π , as it is not an independent quantity for $\Lambda = 0$ states and is given by $\pi = (-1)^J$. The electronic channels $1s\sigma_g$ and $2p\sigma_u$ are labeled by $\alpha = g$ and $\alpha = u$. As in Chap. 3, E and θ_k are the energy and angle (measured relative to the polarization axis) corresponding to the momentum $\mathbf{k}$. Integration over the azimuthal angle of the momentum $\mathbf{k}$ has already been carried out. It is worth noting that calculations of the momentum distribution and observables derived from it have been previously carried out for the two-color dissociation of D_2^+ and its isotopologues (see, for example Ref. [230–235]). However, our parametric formalism provides additional information on

the pathways that can interfere to produce control over a given observable, and gives information about the properties of this control.

Expanding the total wavefunction within our parametric formalism with $\varphi_2 = -2\omega\tau + 2\varphi_1$ and $\omega_2 = 2\omega$, Eq. (2.3) gives

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \frac{1}{R^{5/2}} \sum_{\alpha J n_1 n_2} F_{\alpha J M n_1 n_2}(R, t) \tilde{\Omega}_{M0}^{J\pi}(\theta, \phi, 0) \Phi_{\alpha}(R; \mathbf{r}) e^{-in_1\varphi_1} e^{i2n_2(\omega\tau - \varphi_1)}. \quad (6.6)$$

Although writing φ_2 in such a way that it depends on φ_1 breaks from our convention in Sec. 2.2.3, substituting Eq. (6.6) into the TDSE in Eq. (6.3) will still give the appropriate $-\mathbf{n} \cdot \boldsymbol{\omega}$ energy shift and the usual interpretation of $\mathbf{n}$. The momentum distribution can be expressed in terms of interfering pathways as

$$\begin{aligned} \frac{\partial^2 P}{\partial E \partial \theta_k} = & \sum_{\substack{\alpha \\ J n_1 n_2 \\ J' n'_1 n'_2}} A_{n_1 n_2 J}^{(\alpha)} A_{n'_1 n'_2 J'}^{(\alpha)*} Y_J Y_{J'} e^{-i[(n_1 - n'_1) + 2(n_2 - n'_2)]\varphi_1} e^{i2(n_2 - n'_2)\omega\tau} \\ & + 2 \text{Re} \sum_{\substack{J n_1 n_2 \\ J' n'_1 n'_2}} A_{n_1 n_2 J}^{(g)} A_{n'_1 n'_2 J'}^{(u)*} Y_J Y_{J'} e^{-i[(n_1 - n'_1) + 2(n_2 - n'_2)]\varphi_1} e^{i2(n_2 - n'_2)\omega\tau}, \end{aligned} \quad (6.7)$$

where $A_{n_1 n_2 J}^{(\alpha)} = \sqrt{2\pi}(-i)^J e^{i\delta_{J\alpha}} \langle E J M \alpha | F_{\alpha J M n_1 n_2} \rangle$ is associated with the absorption of n_1 fundamental and n_2 harmonic photons to end in the electronic state α with energy E and angular momentum J . We choose not to label photon-pathway amplitudes by M , as only a single M is involved in any of our individual calculations. The summations in Eq. (6.7) are restricted by dipole-selection rules: $A_{n_1 n_2 J}^{(\alpha)}$ will be summed only over even J and even values of $n_1 + n_2$ for $\alpha = g$, and only over odd J and odd values of $n_1 + n_2$ for $\alpha = u$.

In addition to the momentum distribution, we will also examine the normalized spatial asymmetry — defined here as

$$\mathcal{A}(E) = \left[P_{\text{up}}(E) - P_{\text{down}}(E) \right] \left(\frac{dP}{dE} \right)^{-1}. \quad (6.8)$$

Because the calculations shown in Sec. 6.1.4 were originally carried out as part of a collaboration with Dr. Ben-Itzhak's experimental group — who made the first ever measurements on two-color control in D_2^+ and HD^+ ion beams [3] — our choice to normalize by the total KER rather than

the CEP-averaged as in Eq. (3.18) was made to match their measurements. The numerator of this expression can be shown to give

$$P_{\text{up}}(E) - P_{\text{down}}(E) = \sqrt{\pi} \text{Re} \sum_{\substack{J n_1 n_2 \\ J' n'_1 n'_2}} C_{JJ'} A_{n_1 n_2 J}^{(g)} A_{n'_1 n'_2 J'}^{(u)*} e^{-i[(n_1 - n'_1) + 2(n_2 - n'_2)]\varphi_1} e^{i2(n_2 - n'_2)\omega\tau}, \quad (6.9)$$

where $C_{JJ'}$ are given by Eq. (3.22). The KER in the denominator is given by

$$\frac{dP}{dE} = P_{\text{up}} + P_{\text{down}} = \sum_{\substack{J \alpha \\ n_1 n_2 \\ n'_1 n'_2}} A_{n_1 n_2 J}^{(\alpha)} A_{n'_1 n'_2 J}^{(\alpha)*} e^{-i[(n_1 - n'_1) + 2(n_2 - n'_2)]\varphi_1} e^{i2(n_2 - n'_2)\omega\tau}. \quad (6.10)$$

The integration over all angles in the KER has eliminated the interference between any pathways not ending with the same J — which includes all the terms in Eq. (6.9). In contrast, the numerator in $\mathcal{A}$ exclusively allows for interference between states with different J — eliminating all interference between pathways ending in the same electronic channel. In all the sums above, the values of $n_1 + n_2$ associated with $A_{n_1 n_2 J}^{(\alpha)}$ are restricted to have the same parity as J , following from Eq. (6.7).

It is worth noting that the results in Eq. (6.9) and Eq. (6.10) are incredibly similar to those for HeH^+ in Eq. (3.21) and Eq. (3.23) — with the obvious exception that the latter are for a single color. The expression for $\mathcal{A}$ in the two systems is identical up to a factor of 2, with the spatial asymmetry in both systems allowing only for interference between pathways that end at the same energy and with different J . The KER spectra of the two systems also have the same analytic expression, with both only allowing for the interference between pathways ending at the same energy and with the same J .

Setting $n_2 = n'_2 = 0$ in Eq. (6.9) and Eq. (6.10) would give the single-color CEP control over the two observables for D_2^+ . The resultant expression shows that the control over the interfering pathways is also identical to that seen in HeH^+ . The only real difference between the results for the two systems is that the different parity J are split between two electronic channels in D_2^+ . The similarity between observables for different systems in our parametric formalism is, of course, the basis of the argument that the methods in Chap. 5 could be extended to many systems.

6.1.4 D_2^+ — Results and Discussion

We begin by examining the momentum distribution — which is shown in Fig. 6.1 for a field with only the fundamental, only the harmonic, and with both colors (with $\tau = 0$). The results shown include a Frank-Condon average over all 28 initial vibrational states within the $J = 2$, $1s\sigma_g$ channel. This averaging is done to better match the conditions in the relevant experiment, where D_2^+ ions were created in a distribution of initial states through electron-impact ionization of D_2 .

In a Frank-Condon average, the ionization step is assumed to be sudden (relative to the time scale of nuclear motion) resulting in the nuclear state of the D_2^+ ion being approximately unchanged from that of D_2 [20]. Therefore, the D_2 nuclear state is expanded on the D_2^+ rovibrational basis, with the expansion coefficients giving the Frank-Condon distribution of the ion states for a given J . The Frank-Condon distribution has been shown to give a good approximation to the actual distribution for electron-impact ionization [236]. We choose to use $J = 2$ because it is the most populated rotational state in a thermal distribution for temperatures exceeding 300 K, and such temperatures are expected in an ion-beam experiment. A statistically weighted average over all M values was also included in the spectra in Fig. 6.1.

The single-color momentum distributions in Fig. 6.1 show peaks associated with the absorption of one net-photon from the individual initial vibrational states. We explain the pathways associated with these peaks using the diabatic dressed potential energy curves discussed in Sec. 2.3.1; a slightly modified version of Fig. 2.4 is included here as Fig. 6.2 for ease of reading. As discussed in Sec. 2.3.1, the use of diabatic dressed potentials to study dissociation is nothing new (see, for example, Ref. [191–200]). What our work provides is the ability to use the information found in these potentials to construct a given observable and make predictions about the control that can be obtained over it — using a formalism that is essentially exact.

In the single-color, 790-nm field ($\omega = 1.58$ eV), one-photon dissociation proceeds through the pathway labeled α . From our discussion in Sec. 2.3.2, we know that resonant transitions occur near crossings of the diabatic potentials. Comparing the crossing energy of $1s\sigma_g$ and $2p\sigma_u - 1\omega_1$ (pathway α) to the $1s\sigma_g$, $J = 2$ vibrational energies, we see that $v = 13$ is closest to resonant

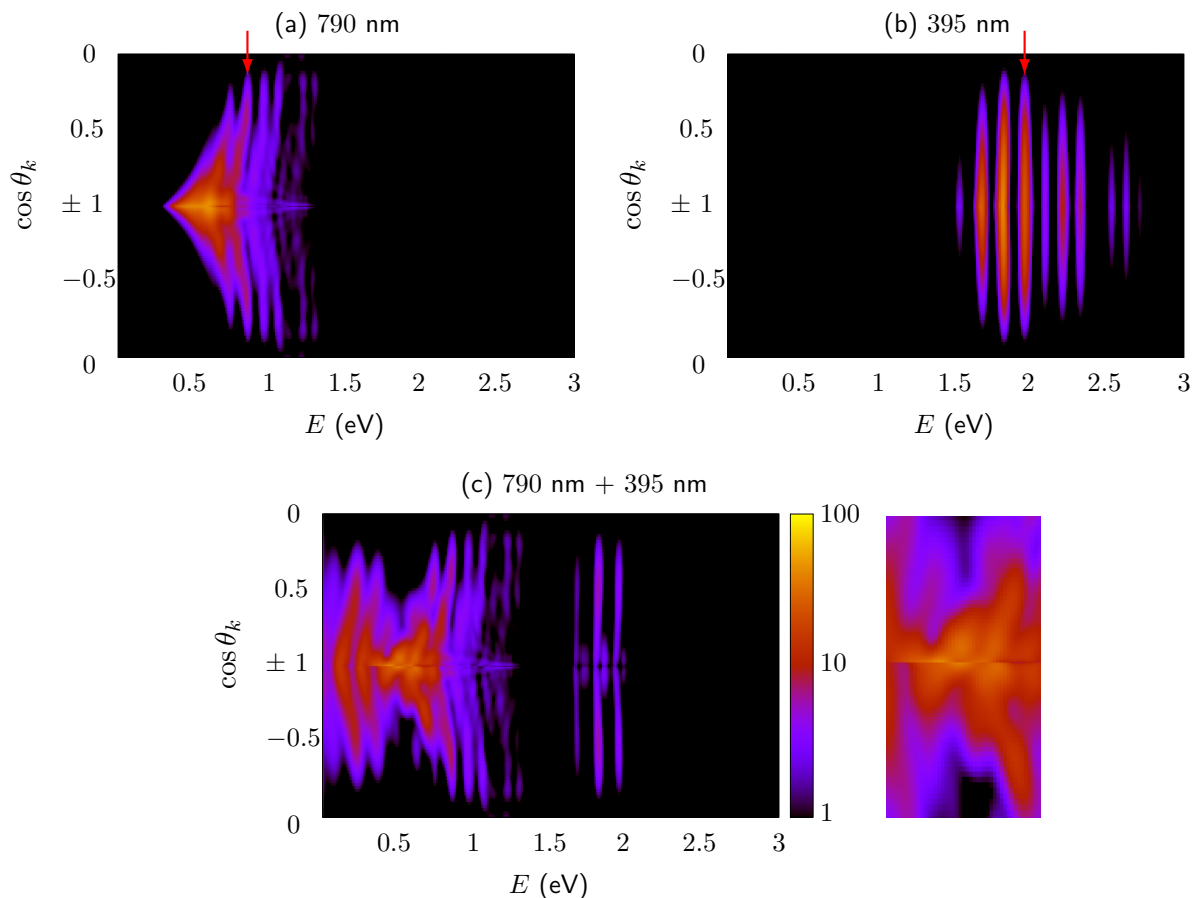


Figure 6.1: (a) Franck-Condon averaged momentum distribution for D_2^+ dissociation in (a) a 790-nm pulse (b) a 395-nm pulse, and (c) the combined two-color 790+395-nm pulse. A zoomed-in cut near $E = 0.5$ eV is included in (c) to illustrate the asymmetry about $\cos \theta_k = \pm 1$ that is created in the two-color case by the interference of pathways α and γ (Fig. 6.2). Red arrows indicate the dissociation energy expected for near-resonant dissociation from (a) $v = 13$ and (b) $v = 8$.

and, therefore, should be the most likely to dissociate. Nearby vibrational states also dissociate, which can be understood from the adiabatic representation since the avoided crossing can grow large enough to allow a range of vibrational states to escape [192, 195, 237–240]. Our calculations for individual vibrational states show that a dissociation probability greater than ten percent can be seen as low as $v = 7$. For vibrational states separated by energies larger than the bandwidth of the pulse, dissociation from each vibrational state creates a clear peak — such peaks can be seen in Fig. 6.1(a).

The single-color, 395-nm momentum distribution can be understood in the same fashion. Figure 6.2 shows that the one-photon process for this wavelength follows the pathway labeled β . The crossing associated with this pathway — $1s\sigma_g \rightarrow 2p\sigma_u - 1\omega_2$ — is nearly resonant with

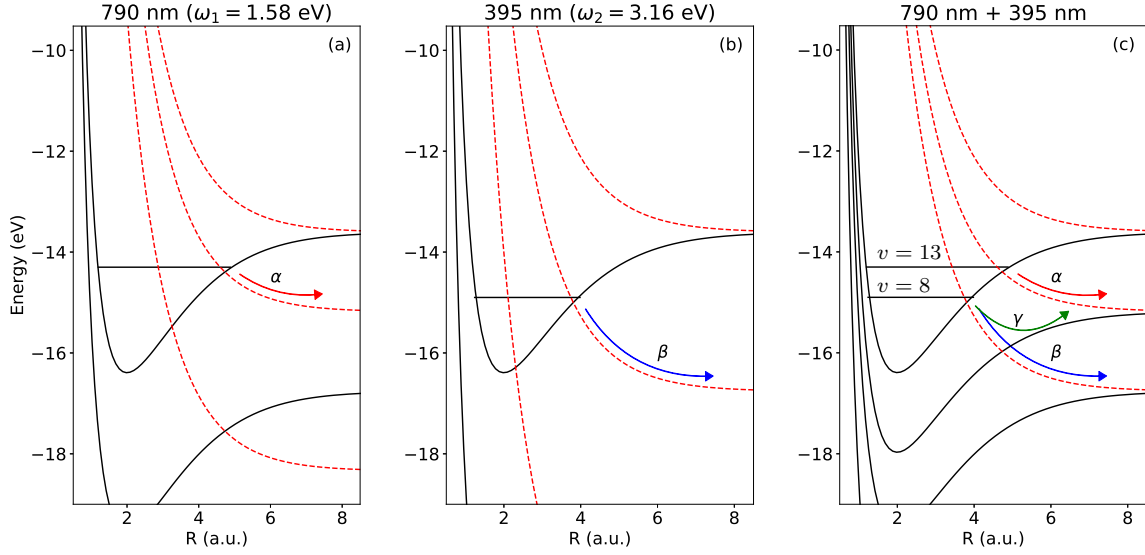


Figure 6.2: Dressed potentials for D_2^+ molecular ion in a 790-nm (a), 395-nm (b), and two-color 790+395-nm field (c). $1s\sigma_g$ potentials are shown in black, $2p\sigma_u$ channels in red. The horizontal lines give the $v = 8$ and $v = 13$ eigenenergies, the individual arrows represent different pathways for dissociation.

the $v = 8$ vibrational state. As with the 790-nm pulse, multiple distinct peaks associated with dissociation from states near $v = 8$ can be seen in the spectrum. The clearer vibrational structure seen in the spectrum for 395 nm (when compared to 790 nm) can potentially be explained by two things. One, the larger separation in energy of the lower-lying vibrational states near $v = 8$ allows for a clearer resolution of the vibrational structure. Two, the ratio $\Delta\omega_{\text{FWHM}}/\omega$ is smaller for 395 nm than 790 nm since both pulses have the same duration.

Figure 6.2 shows that the combined two-color field opens up a new pathway γ , which proceeds via the absorption of a single harmonic photon onto the $2p\sigma_u - 0\omega_1 - 1\omega_2$ channel, followed by the emission of a single fundamental photon to end on the $1s\sigma_g + 1\omega_1 - 1\omega_2$ channel. Because the initial crossing associated with γ occurs at the same energy as β 's crossing, dissociation along γ will also be most probable for states near $v = 8$ — providing contributions to the momentum distribution similar to those in Fig. 6.1(b), but shifted down in energy by 1.58 eV due to the stimulated emission of a 790-nm photon at the next crossing. The single-color pathway α associated with the 790-nm pulse produces dissociation for vibrational states as low as $v = 7$, and for a given initial vibrational state will result in dissociation at the same energy as pathway γ . This means that for a small range of vibrational states above $v = 7$, there will be two pathways

that dissociate to different channels and end at the same energy.

From Eq. (6.10), we see that pathways α and γ will not interfere in the KER — due to the two pathways ending in different channels (and thus different J_s). However, these pathways will interfere in the momentum distribution and the spatial asymmetry — as shown in Eq. (6.7) and Eq. (6.9). This interference in the momentum distribution can be seen in Fig. 6.1(c), where a clear (although somewhat subtle) asymmetry can be seen about the $\cos \theta_k = \pm 1$ line of the plot. This asymmetry is most prominent at roughly $E = 0.5$ eV. Equation (6.9) explicitly shows that asymmetry can only arise from the interference between states ending in different electronic channels; *i.e.*, the features seen in Fig. 6.1(c) can only be created by interference between pathways α and γ .

Moreover, because α and γ differ in both n_1 and n_2 — $\mathbf{n} = (1, 0)$ and $\mathbf{n} = (-1, 1)$, respectively — the interference between these pathways will be controllable via either the CEP or the delay τ . Control over the spatial asymmetry via τ is shown in Fig. 6.3 for calculations from the initial vibrational states $v = 8$ and $v = 9$. These calculations include the average over M and allow us to directly examine the vibrational states expected to provide the largest contribution to the interference seen in Fig. 6.1(c). Both the numerator and denominator of the asymmetry — Eq. (6.9) and Eq. (6.10) — are independently integrated over the low-energy range where the two-color effects are most prominent (energies from 0.14 to 0.49 eV, or 0.005 to 0.018 a.u.).

Because only the numerator of the spatial asymmetry allows for interference between α and

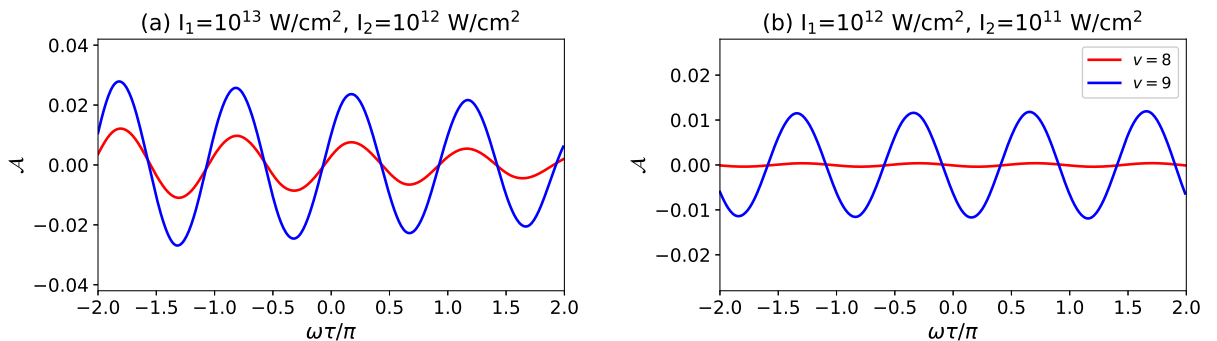


Figure 6.3: Spatial asymmetry in Eq. (6.8), with both the numerator and denominator independently integrated over the energy range of 0.14 to 0.49 eV (0.005 to 0.018 a.u.). Initial states of $v = 8$ and $v = 9$ are used, with fundamental (790 nm) and harmonic (395 nm) pulses of intensities (a) 10^{13} W/cm² and 10^{12} W/cm², respectively, and (b) 10^{12} W/cm² and 10^{11} W/cm², respectively.

γ , all τ -dependence is shown in Eq. (6.9). The predicted periodicity in $\omega\tau$ from Eq. (6.9) is given by $\pi/(n_2 - n'_2)$, giving a period of π for α and γ . This prediction matches the period in the calculations, as seen in from Fig. 6.8.

All calculations were repeated for a fundamental pulse with intensity 10^{12} W/cm² and harmonic pulse with intensity 10^{11} W/cm²; this result is shown alongside the higher intensity calculations in Fig. (6.8). The control in τ provided over both states in Fig. 6.8(b) is considerably smaller than for the higher-intensity case. Clear τ -control can still be seen for $v = 9$, indicating that both pathways α and γ remain open for this vibrational state (albeit with lower associated probabilities). Control via τ over the $v = 8$ state, however, has all but disappeared. It seems unlikely that γ has closed to $v = 8$, as γ is resonant with this state (and the pathway is still open in $v = 9$). It is possible that α has closed to the $v = 8$ state, as sufficient intensity is needed to open the crossing for lower-lying vibrational states to dissociate on this pathway. However, more work needs to be done to see if this is the case.

6.1.5 Branching Ratio in Heteronuclear Systems — HD⁺

In the dissociation of D₂⁺ — and other homonuclear diatomics — the Hamiltonian is symmetric under the exchange of the nuclei. This symmetry results in electronic wavefunctions with well-defined parity under reflection about the nuclear center of mass in the body-fixed frame. As such, taking a linear combination of scattering states in the different channels is necessary in order to construct a scattering state with the correct asymptotic behavior. Once permutation eigenstates are constructed from these linear combinations, and identical particle symmetries are taken into account, the end result is that multiple electronic channels with the same asymptotic energy give only a single momentum distribution. This corresponds to the fact that in experiment, there is only one state to be measured.

In contrast, for heteronuclear molecules — where the reflection symmetry is broken by charge or mass asymmetry — a momentum distribution can be calculated/measured in each individual channel. This, of course, is where control over electron localization actually lies — the ability to steer the electron to different nuclear centers and create unique products. As such, it is useful to examine this control within our parametric formalism. While it is more common to use angle-

and energy-integrated quantities, we will look directly at control over the difference between two momentum distributions. We will refer to these as channel asymmetries throughout this section, although that is not the typical use of the term. Of course, it is possible to define more standard quantities such as branching ratios from these momentum distributions, so these results can easily be extended to those observables.

The simplest heteronuclear molecule, HD^+ , has potentials identical to H_2^+ in the Born-Oppenheimer approximation. The inclusion of non-Born-Oppenheimer effects will create two electronic channels separated by 3.7 meV due to the mass asymmetry — corresponding to dissociation products $\text{H}(1s) + d$ and $\text{D}(1s) + p$. While this system has served as a benchmark for calculations including effects beyond Born-Oppenheimer [102, 206, 241–244], our parametric formalism enables predictions about control via the CEP or τ over the channel asymmetries without the need for calculations. In this section, we will focus on how the presence of permanent-dipole transitions can be identified from a two-color channel asymmetry.

For HD^+ in the two-color field defined by Eq. (6.4), the momentum distribution for one of the lowest two channels, α , is given in our parametric formalism by

$$\frac{\partial^2 P_\alpha}{\partial E \partial \theta_k} = \sum_{\substack{J n_1 n_2 \\ J' n'_1 n'_2}} A_{n_1 n_2 J}^{(\alpha)} A_{n'_1 n'_2 J'}^{(\alpha)*} Y_J Y_{J'} e^{-i[(n_1 - n'_1) + 2(n_2 - n'_2)]\varphi_1} e^{i2(n_2 - n'_2)\omega\tau}. \quad (6.11)$$

Equation (6.11) is simply Eq. (6.7) for D_2^+ without the cross term between channels, and $A_{n_1 n_2 J}^{(\alpha)}$ has the same definition and physical interpretation that it had for D_2^+ . Parity restrictions still require $n_1 + n_2$ to have the same parity as J , but here all J are included in every electronic channel as a result of the permanent dipole. In Eq. (6.11), E will refer to total energy as opposed to KER in order to avoid the complication of measuring E in the two distributions with respect to a different threshold.

Because the channel asymmetry we defined is simply the difference between the two momentum distributions, Eq. (6.11) shows that control via τ is possible only when two pathways defined by (n_1, n_2) and (n'_1, n'_2) from the same initial state end at the same energy E and in the same electronic channel. Additionally, energy conservation — assuming absorption at the central frequency — requires that $n_1 + 2n_2 = n'_1 + 2n'_2$, implying that n_1 and n'_1 must always have the

pathways with odd $n_2 - n'_2$ will require a permanent-dipole or non-adiabatic transition, while any interference between pathways with even $n_2 - n'_2$ can occur exclusively through electronic transitions. As such, the observation of any periodicity corresponding to odd $n_2 - n'_2$ is indicative of the occurrence of permanent-dipole or non-adiabatic transitions.

Integrating the momentum distributions in Eq. (6.11) over all angles adds the constraint that pathways ending in the same electronic channel must also have the same angular momentum J . Because $J \rightarrow J \pm 1$ for each photon exchange, this requires that $(n_1 + n_2)$ and $(n'_1 + n'_2)$ have the same parity, *i.e.*, a pathway involving an odd number of total photons can't end with the same J as a pathway involving an even number. As was previously indicated, energy conservation gives $n_1 - n'_1 = 2(n'_2 - n_2)$ — which requires n_1 and n'_1 to have the same parity in order to be a multiple of two. Combining these two parity restrictions, we see that n_2 and n'_2 must have the same parity to interfere. Because only even $n_2 - n'_2$ can interfere in the angular-integrated branching ratio, there is no clear signature of permanent-dipole or non-adiabatic transitions in this spectrum. Such transitions can, of course, still be present. However, there won't be a way to identify them solely from a two-color spectrum using our formalism.

6.2 Closing Remarks

In this chapter, we have applied the more general form of our parametric formalism in order to understand the multi-color control that can be obtained through variation of the relative phase between multiple colors. The dressed, diabatic potentials that are a direct consequence of our formalism provided a simple method for identifying relevant pathways that lead to control in the dissociation of D_2^+ . Calculations for the system served to validate the predictions of our theory. Similarly, pathway analysis applied to heteronuclear HD^+ was able to make predictions about control over the channel asymmetry without the need for detailed calculations.

Because of the generality of our formalism, our methodology can be extended to many other systems. Expressing the observables of other diatomic molecules in terms of photon-pathways — and identifying the most relevant pathways from Born-Oppenheimer potentials — is incredibly straightforward. Similarly, multi-electron atoms can be studied in an adiabatic hyperspherical

representation [245] in the same fashion. Indeed, we have taken this approach to study the ionization of helium in an attosecond pulse train [2]. More generally, however, any system that can be understood in terms of motion along potential curves is a good candidate for study within our picture. For example, a complex chemical process with dynamics that occur mainly along a specific reaction coordinate could also be understood within a dressed potential picture, allowing for the possibility of understanding how the reaction can be controlled through the use of CEP or multi-color pulses.

Chapter 7

Final Remarks

In this thesis, we have outlined our group's parametric formalism for CEP and multi-color control. The derivation of this formalism is based solely on the properties of the incident laser pulse; as such, it can be applied to intense field interactions with any system — provided that the electric field is given by Eq. (2.2). The work in this thesis, and our group's previous works, have only begun to scratch the surface of the potential applications of our formalism. It is almost certain that it will continue to be applied to increasingly complex problems in the years to come.

We have shown in this thesis how our formalism leads to the natural interpretation of control in terms of the interference between different net photon pathways. The most likely pathways taken by a system can be predicted from the dressed potentials that arise naturally from in formalism (Sec. 2.3.1 and Sec.2.3.2), or through the use of photon diagrams like those in Sec. 2.2.3 and Sec. 2.2.4. Because all observables can be expressed in terms of the interference between these pathways, information about the relevant pathways allows us to easily predict the form of a given observable and the control provided over it by varying the CEP or relative phase between colors. These methods were applied successfully in this thesis to understand CEP control over dissociation of HeH^+ and two-color control of D_2^+ dissociation. We were also able to make predictions about expected channel asymmetries in HD^+ .

In addition to applying our formalism in the above manner to a variety of new problems, this thesis contained our group's first work on using the formalism to directly extract information from a measured spectrum. In Chap. 4, we were able to provide new insights into the physical

mechanisms that determine the shape of experimental PAPs commonly used for CEP characterization. There, we were able to show that deviations from the ideal circular PAP occur due to the interference between photon pathways with $\Delta n \geq 2$. We were not only able to make suggestions for way to minimize these higher-order effects, but also provided a general formula that applied to CEP extraction from any PAP when only $\Delta n = 1$ pathways interfere — even when the PAP was not circular. Furthermore, we explored the idea of using our formalism to improve CEP extraction for a PAP with higher-order interferences. While the improvement provided by our suggested method was small, it was still interesting to see how well our method fit the test data to which it was applied.

We continued this idea of extracting information from a measured spectrum in Chap. 5, where we developed a novel method for directly extracting photon pathways from a momentum distribution. By applying our method to a simple model system, we were able to identify potential problems with non-unique solutions, and to provide simple methods for overcoming these issues. With these insights, we were able to accurately extract photon-pathway amplitudes and relative phases for HeH^+ from our calculated CEP-dependent momentum distribution. Although Chap. 5 mainly served to outline our method and demonstrate its accuracy, we were able to see a number of interesting features in the extracted amplitudes for HeH^+ . For example, the REMPD peak-broadening we discussed in Chap. 3 was incredibly apparent in the individual photon pathways.

Most of the features of the photon pathways for HeH^+ were easily understood without direct calculation — which was, of course, our method for predicting the form of the momentum distribution in Chap. 3. In other systems, the form of these pathways will not always be so apparent. The next step in our this work will be to study the cause of more complicated features — for example, the extraction of the pathways responsible for creating the characteristic plateau in an ATI spectrum. Of course the main benefit of our method is its ability to be applied to experimental spectra, which can be measured for much more complicated systems than those that can be studied through calculations. A clear future direction is also to apply our methods to these spectra.

While there is still much work to be done with pathway extraction, our work thus far provides us with confidence for future applications. The extraction of pathways for HeH^+ used a fit with

62 amplitudes; considering the possibility of partitioning the energies in the spectrum, such a large number of pathways will likely be sufficient for studying a wide range of problems in strong-field physics. Also, while our method has yet to be tested on experimental spectra, our work in CEP extraction provides optimism that the the parametric formalism can provide a quality fit on data with error bars.

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