

Chapter 1

Introduction

Ultrafast phenomena comprise a vast field of study in chemistry and physics, with many types of applications, particularly the direct study of processes happening on sub-picosecond timescales. The short timescales inherent to ultrafast pulses correlate to a wide bandwidth in the frequency domain. During excitation, especially to a first order approximation, several transitions can often simultaneously become excited. In the case of dissipative or quasi-continuum systems, such as a solid state semiconductor or a repulsive molecular electronic potential, a predominant characteristic of the wide bandwidth excitation is a rapid decay of signal[1-3]. In an atom or molecule in the gas phase, the energy level structure can contain narrow bandwidth resonances, implying the presence of slowly decaying states. In the presence of resonances, the dynamics of ultrafast excitation can drastically change from a monotonic exponential decay to series of recurrences, or temporal interferences[4-8]. Thus, if more than one state is excited, a time dependent wave function, or wave packet, results. By defining a wave packet as a superposition of multiple states, a continuum process—such as molecular dissociation—represents the limit of wave packet behavior with an infinite number of component states, but in this case a wave packet consists of a limited number of states[1, 2, 4, 9-11]. In the presence of a limited number of transitions, an oscillatory behavior can show up in time as the time dependent wave function returns to a configuration in state space that is favorable for

observation. This regular recurrence of the wave function to a favorable configuration can be thought of as a re-phasing process. Once launched, the component states of the wave packet accumulate variable amounts of phase as determined by their energy and eventually they can all come into phase at some later time. This re-phasing time depends on both the number of states involved and their relative energy spacing, so it is not necessarily predictable.

The recurrence phenomenon of wave packets leads to the possibility of directing the wave packet's path as it travels through its configuration space and has come to be realized in many forms. Known as coherent control, this study of directing wave packet creation and propagation has seen attention in a wide range of systems from the relatively simple to the seemingly impossibly complex[9, 12-26]. Although early hopes that coherent control would be viable as a synthetic tool have yet to come to fruition, the process of performing coherent control can lead to a better understanding of many types of molecular and spectroscopic processes[22]. Many examples of coherent control have been implemented in the past, with one primary method of control revolving around manipulating the phase and amplitude of the component wave functions of a wave packet by manipulating the excitation laser source[16, 21, 27-31]. In effect, a laser is manipulated, and information from the laser is written onto the wave packet[32, 33].

This thesis addresses several aspects of using ultrafast pulse shaping to control both transient and stable wave packet dynamics. The dynamics to be studied are state resolved, allowing very precise investigations into the spectral

aspects of the dynamics of ultrafast excitation. Most of the studies involved in this thesis address the creation and propagation of precisely prepared wave packets. A wave packet is defined as a superposition of stationary state wave functions that displays time dependent dynamics. A basic description of a wave packet is included here, where the total wave function is a summation of component wave functions:

$$\Psi(t) \propto \sum_i c_i(t) \psi_i e^{i\omega_i t}, \quad (1.1a)$$

where n is a normalization constant, $c_i(t)$ is simply a weighting coefficient, and ψ_i is a component stationary state wave function, and the exponential factor is a time dependent phase factor that depends on the wave function energy. Since an observable consists not of a wave function but a modulus squared of the wave function over some coordinate, the above equation needs to be rewritten to reflect the qualitative act of observation:

$$|\Psi(t)|^2 \propto \sum_i \sum_j |c_i(t) \psi_i|^2 + |c_j(t) \psi_j|^2 + |c_i(t) c_j(t)| \cos(\omega_{ij} t), \quad (1.1b)$$

where ω_{ij} is the energy difference between states in a wave function, and the overlap integral between the component wavefunctions along an observation coordinate is assumed to be unity. In the above equation, the observable time dynamics come from the cosine term representing an interference between states, accounting for the “rephasing” processes mentioned above. In the weak field limit the non-transient weighting coefficients are expressed as

$$c_i \propto \varepsilon(\omega_{ig}) \mu_{ig}, \quad (1.1c)$$

where the excited state coefficient depends upon both the transition dipole between the launch and excited state (μ_{ig}) and the electric field strength at the resonant frequency between the launch and target state [$\mathcal{E}(\omega_{ig})$]. Note that in the presence of an electric field, $c_n(t)$ can change but after an excitation pulse, these factors are effectively constant over timescales on the order of over a nanosecond. Various permutations of Eq. (1) will be invoked several times in the text, and additional details will be added in or expanded upon in the following chapters. The equations above show that, qualitatively, we observe wave packets that get stronger as the excitation laser gets stronger and that contain an oscillatory component in time. At the beginning of each chapter, a justification and a frame of reference will first be established, so that it will come as no surprise when a specific detail is included.

To begin, a summary of important experimental considerations will be considered in chapter 2. The summary will include a short discussion of the experimental setup, excitation scheme, and a somewhat detailed analysis of the limitations of the pulse shaping apparatus. This pulse shaper is very similar to a number of other pulse shapers and has been analyzed in the literature[30, 34], but since its use plays such a large role in many of the experiments of later chapters, a discussion is included. Another experimental technique, here referred to as Wavelength Subtraction Spectroscopy (WSS), is examined. This technique consists of looking at a signal as narrow bands within an ultrafast spectrum are attenuated. This is similar to observing an absorbance process, except

interference effects between different wavelengths in the ultrafast pulse can be examined with WSS.

Chapter 3 describes the use of an Evolutionary Algorithm (EA) to optimize several types of processes in the weak field limit (*i.e.* peak power $<10^{10}$ W/cm² in these experiments in Li₂). After a brief exposition of the routines used by the EA, a sample pulse compression is performed. In this case, the EA performs the same task as a pulse reconstruction algorithm in that it finds the spectral phase of an input pulse. This is followed by an optimization of weak field wave packet dynamics at times after the pump pulse is over, in effect addressing issues related to resonant absorption processes within ultrafast pulses. An optimization of transient weak field wave packets shows that during a pulse, various nonresonant processes can be controlled, as verified by the good agreement of a modeled optimization with experimental results.

Chapter 4 explores in more detail the limits of controlling transient population transfer processes in the weak field. It is shown that the spectrum of an ultrafast pulse can be divided into multiple spectral regions resulting in spectral channels, or groups of wavelengths, that can be used for ultrafast pulse shaping. Resonant and nonresonant effects are shown to be independently controllable, with the nonresonant effects providing the basis for controlling transient dynamics. Even though this sounds similar to Wavelength Division Multiplexing, it differs in that it really pushes the degree to which the control channels can be separated, and it takes advantage of nonresonant effects in a way not previously exploited.

Chapter 5 demonstrates a method for controlling the instantaneous phase of a wave function, as observed by a change in wave packet phase. This is a case of an application of the lessons learned in chapter 4. The observed dynamics are shown to transform a superposition of wave functions in a way that is consistent with a quantum computational Z-gate.

One of the limitations of the wave function manipulations described in Chapter 5 as applied to quantum computation is that the excited state superposition contains significant launch state character. One way around this coherence is to fully transfer the population out of the launch state. This is addressed in chapter 6 as a goal of strong field coherent control (with peak laser powers up to $\sim 10^{12}$ W/cm²), where significant launch state population depletion is possible. In this regime, Eqs. (1a-c) fail to describe the population dynamics, as it is seen that both the ground and excited state populations oscillate as a function of electric field strength. In a two level system, this population oscillation is known as a Rabi oscillation[5]. This chapter starts with a theoretical examination of wave packet dynamics in the presence of both a uniform electric field and a spatially Gaussian electric field. Finally, a chirped pulse Rapid Adiabatic Passage scheme is proposed and implemented to transfer population through specific excited states. Specifically, a Raman transition is excited such that the population that transfers through the E electronic states gets depleted to nearly zero along with the launch state. Stokes/anti-Stokes excitation is selected by simply changing the sign of chirp.

Finally, chapter 7 summarizes studies using a tunable ultrafast laser, with the ultimate goal of identifying energetic regions favorable to studying electronic wave packets. Chapter 7 begins with a study of wave packet dynamics between two bound electronic states. In this low lying Rydberg state regime, it is shown that quantum beats can be observed between individual states on the separate curves. Additional work verifies that the observations are of primarily rotational states, as progressions of rotational quantum beats for increasing vibrational quanta are observed. Within this vibrational progression of rotational beats lie additional coherences that are attributed to quantum beats between electronic states. It is shown that the electronic beats are between states with $\Delta\Lambda=1$, suggesting a potential handle for further controlling the wave packet dynamics via Stark shifting one state relative to the other. Chapter 7 concludes with a series of experiments exploring an ultrafast transient effect that is ultimately deemed to be atomic in nature. This final series of experiments is left with open questions to be revisited at a later date.