

CHAPTER I

Introduction

From a practical point of view, atoms are the basic building blocks that we can use to manipulate our natural world. Molecules are collections of atoms with behavior drastically different from that of the atoms of which they are composed. The ability to control these atoms and molecules has driven the creation of materials that has revolutionized every aspect of technology that impacts our daily lives. Furthermore, the synthesis of chemicals (including life-saving drugs) also relies on our ability to control atoms and molecules. Current methods used to control the atoms and molecules that drive much of our technology are based on thermodynamics. An understanding of those laws allows us to exploit the predicted behavior of atoms and molecules for the synthesis of materials. Improvements in our ability to control atoms and molecules beyond what is allowed by thermodynamics will usher in a new era of technologies based on the control and not just the observation of nature.

At the turn of the previous century, it became apparent that a thermodynamic and deterministic mechanics description of matter, especially for the case of small objects like atoms and molecules, could not explain all of the observed behaviors.

This led to the development of quantum mechanics, which uses wave mechanics of matter to explain much of the observed behavior. Because the behavior of atoms and molecules can be described as waves, they exhibit interference effects between these matter waves. However, in order to observe the wave interferences of an ensemble of quantum-mechanical objects, the waves must be stable with respect to one another, i.e., the ensemble must be coherent. The coherence of a system is not preserved in the presence of collisions or spontaneous radiation, and all quantum-mechanical systems are subject to these de-coherence mechanisms. The time-scales for de-coherence of atoms and molecules at room temperature are on the order of pico and femto-seconds.

Provided there is a coherence, the wave interferences of atomic and molecular quantum-mechanical wavefunctions can be manipulated by the application of an external electro-magnetic field. By manipulating this external control field, the wave interferences can be tailored to produce a desired final quantum-mechanical state that may result in the production of a specific chemical reaction product, or the shaping of the power spectrum of radiation produced by the atom or molecule. Efficient control requires that the control field interact with a coherent ensemble. In order to create and manipulate a quantum-mechanical population efficiently, the time-duration of the control field must be shorter than the de-coherence time. Furthermore, the natural time-scale of evolution of atoms and molecules is femto to picoseconds. As a result, in order to efficiently control the wave interferences of atoms and molecules, the use of coherent, ultrashort pulses of light is required. Atoms in molecules with negligible thermal population vibrate with characteristic periods of

< 50 femtoseconds, while electronic wave functions in molecules in our experiments have sub-femtosecond lifetimes. In order to access these natural timescales, an optical source with a broad-bandwidth, corresponding to controlled sub-20 femtosecond pulse durations is required.

This thesis work sought to control the dynamics of quantum-mechanical systems using shaped light pulses [1, 2].

The new scientific advances discussed in this thesis are:

- The application of coherent control techniques to a highly nonlinear quantum system.
- Attosecond control of a process for the first time by controlling the phase of an electron wave packet with a shaped light pulse.
- Demonstration that a learning algorithm can be used as a powerful tool to discover new science.
- Discovery of a new phase matching mechanism in the high-field regime that occurs between a single atom and a light field.
- The first demonstration that a non transform-limited pulse can optimize a purely electronic nonlinear process.
- The generation of nearly transform-limited soft x-ray pulses.
- Demonstration of learning control of molecular vibrational coherences at room temperature and atmospheric pressure.

- Observation of molecular wave packet dynamics by analyzing the phase modulation imposed by a time-varying molecular polarizability.
- Self-seeding of impulsive stimulated Raman scattering.
- Use of modified cost functionals in a learning algorithm to learn about a system under study.
- Generation of a perfectly spatially coherent XUV beam for the first time.
- The first demonstration of the measurement of the spectrum of a light field by analyzing a double-pinhole interferogram.
- The demonstration of a new pulse compression scheme using phase modulation from controlled molecular rotations.

We achieve control of quantum systems by interacting a very broad bandwidth, shaped light pulse with atoms and molecules. To determine how to shape the optimal light field, I used an idea proposed by Herschel Rabitz in 1992 [3] that suggests using a feed-back loop (or more appropriately, a learning loop) to allow the quantum system under investigation to determine which pulse shape best controls the system.

The idea of using learning control was a revolutionary advance for the field of "coherent control" because of the difficulty in determining optimally shaped fields to control complex, real-world, quantum systems; however, it is an approach that is borrowed from engineering. A number of scientists have implemented this idea in the laboratory, but the experiments focused on systems easily understood [4, 5, 6, 7, 8], where the optimal field was easily calculated, or extremely complex systems that

could not be understood theoretically [9, 10]. Furthermore, none of these prior experiments demonstrated that optical control of a quantum system could have practical applications outside of understanding and controlling quantum dynamics, leading critics of the field to complain that coherent control is an impractical way to control systems. Moreover, many thought that there is no hope of understanding the control mechanism for complex systems and that, once controlled, the systems were of no practical value to scientists in other fields. Herschel Rabitz's idea of learning control was also criticized as a naïve approach to science and that experiments are best performed under the direct control of the scientist.

In this thesis, I describe a set of experiments that address these major criticisms of coherent control, and shows that learning control algorithms can, in fact, act as powerful tools for discovering new, useful science. The work described in this thesis represents scientific advances physics, chemical physics, chemistry, and optical engineering. We have applied these learning, coherent control techniques to the control of electron wave packets in atoms, and to the control of rotational and vibrational wave functions in molecules.

The format of this thesis is as follows: the second chapter gives a brief description of learning control and evolutionary algorithms, the third chapter discusses control in atoms, the fourth chapter discusses the control of molecular systems, the fifth chapter discusses useful applications of controlled quantum systems, and the sixth chapter summarizes this work.

In the third chapter, I explain how to achieve the control of high harmonic genera-

tion (HHG) [11, 12, 13] using broad-bandwidth, shaped light pulses. HHG normally produces a frequency comb of harmonic lines that are an odd integer multiple of the driving laser frequency. I demonstrate that a learning algorithm can be used to find an optimal HHG spectrum to produce a single harmonic, resulting in a quasi-monochromatic x-ray spectrum that is concentrated in a femtosecond duration pulse. In this experiment, the learning algorithm found a new solution that was previously unknown, and would have likely gone undiscovered. This spectrum has applications to a wide variety of time-resolved x-ray experiments because it generates a very short duration x-ray pulse without the need for spectral filtering that might broaden the pulse. Not only does the optimal pulse shape modify the HHG spectrum, it also increases the conversion efficiency of energy from the fundamental driving laser pulse to the x-ray pulse, compared to the conversion efficiency of a transform-limited pulse into HHG light. This result was very surprising, and is the first demonstration of the optimization of a nonlinear process by a non transform-limited laser pulse. Finally, since HHG is the most "extreme" nonlinear process that has ever been observed. This thesis describes the coherent control of a quantum system with the highest nonlinearity to date.

Chapter 3 also discusses models of HHG generation [14, 15, 16, 17, 18] that can describe most of the experimentally observed features. A theoretical model was used in conjunction with a learning algorithm, and the result was that the model exhibits excellent agreement between theory and experiment. Through our understanding of the control of HHG [13], we discovered a new phase-matching mechanism that occurs

between the interaction of a single atom and a pulse of light. This phase matching mechanism is the result of the control of the phase of an electron wave packet with 25 attosecond precision. Thus, this work is the first experimental demonstration of the control of any process with attosecond precision. These results directly refute assertions that the control mechanism of a complex quantum mechanical system can not be determined from a learning control experiment. In fact, in our experiment, the learning algorithm discovered new science.

In the fourth chapter, I apply the learning control "machine," developed originally for the HHG experiments, to the problem of controlling molecular systems. The ultimate goal of such control is to manipulate chemical reactions [19], resulting in the synthesis of products that would be otherwise difficult, or impossible, to synthesize by other methods. The essential idea is to use an optimal control pulse to distort molecules in such a way that a barrier to a reaction pathway is reduced or eliminated, allowing a reaction to proceed. A surface catalyst acts in much the same way in that the surface itself distorts the reactants in order to initiate a chemical reaction. Thus, the shaped laser pulse in this scheme acts as a laser catalyst.

Using the learning machine, we performed experiments that manipulated vibrational and rotational degrees of freedom in molecular gasses and vapors [20, 21]. Due to the short duration of our laser pulses, we are able to induce coherent motion in molecules that exhibit substantial "random" motion, i.e., in gasses at room temperatures, and where the gas is held at atmospheric pressure. This approach holds the promise of coherently "driving" chemical reactions in "real-world" condi-

tions, resulting in macroscopic quantities of products. Furthermore, our approach is non-resonant and can be applied to any molecular system.

In these experiments, we demonstrated selective control (or heating) of specific vibrational modes in multimode molecules. We have also developed a new form of molecular spectroscopy that monitors molecular wave packet motion by analyzing the modified power spectrum of a probe pulse. The probe spectrum experiences changes when phase modulated by the time-dependent molecular polarizability generated by the pump pulse. This approach allows us to monitor the evolution of ro-vibrational wave packets and observe and control overtone and combination band vibrational excitation. The observation of overtone excitation using this technique [21] is an important development towards mode-selective chemistry. Finally, we observe indications of control of the reaction rate of a bimolecular chemical reaction with shaped laser pulses.

Learning control has been shown to be a powerful tool for the control of complex quantum systems. This approach allows one to control the system, even if the details of the system are unknown. During the course of an optimization, many "experiments" are performed, each with a different pulse shape. These distinct pulse shapes each probe the quantum system in a different way. By collecting and analyzing these experimental results, it may be possible to uncover information about the system under control.

We have taken a first step towards using the learning algorithm itself to determine information about the system under control. The learning algorithm was modified

so that the pulse shaper was "penalized" (i.e., reducing the fitness value) for pulse shapes that deviated from a target shape. The effect is that control knobs that do not result in an improvement of the system control are not used. The result is that the optimal pulse shapes are simplified, and only the essential control features are preserved. These experiments are the first demonstration of the use of modified cost functionals to learn about the system under control. The simplified optimal pulse shapes clearly demonstrate the control mechanism and illustrate the promise of using the algorithms to learn about the systems under investigation.

In the first section of chapter 5, I discuss the generation of controlled molecular rotational wave packets, and demonstrate a new technique for compressing ultrafast optical pulses [22]. This technique is applicable at any wavelength from the deep ultraviolet (deep-UV) to the infra-red (IR) regions of the spectrum. In our scheme, one light pulse was used to create a set of "designer" spinning CO_2 molecules inside a hollow glass fiber. The "designer" nature of the spinning CO_2 molecules is that they align and realign periodically, having been set spinning (or "kicked") at the same time by the light pulse. This light pulse is 20 femtoseconds in duration at a wavelength of 800nm, in the near-IR (where it is easy to generate such fast pulses of light). A second, longer duration light pulse with a different wavelength (color) is then sent into the same fiber, at precisely the right time where it encounters the spinning molecules. The aligning molecules act like microscopic molecular modulators - tiny versions of the modulators used to encode optical pulses for transmitting voice and data information across optical networks. This coherently-evolving molec-

ular system exhibits faster modulation times (ps) than is possible using electro-optic modulators, corresponding to the time of less than one picosecond during which the molecules come into and then go out of alignment. This system thus has an enormous bandwidth exceeding 40 THz. Such ultrafast modulation causes dramatic spectral modulation of the second pulse, increasing its bandwidth by over an order of magnitude. This increased spectrum means that the time duration of the second pulse can also be compressed by an order of magnitude, provided that all the new colors in the light pulse can be made to arrive at the same time. One very attractive feature of this scheme is that this second pulse can be compressed by simply sending it through a piece of glass. This is much simpler to implement than traditional approaches to compressing light pulses that require sending the spectrally-broadened pulse through a prism or grating pair. It is also far less lossy (particularly in the UV), and far more compact. Thus far we have demonstrated that this scheme can easily generate 30 femtosecond duration light pulses. The next step will be to generate < 5 femtosecond light pulses in the deep-UV and vacuum-ultraviolet, where materials and many small molecules can be probed.

In the second section of chapter 5, we show that, by using a phase-matched hollow-fiber geometry, the EUV light generated exhibits the highest inherent spatial coherence of any source in this region of the spectrum [23]. Since this source exhibits full spatial coherence at very short wavelength, this light source represents the smallest inherent effective source-size of any light source yet created. While studying the spatial coherence of HHG, I realized that by measuring the spatial coherence, the

power spectrum of the incident field could be determined [24]. We demonstrate this by comparing the deconvolved spectrum with that obtained by a traditional grating spectrometer. HHG generated in a hollow-fiber geometry is constructed on a fraction of an optical table. Finally, in the third section of Chapter 5, I show the application of this versatile source to coherent x-ray imaging that may be useful for plasma and biological imaging.