Chapter 1

Introduction

Being able to change the properties of physical objects, to manipulate the forces of nature is one of the key desires that defines human nature. Controlling one's surrounding triggered the development of more and more sophisticated tools. Today, we have tools to affect matter and light within many orders of magnitude in size and power, reaching scales where the quantum nature of all objects becomes apparent and new tools are required. A femtosecond (10^{-15} s) pulse shaper is such a tool, being able to control light on such short time scales by modulating the frequency components which comprise an ultrashort laser pulse. Originally intended for counteracting phase distortions, they were refined to synthesize customized waveforms [1, 2], enabling them to be used for studying and influencing the motion of molecules, a technique now known as coherent control [3] which became a renowned field within molecular physics and chemistry [4, 5, 6]. Another boost in applicability occurred when general search strategies were incorporated into the pulse shaping routine [7], enabling it to experimentally find light fields suitable to perform specific tasks, contrary to traditional chemical methods, by utilizing quantum wave interferences (optimal control experiments, OCE) as predicted by optimal control theory (OCT) [8, 9, 10].

These search algorithms borrow concepts from biology - mutation, selection, and reproduction - and are therefore called evolutionary algorithms. They were invented in the 1960's [11, 12] and are widely applied: in design, logistics, computational intelligence, manufacturing, for classification and management purposes, even evolutionary art and music [13]. Despite the vast parameter space of possible light fields producible by a pulse shaper, they have shown to be extremely efficient in finding solutions and optimizing molecular processes. However, there are usually some open questions that remain: if there is one outstanding optimal solution or many approximately equally suited solutions, how search space topology looks like, or if other strategies might be more successful.

Also, by all appearance, the algorithmic techniques commonly employed in OCEs did not keep pace with the rapidly evolving conceptual methods of evolutionary computation, forgetting the fact that it was the interdisciplinary leap of Rabitz et al. to computer sciences which brought so much insight to physical and chemical processes. More recent advances [14], amongst them specialized algorithms that target several goals at once (multi-objective evolutionary algorithms) could, for example, become a valuable addition to the experimentalist's repertoire, helping to answer some of the fundamental questions of the field [15].

But optical techniques for pulse shaping have also evolved, adding the polarization of the electromagnetic field to its manipulative capabilities [16, 17]. Femtosecond polarization pulse shaping produces waveforms where the electrical field oscillates in three dimensions, which potentially improves control over quantum objects (whose wavefunctions are also three-dimensional) and all kinds of methods of optical spectroscopy considerably, including improved interaction of rapidly changing polarization states with chiral molecules, and many other applications [18]. Such pulse shaper setups modulate the spectral phase and polarization in a restricted manner, recent advances [19, 20, 21] in pulse shaper design enabled a more sophisticated degree of control over the fields.

This thesis sets out to examine new concepts of pulse shaping, on a terrain where experiment and methodology have a common focal point, increasing systematization, exploring several novel approaches, and implementing them in first, proof-of-principle experiments. Small alkali clusters such as NaK are a suitable model system for testing new control schemes as they are theoretically well enough understood, still have distinguishable control paths, and can be photoionized by a three-photonic process within the bandwidth range of commercially available Ti:sapphire lasers. Their vibrational dynamics can be resolved with femtosecond pulses [22, 23]. Their controllability, which exploits laser-induced wavepacket dynamics [24, 25, 26, 27] makes them ideal candidates for comparative studies. In Chapters 2 and 3, the experimental setup and theoretical concepts will be introduced. Chapter 4 will, for the first time in an OCE, explore the concept of multi-objective optimization by revealing the transition frequencies utilized in ionizing the sodium-potassium dimer in a three-photonic process, introducing the "control pulse cleaning" technique. Chapter 5's objective is to strengthen the persuasiveness of OCE results by monitoring an evolutionary algorithm "at work", while optimizing molecular processes (ionization of NaK and isotope selective ionization on K_2). By tracking the development of temporal and spectral features of the electrical field, such as sub pulses or spectral peaks throughout an experiment, a "course analysis" can be performed, which will be employed frequently in this work. Sub pulses will be starring in Chapter 6, being the means of restricting the amount of possible pulse shapes by restructuring search space in a physically intuitive way, which is commonly referred to as parametric pulse shaping while performing comparative experiments on NaK using both pixel-by-pixel and parametric encodings.

The major developmental part of this thesis is investigating the temporal polarization shaping capabilities of two new pulse shaper designs, one incorporating the amplitude (Chapter 7), and one providing full interferometric field control (Chapter 8), simultaneously developed during the timeframe of this work [28]. In both chapters, a parametrization of the temporal electrical field is applied, allowing to tailor customized polarization transients, which were also implemented experimentally. With the parametrization, comparative experiments on the ionization of NaK with polarization shaped pulses compared to 'free' optimization of phase, amplitude, and polarization will be carried out at the end of Chapter 7. After discussing arbitrary temporal profiles at the end of Chapter 8, an attempt to retrieve interferometrically generated polarization pulse trains using a multiobjective evolutionary algorithm concludes the thesis.