Chapter 10

Summary and Outlook

This thesis set out to expand the available techniques of femtosecond pulse shaping on an applicatory and methodological level, testing new procedures on model-system alkali dimers. Deploying the two instruments of choice, fs-pulse shapers and evolutionary algorithms, a number of novel approaches on how molecular processes can be influenced were tested.

The first strategy applied was *influencing* the control algorithm in a way that it detects otherwise hidden features, such as the transition frequencies ionizing the NaK molecule. By changing the cleaning strength it was shown that the results of the experiment change while simultaneously, the observed amplitude patterns became more structured, allowing to identify a number of $B(3)^1\Pi \leftarrow A(2)^1\Sigma^+$ and $A(6)^1\Sigma^+ \leftarrow A(2)^1\Sigma^+$ transitions. The method of exposure in a general scheme of things was a multi-objective, Weighted-Sum Approach with Weight Scanning, applied in order to determine the Pareto-optimal front resulting from the conflicting objectives: ion yield and minimal spectral effort.

To survey the inner workings of free optimization, a method, dubbed *course analysis*, was devised - visualizing the progress of predefined parameters in scatter diagrams. This way, a general overview could be drawn, the chronology of convergence could be studied, the credibleness of optimized solutions assessed by statistical means, and even correlations between parameters became apparent. For an optimization of the NaK ion yield, the order of convergence could be established, with temporal sub pulse positions first, and relative intensities later; for isotope-selective ionization on K_2, the dominance of spectral over temporal features could be substantiated. The results express a general recommendation to perform a course analysis when "experimenting" with algorithm settings, incorporating new operators, defining new search spaces, and optimizing new (molecular) targets to ensure a proper execution and convergence.

With the successfulness of "reading" parameters, the obvious next step, *redefining* search space, using physically motivated parameters such as the properties of temporal sub pulses were applied in order to reduce search space's size by a substantial amount, resulting in faster convergence times and less complex results. Having the pulse shaper dependably create pulse forms which may be also unsymmetrical in time, results from NaK^+, from free optimization could be approached in a stepwise manner by allowing first three, then six sub pulses to be parametrically adapted. Another spectral parametrization, crafted to locate transition frequencies was able

to demonstrate its usefulness as a complementary approach to pulse cleaning.

The new horizons accessible with polarization pulse shaping enable an *expanding* field of applications; providing an improved access to the three-dimensional nature of matter. To that topic, a scheme of calculating, generating, and visualizing custom-tailored, polarization-enabled waveforms in the time domain was developed. The recently developed serial setup which, for the first time, adds the amplitude to polarization shaping, was studied for its capabilities to generate such waveforms, including the impact of the spectral amplitude on temporal fields. For an implementation of the pulse parameters into the algorithm, a decoupled scheme was compiled by restricting the major axis angles of the temporal polarization ellipses. As a first demonstration, an experimental comparison of free and parametric optimizations on NaK was conducted with the result that the parametric optimization gained comparably high ion yields with half the number of alternating linearly polarized, orthogonal sub pulses via consecutive $\Sigma - \Sigma$ to $\Sigma - \Pi$ transitions. Furthermore, an experiment with different boundary conditions successfully excluded ionization via the first round-trip of the first excited state wavepacket.

Afterwards, an examination of the interferometric, parallel setup's potentiality to create arbitrarily polarization-shaped pulse forms in time was conducted, demonstrating parametrically calculated, and experimentally obtained double pulses without artifacts like side pulses. Additionally, the feasibility of bandwidth-limited laser systems to generate general temporal profiles, including intrapulse modulation, was discussed.

In the last chapter, both concepts polarization shaping and multi-objective algorithms were combined in order to retrieve interferometrically generated pulse forms with a detection scheme that does not involve interferometry by itself. The scheme involves a set of SFG-cross-correlations and pulse spectra which are simultaneously fitted to the measured target values. As a proof-of-principle, the algorithm was utilized to recollect simulated input data, demonstrating that there is indeed enough information contained and showed convergence to a set of experimental traces.

Future prospects. A first experiment involving a multi-objective algorithm incorporating Pareto-optimality in femtochemistry could be optimizing ionization versus ionization and fragmentation simultaneously, potentially retrieving the Pareto-optimal front in one single run with a solution set, containing detailed information about the objective correlations. The introduced methods monitoring the progress in search could be improved to deliver the current focus of the algorithm. Also, the search space redefinition of a parametrization could be automated to some degree, reducing the dimensionality to a necessary minimum and providing a correlation of complexity and yield; potentially executed by a multi-objective algorithm. A procedure could be thought of which simultaneously incorporates optimal control theory into the experimental feedback loop. With accurate pulse shaping and enough computing power, testing theoretically obtained pulse forms experimentally and the other way around could, in principle, achieve an immediate convergence between theory and experiment. Even more exotic strategies could be employed for femtochemistry: For example to train a neural network to "respond" similarly as a molecule or a molecular reaction. Having training grounds like feedback-loop exper-

iments, a fully-qualified network could theoretically be able to operate on its own, responding to input pulse shapes with the same output as a real molecule.

As a prospect, polarization shaping might become one of the standard tools for enquiring molecular systems, providing a higher efficiency, and opening new levels of control. For pulse shaping techniques, apart from a commercially manufactured quadruple-layer modulator, which would be able to provide full polarization control without interferometry, 2D pulse shapers [176] could be upgraded with polarization shaping, providing new possibilities of spatio-temporal control. Being able to project different polarization states to particular locations would generate interesting field properties with possible applications in nanophotonics [177]. When broadband, white-light sources were used with polarization shaping, rather unusual electrical fields, where the field vector bends with a strong curvature, could be generated.

With 3D-molecular alignment using intense, nonresonant, elliptically polarized fields [154], a higher degree of controllability can be obtained. Performing photoisomerization [178] with polarization shaped pulses could gain particular attention in the next years. For such a process, the altering geometry causes adiabatically changing orbitals and transition dipole moments which could be induced/addressed by polarization shaped light with the right frequency/polarization state at the right time. Similarly, "laser distillation" of chiral enantiomers [157, 179] including complex biological molecules could become a wide-spread reality and benefit, for example, pharmaceutical research, as many drugs are chiral. For optics, the dependence of high-harmonic generation on linear polarization could be exploited in order to produce attosecond pulses, using intrapulse-shaped, elliptical-to-linear polarization states [159, 180]. A recent application used polarization shaped pulses to manipulate the optical near-field in the vicinity of silver nanostructures. Achieving subwavelength control [142] could possibly be further extended to quantum dots or wells [181] or for quantum information processing. Further possible fields of application include super-continuum-generation, filamentation in air, data communication, or periodic electron circulation in molecules [182].