1. INTRODUCTION

In 1926 E. Schrödinger published his work "An Undulatory Theory of the Mechanics of Atoms and Molecules" [1], in which he stated the equation of motion for microscopic particles, like molecules, atoms, or electrons. This equation is known today as the time-dependent Schrödinger equation. The motion of these microscopic particles can be influenced by external electric or magnetic fields, for example by a laser field. The first working implementation of the laser by T.H. Maiman in 1960 opened up a practical way to control this microscopic world. One objective of such laser control was the formation or breaking of a certain bond in a molecule. This seemed to be possible if the laser was tuned to the resonance frequency of that particular bond. However, it turned out that the molecule was redistributing the laser energy too quickly so that a "resonance catastrophe" did not occur. This effect, the so called internal vibrational relaxation (IVR), required a more clever excitation strategy and further technological advances. The advent of femtosecond laser pulses in the 1980's and the possibility to observe the ultrafast motion of the nuclei in molecules [2, 3] for which A. Zewail was awarded the Nobel Prize in chemistry in 1999, meant the next big step towards laser-assisted chemistry.

The last missing piece was a sophisticated technology [4] for shaping the laser pulse. Not too long ago, the goal of controlling a complex chemical reaction with coherent light was finally achieved: For example, in 1998 Assion $et\ al.$ [5] showed that the product ratio $CpFeCOCl^+/FeCl^+$ of the organo-metallic compound ($CpFe(CO)_2Cl$) can be either maximized or minimized by a specially tailored light pulse; or in 2001, Levis $et\ al.$ [6] demonstrated a rearrangement of molecular fragments. In both of these experiments adaptive laser pulse shaping techniques [4, 7] have been applied, i.e., a computer analyzes the outcome of the experiment and modifies the laser pulse shape to optimize the yield of a predefined reaction product (discussed in detail in Sec. 1.1). This process is repeated until the optimal laser pulse is found. The pulse contains a lot of additional information about the reaction pathway, from which in turn we can learn about the molecule and its interaction with light. This has been demonstrated recently in a joint effort of theory and experiment: Daniel $et\ al.$ [8] (2003) were able to optimize a pulse to control the product ratio $CpMn(CO)_3^+/CpMn(CO)_2^+$ of the organo-metallic compound $CpMn(CO)_3$, and subsequently decipher the mechanism with theoretical models.

However, laser controlled assembly of arbitrary molecules, especially in large quantities, is still a long-term objective. In addition to further technological advances, it is of utmost importance to have powerful theoretical methods available. The questions that theory has to answer can be divided into two classes: The first class is that of $controllability$ [9], or in other words: Given a certain quantum system (e.g. a molecule) can the control target (a certain reaction product) be reached at all with the given controller (e.g. a laser)? The second class concerns the problem of finding the best way to achieve a given control objective, e.g., the optimal laser pulse to break a particular bond in a molecule. Such theoretical predictions are very important to gain insight into the complexity of the control process, to determine the

experimental parameters, to transfer laser pulse designs to the laboratory, or to compare the optimized pulse from an experiment with the calculated one [10].

Several theoretical approaches have been developed to find optimal laser pulses, ranging from brute-force optimization of a few pulse parameters [11], pulse-timing control [12, 13, 14], Brumer-Shapiro coherent control [15], stimulated-Raman-Adiabatic-Passage (STIRAP) [16, 17, 18], to genetic algorithms [19]. The most powerful approach, in our opinion, is optimal control theory (OCT) which is commonly applied in engineering, for example to design trajectories for satellites and space probes. We will discuss the method and its origins in greater detail in Sec. 1.2. The application of optimal control theory to quantum mechanics (see Chap. 2) started in the late 1980's [20, 21] and shows continuous advances until today. Among the most important developments were the introduction of rapidly converging iteration schemes [22, 23, 24], the generalization to include dissipation (Liouville space) [25, 26, 27], and to account for multiple control objectives [28].

However, computationally optimized pulses have one drawback, namely they often show a very complicated spectrum, especially in the strong field regime. To restrict the spectrum of the pulse to an experimentally feasible one still remains a challenge. In Chap. 3 we suggest an optimization algorithm based on OCT, which is able to deal with constraints on the pulse spectrum and on the pulse energy. We illustrate the algorithm for a one dimensional electron transfer problem and different constraints on the laser pulse. In these examples we calculate laser pulses that drive a quantum system from an initial state to a given final state. That an even more precise control of the quantum system is possible will be demonstrated in Chap. 4. The rapidly convergent schemes [29, 30, 31] and the algorithms developed in Chap. 3 can be used to tailor laser pulses that drive the system along a predefined path in Hilbert space. In particular, we demonstrate the capabilities of this extension to quantum optimal control for a two-dimensional electron transfer problem.

In the last chapter of this work we address the question of extending quantum optimal control to many-particle systems. We will illustrate that this is not a problem in principle, but in practice the numerical solution of the time-dependent Schrödinger equation for the many-particle system proves to be a severe bottleneck. This problem can be solved by using time-dependent density-functional theory (TDDFT), a non-perturbative and in principle exact method that replaces the interacting many-body problem with a noninteracting one. Its "marriage" with optimal control theory will be discussed in Chap. 5.

To summarize, the goal of this work is to develop and improve methods to find optimal controls for quantum systems. An important aspect is the illustration of these methods for generic examples to show that these methods work, to gain experience about the computational effort, and to lay the ground for further research on this exciting subject. Note that the theoretical methods developed here are not restricted to the control of chemical reactions. In particular, the realization of quantum computers [32, 33, 34, 35, 36] or molecular electronics will require tools for a very precise and complete control where technological limitations can be incorporated.

Before we discuss the theorectical foundations of this work we will present a more detailed review on the experimental method of closed-loop learning and the origin of optimal control theory.

1.1   Closed-loop learning experiments

In the following we describe the principles of a closed-loop quantum control experiment using femtosecond laser pulses. In particular, we will focus on the process of laser pulse shaping which provides the connection with our theoretical work. These quantum control experiments have become possible due to the improvement of laser pulse shaping [4, 37, 38] and the implementation of closed-loop learning (CLL) techniques [7]. Experiments using CLL have delivered highly encouraging results, ranging from the control of chemical reactions [5, 6, 8, 39, 40, 41, 42, 43] to the control of high-harmonic generation [44, 45].
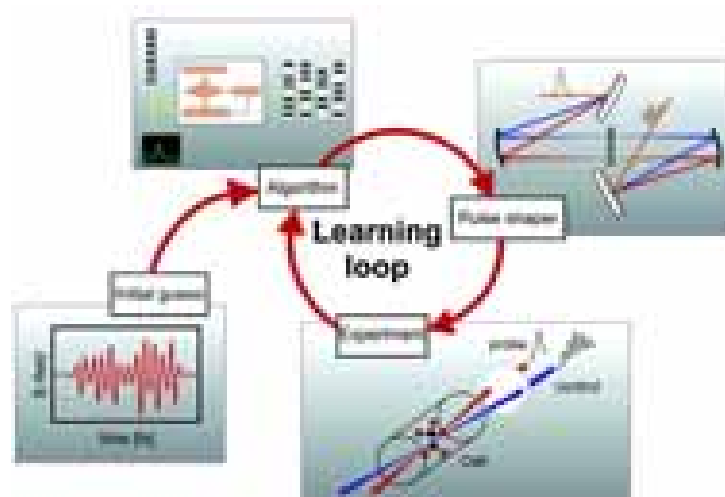

Fig. 1.1: (Color online). Scheme of a closed-loop learning experiment (from Ref. [46]).

To describe the framework of such an experiment we imagine a molecule which consists of three parts: $A-B-C$. The objective is to optimize a laser pulse that breaks the bond between A and B, or in other words, maximizes the yield of $B-C$ fragments over $A-B$ fragments. The optimization proceeds iteratively within a learning loop. The loop starts with using an initial guess for the laser pulse. The pulse hits the molecules (in the gas phase) in a reaction chamber. After the laser interaction the product is analyzed with a mass-spectrometer. The resulting mass spectrum is then fed back into a computer which generates a new pulse shape. The prediction of the new pulse shape is usually done by a genetic algorithm [47]. When the reaction chamber is loaded with a new sample of the molecule the procedure starts again. The loop is continued until the best pulse is found.

To understand some of the problems in these control experiments we have to take a closer look at the process of pulse shaping. The first point to realize is that a femtosecond pulse is broad in frequency space, i.e., many frequency components are needed to form this pulse $(20\,\text{fs} \sim 1000\,\text{cm}^{-1})$. The idea of pulse shaping is to manipulate the phases and the amplitudes of these frequencies which can be achieved in the following way (see the upper right picture in Fig. 1.1): The incoming pulse is targeted on a grating which separates the frequencies in space. Then the light beam enters a liquid crystal modulator (LCM or SLM: spatial light modulator) which consists of several (typically 128 to 512) small "windows" (pixels). Every pixel modifies the amplitude and phase of the incoming light separately, controlled by the computer algorithm. The transmitted beam is then transformed back using a second grating. The first loop of the experiment has to be started with an initial guess for the settings of the

LCM. Since the convergence of the genetic algorithm (speed and final result) might depend on the initial guess a good choice is very important.

Note that this setup presents just the basic principle. The actual experimental setup will be more complicated due to technical aspects. We would like to point out a few limitations relevant for this work. The computational scheme for the determination of the next pulse has to be very robust [48], because the laser might not hit the same amount of molecules at the same place, which will influence the product yield (and cannot be controlled by the algorithm). Apart from these fluctuations the learning algorithm will also "learn about" the influence of the whole apparatus and its environment, i.e., the optimal pulses from an experiment will also contain information about the environment. These two issues make the comparison between theory and experiment difficult.

In the calculation we also have to take into account that the length of the pulse depends on the central wavelength, for example in the infrared (IR) regime pulses can (currently) not be made as short as in the ultraviolet (UV) regime [46]. Note that the spectral resolution also depends on the number of pixels of the LCM.

Finally, we would like to discuss the enormous search space that the genetic algorithm has to deal with. Let us assume a resolution of the amplitude and the phase in each LCM pixel of 4 bit which corresponds to $2^4 = 16$ different settings. With 128 Pixels we have $128^{(2 \cdot 16)} \approx 10^{67}$ different pulses that can be generated. If we fix the amplitude setting and use *phase-only shaping*, we can reduce the number of configurations by a factor $1/2$. If we give up the idea of free optimization and assume a function which describes the settings of the LCM with n parameters [47] we can reduce the search space from 128 to n dimensions and therefore $n^{(2 \cdot 16)}$ configurations. To determine a good parameterization of the pulse, theoretical calculations which take into account the experimental constraints are extremely important.

1.2   Optimal control theory

In this work we use optimal control theory (OCT) to calculate tailored laser fields for the control of quantum systems. This section gives a brief introduction to the origin of OCT and illustrates its use by a simple example within classical mechanics. The application on quantum mechanics will be discussed in Chap. 2.

The birth of OCT dates back to 1697 when Johann Bernoulli published his solution of the brachystochrone problem [49], i.e., to find the shape of the curve down which a bead sliding from rest and accelerated by gravity will slip (without friction) from one point to another in the least time [50]. The next important milestone was the announcement of a maximum principle, which we will discuss below, by the group of L. S. Pontryagin in 1958. Since then the field grew exponentially, triggered by the space race which required applicable and practicable methods to find optimal trajectories for space vehicles, e.g., the re-entry into the Earth's atmosphere (see Ref. [51]).

Nowadays, OCT is used in almost every engineering discipline. Applications employing OCT cover the control of electronic circuits [52], optimal financial investment strategy, optimal control of the immune response [53], and the optimal control of the Earth's climate [54]. It is present in our everyday life, for example, in the control of the airconditioning or the cruise control of cars. Nearly every process in technology that is described by a differential equation and that can be influenced by an external control is optimized with the help of OCT.

The *basic optimal control problem* [55] is formulated in the following way. Given the

equation of motion of a system

$$\dot{\mathbf{x}}(t) = \mathbf{f}\left[\mathbf{x}(t), \mathbf{v}(t)\right], \tag{1.1}$$

with a fixed initial condition $\mathbf{x}(t = 0) = \mathbf{x}_0$ and a set of allowable controls $\mathbf{v}(t) \in U$, we have to determine $\mathbf{u}(t)$ such that the objective function

$$J = J_1[\mathbf{x}(T)] + \int_0^T dt \, J_2[\mathbf{x}(t), \mathbf{v}(t)] \tag{1.2}$$

is maximized. Depending on the control system [Eq. (1.1)] and U, many optimal solutions may exist, in other words $\tilde{\mathbf{u}}(t)$ need not be unique.

To find an optimal control one would have to do a variation of J with respect to $\mathbf{u}(t)$. In practice, it may be rather difficult to determine the change of the objective J for a variation of $\mathbf{u}(t)$ directly. Therefore, one replaces the original objective by

$$\tilde{J} = J - \int_0^T dt \, \boldsymbol{\lambda}^\dagger(t) \left\{ \dot{\mathbf{x}}(t) - \mathbf{f}\left[\mathbf{x}(t), \mathbf{v}(t)\right] \right\}, \tag{1.3}$$

which means substracting "0" from J, since the term in the curly brackets yields zero for any state trajectory $\mathbf{x}(t)$. We have transformed the constrained optimization into an unconstrained one.

To determine the optimal control we now set the variation $\delta \tilde{J} = 0$. This will result in a set of equations, or conditions for optimality, which are called *Pontryagin Maximum Principle (PMP)*.

Theorem (PMP): Suppose $\mathbf{u}(t) \in U$ and $\mathbf{x}(t)$ represent the optimal control and state trajectory for the optimal control problem defined by Eqs. (1.1) and (1.2). Then there is an adjoint trajectory $\boldsymbol{\lambda}(t)$ such that together $\mathbf{u}(t)$, $\mathbf{x}(t)$, and $\boldsymbol{\lambda}(t)$ satisfy

$$
\begin{aligned}
\dot{\mathbf{x}}(t) &= \mathbf{f}[\mathbf{x}(t), \mathbf{u}(t)] & \text{(system equation)}, & \tag{1.4}\\
\mathbf{x}(t = 0) &= \mathbf{x}_0 & \text{(initial state condition)}, & \tag{1.5}\\
-\dot{\boldsymbol{\lambda}}^\dagger(t) &= \boldsymbol{\lambda}^\dagger(t)\mathbf{f}_{\mathbf{x}}[\mathbf{x}(t), \mathbf{u}(t)] + \nabla J_2[\mathbf{x}(t), \mathbf{u}(t)] & \text{(adjoint equation)}, & \tag{1.6}\\
\boldsymbol{\lambda}^\dagger(t) &= \nabla J_1[\mathbf{x}(T)] & \text{(adjoint final condition)}, & \tag{1.7}
\end{aligned}
$$

where $\mathbf{f}_{\mathbf{x}}$ represents the matrix of partial derivatives

$$\mathbf{f}_{\mathbf{x}} = \nabla \mathbf{f} = \left(\frac{\partial}{\partial x_j} f_i(\mathbf{x}, \mathbf{u}) \right).$$

For all t, $0 \leq t \leq T$, and all $\mathbf{v} \in U$

$$H[\boldsymbol{\lambda}(t), \mathbf{x}(t), \mathbf{v}(t)] \leq H[\boldsymbol{\lambda}(t), \mathbf{x}(t), \mathbf{u}(t)] \qquad \text{(maximum condition)}, \tag{1.8}$$

where H is the Hamiltonian

$$H[\boldsymbol{\lambda}(t), \mathbf{x}(t), \mathbf{u}(t)] = \boldsymbol{\lambda}^\dagger(t)\mathbf{f}[\mathbf{x}(t), \mathbf{u}(t)] + J_2[\mathbf{x}(t), \mathbf{u}(t)].$$

Classical mechanics example The use of the PMP can be demonstrated for a simple example in classical mechanics, the so called pushcart problem (taken from Ref. [55]). The goal is to find the optimal acceleration strategy for a cart (in one dimension) such that we maximize the travelled distance but at the same time minimize the total effort. The equation of motion for this problem is simply

$$\ddot{x}(t) = u(t), \tag{1.9}$$

with the initial conditions $x(0) = 0$ and $\dot{x}(0) = 0$. The objective can be expressed in a more mathematical way as

$$J = x(T) - \frac{1}{2} \int_0^T dt\, u^2(t), \tag{1.10}$$

where the first term expresses the maximization of the distance and the second term penalizes the effort. The second-order differential equation (1.9) can be rewritten to a system of first-order differential equations using $x_1 = x$ and $x_2 = \dot{x}$,

$$\begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \end{pmatrix} = \underbrace{\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} u}_{=f(x,u)},$$

and the initial conditions are $x_1(0) = x_2(0) = 0$. The adjoint system Eq. (1.6) is given by

$$\begin{aligned} -\dot{\lambda}_1(t) &= 0, \\ -\dot{\lambda}_2(t) &= \lambda_1, \end{aligned} \tag{1.11}$$

with the final conditions Eq. (1.7),

$$\begin{aligned} \lambda_1(T) &= 1, \\ \lambda_2(T) &= 0. \end{aligned}$$

The solution of the adjoint system yields

$$\begin{aligned} \lambda_1(t) &= 1, \tag{1.12} \\ \lambda_2(t) &= T - t. \tag{1.13} \end{aligned}$$

The Hamiltonian of this system is

$$H[\boldsymbol{\lambda}, \mathbf{x}, \mathbf{u}] = \lambda_1 x_2 + \lambda_2 u - \frac{1}{2} u^2.$$

Since there is no other constraint on $u(t)$, the maximum of the Hamiltonian can be obtained by setting its derivative equal to zero which yields the condition

$$u(t) = \lambda_2(t),$$

and therefore [using Eq. (1.13)]

$$u(t) = T - t.$$

The optimal acceleration strategy is to linearly decrease the applied force with time.

2. QUANTUM OPTIMAL CONTROL THEORY

2.1 Concepts and conventions

This work deals with the control of matter using laser pulses. The problem of light-matter interaction requires three theoretical concepts, namely in which way we describe matter, light, and the interaction between them. Within this section we introduce these concepts, the approximations, and a few naming conventions which shall prevent misunderstandings.

Matter, i.e. atoms, molecules, or solids, is described with the time-dependent Schrödinger equation, while the laser is characterized by an electromagnetic (classical) field. The interaction between them is modeled by the dipole approximation in length gauge (see Appendix B for the derivation). The proper framework to describe the interaction of photons with charged particles (electrons, nulei) is quantum electrodynamics (QED). In this work we will exclusively deal with situations where the photon density is sufficiently high to treat the photon field by a *classical* electromagnetic wave.

Note that all equations and quantities throughout this work are presented in atomic units [a.u.], i.e., $\hbar = e = m_e = a_0 = 1$. The resulting conversion factors for other physical quantities can be found in Appendix A.

The laser pulse is assumed to propagate in z direction and therefore has two polarizations, x and y, so that a test charge is accelerated only in the plane perpendicular to the z axis.

Until Chap. 5 we solely deal with single particles which obey the time-dependent Schrödinger equation

$$
\begin{aligned}
\mathrm{i}\partial_t \Psi(\mathbf{r}, t) &= \hat{H}(t)\Psi(\mathbf{r}, t), \\
\hat{H}(t) &= \hat{H}_0 - \hat{\boldsymbol{\mu}}\boldsymbol{\epsilon}(t), \\
\hat{H}_0 &= \hat{T} + \hat{V},
\end{aligned} \tag{2.1}
$$

where we define

$$
\partial_t \equiv \frac{\partial}{\partial t}.
$$

Furthermore, we have the kinetic energy operator $\hat{T} = -\nabla^2/2$, the potential energy operator $\hat{V}$ which defines the quantum system, and the dipole moment operator $\hat{\boldsymbol{\mu}} = q\hat{\mathbf{r}}$ with the charge q of the particle. For an electron we simply have $\hat{\boldsymbol{\mu}} = -\hat{\mathbf{r}}$.

As mentioned above, the laser is described by its classical electric field which has a total energy of

$$
E_p = \epsilon_0 c A \int_0^T dt \; \boldsymbol{\epsilon}^2(t), \tag{2.2}
$$

where $A = \pi r^2$ is the area covered by the laser focus. Usually r is around hundred μm ($\approx 10^6$ a.u.). In this work we consider the value

$$E_0 = \int_0^T dt \, \boldsymbol{\epsilon}^2(t), \tag{2.3}$$

and refer to it as the laser fluence.

Limitations of this theoretical framework are reached if the spatial extension of the quantum system approaches the wavelength of the radiation, i.e., if we violate

$$L \, 2\pi/\lambda \ll 1. \tag{2.4}$$

In this case we have to go beyond the dipole approximation (see Appendix B). The dipole approximation will also fail in the case of very strong fields when the electron velocity becomes comparable to the speed of light. This can be seen from Eq. (2.4) if we insert $1/\lambda = 1/(cT)$ and $L = vT$. It follows that $v \ll c$. If this relation does not hold it will be necessary to replace the time-dependent Schrödinger equation by the Dirac equation.

If optimal control theory is applied to (non-relativistic) quantum mechanics the more precise term quantum optimal control is only rarely used and most authors refer to it simply as optimal control theory (OCT). This might be misleading when referring to the mathematical literature, where OCT refers to a whole subject. On the other hand, in the experimental physics literature the term optimal control is often used if the laser pulse is optimized with the help of a pulse shaping device in a feedback loop. This is done to distinguish these closed-loop learning (CLL) experiments (see Sec. 1.1) from coherent control experiments where only a very small number of parameters are scanned. To prevent misunderstandings we want to clarify the meaning of the following terms related to this work:

- *Coherent control (CC)*, which is based on the idea that manipulating the interference between different quantum pathways provides a possibility to control the yield of a given observable. As an example consider the transition between two states via two competing pathways, e.g. a one-photon and a three-photon process. By controlling the phase difference between these pulses the occupation of the target state can be controlled. See for example the pioneering work by Shapiro and Brumer [15, 56] and the experimental realization for the control of the product distribution of hydrogen iodide (HI) [57].

- *Closed-loop learning (CLL)*, which is a method to generate optimized laser pulses in the experiment. The basic idea is to couple the output of the experiment after laser irradiation and the pulse shaping device via a computer [7]. In each cycle an algorithm (usually a non-deterministic one, like a genetic algorithm) generates a new laser pulse. Therefore the pulse is adjusted cycle-by-cycle such that it optimizes a given control target. The framework of such experiments is explained in more detail in Sec. 1.1. Note that the method is strictly speaking an open-loop control (see below).

- *Optimal control theory (OCT)*, which is a mathematical technique applied to calculate the (optimal) control functions of a given equation of motion, e.g., the laser pulse in the time-dependent Schrödinger equation. The technique consists in rewriting the constrained optimization problem to an unconstrained one [55, 58]. This work deals exclusively with the application of this method to quantum mechanical systems. The details are discussed in the next section.