Chapter 6

Introduction to Quantum Control

Controlling the motion of atoms and molecules has been a dream since the early days of Quantum Mechanics. Although this quest initially met with failure, the foundation of the Quantum Control (QC) field in the 1980s, throughout the development of various approaches [111, 112, 113], has finally brought this dream to fruition. Quantum Control, sometimes referred to as Optimal Control or Coherent Control, aims at altering the course of quantum dynamics phenomena for specific target realizations. There are two main threads within Quantum Control, theoretical versus experimental control, as typically encountered in Physics. They have experienced an amazing increase of interest during the past 10 years, in parallel to the technological developments of ultrafast laser pulse shaping capabilities, that obviously made it possible to turn the dream into reality. For a broad field review see [114, 115, 116].

The list of successfully closed-loop quantum controlled systems in Physics and Chemistry is practically endless. Examples of early work contain successful applications in fluorescence spectrum manipulation [117], control of quantum wavefunctions [118], vibrational excitation tailoring in polymers [119], molecular rearrangement selectivity [120], chemical discrimination [121], ultrafast solid-state optical switching [122], and photosynthetic bacteria energy transfer [123].

In this chapter we review the fundamental principles of Quantum Control, both in theory and in experiments. Should the reader choose to explore this chapter, an understanding of the basic quantum mechanics principles is assumed, as well as being familiar with the Dirac notation. The reader who wishes to abstract from the physics details could simply view the Quantum Control applications in this study as a non-linear high-dimensional set of problems with real-world applications.
6.1 Optimal Control Theory

Optimal Control Theory (OCT) [124, 125] aims at manipulating the quantum dynamics of a simulated system by means of an external control field, $\epsilon(t)$, which typically corresponds to a temporal electromagnetic field arising from a laser source. The objective to be met in this control process is defined by means of a given physical observable, whose yield is subject to maximization. A quantum control landscape is thus defined as the functional dependence of an observable yield on the control variables, and may be visualized as a surface over the space of all possible controls.

This section is mainly based on [126] (definitions) and on [127, 128] (QC derivations).

6.1.1 The Quantum Control Framework

Formally, we consider quantum systems which are described by Hamiltonians of the form

$$\mathcal{H}(t) = \mathcal{H}_0 - \vec{\mu} \cdot \vec{E}(t)$$

(6.1)

with $\mathcal{H}_0$ as the free-field Hamiltonian, $\vec{\mu}$ the dipole moment operator, and $\vec{E}(t)$ the electric field, within the so-called electric dipole approximation. The electric field is often reduced to a scalar, due to the common assumption of a linear polarization. In practice, a finite number $N$ of states is considered, and thus the Hilbert infinite-dimensional space is practically reduced to an $N$-dimensional space, and therefore the Hamiltonian is typically an $N \times N$ Hermitian matrix.

Given some initial quantum state $|\psi(t=0)\rangle = |\psi_0\rangle$, the time evolution of the quantum state $|\psi(t)\rangle$ is dictated by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \mathcal{H}(t) |\psi(t)\rangle$$

(6.2)

Equivalently, the time propagation operator, typically referred to as the propagator, acts on quantum states in the following manner:

$$|\psi(t)\rangle = \mathcal{U}(t, t') |\psi(t')\rangle \Leftrightarrow |\psi(t')\rangle \rightsquigarrow |\psi(t)\rangle$$

(6.3)

and has the form:

$$\mathcal{U}(t, t') = \mathcal{T} \exp \left( -\frac{i}{\hbar} \int_{t'}^{t} \mathcal{H} (t') \, dt' \right) = \exp (i \mathcal{A}(t))$$

(6.4)

where $\mathcal{T}$ is Dyson’s time-ordering operator, and $\mathcal{A} = \mathcal{A}^\dagger$ is an $N \times N$ Hermitian matrix. Figure 6.1 provides an illustration for the concept of multiple quantum pathways from an initial state to a final state.
Figure 6.1: [Left] Given a quantum system with an initial state $|\psi_i\rangle$, the Quantum Control process aims at steering the system into a desired target state, $|\psi_f\rangle$, by means of the control laser field $\vec{\varepsilon}(t)$. Coherent control relies on the existence of multiple quantum pathways between the two states, as illustrated, which result in interference; The goal is thus obtaining constructive interference in the desired final state, and destructive interference elsewhere. [Right] The quantization of the multiple quantum pathways picture; The transition from the initial state to the target state may be attained in multiple pathways.

Let the target observable operator be $\mathcal{O}$, then the yield of the control process for a pure quantum state is defined as the expectation of the observable operator at time $t = T$:

$$\mathcal{J} = \langle \mathcal{O} \rangle_T = \langle \psi_T | \mathcal{O} | \psi_T \rangle = \left\langle \psi_0 | \mathcal{U}^\dagger \mathcal{O} \mathcal{U} | \psi_0 \right\rangle = \langle \psi_0 | \mathcal{O}_T | \psi_0 \rangle$$  \hfill (6.5)$$
while referring from now on to $\mathcal{U}$ as $\mathcal{U}(T, 0)$, unless specified otherwise.

Let $\mathcal{O}_T$ be diagonalized and spanned by means of its eigenvectors:

$$\mathcal{O}_T = \mathcal{U}^\dagger \mathcal{O} \mathcal{U} = \sum_j \sigma_j |\phi_j\rangle \langle \phi_j|,$$  \hfill (6.6)$$
then the highest eigenvalue $\sigma_{\text{max}}$ corresponds to the maximal attainable observable value.

When an ensemble of quantum states is under investigation,

$$|\Psi(t)\rangle = \sum_j p_j(t) |\psi_j\rangle,$$

it is characterized by the density operator $\rho(t) = |\Psi(t)\rangle \langle \Psi(t)|$. The dynamics of the ensemble is then dictated by the von Neumann equation for the
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density operator $\rho(t)$:
\[ i\hbar \frac{\partial \rho(t)}{\partial t} = [\mathcal{H}(t), \rho(t)] \quad (6.7) \]

where $[A, B] = AB - BA$.

An observable is measured by $\text{Tr} (\rho O)$, and the Quantum Control yield is defined respectively by:
\[ J = \langle O_T \rangle = \text{Tr} (\rho_T O) = \text{Tr} \left( U \rho_0 U^\dagger O \right) \quad (6.8) \]

where
\[ \rho_T = \rho(T) = U \rho_0 U^\dagger \]

Additional auxiliary costs may be imposed on the controls due to constraints, e.g., minimal fluence, and construct respectively a quantum control cost functional of the form:
\[ J' = J - \lambda \int_0^T g(\epsilon(t)) \, dt \quad (6.9) \]

However, in this chapter we restrict our treatment to quantum optimal control problems in the absence of these constraints.

**Critical Points: Kinematic Treatment** At a critical point the differential of the control landscape with respect to $U$ vanishes. This is the so-called kinematic treatment of the critical point analysis, and it reads:
\[ \frac{\delta J}{\delta U} = 0 \quad (6.10) \]

Since $U^\dagger U = I$, we get
\[ \delta U^\dagger U + U^\dagger \delta U = 0 \]

for any $\delta U$. Eq. 6.10 may be rewritten now as
\[ \frac{\delta J}{\delta U} = \text{Tr} \left( \delta U \rho_0 U^\dagger O + U \rho_0 \delta U^\dagger O \right) = \text{Tr} \left( \delta U U^\dagger \rho_0 O - U \rho_0 U^\dagger \delta U^\dagger O \right) = \text{Tr} \left( \left[ \rho_0, U^\dagger O \right] U^\dagger \delta U \right) = \langle U \left[ U^\dagger O \rho_0 \right], \delta U \rangle = 0 \quad (6.11) \]

leading to the important result that at a critical point
\[ \left[ O_T, \rho_0 \right] = \left[ U^\dagger O \rho_0 \right] = 0 \quad (6.12) \]

Hence, $O_T$ and $\rho_0$ commute, and thus are simultaneously diagonalizable, according to this kinematic treatment.
6.1. Optimal Control Theory

Critical Points: Dynamic Treatment The *dynamic treatment*, which considers the differential of the observable with respect to the control field \( \epsilon(t) \), is typically based on the chain rule:

\[
\frac{\delta J}{\delta \epsilon(t)} = \frac{\delta J}{\delta U} \cdot \frac{\delta U}{\delta \epsilon(t)} \tag{6.13}
\]

The dynamic picture is more complex, and is subject to a more delicate treatment, accordingly. At a critical point, it could be shown [127] that this differential yields:

\[
\frac{\delta J}{\delta \epsilon(t)} = \text{Tr} \left( [O_T, \rho_0] B(t) \right) = 0, \tag{6.14}
\]

where \( B(t) = (i/\hbar) U^\dagger(t,0) \nabla \mathcal{H}(t) U(t,0) \).

The crucial assumption which is made by the *dynamic treatment* states that the matrix \( B(t) \) forms a set of \( N^2 \) linearly independent functions for all time \( 0 \leq t \leq T \). This assumption obviously leads to \( [O_T, \rho_0] = 0 \), as in Eq. 6.12, and to the conclusion that the observable and the density matrix commute in the dynamic picture as well.

When diagonalizing the density matrix, the same eigenvectors of the observable (Eq. 6.6) are used:

\[
\rho_0 = \sum_j \lambda_j |\phi_j\rangle \langle \phi_j| \]

The control yield now reads:

\[
J = \text{Tr} \left( \sum_i \sum_j \sigma_i \lambda_j |\phi_i\rangle \langle \phi_j| \phi_j\rangle \langle \phi_j| \right) = \text{Tr} \left( \sum_j \lambda_j \sigma_{\pi(j)} |\phi_j\rangle \langle \phi_j| \right) = \sum_j \lambda_j \sigma_{\pi(j)} \tag{6.15}
\]

where \( \pi(j) \) denotes a permutation, out of \( N! \) possible permutations of these eigenvalues, assuming that there is no degeneracy.

Special Case: \( P_{i \rightarrow f} \) A special state-to-state case is commonly considered, where the transfer of a pure initial state \( |i\rangle \), into a desired final state \( |f\rangle \), is subject to maximization. It is expressed accordingly through pure density projectors: A density matrix \( \rho_0 = |i\rangle \langle i| \), and an observable \( \mathcal{O} = |f\rangle \langle f| \). This *population transfer* problem has a simpler theoretical treatment, and moreover, is also commonly encountered in real-world applications. More explicitly, let us consider the time evolution operator by its matrix element,

\[
U_{if} = \langle i| U |f\rangle \tag{6.16}
\]

being a functional of the control field, \( U = U [\epsilon(t)] \). Then the quantum control *population transfer problem* is posed as maximizing the probability:

\[
P_{i \rightarrow f} = |U_{if}|^2 \tag{6.17}
\]
6.1.2 Controllability

By assessing the controllability of the quantum system we aim at attaining the existence of a control field which obtains the maximal target yield, without studying the nature of the landscape. This is essentially different from optimality analysis, which aims at locating extrema on the landscape, without necessarily conducting controllability assessment.

A powerful aspect of Quantum Control theoretical landscapes is the ability to assess perfect controllability of the system, with hardly any assumptions on the quantum system, as presented in the following theorem:

**Theorem 6.1.1.** Assuming controllability of the system, the only extrema values for Quantum Control of population transfer corresponds to perfect control:

\[ \mathcal{P}_{i\rightarrow f} = 1 \]

In the following we shall outline the principal steps of the proof for this claim, following [129, 130]. For simplicity, we choose to consider the special case of \( \mathcal{P}_{i\rightarrow f} \), subject to dynamic treatment. Note that \( \mathcal{P}_{i\rightarrow f} = |U_{if}|^2 \).

**Proof Idea** A dynamic treatment of a landscape extremum reads:

\[ \frac{\delta \mathcal{P}_{i\rightarrow f}}{\delta \epsilon(t)} = 0 \]  

(6.18)

Using the identity

\[ \langle i | U | f \rangle = \langle i | \exp (iA) | f \rangle, \]

where \( A = A^\dagger \) is an \( N \times N \) Hermitian matrix, Eq. 6.18 may be rewritten as

\[ \frac{\delta \mathcal{P}_{i\rightarrow f}}{\delta \epsilon(t)} = \sum_{p,q} \frac{\partial |U_{ij}|^2}{\partial A_{pq}} \frac{\delta A_{pq}}{\delta \epsilon(t)} = 0 \]  

(6.19)

The same crucial assumption made regarding Eq. 6.14 is made here, reducing the dynamic picture into the kinematic picture: The uniqueness of the functional dependence of the matrix elements \( A_{pq}[\epsilon(t)] \) on \( \epsilon(t) \) is implied by the assumed controllability of the system.

Eq. 6.18 can now be satisfied by

\[ \frac{\partial |U_{ij}|^2}{\partial A_{pq}} = \frac{\partial}{\partial A_{pq}} \langle i | \exp (iA) | f \rangle^2 = U_{ij}^* \frac{\partial U_{ij}}{\partial A_{pq}} + U_{ij} \frac{\partial U_{ij}^*}{\partial A_{pq}} = 0 \quad \forall p\forall q \]  

(6.20)

Further examination of this equation (see Supplemental Online Material of [129]) leads to the following conclusion:

\[ U_{ij} = \exp (i\alpha), \quad \alpha \in \mathbb{R} \]  

(6.21)
and thus $|U_{ij}| = 1$, and the claim is satisfied accordingly:

$$\mathcal{P}_{i \rightarrow f} = 1$$  \hfill (6.22)

The most general case would be the dynamical treatment of the extrema of $\mathcal{J} = \text{Tr} (\rho T \mathcal{O})$. An equivalent theorem, stating that the extrema of such landscapes would correspond to perfect control or no-control, exists and is proven in [127]. Furthermore, the latter article presents important results regarding the nature of the landscape, which we choose to review here briefly:

1. **The Slope** An upper bound of the gradient reads:

$$\left| \frac{\delta \mathcal{J}}{\delta \epsilon(t)} \right| \leq \frac{2}{\hbar} \| \mathcal{O} \| \times \| \tilde{\mu} \|$$  \hfill (6.23)

where the linear polarization of the electric field was assumed for simplicity. In practical realizations, it is reasonable to expect that the landscape slope up to the global maximum will have no steep regions, suggesting that the **optima are robust**.

2. **Hessian at the Global Maximum** The Hessian matrix has typically at most $(2N - n_p - 1)$ non-zero negative eigenvalues ($n_p$ is the number of non-zero eigenvalues of $\rho_0$), where the rest correspond to the null space, which is spanned by their eigenfunctions. Thus, there exist saddle points, but they do not introduce any obstacle toward locating the global maximum.

3. **Robustness** The trace of the Hessian matrix at the top of the landscape suggests a robust global maximum in any practical realization, and gets more robust as the dimensionality $N$ increases.

We conclude this section by stating the following corollary:

**Corollary 6.1.2.** *Quantum Control landscapes have extrema that correspond to perfect control or no-control. Furthermore, given a controllable quantum system, there is always a trap-free pathway up to the top of the control landscape from any location, allowing the location of the global maximum with first-order (gradient) information.*

### 6.1.3 Control Level Sets

Given the results obtained in the previous section, stating that the gradient of the yield function vanishes only at the top of the landscape, it is possible to draw an important conclusion regarding the existence of **level sets**\(^1\) in the landscape.

\(^1\)This important concept, which was discussed previously in the context of global minimum definition (see Eq. 1.2 and Theorem 1.1.1) or the basin definition (see Definition 2.3.1), is revisited here in the context of success-rate.
Let \( f : \mathbb{R}^n \to \mathbb{R} \) be under investigation, with a point in the landscape which satisfies:

\[ f^* = f(\bar{x}^*), \quad \nabla f(\bar{x}^*) \neq 0 \]

The so-called Implicit Function Theorem states that there exists an \((n - 1)\)-dimensional manifold near \( \bar{x}^* \) with the same function value of \( f^* \), and its tangent plane at \( \bar{x}^* \) is perpendicular to \( \nabla f(\bar{x}^*) \).

This theorem can be applied directly to Quantum Control landscapes, due to the results presented previously. While climbing up the QC landscape, every associated yield value along the way has a corresponding manifold, which can potentially be explored by continuous trajectories.

Obviously, we cannot apply the same theorem in order to draw an equivalent conclusion regarding the existence of a level set at the top. However, it is possible to show that a denumerable infinite number of solutions exists at the top of the landscape. Under mild assumptions, it was shown in \([131, 132]\) that in the absence of constraints an infinite number of solutions will exist for a general Quantum Control problem. The proof is based on functional analysis treatment, subject to perturbation formulation, and is beyond the scope of this study.

We may conclude that Quantum Control landscapes are not only easy in terms of the location of its maxima, i.e., optimal controls, as suggested previously, but also offer a rich diversity of multiple solutions.

The careful reader should note that the above conclusions are valid only for Theoretical Quantum Control landscapes, where no constraints whatsoever are posed. In the context of our work on Quantum Control optimization, to be presented in the following chapters, the landscapes under study will always be underposed by multiple constraints, and thus the degree to which these theorems are applicable is generally unknown. However, possible corroboration of the given Quantum Control landscape analysis might be identified in our work, and will be discussed.

The D-MORPH Algorithm  Standard algorithms for the optimization of optimal control are designed for climbing-up the control landscape and locating its extrema at the top, but are not capable of examining the level-sets of the landscape.

A special algorithm for exploring control fields on a given landscape level-set was designed by Rothman et al. \([133, 134]\), aiming to produce trajectories throughout control fields which correspond to a preserved observable. This algorithm is referred to as Diffeomorphic Modulation under Observable-Response-Preserving Homotopy (D-MORPH), and it allows an examination of various control fields which attain the same yield, but may have different physical properties, e.g., fluence.
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The basic idea of the D-MORPH algorithm is to constrain the quantum dynamics such that the observable is preserved for all control fields at a given time. It is convenient to introduce a dummy exploration variable \( s \), and present the quantum dynamics accordingly (\( 0 \leq s \leq 1 \)):

\[
\epsilon(s, t) \leftarrow \epsilon(t) \\
\mathcal{H}(s, t) = \mathcal{H}_0(s) - \bar{\mu}(s) \cdot \bar{\varepsilon}(s, t) \\
i\hbar \frac{\partial}{\partial t} |\psi(s, t)\rangle = \mathcal{H}(s, t) |\psi(s, t)\rangle \\
\langle \mathcal{O}(s) \rangle_T = \langle \psi(s, T) | \mathcal{O} | \psi(s, T) \rangle
\]

Given the desired target observable value at time \( T \), denoted by \( C_T \), the D-MORPH algorithm aims at locating control fields \( \epsilon(s, t) \) that satisfy the following non-linear equation:

\[
F(s) = \langle \mathcal{O}(s) \rangle_T - C_T = 0
\]

A homotopy path can then be obtained by solving the following differential equation:

\[
\frac{dF(s)}{ds} = \frac{d\langle \mathcal{O}(s) \rangle_T}{ds} = 0
\]

We only outline the D-MORPH algorithm above, while omitting most of the explicit derivations of the integration process to be followed. We refer the reader to [133, 134] for those details.

We conclude this section with the following corollary:

**Corollary 6.1.3.** A general controllable Quantum Control problem has a rich landscape with an infinite number of optimal solutions, corresponding to perfect control. Climbing-up to the top of the landscape reveals control level-sets at every yield value, with manifolds which can be explored with continuous trajectories. The latter may be obtained by means of the D-MORPH algorithm.

6.1.4 Computational Complexity

The framework of this study is global optimization, where the focus here is on optimal control of theoretical quantum systems, by means of optimally determining a control field parameterized by \( n \) function values. As such, studying its computational complexity aspect would traditionally consider the resources required for the optimization algorithm as a function of the dimensionality of the search space, denoted here by \( n \).

Due to the special nature of quantum systems, studying the time complexity of OCT optimization algorithms with respect to the Hilbert space dimensionality \( N \) is of considerable interest. In fact, when considering the computational expense of resources for a given OCT optimization problem,
the propagation of the Schrödinger equation is far more substantial than the scalability of the control field to be optimally determined. Accordingly, the underlying optimization challenge seems to stem from the size of the quantum system $N$, rather than from the number of the electric field function values to be optimally determined, $n$.

Hence, OCT computational complexity research focuses on the Hilbert space dimensionality $N$. It should be noted that *kinematic optimization treatment* of OCT, which is typically not of this study’s focus, considers Hermitian matrices of dimension $O(N^2)$ as the control. Thus, in the latter case the time complexity anyway has to be treated in terms of $N$.

We review here briefly a single test case.

**Time Complexity of a Pure-State Quantum System**

Following Corollary 6.1.2, we know that an OCT search can be algorithmically implemented by means of gradient-based steps. It is thus convenient to consider the *gradient flow*, which is defined as the trajectory followed by the algorithm when the step update follows

$$-\nabla_U J(U)$$

The latter is based upon the *kinematic treatment* (see Eq. 6.10 and its derivations). It is then possible to estimate an upper bound for the required time for convergence into an $\varepsilon$-neighborhood of the global maximum for the class of observable maximization problems [135]. The upper bound for a pure initial state system, $\rho_0 = \vert i \rangle \langle i \vert$, then reads:

$$\tau_{\text{max}} \leq \frac{1}{2(\sigma_1 - \sigma_{k+1})} \left[ \ln \left( \frac{2Nk}{\varepsilon^2} \right) + 2 \cdot \ln \left( \frac{(N - k - 2)\sigma_{k+1}}{k(\sigma_1 - \sigma_{k+1})} \right) \right] \quad (6.27)$$

where $N$ is the Hilbert space dimension, $\sigma_1 > \sigma_{k+1} > \ldots > \sigma_N$ are the eigenvalues of the observable $O$, and $k$ is the degeneracy of the maximal eigenvalue, $\sigma_1$.

OCT optimization has a polynomial number of variables in terms of $N$, and given the estimation of Eq. 6.27 we may conclude that it has a *logarithmic time complexity*. It thus belongs to the complexity class **CLOG** (continuous log) in the context of the relevant complexity literature (see, e.g., [136]).

OCT computational complexity research is still in its early days, and is currently under promising study. It includes the investigation of other test cases, subject to theoretical as well as empirical approaches.
6.2 Optimal Control Experiments

Optimal Control Experiments (OCE) [116, 137] consider the realization of Quantum Control in the real-life laboratory, aiming at employing a learning process for altering the course of quantum dynamics phenomena of specific target-applications. Here, the yield, or the success-rate, is obtained by a physical measurement of the target application, whereas numerical modeling of the system's Hamiltonian is not required.

Initially, there were several qualitatively different quantum control schemes. Brumer and Shapiro proposed the use of multi-color interference to control quantum systems [112, 138]: Combinations of harmonic light fields were used to control the total and differential cross-sections of photo-ionization and dissociation processes. That approach focused on the frequency-domain description of the quantum system, and it was followed by a proposed Quantum Control approach by Tannor and Rice, based on exploiting the time-evolution of wave packets that are produced when quantum systems interact with short laser pulses [111, 139]. Finally, Rabitz introduced the important concept of feedback control, where phase-, amplitude- and/or polarization shaping subject to a closed learning loop are used to guide a quantum system toward a desired final state [113]. Rabitz's approach has been successfully applied in numerous applications, and practically became the common experimental routine in the field. We shall focus in this study on the feedback control approach.

The remainder of this section will review experimental Quantum Control, while focusing in computational and optimization aspects. We do not discuss the technical realization of the actual laser pulse. This part is mainly based on [116, 140], as well as on personal lecture notes

6.2.1 Femtosecond Laser Pulse Shaping

As presented earlier, the control field in OCT corresponds to the electric field, which is tuned in the temporal domain in a straightforward manner by the optimization routine. However, the realization in OCE dramatically differs [116].

When considering laser pulses in the duration of femtoseconds\(^3\), it is not yet possible to shape pulses in the temporal domain: State-of-the-art electro-optic switches can currently modulate only in the order of picoseconds\(^4\). Hence, the pulse shaping in OCE is typically implemented by means of "slow" manipulation of the spectrum, subject to a realization of the Fourier

\(^2\)Notes were taken in the course "Quantum Control" of Prof. Herschel Rabitz (CHM509), Princeton University, Fall 2007

\(^3\)1fs = 10\(^{-15}\)s, i.e., 1 millionth of 1 billionth of a second.

\(^4\)1ps = 10\(^{-12}\)s, i.e., 1 trillionth of a second.
transform. We denote the experimental electric field by \( E(t) \),

\[
E(t) \sim \mathbb{R} \left\{ \int_{-\infty}^{\infty} E(\omega) \exp(i\omega t) \ d\omega \right\}
\]

where \( E(\omega) \) is the spectral field. Pulse shapers allow independent amplitude as well as phase modulations, and the spectral field may be modeled accordingly:

\[
E(\omega) = A(\omega) \exp(i\phi(\omega))
\]

with \( A(\omega) \) as the spectral amplitude, and \( \phi(\omega) \) as the spectral phase.

**Time vs. Frequency** The transition between time to frequency domains is obtained by the Fourier transform, \( \mathcal{F} \), whose action can be summarized as follows:

\[
E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{E}(t) \exp(-i\omega t) \ dt = \mathcal{F} \left[ \tilde{E}(t) \right]
\]

\[
\tilde{E}(t) = A(t) \exp(i\Phi(t)) = \int_{-\infty}^{\infty} E(\omega) \exp(i\omega t) \ d\omega = \mathcal{F}^{-1} [E(\omega)]
\]

where \( A(t) \) is the temporal amplitude and \( \Phi(t) \) is the temporal phase. In practice, the modeling of the experimental electric field is real, and it reads:

\[
E(t) = \mathbb{R} \left\{ \int_{-\infty}^{\infty} A(\omega) \exp(i\phi(\omega)) \exp(i\omega t) \ d\omega \right\}
\]

(6.29)

The Fourier transform also determines the reciprocal relation between the spectral width to the temporal width, which is another form of the uncertainty principle. Given the temporal full-width-half-maximum (FWHM) pulse width, \( \Delta \tau_{\text{laser,FWHM}} \), and the FWHM spectral width, \( \Delta \omega_{\text{laser,FWHM}} \), the time-bandwidth relation reads:

\[
\Delta \omega_{\text{laser,FWHM}} \cdot \Delta \tau_{\text{laser,FWHM}} \geq 2\pi c_B
\]

(6.30)

where \( c_B \leq 1 \) depends on the profile of the spectral amplitude \( A(\omega) \).

It is important to distinguish between the temporal intensity of the field,

\[
I(t) = \left| \tilde{E}(t) \right|^2
\]

(6.31)

and the spectral intensity of the field,

\[
I(\omega) = |E(\omega)|^2
\]

(6.32)

which are strictly not directly related, due to the loss of the phase information.
6.2. Optimal Control Experiments

**The Control Phase** Generally speaking, the control function in spectral modulation consists of the spectral amplitude function $A(\omega)$ as well as of the spectral phase function $\phi(\omega)$. Most Quantum Control processes are more sensitive to the phase than to the amplitude, and phase-only shaping is typically sufficient for attaining optimal control. We thus choose to restrict our study to phase modulation, and to consider the spectral function $A(\omega)$ as fixed. The latter is then well-approximated by a Gaussian which determines the bandwidth, or the pulse duration, accordingly. Note that shaping the pulse with phase-only modulation guarantees the conservation of the pulse energy.

We thus consider only $\phi(\omega)$ as our control function: It defines the spectral phase at $n$ frequencies $\{\omega_i\}_{i=1}^n$, that are equally distributed across the spectrum of the pulse. These $n$ values $\{\phi(\omega_i)\}_{i=1}^n$ correspond to $n$ pixels of the pulse shaper, and they would become the decision parameters to be optimized in the experimental learning loop:

$$\phi(\omega) := (\phi(\omega_1), \phi(\omega_2), ..., \phi(\omega_n))$$

(6.33)

Figure 6.2 illustrates the closed learning loop experimental Quantum Control process.

6.2.2 Laboratory Realization: Constraints

The realization of the quantum system in the laboratory poses constraints on the quantum dynamics, and may lead to a different OCE search landscape, in comparison to its equivalent OCT landscape. The OCT theorems which guarantee a trap-free pathway to perfect control from any location in the
landscape, with gradient-based steps and in logarithmic time complexity, may no longer be valid in OCE landscapes. Generally speaking, it is not clear how do Quantum Control landscapes appear in the laboratory.

We discuss here briefly several aspects of laboratory experiments which are likely to be translated into constraints in the OCE landscape [140].

The crucial component of laser pulse shaping process is the phase modulation, which is typically exposed to waveform distortion effects (for a comprehensive study see [141]). We outline here several modulation components.

**Pixelation and Replica Pulses** In practice, the pulse shaping process is implemented by a so-called Spatial Light Modulator (SLM), which is typically based on Liquid Crystal Display (LCD). This approach considers individual pixels subject to rectangle-activation-functions, squ(ν), ideally sharply-defined and with no gaps between each other. This is referred to as the *staircase approximation*. The time modulation of these step-functions is attained by means of their inverse Fourier transform,

$$\mathcal{F}^{-1} [\text{squ}(\nu)] \sim \text{sinc}(\tau)$$

where the width of \(\text{sinc}(\tau) = \frac{\sin(\tau)}{\tau}\) is inversely proportional to the pixel width. Explicitly, the resulting temporal electric field in this pixelization can be described as follows:

$$e(t) = \sum_n \tilde{e}(t-n\tau) \cdot \text{sinc} \left( \frac{\pi t}{\tau} \right), \quad (6.34)$$

with \(\tilde{e}(t)\) as the desired electric field, and where \(\tau = \frac{1}{\Delta \nu}\) is the inverse frequency spacing per pixel.

Practically, step-function gaps between SLM electrodes are responsible for the construction of so-called parasitic replica pulses in the temporal domain, which are located at the zeros of the \text{sinc} envelope function.

**Pulse Break-Up** A linear phase function results in the time shift of the temporal pulse. This can easily be derived by a change of variables, or by the application of the so-called Fourier Shift Theorem (see, e.g., [142]). The influence of the replica pulses becomes more substantial when they are moved from the zeros of the envelope \text{sinc} function, by breaking-up the pulse energy into multiple parasitic replica pulses. This is equivalent to the following statement: *The steeper the linear phase, the more pronounced become the replica pulses, which generally result in lower suboptimal yields* [140].

**Phase Range: Wrapping** Phases that differ in \(2\pi\) radians are mathematically equivalent. This periodic nature of the phase in \([0, 2\pi]n\) practically
poses periodic boundary conditions on the modulator. Given $0 < \varepsilon \leq 2\pi$, the so-called phase wrapping operator is implemented as follows:

\begin{align*}
\phi_i &= 2\pi + \varepsilon \quad \rightarrow \quad \tilde{\phi}_i := \varepsilon \\
\phi_j &= -\varepsilon \quad \rightarrow \quad \tilde{\phi}_j := 2\pi - \varepsilon
\end{align*}

(6.35)
or simply as $\tilde{\phi}_i := \phi_i \mod 2\pi$.

From an optimization perspective, this means that the search space is practically an $n$-dimensional hypercube spanning a length of $2\pi$ in each dimension. It is likely to have implications on the optimization routine in use. In terms of constraints, wrapped phases may be exposed to singularity effects ($0 - 1$ jumps), but it is not considered to be a significant effect. Thus, we consider it here more as a mathematical feature of the search space, rather than a constraint.

Resolution The number of pixels, $n$, determines the control resolution, and poses a direct constraint on the shaped-pulse in the temporal domain: Due to the reciprocal nature of the Fourier transform with respect to frequency versus time, spectral resolution determines the upper bound for temporal resolution. For instance, typical laboratory realizations currently consider $n = 128$ pixels with spectral resolution of 0.25 nm/pixel, which allow a shaped pulse with maximum temporal length of 8.5 ps at FWHM bandwidth of 10 nm.

We hereby summarize the main laboratory constraints in a typical quantum system realization:

1. **Temporal or spectral resolution of the field** Limited spectral resolution in the realized shaper implies limited pulse temporal resolution. State-of-the-art LCD pulse shapers contain 640 pixels to be tuned.

2. **Limited field fluence, limited field intensity** Potential damage to different experimental components restricts in practice the applied field fluence and its intensity.

3. **Limited spectral bandwidth or pulse duration** State-of-the-art commercial lasers can produce nowadays pulses at the duration of $\sim$ 20 fs.

4. **Proper basis** The actual representation of the control phase, e.g., pixel basis, polynomial expansion basis, etc., poses by itself an additional constraint on the landscape.

5. **Noise** Existence of laboratory noise, by definition, poses constraints on the landscape.
6.3 Experimental Procedure

In this study we are interested both in numerical modeling of quantum systems, as well as in their real laboratory experiments. The numerical modeling is typically driven by a known Hamiltonian, but designed in a laboratory-oriented manner, as will be described shortly. Essentially, it is OCT combined with some OCE characteristics.

In our calculations, we choose to restrict this study mostly to noise-free simulations, as we are interested in the physics of the system, rather than conducting an actual simulation of a real laboratory experiment. On this note, we consider the absence of noise in our calculations as a blessing, as it allows for clean interpretation of the physics of the system. In one particular case, we will carry out simulations with noise.

Generally speaking, considering the various quantum systems under investigation in this study, the goal that we would like to achieve in our experimental work is three-fold, and may be outlined as follows:

1. A preliminary part of our work on each quantum system is devoted to a large extent to an investigation of the performance of specific derandomized Evolution Strategies, as well as parameterizations, with respect to the given optimization task. As suggested in Section 1.4.4, this would include the comma-strategy DES variants.

2. After having identified the routines which perform best on our problems, further work would typically concentrate on the physical interpretation of the obtained optimal solutions, when applicable to the system under study. In particular, we will aim at clarifying why certain pulse structures perform better than other trial solutions. This will also be accompanied with investigation of pulse-intensity, field scalability, and other defining features.

3. Finally, we will be interested in applying miscellaneous optimization techniques, at the level of decision making: multi-objective optimization, and the application of niching.

Next, we provide technical details concerning the two classes of experimental work conducted in this study: numerical simulations and laboratory experiments.

6.3.1 Numerical Simulations

We present here the numerical modeling of our laser pulse shaping framework, which is in essence valid for all the numerical calculations conducted in this work, unless specified otherwise. The idea is to simulate the experimental pulse shaping process, in terms of control definition, physical limitations, etc.
As discussed earlier, in our calculations the control is solely the phase function \( \phi(\omega) \). It defines the phase at \( n \) frequencies \( \{\omega_i\}_{i=1}^n \) that are equally distributed across the spectrum of the pulse. These \( n \) values \( \{\phi(\omega_i)\}_{i=1}^n \) are the decision parameters to be optimally determined. Upon their calibration they are numerically interpolated into \( \tilde{n} = 2^{14} \) points, using the `spline()` procedure [143], for the calculation of the electric field in Eq. 6.29. The latter is implemented by means of the `FFT()` procedure [143].

The numerical resolution is naturally underposed to a conflict with the expected optimization efficiency. In order to achieve a good trade-off between the two, i.e., keeping both resolution and optimization efficiency as high as possible, the value of \( n = 80 \) turned to be a good compromise. The search space is therefore an 80-dimensional hypercube spanning a length of \( 2\pi \) in each dimension.

The spectral function \( A(\omega) \) is taken to be a Gaussian, centered at 800 nm, with a width chosen such that the full-width-at-half-maximum (FWHM) length of the *Fourier transform limited* (FTL) pulse (obtained by setting \( \phi(\omega) \equiv 0 \)) is \( \Delta \tau \approx 100 \text{fs} \).

Most of the simulations were run with FORTRAN code, as written and provided by Prof. Marc Vrakking, of Amolf-FOM, Amsterdam\(^5\). This was later combined with a MATLAB version of the original code, as implemented by the author. For the two-photon processes reported in Chapter 7 we used a LabView simulator of Princeton University, coded by Jonathan Roslund.

### 6.3.2 Laboratory Experiments

The laboratory experiments reported in this work were all conducted at the Frick Laboratory, Rabitz Group, Chemistry Department, Princeton University\(^6\). The laser source was a Ti:sapphire femtosecond system, with a Tsunami oscillator and a 1 kHz 1.8 mJ Spitfire amplifier. A pulse was centered at \( \sim 800 \text{nm} \), with a bandwidth of \( \Delta \lambda \approx 10 \text{nm} \), yielding \( \Delta \tau \approx 100 \text{fs} \) pulse duration at FWHM. The employed SLM consisted of 128 pixels (phase-only modulation, liquid-crystal), but the experiments typically used 64 pixels, by coupling together pairs of adjacent pixels, unless specified otherwise. All algorithms were coded in LabView.

### Reference Routine in the Lab: Genetic Algorithm

Genetic Algorithms (GAs) are the most common optimization routines in QC experiments in the vast majority of physics laboratories, likely due to

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\(^5\)Dedicated training was given by Marc Vrakking and Christian Siedschlag, and I thank them both for that.

\(^6\)All experiments were conducted under the dedicated supervision of Jonathan Roslund of the Rabitz Group, whose support in running the experiments has been priceless.
historical reasons. As a reference to specific derandomized ES that we apply in our experiments, we shall also report on the GA performance.

**The Traditional GA** We use the traditional GA [22], with bitstring representation of \( l = 6 \) bit resolution per pixel. It employs a fixed population of \( \mu = 30 \) individuals. The mutation rate for a bit-flip is \( p_m = 0.005 \), and the selection mechanism keeps the fittest offspring, as well as the single best individual of the previous generation (*elitism*). It should be noted that these parameters were collectively optimized to allow sufficient resolution so as to arrive at the highest quality solution with the fastest convergence.