Quantum Control for Scientists and Engineers

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Contents

Preface

With interest mounting across academic departments in the engineering of quantum systems and the design of quantum information processing devices, the need has arisen to delineate the fundamental principles of quantum engineering in a clear and accessible fashion. At the heart of this subject is the theory of quantum estimation and control namely, how to optimally steer a quantum dynamical system to a desired objective, making the best possible use of the information obtained from observations of that system at intermediate times. Until recently, it has been difficult to find an integrated treatment of these topics in one source, partly due to the rapidly changing nature of the fields. The subject is now sufficiently mature to warrant a text/reference book that extends the classical treatment of both estimation and control to the quantum domain. This book aims to provide a self-contained survey of these topics for use by graduate students and researchers in quantum engineering and quantum information sciences. Due to the interdisciplinary nature of these disciplines, the books audience may be comprised of readers with formal training in a wide variety of fields, including quantum chemistry, physics, electrical or mechanical engineering, applied mathematics, or computer science. The only essential prerequisite is an introductory course in quantum mechanics at the first-year graduate level, as typically taught in physics departments. One of our primary goals is to give the student with limited background in control theory, but a familiarity with quantum dynamical systems, the tools to engineer those systems and the necessary preparation to engage the research literature. A second objective is to offer a convenient reference for active and experienced researchers in quantum engineering and quantum information theory. Along the way, we will endeavor to show that quantum control and estimation penetrate directly to the heart of quantum physics and shed light on some longstanding controversies surrounding the subject through a pragmatic approach to observation and regulation.

Optimal control theory can be subdivided into the related subjects of open loop and closed loop control. The former deals with the identification of control laws based solely on knowledge of the dynamical equations of motion and the systems initial conditions, while the latter additionally employs real-time measurements and feedback in order to correct for the effects of noise and uncertainty and to update the control law. In many experimental incarnations of quantum control such as the original applications to the femtosecond laser control of molecular dynamics real-time feedback is not possible (or necessary) due to the short characteristic time scale of the dynamics. The salient feature of open loop control is that it does not require state estimation.

Part I is dedicated to open loop quantum optimal control. Our treatment of open loop control is based on geometric control theory, which uses the principles of group theory to

assess system controllability and derive optimal control laws. Geometric control theory is particularly powerful in quantum mechanics due to the linearity of quantum dynamics and the existence of manifold quantum symmetries. General theorems on open loop quantum control are easiest to prove from the geometric standpoint. By contrast, in most textbooks on classical open loop control, geometric control theory is de-emphasized. In a point of departure from previous texts, we show how the properties of quantum optimal control landscapes that have rendered open loop control remarkably successful -even for highly complex systems -can be rendered transparent through geometric control. Quantum open loop learning control, wherein control fields are iteratively updated in the laboratory to identify optimal solutions, is also covered in Part I.

In certain certain classes of quantum control problems, real-time feedback can improve fidelity. For example, in quantum computation, real-time error correction may help to stabilize information processing channels in the presence of environmental noise and decoherence. In cases where the time delay between measurement and application of feedback is much smaller than the dynamical time scale of the system, closed loop quantum feedback can be implemented. As of the time of this writing, there are no textbooks available on this important subject of closed loop quantum control. The principles of quantum optimal control introduced in Part I are extended to the derivation of closed loop control laws in Part II.

Closed loop control has been extensively studied in the context of classical systems, and the textbooks by Bryson Ho, or Stengel, may be familiar to many readers with backgrounds in engineering. It is thus important to provide a summary of the major differences between classical and quantum closed loop control. First, the state of a quantum dynamical system can never be precisely known on the basis of a finite number of measurements, even in the absence of measurement error or noise in the system. By contrast, in nonstatistical classical mechanics, the state vector can in principle be precisely determined. Second, measurement of the state of a quantum system generally disturbs the state, resulting in stochastic collapse of the state vector into an eigenstate of the corresponding observable. Even in the presence of weak, continuous (as opposed to projective) measurement, which does not necessarily result in collapse into an eigenstate, the measurement results in the introduction of a stochastic driving term into the dynamical equations governing the systems evolution.

As a result of these two features, there are two fundamentally different types of regulators or feedback controllers in quantum control classical feedback controllers and coherent (or quantum) feedback controllers. Closed loop quantum control involving measurements is referred to as quantum control via classical feedback. Such control is always stochastic in quantum mechanics, although it may be deterministic in classical mechanics. By contrast, coherent controllers exploit coherent sensing i.e., transfer of information in the quantum state of the controlled system through entanglement with the controller, which is itself a quantum system. Coherent feedback controllers are the quantum analog of the classical flyball governor in Watts steam engine. This form of closed loop control, where the controller is a second dynamical system and does not require measurements, is often referred to as self-regulation in the control/systems

engineering literature. In essence, the quantum controller assimilates information on the state of the system through entanglement, rather than classical measurement, and is designed to react accordingly. The coherent controller functions as a quantum computer that monitors the state of the target system and processes it, prior to feeding back optimal controls.

Coherent feedback controllers are somewhat more difficult to design experimentally, because all information regarding the feedback control law must be preprogrammed into the design of the controller (or regulator), and because the controller must be directly interfaced with the target system. However, learning control methods can be used to facilitate design, and the lack of measurement-induced disturbance renders such controllers more suitable for noise-sensitive applications like quantum computation. We therefore examine both coherent and classical feedback controllers in this book.

Given that statistical estimation of the state is required for closed loop control with classical feedback, Part II begins with a self-contained treatment of quantum estimation theory, prior to integrating estimation with control. In order to understand quantum estimation theory, we must be cognizant of a third difference between classical and quantum systems namely, that quantum probability theory is based on noncommutative probability spaces. For example, this means that quantum noise (stochastic processes) must be defined in terms of a noncommutative generalization of the Ito stochastic calculus. There are now several classic texts available on quantum probability and quantum statistical inference, which cover the essential differences with classical probability, noise and estimation. The treatments in these books focus on the formal (asymptotic) properties of the estimators or stochastic processes themselves, but do not cover either practical algorithms for state estimation or filtering theory, which are essential for stochastic optimal control. Here, we address both topics. The necessary background on classical probability theory as well as classical filtering is provided.

As in the classical setting, quantum estimation theory can be approached from two standpoints: frequentist or Bayesian statistics. Bayesian estimation is considerably more general than frequentist estimation, and is rigorous for finite sample sizes. Good finite sample size performance is especially important in quantum estimation problems, because of the inevitable disturbances caused by measurements. Moreover, in filtering problems, where both state variables and dynamical parameters must be estimated, Bayesian methods permit estimates for both -including confidence intervals to be obtained simultaneously, since all information about the system is contained within the posterior plausibility distribution. The Bayesian approach has been adopted in the formal quantum statistical inference literature, due to its rigorous theoretical consistency with the axioms of quantum mechanics, but has thus far been underrepresented in the quantum engineering literature. In this book we adopt the Bayesian framework as the foundation for the treatment of estimation, with the aim of demonstrating that it is the preferred method for both stationary and continuous time statistical inference.

Given the emphasis on controlling real quantum systems in the presence of noise and incomplete information, the approach adopted in this book synthesizes features of pure

mathematics and applied/engineering mathematics. This philosophy extends to the example problems that illustrate the principles introduced in each section. Nearly all problems of practical importance in quantum control especially stochastic control -do not admit analytical solution and must be solved numerically. The application of computers to filtering and control problems has a distinguished history of success in classical control theory. Quantum control is no exception. In contrast to most books on quantum mechanics, therefore, some of the examples and problems in this book include the option of combining analytical problem formulation with numerical solution. Two separate chapters are dedicated to describing the theoretical underpinnings of the numerical methods employed.

These simulations may be carried out using either reader-developed code or a library of publicly available quantum control and estimation programs [note: slated for development; details TBD] under the name of The Quantum Scientific Library (QSL). The QSL project aims to provide an integrated suite of control and estimation codes to quantum engineers, given the aforementioned fundamentally different properties of quantum/classical estimation and control. The QSL estimation routines contain both frequentist and Bayesian algorithms (the latter based on efficient Markov Chain Monte Carlo (MCMC) techniques). QSL optimal control algorithms include stochastic (genetic and evolutionary) algorithms for open-loop control of open and closed quantum systems, as well as gradient-based algorithms for searching control landscapes. Hybrid stochastic(simulated annealing)/deterministic algorithms are also included for overcoming control landscape traps. The QSL will be open source, with freely available online documentation.

The book is organized as follows. The preliminary chapter (0) reviews basic concepts of quantum dynamics. This is meant to be a refresher of concepts covered in a first-year graduate quantum physics course. Part I of the book deals with open-loop optimal control theory -optimal control without feedback based on measurement of the state. In Chapter 1, the basic definitions of control systems are presented. This includes the classification of system dynamics and the establishment of the bilinearity of quantum control systems, definitions of the various types of controllability, and powerful controllability theorems that apply to quantum systems. Necessary background on Lie groups and Lie algebras can be found in the Appendix. In Chapter 2, the basics of quantum optimal control theory are presented, including the Euler-Lagrange equations of Pontryagins maximum principle, from which open loop control laws follow. Analytical solutions are presented for selected low-dimensional control systems with various types of costs. Chapter 3 categorizes generic properties of the solution sets of quantum optimal control problems: regular and singular extremals and features of control landscapes that affect the efficiency of the search for optimal controls. In Chapter 4, we present numerical algorithms for open loop quantum optimal control, including stochastic and gradient-based deterministic techniques. Chapter 5 surveys some of the most important applications of open loop quantum optimal control, namely control of the expectation values of quantum observables for state preparation or chemical reaction control, as well as control of quantum gates for quantum computing.

Part II, quantum estimation theory and stochastic control, begins with Chapter 7, an overview of quantum probability theory and its differences with respect to classical probability theory, emphasizing the advantages of Bayesian techniques in quantum statistical inference. The necessary background in classical probability theory is reviewed in the Appendix. Chapter 8 examines the stochastic processes that are the subject of stochastic quantum control. In Chapter 9, the various forms of quantum measurement, and their stochastic effects on the quantum state -an important difference with respect to classical stochastic control -are described. In Chapter 10, quantum filtering and forecasting theory, which are essential for the control of stochastic systems, are covered. The relationship between the system-theoretic notion of observability namely, the ability to completely specify the state through sequential measurements -and controllability is established. Then, both frequentist (Kalman) filtering and Bayesian filtering of quantum states are considered in turn. In Chapter 11, the two primary variants of closed loop quantum control coherent and classical feedback are discussed. Section

11.1 on deterministic (coherent) feedback control is based primary on the results from Chapters 1 and 2 on OCT, and does not require a thorough reading of Chapters 7-9. Section 11.2 on quantum control via classical feedback combines the dynamic programming results from 11.1 with the filtering theory covered in Chapter 10, in order to develop the quantum stochastic feedback control theory. Finally, Chapter 12 presents numerical methods for (frequentist and Bayesian) quantum filtering as well as dynamic programming, with accompanying examples that can be run using the QSL. This book grew out of an extensive review article on open loop quantum optimal control written by the authors for International Reviews in Physical Chemistry in 2007. Chapters 3 and 4, especially, are based heavily on that work.

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Chapter 1

Introduction

For many decades, physicists and chemists have employed various spectroscopic methods to carefully observe quantum systems on the atomic and molecular scale. The fascinating feature of quantum control is the ability to not just observe but actively manipulate the course of physical and chemical processes, thereby providing hitherto unattainable means to explore quantum dynamics. This remarkable capability along with a multitude of possible practical applications have attracted enormous attention to the field of control over quantum phenomena. This area of research has experienced extensive development during the last two decades and continues to grow rapidly. A notable feature of this development is the fruitful interplay between theoretical and experimental advances.

Various theoretical and experimental aspects of quantum control have been reviewed in a number of articles and books [1, 2, **?**, 97, 98, **?**, 3, 61, **?**, 82, 5, 99, 4, 130, 133, 83, 139, 12, 13, **?**, 6, 134, 141, 62, 135, 8, 7, 136, 137, 14, 138, 15, 16, 17, 18, 10, 9, 131, 147, 11, 19, 20, 21, 22, 23]. This paper starts with a short review of historical developments as a basis for evaluating the current status of the field and forecasting future directions of research. We try to identify important trends, follow their evolution from the past through the present, and cautiously project them into the future. This paper is not intended to be a complete review of quantum control, but rather a perspective and prospective on the field.

In section 1.1, we discuss the historical evolution of relevant key ideas from the first attempts to use monochromatic laser fields for selective excitation of molecular bonds, through the inception of the crucial concept of control via manipulation of quantum interferences, and to the emergence of advanced contemporary methods that employ specially tailored ultrafast laser pulses to control quantum dynamics of a wide variety of physical and chemical systems in a precise and effective manner. After this historical summary, we review in more detail the recent progress in the field, focusing on significant theoretical concepts, experimental methods, and practical advances that have shaped the development of quantum control during the last decade. Section **??** is devoted to quantum optimal control theory (QOCT), which is currently the leading theoretical approach for identifying the structure of controls (e.g., the shape of laser pulses) that enable attaining the quantum dynamical objective in the best possible way. We present the formalism of QOCT (i.e., the types of objective functionals used in various problems and methods employed to search for optimal controls), consider the issues of controllability and existence of optimal control solutions, survey applications, and discuss the advantages and limitations of this approach. In section **??**, we review the theory of quantum control landscapes, which provides a basis to analyze the complexity of finding optimal solutions. Topics discussed in that section include the landscape topology (i.e., the characterization of critical points), optimality conditions for control solutions, Pareto optimality for multi-objective control, homotopy trajectory control methods, and the practical implications of control landscape analysis. The important theoretical advances in the field of quantum control have laid the foundation for the fascinating discoveries occurring in laboratories where closed-loop optimizations guided by learning algorithms alter quantum dynamics of real physical and chemical systems in dramatic and often unexpected way. Section **??**, which constitutes a very significant portion of this paper, is devoted to laboratory implementations of adaptive feedback control (AFC) of quantum phenomena. We review numerous AFC experiments that have been performed during the last decade in areas ranging from photochemistry to quantum information sciences. These experimental studies (most of which employ shaped femtosecond laser pulses) clearly demonstrate the capability of AFC to manipulate dynamics of a broad variety of quantum systems and explore the underlying physical mechanisms. The role of theoretical control designs in experimental realizations is discussed in section **??**. In particular, we emphasize the importance of theoretical studies for the feasibility analysis of quantum control experiments. Section **??** presents concepts and potential applications of real-time feedback control (RTFC). Both measurement-based and coherent types of RTFC are described, along with current technological obstacles limiting more extensive use of these approaches in the laboratory. Future directions of quantum control are considered in section **??**, including important unsolved problems and some emerging new trends and applications. Finally, concluding remarks are given in section **??**.

1.1 Early developments of quantum control

The historical origins of quantum control lie in early attempts to use lasers for manipulation of chemical reactions, in particular, selective breaking of bonds in molecules. Lasers, with their tight frequency control and high intensity, were considered ideal for the role of molecular-scale 'scissors' to precisely cut an identified bond, without damage to others. In the 1960s, when the remarkable characteristics of lasers were initially realized, it was thought that transforming this dream into reality would be relatively simple. These hopes were based on intuitive, appealing logic. The procedure involved tuning the monochromatic laser radiation to the characteristic frequency of a particular chemical bond in a molecule. It was suggested that the energy of the laser would naturally be absorbed in a selective way, causing excitation and, ultimately, breakage of the targeted bond. Numerous attempts were made in the 1970s to implement this idea [24, 25, 26]. However, it was soon realized that intramolecular vibrational redistribution of the deposited energy rapidly dissipates the initial local excitation and thus generally prevents selective bond breaking [27, 28, 29]. This process effectively increases the rovibrational temperature in the molecule in the same manner as incoherent heating does, often resulting in breakage of the weakest bond(s), which is usually not the target of interest.

1.1.1 Control via two-pathway quantum interference

Several important steps towards modern quantum control were made in the late 1980s. Brumer and Shapiro [30, 31, 32, 33] identified the role of quantum interference in optical control of molecular systems. They proposed to use two monochromatic laser beams with commensurate frequencies and tunable intensities and phases for creating quantum interference between two reaction pathways. The theoretical analysis showed that by tuning the phase difference between the two laser fields it would be possible to control branching ratios of molecular reactions [41, 42, 43]. The method of two-pathway quantum interference can be also used for controlling population transfer between bound states [44, 45] (in this case, the number of photons absorbed along two pathways often must be either all even or all odd to ensure that the wave functions excited by the two lasers have the same parity; most commonly, one- and three-photon excitations were considered).

The principle of coherent control via two-pathway quantum interference was demonstrated during the 1990s in a number of experiments, including control of population transfer in bound-to-bound transitions in atoms and molecules [44, 45, 46, 47, 48, 49], control of energy and angular distributions of photoionized electrons [50, 51, 52, 53] and photodissociation products [54] in bound-to-continuum transitions, control of cross-sections of photochemical reactions [55, 56, 57], and control of photocurrents in semiconductors [58, 59]. However, practical applications of this method are limited by a number of factors. In particular, it is quite difficult in practice to match excitation rates along the two pathways, either because one of the absorption cross-sections is very small or because other competing processes intervene. Another practical limitation, characteristic of experiments in optically dense media, is undesirable phase and amplitude locking of the two laser fields [60]. Due to these factors and other technical issues (e.g., imperfect focusing and alignment of the two laser beams), modulation depths achieved in two-pathway interference experiments were modest: typically, about 25–50% for control of population transfer between bound states [45, 46, 47, 49] (the highest reported value was about 75% in one experiment [48]), and about 15–25% for control of dissociation and ionization branching ratios in molecules [55, 56]. Two-pathway interference control is a nascent form of full multi-pathway control offered by operating with broad-bandwidth optimally shaped pulses.

1.1.2 Pump-dump control

In the 1980s, Tannor, Kosloff, and Rice [34, 35] proposed a method for selectively controlling intramolecular reactions by using two successive femtosecond laser pulses with a tunable time delay between them. The first laser pulse (the "pump") generates a vibrational wave packet on an electronically excited potential-energy surface of the molecule. After the initial excitation, the wave packet evolves freely until the second laser pulse (the "dump") transfers some of the population back to the ground potential-energy surface into the desired reaction channel. Reaction selectivity is achieved by using the time delay between the two laser pulses to control the location at which the excited wave packet is dumped to the ground potential-energy surface [3, 5]. For example, it may be possible to use this method to move the ground-state wave-function beyond a barrier obstructing the target reaction channel. In some cases, the second pulse transfers the population to an electronic state other than the ground state (e.g., to a higher excited state) in a pump-repump scheme.

The feasibility of the pump-dump control method was demonstrated in a number of experiments [63, 64, 65, 66, 67]. The pump-dump scheme can be also used as a time-resolved spectroscopy technique to explore transient molecular states and thus obtain new information about the dynamics of the molecule at various stages of a reaction [68, 69, 70, 71, 72, 73, 74, 75]. In pump-dump control experiments, the system dynamics often can be explained in the time domain in a simple and intuitive way to provide a satisfactory qualitative interpretation of the control mechanism. The pump-dump method gained considerable popularity [3, 5, 14] due to its capabilities to control and investigate molecular dynamics. However, the employment of transform-limited laser pulses significantly restricts the effectiveness of this technique as a practical control tool. More effective control of the wave-packet dynamics and, consequently, higher reaction selectivity can be achieved by optimally shaping one or both of the pulses. For example, even a chirp of the pump pulse may improve the effectiveness of control by producing more localized wave packets (the use of pulse chirping will be discussed in section 1.1.6 in more detail). Recent experimental applications of the pump-dump scheme with shaped laser pulses (optimized using adaptive methods) will be discussed in section **??**.

1.1.3 Control via stimulated Raman adiabatic passage

In the late 1980s, Bergmann and collaborators [76, 77, 78, 79] demonstrated a very efficient adiabatic method for population transfer between discrete quantum states in atoms or molecules. In this approach known as stimulated Raman adiabatic passage (STIRAP), two time-delayed laser pulses (typically, of nanosecond duration) are applied to a three-level Λ-type configuration to achieve complete population transfer between the two lower levels via the intermediate upper level. Interestingly, the pulse sequence employed in the STIRAP method is counter-intuitive, i.e., the Stokes laser pulse that couples the intermediate and final states precedes (but overlaps) the pump laser pulse that couples the initial and intermediate states. The laser electric fields should be sufficiently strong to generate many cycles of Rabi oscillations. The laser-induced coherence between the quantum states is controlled by tuning the time delay, so that the transient population in the intermediate state remains almost zero, thus avoiding losses by radiative decay. Detailed reviews of STIRAP and related adiabatic passage techniques can be found in [82, 83]. While the efficiency of the STIRAP method, under appropriate conditions, is very high, its applicability is restricted to control of population transfer between a few discrete states as arise in atoms and small (diatomic and triatomic) molecules. In larger polyatomic molecules, the very high density of levels generally prevents successful adiabatic passage [82, 83].

1.1.4 Control via wave-packet interferometry

Another two-pulse approach for control of population transfer between bound states employs Ramsey interference of optically excited wave packets [**?**, **?**]. In this method, referred to as wave-packet interferometry (WPI) [20], two time-delayed laser pulses excite an atomic, molecular, or quantum-dot transition, resulting in two wave packets on an excited state. Quantum interference between the two coherent wave packets can be controlled by tuning the time delay between the laser pulses. For control of population transfer, constructive or destructive interference between the excited wave packets gives rise to larger or smaller excited-state population, respectively. The same control mechanism is also applicable to other problems such as control of atomic radial wave-functions and control of molecular alignment. WPI was demonstrated with Rydberg [84, 85, 86] and fine-structure [87, 88] wave packets in atoms, vibrational [89, 90, 91, 92, 93] and rotational [94] wave packets in molecules, and exciton fine-structure wave packets in semiconductor quantum dots [95, 96] (for a detailed review of coherent control applications of WPI, see [20]; the use of WPI for molecular state reconstruction is reviewed in [?]). Once again, much more effective manipulation of quantum interferences is possible in this control scheme when shaped laser pulses are used instead of transform-limited ones (see section **??** for details).

1.1.5 Quantum optimal control theory

Although the control approaches discussed in sections 1.1.1–1.1.4 were initially perceived as quite different, it is now clear that on a fundamental level all of them employ the mechanism of quantum interference induced by control laser fields. A common feature of these methods is that they generally attempt to manipulate the evolution of quantum systems by controlling just one parameter: the phase difference between two laser fields in control via two-pathway quantum interference; the time delay between two laser pulses in pump-dump control, STIRAP, and WPI. While single-parameter control may be relatively effective in some simple systems, more complex systems and applications require more flexible and capable control resources. The single-parameter control schemes have been unified and generalized by the concept of control with specially tailored ultrashort laser pulses. Rabitz and co-workers [36, 37, 38] and others [39, 40] suggested that it would be possible to steer the quantum evolution to a desired product channel by specifically designing and tailoring the time-dependent electric field of the laser pulse to the characteristics of the system. Specifically, QOCT may be used to design laser pulse shapes which are best suited for achieving the desired goal [36, 37, 38, 39, 40, 124, 125, 126, 127, 128, ?, 129]. An optimally shaped laser pulse typically has a complex form, both temporally and spectrally. The phases and amplitudes of different frequency components are optimized to excite an interference pattern amongst distinct quantum pathways, to best achieve the desired dynamics. The first optimal fields for quantum control were computed by Shi, Woody, and Rabitz [36] who showed that the amplitudes of the interfering vibrational modes of a laser-driven molecule could add up constructively in a given bond. We will review QOCT and its applications in more detail in section **??** (for earlier reviews of QOCT, see [3, 5, 130, 131, 11]).

1.1.6 Control with linearly chirped pulses

Laser pulse-shaping technology rapidly developed during the early 1990s [97, 98, 99]. However, the capabilities of pulse shaping were not fully exploited in quantum control until the first experimental demonstrations of adaptive feedback control (AFC) in 1997–1998 [440, 478]. Initially, ultrashort laser pulses with time-varying photon frequencies were used to tune just the linear chirp, which represents an increase or decrease of the instantaneous frequency as a function of time under the pulse envelope.[1] Linearly chirped femtosecond laser pulses were successfully applied for control of various atomic and molecular processes, including control of vibrational wave packets [100, 101, 102, 103, 104, 105, 106], control of population transfer between atomic states [107, 108, 109] and between molecular vibrational levels [110, 111, 112] via "ladder-climbing" processes, control of electronic excitations in molecules [113, 114, 115, 116, 117], selective excitation of vibrational modes in coherent anti-Stokes Raman scattering (CARS) [118], improvement of the resolution of CARS spectroscopy [119, 120], and control of photoelectron spectra [121] and transitions through multiple highly excited states [122] in strong-field ionization of atoms. In particular, when the emission and absorption bands of a molecule strongly overlap, pulses with negative and positive chirp excite vibrational modes predominately in the ground and excited electronic states, respectively [100, 104, 105, 106]. Chirped pulses can be also used to control the localization of vibrational wave packets in diatomic molecules, with the negative and positive chirp increasing and decreasing the localization, respectively [101, 102, 103]. Based on this effect, pump pulses with negative chirp were used to enhance selectivity in pump-dump control of photodissociation reactions [103]. Recently, the localization effect of negatively chirped pulses was used to protect vibrational wave packets against rotationally-induced decoherence [123]. Due to their effectiveness in various applications, chirped laser pulses are widely used in quantum control. However, by the end of the 1990s, many experimenters realized that more sophisticated pulse shapes, beyond just linear chirp, provide a much more powerful and flexible tool for control of quantum phenomena in complex physical and chemical systems. Femtosecond pulse-shaping technology is utilized to the fullest extent in AFC experiments where laser pulses are optimally tailored to meet the needs of complex quantum dynamics objectives [4, 133, 12, 13, 134, 135, 8, 7, 136, 137, 138, 9, 19]. The enormous growth of this field during the last decade is reviewed in section **??**.

1.1.7 Control via non-resonant dynamic Stark effect

Optimal control of quantum phenomena in atoms and molecules usually operates at laser intensities sufficient to be in the non-perturbative regime. Thus, controlled dynamics will naturally utilize the dynamic Stark shift amongst other available physical processes in order to reach the target. In a recent quantum control development, Stolow and co-workers proposed and experimentally demonstrated manipulation of molecular processes exclusively employing the non-resonant dynamic Stark effect (NRDSE) [**?**, **?**, **?**, **?**]. In this approach, a quantum system is controlled by an infrared laser pulse in the intermediate field-strength regime (non-perturbative but

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[1] The instantaneous frequency $\omega(t)$ of a linearly chirped pulse with a carrier frequency ω_0 is given at time t by $\omega(t) = \omega_0 + 2bt$, where b is the chirp parameter that can be negative or positive.

non-ionizing). Laser frequency and intensity are chosen to eliminate the complex competing processes (e.g., multiphoton resonances and strong-field ionization), so that only the NRDSE contributes to the control mechanism. By utilizing Raman coupling, control via NRDSE reversibly modifies the effective Hamiltonian during system evolution, thus making it possible to affect the course of intramolecular dynamic processes. For example, a suitably timed infrared laser pulse can act as a "photonic catalyst" by reversibly modifying potential energy barriers during a chemical reaction without inducing any real electronic transitions [**?**]. Control via NRDSE was successfully applied to create field-free "switched" wave packets (which can be employed, e.g., for molecular axis alignment) [**?**, **?**] and modify branching ratios in non-adiabatic molecular photodissociation [**?**, **?**].

1.1.8 Control of nuclear spins with radiofrequency fields

One of the earliest examples of coherent control of quantum dynamics is manipulation of nuclear spin ensembles using radiofrequency (RF) fields [**?**]. The main application of nuclear magnetic resonance (NMR) control techniques is high-resolution spectroscopy of polyatomic molecules (e.g., protein structure determination) [598, **?**, **?**, **?**]. While control of an isolated spin by a time-dependent magnetic field is a simple quantum problem, in reality, NMR spectroscopy of molecules containing tens or even hundreds of nuclei involves many complex issues such as the effect of interactions between the spins, thermal relaxation, instrumental noise, and influence of the solvent. Therefore, modern NMR spectroscopy often employs thousands of precisely sequenced and phase-modulated pulses. Among important NMR control techniques are composite pulses, refocusing, and pulse shaping. In particular, the use of shaped RF pulses in NMR makes it possible to improve the frequency selectivity, suppress the solvent contribution, simplify high-resolution spectra, and reduce the size and duration of experiments [**?**]. In recent years, NMR became an important testbed for developing control methods for applications in quantum information sciences [**?**, **?**, **?**, 355, 356]. In order to perform fault-tolerant quantum computations, the system dynamics must be controlled with an unprecedented level of precision, which requires even more sophisticated designs of control pulses than in high-resolution spectroscopy. In particular, QOCT was recently applied to identify optimal sequences of RF pulses for operation of NMR quantum information processors [356, 284].

Chapter 2

Molecular Interactions: Light as controller

A molecule in an electromagnetic field will have an evolution largely controlled by the field properties such as the amplitude, phase and frequency. When a molecule is exposed to light a variety of things could happen which could trigger one or all, of the degrees of freedom of the molecule. The molecule, in accordance with the law of conservation of energy, will absorb the energy of the field and could lead to mechanical motion such as translational, vibrational and rotational or could excite the electronic energy levels which later de-excite to the ground state by emitting light. The most basic example of this type is often discussed in the case of a two level system as shown in Fig. 2.

This simple example illustrates how light acts as a controller. From a purely mechanistic perspective, the scenario depicted in Fig. 2 is a population inversion due to the incident light of frequency $\omega = \frac{E_2 - E_1}{\hbar}$ and hence controls the dynamics

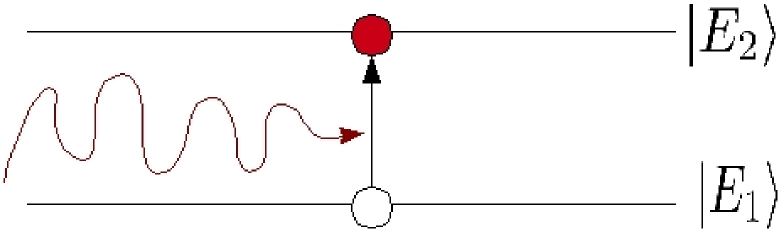

Figure 2.1: A two level atom interacting with light of frequency $\omega = \frac{E_2 - E_1}{\hbar}$. Initially the molecule is in the ground state $|E_1\rangle$ and by absorbing the photon the molecule gets excited and will reach $|E_2\rangle$.

of the system. The field in this case is called as resonant since the frequency of the field is exactly equal to the difference of the energy levels of the system. The frequency difference $\Delta = \omega_0 = \omega$ is called as *d*etuning and is an important factor in practical situations of electromagnetic interaction. *Does this population transfer happen instantaneously ???*

Further insight into the above example reveals that for such a well defined system one does not need any rigorous mathematical and/or numerical modeling to find the electromagnetic field to control the system. However depending on the task that we wish to achieve, it will turn out that employing the concepts for control theory would be useful to optimize the energy of the light pulse. This discussion is taken up in later chapters.

2.1 Molecular dipole interaction

An initially, electrically neutral molecule when placed in an electric field will transform as a dipole(spatially separated equal and opposite charge) due to the pull on the positive charge and push on the negative charge. Thus the molecule, apart from undergoing mechanical twists and turns, will also have a temporal evolution under the potential energy of the light field, which results in driving the molecule's vibrational, rotational and electronic states from an arbitrary initial state.

classically, the energy of a system of charged particles in an electric field can be approximated to first order as $V = \mathbf{D} \cdot \vec{\varepsilon}$, where $\mathbf{D} = \sum_{i=1}^{n} q_i \mathbf{r}_i$, where $\mathbf{r}_i$ denotes the radial position vector for particle i, and where n denotes the number of particles in the molecule

In classical electrodynamics the energy of a system of charged particles is governed by the dipole moment $\vec{d} = q\vec{r}$. The energy in presence of electric field $\vec{\varepsilon}$ is given as $V = -\vec{d} \cdot \vec{\varepsilon}$. A straightforward extension to a system of charged particles in an electric field can be approximated to first order as $V = \cdot \vec{\varepsilon}$, where $= \sum_{i=1}^{n} q_{ii}$, where $\mathbf{r}_i$ denotes the radial position vector for particle i, and where n denotes the number of particles in the molecule. In general we will have three components of the dipole vector D_x, D_y and D_z. Assuming a field polarized in the z-direction and assuming the diameter of the molecule is much smaller than the wavelength of the light, the interaction potential energy of the molecule is given as

$$V = \vec{\varepsilon}(\mathbf{r}, t) \cdot \vec{D} \approx \varepsilon_z(t) D_z. \tag{2.1}$$

When treating the system quantum mechanically, since the free Hamiltonian H_0(corresponding to the kinetic energy of the system) is usually a matrix the interacting dipole moment will now be a matrix dipole moment operator $\hat{\mu}$. Using the energy eigen states of H_0, $|\psi_i\rangle$ we can define the dipole matrix $\hat{\mu} = \langle\psi_i|\hat{\mu}(r)|\psi_j\rangle$, where the position dependent $\mu(\mathbf{r})$ is analogous to . The interaction potential Hamiltonian $\hat{H}_I = -A\cos(\omega t)\cdot\hat{\mu}$ and hence the total Hamiltonian is

$$H = H_0 + H_I = H_0 + \mu\cdot\vec{\varepsilon}(\mathbf{r}, t)$$

and the corresponding Schrödinger equation is

$$\frac{d\psi(t)}{dt} = \frac{-i}{\hbar}(H_0 - \mu\cdot\varepsilon(t))\psi(t). \tag{2.2}$$

The bare Hamiltonian H_0 and the dipole operator μ are hermitian as they are required to have real eigen values to accurately represent a physical situation. In the conventional quantum mechanical description the interaction Hamiltonian H_I is interpreted as a small perturbation to the actual bare Hamiltonian H_0 and there are many approximation methods developed to solve the above equation.

Another way of looking at Eq. (2.2) is to recognize it as a control equation. The mathematical structure of Eq. (2.2) can be recognized as what is popularly known as bilinear control equation which is of the following form for a hermitian matrices A and B,

$$\frac{dx}{dt} = (Ax(t) + Bu(t))x(t)$$

where $u(t)$ is a time dependent control that can designed to for example to drive the state $x(t)$ to a predefined final state $X(T)$. These type of bilinear equations frequently appear in classical optimal control theoretic problems often encountered in engineering designs. *This equation will be discussed more in later chapters??*

Therefore in the Schrödinger equation.2.2 the electric field $\varepsilon(t)$ acts as the time dependent control, solving which leads to time-dependent probability transitions $P_{ij}(t)$ between the energy eigen states $|\psi_i\rangle$ and $|\psi_j\rangle$ of the bare Hamiltonian H_0 which is usually time-independent. For a closed system, where the Schrödinger equation can be exactly solved and the dynamics are Unitary, always leads to time independent probabilities and the states in that case are called as 'stationary states'. In the case of an interaction, the Hamiltonian is not known exactly and the Schrödinger equation cannot be solved exactly and so the time-dependent probabilities.

2.1.1 Representation of the Electric field

The classical theory of light is a well defined field and is discussed in many text books and so in this section we briefly discuss the representation of light for completeness and only pertinent to the quantum control theory.

In performing the quantum control experiments in the actual laboratory, one uses the laser as the light source and the techniques in this book mainly focus on designing the pulse shapes to perform the control task at hand. Usually a pulsed femtosecond laser is used. In theory, laser light is considered as a semiclassical source and so can be described to a remarkably well using the wave theory. In a fully quantum picture the finding an optimal pulse translates to finding an optimal distribution of photons that interact with the physical system under consideration, which is molecule in the present context.

An electromagnetic wave travelling in the z-direction, in general, is composed of all possible frequency modes and is written as,

$$\varepsilon(t - x/c) = \Re\left\{\int_{-\infty}^{\infty} A(\omega)\exp(i\phi(\omega))\exp[i\omega(t - x/c)]\ d\omega\right\} \tag{2.3}$$

where $c = 3 \times 10^8 m/s$, is the speed of light, t is time in seconds and ω is the frequency and $\phi(\omega)$ is the frequency dependent phase. $A(\omega)$ is the complex electric field amplitude in the frequency domain.

In practice, wavelength of highest frequency, which corresponds to the Ultra Violet regime of the electromagnetic spectrum, $c/\omega \approx 10^3$ angstroms, whereas molecular diameter are of the order of single angstroms, and so $\omega x/c$ much larger than molecule. Thus we can approximate Eq. 2.3 as

$$\varepsilon(t) \approx \Re\left\{\int_{-\infty}^{\infty} A(\omega)\exp(i\phi(\omega))\exp(i\omega t)\ d\omega\right\}. \tag{2.4}$$

The most important components of the field apart from the frequency ω, are the phase $\phi(\omega)$ and the amplitude $A(\omega)$ in desiging the optimal pulse shapes. Most Quantum Control processes are sensitive to phase [**?**] and for most physical systems phase-only shaping, by fixing the amplitude $A(\omega)$ is sufficient for attaining optimal control.**ELABORATE....**

The amplitude $A(\omega)$ is typically modelled as Gaussian and is true in most of the practically relevant cases. Thus,

$$\Re[A(\omega)] = \frac{1}{\sqrt{2\pi\sigma}}\exp[-(\omega - \omega_0)^2/\sigma^2] \tag{2.5}$$

for some mean frequency ω_0 and variance of σ. For a pulsed laser this variance σ is called bandwidth of the pulse. Since the shape of the pulse need not be preserved as it propagates, sometimes use of envelope ot shape function will be very helpful. A standard nonlinear chirp is a Gaussian. With an envelope function $s(t)$ the electric field will be

$$\varepsilon(t) = s(t)\Re\left\{\int_{-\infty}^{\infty} A(\omega)\exp(i\phi(\omega))\exp(i\omega t)\ d\omega\right\} \tag{2.6}$$

and typical examples of the envelope function are $s(t) = \sin^2(\pi t/T)$ or $\frac{1}{\sqrt{2\pi\sigma}} \exp[-(t-t_0)^2/\sigma^2]$. The total energy of the of the field is given as the square of the amplitude:

$$\mathbf{E} = \int_{\infty}^{\infty} |\varepsilon(t)|^2 \, dt = \int_{\infty}^{\infty} |\varepsilon(\omega)|^2 \, d\omega \tag{2.7}$$

where $\varepsilon(\omega) = A(\omega)\exp(i\phi(\omega))$ is the electric field in frequency domain and $\varepsilon(t) = A(t)\exp(i\Phi(t))$ in the time domain.

The spectral phase $\phi(\omega)$ and the temporal phase $\Phi(t)$ cannot be measured absolutely and only the relevant phase are important. The phase of an electromagnetic wave is not just a mathematical generlization, but is a well defined property of the wave. The importance of relative phase is demonstrated in the classic double-slit experiment. [**?**].

As an example of the theory developed so far, let us now investigate an harmonic oscillator in an external external electromagnetic field. Consider a di-atomic molecule with atomic masses m_1 and m_2 and are spatially saperated with a distance r_0. The total Hamiltonian H wich is the sum of the free Hamiltonian H_0, consisting of Kinetic and Potential energy, and the interaction Hamiltonian H_I is given as

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{1}{2}kr^2 - \mu(r)\cdot\varepsilon(t)$$

with $m = \frac{m_1 m_2}{m_1+m_2}$ being the reduced mass of the molecule. The corresponding Schrödinger equation is

$$i\hbar\frac{d}{dt}\psi(r,t) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{1}{2}kr^2 - \mu(r)\cdot\varepsilon(t)\right)\psi(r,t). \tag{2.8}$$

The dipole moment matrix μ is an $N \times N$ Hermitian matrix in the eigen basis of H_0 as described earlier in this section. It can be noted from the above equation that although a dipole transition matrix may be well defined for a system, it does not have any effects on the system dynamics in absence of the interaction external field $\varepsilon(t)$.

The diagonal elements of μ are less significant since only the off diagonal elements are what allow the electric field to drive transition between the states. This can be seen more explicitly, if H_0 and μ are both $N \times N$ diagonal matrices, then Eq. 2.8 can have the solution

$$\psi(t+\Delta t) \approx \exp\begin{bmatrix} -\frac{i}{\hbar}(E_1 - m_1\varepsilon(t))\Delta t & & 0 \\ & \ddots & \\ 0 & & -\frac{i}{\hbar}(E_N - m_N\varepsilon(t))\Delta t \end{bmatrix}\psi(t), \tag{2.9}$$

where the diagonal elements of dipole matrix $\mu_{ii} = m_i$. Suppose if we begin in the ground state corresponding to energy E_1 implying $\psi(0) = [1, 0, \cdots, \cdots, 0]^\dagger$, the solution in Eq. 2.9 leads to

$$\psi(T) = \prod_{n=1} \exp(-\frac{i}{\hbar}(E_1 - m_1\varepsilon(t_n))\Delta t)\psi(0)$$

and there is no transition to a different system. The only effect of the evolution is that the initial state is multiplied by an irrelevant global phase, since the expectation value of any observable $\hat{O}$ is same: $\langle\psi(T)|\hat{O}|\psi(T)\rangle = \langle\psi(0)|\hat{O}|\psi(0)\rangle$. Thus the state will not transit to another state. However the ground state energy is being continuously changed as more and more energy is being added via the field $\varepsilon(t)$. This simple example illustrates that we need the off-diagonal transition matrix elements to perform any driving of between the states.

In reality however, as observed in the molecular spectroscopy experiments, only certain direct transitions are possible and may use indirect transitions such as exciting the molecule to short lived intermediate states and then to the final target state can be used for the cases where the direct transtions are not allowed. Whether a direct transition is “forbidded” or “allowed” depends on matrix elements of the dipole moment operators. The matrix elements of μ can be straightforwardly calculated once the Schrödinger equation is solved with the free Hamiltonian H_0 for the eigen state $|\psi_i\rangle$. If the $\mu_{ij} = \langle\psi_i|\mu|\psi_j\rangle = 0$ then the transition between the states $|\psi_i\rangle$ and $|\psi_j\rangle$ is forbidded, while for an allowed transition $\mu_{ij} \neq 0$. For simple harmonic oscillator corresponding to the transitions between the diatomic vibrational states it turns out that the states are given as,

$$\psi_\nu(r) = \frac{1}{\sqrt{2^\nu n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega r^2}{2\hbar}} H_\nu\left(r\sqrt{\frac{m\omega}{\hbar}}\right)$$

where $\omega = \sqrt{\frac{k}{m}}$ and $H_\nu(r) = (-1)^\nu e^{r^2} \frac{d^\nu}{dr^\nu}(e^{-r^2})$ is called as the Hermite polynomial and the corresponding energy eigen values are

$$E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right).$$

Expanding the dipole moment $\mu(r) = \mu_0 + \left(\frac{d\mu}{dr}\right)\hat{r} + \cdots$, where μ_0 refers to the permanent dipole moment at the equalibrium and can be ignored. In the first order term, for most physical systems $d\mu/dr$ is a constant $\alpha(say)$ and $\hat{r}$ is the position operator. Ignoring the hiher order terms, which is reasonable assumption(??), we can calculate the dipole matrix elements quite explicitly as $\langle\psi_\nu(r)|\mu(r)|\psi'_\nu(r)\rangle = \alpha\langle\psi_\nu(r)|\hat{(}r)|\psi'_\nu(r)\rangle$. For harmonic oscillator it turns out that

$$\langle\psi_\nu(r)|\mu(r)|\psi'_\nu(r)\rangle = 0, \quad \forall\nu' \neq \nu \pm 1. \tag{2.10}$$

Thus for the vibrational states one can either excite or de-excite only to the immediate neighbouring states and the selection rule can be succintly written as $\Delta\nu = \pm 1$, for the states that are solely charecterized by the quantum number ν, and the dipole matrix will have a banded structure:

$$\begin{bmatrix} \mu_{11} & \mu_{12} & & & \\ \mu_{21} & \mu_{22} & \mu_{23} & & \\ 0 & \mu_{32} & \mu_{33} & \mu_{34} & \\ \vdots & \vdots & \vdots & \vdots & \ddots \\ 0 & 0 & \cdots & \mu_{N(N-1)} & \mu_{NN} \end{bmatrix}$$

with $\mu_{ij} = \mu_{ji}$ due to the Hermiticity of μ. An important goal in quantum control is finding the laser pulses that drive the transitions between the molecular energy eigenstates. The possibility of such transitions a transition depends on the dipole matrix elements. Conssider the problem of exciting the molecule from the ground vibrational state $\nu = 0$ to the 1^{st} excited vibrational state with $\nu = 1$ using a sinusoidal filed, we would need a non-zero matrix element $\langle \nu = 0|\mu|\nu = 1\rangle$. On the other hand considering the problem of exciting the ground vibrational state to, say 3^{rd} excited vibrational state may be possible, inspite of the fact that $\langle \nu = 0|\mu|\nu = 3\rangle = 0$, by involving a multistep level-level transitions such as following the system in the path: $1 \rightarrow 2 \rightarrow 3$.

- Excercise: Using the Harmonic oscillator eigen functions, derive the selection rules shown in Eq. 2.10

2.2 Pictures in Quantum Mechanics

This section should be in the first chapter.

The time dependent Schrödinger equation for a closed system, mathematically speaking is simply a first order differential equation written as,

$$i\hbar\frac{d}{dt}\psi(r,t) = H_0\psi(r,t) \tag{2.11}$$

and the solutions seeks to find the wavefunction as a function of time: $\psi(t)$. The dynamics of the system are then Unitary, since the norm of the wavefunction $|\langle\psi(t)|\psi(t)\rangle|^2 = |\langle\psi(t)|\psi(t)\rangle|^2 = 1$ is preserved. The solution of the above equation then is

$$\psi(t) = U(t,0)\psi(0), \text{ where } U(t,0) = e^{-\frac{i}{\hbar}\int_0^t H_0(t)dt} \tag{2.12}$$

with $\psi(0)$ being the state at $t = 0$. This is called as *Schrödinger picture* where the states evolve in time and any observable Θ is time independent.

Another conveneint representation is *Heisenberg picture*, where the states are independent of time and the observables are functions of time $\Theta(t)$. Thus the equation of motion for the obeservable is

$$\frac{d\Theta}{dt} = -\frac{i}{\hbar}\left[\Theta, H\right] \tag{2.13}$$

with $[A, B] = Ab - BA$ is the commutator. In the Heisenberg the time development of the operator Θ is also given as $\Theta(t) = U^{\dagger}(t)\Theta U(t)$ and the expectation value of the observable is given as

$$\langle\psi|\Theta(t)|\psi\rangle = \langle\psi|U^{\dagger}(t)\Theta U(t)|\psi\rangle = \langle U(t)\psi|\Theta|U(t)\psi\rangle = \langle\psi(t)|\Theta|\psi(t)\rangle. \tag{2.14}$$

The last term in the above equality is the expectaion value in the Schrödinger picture and it shows that the expectaion values in both pictures is equal. The basic differnce being that in the Schrödinger picture the evolution of the states is governed by the total Hamiltonian, H and the observable do not change, while in the Heisenberg picture the states do not change while the evolution of the observables is governed by the total Hamiltonian H.

In treating the system interacting with an external potential or field, the total Hamiltonian $H(t) = H_0 + H_1(t) = H_0 - \mu \cdot \varepsilon(t)$. It turns out another conveneint picture called as *Interaction picture*, where both the states and observables evolve in time. The evolution of the states is determined by the interaction Hamiltonian $H_1(t)$ and the evolution of the observables in determined by the free Hamiltonian H_0 . This also is equivalent to solving the problem in the system reference reference frame and is performed as,

$$H_I(t) = \exp(\frac{i}{\hbar}H_0 t)H_1(t)\exp(-\frac{i}{\hbar}H_0 t)$$

and the state vectors in this basis are $|\phi(t)\rangle = exp\left(\frac{i}{\hbar}H_0 t\right)|\psi(t)\rangle$ where $\psi(t)$ is the state in the Schrödinger picture. Since at $t = 0$ the exponent $exp\left(\frac{i}{\hbar}H_0 t\right)$ is identity implying that the initial state in both the pictures coincide. We can also get the relation between the matrix elements of the Hamiltonian in both pictures.

$$\begin{aligned}\langle j|H_I|i\rangle &= \langle j|\exp(\frac{i}{\hbar}H_0 t)H_1(t)\exp(-\frac{i}{\hbar}H_0 t)|i\rangle \\ &= \exp^{\frac{i(E_j - E_i)t}{\hbar}}\langle j|H_1(t)|i\rangle\end{aligned}$$

. To derive the Schrödinger equation in the interaction picture consider the time evolution of $|\phi(t)\rangle$,

$$\begin{aligned}
\frac{d}{dt}|\phi(t)\rangle &= \frac{i}{\hbar}H_0|\phi(t)\rangle - \frac{i}{\hbar}\exp(\frac{i}{\hbar}H_0 t)H(t)|\psi(t)\rangle \\
&= \frac{i}{\hbar}H_0|\phi(t)\rangle - \frac{i}{\hbar}H_0\exp(\frac{i}{\hbar}H_0 t)|\psi(t)\rangle - \frac{i}{\hbar}\exp(\frac{i}{\hbar}H_0 t)H_1(t)|\psi(t)\rangle \\
&= \frac{i}{\hbar}H_0|\phi(t)\rangle - \frac{i}{\hbar}H_0|\phi(t)\rangle - \frac{i}{\hbar}\exp(\frac{i}{\hbar}H_0 t)H_1(t)|\psi(t)\rangle \\
&= -\frac{i}{\hbar}\exp(\frac{i}{\hbar}H_0 t)H_1(t)\exp(-\frac{i}{\hbar}H_0 t)|\phi(t)\rangle \\
&= -\frac{i}{\hbar}H_I(t)|\phi(t)\rangle
\end{aligned}$$

We therefore can define the unitary propagator in the interaction picture as

$$U_I(t) = \mathcal{T}exp\left[-\frac{i}{\hbar}\int_0^t H_I(t')dt'\right] \tag{2.15}$$

where $\mathcal{T}$ is called the time ordering operator. We can derive the relation between the unitary propagator in Schrödinger picture and interaction picture which may be useful when dealing with the change in representations. Noting that the free hamiltonian H_0 is always time independent and $|\phi(t)\rangle = U_I(t)\,|\phi(0)\rangle$ and by denoting $U_0 = \exp\left(\frac{i}{\hbar}H_0 t\right)$, starting from the state in the interaction picture

$$\begin{aligned}
|\phi(t)\rangle &= U_0\,|\psi(t)\rangle \\
U_I\,|\phi(0)\rangle &= U_0\exp\left(-\frac{i}{\hbar}\int_0^t H(t')dt'\right)|\psi(0)\rangle \\
U_I\,|\phi(0)\rangle &= U_0 U_s\,|\psi(0)\rangle \\
U_I &= U_0 U_s
\end{aligned}$$

since the initial state in both pictures is identical.

2.3 Time-dependent Perturbation theory

The Schrödinger equation in give Eq. 2.2 often cannot be solved exactly except in very few lower dimensional such as a two energy level systems. In general, as the dimension of the Hilbert space grows, the Schrödinger equation in presence of external field often becomes intractable. It is a common practice to treat the external field as a perturbation to the free Hamiltonian H_0 and assume that the perturbation be small when compared to the eigen values of H_0. This theory is called perturbation theory and the corrections to the energy eigen functions as well as to the energy eigen values can be found to reasonable degree of accuracy.

Perturbation theory seeks to compute the time evolution of state of the system in the presence of the applied field in terms of linear combination of the unperturbed wavefunctions by using a Taylor expansion of the $\psi(t)$ in orders of the interaction Hamiltonian strength λ which is typically used to compute the transition probabilities in weak fields. In general this indicates that the optimal fields are resonant, since in spectroscopic experiments the absorption and emission of charecteristic spectral frequencies corresponding to transitions between the energy levels E_i, E_j of a molecule. However, these solutions are approximate, and control theory is required to compute the optimal fields. For analytical insight, we will begin with a study of perturbation theory calculations of the transition probability.

The dynamics of the system in the interaction picture can be obtained from the unitary propagator given in Eq. 2.15, which also can be rewritten as a differential equation from the Schrödinger equation for $|\phi(t)\rangle$,

$$\begin{aligned} \frac{d}{dt}\left|\phi(t)\right\rangle &= -\frac{i}{\hbar}H_I(t)\left|\phi(t)\right\rangle \\ \frac{d}{dt}U_I(t)\left|\phi(0)\right\rangle &= -\frac{i}{\hbar}H_I(t)U_I\left|\phi(0)\right\rangle \end{aligned}$$

which immediately leads to

$$\frac{d}{dt}U_I(t) = -\frac{i}{\hbar}H_I(t)U_I(t). \tag{2.16}$$

with $U_I(0) = I_N$.

This differential equation 2.16 is often becomes cumbersome for higher dimensional systems since it involves matrices. A formal solution for Eq. 2.16 can be written as, along with the initial condition

$$U_I(t) = I_N - \frac{i}{\hbar}\int_0^t H_I(t')U_I(t')\,dt'. \tag{2.17}$$

Instead of representing this as a matrix exponential, we may expand the exponential in a series and is called as Dyson series, which is equivalent to the following iterative representation of $U_I(t)$:

$$
\begin{aligned}
U_I(t) &= I_N - \frac{i}{\hbar}\int_0^t H_I(t')U_I(t')\ dt' \\
&= I_N - \frac{i}{\hbar}\int_0^t H_I(t')\left[I_N - \frac{i}{\hbar}\int_0^{t'} H_I(t'')U_I(t'')\ dt''\right] dt' \\
&= I_N - \frac{i}{\hbar}\int_0^t H_I(t')\ dt' + (-\frac{i}{\hbar})^2\int_0^t\int_0^{t'} H_I(t')H_I(t'')\ dt''dt' + \cdots + \\
&\quad (-\frac{i}{\hbar})^n\int_0^t\int_0^{t'}\cdots\int_0^{t^{n-1}} H_I(t')H_I(t'')\cdots H_I(t^n)\ dt^n\cdots dt'\cdots
\end{aligned}
$$

Since one is more interested in finding the transition amplitudes $c_{ji}(t) = \langle j|U_I(t)|i\rangle$ and to approximate it to arbitrary order using the above series expansion of $U_I(t)$

$$
\begin{aligned}
c^1_{ji}(t) &= -\langle j|\lambda\frac{i}{\hbar}\int_0^t H_I(t')\ dt'|i\rangle \\
c^2_{ji}(t) &= \langle j|\frac{2}{\hbar^2}\int_0^t\int_0^{t-1} H_I(t'')\ dt''\ dt'|i\rangle \\
&\vdots \\
c^n_{ji}(t) &= \langle j|(-\lambda\frac{i}{\hbar})^n\int_0^t\cdots\int_0^{t^n-1} H_I(t')\cdots H_I(t^n)\ dt^n\cdots dt'|i\rangle
\end{aligned}
$$

2.4 Quantum interference between pathways

The transition of the molucule from state i to state j in reality takes several routes. In the perturbation expansion for the probability amplitudes in the previous section, each order of the probability amplitude is called as a *pathway*. Due to the presence of the imaginary number i(not to be confused with the state$|i\rangle$) these amplitudes in general are complex number and carry a imaginary phase which cannot be neglected since c^n_{ji} is only a part contributing to the total probability. Quite intuitively we can compare the amplitudes with the amplitudes of the electric field in the famous double-slit experiments, where the final intensity on the screen is a definite function of the relative phase between the amplitudes that are emerging from the two pinholes. In the present case the total transition probability(which is analogous to the intensity on the screen) between the states i and j at time t upto n^{th} order is then given as

$$P_{ij}(t) = |c^1_{ji}(t) + c^2_{ji}(t) + \cdots + c^n_{ji}(t)|^2 = \left[c^1_{ji}(t) + c^2_{ji}(t) + \cdots + c^n_{ji}(t)\right]^* \\ \times \left[c^1_{ji}(t) + c^2_{ji}(t) + \cdots + c^n_{ji}(t)\right].$$

This is a remarkable result and is hallamark of quantum mechanics in the context of molecules and demonstrates the property of *quantum intereference between paths* due to the presence of coherence terms $c^x_{ji}(t))^* c^y_{ji}(t)$.

In presence of a well defined external electric field we can derive explicit expression for various orders of the probability amplitudes. Consider a field in Fourier series representation

$$\varepsilon(t) = \int_{-\infty}^{\infty} d\omega\ A(\omega) \exp(i\phi(\omega)) \exp(-i\omega t)$$

and the interaction Hamitonian $H_I(t)$

$$H_I(t) = \exp(\frac{i}{\hbar} H_0 t)[-\mu \cdot \varepsilon(t)] \exp(-\frac{i}{\hbar} H_0 t)$$

and noting that $\langle j| \int_0^t H_I(t)\ dt |i\rangle = -\int_0^t \varepsilon(t) \langle j| \exp(\frac{i}{\hbar} H_0 t) \mu \exp(-\frac{i}{\hbar} H_0 t) |i\rangle\ dt$ we get for the first order probability amplitude as

$$\begin{aligned} c^1_{ji}(t) &= \frac{i}{\hbar} \langle j|\mu|i\rangle \int_0^t \varepsilon(t) \exp(\frac{i}{\hbar}(E_j - E_i)t) dt \\ &= \frac{i}{\hbar} \langle j|\mu|i\rangle \int_{-\infty}^{\infty} d\omega\ A(\omega) \exp(i\phi(\omega)) \int_0^t \exp((\frac{i}{\hbar}(E_j - E_i) - i\omega)t) dt. \end{aligned}$$

Making the substitution $\omega_{ji} \equiv \frac{E_j - E_i}{\hbar}$ and considering the long-time limit, $t \longrightarrow \infty$, the temporal integration is easy to compute in a closed form if we further set the initial time as $-\infty$ and the final time as $+\infty$ we get

$$\int_{-\infty}^{+\infty} \exp[i(\omega_{ji} - \omega)t']\ dt' = 2\pi\delta(\omega_{ji} - \omega)$$

we get the first order probability amplitude as

$$c^1_{ji}(\infty) = \langle j|\mu|i\rangle \int_{-\infty}^{\infty} d\omega\ A(\omega) \exp(i\phi(\omega)) 2\pi\delta(\omega_{ji} - \omega)$$

and due to the delta function it requires $\omega = \omega_{ij}$ in order to have a nonzero contributions and thus in this asymptotic time limit, the perturbation theory demands the external field be in *resonance* with the molecular frequency. Therefore we have

$$c^1_{ji}(\infty) = \frac{2\pi i}{\hbar} \langle j|\mu|i\rangle A(\omega_{ji}) \exp(i\phi(\omega_{ji})). \tag{2.18}$$

Earlier we have mentioned that the phase of the pulse is extremely important and now from the above equation we can see that the optical phase now translates to the phase between the pathways. But if we use only the transition probability amplitude with just the first order we immediately see that

$$|c^1_{ji}(\infty)|^2 = \frac{4\pi^2}{\hbar^2}|\langle j|\mu|i\rangle|^2|A(\omega_{ji})|^2 \tag{2.19}$$

and the phase is irrelavant for the net probability, thus we are not using all information contained in control to drive system to target state.

In an optimal control experiment very often we may want to control the transition between different final states of the molecule. A simple example could be preparing a superposition states for application in quantum computing. Controlling different final states indeed translates to controlling the ration of the probabilities P_{ji} and P_{ki} and is called as *branching ratio*, $R = \frac{P_{ji}}{P_{ki}} = \frac{|c_{ji}(\infty)|^2}{|c_{ki}(\infty)|^2}$. Ideally we would want to control this ration by adjusting the field parameters such as phase and amplitude. Using Eq. 2.19 we get,

$$R = \frac{|c_j(\infty)|^2}{|c_k(\infty)|^2} = \frac{|A(\omega_{ji})|^2|\langle i|\mu|j\rangle|^2}{|A(\omega_{ki})|^2|\langle i|\mu|k\rangle|^2}.$$

which is independent of the field phases. The presence of two different frequencies ω_{ji} and ω_{ki}, the multichromaticity of the laser field is important because each transition pathway requires a corresponding field mode tuned to ω_{ji}.

Chapter 3

(Classical)Optimal Control theory

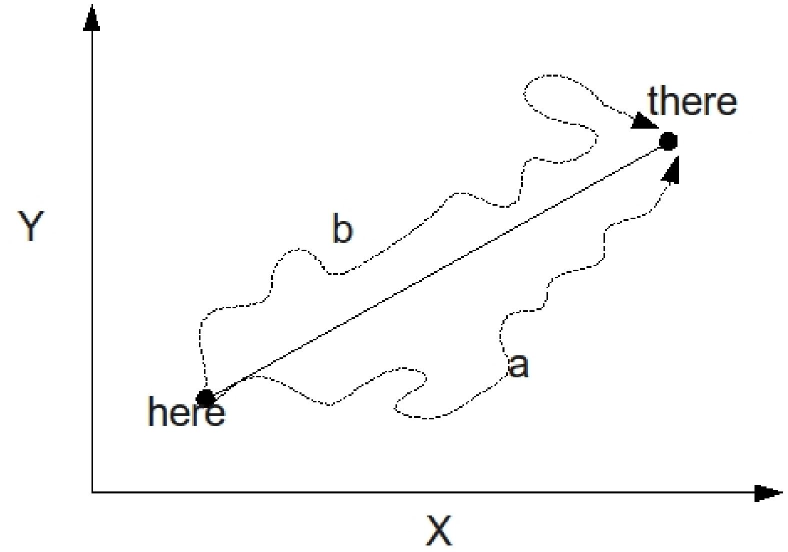

Figure 3.1: A system evolving or driven by external forces from *here* to *there* can take several paths for instance a and b. The theory of optimal control aims at designing the external control such that the evolution will follow a desired path that makes optimal use of the resources at hand.

Very often, as in the case of every invention, engineering new devices and technologies primarily we are interested in controlling the system, and making it perform in a precisely defined manner. Optimal control theory aims at designing controls,optimized over the requirements, which either control a system at a set point such as temperature of a room or drive the system to a well defined final state starting from an arbitrary initial state. Without a well designed control, often a well designed system could not be of much use. A simple and everyday example is the accelerator(gas pedal) and the brake of a car. Without the brake, the accelerator is not of much use, and brake is the controller of the car speed. In this simple case the control(brake) is applied by judging the speed of the car by the driver and therefore not a fully automated control since the human intervention is inevitable. On the other hand, another simple and everyday example of a fully automated control is the thermistor that we use to control the temperature of a room. In this case the thermocouple acts as a control which monitors the temperature and heats the room when the surrounding temperature is below the set value and vice-versa.

Lets consider a simple dynamical system, and whose state $x(t)$ can be determined by a first order differential equation,

$$\frac{dx(t)}{dt} = f(x(t), u(t), t), \tag{3.1}$$

where f could be any function which in general depends on state $x(t)$, control $u(t)$ and time t......

3.1 Euler-Lagrange equations

Optimal control theory has its roots in calculus of variation which aims at maximizing a functional(functional is a function of a function). In general a functional could be a a function of initial state, final state and the cost associated in reaching the final state, all of which could be functions of some system dependent parameters. There are three types of optimal control functionals,*Bolza*, *Lagrange* and *Mayer* that are used in the literature and are suffice to deal with most of the physical systems. *(Are there any other functionals besides these??)*

Consider the state of the system denoted by $x(t)$ and the control $u(t)$, the most "general" cost functional called as *Bolza functional* is given as:

$$J[x(\cdot),\ u(\cdot)] = F(x(T)) + \int_0^T L(x(t), u(t))\ dt. \tag{3.2}$$

The term $J[x(\cdot),\ u(\cdot)]$ is *functional*, since $F(x(T))$ is the *function* often depends only on the final state $x(T)$ and be thought of as an input-output relation, and $L(x(t), u(t))$ is lagrange *function* and is same is the one we encounter in calculus of variation.

The integral $\int_0^T L(x(t), u(t))\ dt$ represents the cost associated, and if this is the only term present then the cost functional J is called as the *Lagrange* type, which physically represents the case where accuracy of reaching the final state can be compromised, but the main goal is to minimize the cost, energy, in reaching the target. On the other hand in the event when we demand the system to reach the exact final state and do not mind in the cost(energy) expended, we will only have the term $F(x(T))$ and the cost functional is then said to be *Mayer* type.

Once the type of problem is decided the optimal control problem in Eq. 3.2 can be stated as

$$\max_{u(\cdot)} J[x(\cdot),\ u(\cdot)] \tag{3.3}$$

subject to the constraints involved in the system as represented by dynamical differential equation of the system.

In Eq. 3.2 the Lagrange term does not necessarily incorporate the constraints of the system as given by the dynamical equations the system follows. Therefore, define a Lagrangian functions $\bar{J}$ that incorporates the constraints of the dynamical system and is given as

$$\bar{J}[\ x(\cdot),\phi(\cdot)] = F(x(T)) + \int_0^T [\lambda L(x(t),u(t)) + \langle \phi(t), f(x(t),u(t),t) - \dot{x}\rangle]\ dt \tag{3.4}$$

where is the lagrange multiplier and $\phi(t)$ is????.

Following the calculus of variations we can define a *Hamiltonian* function, also known as *PMP-Hamiltonian* in control theory for the reasons explained in the next section,

$$\mathbf{H}(x(t),\phi(t),u(t)) = \lambda L(x(t),u(t)) + \langle \phi(t), f(x(t),u(t),t)\rangle \tag{3.5}$$

where $\phi(t)$ is called the costate *for reasons that will be explained later.* Since the inner product is linear, $\langle \phi, f - \dot{x}\rangle = \langle \phi, f\rangle - \langle \phi, \dot{x}\rangle$ and expressing the Lagrangian in terms of $\mathbf{H}$ in Eq. 3.4 we get,

$$\bar{J}[\ x(\cdot),\phi(\cdot)] = F(x(T)) + \int_0^T \mathbf{H}(x(t),\phi(t),u(t))\ dt - \int_0^T \langle \phi, \frac{dx}{dt}\rangle\ dt \tag{3.6}$$

and integrating $\langle \phi(t), \frac{dx(t)}{dt}\rangle$ by parts we arrive at

$$\bar{J} = F(x(T)) - \langle \phi(T), x(T)\rangle + \langle \phi(0), x(0)\rangle + \int_0^T \mathbf{H}(x(t),\phi(t),u(t)) + \langle \frac{d\phi(t)}{dt}, x(t)\rangle\ dt. \tag{3.7}$$

Adopting calculus of variation the solution of the optimal control$u(t)$ can be found by maximizing $\bar{J}$. The first-order variation will be given as,

$$\delta\bar{J} = \langle \nabla_{x(T)} F(x(T)) - \phi(T), \delta x(T)\rangle + \langle \phi(0), \delta x(0)\rangle + \\ + \int_0^T \langle \nabla_{x(t)}\mathbf{H} + \frac{d\phi(t)}{dt}, \delta x(t)\rangle + \nabla_{u(t)}\mathbf{H}\cdot \delta u(t)\ dt.$$

As stated above an ideal control can be obtained by minimizing the cost functional designed, i.e. by setting

$$\delta \bar{J} = 0$$

for any δu, and for any $\delta x(t)$. This condition is analogous to the principle of least action in calculus of variation in which the action is minimized and thus the cost function $\bar{J}$ is an analogous quantity to action in classical Hamiltonian dynamics. This condition further implies the integrand in the equation for $\delta \bar{J}$ is zero and thus leads to the following two Euler-Lagrange equations:

$$\nabla_{x(t)} \mathbf{H} + \frac{d\phi(t)}{dt} = 0 \tag{3.8}$$

$$\nabla_{u(t)} \mathbf{H} = 0, \quad 0 \leq t \leq T. \tag{3.9}$$

The first Euler-Lagrange equation 4.15 along with the definition of the *PMP-Hamiltonian*can be used to generate the dynamical equation of the co-state or adjoint state:

$$\frac{d\phi(t)}{dt} = -\nabla_{x(t)} \mathbf{H} = -\lambda \nabla_{x(t)} L(x(t), u(t)) - \nabla_{x(t)} \langle \phi(t), f(x(t), u(t))) \rangle,$$

3.1.1 Examples of various types of cost functionals

3.1.2 Linear and Bi-linear control systems

For linear control systems such as

$$\frac{dx(t)}{dt} = Ax(t)$$

for an hermitian matrix A for a generic case, we can make the identification (*How is this identification done???*)

$$\nabla_{x(t)} (\mathbf{H} - \lambda L) = A^T \phi(t)$$

and subsequently using the first Euler-Lagrange equation 4.15 we get the co-state dynamical equation for linear control:

$$\frac{d\phi(t)}{dt} = -\lambda \left(\nabla_{x(t)} L \right) - A^T \phi(t). \tag{3.10}$$

Note that the co-state in this case of linear system is not written interms of the state $x(t)$ for reasons that will be made clear in a moment.

Now consider a bilinear control system

$$\frac{dx(t)}{dt} = (A + Bu(t))\, x(t)$$

where A and B are hermitian matrices, $u(t)$ is the control. Bilinear control systems are close to many practical situations such as a molecular system interacts with an external field $\varepsilon(t)$ we have the Schrödinger equation as

$$\frac{d}{dt}\psi(t) = \frac{-i}{\hbar}\left(H_0 - \mu \cdot \varepsilon(t)\right)\psi(t)$$

for an hermitian matrices H_0 and μ which is a bilinear control system where $\varepsilon(t)$ is the control. *The second Euler-Lagrange equation is simply the ODE of the control system, which is said to be the dynamical equation of the variational system. For bilinear systems, we have* $\langle \delta\phi(t), (A + Bu(t))x(t) - \frac{dx(t)}{dt} \rangle = 0,\ \forall\ \delta\phi(t)$*.Based on the dynamical and adjoint equations, we have*

$$\begin{aligned}\frac{d}{dt}\left(\phi(t)x^\dagger(t)\right) &= \frac{d\phi(t)}{dt}x^\dagger(t) + \phi(t)\frac{dx^\dagger(t)}{dt}\\ &= \phi(t)(A + \sum_i B_i u_i(t))x(t) - \phi(t)(A + \sum_i B_i u_i(t))x(t) = 0\end{aligned}$$

i.e., matrix elements of $\phi(t)x^\dagger(t)$ *are constants of the motion and, in particular,* $x^\dagger(t)\phi(t) = x^\dagger(T)\phi(T)$*, so we may express the costate vector in terms of the state vector:* $\phi(t) = x(t)x^\dagger(T)\phi(T)$*.*

For linear systems, it is not possible to express $\phi(t)$ *in terms of* $x(t)$ *in this simple general way because an analogous constant of the motion does not exist. The explicit expression for* $\phi(t)$ *will depend on the specific form of the matrices* A*,* B*.*

If the cost function is of Mayer or Bolza type (latter required for linear systems), the 1st E-L equation is associated with boundary condition

(3.11) $\phi(T) = \nabla_{x(T)} F(x(T))$, [**Show the proof**]

Note that the boundary conditions for the optimal control problem with endpoint cost, specified in the variational and adjoint equations, are "split" between the initial and final times; the costate $\phi(t)$ is propagated backwards in time starting from $\phi(T)$, whereas the "state" $x(t)$ is propagated forward in time starting from $x(0)$.

Example:

3.2 The Pontryagin Maximum Principle

The Euler-Lagrange equations described in the previous section can also derived from Pontryagin Maximum Principle, which also states the necessary condition to find an optimal control with a fixed final time T.

Theorem 3.2.1 *(Pontryagin maximum principle) Consider the problem of steering the control system*

$$\dot{x} = f(x, u), \quad x \in M, \quad u \in \Omega \subset R^k,$$

where M is the state space of the system, from some initial state $x(0) = x_0$ to some final state x_1 while minimizing a cost of the form $\int_0^T f^0(x, u)\mathrm{d}t$. The maximum principle states that if the couple $\bar{u}(t), \bar{x}(t)$ is optimal, there exists an absolutely continuous vector $\lambda(t) \in \mathbb{R}^n$ and a constant $\lambda \leq 0$, such that the PMP-Hamiltonian function $h(x(t), \lambda(t), u(t)) = \langle \lambda(t), f(x(t), u(t)) \rangle + \lambda_0 f^0(x(t), u(t))$ satisfies

$$h(\bar{x}(t), \lambda(t), \bar{u}(t)) = max_u h(\bar{x}(t), \lambda(t), u)$$

and

$$\lambda_j(t) = -\frac{\partial h}{\partial x_j}, \quad j \in 1, ..., n.$$

Moreover, denoting the tangent space to the manifold M at state $x(t')$ by $T_{x(t')}M$, we have $\langle \lambda(0), T_{x(0)}M \rangle = \langle \lambda(T), T_{x(T)}M \rangle$ (transversality condition) [249]. If the final time T is fixed, $h(\bar{x}(t), \lambda(t), \bar{u}(t))$ is constant, whereas if T is allowed to vary, $h(\bar{x}(t), \lambda(t), \bar{u}(t)) = 0$.

This theorem is analogous to the Hamiltonian dynamical equations in Newtonian dynamics. If the control objective is to minimize the final time T insteadof a cost of the form above, the optimal trajectory on $[0, T]$ is associated with the Hamiltonian $-\lambda_0 + \langle \lambda(t), f(x(t), u(t)) \rangle$. In this case, $\max_u h(\bar{x}(t), \lambda(t), u) = 0$ in $[0, T]$, and we have the additional condition that if $\lambda_0 = 0$, then $\lambda(t) \neq 0$ for any t [249].

A corollary of the above PMP-theorem for Mayer type problems is
Corollary: An optimal control $\bar{u}(\cdot)$ that solves the control problem $\max \bar{J}$ satisfies $\frac{\partial \mathbf{H}}{\partial u(t)} = 0$ for a matrix $\phi(T) = \nabla_{x(T)} F(x(T))$ for Bolza or Mayer functionals (otherwise unspecified for Lagrange functionals) and scalar λ where at least one of $\phi(T), \lambda$ is nonzero.

3.3 Optimality conditions: Linear Control problems

From the *PMP-theorem* we can deduce the conditions that determine if the system is optimally controllable. Satisfaction of the first-order conditions following from the PMP is a necessary but not sufficient condition for optimality of a control $\varepsilon(\cdot)$. So-called *Legendre* conditions on the Hessian $\frac{\partial^2 \mathbf{H}}{\partial u(t) \partial u(t')}$, which depend on the type of cost, are also required for optimality. In this section we elucidate the optimality conditions for linear systems..

The first Euler-lagrange equation for linear system is given in Eq. 3.10, which gives us the dynamical equation for the adjoint state. The second Euler-Lagrange equation for linear system leads us to

$$\begin{aligned} \nabla_{u(t)}\mathbf{H} &= 0, \quad 0 \leq t \leq T \\ &= \lambda \nabla_{u(t)} L(u(t)) + \langle B, \phi(t) \rangle = 0 \end{aligned} \tag{3.12}$$

Eq. 3.12 can also be deduced from the *PMP-theorem*, which for linear systems demands that

$$\frac{\partial \mathbf{H}_L}{\partial u_i(t)} = \lambda \frac{\partial L(u(t))}{\partial u_i(t)} + \langle \phi(t), \vec{b}_i \rangle = 0, \quad 0 \leq t \leq T, \tag{3.13}$$

where $\mathbf{H}_L$ represents the *PMP-Hamiltonian* for cost functionals of the Lagrange type and $\vec{b}_i$ is i-th column of B. In general the space of admissible controls $u(\cdot)$ denoted $\mathbb{K}$ is not completely acessible. Impostion of endpoint constraint on the state for Lagrange functionals places restrictions on the adjoint state $\phi(T)$ and hence restricts admissible optimal solutions(controls) to a subspace $\mathcal{S}_L \subset \mathbb{K}$ and *thus a unique control is then specified.*

For cost functionals of the *Bolza* type we have a similar equation with $\mathbf{H}_L$ replaced with $\mathbf{H}_B$, the *PMP-Hamiltonian* for Bolza type. Thus we have

$$\frac{\partial \mathbf{H}_B}{\partial u_i(t)} = \lambda \frac{\partial L(u(t))}{\partial u_i(t)} + \langle \phi(t), \vec{b}_i \rangle = 0, \quad 0 \leq t \leq T, \tag{3.14}$$

along with the boundary condition for the adjoint state, $\phi(T) = \nabla_{x(T)} F(x(T))$ for linear systems. Due to an explicit boundary condition, $\phi(T)$, for Bolza-type functionals, the PMP can explicitly specify a unique optimal control $\bar{u}(\cdot) \in \mathbb{K}$ in the absence of an endpoint constraint, since it may be possible to solve for $\bar{u}(\cdot)$ when $\phi(T) = \nabla F(x(T)) \neq 0$; a unique control is specified there is a unique state that maximizes $F(x)$.

In case of Mayer type cost functionals we do not have the Lagrangian L and hence we have

$$\frac{\partial \mathbf{H}_M}{\partial u_i(t)} = \langle \phi(t), \vec{b}_i \rangle = 0, \quad 0 \leq t \leq T, \tag{3.15}$$

along with the boundary condition $\phi(T) = \nabla_{x(T)} F(x(T))$ for the adjoint state and for this type of cost functionals the PMP condition defines a submanifold $\mathcal{S}_M \subset \mathbb{K}$ of *co*dimension equal to the number of constraints present in the condition $\nabla F(x(T)) =$

0(e.g., N^2, N^2-1, or 1 for unitary propagator, density matrix or observable control, respectively). We will focus on analytical solutions to OCT problems with Bolza costs or Lagrange costs with a terminal constraint, because a unique optimal control exists for these problems.

Example that connects with the previous example in this chapter

3.4 Analytic Solutions: General Guidelines

The existance of the solution, an optimal control is discussed in the previous section. In order to achieve the task usually one has to pay the cost which is enocoded in the Lagrange term of Eq. 3.4. There are mainly two types of Lagrange cost function in determining the solution strategy and charecteristics of closed form optimal control solutions. The first type is *linear cost function*, which has the form:

$$\int_0^T c^T x(t)\ dt$$

for some constant c. The second type of cost function is called the *quadratic cost function* and is has the general form

$$\frac{1}{2}\int_0^T x^T(t) Q x(t)\ dt$$

where Q is not necessarily positive-definite, but symmetric and hence a quadratic form of cost function.

Solving optimal control problems in closed form is non-trivial task because one must not only integrate systems of coupled differential equations as the differential equations are expressed parametrically in terms of controls and one must simultaneously solve for the optimal values of all these parameters. The solution to a control problem, either in the parametric form of the controls or the explicit function is called as the *control law.*

One can solve the optimal control problems either from *Euler-Lagrange* equations or the *PMP-theorem.* In general solving an optimal control problem involves the following steps:

1. Find the dynamical equations for the adjoint state $\phi(t)$, for the control system.
2. Express the control $u(t)$ in terms of the state $x(t)$ and the costate $\phi(t)$
3. If the adjoint equations are uncoupled to the dynamical equations,

   (a) integrate them and express undetermined integration constants in terms of $\phi(T)$.
   (b) Insert this solution for $\phi(t)$ into the dynamical equations and solve for the optimal control.

4. If the adjoint equations are coupled to the dynamical equations,
   (a) solve the system simultaneously (e.g.,using Laplace transforms) express integration constants in terms of $\phi(T)$ and the known initial conditions $x(0)$.
   (b) *If the cost functional is Lagrange*, with an endpoint constraint on the state, use this constraint to obtain $\phi(T)$ and hence explicit solutions for $\phi(t), x(t)$.
   (c) *If the cost functional is Bolza*, use $\phi(T) = \nabla F(x(T))$ to obtain a relation between $\phi(T)$ and $x(T)$; substitute this implicit expression for $\phi(T)$ into all equations to obtain explicit expressions for all constants and determine $x(t), \phi(t)$.
   (d) Use the resulting explicit solutions for $x(t), \phi(t)$ in the equation for $u(t)$ to obtain the optimal control $\bar{u}(t)$.

3.4.1 Linear system: An example

As an application of the theory developed so far, let us take up the example of solving the optimal contorl, i.e. finiding the *control law* for controlling the temperature in a room. The temperature in a room is denoted $y(t)$. It is desired to heat the room (to a target temperature) using the smallest possible amount of energy (heat). Let the ambient (external) temperature be denoted y_e. The rate of heat supply to the room is denoted $u(t)$. The dynamics of temperature change are then given by

$$\frac{dy}{dt} = -a(y(t) - y_e) + bu(t) \tag{3.16}$$

where a, b are constants depending on the insulation and rate of heat transfer. Let the total energy (heat) be given by $\frac{1}{2}\int_0^T u^2(t)\, dt$. We are given the initial temperature $x(0)$.

The problem: Calculate the control function $\bar{u}(t)$ that heats the room to temperature y_f at time T while minimizing the energy used, using two possible performance indices: a) $J = \frac{1}{2}\int_0^T u^2(t)\, dt$ this case corresponds to the demand that the final state must be precisely y_f; b) $J = k[y(T) - y_f]^2 + \frac{1}{2}\int_0^T u^2(t)\, dt$, this case corresponds to the situation that the final temperature need not be precisely y_f.

Solution: To simplify the problem, first let us perform a change of variable in the system differential equation 3.16. Making $x(t) = y(t) - y_e$ and $x_f = y_f - y_e$ leads us to

$$\frac{dx}{dt} = -ax(t) + bu(t) \tag{3.17}$$

which has a bi-linear form and in case of (a) where the cost functional is of Lagrange type, the problem now is $\min\limits_{u(t)} J$ subject to the above equation and $x(T) = X(T) = 100$(say).

On the other hand when the cost functional is Bolza type

$$J = F(x(T)) + \int_0^T L(t)\ dt$$

Following the guidelines outlined in the previous section, first we need to obtain the dynamical equation for the adjoint state $\phi(t)$ and we need to first find the PMP-Hamiltonian which is given as,

$$\begin{aligned}\mathbf{H}(\mathbf{x}(t), \phi(t), \mathbf{u}(t)) &= \lambda L(\mathbf{x}(t), \mathbf{u}(t)) + \langle \phi(t), A\mathbf{x}(t) + B\mathbf{u}(t)\rangle \\ &= \frac{1}{2}\lambda u^2(t) - \phi(t)ax(t) + \phi(t)bu(t)\end{aligned}$$

and using the First Euler-Lagrange equation, the adjoint dynamical equation is given as,

$$\begin{aligned}\frac{d\phi(t)}{dt} &= -\nabla_{\mathbf{x}}\mathbf{H}(\mathbf{x}(t), \phi(t), u(t)) \\ &= -\frac{\partial}{\partial x(t)}[-\phi(t)ax(t) + \phi(t)bu(t)] \\ &= \phi(t)a\end{aligned}$$

To obtain the functional form of the adjoint equation $\phi(t)$, we need to integrate the above 1^{st} order ODE with a being a constant coefficient. We thus obtain,

$$\phi(t) = c\exp(at)$$

where c is integration constant and can be obtained from the boundary condition for $\phi(T)$. Therefore

$$c = \exp(aT)\phi(T)$$

gives us the solution of the adjoint equation as

$$\phi(t) = \exp[-a(T-t)]\phi(T) \tag{3.19}$$

Now applying the second Euler-Lagrange equation we get

$$\begin{aligned} \frac{\partial \mathbf{H}}{\partial u(t)} &= \phi(t)b + \bar{u}(t) = 0, \quad 0 \leq t \leq T \\ &\Longrightarrow \bar{u}(t) = -\phi(t)b \end{aligned} \tag{3.20}$$

where $\bar{u}(t)$ is the optimal control. Now using the solution for the adjoint equation, $\phi(t)$ from above in the dynamical equation for the system we get

$$\begin{aligned} \frac{dx}{dt} &= -ax(t) - b^2\phi(t) \\ &= -ax(t) - b^2 \exp[-a(T-t)]\phi(T) \end{aligned} \tag{3.21}$$

The above dynamical equation for the system, can be analytically integrated using Laplace transforms [**?**]. The following three identifications will be useful

- The Laplace transform of $ax(t)$ is $aX(s)$
- The Laplace transform of $\exp(-at)$ is $\frac{1}{s-a}$
- Laplace transform of $\frac{dx}{dt}$ is $sX(s) - x(0)$

where s is frequency. Thus in the frequency domain the system dynamical equation will take the form,

$$X(s) = \frac{x(0)}{s+a} - b^2 \exp(aT)\phi(T)\frac{1}{(s+a)(s-a)}. \tag{3.22}$$

Performing an inverse Laplace transform we arrive at,

$$x(t) = x(0)\exp(-at) - \frac{x(0)b^2\exp(aT)\phi(T)}{a}\sinh(at) \tag{3.23}$$

where we used the inverse Laplace transforms: $\mathcal{L}^{-1}(\frac{1}{s+a})$ is $\exp(-at)$ and $\mathcal{L}^{-1}(\frac{1}{(s+a)(s-a)}) = \frac{\sinh(at)}{a}$.

From Eqs. **??** we can see that both optimal control and the state are solved but are implicitly expressed in terms of the boundary condition on the adjoint state $\phi(T)$, and so the problem will be completely solved once we have the $\phi(T)$. There are two ways to obtain $\phi(T)$ depending on the cost functional type: Lagrange or Bolza. When dealing with the Lagrange cost we have well defined boundary condition on the state, $x(T) = x_f$ which can be used in Eq. 3.23 leading to

$$\begin{aligned} x_f &= x(0)\exp(-aT) - \frac{x(0)b^2\exp(aT)\phi(T)}{a}\sinh(aT) \\ \phi_L(T) &= \frac{a}{x(0)b^2\exp(aT)\sinh(aT)}\left(x(0)\exp(-aT) - x_f\right) \end{aligned} \tag{3.24}$$

where the subscript L denotes the Lagrange type. When the cost function is of the Bolza type we can use the boundary condition, noting for the current problem at hand $F = k\left[x(T) = x_f\right]^2$, we have

$$\phi_B(T) = \nabla_x F(x(T)) = 2kx(T) \tag{3.25}$$

where the subscript B denotes the Bolza type. Thus we have the solution for the state in both the cases.

To obtain the optimal control $\bar{u}(t)$ we can use Eqs. **??**, leading us to

$$\begin{aligned} \bar{u}(t) &= -\phi(t)b \\ \bar{u}_k(t) &= \exp[a(T-t)]\phi_k(T)b \end{aligned}$$

where $k = L$ refers to Lagrange type and Eq. 3.24 must be used, for $k = B$ Eq. 3.25 must be used.

Chapter 4

Quantum optimal control theory

4.1 Introduction

Optimal control theory[OCT] as described in chapter 4, has been tremendously successful in many of the classical engineering application ranging from sophisticated robotics to the design on thermistors for everyday use. Carrying forward the tremendous success of the OCT to the molecular system requires the basic formalism of the OCT to be treated in accordance with the laws of quantum mechanics and hence is termed as *quantum optimal control theory* or more generally *quantum control*. Historically, the origins of quantum control can be traced back to early attempts at the use of lasers for the selective breaking of bonds in molecules. The concept was based on the application of monochromatic laser radiation tuned to the particular vibrational frequency that would excite and, ultimately, break the targeted chemical bond. A relatively new paradigm of quantum control is towards the quantum information processing, where control of the temporal evolution of states, which are used as information carriers, is desired.

4.2 State manifolds and tangent spaces

In quantum mechanics the states, $|\psi(t)\rangle$ are described by complex vectors in Hilbert space H, with a well defined norm at all times t. The Hilbert sphere $S_{\mathcal{H}}$ is the space of pure states. The quantum states $|\psi\rangle$ evolve on this sphere according the Schrödinger equation for the state matrix or unitary propagator $U(t)$. The manifold of states is described by the unitary group $\mathcal{U}(N)$. Quantum control is achieved by controlling the propagator $U(t)$ and since the map $U(t) \mapsto \psi(t)$ is many-to-one, achieving a control over $U(t)$ is generally more difficult. Further a point on this sphere represents a state at the respective time. From geometrical point of view we can define *tangent space* to a point on the Hilbert sphere $S_{\mathcal{H}}$ as intuitively the flat place touching the manifold at that point. It is generally important when there are constraints on the components of the state vector (e.g., sphere S^2 embedded in $\mathbb{R}^3$). Formally, the tangent space at p is the set of all tangent vectors to the manifold at p, with each tangent vector of a smooth curve σ (in the ambient space) passing through p. $\sigma(0) = p$, $\frac{d\sigma}{dt}|_{t=0} = v$.

Tangent spaces form an important component in quantum control as the existence of tangent vectors represents various possible controls that can then be designed and so it is helpful to define the tangent spaces for both Hilbert sphere $S_{\mathcal{H}}$ and to the unitary group $U(N$.

- Tangent space to $S_{\mathcal{H}}$: Let $S_{\mathcal{H}}$ denote the Hilbert (complex) sphere, the $2N-1$ dimensional space of all N-component complex vectors whose (Hermitian) norm $\langle\psi|\psi\rangle = 1$. Then the tangent space T_S is the set of all complex vectors $\psi_\perp$ satisfying $\langle\psi|\psi_\perp\rangle = 0$.
- Tangent space to $U(N)$: $\mathcal{T}_U U(N) := \{UA : A^\dagger = -A\}$ is the *tangent space* to the unitary group $U(N)$ at U. Here, $A = iB$ $(B = B^\dagger)$ is a skew-Hermitian $N \times N$ matrix, an arbitrary element of the Lie algebra $u(N)$.

the above discussion on tangent spaces needs to be followed by examples and pictorial illustrations??

4.3 Controlled quantum mechanical systems

In this section, we present basic results from quantum theory, which are needed to describe the dynamics of closed quantum systems, that are isolated from any possible environmental interaction. Such an evolution is always unitary propagator, $U(t)$. Coherent control of quantum phenomena involves the application of classical fields (e.g., laser pulses) to quantum systems (e.g., atoms, molecules, quantum dots, etc.). Consider first a coherently controlled closed quantum system (i.e., a system isolated from the environment during the control process), whose evolution is governed by the time-dependent Hamiltonian of the form

$$H(t) = H_0 + H_{\mathrm{c}}(t). \tag{4.1}$$

Here, H_0 is the free Hamiltonian of the system and $H_{\mathrm{c}}(t)$ is the control Hamiltonian (at time t) that represents the interaction of the system with the external field. In the mathematically oriented literature, the control Hamiltonian is usually formally written as $H_{\mathrm{c}}(t) = \sum_m c_m(t) H_m$, where $\{c_m(t)\}$ are real-valued control functions at time t and $\{H_m\}$ are Hermitian operators through which the controls couple to the system. In physical and chemical applications, the control Hamiltonian is often given by

$$H_{\mathrm{c}}(t) = -\varepsilon(t)\mu, \tag{4.2}$$

where μ is the dipole operator and $\varepsilon(t)$ is the control field at time t. The Hamiltonian of the form (4.2) adequately describes the interaction of an atomic or molecular system with a laser electric field in the dipole approximation or the interaction of a spin system with a time-dependent magnetic field. However, other forms for $H_{\mathrm{c}}(t)$ can arise including those nonlinear in $\varepsilon(t)$. For the control fields, we will use the notation $\varepsilon(\cdot) \in \mathbb{K}$ and $c_m(\cdot) \in \mathbb{K}$, where $\mathbb{K}$ is the space of locally bounded, sufficiently smooth, square integrable functions of time defined on some interval $[0, T]$, with T being the target time for achieving the desired control outcome.

The Hilbert space $\mathcal{H}$ of a quantum system is spanned by the eigenstates of the free Hamiltonian H_0. Let $\mathcal{T}(\mathcal{H})$ be the space of trace-class operators on $\mathcal{H}$. For example, for an N-level quantum system, $\mathcal{H} = \mathbb{C}^N$ is the space of complex vectors of length N and $\mathcal{T}(\mathcal{H}) = \mathcal{M}_N$ is the space of $N \times N$ complex matrices. The set of admissible states of a quantum system, which are represented by density matrices on the Hilbert space $\mathcal{H}$, is denoted as $\mathcal{D}(\mathcal{H})$. Any density matrix $\rho \in \mathcal{D}(\mathcal{H})$ is a positive operator of trace one, i.e., $\rho \geq 0$ and $\mathrm{Tr}(\rho) = 1$ [thus, $\mathcal{D}(\mathcal{H}) \subset \mathcal{T}(\mathcal{H})$]. The density matrix of a pure state satisfies $\mathrm{Tr}(\rho^2) = 1$ and can be expressed as $\rho = |\psi\rangle\langle\psi|$, where $|\psi\rangle$ is a normalized complex vector in $\mathcal{H}$. Any quantum state which is not pure can be represented as a statistical mixture of pure states and therefore is called mixed; the density matrix of a mixed state satisfies $\mathrm{Tr}(\rho^2) < 1$. In the presence of environmental interactions the states will be described using the density matrices ρ as the state is often incoherent and hence is a mixed state.

The time evolution of a closed quantum system from $t = 0$ to t is given in the Schrödinger picture by

$$\rho(t) = U(t)\rho_0 U^\dagger(t), \tag{4.3}$$

where $\rho(t)$ is the density matrix of the system at time t, $\rho_0 = \rho(0)$ is the initial state, and $U(t)$ is the system's unitary evolution operator [for an N-level quantum system, $U(t)$ is an $N \times N$ unitary matrix]. If the state is initially pure: $\rho_0 = |\psi_0\rangle\langle\psi_0|$, it will always remain pure under unitary evolution: $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$, where

$$|\psi(t)\rangle = U(t)|\psi_0\rangle. \tag{4.4}$$

The evolution operator satisfies the Schrödinger equation:

$$\frac{d}{dt}U(t) = -\frac{i}{\hbar}H(t)U(t), \quad U(0) = I, \tag{4.5}$$

where I is the identity operator on $\mathcal{H}$. The corresponding evolution equation for the density matrix (called the von Neumann equation) is

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[H(t), \rho(t)], \quad \rho(0) = \rho_0, \tag{4.6}$$

and the Schrödinger equation for a pure state is

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}H(t)|\psi(t)\rangle, \quad |\psi(0)\rangle = |\psi_0\rangle. \tag{4.7}$$

In practice, it is often necessary to take into account interactions between quantum systems called as open quantum systems (e.g., between molecules in a liquid or between electron spins and nuclear spins in a semiconductor material) . We will return to the case of open quantum systems in section 4.5.

4.4 Quantum optimal control theory

4.4.1 Controllability of closed quantum systems

Before considering the design of a control or a control experiment, a basic issue to address is whether in principle a control exists to meet the desired objective. Assessing the system's controllability is an important issue from both fundamental and practical perspectives. A quantum system is called controllable in a set of configurations, $\mathcal{S} = \{\zeta\}$, if for any pair of configurations $\zeta_1 \in \mathcal{S}$ and $\zeta_2 \in \mathcal{S}$ there exists a control that can drive the system from the initial configuration ζ_1 to the final configuration ζ_2 in a finite time T.[1] Here, possible types of the configuration ζ include the system's state ρ, the expectation value $\mathrm{Tr}(\rho\Theta)$ of an observable (a Hermitian operator) Θ, the evolution operator U, and the Kraus map Φ, with the particular choice depending on the specific control problem.

Consider first the well studied issue of controllability of closed quantum systems with unitary dynamics [142, 143, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179]. A closed quantum system is called kinematically controllable in a set $\mathcal{S}_\mathrm{K}$ of states if for any pair of states $\rho_1 \in \mathcal{S}_\mathrm{K}$ and $\rho_2 \in \mathcal{S}_\mathrm{K}$ there exists a unitary operator U, such that $\rho_2 = U\rho_1 U^\dagger$. Any two quantum states that belong to the same kinematically controllable set $\mathcal{S}_\mathrm{K}$ are called kinematically equivalent. As unitary evolution preserves the spectrum of a density matrix, two states ρ_1

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[1] More generally, the definition of controllability can be extended by considering the asymptotic evolution in the limit $T \to \infty$. For the sake of simplicity, we will consider here only finite-time controllability.

and ρ_2 of a closed quantum system are kinematically equivalent if and only if they have the same eigenvalues [171, 172]. Therefore, all quantum states that belong to the same kinematically controllable set have the same density-matrix eigenvalues (and, correspondingly, the same von Neumann entropy and purity [158]). For example, all pure states belong to the same kinematically controllable set. However, any pure state is not kinematically equivalent to any mixed state. For a closed quantum system, all states on the system's Hilbert space are separated into disconnected sets of kinematically equivalent states.

It is also possible to consider controllability in the dynamic picture. Assume that the Hamiltonian $H(t)$ which governs the dynamics of a closed quantum system through the Schrödinger equation (4.5) is a function of a set of time-dependent controls: $H(t) = H(c_1(t), \ldots, c_k(t))$. A closed quantum system is called dynamically controllable in a set $\mathcal{S}_{\mathrm{D}}$ of states if for any pair of states $\rho_1 \in \mathcal{S}_{\mathrm{D}}$ and $\rho_2 \in \mathcal{S}_{\mathrm{D}}$ there exist a finite time T and a set of controls $\{c_1(\cdot), \ldots, c_k(\cdot)\}$, such that the solution $U(T)$ of the Schrödinger equation (4.5) transforms ρ_1 into ρ_2: $\rho_2 = U(T)\rho_1 U^{\dagger}(T)$. Since a closed system is controllable only within a set of kinematically equivalent states, a dynamically controllable set of states $\mathcal{S}_{\mathrm{D}}$ is always a subset of the corresponding kinematically controllable set $\mathcal{S}_{\mathrm{K}}$. If the dynamically controllable set of pure states coincides with its kinematically controllable counterpart (i.e., the set of all pure states), the closed quantum system is called pure-state controllable. If for any pair of kinematically equivalent states ρ_1 and ρ_2 there exists a set of controls that drives ρ_1 into ρ_2 in finite time (i.e., if all dynamically controllable sets of states coincide with their kinematically controllable counterparts), the closed system is called density-matrix controllable.

It is also possible to consider controllability of closed quantum systems in the set of unitary evolution operators. A closed quantum system is called evolution-operator controllable if for any unitary operator W there exists a finite time T and a set of controls $\{c_1(\cdot), \ldots, c_k(\cdot)\}$, such that $W = U(T)$, where $U(T)$ is the solution of the Schrödinger equation (4.5) with $H(t) = H(c_1(t), \ldots, c_k(t))$. For an N-level closed quantum system, a necessary and sufficient condition for evolution-operator controllability is [143, 171, 172, 173] that the dynamical Lie group $\mathfrak{G}$ of the system (i.e., the Lie group generated by the system's Hamiltonian) be $\mathrm{U}(N)$ [or $\mathrm{SU}(N)$ for a traceless Hamiltonian]. It was also shown [171, 172, 173] that density-matrix controllability is equivalent to evolution-operator controllability. For specific classes of states, the requirements for controllability are weaker [165, 166, 167]. For example, pure-state controllability requires that the system's dynamical Lie group $\mathfrak{G}$ is transitive on the sphere $\mathbb{S}^{2N-1}$. For infinite-level quantum systems evolving on non-compact Lie groups, such as those arising in quantum optics, the conditions for controllability are more stringent [179, 180].

4.4.2 Theoretical formulation of quantum optimal control theory

In the majority of physical and chemical applications, the most effective way to coherently control complex dynamical processes in quantum systems is via the coordinated interaction between the system and electromagnetic field whose temporal profile may be continuously altered throughout the control period. For a specified control objective, and with restrictions imposed by many possible constraints, the time-dependent field required to manipulate the system in a desired way can be designed using Quantum Optimal Control Theory(QOCT)

The control theory rests on the fact that an objective function, which means the actual purpose of the problem, can be described and so the formulation of a quantum control problem should begin the definition of a quantitative control objective.

Consider a coherently controlled N-level closed quantum system, with the Hamiltonian

$$H(t) = H_0 - \varepsilon(t)\mu \tag{4.8}$$

and the unitary evolution operator $U(t) \in \mathrm{U}(N)$ that obeys the Schrödinger equation (4.5). In QOCT, the control objective for such a system can be a functional of the set of evolution operators $U(\cdot) = \{U(t) \mid t \in [0, T]\}$ (where T is the target time), as well as of the control fields $\varepsilon(\cdot)$. The general class of control objective functionals (also referred to as cost functionals) can be written as

$$J[U(\cdot), \varepsilon(\cdot)] = F(U(T)) + \int_0^T G(U(t), \varepsilon(t))dt, \tag{4.9}$$

where F, also called as the kinematic objective function, is a continuously differentiable function on $\mathrm{U}(N)$, and G is a continuously differentiable function on $\mathrm{U}(N) \times \mathbb{R}$. Usually, the first term in (3.2) represents the main physical goal, while the second term is used to incorporate various constraints on the dynamics and control fields.

On the Hilbert sphere $S_{\mathcal{H}}$, the optimal control problem may be stated as

$$J_{\text{opt}} = \max_{\varepsilon(\cdot)} J[U(\cdot), \varepsilon(\cdot)], \tag{4.10}$$

subject to the dynamical constraint of the Schrödinger equation. The maximization in Eq.(4.4.1) equivalent to minimization with a change of sign of the functional, but does not alter the basic formalism. The cost functional of the form (3.2) is said to be of the Bolza type. If only the term $\int_0^T G(U(t), \varepsilon(t))dt$ is present, the cost functional is said to be of the Lagrange type, whereas if only the term $F(U(T))$ is present, the functional is said to be of the Mayer type [204]. The choice of $F(U(T))$ depends on the problem at hand and will be discussed in more detail.

The cost functional for a pure state subject to Schrödinger can be written as,

$$\bar{J}[\ \psi(\cdot),\phi(\cdot),\ \varepsilon(\cdot)] \;=\; F(\psi(T))+\int_0^T\Big[\lambda L(\psi(t),\varepsilon(t)) \\ +\;\langle\phi^\dagger(t)|\big(-\frac{i}{\hbar}(H_0-\varepsilon(t)\cdot\mu)-\frac{d}{dt}\big)|\psi(t)\rangle\Big]\,dt \tag{4.11}$$

where λ is a scalar weight and $|\phi(t)\rangle$ is a Lagrange multiplier to satisfy the Schrödinger and can be treated as an auxiliary state often called as *costate*.

A necessary condition for a solution of the optimization problem (4.4.1) subject to the dynamical constraint (4.5) is that the first-order functional derivatives of the objective functional $\tilde{J}[U(\cdot),V(\cdot),\varepsilon(\cdot)]$ of Eq. (4.20) with respect to $V(\cdot)$, $U(\cdot)$, and $\varepsilon(\cdot)$ are equal to zero. The resulting set of Euler-Lagrange(EL) equations is given by

$$\frac{d}{dt}U(t)=-\frac{i}{\hbar}H(t)U(t),\quad U(0)=I, \tag{4.12}$$

$$\frac{d}{dt}V(t)=-\frac{i}{\hbar}H(t)V(t),\quad V(T)=\nabla F(U(T)), \tag{4.13}$$

$$\frac{\partial}{\partial\varepsilon(t)}G(\varepsilon(t))-\frac{2}{\hbar}\mathrm{Im}\left\{\mathrm{Tr}\left[V^\dagger(t)\mu U(t)\right]\right\}=0, \tag{4.14}$$

where $\nabla F(U(T))$ is the gradient of F at $U(T)$ in $\mathrm{U}(N)$. Critical points of the objective functional, which include optimal controls, can be obtained by solving this set of equations.

Following the above, the EL equations, leads to an equation of motion for the costate $|\phi(t)\rangle$. Noting that H_0 and μ in the bilinear system (4.1) are Hermitian and based on the objective functional in (4.20) we get,

$$\frac{d\phi(t)}{dt}=-\frac{i}{\hbar}(H_0-\varepsilon(t)\cdot\mu)\phi(t). \tag{4.15}$$

1. Exercise: Derive Eq. (4.15)...**we may need to fill the proof**

To solve the costate equation (4.15) we can use the fact that the matrix elements $\langle\psi(t)|\phi(t)\rangle$ are constant of motion, i. e.,

$$\begin{aligned}\frac{d\langle\psi(t)|\phi(t)\rangle}{dt} &= \frac{d\,\langle\psi(t)|}{dt}\,|\phi(t)\rangle+\langle\psi(t)|\,\frac{d\,|\phi(t)\rangle}{dt}\\ &=\frac{i}{\hbar}\left[\langle\psi(t)|\,(H_0-\mu\varepsilon(t))\,|\phi(t)\rangle-\langle\psi(t)|\,(H_0-\mu\varepsilon(t))\,|\phi(t)\rangle\right]\\ &=0.\end{aligned}$$

This implies that $\langle\psi(t)|\phi(t)\rangle = \langle\psi(T)|\phi(T)\rangle$ and hence we can express the costate equation in terms of state vector as,

$$|\phi(t)\rangle = \langle\psi(T)|\phi(T)\,|\psi(t)\rangle\rangle. \tag{4.16}$$

An equivalent approach to solve the optimal controls is based on applying Pontryagin Maximum Principle(PMP), which is,

Theorem 4.4.1 (Pontryagin) *An optimal control* $\bar{\varepsilon}(\cdot)$ *that solves*

$$\max_{\varepsilon(\cdot)} J[\psi(\cdot),\ \varepsilon(\cdot)]$$

satisfies $\frac{\partial \boldsymbol{H}}{\partial\varepsilon(t)} = 0$ *for a matrix* $\phi(T) = \psi(T)\psi^\dagger(t)\phi(t)$ *and scalar* λ *where at least one of* $\phi(T), \lambda$ *is nonzero.*

where H is called as PMP-Hamiltonian or PMP-function and for a generic optimal control problem as given in Eq. 4.9 and is defined as

$$\begin{aligned}\mathbf{H}[U(t),V(t),\varepsilon(t)]G(\varepsilon(t)) - 2\mathrm{Re}\left[\langle V(t), \frac{i}{\hbar}H(t)U(t)\rangle\right]\\ = G(\varepsilon(t)) + \frac{2}{\hbar}\mathrm{Im}\left\{\mathrm{Tr}\left[V^\dagger(t)H(t)U(t)\right]\right\},\end{aligned} \tag{4.17}$$

where $\langle A,B\rangle = \mathrm{Tr}(A^\dagger B)$ is the Hilbert-Schmidt inner product. According to the PMP, all solutions to the optimization problem (4.4.1) satisfy equations

$$\frac{dU(t)}{dt} = \frac{\partial\mathbf{H}}{\partial V(t)}, \quad \frac{dV(t)}{dt} = -\frac{\partial\mathbf{H}}{\partial U(t)}, \quad \frac{\partial\mathbf{H}}{\partial\varepsilon(t)} = 0, \quad \forall t\in[0,T], \tag{4.18}$$

with the boundary conditions $U(0) = I$, $V(T) = \nabla F(U(T))$. It is easy to see that for the PMP function of the form (4.31), the conditions (4.32) produce Eqs. (4.22)–(4.24). Satisfaction of the first-order condition $\delta\tilde{J}/\delta\varepsilon(\cdot) = 0$ or, equivalently, $\partial\mathbf{H}/\partial\varepsilon(t) = 0$ ($\forall t\in[0,T]$) is a necessary but not sufficient condition for optimality of a control $\varepsilon(\cdot)$. So-called Legendre conditions on the Hessian $\partial^2\mathbf{H}/\partial\varepsilon(t')\partial\varepsilon(t)$ are also required for optimality [204, 273]. The optimality criteria are discussed in Section **to be written**.

For the pure state optimal control problem described in (4.20) which basically describes a control on the Hilbert sphere $S_{\mathcal{H}}$ the PMP Hamiltonian can be written as,

$$\mathbf{H}[\psi(t),\phi(t),\varepsilon(t)] = \lambda L(\psi(t),\varepsilon(t)) - \langle\phi(t), \frac{i}{\hbar}H_0\psi(t)\rangle + \varepsilon(t)\langle\phi(t), \frac{i}{\hbar}\mu\psi(t)\rangle,$$

and by using the costate solution in Eq. (4.16)

$$\mathbf{H}[\psi(t),\phi(t),\varepsilon(t)] = \lambda L(\psi(t),\varepsilon(t)) - \langle \psi(t)\psi^\dagger(T)\phi(T), \frac{i}{\hbar}H_0\psi(t)\rangle + \varepsilon(t)\langle \psi(t)\psi^\dagger(T)\phi(T), \frac{i}{\hbar}\mu\psi(t)\rangle.$$

Applying the Pontryagin theorem, i.e. maximizing the PMP-Hamiltonian leads us to

$$\frac{\partial \mathbf{H}}{\partial \varepsilon(t)} = \lambda \frac{\partial L(\varepsilon(t))}{\partial \varepsilon(t)} - \frac{i}{\hbar}\phi^\dagger(t)\mu\psi(t) = 0, \quad 0 \le t \le T.$$

4.4.3 Searching for optimal controls

To identify optimal controls that maximize an objective functional J (of the types discussed in Section **??**), it is convenient to define a functional $\tilde{J}$ that explicitly incorporates the dynamical constraint. For example, many QOCT studies [11, 130, 131] considered pure-state evolution of a closed quantum system, for which the dynamical constraint is satisfaction of Eq. (4.7). The corresponding objective functional (e.g., for observable control) $\tilde{J} = \tilde{J}[\psi(\cdot),\chi(\cdot),\varepsilon(\cdot)]$ often is taken to have the form

$$\tilde{J} = \langle \psi(T)|\Theta|\psi(T)\rangle - \int_0^T \alpha(t)\varepsilon^2(t)dt - 2\mathrm{Re}\int_0^T \langle \chi(t)| \left[\frac{d}{dt} + \frac{i}{\hbar}H(t)\right] |\psi(t)\rangle dt. \tag{4.19}$$

Here, the first term represents the main control goal of maximizing the expectation value of the target observable Θ at the final time T; the second term is used to restrict the fluence and shape of the control field, with $\alpha(t)$ being a weight function; the third term includes an auxiliary state $|\chi(t)\rangle$ that is a Lagrange multiplier employed to enforce satisfaction of the Schrödinger equation for the pure state [Eq. (4.7)], and $H(t)$ is the Hamiltonian (4.8) that includes the time-dependent control term. More generally, satisfaction of the Schrödinger equation for the evolution operator of a closed quantum system [Eq. (4.5)] can be used as the dynamical constraint for different types of objectives, including evolution-operator, state, and observable control. The corresponding general form of the objective functional $\tilde{J} = \tilde{J}[U(\cdot),V(\cdot),\varepsilon(\cdot)]$ is

$$\tilde{J} = F(U(T)) + \int_0^T G(\varepsilon(t))dt - 2\mathrm{Re}\int_0^T \mathrm{Tr}\left\{V^\dagger(t)\left[\frac{d}{dt} + \frac{i}{\hbar}H(t)\right]U(t)\right\}dt. \tag{4.20}$$

Here, an auxiliary operator $V(t)$ is a Lagrange multiplier employed to enforce satisfaction of Eq. (4.5), and, for the sake of simplicity, we assumed that G depends only on the control field.

QOCT can be also formulated for open systems with non-unitary dynamics [128, 251, 252, 253, 254, 255, 256, 257, 258]. For example, for a quantum system coupled to a Markovian environment, the Liouville-von Neumann equation (4.45) must be satisfied. The corresponding objective functional (e.g., for observable control) $\tilde{J} = \tilde{J}[\rho(\cdot), \sigma(\cdot), \varepsilon(\cdot)]$ has the form

$$\tilde{J} = \mathrm{Tr}\left[\rho(T)\Theta\right] - \int_0^T \alpha(t)\varepsilon^2(t)dt - \int_0^T \mathrm{Tr}\left\{\sigma^\dagger(t)\left[\frac{d}{dt} + i\mathcal{L}\right]\rho(t)\right\} dt. \tag{4.21}$$

Here, $\mathcal{L}$ is the Liouville super-operator (the generator of the dynamical semigroup), and an auxiliary density matrix $\sigma(t)$ is a Lagrange multiplier employed to enforce satisfaction of Eq. (4.45). Extensions of QOCT to non-Markovian open-system dynamics were also considered [256, 259, 257, 260].

Various modifications of the objective functionals (4.19), (4.20), and (4.21) are possible. For example, modified objective functionals can comprise additional spectral and fluence constraints on the control field [261, 262], take into account nonlinear interactions with the control field [263, 264], deal with time-dependent and time-averaged targets [258, 265, 266, 267], and include the final time as a free control parameter [268, 269]. It is also possible to formulate QOCT with time minimization as a control goal (time optimal control) [270, 271, 272]. As we mentioned earlier, QOCT can be also extended to incorporate optimization of multiple objectives [242, 243, 244, 245].

A necessary condition for a solution of the optimization problem (4.4.1) subject to the dynamical constraint (4.5) is that the first-order functional derivatives of the objective functional $\tilde{J}[U(\cdot), V(\cdot), \varepsilon(\cdot)]$ of Eq. (4.20) with respect to $V(\cdot)$, $U(\cdot)$, and $\varepsilon(\cdot)$ are equal to zero. The resulting set of Euler-Lagrange equations is given by

$$\frac{d}{dt}U(t) = -\frac{i}{\hbar}H(t)U(t), \quad U(0) = I, \tag{4.22}$$

$$\frac{d}{dt}V(t) = -\frac{i}{\hbar}H(t)V(t), \quad V(T) = \nabla F(U(T)), \tag{4.23}$$

$$\frac{\partial}{\partial\varepsilon(t)}G(\varepsilon(t)) - \frac{2}{\hbar}\mathrm{Im}\left\{\mathrm{Tr}\left[V^\dagger(t)\mu U(t)\right]\right\} = 0, \tag{4.24}$$

where $\nabla F(U(T))$ is the gradient of F at $U(T)$ in $\mathrm{U}(N)$. Critical points of the objective functional, which include optimal controls, can be obtained by solving this set of equations (various algorithms employed for numerical solution are discussed below). In the special case of the objective functional $\tilde{J}[\psi(\cdot), \chi(\cdot), \varepsilon(\cdot)]$ of Eq. (4.19), setting the first-order functional derivatives of $\tilde{J}$ with respect to $\chi(\cdot)$, $\psi(\cdot)$, and $\varepsilon(\cdot)$

to zero results in the following Euler-Lagrange equations:

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}H(t)|\psi(t)\rangle, \quad |\psi(0)\rangle = |\psi_0\rangle, \tag{4.25}$$

$$\frac{d}{dt}|\chi(t)\rangle = -\frac{i}{\hbar}H(t)|\chi(t)\rangle, \quad |\chi(T)\rangle = \Theta|\psi(T)\rangle, \tag{4.26}$$

$$\varepsilon(t) = -\frac{1}{\hbar\alpha(t)}\mathrm{Im}\left\{\langle\chi(t)|\mu|\psi(t)\rangle\right\}. \tag{4.27}$$

Analogously, in the special case of the objective functional $\tilde{J}[\rho(\cdot),\sigma(\cdot),\varepsilon(\cdot)]$ of Eq. (4.21), setting the first-order functional derivatives of $\tilde{J}$ with respect to $\sigma(\cdot)$, $\rho(\cdot)$, and $\varepsilon(\cdot)$ to zero results in the following Euler-Lagrange equations:

$$\frac{d}{dt}\rho(t) = -i\mathcal{L}\rho(t), \quad \rho(0) = \rho_0, \tag{4.28}$$

$$\frac{d}{dt}\sigma(t) = -i\mathcal{L}^{\dagger}\sigma(t), \quad \sigma(T) = \Theta, \tag{4.29}$$

$$\varepsilon(t) = -\frac{1}{\hbar\alpha(t)}\mathrm{Im}\left\{\mathrm{Tr}\left[\sigma^{\dagger}(t)\mu\rho(t)\right]\right\}. \tag{4.30}$$

An equivalent method for deriving optimal control equations is based on applying the Pontryagin maximum principle (PMP) [249, 250, 273]. For a bilinear control system of the form (4.5) evolving on the unitary group, the PMP function (also referred to as the PMP-Hamiltonian) is defined as

$$\begin{aligned}\mathbf{H}[U(t),V(t),\varepsilon(t)]G(\varepsilon(t)) - 2\mathrm{Re}\left[\langle V(t), \frac{i}{\hbar}H(t)U(t)\rangle\right] \\ = G(\varepsilon(t)) + \frac{2}{\hbar}\mathrm{Im}\left\{\mathrm{Tr}\left[V^{\dagger}(t)H(t)U(t)\right]\right\},\end{aligned} \tag{4.31}$$

where $\langle A,B\rangle = \mathrm{Tr}(A^{\dagger}B)$ is the Hilbert-Schmidt inner product. According to the PMP, all solutions to the optimization problem (4.4.1) satisfy equations

$$\frac{dU(t)}{dt} = \frac{\partial\mathbf{H}}{\partial V(t)}, \quad \frac{dV(t)}{dt} = -\frac{\partial\mathbf{H}}{\partial U(t)}, \quad \frac{\partial\mathbf{H}}{\partial\varepsilon(t)} = 0, \quad \forall t\in[0,T], \tag{4.32}$$

with the boundary conditions $U(0) = I$, $V(T) = \nabla F(U(T))$. It is easy to see that for the PMP function of the form (4.31), the conditions (4.32) produce Eqs. (4.22)–(4.24). Satisfaction of the first-order condition $\delta\tilde{J}/\delta\varepsilon(\cdot) = 0$ or, equivalently, $\partial\mathbf{H}/\partial\varepsilon(t) = 0$ ($\forall t\in[0,T]$) is a necessary but not sufficient condition for optimality of a control $\varepsilon(\cdot)$. So-called Legendre conditions on the Hessian $\partial^2\mathbf{H}/\partial\varepsilon(t')\partial\varepsilon(t)$ are also required for optimality [204, 273]. The optimality criteria are discussed in Section **??**.

4.4.3.1 Existence of optimal controls

An important issue is the existence of optimal control fields (i.e., maxima of the objective functional) for realistic situations that involve practical constraints on the applied laser fields. It is important to distinguish between the existence of an optimal control field and controllability; in the former case, a field is designed, subject to particular constraints, that guides the evolution of the system towards a specified target until a maximum of the objective functional is reached, while in the latter case, the exact coincidence between the attained evolution operator (or state) and the target evolution operator (or state) is sought. The existence of optimal controls for quantum systems was analyzed in a number of works. Peirce *et al.* [37] proved the existence of optimal solutions for state control in a spatially bounded quantum system that necessarily has spatially localized states and a discrete spectrum. Zhao and Rice [144] extended this analysis to a system with both discrete and continuous states and proved the existence of optimal controls over the evolution in the subspace of discrete states. Demiralp and Rabitz [145] showed that, in general, there is a denumerable infinity of solutions to a particular class of well-posed quantum control problems; the solutions can be ordered in quality according to the achieved optimal value of the objective functional. The existence of multiple control solutions has important practical consequences, suggesting that there may be broad latitude in the laboratory, even under strict experimental restrictions, for finding successful controls for well-posed quantum objectives. The existence and properties of critical points (including global extrema) of objective functionals for various types of quantum control problems were further explored using the analysis of QCLs [208, 209, 210, 217, 218, 219, 220, 146, 221, 274] (see Section **??**).

A number of optimization algorithms have been adapted or specially developed for use in QOCT, including the conjugate gradient search method [39], the Krotov method [206, 275, 276], monotonically convergent algorithms [277, 278, 279, 280, 259, 281, 282], non-iterative algorithms [283], the gradient ascent pulse engineering (GRAPE) algorithm [284], a hybrid local/global algorithm [258], and homotopy-based methods [285, 286, 287]. Faster convergence of iterative QOCT algorithms was demonstrated using “mixing” strategies [288]. Also, the employment of propagation toolkits [289, 290, 291] can greatly increase the efficiency of numerical optimizations. Detailed discussions of the QOCT formalism and algorithms are available in the literature [5, 130, 131, 11].

4.4.4 Applications of QOCT

In this section we first survey various applications of the QOCT and present an example of the theory developed so far. The applications of QOCT to the open quantum systems will be discussed in the next section.

Originally, QOCT was developed to design optimal fields for manipulation of molecular systems [36, 37, 38, 39, 40, 124, 125, 126, 127, 128, 129] and has been applied to a myriad of problems (e.g., rotational, vibrational, electronic, reactive, and other processes) [5, 130, 11]. Some recent applications include, for example, control of molecular isomerization [292, 293, 294, 295], control of electron ring currents in chiral aromatic molecules [296], and control of heterogeneous electron transfer from surface attached molecules into semiconductor band states [297]. Beyond molecules, QOCT has been applied to various physical objectives including, for example, control of electron states in semiconductor quantum structures [298, 299, 300], control of atom transport in optical lattices [301], control of Bose-Einstein condensate transport in magnetic microtraps [302], control of a transition of ultracold atoms from the superfluid phase to a Mott insulator state [303], control of coherent population transfer in superconducting quantum interference devices [304], and control of the local electromagnetic response of nanostructured materials [305].

Recently, there has been rapidly growing interest in applications of QOCT to the field of quantum information sciences. One of the important problems in this field is optimal protection of quantum systems against decoherence, as mentioned above. Applications of QOCT to quantum information processing also include optimal operation of quantum gates in closed systems [180, 205, 206, 250, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335] and in open systems (i.e., in the presence of decoherence) [213, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351], and optimal generation of entanglement [268, 269, 350, 352, 353, 354]. One particular area where QOCT methods have proved to be especially useful is design of optimal sequences of radiofrequency (RF) pulses for operation of quantum gates in systems of coupled nuclear spins in a nuclear magnetic resonance (NMR) setup [284, 355, 356]. In a recent experiment with trapped ion qubits, shaped pulses designed using QOCT were applied to enact single-qubit gates with enhanced robustness to noise in the control field [357]. Optimal control methods were also applied to the problem of storage and retrieval of photonic states in atomic media, including both theoretical optimization [358, 359, 360] and experimental tests [361, 362, 363].

Let us now consider an instructive example by applying the theory developed so far developed to a molecular system. In one of the pioneering QOCT studies, Kosloff *et al.* [39] considered two electronic states (ground and excited) of a model molecular system, with the wave function (in the coordinate representation) of the form[2]

$$\psi(\mathbf{r},t) = \langle \mathbf{r}|\psi(t)\rangle = \begin{pmatrix} \psi_{\mathrm{e}}(\mathbf{r},t) \\ \psi_{\mathrm{g}}(\mathbf{r},t) \end{pmatrix}, \tag{4.33}$$

where ψ_{g} and ψ_{e} are the projections of the wave function on the ground and excited state, respectively. The time evolution of the wave function is determined by the Schrödinger equation:

$$\hbar\frac{\partial}{\partial t}\begin{pmatrix} \psi_{\mathrm{e}}(\mathbf{r},t) \\ \psi_{\mathrm{g}}(\mathbf{r},t) \end{pmatrix} = \begin{pmatrix} H_{\mathrm{e}}(\mathbf{r}) & H_{\mathrm{ge}}(\mathbf{r},t) \\ H_{\mathrm{ge}}^{\dagger}(\mathbf{r},t) & H_{\mathrm{g}}(\mathbf{r}) \end{pmatrix}\begin{pmatrix} \psi_{\mathrm{e}}(\mathbf{r},t) \\ \psi_{\mathrm{g}}(\mathbf{r},t) \end{pmatrix}, \tag{4.34}$$

where $H_i(\mathbf{r}) = \mathbf{p}^2/(2m) + V_i(\mathbf{r})$ ($i = \mathrm{g}, \mathrm{e}$), $\mathbf{p}$ is the momentum operator, $V_{\mathrm{g}}(\mathbf{r})$ and $V_{\mathrm{e}}(\mathbf{r})$ are the adiabatic potential energy surfaces for the ground and excited state, respectively. The off-diagonal term $H_{\mathrm{ge}}(\mathbf{r},t)$ represents the field-induced coupling between the molecular states:

$$H_{\mathrm{ge}}(\mathbf{r},t) = -\mu_{\mathrm{ge}}(\mathbf{r})\varepsilon(t), \tag{4.35}$$

where $\mu_{\mathrm{ge}}(\mathbf{r})$ is the electric dipole operator and $\varepsilon(t)$ is the time-dependent electric field of the control laser pulse applied to the molecule.

The goal is to control a dissociation reaction in the presence of two distinct exit channels on the ground potential energy surface. The corresponding objective functional (including the dynamical constraint) is given by

$$\tilde{J} = \langle\psi(T)|P|\psi(T)\rangle - \lambda\int_0^T \varepsilon^2(t)\,t - 2\Re\int_0^T \langle\chi(t)|\left(\frac{\partial}{\partial t} + \frac{}{\hbar}H\right)|\psi(t)\rangle\,t, \tag{4.36}$$

The first term in (4.36) represents the main control goal, where P is the projection operator on the state corresponding to the target exit channel (i.e., the part of the wave function which is beyond the target saddle point on the ground-state surface and is characterized by the outgoing momentum); the second term is used to manage the fluence of the control field, with λ being a scalar weight factor; the third term includes an auxiliary state $|\chi(t)\rangle$ that is a Lagrange multiplier employed to enforce satisfaction of the Schrödinger equation (H is the 2×2 Hamiltonian matrix defined by (4.34)). In order to find the control field that maximizes the objective, the first-order functional derivatives of $\tilde{J}$ with respect to $\chi(\cdot)$, $\psi(\cdot)$, and $\varepsilon(\cdot)$ are set to zero, producing the following Euler-Lagrange equations:

$$\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle, \quad |\psi(0)\rangle = |\psi_0\rangle, \tag{4.37}$$

$$\hbar\frac{\partial}{\partial t}|\chi(t)\rangle = H|\chi(t)\rangle, \quad |\chi(T)\rangle = P|\psi(T)\rangle, \tag{4.38}$$

$$\varepsilon(t) = -\frac{1}{\hbar\lambda}\Im\left\{\langle\chi_{\mathrm{g}}(t)|\mu_{\mathrm{ge}}|\psi_{\mathrm{e}}(t)\rangle + \langle\chi_{\mathrm{e}}(t)|\mu_{\mathrm{ge}}|\psi_{\mathrm{g}}(t)\rangle\right\}. \tag{4.39}$$

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[2] For the sake of notation consistency, the control problem is presented here slightly differently than in the original work [39].

An initial guess is selected for the control field (e.g., a pair of transform-limited pulses with a time delay between them, as in pump-dump control), and equations (4.37)–(4.39) are solved using an appropriate algorithm, as discussed in section 4.4.3 above. This optimization procedure identifies a shaped control field $\varepsilon_{\text{opt}}(\cdot)$ that maximizes photoinduced molecular dissociation into the target channel. Successful application of QOCT to this model molecular system [39] demonstrated the benefits of optimally tailoring the time-dependent laser field to achieve the desired dynamic outcome.

Example: Let us consider a more detailed problem of controlling a single nuclear spin subjected to a static magnetic field along the z-axis and a time varying radio frequency magnetic field along the x and y-axes. Since the electric and Magnetic fields are related via Maxwell equations, the controls are denoted as $\varepsilon_x(t), \varepsilon_y(t)$ instead of $B_x(t), B_y(t)$. The dynamics of a spin are described using the Pauli-spin operators, σ_x, σ_y and σ_z or with the spin vector $\vec{\sigma} = \sigma_x\hat{\imath} + \sigma_y\hat{\jmath} + \sigma_z\hat{k}$.

The problem:Find the time-varying fields $\varepsilon_x(t)$ and $\varepsilon_y(t)$ that drive the system to a specified final state ψ_f at time T using minimal energy. The dynamical equation (Schrödinger equation) is

$$\begin{aligned}\frac{d}{dt}|\psi(t)\rangle =& -\frac{i}{\hbar}\vec{\sigma}\cdot\vec{\varepsilon}(t)|\psi(t)\rangle \\ =& -\frac{i}{\hbar}\left[\sigma_z B_z + \sigma_x\varepsilon_x(t) + \sigma_y\varepsilon_y(t)\right]\psi(t)\rangle\end{aligned}$$

Solution: First lets define the Lagrange for the problem which is now a function of the two controls $\varepsilon_x(t), \varepsilon_y(t)$ and is given as,

$$L(\varepsilon_x(t), \varepsilon_y(t)) = -\frac{1}{2}(\varepsilon_x^2(t) + \varepsilon_y^2(t)).$$

Since the final state ψ_f is assumed to be pre-defined the cost function will now have the form,

$$F(\psi(T)) = \Re\langle\psi_f|\psi(t)\rangle$$

and ideally we want to reach the final state exactly within a global phase , we have the condition

$$\max F(\psi(T)) = 1. \tag{4.40}$$

Thus proceeding we get the cost functional J in the Lagrange formulation as,

$$J = \frac{1}{2}\int_0^T \varepsilon_x^2(t) + \varepsilon_y^2(t)\ dt$$

and the PMP-Hamiltonian, which is a function of state $\psi(t)$, costate $\phi(t)$ and control $\vec{\varepsilon}(t)$, is given as,

$$\mathbf{H}(\psi(t), \phi(t), \vec{\varepsilon}(t)) = \frac{1}{2}(\varepsilon_x^2(t) + \varepsilon_y^2(t)) + \langle\phi(t)| - \frac{i}{\hbar}[\sigma_z B_z + \sigma_x\varepsilon_x(t) + \sigma_y\varepsilon_y(t)|\psi(t)\rangle.$$

From the first Euler-Lagrange equation we have the dynamical equation for the costate $\phi(t)$ as,

$$\begin{aligned}\frac{d\phi^\dagger(t)}{dt} &= \nabla_{\psi(t)}\mathbf{H}(\psi(t),\phi(t),\varepsilon(t))\\ &= -\frac{i}{\hbar}\phi^\dagger(t)\left[\sigma_z B_z + \sigma_x\varepsilon_x(t) + \sigma_y\varepsilon_y(t)\right]\end{aligned}$$

or equivalently

$$\frac{d\phi(t)}{dt} = \frac{i}{\hbar}\left[\sigma_z B_z + \sigma_x\varepsilon_x(t) + \sigma_y\varepsilon_y(t)\right]\phi(t).$$

Employing the second Euler-Lagrange equation or directly from the Pontraygin maximum principle we have the maximization of the PMP-Hamiltonian over the control as,

$$\nabla_{\vec{\varepsilon}(t)}\mathbf{H}(\psi(t),\phi(t),\vec{\varepsilon}(t)) = 0$$

which leads to

$$\varepsilon_x(t) = \frac{i}{\hbar}\langle\phi(t)|\sigma_x|\psi(t)\rangle\varepsilon_y(t) = \frac{i}{\hbar}\langle\phi(t)|\sigma_y|\psi(t)\rangle$$

and further leads to the equations for the controls,

$$\begin{aligned}\frac{d\varepsilon_x(t)}{dt} &= \frac{i}{\hbar}\left\{\langle\frac{d}{dt}\phi(t)|\sigma_x|\psi(t)\rangle + \langle\phi(t)|\sigma_x|\frac{d}{dt}\psi(t)\rangle\right\}\\ \frac{d\varepsilon_y(t)}{dt} &= \frac{i}{\hbar}\left\{\langle\frac{d}{dt}\phi(t)|\sigma_y|\psi(t)\rangle + \langle\frac{d}{dt}\phi(t)|\sigma_y|\frac{d}{dt}\psi(t)\rangle\right\}\end{aligned}$$

Since the Pauli matrices obey the commutation rules $[\sigma_i,\sigma_j] = i\epsilon_{ijk}\sigma_k$ where ϵ_{ijk} is called structure constants that determine the structure of the Lie-Algebra.Now we can use the co-state equations, $\dot{\phi(t)}$ and rewrite the RHS of the above equations as,

$$\begin{aligned}\langle\frac{d}{dt}\phi(t)|\sigma_y|\psi(t)\rangle &= \frac{i}{\hbar}\phi^\dagger(t)\left[\sigma_z B_z + \sigma_x u_x(t) + \sigma_y u_y(t)\right]\sigma_x\psi(t)\\ \langle\phi(t)|\sigma_y|\frac{d}{dt}\psi(t)\rangle &= \frac{i}{\hbar}\phi^\dagger(t)\sigma_x\left[\sigma_z B_z + \sigma_x u_x(t) + \sigma_y u_y(t)\right]\psi(t)\end{aligned}$$

and the control equations can be rewritten as,

$$\begin{aligned}\dot{\varepsilon}_x(t) &= (\frac{i}{\hbar})^2\phi^\dagger(t)[\sigma_x,\sigma_y]u_y(t)\psi(t) = -{\frac{i}{\hbar}}^2(\phi^\dagger(t)\sigma_z\psi(t)u_y(t) - \phi^\dagger(t)\sigma_y\psi(t)B_z)\\ \dot{\varepsilon}_y(t) &= (\frac{i}{\hbar})^2\phi^\dagger(t)[\sigma_y,\sigma_x]u_x(t)\psi(t) = {\frac{i}{\hbar}}^2(\phi^\dagger(t)\sigma_z\psi(t)u_x(t) - \phi^\dagger(t)\sigma_x\psi(t)B_z).\end{aligned}$$

Additional Conserved quantities: PMP-Hamiltonian *Slides not clear to me*

4.5 Open quantum systems

In practice, it is often necessary to take into account interactions between quantum systems (e.g., between molecules in a liquid or between electron spins and nuclear spins in a semiconductor material). If for a particular problem only one of the interacting subsystems is of interest (now referred to as the system), all other subsystems that surround it are collectively referred to as the environment. A quantum system coupled to an environment is called open [154]. A molecule in a solution or an atom coupled to the vacuum electromagnetic field are examples of open quantum systems. The interaction with the environment typically results in a process of decoherence, in which a coherent superposition state of an open quantum system is transformed into a statistical mixture (decoherence is often accompanied by dissipation of the initial excitation, although in some situations pure dephasing is possible; see [154, 155] for details). Generally, all quantum systems are open, however, whether or not environmentally-induced processes are important depends on their rate relative to the rate of the coherent evolution. From a practical perspective, the importance of decoherence also depends on the control objective. In chemical applications such as control over the yield of a reaction product, environmental effects may play a significant role in the liquid phase where relaxation processes happen on the time scale of the order of one picosecond [8, 9, 156, 157]. On the other hand, decoherence induced by collisions in the gas phase can often be neglected (at least at low pressures), as the time between collisions is much longer than the characteristic period of vibronic dynamics controlled by femtosecond laser pulses [8]. In contrast, in quantum information processing, an unprecedented level of control accuracy is required to minimize quantum gate errors, and therefore decoherence needs to be taken into account for practically all physical realizations [158].

The state of an open quantum system is described by the reduced density matrix $\rho = \mathrm{Tr}_{\mathrm{env}}(\rho_{\mathrm{tot}})$, where ρ_{tot} represents the state of the system and environment taken together, and $\mathrm{Tr}_{\mathrm{env}}$ denotes the trace over the environment degrees of freedom. There are many models of open-system dynamics depending on the type of environment and character of the system-environment coupling [154, 155]. If the system and environment are initially uncoupled, $\rho_{\mathrm{tot}}(0) = \rho(0) \otimes \rho_{\mathrm{env}}$, then the evolution of the system's reduced density matrix from $t = 0$ to t is described by a completely positive, trace preserving map Φ_t:

$$\rho(t) = \Phi_t \rho_0, \tag{4.41}$$

where $\rho_0 = \rho(0)$. A linear map $\Phi : \mathcal{T}(\mathcal{H}) \to \mathcal{T}(\mathcal{H})$ is called completely positive if the map $\Phi \otimes I_l : \mathcal{T}(\mathcal{H}) \otimes \mathcal{M}_l \to \mathcal{T}(\mathcal{H}) \otimes \mathcal{M}_l$ (where I_l is the identity map in $\mathcal{M}_l$) is positive for any $l \in \mathbb{N}$. A map Φ is called trace preserving if $\mathrm{Tr}(\Phi\rho) = \mathrm{Tr}(\rho)$ for any $\rho \in \mathcal{T}(\mathcal{H})$. The map (4.41) can be defined for any time $t \geq 0$, and the entire time evolution of the open quantum system is described by a one-parameter family $\{\Phi_t \mid t \geq 0\}$ of dynamical maps (where Φ_0 is the identity map I).

Any completely positive, trace-preserving map has the Kraus operator-sum representation (OSR) [159, 160, 161]:

$$\rho(t) = \Phi_t \rho_0 = \sum_{j=1}^{n} K_j(t) \rho_0 K_j^{\dagger}(t), \tag{4.42}$$

where $\{K_j\}$ are the Kraus operators ($N \times N$ complex matrices for an N-level quantum system). The trace preservation is ensured by the condition

$$\sum_{j=1}^{n} K_j^{\dagger}(t) K_j(t) = I. \tag{4.43}$$

Here, $n \in \mathbb{N}$ is the number of Kraus operators. We will refer to completely positive, trace-preserving maps simply as Kraus maps. Unitary transformations form a particular subset of Kraus maps corresponding to $n = 1$. There exist infinitely many OSRs (with different sets of Kraus operators) for the same Kraus map. For any Kraus map for an N-level quantum system, there always exists an OSR with a set of $n \leq N^2$ Kraus operators [161].

While the Kraus-map description of open-system dynamics is very general, it is often not the most convenient one for numerical calculations. With additional assumptions, various types of quantum master equations can be derived from the Kraus OSR [154, 155]. In particular, for a Markovian environment (i.e., when the memory time for the environment is zero), the set of Kraus maps $\{\Phi_t \mid t \geq 0\}$ is a semigroup, which means that any two maps in the set satisfy the condition [154]

$$\Phi_{t_1} \Phi_{t_2} = \Phi_{t_1 + t_2}, \quad t_1, t_2 \geq 0. \tag{4.44}$$

In this situation, the dynamics of an open quantum system is described by the quantum master equation of the form [154]

$$\frac{d}{dt} \rho(t) = -i \mathcal{L} \rho(t), \tag{4.45}$$

where the linear map $\mathcal{L}$ (also referred to as the Liouville super-operator) is the generator of the dynamical semigroup, i.e., $\Phi_t = \exp(-i\mathcal{L}t)$. The evolution equation of the form (4.45) is often referred to as the Liouville-von Neumann equation. For an N-level quantum system coupled to a Markovian environment, the most general form of the map $\mathcal{L}$ can be constructed, resulting in the quantum master equation of the Lindblad type [154, 155, 162]:

$$\frac{d}{dt} \rho(t) = -\frac{i}{\hbar} [H(t), \rho(t)] + \sum_{i=1}^{N^2-1} \gamma_i \left[L_i \rho(t) L_i^{\dagger} - \frac{1}{2} L_i^{\dagger} L_i \rho(t) - \frac{1}{2} \rho(t) L_i^{\dagger} L_i \right]. \tag{4.46}$$

Here, $\{\gamma_i\}$ are non-negative constants and $\{L_i\}$ are the Lindblad operators ($N \times N$ complex matrices) that form (together with the identity operator) an orthonormal operator basis on $\mathcal{H}$. By convention, $\{L_i\}$ are traceless. The first term in Eq. (4.46) represents the unitary part of the dynamics governed by the Hamiltonian H and the second (Lindblad) term represents the non-unitary effect of coupling to the environment. The constants $\{\gamma_i\}$ are given in terms of certain correlation functions of the environment and play the role of relaxation rates for different decay modes of the open system [154].

4.5.1 Applications of QOCT for open quantum systems

In the context of open-system dynamics in the presence of coupling to a Markovian environment, QOCT applications include control of unimolecular dissociation reactions in the collisional regime [128], laser cooling of molecular internal degrees of freedom coupled to a bath [252, 253, 306], control of vibrational wave packets in a model molecular system coupled to an oscillator bath at finite temperatures in the weak-field (perturbative) regime [251, 307], creation of a specified vibronic state, population inversion, wave packet shaping in the presence of dissipation in the strong-field regime [255], control of ultrafast electron transfer in donor-acceptor systems where the reaction coordinate is coupled to a reservoir of other coordinates [308], control of photodesorption of NO molecules from a metal surface in the presence of strong dissipation [309], control of excitation of intramolecular and molecule-surface vibrational modes of CO molecules adsorbed on a metal surface in the presence of dissipation to baths of substrate electrons and phonons [310, 258], and control of current flow patterns through molecular wires coupled to leads [311]. Also, QOCT was actively applied to the problem of protection of open quantum systems against environmentally-induced decoherence [216, 257, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321].

Chapter 5

Quantum control landscapes

5.1 Introduction

An important practical goal of quantum control is the discovery of optimal solutions for manipulating quantum phenomena. Early studies [37, 145, 144] described conditions under which optimal solutions exist, but did not explore the complexity of finding them. Underlying the search for optimal controls is the landscape which specifies the physical objective as a function of the control variables. Analysis of quantum control landscapes [147] can not only establish the existence of optimal control solutions and determine their types (e.g., global versus local maxima and true maxima versus saddle points), but also deal with establishing necessary conditions for convergence of optimization algorithms to global maxima along with bounds on the scaling of convergence effort. Surprisingly, these properties are independent of details of a particular Hamiltonian (provided that the system is controllable), which makes the results of landscape analysis applicable across a wide range of controlled quantum phenomena.

The notion of controlling quantum systems seems inherently problematic on several counts. First, the extreme sensitivity of quantum systems to environmental interactions would appear to place limits on the maximal achievable control fidelity. Second, from a numerical perspective, given the considerable cost of propagating the Schrodinger equation, unless the search space for optimal controls has particularly simple properties, it would appear impossible to locate controls for all but the smallest quantum systems in reasonable time. However, once the methods of optimal control began to be applied to molecular systems (thanks to remarkable advances in laser pulse shaping technology) it rapidly became clear that quantum control was not an ill-fated concept, but rather, that controlling quantum systems was surprisingly easy. In the laboratory, this conclusion was particularly apparent in the case of so-called adaptive learning control of quantum dynamics, wherein learning (i.e., typically genetic) algorithms are applied to search the space of laser control parameters for the maximization of the expectation value of a quantum observable. This search space is high-dimensional, normally suggesting that it should be replete with local optima and other unfavorable features that would trap unsophisticated search algorithms, especially in the presence of environmental decoherence. The repeated successes of quantum optimal control experiments and simulations indicated that the so-called "curse of dimensionality", common in the theory of optimization in high-dimensional spaces, was not prohibitive here.

Figure 5.1: A control landscape is defined as the map between the time-dependent control Hamiltonian and associated values of the control cost functional. The entry point into their study is (a) the controllability of the quantum system, which allows search algorithms to freely traverse the landscape. Quantum control landscape features can be conveniently subdivided into those pertaining to (b) critical topology, i.e., the maxima, minima and saddle points of the landscape, and (c) landscape geometry, namely the characteristic local structures encountered while climbing toward the global optimum. Study of the geometry of quantum control landscapes reveals (d) the existence of multiple control solutions corresponding to any given objective function value. The topology and geometry of quantum control landscapes together determine (e) the search complexity of the control problems, i.e. the scaling of the effort required to locate optimal controls. An ultimate goal in the study of quantum control landscapes is the design of global search algorithms that attain lower bounds on this search complexity. Such algorithms may be applied to either of the two major classes of quantum system manipulation problems, (f) control of quantum observables and (g) control of quantum dynamical transformations (i.e., unitary propagators). An overarching conclusion pertaining to both these types of landscapes is that they contain no suboptimal traps, which has broad-scale implications for both the experimental and computational feasibility of quantum control.

This attractive circumstance for quantum control rests on the mathematical underpinnings of quantum theory being surprisingly simple, owing to the linearity of quantum mechanics and the unitarity of the accompanying transformations. Although quantum systems can be highly sensitive to environmental perturbations, the rules governing their dynamics are in many ways simpler than those governing classical dynamics. Furthermore, the presence of an environment, rather than being an impediment, may under the right conditions aid the control process. Recent work has aimed to understand the precise mathematical properties of quantum mechanics are responsible for the surprising simplicity with which quantum phenomena can be controlled. Analytical, numerical and experimental treatments of the problem have been explored. In order to enable the systematic study of these features, the notion of a quantum control landscape, defined as the map between the space of time-dependent controls and associated values of the objective functional, was introduced (Figs. 5.1, **??**).

From an analytical perspective, it was recently found that for several classes of low-dimensional problems, it is possible to exactly solve for quantum optimal controls, without any need for numerical search. By contrast, for the analogous classical problems, analytical solutions do not exist. Of course, analytical solutions are still only possible for special small systems; however, beyond this, it has become clear that the numerical or experimental search for optimal controls is often easier for quantum systems than for classical systems. In this regard, the topology of the search space is of fundamental importance. Evidence suggests that the landscapes for both observable maximization and control of dynamical transformations have simpler topological properties for quantum versus classical systems, contributing to rapid convergence of numerical or experimental searches for effective controls. Moreover, besides the simplicity of locating quantum controls, it has been observed that the controls themselves have remarkably simple functional properties, in some cases enabling a direct interpretation of the mechanisms involved in steering about the dynamics.

The ease of locating optimal quantum controls, and the comparatively simple structure of these controls, have pervasive implications for a wide range of quantum technologies. The study of quantum control landscapes is motivated by the practical goals of achieving higher objective function yields and designing control fields with desired properties, but in order to attain these goals, it is necessary to embrace the mathematical framework that underlies the remarkable properties of these landscapes. The origin of these counterintuitive properties, and their differences with respect to classical control, constitute the primary subject of this review.

subsectionControl landscape definition and critical points

Properties of the search space associated with Mayer-type cost functionals play a fundamental role in the ability to identify optimal controls. To characterize these properties, it is convenient to express the cost functional in a form where the dynamical constraints are implicitly satisfied. Consider a control problem with a fixed target time T for a closed quantum system with unitary evolution. Denote by $V_T : \varepsilon(\cdot) \mapsto U(T)$ the endpoint map from the space of control functions to the space of unitary evolution operators, induced by the Schrödinger equation (4.5), so that $U(T) = V_T(\varepsilon(\cdot))$. A Mayer-type cost functional $F(U(T))$ itself describes a map F from the space of evolution operators to the space of real-valued costs. Thus the composition of these maps, $J = F \circ V_T : \ \mathbb{K} \to \mathbb{R}$, is a map from the space of control functions to the space of real-valued costs. This map generates the functional $J[\varepsilon(\cdot)] = F(V_T(\varepsilon(\cdot)))$. We will refer to the functional $J[\varepsilon(\cdot)]$ as the *control landscape.* The optimal control problem may then be expressed as the unconstrained search for

$$J_{\mathrm{opt}} = \max_{\varepsilon(\cdot)} J[\varepsilon(\cdot)]. \tag{5.1}$$

The topology of the control landscape (i.e., the character of its critical points, including local and global extrema) determines whether local search algorithms will converge to globally optimal solutions to the control problem [148]. Studies of quantum control landscape topology are presently an active research area [147, 208, 209, 210, 217, 219, 220, 146, 221, 169, 627].

The critical points (extrema) of the landscape are controls, at which the first-order functional derivative of $J[\varepsilon(\cdot)]$ with respect to the control field is zero for all time, i.e.,

$$\frac{\delta J[\varepsilon(\cdot)]}{\delta \varepsilon(t)} = 0, \quad \forall t \in [0, T]. \tag{5.2}$$

The critical manifold $\mathcal{M}$ of the control landscape is the collection of all critical points:

$$\mathcal{M} = \{\varepsilon(\cdot) \mid \delta J / \delta \varepsilon(t) = 0, \ \forall t \in [0, T]\}. \tag{5.3}$$

A central concept in landscape topology is the classification of a critical point as regular or singular [628, 629]. Most generally, a critical point of $J[\varepsilon(\cdot)]$ is regular if the map V_T is locally surjective in its vicinity, i.e., if for any local increment $\delta U(T)$ in the evolution operator there exists an increment $\delta\varepsilon(\cdot)$ in the control function such that $V_T(\varepsilon(\cdot) + \delta\varepsilon(\cdot)) = V_T(\varepsilon(\cdot)) + \delta U(T)$. This condition is equivalent to requiring that the elements $\mu_{ij}(t)$ of the time-dependent dipole-operator matrix (in the Heisenberg picture) form a set of N^2 linearly independent functions of time [210]. In its turn, this condition is satisfied for all non-constant admissible controls if and only if the quantum system is evolution-operator controllable [143, 210]. Note that for landscapes of some particular physical objectives the conditions for regularity of the critical points can be less stringent. For example, in the important special case of state-transition control, a critical point is regular if the matrix elements $\mu_{ij}(t)$ contain a set of just $2N - 1$ linearly independent functions of time. This condition is satisfied for all non-constant admissible controls if and only if the quantum system is pure-state controllable (which is a weaker condition than evolution-operator controllability, as discussed in section **??**).

A critical point of $J[\varepsilon(\cdot)]$ is singular if the map V_T is not locally surjective in the point's vicinity. Using the chain rule, one obtains:

$$\frac{\delta J}{\delta \varepsilon(t)} = \left\langle \nabla F(U(T)), \frac{\delta U(T)}{\delta \varepsilon(t)} \right\rangle, \tag{5.4}$$

where $\nabla F(U(T))$ is the gradient of F at $U(T)$, $\delta U(T)/\delta\varepsilon(t)$ is the first-order functional derivative of $U(T)$ with respect to the control field, and $\langle A, B\rangle = (A^\dagger B)$ is the Hilbert-Schmidt inner product. From (5.4), if a critical point of J is regular, $\nabla F(U(T))$ must be zero. A critical point is called kinematic if $\nabla F(U(T)) = 0$ and non-kinematic if $\nabla F(U(T)) \neq 0$. Thus, all regular critical points are kinematic. A singular critical point may be either kinematic or non-kinematic; in the latter case, $\delta J/\delta\varepsilon(t) = 0$ whereas $\nabla F(U(T)) \neq 0$ [629]. On quantum control landscapes, the measure of regular critical points appears to be much greater than that of singular ones [629]. Therefore attention has been focused on the characterization of regular critical points, and several important results have been obtained [147]. Nevertheless, singular critical points on quantum control landscapes have been recently studied theoretically [629] and demonstrated experimentally [630].

The condition for kinematic critical points, $\nabla F(U(T)) = 0$, can be cast in an explicit form for various types of quantum control problems. For evolution-operator control with the objective functional $J = F_1(U(T))$ of (**??**), this condition becomes [208, 209]

$$W^\dagger U(T) = U^\dagger(T)W, \tag{5.5}$$

i.e., $W^\dagger U(T)$ is required to be a Hermitian operator. It was shown [208, 209] that this condition implies $W^\dagger U(T) = Y^\dagger(-I_m \oplus I_{N-m})Y$, where Y is an arbitrary unitary transformation and $m = 0, 1, \ldots, N$. There are $N + 1$ distinct critical submanifolds labeled by m, with corresponding critical values of J given by $J_m = 1 - (2m/N)$. The global optima corresponding to $m = 0$ and $m = N$ (with $J_0 = 1$ and $J_N = -1$, respectively) are isolated points, while local extrema corresponding to $m = 1, 2, \ldots, N - 1$ are smooth, compact, Grassmannian submanifolds embedded in $\mathrm{U}(N)$. It can be shown that all regular local extrema are saddle-point regions [209].

For observable control with the objective functional $J = F_3(U(T))$ of (**??**), the condition for a kinematic critical point becomes [217, 146, 169]

$$[U(T)\rho_0 U^\dagger(T), \Theta] = 0, \tag{5.6}$$

i.e., the density matrix at the final time is required to commute with the target observable operator. This condition was studied in the context of optimization of Lagrange-type cost functionals with an endpoint constraint [627, 631, 632] as well as in the context of regular critical points for Mayer-type cost functionals [217, 169]. Let R and S denote unitary matrices that diagonalize ρ_0 and Θ, respectively, and define $\tilde{U}(T) = S^\dagger U(T)R$. The condition (5.6) that $\rho(T)$ and Θ commute is equivalent to the condition that the matrix $\tilde{U}(T)$ is in the double coset $\mathcal{M}_\pi$ of some permutation matrix P_π [219]:

$$\tilde{U}(T) \in \mathcal{M}_\pi = \mathrm{U}(\mathbf{n})P_\pi\mathrm{U}(\mathbf{m}). \tag{5.7}$$

Here, $\mathrm{U}(\mathbf{n})$ is the product group $\mathrm{U}(n_1) \times \cdots \times \mathrm{U}(n_r)$, where $\mathrm{U}(n_l)$ corresponds to the lth eigenvalue of ρ_0 with n_l-fold degeneracy, and $\mathrm{U}(\mathbf{m})$ is the product group $\mathrm{U}(m_1)\times\cdots\times\mathrm{U}(m_s)$, where $\mathrm{U}(m_l)$ corresponds to the lth eigenvalue of Θ with m_l-fold degeneracy. Thus, each critical submanifold $\mathcal{M}_\pi$ corresponds to a particular choice of the permutation π. All permutations on N indices form the symmetric group $\mathfrak{S}_N$, and the entire critical manifold $\mathcal{M}$ is given by $\mathcal{M} = \bigcup_{\pi\in\mathfrak{S}_N} \mathcal{M}_\pi$. The structure of $\mathcal{M}$ depends on any degeneracies in the spectra of ρ_0 and Θ. When both ρ_0 and Θ are fully nondegenerate, then $\mathrm{U}(\mathbf{n}) = \mathrm{U}(\mathbf{m}) = [\mathrm{U}(1)]^N$, and $\mathcal{M}$ consists of $N!$ disjoint N-dimensional tori, labeled by the permutation matrices. The occurrence of degeneracies in the spectra of ρ_0 and Θ will merge two or more tori together, thereby reducing the number of disjoint critical submanifolds and increasing their dimensions [219].

5.1.1 Optimality of control solutions

Satisfaction of the condition (5.2) for a critical point is a necessary but not sufficient condition for optimality of a control [204, 249]. For Mayer-type cost functionals, a sufficient condition for optimality is negative semidefiniteness of the Hessian of J, which is defined as

$$\mathcal{H}(t,t')\frac{\delta^2 J}{\delta\varepsilon(t')\delta\varepsilon(t)}. \tag{5.8}$$

The characteristics of critical points (in particular, the presence or absence of local optima) are important for the convergence properties of search algorithms [147]. To classify critical points as global maxima and minima, local maxima and minima, and saddle points, one examines the second-order variation in J for an arbitrary control variation $\delta\varepsilon(\cdot)$, which for Mayer-type functionals can be written as

$$\delta^2 J = \mathcal{Q}_F(\delta U(T), \delta U(T)) + \langle \nabla F(U(T)), \delta^2 U(T)\rangle, \tag{5.9}$$

where $\delta U(T)$ and $\delta^2 U(T)$ are the first- and second-order variations, respectively, of $U(T)$ caused by a control variation $\delta\varepsilon(\cdot)$, and $\mathcal{Q}_F$ is the Hessian quadratic form of $F(U)$. Assuming that the critical point $\varepsilon(\cdot)$ is regular, one obtains:

$$\delta^2 J = \mathcal{Q}_F(\delta U(T), \delta U(T)). \tag{5.10}$$

Explicit expressions for the Hessian and/or Hessian quadratic form were obtained for evolution-operator control [208, 209, 210] and observable control [218, 148].

The optimality of regular critical points can be determined by inspecting the number of positive, negative and null eigenvalues of the Hessian (or, equivalently, the coefficients of the Hessian quadratic form when written in a diagonal basis).

An issue of special interest is to determine whether any of the regular critical points are local maxima (frequently referred to as local traps due to their ability to halt searches guided by gradient algorithms before reaching the global maximum). Detailed analyses for evolution-operator control and observable control reveal [147, 208, 209, 210, 218, 148] that all regular optima are global and the remainder of regular critical points (i.e., except for the global maximum and global minimum) are saddles. This discovery means that no local traps exist in the control landscapes of controllable closed quantum systems. The same result was also obtained for observable-control landscapes of controllable open quantum systems with Kraus-map dynamics [274]. Due attention still needs to be given to consideration of singular critical points, although numerical evidence suggests that their effect on optimization is likely insignificant [629].

5.1.2 Pareto optimality for multi-objective control

Many practical quantum control problems seek to optimize multiple, often competing, objectives. In such situations the usual notion of optimality is replaced by that of Pareto optimality. The *Pareto front* of a multi-objective control problem is the set of all controls such that all other controls have a lower value for at least one of the objectives [246, 247, 248]. The analysis of the Pareto front reveals the nature of conflicts and tradeoffs between different control objectives. The structure of the landscape for multi-observable control is of interest and follows directly from that of single-observable control [244]. Of particular relevance to many chemical and physical applications is the problem of simultaneous maximization of the expectation values of multiple observables. Such simultaneous maximization is possible if the intersection $\bigcap_k \mathcal{M}_k^{(\max)}$ (where $\mathcal{M}_k^{(\max)}$ is the maximum submanifold for the kth observable) is nonempty and a point in the intersection can be reached under some control $\varepsilon(\cdot)$; in this regard, the dimension of the intersection manifold $\bigcap_k \mathcal{M}_k^{(\max)}$ has been analyzed [245]. It has been shown that the common QOCT technique of running many independent maximizations of a cost functional like (**??**) (using different weight coefficients $\{\alpha_k\}$) is incapable of sampling many regions of the Pareto front [245]. Alternative methods for Pareto front sampling are discussed further below.

5.1.3 Landscape exploration via homotopy trajectory control

The absence of local traps in landscapes for observable control and evolution-operator control with Mayer-type cost functionals has important implications for the design of optimization algorithms. Many practical applications require algorithms capable of searching quantum control landscapes for optimal solutions that satisfy additional criteria, such as minimization of the field fluence or maximization of the robustness to laser noise. So-called *homotopy trajectory control* algorithms (in particular, diffeomorphic modulation under observable-response-preserving homotopy, or D-MORPH) [285, 286, 287] can follow paths to the global maximum of a Mayer-type cost functional, exploiting the trap-free nature of the control landscape, while locally optimizing auxiliary costs. The essential prerequisite for successful use of these algorithms is the existence of a connected path between the initial and target controls. Homotopy trajectory control is closely related to the notion of a level set which is defined as the collection of controls that all produce the same value of the cost functional J. Theoretical analysis [147, 286, 287] predicts that for controllable quantum systems each level set is a continuous manifold. A homotopy trajectory algorithm is able to move on such a manifold exploring different control solutions that result in the same value of the cost functional, but may differ in other properties (e.g., the field fluence or robustness). A version of the D-MORPH algorithm was also developed for evolution-operator control of closed quantum systems; it was able to identify optimal controls generating a target unitary transformation up to machine precision [328].

Homotopy trajectory algorithms are also very useful for exploring quantum control landscapes for multiple objectives. For example, in order to track paths in the space of expectation values of multiple observables while locally minimizing a Lagrange-type cost, multi-observable trajectory control algorithms were developed [244]. Such algorithms are generally applicable to the treatment of multi-objective quantum control problems (Pareto quantum optimal control) [245]. They can traverse the Pareto front to identify admissible tradeoffs in optimization of multiple control objectives (e.g., maximization of multiple observable expectation values). This method can continuously sample the Pareto front during the course of one optimization run [245] and thus can be more efficient than the use of standard QOCT with cost functionals of the form (**??**). Also, the D-MORPH algorithm was recently extended to handle optimal control problems involving multiple quantum systems and multiple objectives [**?**].

5.1.4 Practical importance of control landscape analysis

The absence of local traps in control landscapes of controllable quantum systems has very important implications for the feasibility of AFC experiments (see section **??**). The relationship between the quantum control landscape structure and optimization complexity of algorithms used in AFC has been the subject of recent theoretical analyses [147, 149, 150, 151]. Results of these studies support the vast empirical evidence [148] indicating that the favorable landscape topology strongly correlates with fast mean convergence times to the global optimum. The trap-free control landscape topology also ensures convergence of gradient-based optimization algorithms to the global maximum. These algorithms can be used to search for optimal solutions to a variety of quantum control problems. In addition to theoretical studies (mostly using QOCT), gradient algorithms are also applicable in quantum control experiments [152], provided that measurement of the gradient is sufficiently robust to laser and detection noise. The use of deterministic algorithms in AFC experiments is discussed in more detail in section **??**.

5.1.5 Experimental observation of quantum control landscapes

Significant efforts have been recently devoted to experimental observation of quantum control landscapes, aiming both at testing the predictions of the theoretical analysis and at obtaining a better understanding of control mechanisms. Roslund *et al.* [634] observed quantum control level sets for maximization of non-resonant two-photon absorption in a molecule and second harmonic generation (SHG) in a nonlinear crystal and found them to be continuous manifolds (closed surfaces) in the control landscape. A diverse family of control mechanisms was encountered, as each of the multiple control fields forming a level set preserves the observable value by exciting a distinct pattern of constructive and destructive quantum interferences.

Wollenhaupt, Baumert, and co-workers [635, 636] used parameterized pulse shapes to reduce the dimensionality of the optimization problem (maximization of the Autler-Townes contrast in strong-field ionization of potassium atoms) and observed the corresponding two-dimensional quantum control landscape. In order to better understand the performance of AFC, the evolution of different optimization procedures was visualized by means of trajectories on the surface of the measured control landscape. Marquetand *et al.* [637] observed a two-dimensional quantum control landscape (for maximization of the retinal photoisomerization yield in bacteriorhodopsin) and used it to elucidate the properties of molecular wave-packet evolution on an excited potential energy surface.

The theoretical analysis of control landscape topology has been carried out with no constraints placed on the controls (see section 5.1). A main conclusion from these studies is the inherent lack of local traps on quantum control landscapes under normal circumstances. Recently, Roslund and Rabitz [**?**] experimentally demonstrated the trap-free monotonic character of control landscapes for optimization of frequency unfiltered and filtered SHG. For unfiltered SHG, the landscape was randomly sampled and interpolation of the data was found to be devoid of traps up to the level of data noise. In the case of narrow-band-filtered SHG, trajectories taken on the landscape revealed the absence of traps, although a rich local structure was observed on the landscape in this case. Despite the inherent trap-free nature of the landscapes, significant constraints on the controls can distort and/or isolate portions of the erstwhile trap-free landscape to produce apparent (i.e., false) traps [**?**]. Such artificial structure arising from the forced sampling of the landscape has been seen in some experimental studies [635, 636, 637], in which the number of control variables was purposely reduced.

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