OPTIMAL CONTROL OF MOLECULAR SCALE PHENOMENA

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Contents

1. Introduction
2. Theoretical Principles of Quantum Control
2.1. Control via Two-Path Quantum Interference
2.2. Control with the Pump-Dump Technique
2.3. Optimal Quantum Control
2.4. Tracking Control
2.5. Controllability of Quantum Systems
2.6. Existence and Robustness of Optimal Control
3. Quantum Learning Control
3.1 Structure of Laboratory Learning Control
3.2. Learning Algorithms
4. Laboratory Realizations of Quantum Control
4.1. Manipulations via Laser-Induced Two-Pathway Interferences
4.2. Manipulations with Ultrashort Laser Pulses
4.3. Closed-Loop Laboratory Learning Control
5. Control-Assisted Extraction of Microscopic Information
6. The Future of Quantum Control
Acknowledgements
Glossary
Bibliography
Biographical Sketches

Summary

Coherent control of quantum phenomena is a rapidly developing field with important applications in chemistry and physics. The basic principle of control over microscopic systems such as atoms and molecules is the manipulation of quantum interferences. Transitions between atomic or molecular levels are excited by external laser fields which can be tuned to produce either constructive or destructive interference of the transition amplitudes and thereby control the evolution of the system. For example, laser-induced quantum interferences can be used to selectively break bonds in polyatomic molecules and control branching ratios of photo-induced molecular reactions. This article presents an overview of theoretical and experimental advances in the field of coherent laser control over molecular-scale phenomena. The emphasis is on theoretical and laboratory methods for design of laser fields which are optimal for achieving the desired control objective. Effective control of the molecular dynamics can

be achieved by using ultrashort tailored laser pulses with femtosecond temporal resolution and complex spectral structure needed to create the desired interference pattern. The spectral components of an ultrashort pulse can be tuned simultaneously in a pulse shaper. In principle, the most suitable pulse shape can be designed by means of optimal control theory. However, theoretical methods of design are hampered by the lack of complete information about the interatomic forces and by inevitable experimental uncertainties and errors. Laser control designs which are optimal for the true molecular Hamiltonian and robust to experimental disturbances can be obtained in the closed-loop laboratory learning process. In this method, results of measurements on the laser-driven quantum system are analyzed by a learning algorithm which evaluates the applied control field design and refines it, until the achieved result is as close as possible to the control objective. The overview of the field presented here indicates that the application of emerging theoretical concepts and laboratory techniques can bring about important advances in the control of molecular-scale phenomena and in the ability to learn about interatomic forces.

1. Introduction

In recent years remarkable theoretical and experimental progress has been achieved in the rapidly developing area of control over quantum phenomena. Most applications have considered the use of coherent laser radiation for control of electronic, atomic, and molecular processes. This article discusses the development of the field of laser control of molecular-scale phenomena, the present state of the art of theoretical concepts and experimental techniques, and future trends and directions.

Historically, since their earliest days in the 1960s, lasers were considered the ideal candidates for microscopic manipulation of chemical reactions, that is, selective breaking and making of chemical bonds in molecules. Initial analysis suggested that lasers with their tight frequency control and high intensity could be put to use as molecular-scale ‘scissors’, with the capability of precision cutting of an identified bond, without damage to others. It was thought that there would be only simple steps between this dream and its transformation to reality. The logic involved was intuitive and appealing. Each chemical bond in a molecule has its own characteristic frequency, and radiation will preferentially be absorbed locally at that frequency. Thus, it was suggested that monochromatic laser radiation tuned to the desired bond frequency would naturally be absorbed in a selective way, causing activation and, possibly, breakage of the particular chemical bond. Matches were found between available laser frequencies and suitable chemical bonds for testing this idea, but it was soon realized that other processes were intervening and preventing the desired outcome. The main difficulty was found to be undesirable intramolecular energy transfer rapidly dissipating the initial local excitation.

The modern approach to the problem of laser control of molecular processes has come a long way from the naive early ideas described above. The present progress in this area originates from both conceptual and practical laboratory developments. First, a conceptual breakthrough was achieved when researchers understood that the key fundamental principle of control over molecular-scale dynamics is the manipulation of quantum interferences. Second, this conceptual understanding has led to an identification of the necessary laboratory tools for achieving the desired control. These sophisticated tools were not available until recently, but the last few years have witnessed enormous progress in the development of new and effective experimental methods and techniques for laboratory laser control.

The modern era of laser control started in the late 1980s when Brumer and Shapiro showed theoretically that quantum interference between two reaction pathways driven by two monochromatic lasers with commensurate frequencies and tunable intensities and phases can be used to control branching ratios of molecular reactions. In another scheme, proposed by Tannor, Kosloff, and Rice, control over intramolecular reactions is achieved by tuning the time delay between two ultrashort laser pulses. A generalization of these two approaches is the idea to control molecular processes with specially tailored ultrashort laser pulses. In order to reach a specific reaction channel, the electric field of the laser pulse should be specifically designed and tailored to the molecule. Rabitz and coworkers and others applied optimal control theory for calculations of laser pulse shapes which are most suited for achieving the desired goal. An optimally shaped laser pulse typically has a complicated spectral form, with intensities and phases of different frequency components tuned to excite an optimal interference pattern to manipulate the distinct reaction pathways of a complex molecule. Shi, Woody, and Rabitz were the first to use optimal control theory to design laser pulse shapes and showed that the amplitudes of the different interfering vibrational modes of a laser-driven molecule could add up in a given bond ultimately leading to its breakage.

A further step of fundamental importance in laser control of molecular-scale phenomena was made in 1992 when Judson and Rabitz proposed to employ a closed learning loop around the quantum system in the laboratory. In this method, the output of a control experiment is directly included in the optimization procedure, as an adaptive learning algorithm compares the measurement results with the selected target value and iteratively improves the shape of the applied laser field to better meet the goal. Recently, a number of successful experiments with atoms, molecules, and nonlinear optical systems have unequivocally demonstrated the usefulness of closed-loop laboratory learning control. These experiments became possible due to remarkable progress in femtosecond laser pulse-shaping technology.

The original goal of laser manipulation of molecular bonds has greatly broadened out in chemistry, as well as in physics and engineering, to embrace a variety of coherently controlled quantum phenomena. New types of applications in this rapidly growing field include non-linear optical processes, motion of atomic beams, quantum electron motion in semiconductors, and quantum information processing elements, as well as others. Although these directions are distinct from the original goal of controlling chemical reactions, the operating principle for quantum control of any type is the same. One may envision numerous applications of quantum control in many areas of chemistry and physics. In addition to practical applications, research aimed at manipulating molecular-scale events may also bring important fundamental results. An important long term outcome of progress in the control of quantum phenomena may be its consequences for providing a more precise means of identifying and understanding the fundamental interactions operative at the molecular scale.

The goal of this article is to provide an overview of concepts and techniques as they are now emerging in the present modern era of coherent quantum control. The topics considered include the nature of physical and chemical control objectives, the theoretical design of optimal laser shapes for coherent quantum control, general issues of controllability, closed-loop learning control in the laboratory, and the ability to utilize coherent quantum manipulation as a means for extracting microscopic information. This overview aims to outline the basic principles, the status of laboratory studies, and an indication of key milestones ahead, as well as cautious predictions on new challenges and directions.

2. Theoretical Principles of Quantum Control

2.1. Control via Two-Path Quantum Interference

Modern strategies of coherent control are based on the fundamental principle of quantum interference. Consider, for example, a photo-induced branching reaction, in which the reactant molecule is excited from the initial bound state to a final state in the continuum and can form at least two distinct product species. Brumer and Shapiro showed that the branching ratio of the reaction products can be controlled via interference created by coherent laser excitations of two reaction pathways. In quantum theory, the probability of forming a specified product is proportional to the square of the sum of the transition amplitudes for the two pathways between the initial and final states.

In the Brumer-Shapiro method, the transitions from the initial to the final state are driven by two monochromatic lasers with commensurate frequencies. The intensities and phases of the two lasers can be tuned to change the transition amplitudes. This will cause constructive or destructive interference between the two excitation pathways resulting in enhancement of one reaction channel and suppression of others. The Brumer-Shapiro technique of quantum interference between competing paths can be also used for control of transfer of population between bound states. The number of photons absorbed along two paths 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, competition between one- and three-photon excitations is employed. The overall transition rate can be controlled by tuning the relative phase of the two laser beams.

2.2. Control with the Pump-Dump Technique

Tannor, Kosloff, and Rice proposed a different method for controlling selectivity of product formation in an intramolecular reaction, by tuning the time delay between two successive ultrashort laser pulses. The first laser pulse transfers probability amplitude from the electronic ground state to an excited state, creating a wave packet on the excited potential-energy surface. This wave packet evolves freely until the second laser pulse, incident after a time interval t, dumps some of the wave-function amplitude from the excited state into a selected reaction channel on the ground potential-energy surface beyond any barrier obstructing the exit channel. Another version of this "pump-dump" technique can be used to control the transfer of population between two electronic surfaces. In this case, the phases of the two laser pulses are locked, and the probability amplitudes transferred to the excited electronic state by the two successive pulses interfere. Constructive or destructive interference, giving rise to larger or smaller excited-state population, can be achieved by tuning the time delay between the two pulses.

2.3. Optimal Quantum Control

Both types of control schemes discussed above are based on a limited number of optimization parameters: the phase difference between two monochromatic lasers and the time delay between the pump and dump laser pulses, respectively. Given the complexity of the potential-energy surfaces of polyatomic molecules, the use of time-independent fields or simple pulse sequences is generally not likely to yield the most efficient control of chemical reactions and other quantum phenomena. The most comprehensive means for controlling the evolution of a molecule undergoing a complex dynamical process is through the coordinated interaction between the molecule and the electromagnetic field whose spectral content and temporal profile are continuously altered throughout the process. For specified initial and final states of a given molecule, and with restrictions imposed by any of a variety of constraints, the time-dependent field required to control the desired dynamical process can be designed using optimal control theory. This general formulation encompasses both the weak and strong field limits and incorporates as special cases the control method based on two-path interference induced by monochromatic laser fields and the “pump-dump” technique based on the sequence of two ultrashort laser pulses.

Optimal control theory has an extensive history in traditional engineering applications, but the quantum nature of molecular-scale phenomena imposes special features. Consider a quantum system (e.g., a molecule), whose free evolution is governed by the Hamiltonian H_0. The system can be controlled by the optical electric field of an external laser. The full Hamiltonian of the laser-driven system is $H = H_0 - \mu\varepsilon(t)$ where $\varepsilon(t)$ is the time-dependent electric field and μ is the system dipole moment (it is assumed that the laser beam is linearly polarized and μ is the component of the dipole moment in the direction of the laser field). The basic idea of control is to design the form of the electric field which will allow manipulation of the system dynamics in a desired way.

A typical quantum control objective is to manipulate the expectation value $\left\langle \psi(t) \middle| O \middle| \psi(t) \right\rangle$ of an operator O at the final time $t = T$. For example, O may be the projection operator on a bound quantum state, and the control objective then typically will be to maximize the population of this state. In practice, there may be multiple objectives involving distinct observable operators corresponding to the desire to simultaneously manipulate several physical aspects of the same system (e.g., control the fate of multiple bonds, in a polyatomic molecule). In addition, there may be costs or constraints on the form, magnitude, frequency, or other characteristics of the control field. These various objectives and constraints will often be in competition with each other. This recognition suggests posing the control design problem as an optimization attempting to strike a balance between the competing physical components or goals. Such an approach is the essence of optimal control theory. The physical objectives are expressed in the form of a cost functional, $J\left[\psi(t),\varepsilon(t)\right]$, dependent on the evolving wave function, the target states or expectation values, any constraints, and the electric field. The cost functional is optimized with respect to the control field $\varepsilon(t)$, to yield the best possible control performance in balance with any competing factors.

Consider, for example, the case of control over maximizing the expectation value $\left\langle \psi(t)\middle|O\middle|\psi(t)\right\rangle$ of a positive definite operator *O* at the final time *T*, while minimizing the laser field fluence. In this case, the cost functional takes the form

$$\begin{aligned} J &= \left\langle \psi(T)\middle|O\middle|\psi(T)\right\rangle \\ &-\alpha_0\int_0^T[\varepsilon(t)]^2\,dt - 2\,\mathrm{Im}\left[\int_0^T\left\langle \chi(t)\middle|i\hbar\partial_t - H\middle|\psi(t)\right\rangle dt\right]. \end{aligned} \tag{1}$$

Here, $\partial_t = \partial/\partial t$, $i=\sqrt{-1}$, $\hbar$ is Planck's constant, Im denotes imaginary part, α_0 is a positive parameter chosen to weight the significance of the laser fluence, $\left|\psi(t)\right\rangle$ is the system wave function, satisfying the initial condition $\left|\psi(0)\right\rangle = \left|\psi_0\right\rangle$, and $\left|\chi(t)\right\rangle$ can be regarded as a Lagrange multiplier introduced to assure satisfaction of the Schrödinger equation. Requiring the first variation of *J* with respect to $\left|\psi(t)\right\rangle$, $\left|\chi(t)\right\rangle$, and $\varepsilon(t)$ satisfy $\delta J = 0$ will give equations for the wave function, Lagrange multiplier, and optimized laser field:

$$i\hbar\partial_t\left|\psi(t)\right\rangle = H\left|\psi(t)\right\rangle, \quad \left|\psi(0)\right\rangle = \left|\psi_0\right\rangle, \tag{2}$$

$$i\hbar\partial_t\left|\chi(t)\right\rangle = H\left|\chi(t)\right\rangle, \quad \left|\chi(T)\right\rangle = O\left|\psi(T)\right\rangle, \tag{3}$$

$$\alpha_0\varepsilon(t) = -\,\mathrm{Im}\left\langle \chi(t)\middle|\mu\middle|\psi(t)\right\rangle. \tag{4}$$

Numerical solution of the above equations will give the desired optimal control field design, although this is a problem of significant computational complexity. Various iterative algorithms have been developed for the calculation of optimal control fields. In particular, Zhu and Rabitz demonstrated recently a number of rapid monotonically convergent iterative algorithms as well as some approximate noniterative methods. Many numerical examples have illustrated quantum optimal control of various molecular-scale phenomena, e.g., rotational, vibrational, electronic, reactive, and other processes.

2.4. Tracking Control

In typical optimal control problems, objectives are specified at the end of the control period, leaving significant freedom for the intermediate dynamics. However, it is possible to search for the laser field which will guide the system evolution along a specified track connecting the initial and final states. For example, the system may be required to follow a track $f(t)$ for the expectation value, $\langle \psi(t) | O | \psi(t) \rangle = f(t), 0 \leq t \leq T$. The corresponding Heisenberg equation of motion can be rearranged to give

$$\varepsilon(t) = \left(\langle \psi(t) | [O, \mu] | \psi(t) \rangle \right)^{-1} \left[i\hbar \frac{df(t)}{dt} - \langle \psi(t) | [O, H_0] | \psi(t) \rangle \right] . \qquad (5)$$

This expression can be substituted into the Schrödinger equation $i\hbar\partial_t | \psi(t) \rangle = [H_0 - \mu\varepsilon(t)] | \psi(t) \rangle$ and numerically solved for $| \psi(t) \rangle$. Finally, the wave function $| \psi(t) \rangle$ can be substituted back into Eq. (5) to give the field $\varepsilon(t)$ that exactly produces the imposed track $f(t)$. Note, that if the denominator in Eq. (5) vanishes, then the field $| \psi(t) \rangle$ can be calculated using higher-order time derivatives of $\langle \psi(t) | O | \psi(t) \rangle$.

The method of tracking control requires no iterations in the numerical solution process and is computationally much simpler than the corresponding optimal control problem with only initial and final conditions specified. This simplicity follows from the fact that a specified track contains much more information on the evolution of the system than just the final expectation value or the final state. In tracking control, this information is used to extract the laser electric field driving the system. This approach emphasizes the fact that control is a type of inversion problem, where information about a part of the system Hamiltonian (specifically, the driving electric field) is extracted from partial knowledge of the system dynamics. From the practical point of view, the tracking algorithm may be considered as a test of one's intuition, as well as a means for control design. That is, if the intuitively imposed track $f(t)$ leads to a physically acceptable control field, then a successful design will have been achieved.

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Biographical Sketches

Constantin Brif obtained his B.A. in Physics in 1993, M.S. in Physics in 1995, and Ph.D. in Physics in 1998, all from the Technion - Israel Institute of Technology. In 1998-1999 he was a post-doctoral scholar in California Institute of Technology. In 1999 he joined the group of Professor Herschel Rabitz in the Department of Chemistry at Princeton University as a post-doctoral associate. Dr. Brif's research interests include a broad variety of topics in quantum theory and chemical physics, with a focus on coherent control of quantum phenomena, inverse quantum dynamics, quantum noise reduction in interferometry and spectroscopy, quantum dynamics of field-matter interactions, nonclassical photon states, phase-space methods in quantum mechanics and quantum optics, quantum entanglement, and group-theoretic and analytic methods in quantum physics. In 1997 and 1998 Constantin Brif received Miriam and Aaron Gutwirth Memorial Fellowship and in 1998 he was awarded Israel Knesset Education Committee Prize of Excellence and Lester Deutsch Post-doctoral Fellowship.

Herschel Rabitz obtained his B.S. in Chemistry from University of California, Berkeley, in 1966 and Ph.D. in Chemical Physics from Harvard University in 1970. In 1970-1971 he was a post-doctoral associate at University of Wisconsin. In 1971 he joined the faculty of the Department of Chemistry at Princeton University. Since 1974, he has been an affiliated member of Program in Applied and Computational Mathematics at Princeton University and was acting director of the Program in 1981. In 1993-1996 Professor Rabitz chaired the Department of Chemistry at Princeton University. In 2000 he was named Charles Phelps Smyth Professor of Chemistry. Professor Rabitz's research interests lie at the interface of chemistry, physics, and engineering, with principal areas of focus including molecular dynamics, biophysical chemistry, chemical kinetics, and optical interactions with matter. An overriding theme throughout his research is the emphasis on molecular-scale systems analysis. Professor Rabitz was an Alfred P. Sloan Fellow in 1975-1979, Camille and Henry Dreyfus Teacher-Scholar in 1974-1979, and received an Alexander von Humboldt Award in 2000.