

# COHERENT CONTROL OF PHYSICAL AND CHEMICAL PROCESSES

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## Summary

The method of coherent control allows one to exploit classical and quantum-mechanical interferences to control the dynamics of atomic, molecular, and solid-state systems, and to drive them into novel, non-equilibrium states. This technique has been widely applied to control both electronic and vibrational degrees of freedom in a variety of systems. Typically, a sequence of femtosecond pulses excites some arbitrary system into a state dependent on the temporal delay between pulses, and the resulting dynamics are probed optically. Various experiments in chemistry, biology, nanoparticles, and physics are considered showing great possibilities of these new techniques in investigation of dynamics of different systems.

## 1. Introduction

Quantum mechanics, though a probabilistic theory, gives a “deterministic” answer to the question of how the present determines the future. In essence, in order to predict future probabilities, we need to (numerically) propagate the time-dependent Schrödinger equation from the present to the future. It is interesting to note that classical mechanics of macroscopic bodies, though reputed to be a deterministic theory, does not allow, due to chaos (which unfortunately is more prevalent than integrability), such clear insights into the future. In contrast, small (e.g., atomic, molecular and photonic) systems which are best understood using the tools of quantum mechanics, do not suffer from chaos, rendering the prediction of the probability-distributions of future events possible.

The field of quantum control deals with an important modification of this task, namely, it asks: given a wave function in the present, what dynamics, i.e. what Hamiltonian, guarantees a desired outcome or “objective” in the future? In practice one may achieve this goal of modifying and finding the desired Hamiltonian by introducing external fields, e.g. laser light. It is then possible to reach the objective in a “trial-and-error” fashion, performed either numerically or in the laboratory. We can guess or build a Hamiltonian, do an experiment, or propagate the initial wave function to the future, compare the result with the desirable objective, and correct the guess for the Hamiltonian until satisfactory agreement with the objective is reached. A systematic way of executing this procedure is the sub-field called “optimal control”.

The trial-and-error method is often very time consuming and rarely provides mechanistic insight. There are situations where analytical solutions exist, rendering the control strategies more transparent. This is especially so when one can identify quantum interferences as the heart of quantum control, the essence of the field called “coherent control”.

The experience accumulated so far by many groups is that quantum interferences are the mechanism underlying most successful control scenarios and control experiments. The identification of the control mechanism is especially facile when the time-dependence of the Hamiltonian merely serves to prepare a state which then evolves in the absence of external fields. Analytical theories also exist when the explicit time dependence of the Hamiltonian can be treated adiabatically.

Under these circumstances one can identify the quantum interfering pathways that lead to control, allowing for the simultaneous exploration of entire “landscapes” (and not just a single “desirable” objective) resulting from varying all the experimental “knobs” at our disposal, e.g., relative- and envelope-phases, intensities, polarizations, and pulse-sequencing. Such “pulse-shaping” knobs are now available down to the sub-femtosecond regime in broad spectral regions ranging from the UV to the IR.

Comprehensive investigations of the quantum interference required to control dynamical processes will result in a more detailed understanding of the dynamics themselves. Together with experimental progress –the stage is now set for many exciting applications in fundamental and applied sciences by “tailoring” light-matter interactions essentially at will. We consider below some examples of coherent control techniques in physics, chemistry and biology.

## **2. Coherent Control of Dynamics of Chemical Processes and Product Yield**

In a stochastic (traditional) reaction, energy localization in a desired region is governed by statistical fluctuations. However, when lasers were invented they were considered the ideal tool for microscopic control of chemical reactions, that is, selective cleavage or formation of chemical bonds. By exactly tuning the monochromatic laser light according to the local mode frequency of a specific chemical bond, it was thought that enough energy could be deposited in this specific mode to cause selective bond breakage. In most experiments, however, selectivity is lost because of rapid intramolecular energy redistribution. Several control schemes have been proposed that make use of the coherent

nature of laser radiation. Known as "coherent control"(this is sometimes called "quantum"), these schemes access the broad range of quantum interference effects. The key principle of coherent control of various systems to obtain a desired result consists in targeted control of quantum interference.

Brumer and Shapiro (1986), for example, showed theoretically that in a quantum mechanical system simultaneous one- and three-photon excitation can lead to constructive or destructive interference of different reaction pathways, depending on the relative phase of the light waves. Experimental realizations have been carried out on atomic and small molecular systems. A somewhat different control scheme makes use of the rapid progress in ultrashort laser pulse technology. For example, Tannor, Kosloff, and Rice (1986) suggested a "pump-dump" technique, which has been realized experimentally by several groups.

Progress in research on the possibility of coherent control follows two avenues. The most widely used method is based on the theory of optimal control and construction of self-learning feedback algorithms. It was developed because the PES (potential energy surface of the reaction) parameters are usually unknown. The approach (Figure 1) involves experimental determination of the ratio of product yields in two channels. This information is transferred to a computer. A computer program makes it possible to vary the parameters of the excitation pulse (phases, amplitudes, and polarizations of spectral components) and to determine the fields corresponding to the maximal and minimal product yields.

The drawbacks of this approach are unpredictability of results and ambiguity of correspondence between the optimal femtosecond pulse found and the global extremum.

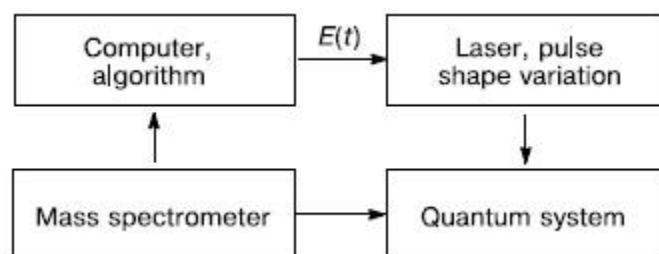


Figure 1. Scheme of coherent control of the yield of reaction products based on the theory of optimal control.

This approach is developed in many studies of samples of different degree of complexity. For instance, photo fragmentation of  $\text{MeCOOCF}_3$ ,  $\text{MeCO}\tilde{\text{N}}\text{D}_3$ , and  $\text{MeCOCCl}_3$  was studied by D. Gardoza, M. Baertschu and T. Weinacht (2005). Reaction products were detected using a mass spectrometer. It was shown that variation of the amplitudes and phases can be used for generation of different fragment ions and, therefore, for optimization of the product yield ratio. The relative yields of products having two different weights can vary from 1 to 3. Interesting results were obtained by F. Vetter with colleagues (2005) in studies of photo dissociation of  $\text{Na}_m\text{K}_n$  clusters. It was shown that coherent control can be used for controlling the wave-packet motion

dynamics if the frequency of incident light is equal to the frequency of vibrational transitions. This approach is appropriate in the case of optical detection of products.

The second avenue of research includes the development of concepts of microscopic mechanisms of coherent control. The main idea of the approach is to choose branching intramolecular processes, to study them experimentally, and to construct theoretical models for various types of branching. Comparison of theoretical models with experimental data will provide a qualitative picture of the processes, which makes it possible to predict the possibility of coherent control in various systems. However, this approach is of limited use because of difficulties in calculations of polyatomic systems.

### 3. Specific Features of Experiments on Coherent Control

The development of coherent control of processes in electronic-excited states shows the greatest progress, because by varying the amplitudes and phases of spectral components of the excitation pulse one can with relative ease create coherent wave packets with different parameters in the electronic-excited state. The amplitudes and phases of femtosecond pulses can be varied using some devices. One of them is schematically shown in Figure 2.

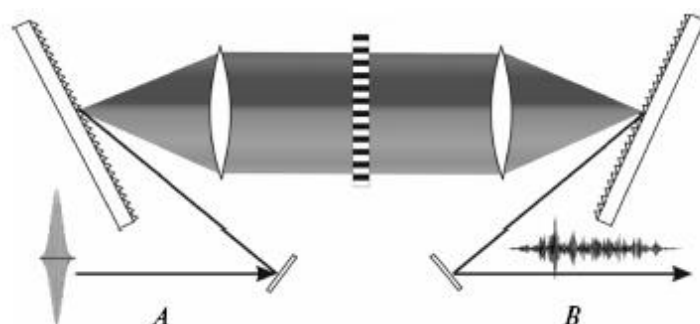


Figure 2. Scheme of a device for variation of the amplitude and phase of femtosecond pulse. Initial (A) and transformed (B) shapes of femtosecond pulse

A femtosecond pulse is decomposed over spectral components. The device permits variation of the (i) optical path length of spectral components to vary the phases  $\gamma_k$  of the stationary excited vibrational states contributing to the coherent wave packet and (ii) polarization of each spectral component to vary their amplitudes  $C_k$  (this is attained using polarizers). Figure 3 presents a possible initial (A) and a possible final (B) coherent wave packet. By varying the parameters of the excitation pulse one can achieve targeted manipulation of the structure and interference of the coherent wave packet.

The authors of some studies on coherent control used a simplified approach involving variation of only phase characteristics of the femtosecond excitation pulse. In the simplest case this is achieved by varying the linear chirp  $\beta$  (parameter that characterizes the rate of phase modulation). The parameter  $\beta$  defines which spectral components irradiate the sample earlier and which do it later. This means that a change

in the parameter  $\beta$  causes the phase of vibrations, *i.e.*, synchronization of nuclear motion, to vary. By varying the linear chirp magnitude the structure and interference of the coherent wave packet created can be varied in targeted manner to achieve coherent control.

At present, coherent control in small systems was experimentally implemented in gases and solutions, in nanoscale and microscopic solid particles, in condensed matter, and in biological compounds. We will consider them separately.

#### 4. Processes and Elementary Photoreactions in Gases and Solutions.

Examples of coherent control of various processes in small systems are presented in Table 1.

Process type	System	Reference
Multiphoton light absorption	Diatomic molecules	Krivoguz (2004, 2005)
Dynamics of nuclear vibrations	Iodine molecules in gas phase	Lozovoy (1999)
Multiphoton photodissociation	Ammonia molecules in gas phase	Sarkisov (2001)
Proton transfer reactions	(2,2 – Bipyridine)–3,3 –diol in solution	Sarkisov (2001)
Bifunctional compounds		Sarkisov (2006)
Isomerization	Spiropyran	Konorov (2003)

Table 1. Examples of coherent control of various processes in small systems

It was theoretically shown that in two-level systems the dependence of the probability of three-photon absorption on the linear chirp  $\beta$  of the femtosecond excitation pulse is governed by the pulse duration only. In the presence of an intermediate resonant electron level the dependence of the probability of three-photon absorption of a femtosecond pulse depends strongly on the phase characteristics (sign and magnitude) of the linear chirp. This can be explained by important role of the evolution of the coherent wave packet in the intermediate electronic state. According to calculations, the character (fall or raise) of the monotonic dependence of the three-photon absorption probability on  $\beta$  depends strongly on the character (repulsive or attractive) of the intermediate term.

Coherent control of the vibrational dynamics of nuclear motion in iodine molecule (Figure3) was studied theoretically and experimentally. In the experiments, the excitation energy was too low to initiate the chemical reaction. The excitation energy of a molecule is such that no chemical reaction occurs. Figures 3 *a, b* present the experimental dependences of the detected signal on the time delay between the probe pulse and excitation pulse at different signs of the chirp  $\beta$ . As can be seen, vibrations of even a small diatomic molecule are a complex process, which is strongly dependent on the sign of the parameter  $\beta$ . Since the excited-state PES is known, theory describes experimental data without fitting parameters. Figures 3, *c–f* present the density probability maps for the system location at different points of the phase space. At

negative  $\beta$  values, the wave packet is localized at 3.2–3.4 Å, whereas at positive  $\beta$  values, it is delocalized over almost the whole molecule.

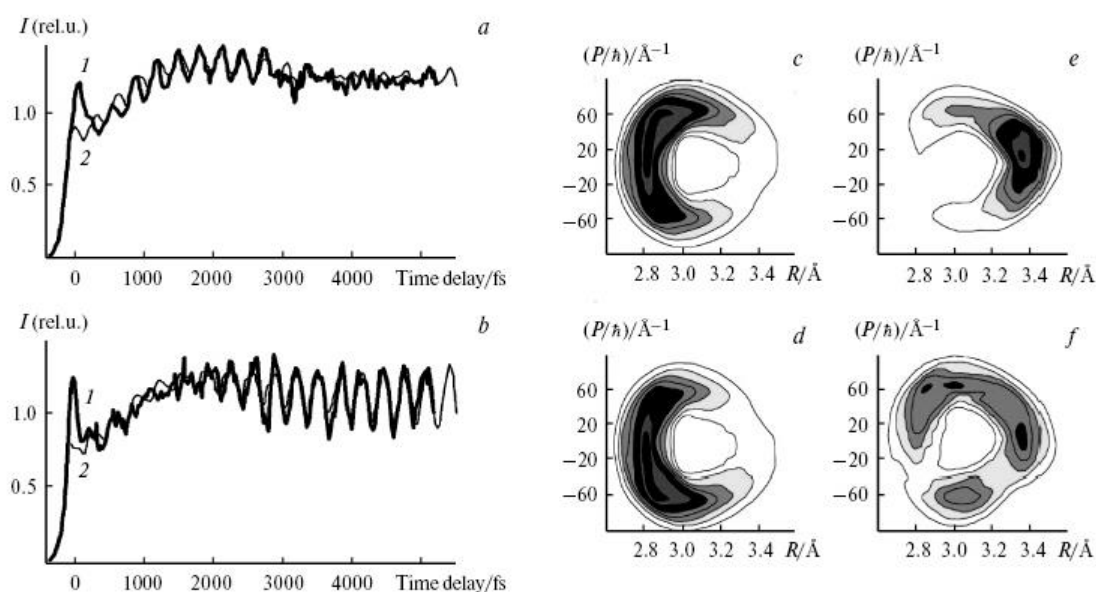


Figure 3. Experimental (1) and theoretical (2) results obtained in studies of the dynamics of coherent vibrational wave packets ( $\beta = -2000$  (a) and  $2000 \text{ fs}^2$  (b); density probabilities for the system to have a preset pulse ( $P$ ) and to be located at particular internuclear distance ( $R$ ) at  $\beta = -2000$  (c, e) and  $2000 \text{ fs}^2$  (d, f) and a time delay of 0 ( $\tilde{n}, d$ ) and 200 fs (e, f). Darker areas correspond to higher probability densities.

The results of coherent control of product yield upon multiphonon photo dissociation of ammonia are shown in Figure 4. As the system absorbs the femtosecond pulse, the reaction proceeds by two channels involving (i) cleavage of one bond to produce a hydrogen atom and a radical and (ii) formation of dihydrogen and electronic-excited  $\text{N}\dot{\text{I}}$  molecule. From Figure 4 it follows that the yield of  $\text{N}\dot{\text{I}}$  varies over a wide range depending on the parameter  $\beta$ .

Tautomerization of (2,2'-bipyridine)-3,3'-diol was studied in 2001 by Sarkisov *et al.* Excitation of the molecule is followed by the processes proceeding by two intramolecular concurrent channels, namely, concerted transfer of two protons and transfer of a single proton only (Scheme 1). Figure 5 presents the stimulated emission spectrum of the two tautomers formed at a time delay of 250 fs (no other processes do occur under these conditions). The difference in the stimulated emission spectra between these two tautomers at different  $\beta$  values unambiguously indicates a change in the transfer rates of one and two protons.

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D'Alessandro Domenico (2004). *Introduction to Quantum Control and Dynamics*. Chapman & Hall/CRC Applied Mathematics & Nonlinear Science , pp.360. [This book presents the mathematical concepts and fundamental physics behind the analysis and control of quantum dynamics, emphasizing the application of Lie algebra and Lie group theory. After introducing the basics of quantum mechanics, the book derives a class of models for quantum control systems from fundamental physics. It examines the controllability and observability of quantum systems and the related problem of quantum state determination and measurement. The author also uses Lie group decompositions as tools to analyze dynamics and to design control algorithms. In addition, he describes various other control methods and discusses topics in quantum information theory that include entanglement and entanglement dynamics. The final chapter covers the implementation of quantum control and dynamics in several fields. Armed with the basics of quantum control and dynamics, readers will invariably use this interdisciplinary knowledge in their mathematical, physics, and engineering work.]

Martin M.M. (ed.), Hynes J.T. (ed.). (2004) *Femtochemistry and Femtobiology*, Elsevier B.V. pp.800. [This book contains important contributions from top international scientists on the-state-of-the-art of femtochemistry and femtobiology at the beginning of the new millennium. It consists of reviews and papers on ultrafast dynamics in molecular science. The coverage of topics highlights several important features of molecular science from the viewpoint of structure (space domain) and dynamics (time domain). First of all, the book presents the latest developments, such as experimental techniques for understanding ultrafast processes in gas, condensed and complex systems, including biological molecules, surfaces and nanostructures. At the same time it stresses the different ways to control the rates and pathways of reactive events in chemistry and biology. Particular emphasis is given to biological processes as an area where femtodynamics is becoming very useful for resolving the structural dynamics from techniques such as electron diffraction, and X-ray and IR spectroscopy. Finally, the latest developments in quantum control (in both theory and experiment) and the experimental pulse-shaping techniques are described.]

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### Biography Sketch

**Oleg Mikhailovich Sarkisov** currently is the Professor of Chemistry and vice director at the Institute of Chemical Physics of the Russian Academy of Sciences and the Professor at the Faculty of Molecular and Biological Physics of Moscow Institute of Physics and Technology. He received his MS degree from Moscow Institute of Physics and Technology (1967) and his Ph.D. from the Institute of Chemical Physics of the Russian Academy of Sciences (1971). In 1981 he obtained the degree of Doctor of Physical and Mathematical Sciences, in 1984 he obtained the diploma of Full Professor. Since 1983 up to now, he is the head of the Laboratory of Laser Photochemistry and Spectroscopy. Since 1997 up to now, he is vice director of the Institute. The author of more than 200 publications. Oleg M. Sarkisov is the Member of Scientific Council on "Chemical Kinetics and Structure" of the Russian Academy of Sciences; Chairman of chemical dynamics section of Scientific Council on "Chemical dynamics" of Russian Academy of Sciences; the Member of Russian Committee of International Geosphere-Biosphere Programme. He is the supervisor of more than 30 post-graduate students and post-doctoral fellows. O.M. Sarkisov is the



coauthor of two monographs and more than 150 scientific articles. His main scientific interests are kinetics and dynamics of elementary reactions, intramolecular and intermolecular energy transfer processes, laser spectroscopy, photochemistry, and atmospheric chemistry.