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Coherent Control of Quantum Dynamics: The Dream Is Alive

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Current experimental and theoretical progress toward the goal of controlling quantum dynamics is summarized. Two key developments have now revitalized the field. First, appropriate ultrafast laser pulse shaping capabilities have only recently become practical. Second, the introduction of engineering control concepts has put the required theoretical framework on a rigorous foundation. Extrapolations to determine what is realistically possible are presented.

Since the early days of quantum mechanics, an implicit dream has been the desire to manipulate and control quantum-mechanical phenomena. This dream crystallized into an active pursuit with the development of the first high-power pulsed lasers in the 1960s. The objectives were focused toward manipulating events at the molecular scale. Special emphasis was given to the goal of selectively breaking bonds in polyatomic molecules, as this capability could, in principle, significantly improve chemists' ability to build and otherwise alter complex molecular frameworks with high specificity. With this objective in mind, a flurry of activity ensued, extending over some 30 years, by chemists and physicists attempting especially to selectively break one bond versus another in polyatomic molecules, using a variety of laser sources (1). The basic approach seemed simple: identify the local mode frequency associated with the targeted bond, then pump intensely with a laser tuned to that frequency until the bond breaks.

Many years of work and variations on

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this theme were attempted, with essentially no substantial success. The crux of the problem eventually became clear: in all but the smallest molecules, locally deposited energy very rapidly redistributes throughout the molecule, destroying the selectivity. As a result, while these studies revealed a great deal about intramolecular energy redistribution, they made the dream lose much of its allure.

In fact, this early paradigm effectively ignored a key aspect of quantum phenomena—quantum dynamical processes are wave phenomena, subject to constructive and destructive interferences. In the past few years, a resurgence of activity has occurred in this field as researchers have finally recognized that actively manipulating these constructive and destructive interferences is the essential step. This recognition has both theoretical and experimental components. On the theoretical side, the active manipulation of quantum dynamics phenomena is now realized to be a problem of control theory or optimal design analogous to efforts carried out in the traditional macroworld engineering disciplines, where the control of airplanes or mechanical and electrical devices is commonplace. The introduction of control theory concepts has finally put the subject of active manipula-

tion of quantum phenomena on a firm theoretical footing. In the laboratory, with hindsight, the laser tools needed to actively manipulate quantum phenomena were, in fact, not available until very recently. These tools particularly include the ability to tailor the time or frequency structure of optical pulses to precisely meet the needs of the quantum system being manipulated. Molecules or other quantum systems are capable of quite complex dynamical behavior. The controlling optical field must work cooperatively with this behavior, and hence, is expected to typically contain concomitant structure reflecting this situation. Computer-controlled optical pulse shaping tools with features in the near femtosecond regime are now becoming practical, and this capability will have an important enabling impact on the field.

Since the original inception of control over quantum phenomena as a goal, the potential applications have broadened out beyond chemical reactivity. In principle, quantum phenomena of any variety could be amenable to control by optical or other means. Thus, attention is being given to controlling electrons in solid-state multiple quantum wells, encoding or decoding of information in the wavepacket of moving electrons in semiconductors, and possibly using the active manipulation of molecular dynamics as a means for extracting information on the underlying Hamiltonian. The old dream, as stated earlier, is not only alive, but also broadened out in its significance. With the present recognition of the essential nature of the problem and the availability of powerful new laboratory tools, the prospect of making these dreams a reality is here (2). For this to happen, it is also clear that laboratory studies or theory alone cannot lead to success. These all-too-often disparate activities in chemical physics must work cooperatively for the subject to reach fruition. Glimmers of this success are already in hand. An algorithm has been put forth, drawing on the best capabilities of the emerging experimental and theoretical tools, and the capabilities are discussed in this article.

Theoretical Developments: What Might Be Possible?

We begin by discussing the theoretical possibilities for coherent control, which are absolutely spectacular—calculations suggest that appropriate laser pulses or pulse sequences can break strong bonds (3), force molecules to climb anharmonic ladders (4, 5) or change reaction pathways (6, 7), manipulate curve crossings between states (8), or transform local modes into energy eigenstates (9). These exciting prospects and methods for bringing these ideas to

experimental realization have been the subject of much discussion in the coherent control community over the last few years and the focus of several meetings. The theoretical developments in active laser control have been spurred by technological progress, which has also been substantial, and a variety of intriguing experiments have shown that active control can directly affect molecular dynamics. It is also clear that the gap between theory and experiment is narrowing, as experimental capabilities become more sophisticated, and as calculations begin to incorporate such experimental complications as laser imperfections and spectral complexity.

Weak versus strong response. In discussing active laser control experiments it is useful to distinguish between weak-response and strong-response experiments, on the basis of how the observables change when the intensity is made arbitrarily small. If the expected signal or excitation is unchanged in functional form as the intensity is changed, but merely scales as some power of the intensity, then we are describing a weak-response phenomenon. In general, weak-response experiments are readily described by perturbation theory: the field does not appreciably alter the energy level structure of the molecule when it is on.

The simplest examples of weak-response experiments involve one-photon resonances, with signals (absorption or laser-induced fluorescence) that are linearly proportional to the applied intensity. In this limit (often called linear response), pulse shape and sequence effects are easily visualized. The induced polarization at frequency ω is proportional to the Fourier component of the electric field at that frequency, and the excited population at frequency ω is proportional to the Fourier component of the intensity. However, the concept of weak-response experiments is more general. For example, multiphoton absorption spectroscopy, four-wave mixing, and pump-dump experiments are usually done in the weak-response limit.

Strong-response experiments do not necessarily imply intense radiation fields. Although it is certainly true that fields that are large enough to blow apart molecules produce a strong response, so do much weaker fields that merely shift energy levels or transfer substantial population to excited states. At these intensities, the fields effectively alter the molecular eigenstates while they are on and can thus affect intramolecular dynamics. No simple scaling relations describe the energy dependence; the sequences generate a much more complex behavior, which cannot be understood simply by Fourier transformation because population in the ground state is strongly depleted.

Coherent control has been demonstrat-

ed theoretically and experimentally in both the weak- and strong-response regimes. Neither is universally preferred; each has advantages and disadvantages.

Weak-response experiments and calculations. A great conceptual advantage of the weak-response regime is that Fourier analysis usually permits equivalent time-domain or frequency-domain descriptions. The combination of the two can give more insight than either description by itself. For example, suppose a sequence of two amplitude-modulated laser pulses is generated, with the second pulse exactly π radians out of phase with the first; then the Fourier component at the carrier wave frequency vanishes, and there is no excitation at that frequency. However, if the two pulses were exactly in phase, the resonant Fourier component would be large, and excitation would be observed. Thus phase-shifted, low-energy picosecond or subpicosecond pulse trains can modulate excitation (10–13). However, by definition, the weak-response limit implies a low product yield. As the pulse energy increases, making these strong-field experiments, the intuitive explanations and guidance for experimental design begins to fail.

This type of Fourier analysis is easily generalized to include off-resonance effects or complicated pulse shapes and can be used to predict the signal precisely. If the spectrum within the excitation bandwidth is complex, this time evolution may appear extremely complicated in the time domain. For example, Scherer, Fleming, and co-workers (13) demonstrated that the excitation produced in molecular iodine by a pair of femtosecond pulses with a well-defined interpulse phase relation oscillates dramatically as the delay between the pulses is incremented. It is possible to rationalize this in the time domain by noting that the first pulse prepares a wave packet, which evolves with time between the two pulses; the second pulse then creates a complex interference pattern as it drops some of this population back down to the ground state. An equivalent frequency domain picture simply looks at the Fourier components associated with a pair of pulses separated by a delay, and matches these components to the absorption spectrum. In such a picture, it becomes apparent that this experiment is the first demonstration of true optical Fourier transform spectroscopy and that the complex-looking signal which is produced is essentially the Fourier transform of the conventional absorption spectrum.

Another large group of weak-field experiments generates a signal with greater than linear dependence on the input power, usually because of multiphoton resonance. For example, a train of infrared pulses with constant spacing T (for example, the out-

put of an interferometer) can efficiently excite population up an anharmonic vibrational ladder (4). A time-domain description would point out that each pulse moves a wavepacket to the excited states, which oscillates back and forth at the vibrational frequency; hence if T is chosen to be one cycle at the vibrational frequency, the contributions from successive pulses reinforce. In a frequency-domain description, the periodicity of the pulse train concentrates intensity into frequency components at the carrier frequency $\pm 1/T$, $3/T$, and so forth; these sidebands can be made to coincide with the anharmonic resonances. In the low-power limit, the population in the n th vibrational level scales as the n th power of the field. Similarly, the elegant impulsive stimulated Raman scattering experiments of Nelson, Weiner, and co-workers (14) use a periodic laser pulse train to deliver impulsive energy to a vibrational mode; if the mode frequency is a multiple of the pulse spacing, the resonant Fourier component is enhanced. In demonstrations to date, the excitation does not seriously deplete population in the lowest vibrational state, and the excited population scales as the square of the field strength.

Coherent control is certainly not restricted to ultrafast pulses. A variety of control schemes with multiple continuous lasers have been suggested (7) with the canonical process involving the manipulation of two interfering pathways to a degenerate pair $|\phi_\alpha\rangle$ and $|\phi_\beta\rangle$ of final states distinguished by their quantum numbers α and β . Typically, the two pathways will differ by accessing distinct intermediate states, thus calling for the incorporation of several control fields coherently locked together. For example, manipulation of the phase relations between the fields can, in turn, manipulate the amplitude for one or another of the final states. This scheme is analogous to the fundamental double-slit experiment and its ensuing interference patterns. Modulation of total excitation or angular distribution of products has been demonstrated, but it is clear that establishing the required phase relation over a macroscopic sample between multiple lasers of different colors is experimentally quite difficult.

To the degree that simple systems with a small number of isolated intermediate and final states can be found, this approach may well be attractive for practical implementation. It has the advantages of intuitive correctness and robustness to certain experimental difficulties. For example, lasers typically have spatially nonuniform electric field strengths ϵ , and transition dipoles μ are often randomly oriented in space so that pumping rate $\mu \cdot \epsilon$ will have a wide range of values. Fortunately, in a true weak-response experiment, this nonuniformity would af-

fect only the total yield, not the selectivity. In fact, calculations have been published which use quite sophisticated model Hamiltonians, and enhancement or suppression of excitation by phase-shifting two lasers has been demonstrated (15, 16).

However, complexities abound, particularly for polyatomic molecules, which are expected to have many potentially different interfering pathways. In addition, if the "product" is molecular dissociation, in principle all of the molecules will ultimately be converted, but the rate might be expected to be quite low ("no field, no yield"). A continuous laser will only affect a small portion of the thermal distribution of initial states, even at very low temperature (at 1 K, the thermal energy $kT \approx 20$ GHz, far larger than the bandwidth of even a transform-limited nanosecond pulse). At higher temperatures, inhomogeneous effects further reduce the resonant population. It then becomes necessary to rely on collisional processes to refill the resonant "hole" burned by the lasers; but too high a collision rate would surely change the reaction dynamics as well. Second, as pointed out in the introduction, there are other applications for controlling quantum phenomena besides bond breaking, and some do not fit the simple scheme suggested here.

Strong-response experiments and calculations. The history of failed attempts to control quantum dynamics phenomena amply illustrate the point that laboratory experiments alone usually cannot meet the sought-after objectives. The traditional foundation of experimental design is simply good physical intuition, and in the present context, this also has been the route of previous laboratory efforts. The control of quantum phenomena has proven to be singularly not amenable to this traditional approach. The essential process for achieving control within quantum mechanics consists of the active manipulation of constructive and destructive interferences. This point can be made clearer by realizing that there will be generally many, if not an infinite number of, significant paths between the prescribed initial and desired final quantum states. The latter final state may be a coherent superposition of the field-free eigenstates to meet some objectives. It is the delicate destructive and constructive interference of the multiple pathways that will dictate whether successful control is achieved. Except under the simplest of circumstances, the creation of such a delicate interference process will not be amenable to intuition, so experimental explorations without more sophisticated theoretical guidance may well be futile. Similarly, theory acting alone will be sterile, as it is ultimately the laboratory realization of quantum control that is of true interest.

With the overall goal being the active manipulation of quantum dynamics, an ability to operate with higher intensities broadens the capabilities of achieving control. In the higher intensity regime, perturbation theory and its simple phase- or amplitude-control arguments will no longer be valid. In some cases, it is possible to use known analytical solutions for the strong-response limit [typically first demonstrated in nuclear magnetic resonance (NMR)] (17). For example, picosecond adiabatic passage with frequency-swept laser pulses has been shown experimentally to generate clean population inversions, even when many transitions are simultaneously resonant (18), and a variety of phase- and amplitude-modulated shapes have been used both as shaped laser pulses and as shaped NMR pulses. Adiabatic half passage (sweeping to resonance) is capable of shifting bright states away from coupled dark states, thus changing the intramolecular relaxation dynamics (9). In these cases, there is a solid mathematical justification for expecting the waveforms to be robust with respect to experimental complications, and this tremendously increases their practical utility.

More generally, a key recent development has been the introduction of formal control theory concepts (19), within the domain of quantum mechanics (2). Early work along this line goes back approximately a decade (20), but only recently has considerable activity occurred. These developments have, once and for all, put the control of quantum phenomena on a broad, rigorous footing. The problem is now recognized as one of design and manipulation within quantum mechanics, in analogy with many other such similar problems traditionally studied in the engineering disciplines (such as in the design of high-performance aircraft). The subject of control theory in quantum mechanics covers many issues, and at this juncture, only the basic rudiments have been explored. A fundamental point is the topic of controllability (20, 21), which addresses the matter of whether it is, in principle, possible to steer a particular quantum mechanical system from one state to another. Even if such precise control is not achievable, the latitude in specifying many quantum control objectives allows for considerable freedom (that is, we may seek bond dissociation, but do not need to specify the energy of the separating fragments). In this regard, a more practical approach is provided by the tools of optimal control theory (22), which aim to achieve control as best as possible, given competing criteria. Even when the optical fields are weak, there can be competing physical processes, such as accessing undesirable intermediate or final product states.

Optimal control theory within quantum mechanics has a rather generic structure, regardless of the application. The first step is to delineate the physical objectives and any costs or penalties that may arise in competition with the objectives. These objectives and costs may be translated into mathematical expressions to construct an overall objective functional

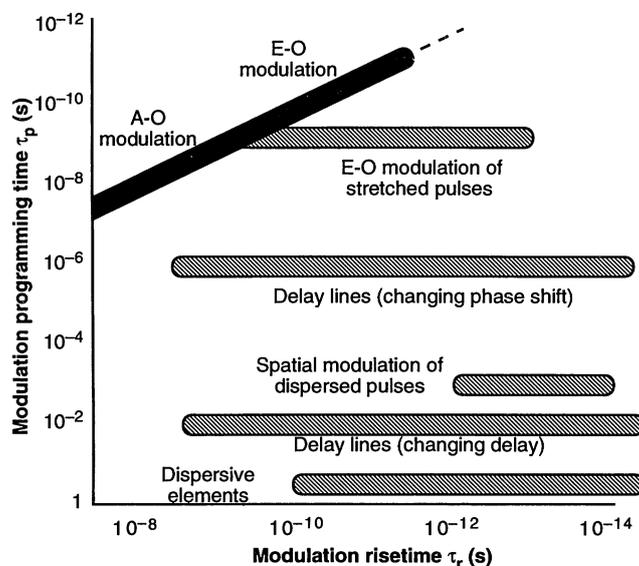
$$J = J_o + J_c \quad (1)$$

where J_o contains the objectives and J_c contains any relevant competing costs. For example, a possible objective might be to maximize the expectation value $\langle \psi(T) | O | \psi(T) \rangle$ of an observable operator O (such as a bond length) at target time T . Simultaneously, it may be important to minimize the expectation value of another operator O' (such as another bond length) over the entire control interval $0 < t \leq T$. Competition can arise here, as the objective and cost may be inconsistent to some degree. In addition, a typical further cost is the criteria of achieving the desired results at minimal work performed by the optical field (that is, minimal field intensity). As the quantum system becomes more complex, the number of objectives, and especially competing costs, will generally rise. The physical mechanism of striking, hopefully, a favorable balance in this competition exists in the ability to manipulate quantum interferences. The task of theory reduces to finding an optimal optical field $\epsilon(t)$, considered as electric here, that creates the necessary interferences.

Optimal control theory provides a precise set of mathematical tools for translating the above problem to one amenable to numerical implementation. By construction, the cost functional satisfies the property $J \geq 0$, and the field design process consists of the minimization of J with respect to the unknown control field $\epsilon(t)$, subject to the overall constraint that Schrödinger's equation be satisfied. The ensuing variational problem can be approached with a number of techniques familiar in the field of optimization. A complete theory would also need to consider not only how the field manipulates the quantum system but also how the quantum system alters the field (considered as classical here). Naturally, to achieve control field design, it is necessary to solve Schrödinger's equation, and in addition, further equations and relations need to be dealt with (3). As a result, a serious although not insurmountable computational task arises as recent illustrations have shown.

A variety of model problems have been explored (2, 3, 6) that span objectives involving the control of rotational (23), vibrational (24), and electronic degrees of freedom (25), with manipulation of chem-

Fig. 1. Characterization of a variety of different techniques for active laser pulse control, in terms of the fastest achievable risetime (τ_r) and the speed at which the waveform can be changed or reprogrammed (τ_p). The solid bar represents direct modulation techniques [electro-optic (E-O) and acousto-optic (A-O) modulation], that have $\tau_p \approx \tau_r$. Indirect techniques are capable of quite fast risetimes but they often cannot be updated quickly. Both τ_p and τ_r are important parameters for combining optimal control with experimental measurements to produce useful laser pulses, as discussed in the text.



ical reactivity being an objective in some cases. The detailed particulars of each case are not so much of concern here, but rather some general points of understanding. First, a natural trade-off exists between the allowed control time interval T and the optical field intensity; lower intensities call for longer control intervals to achieve comparable quality of the physical objectives (22). Second, in keeping with the fact that typical quantum systems are capable of quite complex dynamical behavior, the control fields that yield high-quality results will reflect this fact by matching this complexity in order to work cooperatively with the dynamical capabilities of the system. Control field complexity can show up in both the time or frequency domain representations of the field. Although it is understandable that optimally designed fields without constraints on their form may take on a high degree of complexity, this does not imply that viable solutions may also exist of less complexity. In this regard, various computations have introduced spectral (8, 26) or other types of constraining relations on the structure of the field and still have yielded acceptable control results.

The latter observation brings into question whether, in general, there are multiple solutions to the problem of achieving optimal control within quantum mechanics. It has been shown, under rather mild assumptions, that there can arise a denumerably infinite number of solutions to such problems (27). Although many of these solutions may produce poor quality results, on the other hand, many may also be quite adequate. The existence of multiple solutions is due to the inherently nonlinear nature of the problem of controlling quantum dynamical processes. It is a curious fact that quantum mechanics, traditionally a

mathematically linear problem for a prescribed Hamiltonian, becomes a highly nonlinear problem when its control is the issue being addressed. The prospect of choosing among multiple solutions is certainly physically attractive from the ultimate laboratory perspective, but can cause numerical difficulties in searching for the designs on the computer. Computational limitations have restricted the design efforts to problems that are tractable by quantum wave packet propagation techniques. In practice, this approach is presently at the level of di- and triatomic molecules, using high-accuracy methods. This capability will surely evolve, and the introduction of acceptable approximate solutions could greatly extend the range of systems amenable to design.

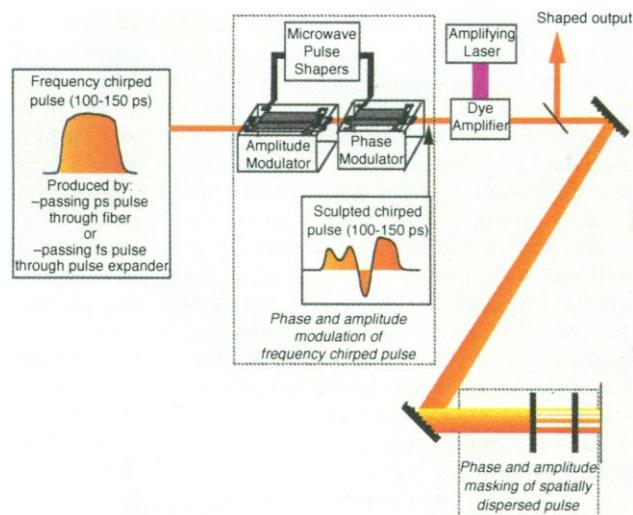
Regardless of the physical objective, the result of the theoretical effort will be an optical field template $\epsilon(t)$ to be taken into the laboratory for creation and application to the physical system. A central issue is the stability or robustness of such designs to inherent uncertainties in the molecular Hamiltonian as well as errors in the creation of the field in the laboratory. Experience has already shown that, without explicitly requesting robustness, the designs will often be highly sensitive to uncertainties and errors. This conclusion is not surprising, as the control mechanism is one of delicate manipulation of quantum interferences. However, the problem is not without recourse; as pointed out, there will typically be many possible solutions, and this flexibility allows for incorporation of robustness as an additional cost into the design process. Computations have already shown that such an incorporation can make a significant difference in assuring the robustness of the control field designs (28).

Laboratory Developments: What Is Possible Now?

With hindsight, it can be shown that all of the early attempts at laser control of chemical reactions would fail. The parameters that we now know are important for such applications—careful pulse shaping, interpulse phase shifts, or phase shifts between two collinear continuous lasers—were initially not very controllable. Early lasers generally gave pulses with residual phase and frequency modulation. In addition, the shape and amplitude were not perfectly reproducible from shot to shot. Multiple pulse sequences were usually created with optical delay lines. Thus, for a number of years the important spectroscopic applications of laser pulse sequences were essentially “pump and dump” experiments (where only population transfer counted) and echoes or four-wave mixing experiments, which can use “incoherent pulses” (29).

Technological developments over the last decade to enhance control over radiation fields have been dramatic and have certainly spurred the current interest in this field by theoretical groups. Various research groups have demonstrated simple pulse sequences with small-flip-angle femtosecond pulses and arbitrary phase shifts (13), arbitrary phase shifts and $\pi/2$ or π pulses of 1- to 100-ps duration (10–12), and complex sequences with phase and frequency shifts on a timescale of tens of nanoseconds (30). Laser pulse shape control with subpicosecond resolution has been demonstrated by several different methods. Specific shaped pulses or sequences of pulses with well-defined phase shifts have been used in optical communications applications to generate solitons (31) or to provide very high bit-rate information transmission. In spectroscopic applications, such pulses have been used to increase the signal generated

Fig. 2. Two examples of indirect laser pulse shape control to generate subpicosecond resolution are shown here. If the laser pulses are temporally dispersed (“chirped”), then very fast electro-optic modulators can alter their phase and amplitude. If they are spatially dispersed, masks or programmable liquid crystal modulators can alter their frequency content.



by impulsive stimulated Raman scattering, generate population inversions, modulate harmonic generation (10), modulate dissociation or fluorescence (10, 12, 13), monitor wave packet evolution (13), or force narrowband excitation with broadband pulses (32).

In this section, we summarize the capabilities for active laser control which exist at present, which are certainly formidable, and try to extrapolate these capabilities. Of course, not every conceivable waveform can actually be made in the laboratory, even in principle. For example, waveforms with spatial as well as frequency modulation have to be carefully checked for consistency with Maxwell's equations. Even if a waveform does not violate any physical laws, the required modulation might still be impractically severe. For simplicity, we will restrict ourselves here to temporal modulation (assuming a single propagation direction \hat{z} and a single polarization direction \hat{x} for a plane wave) and a nondispersive, optically thin medium. In this case we can write a general waveform as:

$$\epsilon_x(t) = \text{Re} \sum_i A_i(t) \exp [i\omega_i(t)t + \phi_i(t)] \quad (2)$$

which explicitly includes amplitude modulation [$A_i(t)$], frequency modulation [$\omega_i(t)$], and phase modulation [$\phi_i(t)$].

The modulation functions in Eq. 2 are not unique; for example, frequency modulation and phase modulation are closely related, and any waveform can be written using only one of the two. However, experimentally these modulations are produced with different technologies, and some combinations of frequency and phase modulation are only feasible today by combining two approaches. Probably the most important role theory can play (from an experimentalist's perspective) is to prescribe experimentally accessible forms for A_i , ω_i , and

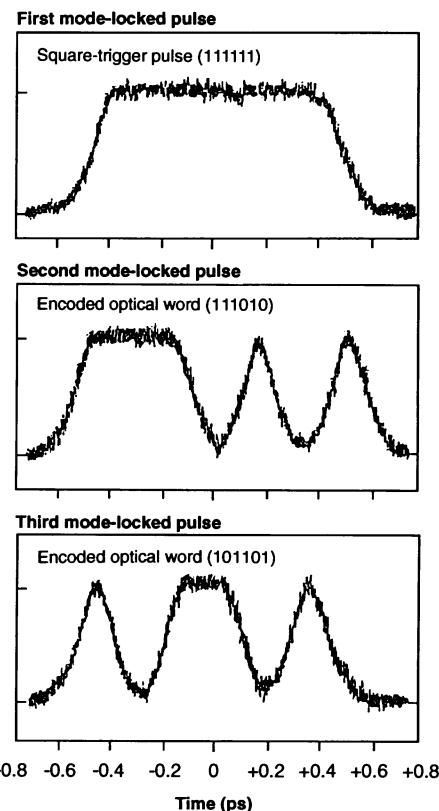


Fig. 3. An example of state-of-the-art pulse-shape programmability. These are consecutive shaped laser pulses out of a mode-locked laser system. The waveform generation, which requires both phase and amplitude modulation, is done in the 10 to 15 ns delay between pulses (data courtesy of M. Haner).

ϕ_i that will achieve quantum control—or at least to provide forms which, if they are not feasible today, can serve as a useful technological objective.

There are two different time scales to consider for any modulation scheme—the fastest modulation risetime that can be generated (which we will call τ_r), and the speed with which the device could be programmed to change the modulation function (which we will call τ_p). Both τ_r and τ_p are important parameters. Most of the phenomena considered for quantum control involve vibrational, electronic, or reactive processes and require $\tau_r \approx 10$ ps or shorter. Small values of τ_p are important to correct for instrumental variations (such as amplitude jitter) or to empirically optimize waveforms in the laboratory.

The difference between τ_p and τ_r helps us divide modulation techniques into two different categories (Fig. 1). Direct modulation techniques act essentially in real time, giving $\tau_r \approx \tau_p$; in effect, a low-frequency electromagnetic waveform (a voltage pulse) becomes one of the modulation functions $A_i(t)$ or $\phi_i(t)$ in Eq. 2. Indirect modulation techniques create tem-

poral modulation by a subterfuge. For example, it is possible to spatially disperse the different frequency components of the light with gratings, insert a mask to alter the pulse spectrum, and then finally recombine the spatially separated components into a temporally modulated pulse. Generally $\tau_r \ll \tau_p$ for indirect techniques; very slow devices can modulate with femtosecond resolution.

Direct modulation techniques. Direct modulation with $\tau_r \approx 1$ to 10 ns had been extensively demonstrated by the mid-1980s. Amplitude and frequency control and interpulse phase shifts were achieved with acousto-optic modulators (30); phase control was also possible with bulk electro-optic modulators (33). Traveling wave electro-optic devices at present can produce amplitude modulation or phase modulation on a picosecond time scale. For example, lithium niobate modulators with waveguides fabricated by titanium indiffusion or proton exchange are commercially available for infrared (IR) applications with bandwidths up to ~ 10 GHz. Modulators in research laboratories are commonly fabricated with 3-dB bandwidths up to ~ 20 GHz but fairly large half-wave voltages (≈ 20 V) (34); a titanium-indiffused Ba-TiO₃ modulator has been made with 20-GHz bandwidth and a half-wave voltage of 3 V, plus much higher damage thresholds in the visible (> 1 mW in 5- μ m waveguides at 600 nm) (35). With these modest power requirements, shaped microwave pulses can be built with GaAs-based field-effect transistor (FET) circuitry; the FETs can have switching times as short as a few picoseconds and can be updated in a few nanoseconds (36).

Direct modulation techniques will surely improve, but there are several formidable barriers to ever-increasing speed. Electro-optic devices have a fundamental trade-off between half-wave voltage and bandwidth, which comes from several different effects. For any specified material with fixed nonlinear coefficients, the half-wave voltage is reduced by increasing the interaction length l , but increasing l also decreases the bandwidth of the microwave electrodes. In addition, there is generally a difference in the velocities of propagation of microwave and optical pulses. This gives a minimum rise time of $\tau_r = \Delta n (l/c)$, where $\Delta n = \sqrt{\epsilon_{\text{eff}}} - n$, ϵ_{eff} is the microwave dielectric constant, n is the optical index of refraction, and c is the speed of light. For a Mach-Zehnder interferometer in LiNbO₃, $\nu_{\text{max}} \approx (1/2\pi)\tau_r \approx (9.6 \text{ GHz cm})/l$, with comparable values for other inorganic ionic crystals (36). Matching the microwave and optical bandwidths is possible to some extent by overcoating with thick ($\sim 1 \mu\text{m}$) buffer layers of SiO₂ or by putting the

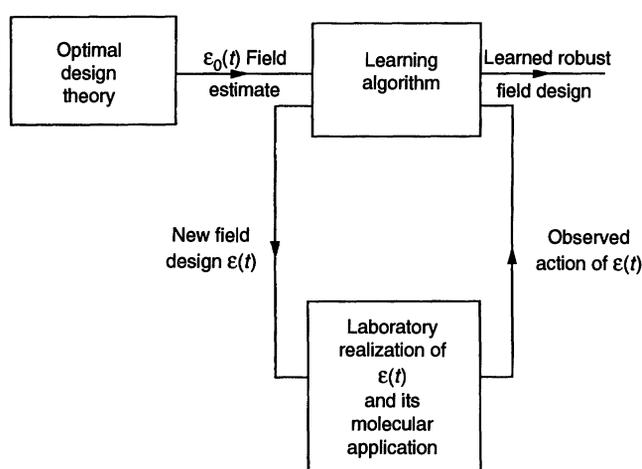


Fig. 4. A schematic of an adaptive-learning algorithm approach for teaching lasers to control molecules. The algorithm is initiated by an optimal control estimate $\epsilon_0(t)$ of the control field, followed by its laboratory refinement in a computer-controlled sequence of experiments coupled to a pattern-recognizing learning algorithm.

electrodes inside a "sandwich" of the nonlinear optical material. This approach has been exploited most dramatically in the development of a 100-GHz GaAs traveling wave modulator (rise time of 3 ps) (37); however, the half-wave voltage of this device is estimated to be 288 V.

Polymer materials have a potential advantage in these applications because the typical $\sqrt{\epsilon} \approx 1.7$ to 1.9 is close to n , so $\nu_{\text{max}} \approx (150 \text{ GHz})/l$; in addition, the nonlinear coefficients can be larger than in conventional materials. An electro-optic polymer Mach-Zehnder modulator with 9-V half-wave voltage, extinction ratio of 10 dB, flat response to 200 MHz, and measurable modulation up to 20 GHz has been developed (38); dc electro-optic polarization rotation has also been verified in diazo-substituted polymers (39).

However, even if significantly higher bandwidths become possible in the next few years, these bandwidths will be difficult to exploit. Microwave technology has benefited from more than half a century of concentrated development; nonetheless, it is far from trivial to generate, amplify, or propagate waveforms that have (for example) frequency components from dc to 100 GHz. Such waveforms ultimately require a transition to waveguide or quasi-optical components.

Indirect modulation techniques. Indirect modulation techniques have also been in use for decades. On a nanosecond time scale, crossing a laser with a molecular beam (40) or Stark-shifting molecules in and out of resonance (41) can alter the effects of a continuous wave (cw) laser as if the pulse shape were altered. In addition, dispersive or nonlinear elements are capable of imposing different kinds of frequency modulation. A pair of gratings can convert a transform-limited femtosecond pulse into a clean, nearly linear frequency sweep; factors of 1000 in pulse stretching, and then subsequent recompression by two gratings

with an effective "negative separation" created by lenses, have been demonstrated (42). An optical fiber, or any other material with a nonlinear index of refraction, also creates frequency sweeps and increases the bandwidth of the pulse. The combination of these techniques, plus other elements to compensate for residual deviations from a linear sweep, were used to create the shortest laser pulses reported to date (6-fs duration) (43). In addition, a high-power pulse can be focused in many media to produce broadband "continuum pulses" with a very large bandwidth but, as we discuss below, it is difficult to do much with such pulses unless they are filtered to restrict the bandwidth.

The output pulse shape of a typical picosecond or femtosecond dye laser system changes enormously if a single optical element is moved; system alignment is done by positioning components for minimum width. If we ignore this type of "empirical pulse shaping," there are only a few demonstrated methods for modulating on a subpicosecond time scale, and all of them are indirect (since no electronic devices can presently generate such rapid modulation). The methods for shaping femtosecond pulses all rely on temporal or spatial dispersion of ultrafast pulses in devices such as grating pairs and optical fibers.

Figure 2 shows a generic apparatus for generating arbitrarily shaped laser pulses and illustrates two different technologies. One approach circumvents the speed limitations of existing modulators by modulating chirped pulses. The time-domain approach uses programmable microwave pulse shapers and traveling wave electro-optic modulators. For example, passing a pulse for a particular output is quite simple because the remaining optical components after the modulator are linear.

An example of the types of waveforms that can be produced by the time-domain approach alone is shown in Fig. 3. The interval between consecutive pulses in the

mode-locked laser system was sufficient to update the waveform generator driving the electro-optic modulator, which permitted generation of completely different shaped pulses.

The frequency-domain approach (47) uses spatial dispersion inside the grating pair (as shown in the lower right corner of Fig. 2) instead of temporal dispersion after the fiber. Initial experiments used amplitude masks that were fabricated by microlithography and induced phase shifts at different frequencies (positions) by inserting optical delays. Recently, it has also been demonstrated that at least the phase shifts can be made programmable (48) by using multielement liquid crystal modulators. Holographic techniques can also be used to create gratings (49).

The different approaches to femtosecond pulse shaping have demonstrated comparable time resolution and peak powers, but they have different strengths and weaknesses. For example, the pulses shown in Fig. 3 could not have been produced by the frequency-domain approach; the programmable masks are many orders of magnitude too slow. On the other hand, a pulse or pulse sequence that is symmetric and amplitude modulated has a purely real Fourier transform, which can be fabricated as an amplitude mask. In addition, spatially periodic phase modulation can efficiently generate a sequence of equally spaced pulses, and this method has recently been used in impulsive stimulated Raman scattering experiments that do not require well-defined phases or transform-limited bandwidths for the individual pulses (14).

An optical delay line is also an amplitude modulator—it creates time-shifted replica pulses of an initial waveform, with no intrinsic risetime limitation. However, it is not trivial to have the delay line produce pulses with known phases. For example, in the simplest case (pure amplitude modulation), all of the pulses have a single carrier wave frequency [$\omega_i(t) \equiv \omega$] and the phase is constant during each pulse [$\phi_i(t) \equiv \phi_i$]. Measuring the delay is easy; for example, a 1-ns delay corresponds to 30 cm in air. However, such a delay corresponds to $\sim 500,000$ cycles of visible light, and the relative phase goes through 2π radians on each cycle. Thus, unless both the length of the delay and the carrier frequency of the laser pulses are stable and known to extremely high precision, the relative phases will be unknown. This problem has been solved in two different ways. It is possible to injection-lock a laser amplifier with a weak cw laser beam, thus creating amplified pulses with exactly the same carrier frequency; in this case, fringes can be monitored to determine the exact phase (12). A more general technique splits off a small portion

of the pulse train and passes the pulses through a monochromator, which selects only a small range of frequencies, hence broadening the pulses until they overlap; then constructive and destructive interference can again be used to determine the phase relation over the bandwidth of the monochromator (13).

Development of additional indirect methods to increase the range of available modulations is desirable, and is likely over the next few years.

Center wavelength and peak power requirements. The techniques described in the last two sections can be combined to create an extraordinarily wide variety of waveforms. However, while the amplitude, phase, or frequency modulation is important for most applications, so is the center wavelength, and this imposes additional constraints. Frequency conversion techniques have been used to produce light from the x-ray region to the far-IR, but the most impressive demonstrations of pulse-shaping capabilities to date have used near-IR or red lasers, in large part because the best programmable modulators operate at those wavelengths. Unfortunately, most molecules do not absorb light in this region.

Sum frequency and harmonic generation can be used to produce waveforms in the ultraviolet, and difference frequency generation can be used to produce vibrationally active IR pulses. These processes can be quite efficient with high-power pulsed laser systems. The development of solid-state tunable laser systems during the last decade has significantly improved the accessible wavelength range, and further progress seems quite likely.

However, adding frequency conversion pushes the devices at the control of the experimentalist (the modulators) one step further back and further complicates the process of generating controlled shapes. Nonlinear processes dramatically change the pulse shape; these changes can be corrected to a limited extent by predistorting the laser pulses, but fluctuations (for example, pulse-amplitude jitter) are also magnified. In addition, maintaining the phase-matching conditions required for efficient frequency conversion becomes quite difficult if the fractional bandwidth of either the input or output pulses is large.

In weak-response applications, it is possible to accept extremely low peak powers at the cost of very low yield. Strong-response applications require sufficient intensity to perturb populations, which means that amplification is usually required. Amplification requires a gain medium with sufficient bandwidth to cover the entire pulse spectrum (usually a dye or materials such as titanium-doped sapphire). In general, one must amplify in the visible or near-IR

and then accept a rather large loss in arranging frequency conversion to produce a reproducible and controlled pulse shape.

Thus, in general, laser pulses with large fractional bandwidths ($>20\%$) cannot be amplified, and details such as the shape of the envelope are extremely difficult to control. Loosening these constraints requires the development of still-broader gain media (or combinations of media) and improved nonlinear crystals.

Discussion and Extrapolation: What Is Realistic Soon?

All of the above work may be summarized by stating that many of the basic concepts of control over quantum phenomena are now established, both theoretically and experimentally. It is certain that applications will continue to increase and that implementation of a wide variety of exciting applications is possible in principle.

The most important stumbling blocks in taking promising proposed active control schemes from concept to the laboratory are:

1) A lack of precise knowledge about the molecular Hamiltonian, including its optical coupling coefficients.

2) The assurance of robustness to laboratory field errors.

3) The ability to accurately execute the numerical problem posed by the design process.

Although these problems are not impossible to surmount, there are certainly severe limitations.

With this as background, a recent suggestion has been put forth to judiciously combine the best capabilities of current theoretical design, with the emerging capabilities of the ultrafast laboratory optical pulse shaping techniques summarized above (50). This combined effort has been referred to as "teaching lasers to control molecules," and the logic involved proceeds as follows. First, although the designers may not know the Hamiltonian precisely, the target molecule, of course, has full knowledge of the Hamiltonian. Second, the molecular sample is fully capable of "solving" its equations of motion in real time, upon exposure to an external control field. Thus, it has been suggested to use the actual molecular sample effectively as an analog computer to surmount the hitherto complex problems arising in the theoretical design effort.

This suggestion appears feasible, given the rapidly evolving state-of-the-art of computer-driven optical pulse shaping techniques, where duty cycles as high as a 10^3 , or even $\sim 10^6$, distinct pulse shapes per second can be envisioned. Second, many of the quantum control objectives can be characterized in terms of steering the system

out of one channel (that is, state) versus another. Such a distinction may often be easily detected in the laboratory by a follow-on rapid probe pulse, without further time-consuming, sophisticated analysis of the results. This latter point is important, as the suggested paradigm combines all of the above statements through a slaved pattern recognition learning algorithm to guide the overall process (Fig. 4). On a computer, the molecular state after a single application of a specific pulse shape is completely known. In the laboratory, inhomogeneities, noise, and practical restrictions on observables reduce the rate at which molecular information can be obtained. The best available theoretical techniques would be used to create the initial design, and its refinement by an overwhelming number of computer-driven experiments would then take over in the laboratory.

This approach is of course intrinsically restricted to pulse shapes that can be generated in the laboratory, and here the distinction between programmability and modulation bandwidth becomes quite important. For example, one might consider a "layered approach" to pulse shaping as shown in Fig. 3, which uses rapidly programmable elements, such as electro-optic modulators, to update the coarse structure of ultrafast waveforms at megahertz rates and uses slower control elements, such as the spatial multielement modulators, to refine the pulse shape.

In essence, this feedback quantum control process may be viewed as reverting to old Edisonian methods, recast in terms of ultrafast computer-controlled optical pulse shaping combined with efficient pattern-recognition learning algorithms. As target molecules become more complex, the initial control field estimate provided by the theoretical input will become much more important, just as it is in purely computational optimization. As noted above, there can be a denumerably infinite number of local minima; in this case, finding the global minimum, or at least a good local minimum, is not at all trivial. Nevertheless, in simple cases, it has already been shown through simulations that the algorithm may be self-starting and still achieve the sought-after objectives, even with random input and no prior knowledge of the system Hamiltonian (50). The approach is also inherently robust, as it is based on utilizing the actual molecular sample with the real laboratory fields. The balance between reliance on design alone versus laboratory experiments alone is flexible, and may swing between the two extremes, as dictated by the particular case. In this regard, the optimization process occurring in the laboratory closed loop of Fig. 4 has the same general character as the optimal design the-

ory occurring in the input box, except the nature of the cost functional may be different. A variant of the adaptive feedback loop of Fig. 4 could be envisioned as a means for seeking an inversion of the laboratory data to yield Hamiltonian information rather than final quantum state control.

Conclusions

In summary, the key advance on the experimental side in recent years has been the development of technologies for active laser control (pulse shaping and phase shifting); the key advance on the theoretical side in recent years has been the recognition that control of quantum phenomena is essentially a design effort at the molecular scale calling for the manipulation of quantum interferences. Much of the control logic developed in traditional macroworld engineering disciplines for analogous problems can be carried over into this new micro-world domain. In addition, quantum control offers new challenges to the traditional control community. Most promising is a combined flexible balance between theoretical design and laboratory implementation, in a cyclic process.

The control of quantum phenomena remains an important challenge to the experimental and theoretical physics and chemistry communities. The ultimate fundamental and practical implications of successful control in quantum mechanics will not become entirely clear until the flexibility to achieve active manipulation is in hand. The subject will surely evolve rapidly in the coming years, and the key advances in the laboratory and theoretical tools addressed in this article have brought the subject to a pivotal threshold. These tools separately are not without limitations, and the real hope for success resides in their combination. The dream is indeed alive.

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