

Paradigms and Algorithms for Controlling Molecular Motion

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Introduction

Physical chemistry on the microscopic scale has traditionally been associated with a passive description of dynamical processes. For many years, interest has been expressed in the possibilities for control of molecular motion. A resurgence of activity in this area is being stimulated both by the dramatic improvement in the theoretical tools for describing few-body processes and, most importantly, by improvements in laser technology. The development of coherent pulses on short time scales of less than ~ 50 fs opens up new prospects for control. For a soft molecular vibration frequency of ~ 500 cm^{-1} , the associated period is ~ 300 fs and intuitively it is clear that narrow laser pulses may be used to possibly "guide" a molecule to a given state. Equally important is the development of programmable laser pulses, where, within experimental limitations, the operator imposes a desired structure with fine temporal or frequency features rather than creating a single narrow pulse.¹⁻⁴ These experimental developments have led theoreticians to suggest specific schemes for utilizing lasers for actual control of molecular motion, as described below.

Brumer and Shapiro developed a scheme in which two alternate routes, each involving few photon transitions, bring the system to a mixture of two degenerate final quantum states.⁵ Appropriate timing or phase control of the two pulses generates the coherence between the final states to produce the required mixture. The logic involved is analogous to control of the interference pattern generated by dual pathways, as in a "double slit" experiment. In a different approach, Tannor and Rice emphasized a molecular wave packet picture in which the operator "follows" the wave packet of the system and, by a series of appropriately timed transitions, guides it from one electronic state to another.⁶ A different paradigm was developed by Nelson and his co-workers, who use trains of pulses to impulsively "kick" the system.²

In addition to these particular schemes, a general optimal control approach has been recently developed, in which the laser field structure is systematically tailored to the desired objective and the available

experimental equipment.⁷ This formalism is not a scheme *per se*, since it may be applied within any given molecular situation. Application of the formalism produces schemes which are optimal for the physical problem and its imposed constraints.

In this account, we briefly review the paradigms of Brumer and Shapiro and of Tannor and Rice. The next section describes the mathematical machinery of the more general optimal control procedure and is followed by a brief review of the applications of molecular optimal control theory to various systems: control of rotational, vibrational, and electronic motion in diatoms; product selectivity in photodissociation of collinear three-body systems; and control of molecular motion in the liquid phase. Finally, a discussion is presented on the inherent difficulties and limitations of coherent field design, followed by a suggestion that takes advantage of the best capabilities of theory and experiment, through an adaptive learning algorithm, to literally teach lasers how to control molecules.

Control of Molecular Motion: Simple Paradigms

The different paradigms and approaches to control of molecular systems will be developed with reference to a very simple system of dissociation (Figure 1), where the molecule initially lies on the ground state of a bound electronic surface (X) and the eventual goal is to bring the system into one of two asymptotes of a dissociative upper surface (A). Other variations of these schemes exist, but these serve to illustrate the basic ideas involved.

In a typical application of the coherent-state approach of Brumer and Shapiro,⁵ the system is partially excited from the ground state to a rovibrationally excited bound-state Ψ on surface X, such that a coherent nonstationary wave packet results:

$$\Psi = a_0 e^{-iE_0 t} \Psi_0(r) + a_1 e^{-iE_1 t} \Psi_1(r)$$

A second pulse then excites the system further, at time t_2 , to the dissociative surface A. By varying the pulse times, different wave packets result, concentrated on

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Herschel Rabitz received his Ph.D. in chemical physics from Harvard University in 1971 and has subsequently been a faculty member in the Department of Chemistry at Princeton University. His research interests lie in the general area of chemical dynamics, especially involving the introduction of systems analysis tools. These latter tools are the basis for his work in the topic of controlling molecular motion.

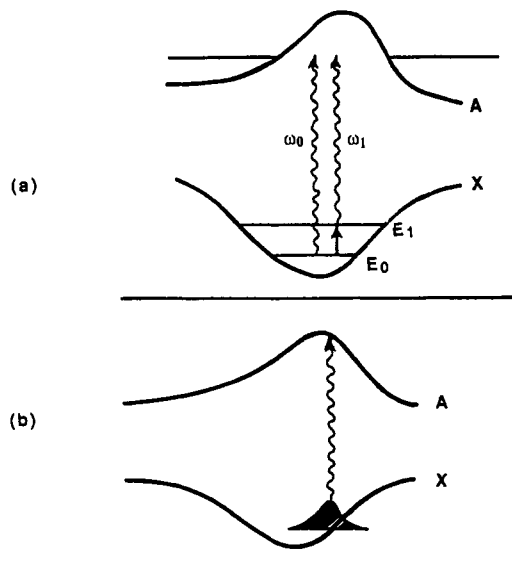


Figure 1. (a) Schematic of the Brumer-Shapiro control paradigm for a model one-dimensional system; appropriate mixing of two pulses generates a quantum state localized to the left (or the right) of a barrier on the upper surface. (b) Schematic of the Tannor-Rice paradigm; two short pulses are used, first to excite an oscillatory wave packet on the ground electronic state surface X, and then, the second pulse excites the wave packet to the desired part of surface A.

the left or right side of the barrier (Figure 1a), i.e., control is exerted on the relative yield. This can be quantitatively described as follows. The final pulse has frequencies ω_0 and $\omega_1 = \omega_0 - (E_1 - E_0)$ and brings the system to a particular mixture of two continuum states (ζ_L , ζ_R) concentrated on the two sides (left L and right R) of the barrier

$$\Psi_0 \rightarrow b_{0L}\zeta_L(E) + b_{0R}\zeta_R(E)$$

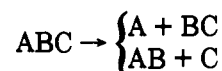
$$\Psi_1 \rightarrow b_{1L}\zeta_L(E) + b_{1R}\zeta_R(E)$$

and by adjusting the relative intensities and phases of the two pulses, it is possible to create states concentrated mainly, or entirely, in ζ_L (or ζ_R), thus gaining control.

Tannor and Rice introduced another approach,⁶ in which the laser fields are pulses "designed" by inspection to move the system wave packet between the two surfaces. A simple example is shown in Figure 1b. A vibrational wave packet is excited on the lower surface by one pulse, and a second pulse excites the wave packet upward to the dissociative electronic surface. Selectivity from a two-pulse scheme may not be sufficient to yield complete control of the system, and thus a series of pulses may be necessary to specifically "move" the wave packet up and down between the two electronic potentials. The choice of appropriate pulse times and phases clearly needs to be automated; indeed, optimal control theory supplies exactly such an algorithm, as will be explained in the next section. However, we need to comment on the necessity to proceed beyond the simple coherent-state approach for complicated triatomics or heavier few-body molecular systems.

The approach of Brumer and Shapiro is attractive for simple systems, such as the one-dimensional example in Figure 1, or for curve-crossing diatomics.⁵ In general, this approach should perform well for any system where, by a series of optical transitions, it is possible to isolate

a small number of required final quantum states. For example, in dissociation of a model collinear triatomic



the dissociated wave function is described outside the reaction region by a sum over vibrational states

$$|\Psi(E)\rangle \approx \sum_{\nu} a_{\nu} \phi_{\nu}(r) \exp[ik_{\nu}R] + \sum_{\nu'} a_{\nu'} \phi_{\nu'}(r') \exp[ik_{\nu'}R']$$

where r and R are Jacobi coordinates corresponding to the AB and C-AB distances and r' and R' are the corresponding values for the BC and A-BC separations. The most favorable situation for coherent-state control arises when the optical coupling is sufficiently large for both pathways to produce significant yields at low dissociation energies E , at which only few vibrational channels are open. Then, by including multiple pulses and adjusting the phase and timing of the dissociation-inducing pulses, it is possible to specifically select the channel to which dissociation occurs.

The utilization of this approach is not guaranteed, however, for systems exhibiting IVR such that short optical excitation couples to many quantum states. Even in systems with resolvable lines, such that the various states are individually accessible (e.g., in the 100-ns time scale regime where optical line coherence can typically be maintained), the dipole transitions to the few desired final states must be strong. Thus, for control of dissociation into various products, the transition to the states that are close to the dissociation thresholds must be very strong, which is not a common case for a polyatomic system.

A different application is control of dynamics in liquids, where it is desirable to have an automated procedure that determines multiphoton transitions in the presence of rapid collisions destroying phase coherence. In a study based on the Bloch equation, it was found that, with designed pulses, selectivity remains even if the pulse width T is equal to (or moderately longer than) T_2 , the time between consecutive collisions.⁹ Specifically, selectivity remains for $T_2/T \gtrsim 1$. It was found that when $T_2 \ll T_1$, where T_1 is the energy exchange time (i.e., for collisions in a molecular beam seeded with rare gases), the approach based on a simple paradigm related to Figure 1a gave poor results,⁹ while an optimal design approach was far superior.⁸ Thus, it is clear that the need arises for a procedure that predicts field structures incorporating any necessary multiphoton processes, as well as external disturbances. Such a procedure, where field structuring is done systematically, is described below. Nevertheless, the essential feature of all coherent molecular control is the manipulation of interfering pathways, as exemplified by the two-pathway paradigm in Figure 1.

The Optimal Control Algorithm

The optimal control algorithm is an iterative procedure where the predicted field is repeatedly corrected for improved overall yield. The procedure will be developed in stages below, with reference to the simple dissociation example in Figure 1 (even though the full

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power of the optimal control procedure is truly evident only for more complex systems).

The first stage in optimal control theory is the representation of the "maximum yield" requirement in mathematical terms as minimization of an objective J_0 , which is taken here as the integrated yield beyond a large distance on one side of the barrier (here the right side is taken):

$$J_0 = 1 - \int_{r>r_1} |\Psi_A(r, \tau)|^2 dr$$

where τ , the final time, is any large time when the full dissociation is complete. Once τ is sufficiently large, the field profile does not depend on it; r_1 is a long distance extending into the asymptotic region.

Next are introduced constraints on the field, that are loosely divided into two overlapping types: physical and paradigm-related. The physical constraints take into account the relative difficulty associated with creating the laser field. For example, the total fluence is often sought to be as small as possible; to effect this, we add a cost term

$$J_{\text{cost}} = \beta \int_0^\tau \epsilon^2(t) dt$$

to the objective, such that the total objective to be minimized is

$$J = 1 - \int_{r>r_1} |\Psi_A(r, \tau)|^2 dr + \beta \int_0^\tau \epsilon^2(t) dt$$

The value of the weight factor $\beta > 0$ is determined by the experimental conditions; β should be large if high intensities are difficult to obtain and one is willing to forego some of the selectivity in exchange for lower intensity. Other penalties are similarly incorporated by adding appropriate physically motivated cost terms to the objective.

The second class of constraints is related to the specific paradigm chosen for the field. In the most unrestricted case, the field $\epsilon(t)$ would simply be discretized into a fine grid of points [$\epsilon(t=0)$, $\epsilon(\Delta t)$, $\epsilon(2\Delta t)$, ... $\epsilon(\tau)$] to be determined. As another example, a two-pulse Tannor-Rice scheme may have free parameters for the location, width, and carrier frequency of the pulses

$$\epsilon(t) = \sum_{i=1}^2 A_i \exp[-(t-t_i)^2/t_i^2] \cos(\omega_i t - \phi_i)$$

Similar expressions can be written for any other specific field paradigms.⁷

Once the actual field form, the objective, and the cost terms are established, the third and final step in the control procedure is the search for the optimal field (i.e., the field that optimizes the objective in competition with the costs, subject to the paradigm-specific field form). A variety of means may be employed, but a simple search procedure is effected by a linear gradient algorithm. Thus, for the two-pulse field form, the field is improved by iteration

$$A_i \rightarrow A_i + \alpha \frac{\partial J}{\partial A_i}$$

and similarly for the other parameters in the field. Such an iteration becomes very expensive for field forms with many parameters, as separate evaluations of J must be done for the calculation of the derivative of each

parameter. However, this difficulty can be easily circumvented using Lagrange multiplier variables, and the modified procedure is developed as follows (first for unrestricted fields). We note that the objective J depends on $\epsilon(t)$ both directly (due to the fluence cost term) and indirectly due to the dependence of $\Psi(t)$ on $\epsilon(t)$, via the Schrödinger equation

$$i\dot{\Psi} = H_0\Psi + \epsilon\mu\Psi = H\Psi$$

The Schrödinger equation is incorporated explicitly by adding a term with a Lagrange state function $\lambda(t)$ into the objective

$$J \rightarrow 1 - \int_{r>r_1} |\Psi_A(r, \tau)|^2 dr + \beta \int_0^\tau \epsilon(\tau)^2 dt + \int_0^\tau \left[\left\langle \lambda(t) \left| i \frac{d}{dt} - H \right| \Psi(t) \right\rangle + cc \right] dt$$

The minimization of J is now done with respect to $\epsilon(t)$, $\Psi(t)$, and $\lambda(t)$ (i.e., $\Psi(t)$ is no longer considered a functional of $\epsilon(t)$). Minimization with respect to Ψ and λ , respectively, leads to

$$i\dot{\lambda} = H\lambda$$

$$i\dot{\Psi} = H\Psi$$

$$\lambda(r, \tau) = i \begin{cases} 0 & r < r_1 \\ \Psi_A(r, \tau) & r > r_1 \end{cases}$$

The above final condition for $\lambda(r, \tau)$ applies to its A-state component, while for the X-state, we have $\lambda(r, \tau) = 0$. Note especially that the boundary condition on λ is given at the *final* time; thus $\lambda(r, t)$ is propagated backward.

The minimization with respect to $\epsilon(t)$ is still done iteratively, where the gradient is now

$$\frac{\delta J}{\delta \epsilon(t)} = 2\beta\epsilon(t) - 2\text{Re}\langle \lambda(t) | \mu | \Psi(t) \rangle$$

The introduction of λ has allowed for the ready evaluation of $\delta J / \delta \epsilon(t)$ once $\lambda(t)$ and $\Psi(t)$ are known at any level of iteration. The optimal control procedure begins by making an initial trial choice of $\epsilon(t)$ and improving it iteratively. At each iteration stage, the Schrödinger equation for Ψ is solved first, and the final-time wave function $\Psi(r, \tau)$ is used to yield the initial value for $\lambda(r, \tau)$. Then, $\lambda(r, t)$ is propagated backward and is used to yield the gradient of the objective functional with respect to $\epsilon(t)$. The field is modified along the gradient. The resultant procedure is generally computationally efficient, since at every iteration step, only two wave packet propagations are required. Moreover, it is useful *even when a specific paradigm for the field is invoked*; for example, in a Tannor-Rice pulse paradigm, the gradient with respect to the field strengths will be calculated as

$$\frac{\partial J}{\partial A_i} = \int \frac{\delta J}{\delta \epsilon(t)} \frac{\partial \epsilon(t)}{\partial A_i} dt = \int \frac{\delta J}{\delta \epsilon(t)} \exp[-(t-t_i)^2/t_i^2] \cos(\omega_i t - \phi_i) dt$$

with similar equations for the pulse frequency, phase, duration, and width. The procedure of Brumer and Shapiro may also be cast as a special case of optimal

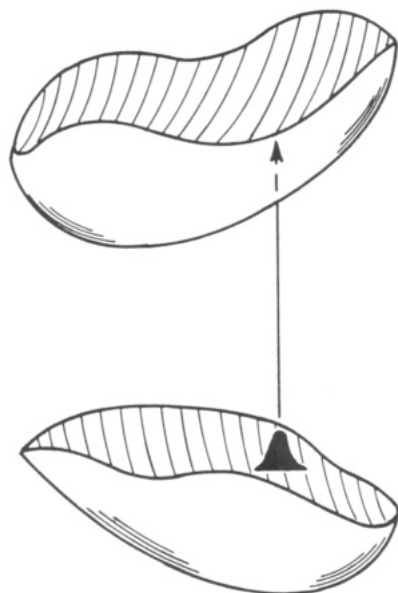


Figure 2. Localization of wave packets in different regions via the control algorithm on a known electronic surface may possibly be used for extracting the potential energy function of an upper electronic surface. The figure schematically indicates the transfer of a localized wave packet on one surface to another. Probing the dynamics of the wave packet can yield information about the potential surfaces.

control theory as it ultimately assesses the product yield in terms of a few constrained field parameters.

Optimal Control Applications

In this section, we briefly review various recent implementations of the optimal control procedure. This procedure has been illustrated for all aspects of molecular motion: rotational alignment,¹⁰ vibrational localization,^{7,11} and electronic selectivity.¹² In both alignment and vibrational localization, the wave packet is required to evolve to a desired form at a particular time τ . The importance of this application is 2-fold. First, effects of rotational alignment in collisions can be studied if the wave packet is made to point in a given direction prior to collisions and before dephasing, or for other reorientation-specific probes. Moreover, by creating a local vibrational wave packet on a given known electronic surface, it may be possible to perform a femtosecond excitation experiment in which the absorption spectrum reveals the position dependence of the potential on an upper curve (see Figure 2; such an experiment would likely rely on the analysis of the temporal signal rather than the bandwidth-limited absorption).¹³ The creation of specific localized wave packets can be valuable for extending femtosecond experiments to determine potentials for multidimensional systems. Vibrational localization was tested both for achieving a special wave packet form⁹ and for general localization of a wave packet. The latter goal was tested

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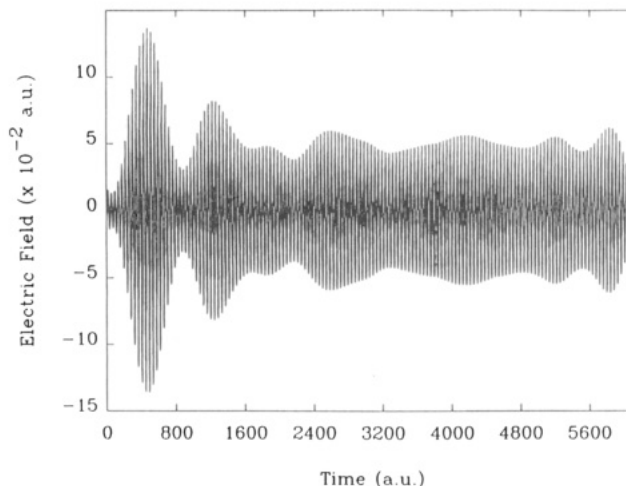


Figure 3. Field for effectively eliminating the adiabatic coupling in a particular case of curve crossing, when the power spectra are restricted to contain only high-frequency components. Here, the field acts between the ground state (1) and the crossing curves (2 and 3) of Figure 4.

on a specific model one-dimensional system where the objective was

$$J_0 = \left(\int |\Psi(r, \tau)|^2 (r - r_0) dr \right)^2 + \int |\Psi(r, \tau)|^2 (r - r_0)^2 dr$$

The first term is responsible for guiding the wave packet to the average position r_0 , and the second term controls how well the wave packet is localized (i.e., its variance). We find that this objective of localization is easily achieved.¹⁵

Another example where optimal control was utilized is selectivity in curve crossing; the example studied was of two dissociation curves, reminiscent of those arising in IBr. The system was studied without including rotations.¹² While full control of purely vibrational motion on two electronic states can be achieved with the Brumer-Shapiro wave packet preparation procedure,⁵ the optimal control study was designed as a precursor to the realistic three-dimensional study of more general motion control (where only simple wave packet preparation can mix in unwanted states and limit selectivity). When the optimal control approach is applied naively to the curve-crossing problem, the procedure predicts, not surprisingly, the need for a dc field of the exactly correct magnitude for elimination (or enhancement) of the effect of the nonadiabatic coupling between the dissociative curves. Since it is not feasible to create very high intensity dc fields, the formalism must be modified to eliminate such fields. The approach is to add a high-pass filter

$$\epsilon(t) = \int_{-\infty}^{\infty} \theta(|\omega| - \omega_1) \epsilon(\omega) e^{i\omega t} dt$$

where ω_1 is a low (IR) frequency above which high intensities can be obtained and $\theta(\omega_1 - |\omega|)$ is a step function, with the effect that the low-frequency components are filtered out. The optimization proceeds exactly as in the unrestricted field case, except that, after every iteration step, the field is filtered again to contain solely high frequencies

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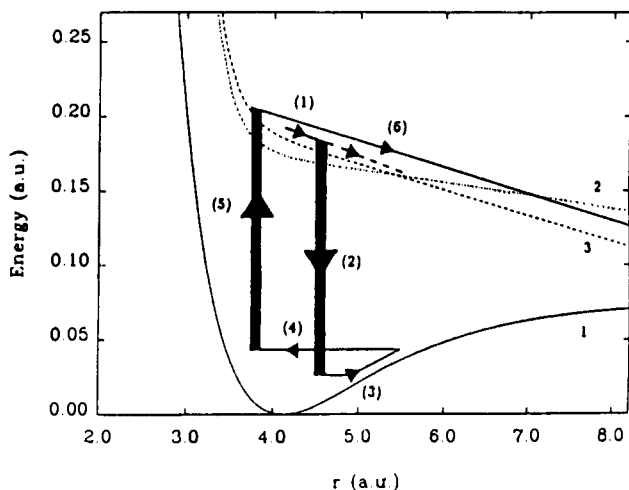


Figure 4. Schematic of the physical mechanism induced by the restricted optimal field on the strong coupling system designed to maximize the channel 3 product. Nominally, without control, the initial wave packet on curve 3 will exit on channel 3 only with 0.127 probability. The control field in Figure 3 reversed this situation, with the probability of exiting on channel 3 now being 0.631. The mechanism is seen to be a dump of amplitude down to surface 1, free evolution with the momentum carried from curve 3 to eventually recycle it at a further distance from the crossing point to once again manipulate the wave packet and thereby significantly enhance the amplitude out of channel 3.

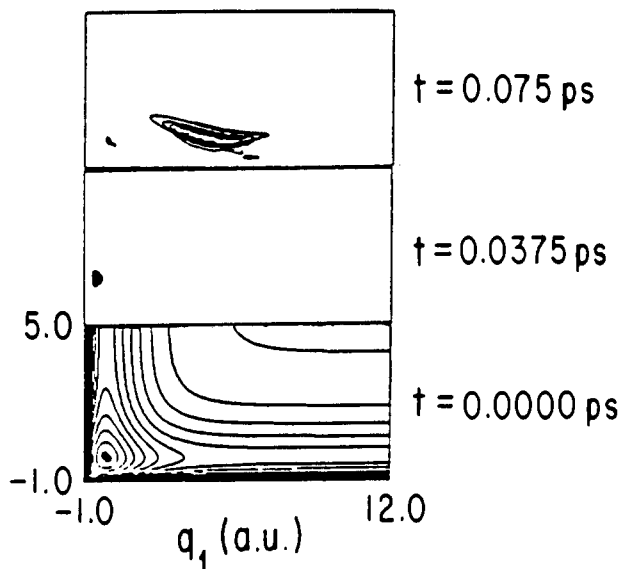


Figure 5. Contour maps of molecular probability density at different times for photodissociation of a model collinear triatomic with an optimally designed field. A contour map of the molecular potential energy is superimposed for reference with the initial ground-state probability density at $t = 0$. The probability density keeps its shape by $t = 0.0375$ ps, but beyond 0.075 ps, it spreads rapidly down the desired channel to the right.¹⁶

$$\epsilon(t) \rightarrow \epsilon(t) + \alpha \int_{-\infty}^{\infty} \Delta\epsilon(\omega) e^{i\omega t} \theta(|\omega| - \omega_T) dt$$

where $\Delta\epsilon(\omega)$ is the frequency transform of the objective gradient, $\delta J / \delta \epsilon(t)$. An example of the resultant field is shown in Figure 3 and the control mechanism is in Figure 4. In general, it was found that the frequency-restrained fields could effectively steer the wave packet out the desired curve-crossing channel in direct competition with the adiabatic coupling.¹²

In addition to diatomics, there have been two applications^{14,15} of the optimal control techniques to

triatomics. In Figure 5, we exhibit a contour map of the potential and some snapshots of the wave packet probability density employed in ref 14 where only the ground electronic potential was utilized. (We note that the inclusion of various electronic states,¹⁵ while physically important for describing the optical transitions between the various electronic states, does not modify the overall formalism.) The initial system is a bound collinear triatomic ABC. By application of the optimal field, the system is preferentially excited to yield AB + C (or A + BC, if required). The objective which the optimal field minimizes is

$$J = \int G(r) |\Psi(r, \tau)|^2 dr$$

where $G(r)$ is any weight function that samples preferentially the AB + C arrangement.

Adaptive Control: Teaching Lasers to Control Molecules

To effectively carry out design calculations for optimal control of molecular motion, it is necessary to have available the system Hamiltonian and the ability to efficiently solve Schrödinger's equation. As is well-known, accurate Hamiltonians, including optical coupling coefficients for polyatomic molecules, are not readily available. The technology for solving large-scale quantum dynamics problems is also limited, although improvements in both of these areas will surely occur in the coming years. From another perspective, the current optimal control design calculations suggest that a marriage of learning algorithms with the potentially high duty cycle of computer-driven optical pulse-shaping techniques and the subsequent rapid probing of the created molecular state may be used to literally teach lasers how to control molecular motion. In this case, the objective should be chosen as simple, such as steering the system out of channel 1 versus channel 2, which could be easily detected by a simple probe measurement without subsequent detailed analysis. The learning algorithm would essentially be employed to discern patterns of advantage in one optical field versus another, suggesting new forms for further improvement, to be rapidly implemented by the pulse-shaping apparatus, and once again probed for their effect. Simulations of this learning algorithm approach were quite successful,¹⁷ even including a case that showed high-fidelity learning about the control field without prior knowledge of the Hamiltonian.¹⁶ The learning process has a strong resemblance to the overall optimal control algorithm. The primary difference is that the wave function does not explicitly appear in the learning algorithm, as only its observable effects could be measured. In actual implementation, a preliminary field design $\epsilon_0(t)$ would best be done using the tools of optimal control theory, followed by its iterative refinement in the laboratory pulsed pump-probe apparatus. Thus, the actual molecules are used as exact analog computers having full knowledge of their own Hamiltonians and solving Schrödinger's equation in real time. The procedure is also inherently robust, as it uses the actual laboratory environment. Figure 6 summarizes this full algorithm. Although feedback

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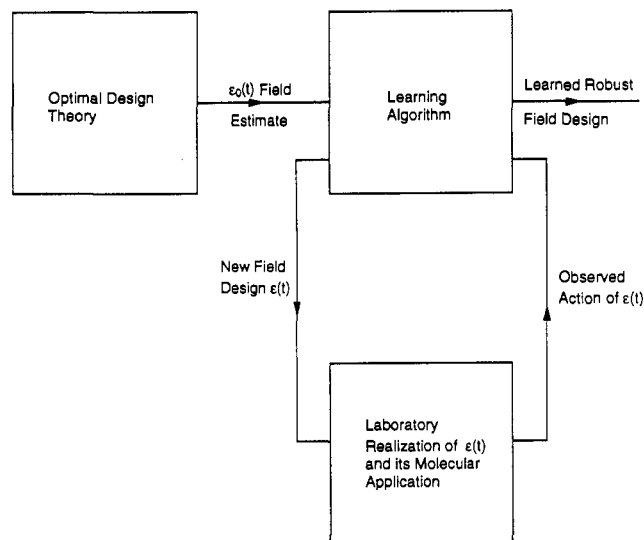


Figure 6. Schematic of an adaptive learning algorithm approach to teaching lasers to control molecules. The algorithm is initiated by an optimal control estimate $\epsilon_0(t)$ of the control field, followed by its laboratory refinement in a computer-controlled sequence of experiments coupled to a pattern-recognizing learning algorithm. The latter cyclic process in the laboratory is exactly analogous to the design operations in the first box labeled "Optimal Design Theory", except the computer model of the molecular dynamics is replaced by the true molecules executing exact dynamics under the actual laboratory fields.

from a single control experiment cannot be done in real time (due to the ultrafast nature of the events), equivalent information could be obtained from a rapid sequence of experiments. In this fashion, we envision that the powerful tools of modern macroworld engineering control can now be brought to bear at the molecular level, where the laws of quantum mechanics are operative. The finesse of rapid optical pulse-shaping techniques and advanced learning algorithms should be capable of systematically finding solutions to the complex problem of molecular control.

Conclusion

In this account, we reviewed the subject of molecular control with an emphasis on the generality of the optimal control procedure. Our focus was on the underlying physical assumptions leading to a framework capable of formulating optical controls of complex molecular motion. Optimal molecular control is not itself a paradigm but rather an algorithm to yield optimal fields, subject to any given paradigm on the field structure. Thus, the application of the optimal control algorithm will be applicable within any of the

experimental and theoretical paradigms which are now being developed for manipulating molecular motion. There is much research to be performed to fully understand the capabilities of the optimal control approach to manipulating molecular motion. From a historic perspective, the technique is quite natural for molecular objectives,¹⁸ although it is quite new in the quantum mechanical context. Many issues need to be explored, and the brevity of this review has not permitted a thorough analysis. Certainly, high on the list of research goals is the need to develop an assurance that the field designs are robust to the various Hamiltonian and laboratory uncertainties that may arise. Molecular optimal control theory contains an abundance of richness, and in this regard, it is possible to show, under rather mild assumptions, that quantum mechanical control problems can exhibit a denumerably infinite number of solutions.¹⁹ Finally, an adaptive learning algorithm was suggested, drawing on the best capabilities of optimal control theory and the emerging optical pulse-shaping tools. This latter approach shows the most promise for success in the immediate future, as it is based on systematic feedback of control field design from a rapid sequence of computer-automated ultrafast pump-probe experiments.

Finally, it is worthwhile to speculate on the classes of chemical problems anticipated to be opened for study with the availability of practical laboratory and theoretical techniques for molecular control.²⁰ First, historically, the objective of manipulating chemical reactivity certainly stands as the outstanding objective. Practical results may ensue from such studies, but perhaps more important will be the insight gained into the underlying dynamics. In this regard, the most significant chemical application of these concepts is anticipated to be their redirection for the purpose of extracting high-quality, detailed information about the underlying molecular Hamiltonian, including intramolecular potential surfaces and optical coupling coefficients. In this context, a feedback algorithm similar to that of Figure 6 could be established with the sequence of iterative experiments specifically designed to ease the notoriously difficult burden of inverting laboratory data to seek out such fundamental information. Beyond chemistry, applications may also be found in controlling quantum electron transport in nanometer-scale semiconductor devices. The sense in the community is that such developments are on the threshold of realization, as once and for all, the theoretical concepts and experimental tools are now becoming available.

H.R. acknowledges the Office of Naval Research, the Air Force Office of Scientific Research, and the Army Research Office for support of this research. D.N. acknowledges support of a Weizmann Fellowship for 1989–91.

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