

# Mathematics Makes Molecules Dance

By Mei Kobayashi

The desire to understand and control chemical reactions can be traced to the origins of civilization. Modern scientists have succeeded in extending their investigations of the control of natural processes into the microscopic domain; ever greater precision and selectivity are required to meet the resulting challenges. These challenges include the control of molecular motion and bonds in the synthesis of new molecules and materials, the control of quantum states of atoms and molecules for the development of quantum computers, the control of nonlinear optical processes, and the control of quantum electronic motion in semiconductors.

As laboratory experimentation becomes more and more difficult, theoretical chemists and physicists are using highly sophisticated mathematical models and simulations of the microscopic world with the aim of guiding the refinement and design of quantum control experiments. In this article we examine (a) the ways in which mathematical models and techniques have been employed by these theoreticians and (b) the future of this relatively young area of research, known as quantum mechanical control.

## The Flawed Origins of Molecular Control

The first steps toward controlling processes at the microscopic level can be traced to the 1960s—the early days of lasers—when this magical new tool, with its tight frequency control and high intensity, showed promise as a molecular-scale “scissors” that could cut specific, targeted bonds in a molecule while leaving others relatively intact:

“The logic involved was intuitive and appealing. Each chemical bond in a molecule has its own characteristic frequency, and radiation will preferentially be absorbed . . . at that characteristic frequency. Thus, it was suggested that laser radiation tuned to the desired bond frequency would be absorbed in a selected way, leading to at least local activation of the particular chemical bond, and possibly even breakage. . . . The logic followed that other waiting reactive reagents would selectively attack the excited or broken bond.” [8]

Experiments conducted soon after the idea was proposed showed that unforeseen events were intervening and preventing the predicted outcome; the scientific community, however, persisted in pursuing experiments that followed this (flawed) logic for almost a quarter of a century.

The rapid dissipation of the energy associated with the initial local excitation is now recognized as the limiting problem of the earlier experiments. The study of intramolecular energy transfer, although it has developed into an interesting field in its own right, did not lead to any significant new insights into the control of molecules and their reactions in the microscopic domain. The break with the earlier paradigm came in the late 1980s, when scientists realized that the key fundamental principle in the control of microworld processes is the manipulation of quantum wave interferences [10].

Although the subject of molecular control originally evolved in the context of developing new tools for site-specific chemistry, it has developed into a broader new area of research. The focus of the subject now extends from control of electronic degrees of freedom and vibrational–rotational motion to dissociation. The prospect of achieving such control gave rise to the appealing notion of “Making Molecules Dance” [9].

## Quantum Mechanical Models

Molecular control is an inverse problem that can be analyzed with quantum mechanical models: Given molecular objectives (e.g., a specific quantum mechanical state), determine an optical field that, when applied, would lead to the objective. (Existence of the field does not guarantee uniqueness. In fact, the number of possible fields is usually infinite; scientists proceed by determining a field that can be produced easily in the laboratory at relatively low cost, which leads to the desired objective efficiently.) Herschel Rabitz and his colleagues at Princeton University formulated the molecular control problem mathematically as follows: Determine a field  $\epsilon(t)$  that minimizes the optimizing functional

$$J(\epsilon) = J_o + J_p + J_{c,d} + J_{c,o},$$

by requiring that  $\delta J(\epsilon)/\delta \epsilon = 0$ . Here,  $J_o$  represents the physical objectives,  $J_p$  the penalties and ancillary costs,  $J_{c,d}$  the dynamic constraints, and  $J_{c,o}$  the objective constraints. Each of the terms on the right-hand side depends either explicitly or implicitly on  $\epsilon(t)$ , and they compete to be simultaneously minimized.

The terms  $J_o$  and  $J_p$  of the optimizing function depend on the physical objective(s) of, and the penalties associated with, the control problem, and their formulation is chosen by the designer. For example, if the objective is for the operator  $\hat{O}$  to have a specified expectation value  $\tilde{O}$  at time  $t = T$ , then a choice for  $J_o$  would be

$$J_o = \left( \langle \psi(T) | \hat{O} | \psi(T) \rangle - \tilde{O} \right)^2.$$

When the expectation value equals the target  $\tilde{O}$ , the objective term  $J_o$  is minimized and the state of the system at time  $T$  will depend

on the field  $\epsilon(t)$  for all times  $0 \leq t \leq T$ . The choice of  $J_o$  is not unique; the example given here, which is reasonable and simple for computations and analysis, was chosen to illustrate how designers introduce objectives. The penalty term  $J_p$  can be expressed as the expectation value of an operator  $\hat{O}'$  with a weight function  $W_p(t)$  such that

$$J_p = \int_0^T dt \cdot W_p(t) \cdot \left| \langle \psi(t) | \hat{O}' | \psi(t) \rangle \right|^2.$$

Suppose, for example, that  $\hat{O} = H_i$  is the  $i$ th localized piece of the Hamiltonian, corresponding, for example, to the desire to maximize energy associated with the  $i$ th bond. A simple choice for  $\hat{O}'$  is then

$$\hat{O}' = H - H_i = \sum_{j \neq i} H_j.$$

Another penalty term commonly considered is the optical field fluence

$$J_p = \int_0^T dt \cdot W_\epsilon(t) \cdot \epsilon(t)^2,$$

where  $W_\epsilon(t)$  is a weighting function. The fluence, which is a measure of the energy in the control field, can be modified to weight against electric fields larger (–) or smaller (+) than  $\epsilon^*(t)$  by replacing the integrand with

$$W_\epsilon(t) \cdot \epsilon(t)^2 \cdot H[\epsilon(t) \pm \epsilon^*],$$

where  $H(\cdot)$  is a Heaviside function. To bias against undesirable frequency components, Rabitz et al. suggest the use of a penalty term associated with frequency filtering, such as

$$J_p = \int_{-\infty}^{+\infty} d\omega \cdot I(\omega)^2 \cdot W_s(\omega),$$

where  $W_s(\omega)$  is a spectral weight and  $I(\omega)$  is the Fourier transform of  $\epsilon(t)$ . A simple term for guaranteeing consideration of robustness to control field errors in a system is the sensitivity penalty function

$$J_p = \int_0^T dt \cdot \left( \frac{\delta O(T)}{\delta \epsilon(t)} \right)^2,$$

where  $O(T)$  is the quantum mechanical expectation value. This penalty term monitors a system and favors greater control by reducing the impact of field fluctuations on the target  $O(T)$ .

A dynamic constraint term  $J_{c,d}$  for a quantum mechanical model has the form

$$J_{c,d} = \int_0^T dt \cdot \left\langle \lambda(t) \left| i\hbar \frac{\partial}{\partial t} - H(t) \right| \psi(t) \right\rangle - c.c.,$$

where  $\lambda(t)$  is a Lagrange multiplier function,  $H(t)$  is the time-dependent Hamiltonian, and  $c.c.$  denotes the complex conjugate (to ensure that the control field is real).

If the physical objectives for the term  $J_o$  must be satisfied exactly, Rabitz et al. suggest the use of an objective constraint term

$$J_{c,o} = \eta [O(T) - \tilde{O}],$$

where  $\eta$  is a Lagrange parameter. In our earlier analysis, the terms  $J_o$  and  $J_p$  are used as a means to quantitatively balance the tradeoff between the objective and penalties and do not guarantee the arrival at user-specified expectation values. In general, use of the objective constraint term  $J_{c,o}$  places heavier demand on the system and may result in less favorable characteristics or conditions for system control, e.g., relaxed satisfaction of the penalty terms  $J_p$ , such as those described above, or the need for a more intense external field. Unless an objective constraint term is necessary, use of a penalty term may be a better compromise for designing a control system.

In the next step in the design of the external field  $\epsilon(t)$ , the variation of the optimizing functional with respect to the unknown functions is computed to produce Euler equations. A simple example from [9] is given here to describe the procedure. Consider a quantum mechanical system with the Hamiltonian

$$H = H_0 + \mu \epsilon(t),$$

where  $H_0$  is the free molecular Hamiltonian and  $\mu$  is a molecular dipole function. If the objective is to steer the molecule to the

state  $\tilde{\phi}$ , then the associated Euler equations are

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H(t)\psi(t), \psi(0) = \psi_0 \quad (1)$$

$$i\hbar \frac{\partial \lambda(t)}{\partial t} = H(t)\lambda(t), \lambda(T) = 2[\tilde{\phi} - \psi(T)] \quad (2)$$

$$\epsilon(t) = \text{Im} \left( \frac{\langle \lambda(t) | \mu | \psi^*(t) \rangle}{\omega_\epsilon} \right) \quad (3)$$

Equation (1) is the Schrödinger equation for the wavefunction  $\psi(t)$  with an initial condition, equation (2) is the Schrödinger equation for the Lagrange multiplier function  $\lambda(T)$  with a specified condition at time  $T$ , and equation (3) expresses the field  $\epsilon(t)$  in terms of these latter functions. The functions  $\epsilon(t)$ ,  $\psi(t)$ , and  $\lambda(t)$  are all unknown.

Determining a solution to the set of equations (1)–(3) is a nontrivial mathematical problem. The condition at target time  $t = T$  in (2) depends explicitly on the difference between the objective target state and the actual state of the system, which was produced by the designer field given by (3). In general, the existence of solutions is assumed. Since a closed-form solution to (1)–(3) usually cannot be found, iterative techniques are used to determine a solution numerically. Tools developed by numerical analysts (e.g., spatial discretization schemes, basis set expansions, variational techniques) are vital to the solution of the equations that arise in the design of controls for manipulating quantum systems.

### The Power of Optimal Control Formalism

Chemists generally take a pragmatic approach to the issue of uniqueness. When a solution exists, there are often multiple (or even an infinite number of) optimal solutions, i.e., fields  $\epsilon(t)$ , corresponding to  $\psi(T)$  of equivalent or at least physically acceptable quality. A control system designer will choose the field that is easiest and least expensive to produce in a laboratory, or that is least likely to produce unwanted side reactions or by-products.

To illustrate the power of the optimal control formalism, Shi, Woody, and Rabitz examined a 20-atom, linear,

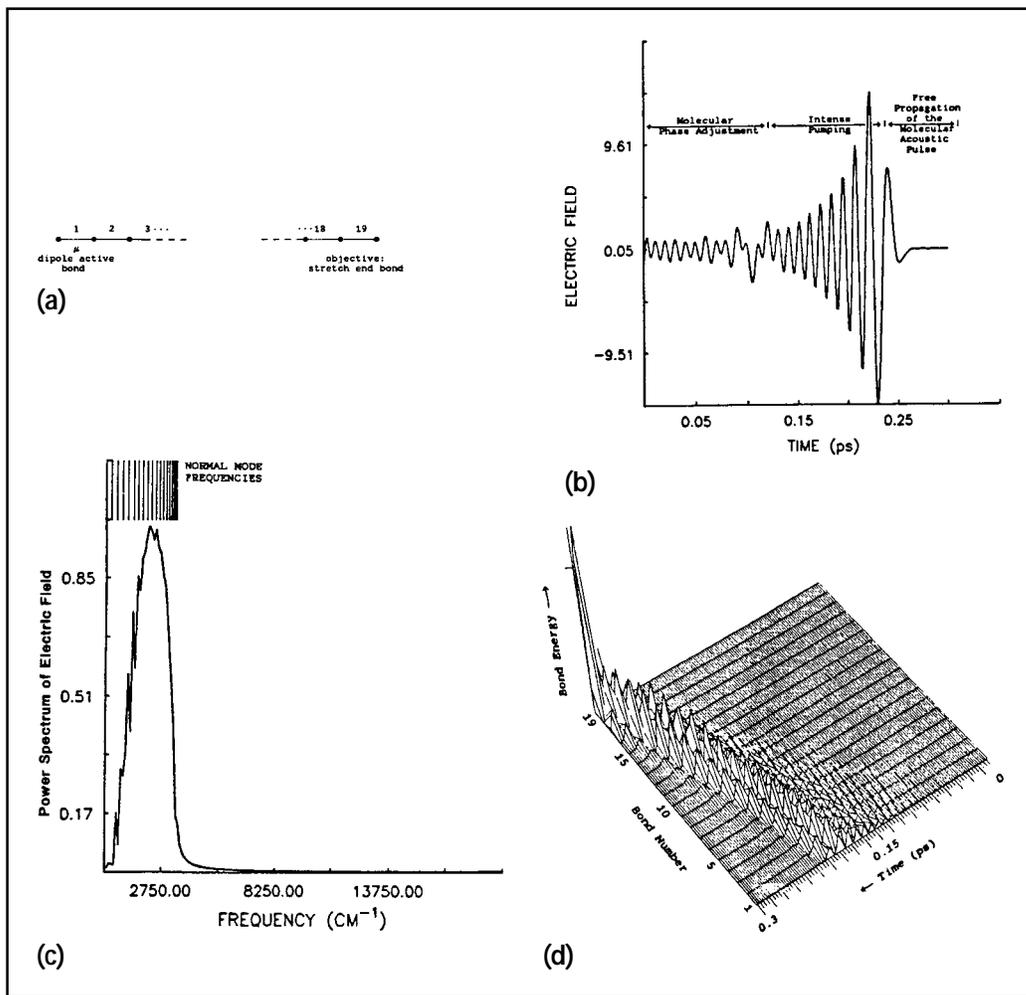


Figure 1. Linear chain bond-stretching objectives: (a) The 20-atom molecule with a dipole at one end and the objective of substantially stretching the bond at the other end at time  $t = 0.3$  ps while minimally disturbing the remainder of the molecule. (b) The time-dependent electric field achieving the desired objective. The phase-adjustment period is central to the preparation of the entire molecule for the subsequent intense pumping, when most of the energy is deposited. Finally, the molecule signals that the radiative field should be turned off to allow for the transmission of the molecular excitation pulse from the energy-absorbing end of the molecule to the target bond at the other end. (c) The frequency spectrum corresponding to the temporal pulse in (b). The discrete normal mode frequencies are shown at the top. A highly broadband excitation is involved. (d) Localized bond energy as a function of time and molecular bond number. The coherent traveling excitation pulse is quite evident and results in a high degree of excitation at the end bond at the desired time.

harmonic molecular system (Figure 1a) in which radiation from the field  $\epsilon(t)$  can enter only through bond 1—between the first and second atoms. The objective is to stretch bond 19—between the 19th and 20th atoms—at the opposite end of the molecule while minimizing the total fluence and disturbance in the remainder of the molecule [14].

The time-varying electric field  $\epsilon(t)$  leading to the objective, which was computed numerically, consists of three distinct periods: molecular phase adjustment, intense pumping, and free propagation of the pulse (Figure 1b). The graph of the frequency spectrum corresponding to the temporal pulse in Figure 1b shows that all modes of the molecule are simultaneously pumped by the field (Figure 1c). More specifically, higher-frequency normal modes are excited first, and lower-frequency modes last, to produce destructive interference during propagation of the energy along the molecular chain from bond 1 to bond 19 (Figure 1d). At target time  $t = T$ , all the waves arrive to form a coherent superposition at bond 19. Once the form of  $\epsilon(t)$  is known, this intuitive explanation seems reasonable (and perhaps almost obvious); without prior knowledge of the solution, however, the mechanism defies guesswork.

Follow-up studies indicate that it is possible to make the peak amplitude of the field, i.e.,

$$\epsilon_{\max} = \max_{0 \leq t \leq T} \epsilon(t),$$

arbitrarily small by increasing the target time  $T$ . This information is valuable to designers of laboratory experiments; although low-amplitude fields over long durations are desirable from a field-intensity perspective, they have an undesirable characteristic: Their coherence over long times requires maintenance. Ultimately, laboratory experiments must be performed to determine which parameter settings are possible to implement and which will yield the best results.

In the late 1980s, Stuart Rice and David Tannor (then at the University of Chicago), Ronnie Kosloff (Hebrew University, Jerusalem), as well as Moshe Shapiro and Paul Brumer (Weizmann Institute of Science) developed a method that uses lasers to control the selectivity of product formation in chemical reactions [7, 11, 12, 15, 16]. Rice and Tannor were among the earliest to consider a multiple-energy-level system. They use conjugate gradient methods to direct the convergence of a variational approach, like that described earlier, in their simulation studies.

Around the same time, G. Huang, T. Tarn, and J. Clark presented an existence theorem for the complete controllability of a class of quantum mechanical systems. The theorem demonstrates that it is possible, in principle, to devise a scheme to control systems with a discrete spectrum so that 100% of a desired final state will be occupied in a finite number of steps. Because the existence proof is not constructive and does not provide a general scheme that can be used to direct reactions, plenty of work is left for experimental designers. The theorem also points the way to a broader area of research, i.e., existence proofs and algorithms for the control of open quantum systems.

Several independent research teams have also used numerical simulations to study simple models of vibrational amplitude control [1, 13], rigid molecular rotor control, transitions between molecular eigenstates [1, 4], and bond-selective dissociation [3]. These examples are drawn from the framework for the optimal control of quantum mechanical systems proposed for more general contexts by Butkovskii and Samoilenko [2]. A direct implementation of the variational design procedure corresponds to open loop control. A laboratory venture of this type could work for simple cases (as has been demonstrated), but it is fraught with difficulties for most realistic laboratory systems, which are more complex. Judson and Rabitz [5] have suggested the use of learning control techniques to circumvent problems associated with open loop control and to take advantage of the high-duty cycle of current pulsed lasers. In practice, a control design would be performed and refined iteratively in the laboratory. For full implementation of the process, stable learning algorithms, capable of operating quickly and reliably with quantum systems, must be identified.

Development of effective and inexpensive systems for molecular control is an exciting and potentially lucrative area of research. Successful endeavors will undoubtedly involve teams of scientists from many different backgrounds who can work in unison and who can appreciate the work of their teammates. The advent of more powerful computers and computational algorithms in recent years is enabling theoreticians to conduct more realistic simulations, which are contributing to experimental and system design. As witnessed already in industrial labs, simulations can help reduce labor and material costs in the development of timely new technologies, and applied mathematicians are in a great position to continue to make an impact. Although it can't be taken literally, "Making Molecules Dance" is a colorful and inspirational slogan for recruiting some of the brightest young minds.

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