Control of Molecular Motion

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Invited Paper

In this paper we present a short introduction to the new field of control of molecular motion. Our intention is to outline how the methods and techniques of control theory play a crucial role in the development of this emerging field, and reciprocally how fundamental new problems are motivated by this interaction.

I. Introduction

A. What Is Molecular Control?

Since the beginning of alchemy one of the primary goals of chemists has been to stimulate chemical reactions to form desired products. Traditionally these stimuli were applied by changing the global thermodynamic variables such as the temperature and the pressure or by adding the appropriate combination of reagents to achieve the desired chemical products. In stimulating such chemical reactions it often happens that only a certain fraction of the reagents combine to form the desired products while the remaining reagents combine to form a number of unwanted by products. Furthermore, there are products that cannot be produced by varying such global control variables. There has therefore been ongoing research to find more selective and efficient ways to manipulate chemical reactions. The possibility of selective excitation at the molecular scale also provides the potential to actively probe and determine unknown parts of the molecular potential energy function.

Neighboring atoms within molecules frequently have net opposite charges on them (the hydrogen and oxygen atoms in a water molecule are a typical example), and the dipoles formed by such pairs of atoms act as microscopic "handles" on the molecules by which it is possible to excite the molecules in a desired way using applied electromagnetic fields. One possible means to control molecular motion or chemical reactions is to take advantage of the radiative coupling and prepare the molecule in selected quantum states which evolve to the desired products. Although these new modes of stimuli offer the possibility of more selective excitation and products, their success depends on being able to determine the correct field to apply in order to achieve the desired objective. In addition, care must be exercised to ensure that the designed field is sufficiently robust to modeling and inevitable laboratory errors.

The idea of using electric or optical fields to achieve selective chemistry is not new, and there has been a great deal of research in this area over the last 30 years. However, the field designs, which were previously based on intuition, have been largely unsuccessful. For example, if there is a need to break a particular bond within a molecule, then simple intuition would suggest that excitation at the fundamental vibration frequency associated with that bond could induce a resonance which would ultimately break the bond. However, due to the coupling between the bond in question and the remainder of the molecule, it is difficult to localize the energy imparted to the molecule within the bond. To overcome this problem the wave nature of the quantum molecular dynamics needs to be exploited. The complicated dynamics and quantum interference structure of the molecule also have to be incorporated in the field-design process. Some progress has been made with perturbation theory based field designs by exploiting quantum wave interference properties of the molecules. Recently, the recognition that the design of fields to manipulate quantum molecular systems is a control theory problem has led to a major advance in this area [1]–[4]. The novel application of control theory to molecular motion is the focus of this article.

A comment about the nature of molecular dynamical equations of motion is appropriate before considering issues of control. Rigorously, the laws of quantum mechanics are operative at the molecular scale, and this necessitates describing the dynamics in terms of Schrödinger's equation which is a partial differential equation in time and $3s$ spatial variables, where s is the number of atoms or particles involved. Thus modeling alone at the molecular scale is a challenging task, even though Schrödinger's

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equation is linear in terms of the unknown wavefunction. In contrast, classical mechanics is typically expressed in terms of Hamilton's equations of motion and can often be applied with reasonable accuracy at the molecular scale, provided the motion describes the movement of the atoms alone and not their electrons (electron motion is strictly quantum mechanical, due to the light mass of the particles). Hamilton's equations of motion are perhaps simpler since they involve 6s first order ordinary differential equations, but they will typically be highly nonlinear and can exhibit chaotic behavior. At this point, most explorations into molecular control have considered the quantum mechanical perspective, and this paper will also follow that line. Nevertheless, classical analogs of the molecular issues involved are expected to play an increasingly important role in the subject.

The balance of the paper is organized as follows. Section II will give an illustrative case of molecular control to set the framework of the topic. Section III will address the role of nonlinear control theory. Sections IV and V deal with some practical issues and applications of molecular control. Finally Section VI will summarize some open challenges presented by molecular control.

II. From Optimal Control to Molecular Control

The evolution of physical systems is often influenced by an externally applied control input. Control theory involves the careful design of such an input to force the system to evolve in a desired fashion. For example, the dynamics of a diatomic molecule may be manipulated by an external laser field that is coupled to the molecule via its dipole moment. The appropriate choice of this external laser field can cause the molecule to rotate, vibrate, or dissociate in a desired fashion. The science of designing such inputs is the essence of the field of molecular control. Over the years, and through the work of many researchers, mathematical techniques have been developed that make possible the design of control inputs to satisfy desired design objectives in the best possible way. Currently, the techniques of optimal control span a wide range of analytical and computational methods, with many variations that apply to models described by ordinary differential equations, partial differential equations, and discrete-event systems. An approach that is currently used in molecular control problems is based on a variational method, which involves the solution of two coupled boundary-value problems that can be derived from the quantum description of the molecular dynamics. The solution of these two boundary-value problems yields gradient information about the desired objective, which can be used in a conjugate gradient search for the optimal control input. We will outline this type of analysis in the next section when we describe the control of a diatomic molecule.

Since the recognition that control theory could be applied to molecular motion, there has been significant progress in the theoretical design of stimulating fields for molecular systems. Applications of this approach include the excitation of vibrational modes of polyatomic molecules, rotational excitations, and dissociation of molecular structures [1]–[12]. Control theory has not only been crucial in the process of designing the required fields, but also in establishing the limits of what these fields can achieve.

A. Molecular Dissociation: A Case Study

In this section we will use an example to demonstrate the type of calculations that are involved in a molecular control problem [1]. The dynamics of a molecular system is described by a Schrödinger equation of the form

$$i\hbar \frac{\partial \psi}{\partial t} = (H_0 + U)\psi$$

where the term H_0 includes a potential energy function $V_0(x)$ and the Laplace operator, and is called the nominal Hamiltonian and U is the externally applied laser field, i.e., the control input. The state of a quantum system, $\psi(x, t)$, prescribes a probability density function, $|\psi(x, t)|^2$, from which the statistical information about the physical observables associated with the quantum system can be calculated. A problem of practical importance is to determine the appropriate externally applied control that will steer a wavepacket, $\psi(x, t)$, about and ultimately dissociate the molecule. The nominal potential for a typical diatomic molecule is qualitatively described by a Morse potential which takes the following form:

$$V_0(x) = D[1 - e^{-\gamma(x-x_0)}]^2.$$

In the neighborhood of the minimum point x_0 the Morse potential resembles a harmonic potential, while away from x_0, the two potentials differ significantly. We first transform coordinates to an equivalent dimensionless form, where the scaled spatial variable is denoted by X. The initial wavepacket is assumed to be a Gaussian:

$$\hat{\psi}(X) = \left(\frac{1}{2\pi}\right)^{1/4} \frac{1}{L^{1/2}} \exp\left[\frac{-(X - X_0)^2}{2L^2}\right].$$

For illustration we take the parameters $L = 20$, $X_0 = 6$. The target wavepacket is also a Gaussian centered at $X_0 = 4$. The goal is to design a control input such that the wavepacket evolves to a state that is as close as possible to a desired state $\hat{\psi}(X)$ at a target time T for which the associated energy is higher than the dissociation energy of the molecule. The applied control is given by $U = B(X)E(t)$, in which the molecular dipole coupling potential is $B(X) = X - X_0$. Thus the optimal control procedure seeks to find the time-dependent external field $E(t)$ that minimizes the difference between the specified target wavepacket $\hat{\psi}(X)$ and the actual final wavepacket $\psi(X, T)$ while simultaneously minimizing the energy of the control term $B(X)E(t)$. We use a Lagrange-multiplier formulation to convert this optimization problem to the solution of two boundary value problems, which provide the information necessary to conduct a conjugate gradient search for a minimum of the cost functional. The results of this computation are shown in Figs. 1–4.

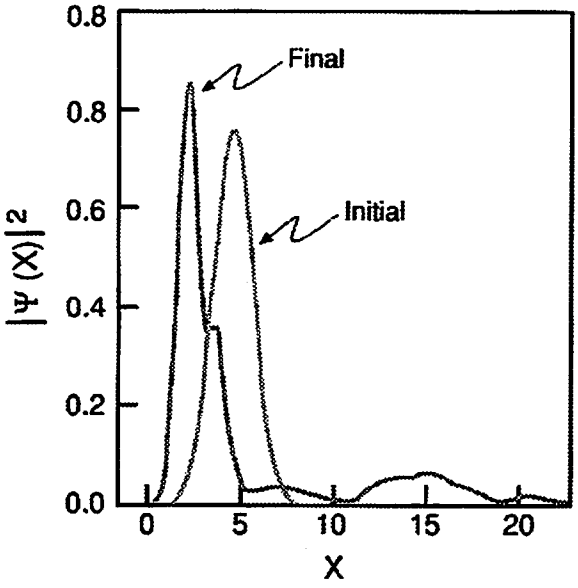

Fig. 1. The initial and final wavepackets of a diatomic molecule.

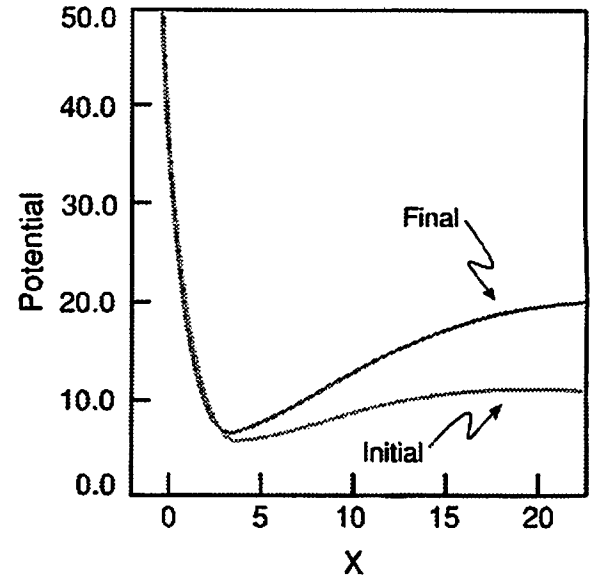

Fig. 2. The initial and final potentials of a diatomic molecule.

Fig. 1 shows the probability density for the initial and the final wavepackets. Dissociation is achieved by translating the wavepacket from 6 to 4, which compresses the bond and releases it at time T. The subsequent dynamics shows that the compressed atoms fly apart to dissociate as desired. Fig. 2 shows the controlled and uncontrolled potential energy functions to which the diatomic molecule is subjected. Notice that the enhanced curvature of the net potential in the target region provides an explanation for the narrowing of the final wavepacket as seen in Fig. 1.

Fig. 3 shows a contour plot of $|\psi(X, t)|^2$ over the space-time domain. In this figure the evolution of the wavepacket can be traced from its initial position around $X_0 = 6$ to its final position around 4. Note that the crest of the Gaussian indicates the average length of the diatomic bond. See the figure on the cover of this journal. The response of the wavepacket to the optimal driving field $E(t)$ (see Fig. 4) can be observed. Initially there is a period of phase adjustments, which is relatively high in frequency and low in amplitude. This period is followed by a large low-frequency pulse which is applied near the end of the time period. The large peak of $E(t)$ near the end of the time interval increases the effective curvature of the combined potential as shown in Fig. 2.

This example demonstrates the use of optimal control methods to design a control field strategy that achieves dissociation within the given time interval and which minimizes the work performed by $E(t)$ to achieve this goal. The control and guidance of the wave packet is achieved by forcing the wave packet in a delicately phased fashion by means of the applied potential $B(X)E(t)$. The optimal field $E(t)$ exhibits many interesting features that could not have been anticipated *a priori* without such an analysis. This nonintuitive structure is typical of many successful molecular designs. A key issue is assuring the practical nature of the control design and this point will be discussed later.

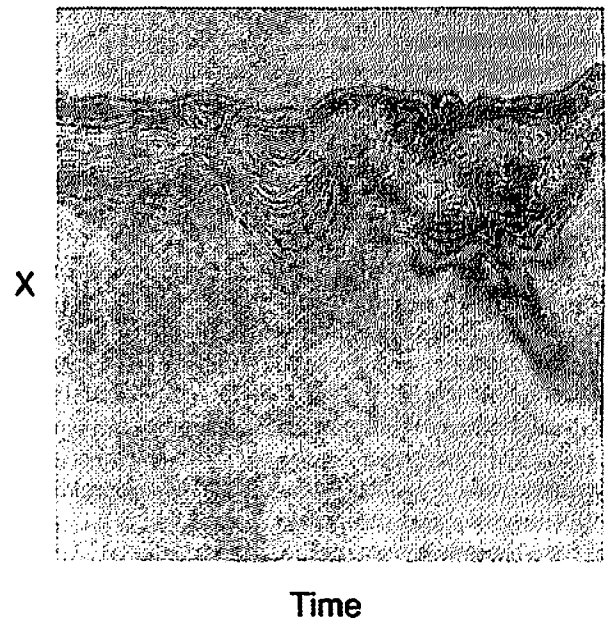

Fig. 3. The time evolution of $|\psi(X, t)|$ for a diatomic molecule.

III. Nonlinear Control Methods

There is a significant role for finite dimensional nonlinear control techniques in the molecular regime. Schrödinger's equation with an external control is a bilinear distributed parameter system. Nevertheless, the theory of the control of nonlinear lumped parameter systems is of great value to molecular control.

For reasons mentioned in Section I, molecular systems are often modeled classically. This naturally gives rise to a Hamiltonian control system (i.e., both the drift and the input vector fields are Hamiltonian). Even when quantum mechanics is employed, ideas from the control of nonlinear

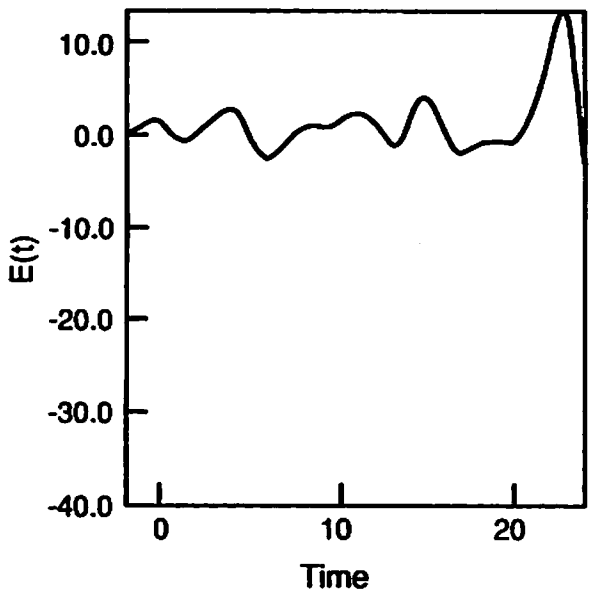

Fig. 4. The time dependence of the control field.

lumped parameter systems play a significant role. In fact, molecular control problems suggest new questions in nonlinear control theory whose solutions ought to be of interest to a wider audience. We will describe these later in the paper.

A. Controllability

Perhaps the most important control objective that arises in molecular dynamics is the problem of the preparation of a desired final state starting from a given initial one, i.e., the problem of constructive controllability. For the sake of greater precision let us first describe how nonlinear (in fact, bilinear) lumped models arise in the quantum regime. We first write Schrödinger's equation with an external control and then make a Galerkin approximation. Explicitly, we make an ansatz, $\psi(x, t) = \sum_i c_i(t)\phi_i(x)$ for the substitution into Schrödinger's equation. Here, the ϕ_i are typically chosen to be the normalized eigenfunctions of the field free Hamiltonian, corresponding to eigenvalues, E_i, $i = 1, \cdots, N$. The eigenvalues E_i represent the energy levels of the molecule in the absence of an external laser field. In practice, the values of the E_i, $i = 1, \cdots, N$ are obtained either experimentally (via, e.g., spectroscopy) or numerically from an approximate model for the molecular potential. The number N depends on the application. Such finite dimensional models are referred to as N-level systems in the atomic and chemical physics literature. The so-called selection rules [13] frequently justify taking only a finite number of states in the evolution of the molecular system. Conversely, they also necessitate the inclusion of intermediate levels, even if there are only two levels which correspond to chemical events and, therefore, need to be controlled. For instance, a five-level system has been used to model the control of selectivity of product formation in a chemical reaction in [12].

The foregoing considerations give rise to the following bilinear control system:

$$\dot{c} = Ac + Bcu. \tag{1}$$

The state c is the N-vector consisting of c_i, $i = 1, \cdots, N$. Typically there is only one control $u = \epsilon(t)$. The matrix A represents the reference Hamiltonian iH_0, and is diagonal with entries equal to the energies iE_j, $j = 1, \cdots, N$ corresponding to the ϕ_j, $i = 1, \cdots, N$. Similarly the matrix B is i times the matrix representation of the interaction Hamiltonian (i.e., it contains information about the dipole coupling). For convenience, we assume that $\hbar = 1$. Clearly A and B are skew-Hermitian matrices. Since the vector c evolves on a $2N-1$ dimensional sphere, we get an invariant system evolving on a homogeneous space. We will explain below what this means [15]. Therefore, its evolution may be analyzed by passing to the control system describing the evolution of the corresponding unitary generators:

$$\dot{U} = AU + u(t)BU. \tag{2}$$

This is now an invariant system evolving on $U(N)$ [15].

To avoid confusion, we will first record the definition of controllability (since the nonlinear control literature is replete with several different variations on this theme). The controllability of the system (1) means the following: "Given any initial condition $c(0)$ and any other arbitrary state d there exists: 1) a positive time τ, and 2) an admissible control function $u(t)$ [τ and $u(t)$ may depend on both $c(0)$ and d], such that under the influence of the latter the state of $c(t)$ of (1), initialized at $c(0)$, satisfies $c(\tau) = d$." We will now briefly describe, via two-level systems, the role of passing to (2) for the analysis of the controllability of (1). This analysis will, we hope, also clearly explain why matrix commutators play a prominent role in the analysis of the controllability of (1). Two level systems are not only simple to analyze, but also have innumerable applications. Phenomena and devices modeled as two-level systems include nuclear magnetic resonance, masers and lasers, and optical pumping. See [13] and [14] for lucid descriptions of these and several more applications of two-level systems.

Consider, therefore, a two-level system (1), which has been initialized at $[c_1(0), c_2(0)] = (c^1, c^2)$, with (c^1, c^2) a pair of complex numbers with unit norm. Suppose that we wish to steer the state of the system to a desired point $(d^1, d^2) \in S^3$ in some finite time τ. We first claim that there is at least one 2×2 unitary matrix V which satisfies $V(c^1, c^2)^T = (d^1, d^2)^T$. We construct V as the product of two unitary matrices $U_2U_1^\dagger$. U_1 has for its first column the vector $(c^1, c^2)^T$. The second column can be any unit norm vector in C^2, which along with $(c^1, c^2)^T$ forms an orthonormal basis for C^2. The matrix U_2 is constructed in exactly the same way with the difference that we replace $(c^1, c^2)^T$ by $(d^1, d^2)^T$. Clearly the V thus constructed has the desired attribute. The existence of such a V is precisely what it means to say that the sphere is a homogeneous space.

The foregoing analysis shows that we will have established controllability of (1) if we can find controls $u(t)$ which take the corresponding system (2) from its initial condition, I_2, to any arbitrary unitary matrix V in some finite time. We will restrict ourselves to piecewise constant controls. For the purposes of assessing controllability, there is no loss of generality in doing so. Let us therefore consider solutions to the equation $\dot{U} = AU + k_1BU$, $U(0) = I_2$ on some finite interval $[0, \tau_1]$. The constant k_1 represents the value of the piecewise control on $[0, \tau_1]$. The solution to this differential equation is $U(t) = \exp t(A + k_1B)I_2$.

To understand, how matrix commutators arise, we will express $\exp t(A + k_1B)$ in the form $g(t) \exp(tA)$, where $g(t)$ is yet to be determined. To evaluate $g(t)$ we differentiate $\exp t(A+k_1B)$ with respect to t. This yields the matrix $\exp t(A+k_1B)(A+k_1B)$, which equals $g(t) \exp(tA)(A+k_1B)$. Likewise differentiating $g(t) \exp(tA)$ with respect to t yields the matrix $g'(t) \exp(tA) + g(t) \exp(tA)A$. We now equate the two to get:

$$g' = g \exp(tA)(k_1B) \exp(-tA)$$

which gives

$$g' = g\, k_1(B + t[A, B] + \cdots).$$

We hope that the last equation partially explains the role played by matrix commutators in the analysis of the controllability of (2) and hence, that of (1). It ought to be now conceivable (and can indeed be demonstrated) that if the linear span of A, B and all their iterated matrix commutators (in other words the *Lie algebra generated by A and B*) equals the set of all skew-Hermitian 2×2 matrices, then indeed every such desired unitary matrix V can be generated by the evolution of (2) under piecewise constant controls. This is the case even for arbitrary N, but demonstrating it requires quite some effort [16]. The fact that the set of $N \times N$ unitary matrices forms what is called a compact and connected Lie group [17] plays a crucial role in the proof.

Some remarks are in order at this stage:

- Typically controllability criteria do not explicitly produce the control which will carry the solutions of (1) or (2) to the desired final state. The above product of exponentials formula appears to imply that one could find the desired control by inverting some matrices. This is feasible only in the case that all sufficiently often iterated brackets of A and B are zero. Unfortunately, unitary groups lie at the opposite end of the spectrum with respect to this attribute. Therefore, the problem of explicitly determining controls which drive the state of (1) from a given initial condition to a desired terminal condition is both open and of great interest. Of course, optimal control seeks to do the same, but what is preferable is a method which employs first principles (i.e., makes explicit use of the Lie algebra generated by A and B) and is computationally less burdensome than optimal control. In particular, the problem of determining sinusoidal controls which do the same is very important, since the external mode of control in these problems is the laser which generates an oscillatory field. We should mention that from the results of [16] it is known that if controllability can be concluded under the assumption that one is allowed to use all admissible controls, then one can conclude controllability under the assumption that one may use only those controls which are bounded in amplitude. This is important from a practical point of view. It is also important in partially justifying the Galerkin approximation. Indeed, it is known that if the external field is not too strong and has only certain frequencies (the correct resonant frequencies) in its Fourier spectrum, then the probability of exciting the neglected modes is extremely small, and thus one can be certain that retaining only the first N modes is quite accurate (to be accurate the field can be strong but $\int_0^T u(t)\,dt$ has to be small). In this regard, we mention the work of [18] where the control of Schrödinger's equation in the weak field limit was studied. In this limit one obtains a linear control system. Since the system is linear one can not only algebraically deduce controllability but also obtain algebraically (i.e., in closed form) the external field which will produce the desired transfer of state. It is interesting to note that the work of [18] obtained, thereby, a field which had only the correct resonant frequencies. Along the same lines, the work of [19] addressed the problem of selective population of quantum states by using only those fields which had only the correct resonant frequencies and were bounded in amplitude. It was found that if one varied the phase of the incident laser field in a suitable manner (something which is within the realms of current technology), then one could indeed achieve the desired objective. It is also noteworthy that in [19] no use of optimal control theory was made.
- The foregoing considerations also apply to more general cases of lumped parameter nonlinear control systems. The matrix commutator now gets replaced by the Lie bracket of two vector fields. The Lie bracket, essentially supplies an extra direction of motion. This point is clearly explained in the survey paper by Brockett [21]. However, we caution the reader that the analog of the rank condition described above (called the reachability rank condition in the literature [20]), is usually not sufficient to conclude the controllability of general classes of nonlinear systems. However, practically all the systems arising in molecular control belong to that rare class where the reachability rank condition actually suffices to determine controllability. As another example we briefly mention the controllability of Liouville's equation which describes the evolution of the density matrix [22]. The density matrix is used in situations when there is (statistical) randomness in the Hamiltonian of the molecular problem. Liouville's equation also gives rise to a bilinear control system with the difference that the corresponding A matrix also belongs to $su(N)$, i.e., it has zero trace

in addition to being skew-Hermitian. However, since the state vector in this case does not have a unique norm we do not obtain an invariant system on a homogeneous space. This is the only obstruction to carrying out the above program for Liouville's equation. However, it permits us to describe the set of states that can be obtained from a given initial condition, under all possible controls in finite time. Finally, we note that the controllability of other problems arising in molecular dynamics and micro(nano)electronics can also be deduced via rank conditions. For instance, the controllability of a classically modeled system can also be deduced via rank conditions due to the Hamiltonian nature of the problem (under certain other assumptions). The same circle of ideas also allows us to analyze and understand some remarkable results on the control of electron scattering amplitudes (at many incident energies) in 1-D semiconductor heterostructures [23].

- In determining the controllability of (1) or (2) one can spare oneself some calculations by just determining if the real dimension of the Lie algebra $span\{B, [A,B], \cdots\}$ is $N^2 - 1$ [24]. This is because in typical applications the only element belonging to the Lie algebra generated by A and B which has nonzero trace is A [24]. In [24] use is made of such calculations to explain certain heuristic results of [12] on a five level (i.e., $N = 5$) system.
- The reader may wonder why the argument above, involving the product of exponentials, which motivated the role of matrix commutators could not have been made at the level of (1) itself. It certainly could have. However, by passing to (2) we need verify the reachability rank condition only at one point of $U(N)$ (namely, the identity matrix), whereas we would have had to verify the reachability rank condition pointwise if only (1) had been employed. There are several other advantages as well. For instance, the fact that (2) is an invariant system on a Lie group leads to the simplification of certain optimal control problems. Indeed for cost functionals which are quadratic it is possible to explicitly solve the resulting two point boundary value problem. This is a direct application of the results of [25].

B. Tracking as an Alternative to Optimization

Optimal control is the method that has been used most for the purpose of designing fields to manipulate molecules. Whilst optimal control is the most flexible (inasmuch as it is capable of handling several competing objectives), it can be computationally expensive. Therefore, it is desirable to explore other techniques which will, at least in some cases, yield the desired external field.

One such technique is the method of "inverse control" or the method of exact tracking. The basic idea is to prescribe a reference track $r(t)$ for some observable of the molecular system. $r(t)$ is so chosen that if the observable follows $r(t)$ exactly over $[0, T]$ then at $t = T$ the state of the molecular system is where one wants it to be. The requisite field is obtained by inverting the equations of motion. Therefore, the method applies equally to classical and quantum models. The only difference, loosely speaking, is that in the latter Heisenberg commutators replace Lie derivatives in the former.

There are two sources of difficulty with the exact tracking method. First, unlike the situation in traditional engineering applications, the track $r(t)$ is secondary in importance to the problem of achieving transfer of state. Thus there will typically be no laboratory guidance for choosing the track. This places a considerable burden on the designer to come up with a suitable track. If the track is not chosen carefully the field produced by this method could well have undesirable characteristics like strong low frequency components. Second, in most typical problems there are at least two observables whose behavior must be controlled in order to achieve the given molecular objective. For instance, if the goal is to break the stronger of the two bonds in a triatomic molecule then one not only wishes to pump more energy into the stronger bond, but also to keep the energy in the other bond at a minimum. Thus at least two outputs have to be exactly tracked with just one input. Usually this problem is difficult.

Various extensions of exact tracking have been proposed to ameliorate the situation [26], [27]. Among these are asymptotic tracking of weighted sums of the competing tracks and various combinations of tracking and optimization. The latter approach is closely related to techniques in chemical process engineering, usually dubbed model predictive control [28]. These methods were tried both in the classical and quantum regime. One physically interesting application was to the dissociation of the HF molecule, and the technique yielded good results. These techniques were also applied to the more challenging situation of breaking the stronger of the two bonds in a model linear rotationless triatomic A-B-C molecule [26], [27]. Some of the extensions proposed in [26], [27] are well established in the nonlinear control literature (e.g., asymptotic tracking). However, there is still some novelty due to the fact that these control laws are state feedback laws, and therefore cannot be used as such in molecular control problems, where real time feedback is not currently feasible.

IV. Practical Laboratory Issues of Molecular Control: The Need for Adaptive Feedback

As with all control problems, the goal of molecular control is to ultimately go into the laboratory and manipulate molecular-scale events, including chemical reactivity. Almost all molecular optimal control theory studies have thus far considered open loop control, since the dynamical events in molecules are occurring at ultrafast time scales, even down to 10^{-12}–10^{-15} s. Thus real time feedback, as traditionally done in engineering applications, appears not feasible for molecular control. Nevertheless, the same basic issues, driving the need for feedback, occur. In particular, the Hamiltonians for all but the simplest molecules

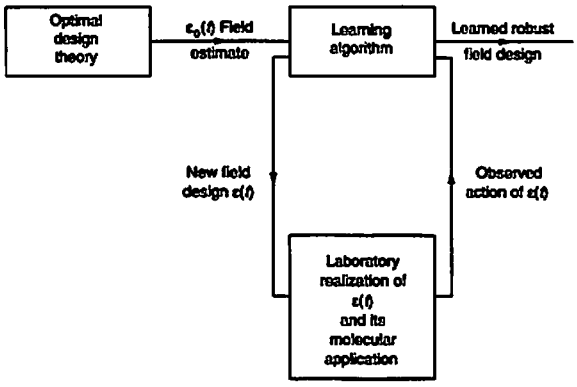

Fig. 5. A schematic of an adaptive-learning algorithm apporach for teaching lasers to control molecules. The algorithm is initiated by an optimal control estimate $\epsilon_0(t)$ of the control field, followed by its laboratory refinement in a computer-controlled sequence of experiments coupled to a pattern-recognizing learning algorithm.

are imprecisely known, leading to control field designs of suspicious quality. Second, even in cases where the Hamiltonian is known to be accurate, solving the control equations can be a formidable task, especially if several atoms or particles are involved. Third, even if the latter two difficulties are surmounted, the actual laboratory realization of the designed field will have errors of a random and systematic nature, and the degree of tolerance to such errors is not fully understood.

Although the above difficulties are serious, there appears to be a very attractive way of dealing with these problems. First, some appreciation of how laboratory control fields are generated is necessary. Current techniques of optical pulse shaping operate most effectively in the frequency domain: an ultrafast raw laser pulse is first Fourier-transformed into its spectral components, followed by application of a frequency and/or phase filter, and lastly, an inverse transform is applied to yield a pulse of desired shape. All of these operations are performed by passive optical devices, except the filter. Most importantly, the laboratory procedure for changing the filter can be implemented, with computer control, leading to the possibility of creating distinct pulses at a high duty cycle of perhaps thousands or millions per second. A canonical single experiment would consist of a rapid control pulse, followed by an interrogating probe pulse, to investigate what happened to the molecule. Thus although direct real time feedback cannot be envisioned now, an unprecedented number of experiments of this type could be sequentially performed, to suggest an adaptive feedback algorithm, as sketched in Fig. 5. Such a learning-based approach for control has analogs in other areas of engineering, but the molecular-scale applications may be unique in terms of the enormous number of independent experiments that may be performed over a short period of time in the laboratory.

The ideal mode of operation in learning-based molecular control would first involve employing various control theoretical design techniques, as a starting estimate for the laboratory control field. This latter first step may be increasingly important in more complex molecular control situations. At the present time, laboratory illustrations of molecular control learning have not been attempted, but a number of highly encouraging simulations have been performed. Most significant are results suggesting a high tolerance to certain classes of noise and systematic errors in the laboratory. It is anticipated that adaptive feedback learning at the molecular scale will become an essential component of virtually all practical molecular control applications in the future [29].

V. Optimal Molecular Control for Inversion Purposes

Historically, the domain of molecular control has been driven by the desire to manipulate molecular motion, and especially, chemical reactivity. This still remains as the central challenge, and results of fundamental significance may indeed emerge. However, in considering these goals, as pointed out above, there is typically a serious lack of information on the underlying Hamiltonian, and in particular, the intramolecular potential function describing the interaction among the atoms of the molecule. Control and inversion theory are closely allied in the overall domain of systems theory. In the case of chemistry and physics, a very large fraction of laboratory studies, especially of a spectroscopic nature, are carried out with the ultimate aim of inversion, to learn about the molecular potential functions. Such efforts have been plagued by a number of difficulties, perhaps the most important one being the lack of a reliable algorithm to guide the inversion process. Given the significance of molecular inversion, it is natural to inquire whether a variation on the theme of molecular control might be employed for inversion purposes. A fundamental issue is to develop an algorithm to guide the process. The subject is at an early stage, but a promising suggestion has been put forth, related to the concepts of molecular tracking and control theory [30]. In tracking, a desired trajectory is imposed on the molecular observable and the dynamical equations effectively inverted, to obtain the control field which will achieve this externally prescribed trajectory. In the present context, the suggestion is not to prescribe *a priori* a trajectory for some observable, but rather it is to actually monitor the evolution of the observable in the laboratory, and then use the knowledge of the initial condition and then perform the inversion procedure used in the theory of tracking to obtain the unknown intramolecular potential function. There is only a loose analogy between these two tracking applications, as in the case of control, the inversion seeks to find a time-dependent function $u(t)$, while the Hamiltonian inversion problem seeks the intramolecular potential $V_0(x)$ as a function of spatial variables. A specific algorithm to perform intramolecular potential inversion has been suggested. Ultimately, a full incorporation of control theory will be needed, as the real issue is identifying the optimal sequence of controlled experimental observations for best extracting the underlying Hamiltonian information. One can

envision the generation of "smart" or adaptively controlled spectrometers, whose operation and design are specifically aimed at inversion. Success in this domain would be of equal, if not greater, importance than merely achieving molecular control.

VI. Challenges to Control Theory

In the history of control theory, major advances have been achieved by the search for solutions to problems that pose significant new challenges, such as those presented by the space program. Molecular control poses new challenges for control theory. First, models for the dynamics of molecules are rich in structure: the approximate classical models are nonlinear dynamical systems that can be chaotic, while the more accurate quantum mechanical models increase rapidly in computational complexity as the number of atoms in the molecule increases. Second, the characteristic time-scale of the molecular systems is very small: the controlling fields for such systems will not be amenable to real time feedback in response to minor perturbations in the trajectory of the molecule. This is a significant deviation from the requirements of traditional control designs in which observation and feedback are fundamental components. However, as argued above adaptive feedback through a sequence of experiments is quite possible. Third, in the design of molecular controllers, knowledge of the molecular Hamiltonian is often incomplete: Robust controllers will have to be designed to make them less sensitive to such uncertainties.

There are some novel problems which arise in nonlinear control that are motivated by molecular control. The first is the problem of "motion planning" for invariant systems with drift on Lie groups. In particular, at the molecular level, one wishes to study the same problem with restrictions on the Fourier spectrum of the input field (this can be studied via optimal control, but one would like to avoid the time consuming computation that goes with it—in other words, we would like to solve this problem from first principles by making a systematic use of the structure of the Lie algebra generated by the A and B matrices of system (1)). A similar question has been studied for *driftless* systems (with, of course, more than one control) in [31] in the context of the path planning problem for mechanical systems with nonholonomic constraints. We should stress that the trick, found in the control literature, of effecting a time-dependent coordinate change to convert the given system into a driftfree one will not be very valuable in the molecular control problem. The main obstruction to this as a systematic technique for the resolution of the above problem at the molecular level is that there is typically only one control, and hence, the resultant driftless system will not be controllable even if the original one was. Incidentally, this trick is well established in the quantum mechanics literature [13]. On the other hand, it seems to us that the main techniques in [31], namely the Wei–Norman and Magnus expansions, are not inherently limited to the driftfree case.

Thus far, the work on molecular controllability theory can be understood in the traditional engineering control sense of attempting to identify the degree to which the system may be steered about, from one arbitrary point to another. However, in fact, at the molecular scale, such an approach is overly confining, as the state of the system described by the wavefunction $\psi(x, t)$ cannot actually be measured. Although the initial condition $\psi(x, 0)$ may be known, the actual observations in the laboratory are of a quadratic functional of the wavefunction involving an integral over all spatial coordinates x. Such a functional inherently washes out much information on the true state $\psi(x, t)$, and it renders the following physically important controllability problem: "Determine if every value that an observable may take, can indeed be achieved via the imposition of a suitable external laser field." Surely, a quantum mechanical system which is controllable in the traditional state space sense would also be controllable in the sense suggested here. However, most importantly, even if a system is not controllable in the state space sense, it may well still be controllable in terms of generating true laboratory observables. Thus a significant challenge is to develop a controllability framework for actual laboratory observables. It is conjectured that a wider class of quantum mechanical systems will be controllable from this physically important perspective, but the mathematical analysis is likely to be more complex, due to the additional nonlinearity of the assessment process.

Another problem is to effectively determine when two given points in the state space of a nonlinear control system can be attained from one another, given that the rank condition fails at isolated points of the state space. In other words, we seek to determine when these two points lie on the same "leaf of the foliation determined by the reachability Lie algebra" [20]. This is particularly important for classical models of molecular control problems and the control systems arising in solid-state electronics. Typically the reachability rank criterion will fail at certain isolated points of the state space in these problems. Thus this problem is not trivial. At least for the classical problem it seems that symmetry considerations will play an important role in resolving this question.

An interesting problem arises in the context of tracking multiple objectives exactly. Typically the limitations on the class of tracks for the second (or more) output are limited by the zero dynamics of the first and primary output. For classical systems this likely rules out any interesting possibilities. However, for quantum systems the associated "zero dynamics" are infinite dimensional, thus leaving some interesting scenarios (see [20] for a definition, in the context of the tracking problem, of "zero dynamics"). At this point, the problem is to make this notion as precise as possible.

The introduction of concepts and tools from control theory at the molecular scale is a new field, and already has raised interesting new issues. Quantum control is rich in terms of its physical significance, and much is to be gained by joining the methods of control theory and quantum physics.

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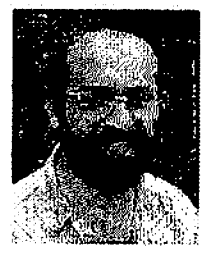

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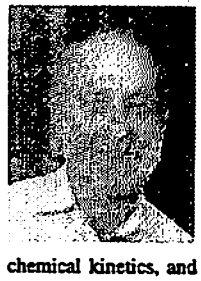

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Viswanath Ramakrishna, photograph and biography not available at time of publication.