PROJECT DESCRIPTION

I. INTRODUCTION AND OBJECTIVES

Quantum control – a discipline that leverages the wave-particle duality of matter to attain control over atoms, molecules and nanosystems using coherent perturbations like lasers – represents a bold new front of 21st century technology [1]. Our ability to control coherent quantum phenomena at the angstrom (10^{-10} m) length scales and femtosecond (10^{-15} s) time scales (characteristic of atomic and electronic motion) promises to have a pervasive impact on molecular manufacturing. By exploiting even the most subtle differences in electronic structure between similar molecules, coherent control can selectively break only a target bond of interest, producing minimal by-products [2]. Moreover, coherent control may allow us to reach the ultimate limits of sustainability in chemical transformations. Shaped laser pulses, or "photonic reagents", offer a promising alternative to conventional inorganic catalysts, since high temperatures, pressures and by-products are avoided – a goal that has been coveted by scientists ever since the dawn of chemistry. This is achieved by manipulating quantum wave interferences that are only accessible in a dynamical picture of chemical reactivity. In this proposal, I will outline a research plan for enabling a comprehensive technology of coherent molecular control that will help pave the way for the sustainable manufacturing of the future.

Control of molecular dynamics [3, 4] has several advantageous features compared to the control of complex chemical process dynamics: a) the dynamical equations of motion are well-understood, rendering model-based control possible if the system is sufficiently isolated from its environment and the system parameters can be efficiently estimated; b) the equations of motion are linear, and the control system is bilinear – this reduces the computational complexity of the optimal control problem and allows analytical assessment of controllability [5]; c) closed quantum systems exhibit unitary evolution, which means that components of the state and other observables are always bounded functions of time, since the system, unlike many classical control systems, is inherently stable; d) the duty cycle of femtosecond laser experiments is extremely high, allowing thousands of experiments to be carried out in a matter of minutes [6]; and e) the ability to directly manipulate quantum wave interferences enables quantum control to influence the outcomes of molecular/nanoscale processes with greater precision than incoherent control.

Despite these favorable features, nearly all reported experiments on control of atomic and molecular systems have been based on model-free, adaptive feedback approaches that do not leverage the latest advances in engineering control and estimation [7]. Moreover, these experiments have largely focused on single input-single output (SISO) control problems. Quantum chemical manufacturing requires the development of a multiple input-output (MIMO) quantum control theory. Examples of multiple inputs include: a) the x an y components of a time-varying magnetic field controlling transitions between spin states in an atomic or molecular nucleus [8] and b) the x,y,z components of a time-varying phase coherent laser electric field [9]. Examples of multiple outputs include: a) the expectation values of several quantum observables, such as the populations of multiple energy levels in a single atom or molecule (manipulated in the control of multiple reaction pathways in a molecular dissociation or rearrangement reaction); b) the populations of the same energy level in distinct atomic or molecular species in a mixture (manipulated to achieve optimal discrimination of similar molecules [10]); and c) phases and amplitudes of quantum state components [11]) or matrix elements of the dynamical propagator of the quantum system, which encode logical operations in quantum information processing [8].

There are several challenges confronting the application of model-based, MIMO control to quantum systems. These are: a) the ultrashort time scales of molecular dynamics (ranging from femtoseconds for electronic transitions to microseconds for spins), which currently renders real-time feedback impossible for many transitions; b) poor knowledge of system parameters, especially for larger atoms and molecules; and c) computational expense of solving the equations of motion for larger atoms and molecules. The objective of this proposal is to develop robust open and closed loop control strategies for MIMO quantum control by addressing each of the issues a-c through a combination of efficient

estimation, robust optimization and adaptive feedback techniques. Doing so will require the confluence of tools from engineering control and estimation theory with the principles of chemical physics.

As such, the Specific Aims of the proposed research are: 1) Development of quantum optimal control theory (QOCT) for multiple outputs, including efficient optimal control algorithms for different classes of molecular outputs; 2) Introduction of new principles and techniques for classifying quantum systems in terms of their robustness to parameter uncertainty and noise in manipulated variables; 3) Development of state and Hamiltonian estimation methods that extract maximal information about molecular parameters by exploiting the properties of quantum states and measurements; and 4) Development of an integrated approach to open loop and adaptive feedback MIMO quantum control, combining ultra high-duty cycle AFC with QOCT, especially for molecular systems with fast dynamics.

II. BACKGROUND AND MOTIVATION

The control of quantum phenomena had its origins in the realm of bond-selective laser chemistry, a goal of chemical physicists ever since the invention of the laser in the 1960s. Early attempts, based on vibrational mode pumping, were unsuccessful because energy is redistributed among all of a molecule's bonds more rapidly than a laser can deposit it into one bond. However, these experiments inspired a few forward-looking scientists to develop an entirely new approach to quantum control, based on the concept of multi-path quantum interference.

Brumer and Shapiro [12–15] proposed to use two monochromatic laser beams with commensurate frequencies and tunable intensities and phases for creating quantum interference between two reaction pathways. In this approach, control over branching ratios of simple molecular reactions can, in principle, be achieved by tuning the phase difference between the two laser fields [16–18]. While the practical effectiveness of this method is limited (e.g., by the difficulty of matching excitation rates along the two pathways and undesirable phase and amplitude locking of the two laser fields in optically dense media [19]), the concept of control via two-pathway quantum interference has played an important role in the historical development of the field [20–23].

Another important step towards selective control of intramolecular reactions was made by Tannor, Kosloff, and Rice [24, 25], who proposed the method of pump-dump control, based on the use of two successive femtosecond laser pulses with a tunable time delay between them. In the related approach known as stimulated Raman adiabatic passage (STIRAP), two time-delayed laser pulses (typically, of nanosecond duration) are applied to a three-level configuration to achieve complete population transfer between the two lower levels via the intermediate upper level [26–31]. The laser-induced coherence between the quantum states is controlled by tuning the time delay, in order to keep the transient population in the intermediate state almost at zero (thus avoiding losses by radiative decay).

The control approaches discussed above share the same fundamental mechanism based on quantum interference induced by control laser fields. However, another common feature of these methods — the use of just one control parameter (the phase difference between two laser fields in control via two-pathway quantum interference and the time delay between two laser pulses in pump-dump control and STIRAP) — is not fundamental at all. While single-parameter control may be relatively effective in some simple systems, more complex systems and applications require more flexible and capable control resources. The single parameter control schemes have been unified and generalized by the concept of control with specially tailored ultrashort laser pulses. Rabitz and coworkers [32–34] and others [35, 36] suggested that it would be possible to steer the quantum evolution to a desired product channel by optimally designing and tailoring the time-dependent electric field of the laser pulse to the characteristics of the system. Specifically, QOCT may be used to design laser pulse shapes which are best suited for achieving the desired goal [32–42], by applying the engineering principles of optimal control theory [5, 43, 44]. An optimally shaped laser pulse typically has a complex form, both temporally and spectrally. The phases and amplitudes of different frequency components are optimized to excite an interference pattern amongst distinct quantum pathways, to best achieve the desired dynamics. The probability of transition between two states i and j can be written

$$P_{ij}(t) = |\, c_{ji}^{1}(t) + \ldots + c_{ji}^{n}(t)\,|^2 = [c_{ji}^{1}(t) + \ldots + c_{ji}^{n}(t)]\;\; [c_{ji}^{1}(t) + \ldots + c_{ji}^{n}(t)]^* \qquad (1)$$

where c_{ji}^{x} denotes a contribution involving x photons of light (m-th order transition). Quantum interference originates in the cross-terms $c_{ji}^{x}(c_{ji}^{y})^*$, which are sensitive to the phases of the laser field.

The above developments heralded the introduction of the principles of engineering control into mainstream chemical physics, and the genesis of a new field of study – quantum control engineering - at the frontier of physical science and systems engineering. It was recognized that quantum systems under the influence of time-varying electromagnetic fields are bilinear control systems, which has enabled the extension of several important results, including controllability and observability, from classical bilinear control engineering [5, 43] to quantum control engineering [45]. The Schroedinger equation

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\mathsf{h}}[H_0 - \varepsilon(t)\,\mu]|\psi(t)\rangle \qquad (2)$$

specifies the dynamics, where the drift Hamiltonian H_0 and molecular dipole moment operator μ are Hermitian matrices of order N, the laser field $\varepsilon(t)$ is the manipulated input variable, and ψ denotes the quantum state. MIMO quantum control aims to achieve control over 1) multiple state populations $|\psi_i|^2$; 2) multiple quantum state phases $\Phi_i = \tan^{-1}[\mathrm{Im}(\psi_i)/\mathrm{Re}(\psi_i)]$; or 3) all components of the unitary dynamical propagator $U(t)$ (where $\psi(t) = U(t)\psi(0)$) simultaneously (see Section IV for further details). Quantum system controllability analysis provides conditions that must be satisfied in order for simultaneous control of multiple components of the state $\psi(t)$ to be possible, as is required for ultraselective chemical manufacturing. This analysis is based on Lie group theory, because molecular quantum systems under the influence of external fields are bilinear control systems that evolve on Lie groups (Section IV) [45]. Application of this theory reveals that for several classes of quantum systems, complete control cannot be guaranteed if a only single manipulated input (e.g., the z-component of a laser's electric field) is used, and that in general, the use of more manipulated inputs allows complete control to be achieved in shorter time [45-48].

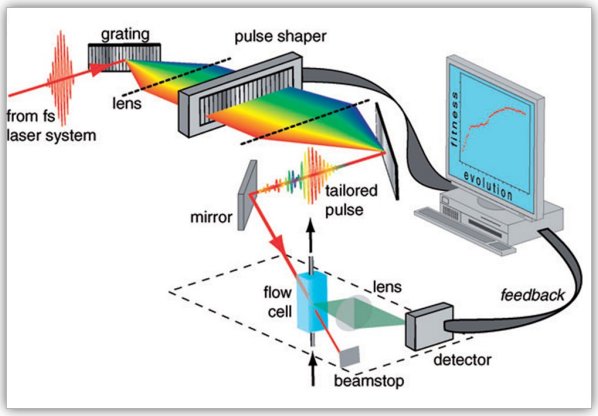

Figure 1. A schematic depiction of a closed-loop process employed in adaptive feedback control (AFC) of quantum phenomena. The input to the loop is an initial control guess. A current design of the laser control field is created with a pulse shaper and then applied to the sample. The outcome of the control action is measured, and the results are fed back to a learning algorithm. The algorithm searches through the space of possible controls and suggests an improved field design. Excursions around the loop are repeated until a satisfactory value of the control objective is achieved.

Simultaneous control of more than 2-3 outputs in molecular systems requires the exploitation of delicate quantum interferences, which can be achieved through QOCT. Experimentally, for control of vibrational, rotational, electronic states in atomic and molecular systems, QOCT has not yet been successfully applied. Instead, quantum optimal control experiments have relied on the principle of adaptive feedback, given the underlying controllability of most molecular systems. In adaptive closed loop feedback control of quantum dynamics (**Fig. 1**), femtosecond lasers (or other forms of coherent radiation) are "taught" to optimally control quantum dynamics in the presence of Hamiltonian uncertainty, noise, and environmental decoherence [6].

The learning loop entails: i) shaping of the laser pulse to generate trial waveforms; ii) application of the shaped pulse to a quantum system sample; iii) measurement of a control objective function, such as the expectation value of a quantum observable; iv) reshaping of the laser pulse based on the measurement outcome, according to an optimization algorithm (implemented online through an integrated high-performance computing system). These four steps are repeated until a control is found that maximizes the objective function through tailored coherent wave interference. The principles of adaptive feedback quantum control are borrowed from classical control, where it has been extensively applied in the field of robotics [49–54].

This approach has been remarkably successful in diverse simple single output applications, including selective chemical dissociation and rearrangement of simple organic molecules [55-57], optimization of laser-induced fluorescence, stimulated Raman emission from molecules, high harmonic generation [58], ultrafast semiconductor switching [59] and more. Importantly, the successes of coherent quantum control are not limited to human engineered designs. Within the past few years, it has been demonstrated that nature also implements quantum control in various biological processes, most notably in the basic energy transduction event of photosynthesis [60-62]. These successes have provided ample motivation for extension of SISO quantum control to MIMO quantum control. In order to determine whether such an extension is possible using only AFC, or whether open loop model-based calculations are needed, we have studied the properties of quantum control landscapes (**Fig. 2**), defined as the map between a control function of time and associated values of the performance measure, which underlie both AFC and QOCT searches for optimal controls. Our preliminary results (see below) indicate that AFC alone is not sufficient for various classes of MIMO quantum control problems, necessitating the application of additional tools from engineering control theory.

In the past decade since the initial successes of AFC, the engineering control community has pioneered new applications of control theory to quantum systems [63-73]. Many of these works have focused on the control of nuclear spin states [63-65], which can be modeled as few-level systems, or the quantum states of electromagnetic radiation itself (linear quantum optics) [66,67]. In contrast to molecular systems, the characteristic dynamical timescales of these systems are sufficiently long that real-time feedback can be applied. In addition, for few-level systems, initial works have appeared on robust control in the presence of field noise and Hamiltonian uncertainty [68]. Engineering control techniques for stability and robustness have been studied for few-level systems [69], with an emphasis on quantum information processing applications.

The majority of near-term technological applications of quantum control require the manipulation many-level molecular systems with femtosecond laser hardware. Comparatively little attention has been devoted to the application of MIMO engineering control tools to the experimental manipulation of such bilinear control systems. For example, multiobservable control of electronic states in even the simplest atoms and molecules is not amenable to the analytical solution techniques reported to-date. Engineering robust control techniques have not yet been introduced for these classes of systems. These circumstances necessitate the proposed research.

III. PRELIMINARY RESULTS

We present below some of our preliminary results in the four categories relevant to the specific aims of this proposal.

Quantum control landscapes:

Our studies of quantum control landscapes [74] have revealed a striking overarching explanation for the success of SISO, adaptive feedback quantum control: The Mayer-type cost functions for quantum observable control landscapes (**Fig. 2**) contain no suboptimal traps, guaranteeing successful control field optimization. The cost function for single observable control may be written:

$$\langle \Theta(T) \rangle = Tr[\rho(T)\Theta] = Tr \ |\psi(T)\rangle\langle\psi(T)||\psi_f\rangle\langle\psi_f| \qquad (3)$$

where ρ denotes the density matrix of the molecule (see below) and $\langle\Theta\rangle$ represents the expectation value of the observed quantity of interest at the final time T; the second equality holds if the molecule is initially in a pure ground state and the observed quantity is population in the target state $|\psi_f\rangle$. In addition to the relative ease of finding optimal solutions, theoretical simulation studies and the many successful quantum single observable control experiments suggest that SISO quantum control has a high degree of robustness to noise. This robustness is of immense practical importance, since there will inevitably be physical inaccuracies in the experimental implementation of a particular solution, and one would like the nonideal fields to also produce dynamics that reach the objective. Again, studies of quantum control landscapes have revealed the origin of this robustness: for any value of the objective functional, there typically exists an infinite number of degenerate control solutions [75–78], collectively denoted a landscape "level set". Moreover, analysis of the Hessian of the single observable control landscape indicates there are many directions leading up to the point of perfect population transfer [76]. These properties underlie the success of AFC experiments to date.

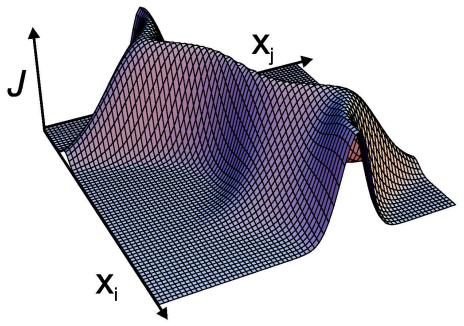

Figure 2. Schematic representation of a quantum control landscape. x_i, x_j indicate two of possibly many control degrees of freedom, and J denotes the objective function value. Any point on the landscape corresponds to a time-dependent control field. Critical points of the map correspond to locally optimal solutions to the control problem. The number of positive, negative, and null Hessian eigenvalues at these points determine whether they are saddle points or local traps.

Although the trap-free nature of control landscapes suggests reasons for optimism in the laboratory control of more complex objectives, it does not in itself guarantee favorable scaling of search effort with system size. We have also characterized the topology of control landscapes for the multioutput control problem of dynamical propagator control. There the landscape is devoid of local traps [77], but the dimension of the level set at the global optimum is significantly smaller, and there are fewer directions leading up to the top of the landscape [79]. For these and other MIMO control problems, landscape topology analysis does not immediately imply that AFC will be successful.

Optimal multiobjective control

To-date, most molecular quantum control experiments have aimed at control of a single observable $\langle\Theta(T)\rangle$. Control over either a single observable in multiple distinct molecules (for substrate selective chemistry or molecular discrimination) or multiple observables in the same molecule (for selective excitation of a particular reaction pathway, while inhibiting other competing pathways) is of great practical interest. In our past work, we have extended the principles of SISO quantum control to multiple outputs. We carried out the first studies of multiple output optimal quantum control in a single chemical species [80]. These studies analytically characterized the types of tradeoffs that occur in the optimization of multiple output performance measures, and introduced fast new algorithms - capable of achieving fidelities approaching machine precision in simulations - for locating optimal laser fields for MIMO quantum control systems [78]. Moreover, we demonstrated that the spectra of optimal pulses required for simultaneously controlling several independent observables are significantly more complex than those for single observables (**Fig. 3**). In particular, even for relatively simple atoms and molecules, MIMO quantum control is generally not achievable by the two-parameter interference methods described in Section II. We established a connection between MIMO quantum control and controllability theory, demonstrating quantitatively that the control resources required for MIMO quantum control are greater than those for SISO control. The notion of a quantum control landscape level set was extended to MIMO control via introduction of

quantum Pareto fronts, which were analytically characterized to assess the fundamental tradeoffs between competing quantum objectives [78].

Optimal dynamical propagator control

As in the case of classical linear dynamical systems, the evolution of quantum systems can be studied from the perspective of either the system state or the so-called system dynamical propagator, which is a matrix [43]. This dynamical propagator contains all information about the system's evolution at any time. In quantum systems the propagator is a unitary matrix that can be interpreted as a logical operation or computation - i.e., as a quantum gate, the building block of quantum information processing. In prior work [79, 81], we have developed optimal control algorithms for the construction of arbitrary unitary transformations, one of the most challenging problems in quantum control. Analytical bounds on the curvature and slope of the propagator control landscape were derived. It was shown that so-called gradient-based homotopy tracking algorithms [82]), rather than the genetic algorithms (GAs) conventionally used in SISO observable control, are essential for propagator control; i.e., the local landscape structural information, rather than simply objective function values, are necessary for locating optimal controls. These gradients are difficult to measure online in AFC.

Quantum state estimation

We have also carried out comprehensive studies on the efficiency of quantum parameter estimation schemes, from the perspectives of both asymptotic and finite sample performance [83]. Here we introduced algorithms for maximizing the likelihood function of the state given quantum observations, and carried out some of the earliest studies on the performance (size and power) of quantum hypothesis testing. These studies demonstrated that while finite sample standard errors are sufficiently small for low-dimensional systems (like nuclear spins), for higher dimensional molecular state estimation, the magnitude of the standard errors on the state estimates increases considerably. This renders it difficult to rely on asymptotic predictions in robust or stochastic control strategies. The magnitudes of the standard errors are significant compared to the parameter values themselves, which will degrade the fidelity of open loop MIMO control. We demonstrated that finite sample performance of quantum state estimation could be improved by optimal choice of measured quantities and the times at which these quantities are measured. These optimal measurements can be applied in both open and closed loop [84] control strategies.

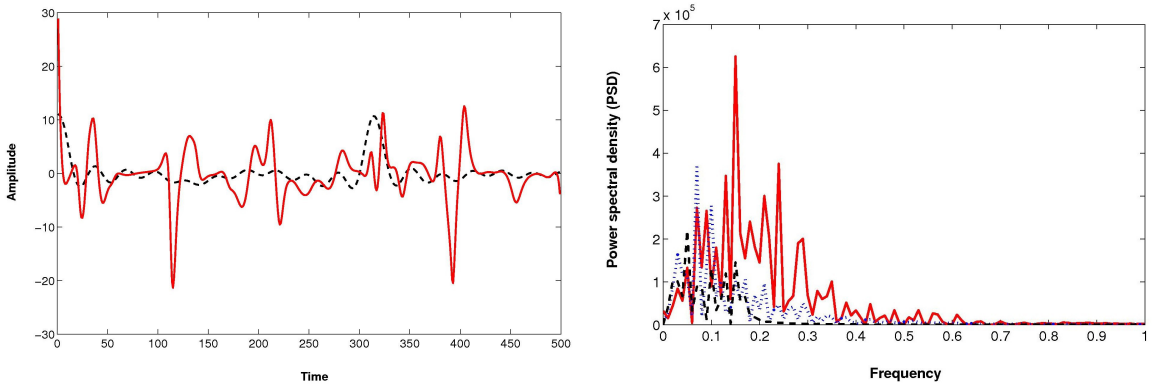

Figure 3. Multiple output quantum control. **Left**: Superimposition of the optimal control fields identified control for 5 (dashed) and 20 (solid) observable control problems. **Right**: Fourier power spectra of optimal control fields for various numbers of observables m. The spectra for m=5 (dashed) and m=20 (solid) are shown alongside the spectrum for m=15 (dotted). From [80].

Future Challenges:

Based on our preliminary results, we have identified the following challenges in the control of molecular systems, in the areas of adaptive feedback, QOCT and parameter estimation. We will address some of these challenges in the present proposal.

1. Challenge for adaptive feedback: Given a control objective and Hamiltonian type, how can one assess whether AFC will be able to locate a control input producing the desired output fidelity?

2. Challenge for QOCT: How can one a) improve the computational efficiency of QOCT, b) assess robustness of QOCT for different types of atoms and especially molecules, and c) obtain more robust control solutions suitable for refinement by adaptive feedback, given this knowledge?

3. Challenge for estimation: How can one extract maximal information from a limited number of quantum measurements, and obtain accurate confidence intervals on parameters suitable for input into QOCT calculations?

IV. PROPOSED RESEARCH

Our specific aims lay out a plan for MIMO quantum control in several classes of atomic and molecular systems, through an integrated open loop/adaptive feedback approach. Before discussing the proposed research under the different Specific Aims, let us first enumerate the *control objectives* and the *quantum systems* of interest:

The *control objectives* are:

- Single observable: Examples include expectation values of Hermitian observable operators, such as the energy of the molecule, or the population of a vibrational, rotational or electronic state.
- Multiple observables: Examples include several molecular state populations or the coherent complex phases characterizing quantum superpositions, which are responsible for the enhanced fidelity of quantum over incoherent control. These objectives can all be formulated in terms of the simultaneous control of multiple quantum observable expectation values.
- Dynamical propagator: The unitary dynamical propagator contains all information about the molecule's time evolution.

The two classes of *quantum systems* that are of interest to us are: a) alkali metal atoms such as K and Rb (in a vapor cell or in an atomic beam); b) the diatomic molecules CO, HCl, and bialkali dimer LiRb, for which accurate Hamiltonian information can be obtained (see below).

Aim 1: Development of MIMO quantum optimal control and control landscape theory for atoms/ molecules. In Aim 1 we will develop a unified treatment of different MIMO quantum control problems in order to lay the groundwork for successful integration of open loop and AFC laboratory approaches. We will assess the search complexity and resource scaling of optimal control strategies for the above objective classes - using realistic Hamiltonians and representations of laboratory pulse shaping devices - and will identify what types of algorithms are necessary for locating optimal controls in each case. This will answer Challenge questions 1 and 2a.

Control optimization search effort [51] is of central importance to any strategy that aims to employ AFC to refine QOCT-derived controls. It is especially relevant for MIMO control problems, because in quantum control experiments, measuring the expectation value of an observable is much easier than estimating the quantum state or dynamical propagator [8, 85–96]. Thus, assessment of search effort for different classes of MIMO objectives will reveal: a) which objectives require precise parameter estimates in the open loop model and b) which can be refined adaptively starting from a more crude open loop prediction. The effects of control landscape features including critical topology, slope, and curvature on the convergence rate of first-order and stochastic algorithms for control optimization will be quantified in the case of each molecule/control objective pair listed above.

Numerically, we will study control optimization using our previously developed

QOCT algorithms in simulations with realistic Hamiltonians for K, Rb, CO and HCl, and field parameterizations that accurately represent current liquid crystal modulator (LCM) pulse shaping technology [97–102]. This technology shapes pulses in the frequency, rather than time-domain, using the parameterization

$$\varepsilon(t) = \sum_{i=1}^{n} A(\omega_i)\cos[\omega_i t + \phi(\omega_i)] \qquad (4)$$

where A, ϕ denote the manipulated amplitude and phase of laser frequency mode ω_i. The QOCT algorithms will assess, based on our prior results on landscape topology and bounds on slope and curvature for each class of objective [74, 76, 79], the influence of landscape critical points and local structure on the search dynamics.

Molecular Hamiltonians (drift Hamiltonian and transition dipole matrix in equation (2)) will be chosen from the following classes: 1) *electronic states* of K, Rb (restricted to alkali metal atoms because the accuracy of many-body calculations of electronic states for diatomic molecules is lower). The Hamiltonians will be obtained from electronic structure calculations reported in [103]. 2) *vibrational* states of CO and HCl; these will use the anharmonic Morse oscillator approximation [104]; 3) *rotational* states of CO, HCl and LiRb; these will use the rigid rotor approximation [105]; 4) *rovibrational* states of CO and HCl [105].

The goal here is to determine the number of observables in the same atom/molecule that can be simultaneously controlled with QOCT or AFC algorithms, using the laboratory laser field parametrization equation (4). Two classes of optimization algorithms will be employed: a) multiobjective evolutionary algorithms (MOEAs), which are implementable in AFC experiments [95-97], and b) homotopy tracking algorithms (so named because they follow a specified path to the desired point in the objective space) that we introduced in our prior work [70]. MOEAs generally have difficulty optimizing more than three objectives simultaneously, but can rapidly sample the frontier of Pareto optimal solutions that strike different tradeoffs among up to three objectives [98-101]. By contrast, homotopy tracking algorithms are not so limited, but can only be applied offline in QOCT. By applying these algorithms to several observables in atomic Rb, we will identify the multiobservable control problems that can be solved by AFC alone, and those that require model-based QOCT algorithms. First, the absolute populations of the 5D3/2 and 5D5/2 Rb electronic states will be simultaneously controlled (**Fig. 3**). Next, we will simultaneously tune four state populations - those of the 5D3/2, 5D5/2, 5P1/2, and 5P3/2 states. Finally, phase coherent control of the 5D3/2, 5D5/2 states will be executed optimally [102-104]. Pending success, simultaneous control over multiple vibrational states of HCl, CO and the methyl halides will be studied in an analogous fashion, due to the applications to selective bond dissociation.

Upon completion of Aim 1, we will have identified which control objectives require open loop QOCT methods and which can be achieved via AFC alone. Moreover, for each objective, we will know a) the scaling of required control resources; b) the effect of field parameterization constraints on control fidelity. The role of system Hamiltonian on MIMO control fidelity and robustness will be further studied in Aim 2.

Aim 2: Mechanism identification of controlled quantum dynamics: methods for assessing robustness to noise and parameter uncertainty. Quantum optimal control involves the manipulation of delicate wave interferences to achieve selective transfer from initial to final states. It is desirable to obtain a picture of how the state transfer is occurring under an optimal control, because control strategies relying on more complex mechanisms will generally require more precisely shaped time-varying fields - which are less robust to noise - in order to attain the target state. The number of interferences required to achieve the control objective increases with the number of parameters of the dynamical propagator being controlled.

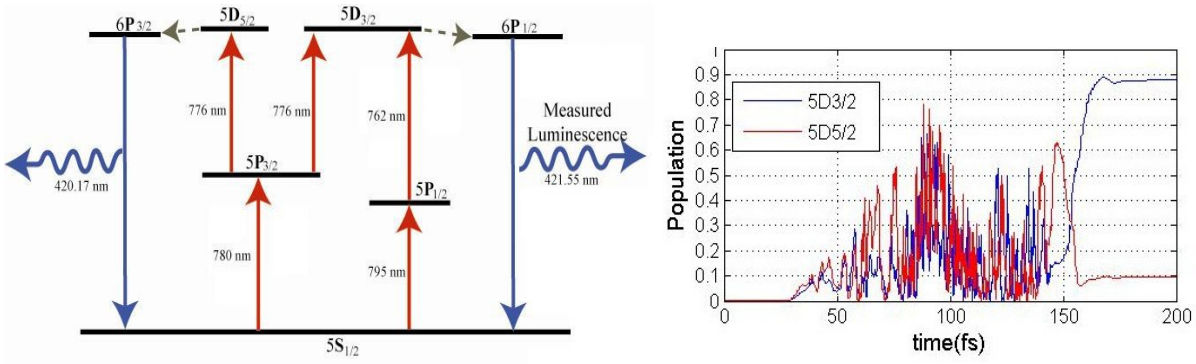

Figure 5. Left: Electronic state level diagram of atomic rubidium (Rb) and dipole-allowed resonant transitions (upward arrows). 5,6 denote the electronic principal quantum number**,** D,P denote term symbols and the subscript denotes the total angular momentum of the electronic configuration. The excited 5D states decay spontaneously to the 6P states, which emit visible photons by fluorescence (blue arrows) that are detected by a spectrometer. **Right:** Controlled populations of the 5D3/2 and 5D5/2 electronic states of atomic rubidium, as a function of the evolution time under the influence of an optimally shaped laser pulse.

Quantum control mechanism identification (MI) through Hamiltonian encoding [117–124] uses signal processing techniques to obtain the amplitudes of all contributing interferences simultaneously. This is achieved by encoding the dipole operator with a timelike variable and taking the Fourier transform [117]. We propose to extend current MI techniques so they can be applied to MIMO quantum control systems. Thus far they have only been applied to single output control. We will develop mechanism identification methodologies to interrogate the pathways responsible for control in MIMO quantum control problems and to assess robustness of the required multi-photon interferences to noise, in order to answer Challenge question 2b. Specifically, for those molecular systems studied in Aim 1 that displayed slow convergence even for single observable control, the control mechanism for the optimal field will be obtained via Hamiltonian encoding (**Fig. 6**). The sensitivity of each required multipathway interference to laser noise will be assessed numerically. Related methods for sensitivity analysis based on series expansions of nonlinear dynamics have been employed in the classical control literature [125, 126], but these have not employed MI techniques.

In order to improve the robustness of optimal laser control fields, two types of quantum robust control strategies will be examined. In the first, a control algorithm will be developed that seeks input fields satisfying a worst-case performance bound suitable to the target objective [127, 128], whereas in the second, a stochastic optimal control strategy will be applied that maximizes the expected performance measure while minimizing its variance [126, 129, 130]. Robust control techniques have not yet been introduced for the laser control of molecular dynamics. Within the traditional engineering literature, the role of wave interferences in robustness has not been studied, since classical mechanical systems do not exhibit unitary evolution. In the quantum engineering literature, the robust control strategies proposed have been specialized to low-dimensional systems like nuclear spin states (NMR). General algorithms for robust control for bilinear quantum systems have not yet been proposed.

These numerical studies will be complemented with new *analytical* techniques for assessing the robustness of optimal control strategies to laser noise and parameter uncertainty. Up to this time, there

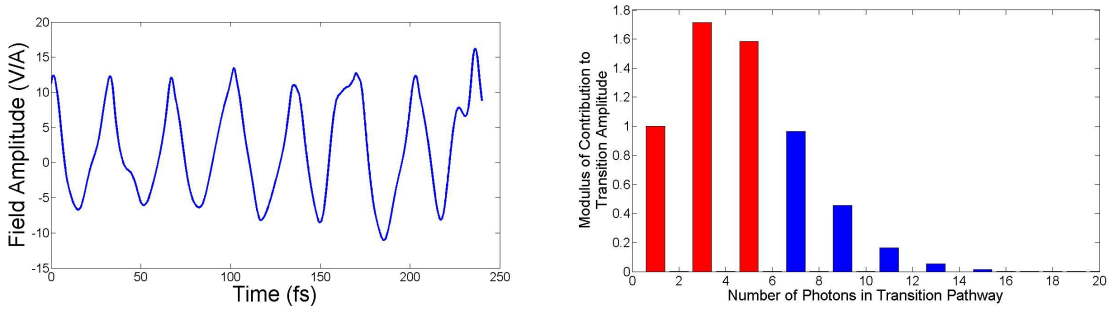

Figure 6. Mechanism identification for controlled quantum dynamical propagators. **Left:** Optimal field for generation of a 2-qubit quantum logic gate on rotational eigenstates of the CO molecule. **Right:** Contribution of various orders in perturbation theory (x-axis) to the 1,2-th element of the dynamical propagator. The first few orders (red) are the only ones accounted for in SISO two-pathway interference schemes.

have been no proposals in the quantum engineering literature for how to quantify the number of orders in perturbation theory required to robustly control quantum states in atoms and molecules of various identities. We propose such a method, based on principles of controllability. Controllability is determined by the equation of motion as well as properties of the Hamiltonian. For a closed quantum system (2) with unitary dynamics, propagator controllability implies that for any unitary operator W there exists a finite time T and a control $\varepsilon(t)$ such that W = U(T), where U(T) is the propagator. For an N-level closed system, a necessary and sufficient condition for propagator controllability is that the dynamical Lie group of the system (i.e., the Lie group generated by the system's Hamiltonian) be the entire unitary group of propagators [45, 131–133]. This so-called "Lie algebra rank condition" can be checked by taking repeated commutators of the drift and control Hamiltonians until there are no more linearly independent basis matrices. We propose to introduce a quantity called the *dynamical Lie algebra depth* that is defined as the number of commutators required to span this algebra. The depth may differ considerably for different molecules. We postulate that systems with greater Lie algebra depth generally require more energy to control and are more difficult to steer in the presence of parameter uncertainty and laser noise. This is because according to the Magnus expansion [134] for the generator iA_t of the unitary propagator U_t, i.e.,

$$iA_t\big(\varepsilon(\cdot)\big) = -i\big(H_0 - \mu\varepsilon(t)\big) + \frac{1}{2!}\big[H_0,\mu\big]\int_0^t\int_0^t \varepsilon(t')\,\varepsilon(t'')\,dt'\,dt'' \quad \ldots$$

(working in units hbar=1), the directions represented by higher-order Lie brackets are associated with higher powers and multiple integrals of the electric field. It is easy to see from this expression that nonresonant higher-order transitions - which exploit more wave interferences originating from multiphoton pathways - are more sensitive to uncertainties in dipole matrix elements, since many such elements are involved in the transition dynamics.

The notion of dynamical Lie algebra depth will be employed as an analytical measure of pathway robustness, in order to predict which molecular systems will be most amenable to open loop QOCT due to their insensitivity to parameter uncertainty and noise. This analytical measure will be validated by comparison to the above numerical results using MI. We will systematically investigate the mechanisms of control fields displaying varying degrees of robustness. Our preliminary results indicate that control of vibrational transitions requires higher-order pathways and more delicate wave interferences than control of rotational transitions, and is more sensitive to laser noise as well. This is consistent with our finding that the Lie algebraic depth of vibrational molecular systems is higher than that of rotational molecular systems [135].

Aim 3: Optimal molecular system identification.
Application of QOCT requires accurate estimates of the time-independent Hamiltonian matrices in equation (2). Prior Hamiltonian identification studies [136–144] applied least squares minimization of a performance measure quantifying the difference between the model-implied expectation values and the measured expectation values. Least squares estimation cannot achieve lower error bounds on parameter estimates, and hence is not suitable for robust control applications. In Aim 3, we will apply system identification methods [7] based on maximum likelihood [145] and Bayesian estimation [146], in conjunction with optimally tailored laser pulses, to improve atomic Hamiltonian parameter estimates and hence answer Challenge question 3.

In quantum mechanics, the same measurement made at different times observes the molecule from different "reference frames", which can be represented by unitary matrices [147]. By appropriate application of tailored laser pulses, the molecular wave function can be made to rotate into a reference frame that maximizes the information obtained from the measurement and hence the accuracy of state parameter estimates. We have shown how appropriate choice of reference frame can minimize state estimation error [83]. Concurrently, our prior work on dynamical propagator QOCT [79] has shown how the optimal reference frame can be generated by proper choice of laser pulse. We propose to combine these findings to achieve optimal system (Hamiltonian) identification. The optimal laser pulses and measurement times for a set of n states $\psi(t_1),...,\psi(t_n)$ of the molecule will be computed using QOCT; each measurement time corresponds to the duration of a femtosecond laser pulse. Then, the likelihood of the system parameters given the measured observations will be maximized numerically using the algorithms applied in [83]. This method will be applied to atomic Rb in computer simulations, with simulated measurements of the populations of the two excited states 5D3/2 and 5D5/2; These populations which can be measured experimentally by fluorescence (**Fig. 5**). We will iterate between cycles of optimal pulse generation and estimation in order to converge at accurate system parameters.

In order to obtain still more accurate confidence intervals on the parameter estimates, we will also apply a Bayesian estimation method [148], similar to that described in [83], within the above framework. Bayesian confidence intervals are rigorous for small sample sizes [146] since they are based on numerical simulation. Moreover, through the specification of a prior plausibility distribution, prior information about the system parameter (based on *ab initio* electronic structure calculations) can be incorporated into the estimation procedure. This renders the parameters completely identifiable. The prior plausibility distribution of the Hamiltonian parameters will be updated to the posterior plausibility distribution based on the measurements. The estimates and confidence intervals will then be obtained through Markov Chain Monte Carlo (MCMC) sampling from the posterior distribution of the Hamiltonian parameters [142, 143], using a Gaussian prior centered at the parameters obtained from two-electron reduced density matrix (RDM) calculations of atomic Rb electronic states [150].

Aim 4: Integrated open loop and adaptive feedback quantum control

In Aim 4, we will apply parameter estimate distributions obtained in Aim 3 along with MIMO optimal control and robustness analysis methods from Aims 1 and 2 to develop an integrated open loop / adaptive feedback approach to experimental MIMO quantum control. The adaptive feedback component will leverage the ultrashort time scales of quantum dynamics (the same factor limiting the application of real-time feedback approaches), which enables large numbers of successive experiments. For problems such as multiobservable [78, 80] or propagator [151, 152] control, QOCT is essential for obtaining an initial guess for the control field, since estimating the entire system propagator or multiple state populations experimentally at each online AFC step is expensive. Hence it is desirable to limit the number of required AFC iterations and rely more heavily on open loop methods, using accurate Hamiltonian parameter estimates. For larger systems where the Hamiltonian estimation error can be considerable (more likely with large molecules), QOCT may be more useful as a means of obtaining an initial guess for the optimal control, which can then be improved by relying heavily on online AFC refinement. This is feasible for problems involving one to three controlled outputs.

First, robust and stochastic optimization techniques described in Aim 2 will be applied in simulations given the Hamiltonian parameter estimates generated in Aim 3. Field noise will be modeled in terms of the known frequency stability of the Ti:sapphire laser provided by the manufacturer and the phase uncertainty of the LCM pulse shaper. The optimization algorithms used will be robust extensions [153] of the deterministic homotopy tracking algorithms we previously developed (Preliminary Results). To our knowledge, no prior studies have considered the problem of maximizing robustness in the presence of parameter uncertainties obtained from Hamiltonian estimation of atomic or molecular systems, nor in the presence of laser field noise spectra estimated from experimental sampling of laser fields.

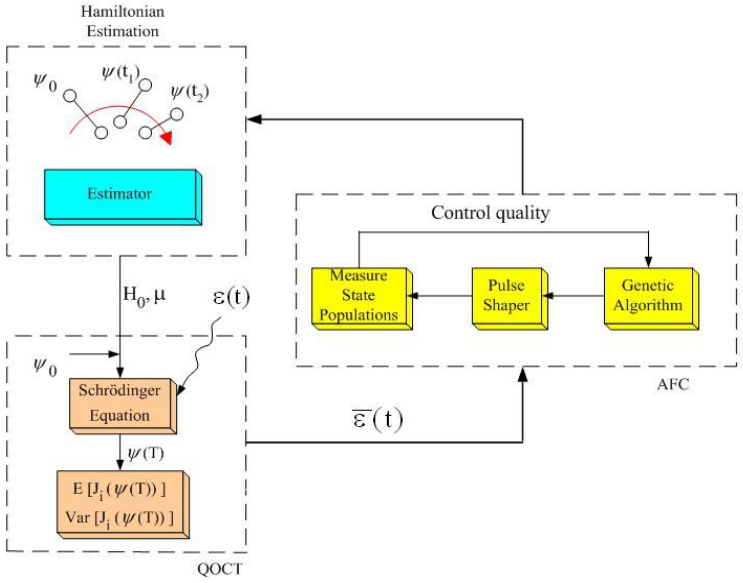

Figure 7. Integrated open loop / adaptive refinement scheme for control of quantum atomic and molecular dynamics. Counterclockwise from top: **1)** Hamiltonian parameter estimates and associated confidence intervals for the atom/molecule are obtained by applying maximum likelihood or Bayesian estimation to observations of state populations (e.g., fluorescence from Rb 6P states). **2)** Parameter distributions are applied in QOCT calculations of an optimal laser field that will drive components of the atomic state to desired values (e.g., target populations of Rb 5D states). A robust field is obtained by maximizing the expectation value of the performance measure while minimizing its variance. **3)** The resulting laser field is generated on a Ti:sapphire laser and the performance measure is refined by AFC using an online multiobjective evolutionary algorithm.

Due to the computational expense of these numerical methods, they will be applied only to those molecules and multiobservable objectives that were found in Aim 1 to display favorable search effort for steepest ascent algorithms. These are the control problems for which the QOCT-derived laser fields can be efficiently refined via adaptive feedback techniques. Atomic Rb will be the priority since its Hamiltonian parameters have been extensively validated. From the set of diatomic molecules HCl, CO, and LiRb, those found to have lower Lie algebra depth in Aim 2 will be chosen for study, since these will display greater robustness to parameter uncertainty. Multiobjective evolutionary algorithms will be used to simulate the AFC refinement process for these systems [106, 107, 109].

The molecular systems and multiobservable performance measures that can be adaptively refined within a desired tolerance in simulations can then be studied in the laboratory. Within the scope of this proposal, only atomic Rb control will be examined experimentally. The populations of the Rb 5D3/2 and 5D5/2 states will be simultaneously controlled in a Rb vapor cell by generating the QOCT-predicted pulse shapes using a Ti:sapphire laser centered at 780 nm with a bandwidth of 36 nm, equipped with 128-pixel liquid crystal spatial light modulator. These state populations will be measured by visible fluorescence from the states 6P1/2 and 6P3/2, to which the target states respectively decay (**Fig 5**). We will determine if the predicted error bars on the performance measure contain the values obtained via the fluorescence measurements. If not, the pulses will be refined online by AFC using an integrated computer system running the MOEA in Labview. If control fidelity is still inadequate, Hamiltonian estimates will be improved in two ways: a) more cycles of MCMC for Bayesian estimation; b) more optimal choice of measurements in Aim 3. If the fidelity cannot be suitably refined, we will replace the Hamiltonian parameter estimates from Aim 3 with *ab initio* parameters calculated using RDM theory with a time-

varying potential surface that directly accounts for the effect of the laser pulse on the electronic structure of the molecule, beyond the dipole approximation [154].

The design cycle (**Fig. 7**) will be repeated until convergence to the desired fidelity is achieved. Pending success, four Rb state populations - those of the 5D3/2, 5D5/2, 6D3/2, and 6D5/2 states - will be subjected to the same procedure. We anticipate this will require more accurate Hamiltonian estimates and less reliance on AFC. In future work, objectives from Aim 1 displaying more unfavorable scaling, and Hamiltonians from Aim 2 with greater Lie algebra depth will be subjected to the same procedure. The ultimate goal is to identify the number of cycles of the design process necessary to achieve MIMO control of arbitrary numbers of observables in molecular systems.

V. RESULTS FROM PRIOR NSF SUPPORT

PI's Ph.D. work (2002) at Princeton University was supported by a NSF Fellowship. This work resulted in several publications including one book chapter (In: PCR Technology: Current Innovations, 2nd Edition. Weissensteiner, HG Griffin and A Griffin, Eds. CRC Press Boca Raton, FL, 2003), and three U.S. Patents (US Patent 7,772,383 B2 issued 2010; US Patent 7,276,357 issued 2007; and US 6,949,368 issued 2005). This process (Chemical PCR) is now extensively used in research laboratories worldwide and is also being licensed by Celera/Abbott Diagnostics for their Fragile X diagnostic kits and by New England Biolab for use in various molecular diagnostic applications.

VI. BROADER IMPACT: INTEGRATION OF RESEARCH AND EDUCATION

In a broad sense, integration of research and education has four dimensions. These are: a) Impact of the research on the society; b) Dissemination of research results c) Integration research with teaching; and d) Compatibility of research-cum-teaching plans with the mission, goals and resources of the university.

a. Impact on the society.

This project is a part of my broad research-cum-teaching agenda in Control Systems, particularly in the field of Quantum Control and Quantum Estimation theory. Realizing the potential of this emerging field, the national research council (NRC) has put *Controlling the Quantum World* at the forefront of its 10-year agenda in atomic and molecular physics, and the US Department of Energy (DOE) has linked four of its *Five Grand Challenges* in energy science on quantum control. This project aims at advancing the cause of this broad national priority. In particular, coherent control of quantum systems has wide-ranging applications in a future economy based on sustainable manufacturing and energy production. The present proposal focuses on applications to chemical engineering. Here, it is remarkable that coherent manipulation of quantum systems via photonic reagents is the only methodology for the control of chemical reactivity that has been shown to be capable of achieving (at least in theory) any type of chemical transformation that is permissible according to the laws of quantum mechanics. Such selectivity can enable new types of bond cleavage and rearrangement reactions [55-59] that exploit intermediate states impossible to achieve with conventional catalysts, minimizing the production of environmentally hazardous by-products. In another application, coherent control can discriminate one particular chemical species within a background of any number of structurally similar species, either for chemical reactions or molecular identification (optimal spectroscopy). Hazardous chemical species can be identified in the presence of arbitrarily similar, benign species – thus redefining the limits of spectroscopy. In the domain of energy production, it has recently been found [60-62] that nearly 100% efficiency of energy transduction in photosynthesis originates in controlled quantum transport. As such, quantum control engineering has the potential to redefine the limits of efficiency of artificially designed photovoltaic devices.

Given the implications of my research for sustainable chemical manufacturing, while at Purdue I was a) the faculty advisor for the Purdue Chemical Engineering Sustainability Initiative (2009-2011); b) advisor to PhD students on environmental sustainability issues; and c) an industry advisor for research on green technologies. To raise awareness in this matter, I organized departmental invited seminars on chemical engineering sustainability (e.g., ACS Green Chemistry Institute Director Robert Peoples).

b. Dissemination of research results.

Our goal here will be to make the results of our research findings reach and benefit the broadest possible audience. In this regard our first and obvious approach will be to publish our results in scholarly journals and/or incorporate them in a book. I have been invited by Taylor & Francis to write a textbook, *Quantum Control Engineering*, which I am planning to write with Prof H. Rabitz of Princeton University. The book will include the latest results both from my research as well as those of others. My group is also currently developing a Quantum Scientific Library (QSL) that includes genetic and evolutionary algorithms (MOEAs) for AFC of atomic and molecular dynamics, as well as gradient-based algorithms for open loop control optimization. In addition, one of my graduate students is developing a web platform for Open Academic Innovation, which will enable university students from around the world to log on to my group's servers and participate in simulated quantum control experiments using the QSL. In this connection it is important to note that as university learning is becoming increasingly global in scope, there is a need to actively promote and partake in exchange of critical operational practices of universities outside our national boundaries. Our Open Academic Innovation platform offers such an opportunity.

c. Integration with Teaching.

The most straightforward way of integrating my research with teaching will be to include it, along with other recent advances in the field, in the curricula of the undergraduate and graduate courses that I teach in Control Systems and Quantum Control. My graduate courses in Quantum Control draw students from various disciplines – physics, mechanical engineering, electrical engineering, aeronautical engineering, electrical engineering and, of course, chemical engineering – some of whom are specifically interested in nanoscale applications.

The other important issue of integration involves reaching out to the K-12 level. We are failing miserably in attracting students, particularly minority students, to STEM education (*Science* 331: 125, 2011). The problem seems to be how to convince students to study science, which is perceived to be hard to learn and yet a degree in science often does not pay more than a degree in softer subjects like business and humanities. Accordingly, in order to change the current situation, we ought to be able to instill in our students the lure of a larger cause, the motive force of which is not simply greed for money. In case of minority students, in particular, we must intervene at the junior through high school levels and be able to convince them that science education is fun and it is also at the heart of the interest of their own ethnicity, their country, and their individual self-respect.

In line with the above logic, my plans for educational outreach will consist of the following steps, the emphasis being on attracting minorities to science.

i) Enlisting the Support and Cooperation of Schools: I will focus on the public school system in Upper St. Clair, PA (USC), a suburb of Pittsburgh, where I received my schooling. While I was a senior there I won first prize at the Intel International Science and Engineering Fair and also was named to USA Today's National Top 20 High School students. I am an indoctrinated member of the Upper St. Clair Academic Hall of Fame. Accordingly, my recommendations carry weight at this school, and I will take advantage of this position to achieve my educational outreach goal. I am assured of cooperation of the school board the school's senior science teacher, Mr. Edward Callahan, who mentored me during my science fair competitions.

ii) Organizing and holding science workshops at the schools. We will invite local science teachers and students to attend these workshops. These workshops will focus on explaining in very simple terms the principles of chemical manufacturing via direct laser manipulation of molecules, and will contrast these techniques with the conventional approaches to catalysis that are taught in mainstream chemistry courses. To increase student participation, we will ask the school to grant credit for attending these workshops.

iii) Massively open online education on quantum manufacturing and energy harvesting. After the workships, we will use our online teaching platform (the same platform that we use to operate Open

Academic Innovation) to continue an immersive educational experience for our workshop participants, with ongoing video tutorials and demonstrations of laser-based chemical manufacturing. We will explain to them how these experiments one day may pave the way to solving global energy problems (artificial photosynthesis) or achieve environmental sustainability (chemical reactions without forming wasteful by-products). Our online platform is already hosted on the Amazon cloud, and will allow tens of thousands of students and teachers from across to US to participate and communicate. It will be launching its first online tutorials in Spring 2013. Our online teaching platform will enable the distribution of knowledge far beyond the boundaries of local Pittsburgh schools. We expect the social networking and collaboration features of the platform to rapidly spread the user base across the US.

Iv) Preparing for Science Fairs. I can speak from my own personal experience that participation in science fairs is a powerful means of putting students on the path for lifelong pursuits of science. From our workshop we will select four middle-to-high school minority students and their science teachers and have them conduct quantum simulation experiments under the guidance of our graduate students. They will then present their projects at regional and national science fairs. Simulations of controlled molecular dynamics using the QSL will be displayed in streaming video format, which the teachers and others from outside the school can access online.

d. Compatibility of teaching plans with the missions, goals and resources of my university.
The strategic goals of the Department of Chemical Engineering at CMU are embedded in its mission, which calls for achieving global recognition thorough leadership, excellence and innovation with emphasis on diversity and respect. It is clear from the above mission statement that my goals regarding broader impact of my research and my plan for integrating research with education, are compatible with and fully supported by the missions, goals and resources of my organization. I am also a faculty member in the Center for Advanced Process Decision-Making at CMU, which is leader in the development of new systems engineering tools and their use in new applications. As such, CMU is an ideal venue to carry out the proposed research and teach the subject.

VII. TIMELINE AND RESOURCE ALLOCATION.
The following table gives a brief outline of specific targets of the project and the personnel resources that will be allocated to each target.

A. Resource allocation

Year	**Project Goals, Deliverables**	**Allocation of Personnel**
1	Development of MIMO quantum optimal control theory for atoms and molecules [**Aim 1**]	1 Graduate Student (100%)
	Mechanism identification of controlled quantum dynamics: methods for assessing robustness to noise/parameter uncertainty [**Aim 2]**	1 Graduate Student: (100%)
2	Optimal molecular system identification [**Aim 3**]	1 Graduate Student (100%)
3	Integrated open loop/adaptive feedback quantum control [**Aim 4**]	1 Graduate Student (100%)

B. Timeline: 1.1 Single observable control optimization (Rb, CO, HCl) 6 mo; **1.2** Multiple observable control optimization (Rb) 12 mo; **2.1** Mechanism identification (MI) for multiobservable control 6 mo; **2.2** Sensitivity analysis, comparison of Lie algebraic depth to MI 12 mo; **2.3** Stochastic and robust control optimization for Rb, HCl 12 mo; **3.1** Maximum likelihood Hamiltonian parameter estimation (Rb) 20 mo; **3.2** Bayesian Hamiltonian parameter estimation (Rb) 24 mo; **4.2** Integrated QOCT/AFC control of Rb 36 mo.