

Report Title

Final Report: RESEARCH AREA 7.1: Exploring the Systematics of Controlling Quantum Phenomena

ABSTRACT

This research is concerned with the theoretical and experimental control quantum dynamics phenomena. Advances include new algorithms to accelerate quantum control as well as provide physical insights into the controlled dynamics. The latter research includes the demonstration of a new protocol for extracting information about control mechanisms directly from laboratory data without the need for simulations. A special focus was also placed on understanding the topology of the underlying fundamental quantum control landscapes, as they dictate the ease of finding effective control fields. A new direction was opened up considering the material or molecular portions of the Hamiltonian as part of the controls along with an applied field. Finally, a review was prepared on the state of quantum control research including some speculation on directions ahead.

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 20.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

08/21/2014 16.00 H. Rabitz, R.-B Wu, T.-S. Ho, K. Moore Tibbetts, X. Feng. Fundamental Principles of Control Landscapes with Applications to Quantum Mechanics, Chemistry, and Evolution, Berlin: Springer-Verlag, (01 2014)

TOTAL: 1

Patents Submitted

Patents Awarded

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>	
David Hocker	
Total Number:	1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Genyuan Li	0.30
FTE Equivalent:	0.30
Total Number:	1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Interactions with Dr. Paul Pellegrino and Dr. Kurt Jacobs, ARL

Final Progress Report 07/31/2013 – 07/31/2016

Research Area 7.1: Exploring the Systematics of Controlling Quantum Phenomena – 63805-CH

Herschel Rabitz

ABSTRACT

This research is concerned with the theoretical and experimental control quantum dynamics phenomena. Advances include new algorithms to accelerate quantum control as well as provide physical insights into the controlled dynamics. The latter research includes the demonstration of a new protocol for extracting information about control mechanisms directly from laboratory data without the need for simulations. A special focus was also placed on understanding the topology of the underlying fundamental quantum control landscapes, as they dictate the ease of finding effective control fields. A new direction was opened up considering the material or molecular portions of the Hamiltonian as part of the controls along with an applied field. Finally, a review was prepared on the state of quantum control research including some speculation on directions ahead.

SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

Single-Molecule Electric Revolving Door

L.-Y. Hsu, E. Li, and H. Rabitz, *Nano. Lett.*, 13, 5020-5025, (2013)

This work proposes a new type of molecular machine, the single-molecule electric revolving door, which utilizes conductance dependence upon molecular conformation as well as destructive quantum interference. We perform electron transport simulations in the zero-bias limit using the Landauer formalism together with density functional theory. The simulations show that the open- and closed-door states, accompanied by significant conductance variation, can be operated by an external electric field. The large on-off conductance ratio ($\sim 10^5$) implies that the molecular machine can also serve as an effective switching device. The simultaneous control and detection of the door states can function at the nanosecond scale, thereby offering a new capability for molecular-scale devices.

Exploring control landscapes for laser-driven molecular fragmentation

K. Moore Tibbetts, X. Xing, and H. Rabitz, *J. Chem. Phys.*, 139, 144201 (2013)

The growing success of quantum optimal control experiments is attributed to the favorable topology of the *control landscape*, which specifies the functional relationship between the physical objective and the control variables describing the applied field. This work explores experimental control landscapes expressing the yields of dissociative ionization products from halogenated hydrocarbons in terms of three control variables specifying a polynomial expansion of the spectral phase of the ultrafast laser pulse. Many of the landscapes in this work exhibit features predicted by control landscape theory,

including a lack of suboptimal extrema, i.e., “traps” and the presence of connected optimal level sets, i.e., continuously varying values of the control variables that produce an optimal objective yield. Placing significant constraints on the control resources, particularly by limiting the laser pulse energy, is found to distort the underlying landscape topology. The control landscapes from a diverse, yet related family of halogenated hydrocarbons are shown to possess similar features, reflecting the chemical similarity of the compounds.

Exploring quantum control landscape structure

A. Nanduri, A. Donovan, T.-S. Ho, and H. Rabitz, Phys. Rev. A, 88, 033425, (2013)

A common goal of quantum control is to maximize a physical observable through the application of a tailored field. The observable value as a function of the field constitutes a quantum-control landscape. Previous papers have shown, under specified conditions, that the quantum-control landscape should be free of suboptimal critical points. This favorable landscape topology is one factor contributing to the efficiency of climbing the landscape. An additional complementary factor is the landscape structure, which constitutes all nontopological features. If the landscape’s structure is too complex, then climbs may be forced to take inefficient convoluted routes to find optimal controls. This paper provides a foundation for understanding control-landscape structure by examining the linearity of gradient-based optimization trajectories through the space of control fields. For this assessment, a metric $R \geq 1$ is defined as the ratio of the path length of the optimization trajectory to the Euclidean distance between the initial control field and the resultant optimal control field that takes an observable from the bottom to the top of the landscape. Computational analyses for simple model quantum systems are performed to ascertain the relative abundance of nearly straight control trajectories encountered when optimizing a state-to-state transition probability. The distribution of R values is found to be centered near remarkably low values upon sampling large numbers of randomly chosen initial control fields. Additionally, a stochastic algorithm is used to locate many distinct initial control fields, each of which corresponds to the start of an almost straight control trajectory with $R \simeq 1.0$. The collected results indicate that quantum-control landscapes have very simple structural features. The favorable topology and the complementary simple structure of the control landscape provide a basis for understanding the generally observed ease of optimizing a state-to-state transition probability.

Exploring the transition-probability-control landscape of open quantum systems: Application to a two-level case

F. Yang, S. Cong, R. Long, T. Ho, R. Wu, and H. Rabitz, Phys. Rev. A, 88, 033420, (2013)

This paper explores the state-to-state transition-probability-control landscape for n -level open quantum systems governed by the Lindblad equation. For generic two-level systems, we show analytically that the control landscape does not possess critical points in the space of square-integrable control fields. Numerical simulations show that for a given target state the transition probability reaches its highest value at a particular finite time, and the corresponding control contains temporal subpulses, similar to that for the time optimal control of analogous closed quantum systems with unbounded controls.

Sampled-data design for robust control of a single qubit

D. Dong, D. Peterson and H. Rabitz, IEEE Trans. on Auto. Control, **58**, 2654, (2013)

This technical note presents a sampled-data approach to the robust control of a single qubit (quantum bit). The required robustness is defined using a sliding mode domain and the control law is designed offline and then utilized online with a single qubit having bounded uncertainties. Two classes of uncertainties are considered involving the system Hamiltonian and the coupling strength of the system-environment interaction. Four cases are analyzed in detail including without decoherence, with amplitude damping decoherence, phase damping decoherence and depolarizing decoherence. Sampling periods are specifically designed for these cases to guarantee the required robustness. Two sufficient conditions are presented for the design of a unitary control for the cases without decoherence and with amplitude damping decoherence. The proposed approach has potential applications in quantum error-correction and in constructing robust quantum gates.

Sampling-based learning control of inhomogeneous quantum ensembles

C. Chen, D. Dong, R. Long, I. Petersen, and H. Rabitz, Phys. Rev. A, **89**, 023402, (2014)

Compensation for parameter dispersion is a significant challenge for control of inhomogeneous quantum ensembles. In this paper, we present the systematic methodology of sampling-based learning control (SLC) for simultaneously steering the members of inhomogeneous quantum ensembles to the same desired state. The SLC method is employed for optimal control of the state-to-state transition probability for inhomogeneous quantum ensembles of spins as well as Λ -type atomic systems. The procedure involves the steps of (i) training and (ii) testing. In the training step, a generalized system is constructed by sampling members according to the distribution of inhomogeneous parameters drawn from the ensemble. A gradient flow based learning and optimization algorithm is adopted to find an optimal control for the generalized system. In the process of testing, a number of additional ensemble members are randomly selected to evaluate the control performance. Numerical results are presented, showing the effectiveness of the SLC method.

Invariance of quantum optimal control fields to experimental parameters

E. de Lima, T.-S. Ho, and H. Rabitz, Phys. Rev. A, **89**, 043421, (2014)

We consider an ensemble of closed finite-level systems described by a density matrix where the goal is to find an optimal control field to maximize the expectation value of an observable. The eigenvalues of the initial density matrix are assumed to depend on an experimental parameter (e.g., the temperature), whereas the eigenvalues of the observable may depend on an additional application-specific experimental parameter. We show that an optimal control will remain optimal for all such experimental parameters, if the relative ordering, by magnitude, of the eigenvalues of the initial density matrix as well as of the observable is unaltered regardless of the parameter values. More generally, we show like invariance of a control associated with any particular critical point on the corresponding control landscape. The invariance of control laser fields with respect to temperature is illustrated for vibrational excitation of diatomic molecules and photoassociation of atoms.

Exploring the Hamiltonian inversion landscape

A. Donovan and H. Rabitz, *Phys. Chem. Chem. Phys.*, **16**, 15615, (2014)

The identification of quantum system Hamiltonians through the use of experimental data remains an important research goal. Seeking a Hamiltonian that is consistent with experimental measurements constitutes an excursion over a Hamiltonian inversion landscape, which is the quality of reproducing the data as a function of the Hamiltonian parameters. Recent theoretical work shows that with sufficient experimental data there should be local convexity about the true Hamiltonian on the landscape. The present paper builds on this result and performs simulations to test whether such convexity is observed. A gradient-based Hamiltonian search algorithm is incorporated into an inversion routine as a means to explore the local inversion landscape. The simulations consider idealized noise-free as well as noise-ridden experimental data. The results suggest that a sizable convex domain exists about the true Hamiltonian, even with a modest amount of experimental data and in the presence of a reasonable level of noise.

Local topology at limited resource induced suboptimal traps on the quantum control landscape

A. Donovan, V. Beltrani, and H. Rabitz, *J. Math. Chem.*, **52**, 407, (2014)

In a quantum optimal control experiment, a system is driven towards a target observable value with a tailored external field. The underlying quantum control landscape, defined by the observable as a function of the control variables, lacks suboptimal extrema upon satisfaction of certain physical assumptions. This favorable topology implies that, upon climbing the landscape to seek an optimal control field, a steepest ascent algorithm should not halt prematurely at suboptimal critical points, or traps. One of the important aforementioned assumptions is that no limitations are imposed on the control resources. Constraints on the control restricts access to certain regions of the landscape, potentially preventing optimal performance through convergence to limited resource induced suboptimal traps. This work develops mathematical tools to explore the local landscape structure around suboptimal critical points. The landscape structure may be favorably altered by systematically relaxing the control resources. In this fashion, isolated suboptimal critical points may be transformed into extensive level sets and then to saddle points permitting further landscape ascent. Time-independent kinematic controls are employed as stand-ins for traditional dynamic controls to allow for performing a simpler constrained resource landscape analysis. The kinematic controls can be directly transferred to their dynamic counterparts at any juncture of the kinematic analysis. The numerical simulations employ a family of landscape exploration algorithms while imposing constraints on the kinematic controls. Particular algorithms are introduced to meet the goals of either climbing the landscape or seeking specific changes in the topology of the landscape by relaxing the control resources.

Gate Control of the Conduction Mechanism Transition from Tunneling to Thermally Activated Hopping

L.-Y. Hsu, N. Wu, and H. Rabitz, *J. Phys. Chem. Lett.*, **5**, 1831, (2014)

We explore gate control of electron transport through molecules with different repeat units. In the framework of reduced density matrix theory, the computational results show

(i) exponential decay in the tunneling regime and (ii) Arrhenius behavior and similar activation energies in the hopping regime, which are qualitatively consistent with experimental observations. Moreover, the gate enables tuning of the activation energy, indicating that the continuous transition from tunneling to hopping could be experimentally observed. The activation energy–gate voltage characteristics are introduced to investigate different conduction regimes.

Fundamental Principles of Control Landscapes with Applications to Quantum Mechanics, Chemistry, and Evolution

H. Rabitz, R.-B Wu, T.-S. Ho, K. Moore Tibbetts, and X. Feng, *Recent Advances in the Theory and Application of Fitness Landscapes: Emergence, Complexity and Computation* 6, 6, 33, (2014)

The concept of a landscape or response surface naturally arises in applications widely ranging over the sciences, engineering and other disciplines. A landscape is the desired output as a function of a set of input variables, often of very high dimension. The relationship between the features of a landscape and the input variables is usually unknown *a priori* and often thought to be highly complex due to the anticipated intricate interactions involved. This chapter reviews recent developments in the analysis of landscape topology with the input variables considered as controls. Taking a control perspective allows for the specification of particular assumptions whose satisfaction permits a general analysis of the landscape topology. Satisfaction of these conditions leads to the conclusion that control landscapes should be devoid of suboptimal critical point traps, thereby permitting ready excursions without hindrance to the highest values of the landscape. These principles are set out in a general framework and then specifically illustrated for applications involving control in quantum mechanics, chemical and material science, and in natural and directed evolution. Perspectives are given on the significance of these findings and potential future directions for additional analysis of landscape principles.

Dynamic Dimensionality Identification for Quantum Control

J. Roslund and H. Rabitz, *Phys. Rev. Lett.*, **112**, 143001, (2014)

The control of quantum systems with shaped laser pulses presents a paradox since the relative ease with which solutions are discovered appears incompatible with the enormous variety of pulse shapes accessible with a standard pulse shaper. Quantum landscape theory indicates that the relevant search dimensionality is not dictated by the number of pulse shaper elements, but rather is related to the number of states participating in the controlled dynamics. The actual dimensionality is encoded within the sensitivity of the observed yield to all of the pulse shaper elements. To investigate this proposition, the Hessian matrix is measured for controlled transitions amongst states of atomic rubidium, and its eigendecomposition reveals a dimensionality consistent with that predicted by landscape theory. Additionally, this methodology furnishes a low-dimensional picture that captures the essence of the light-matter interaction and the ensuing system dynamics.

Efficient retrieval of landscape Hessian: Forced optimal covariance adaptive learning

O. Shir, J. Roslund, D. Whitley, and H. Rabitz, Phys. Rev. E, **89**, 063306, (2014)

Knowledge of the Hessian matrix at the landscape optimum of a controlled physical observable offers valuable information about the system robustness to control noise. The Hessian can also assist in physical landscape characterization, which is of particular interest in quantum system control experiments. The recently developed landscape theoretical analysis motivates the compilation of an automated method to learn the Hessian matrix about the global optimum without derivative measurements from noisy data. The current study introduces the forced optimal covariance adaptive learning (FOCAL) technique for this purpose. FOCAL relies on the covariance matrix adaptation evolution strategy (CMA-ES) that exploits covariance information amongst the control variables by means of principal component analysis. The FOCAL technique is designed to operate with experimental optimization, generally involving continuous high-dimensional search landscapes (≥ 30) with large Hessian condition numbers ($\geq 10^4$). This paper introduces the theoretical foundations of the inverse relationship between the covariance learned by the evolution strategy and the actual Hessian matrix of the landscape. FOCAL is presented and demonstrated to retrieve the Hessian matrix with high fidelity on both model landscapes and quantum control experiments, which are observed to possess nonseparable, nonquadratic search landscapes. The recovered Hessian forms are corroborated by physical knowledge of the systems. The implications of FOCAL extend beyond the investigated studies to potentially cover other physically motivated multivariate landscapes.

Investigating constrained quantum control through a kinematic-to-dynamic-variable transformation

A. Donovan and H. Rabitz, Phys. Rev. A, **90**, 013408, (2014)

A search for the variables that control a quantum system's dynamics occurs over a landscape, defined as the target objective as a function of the variables. Prior studies show that upon satisfaction of three specific assumptions, the topology of the landscape is free of suboptimal traps that could prematurely halt the search for an optimal control. One key assumption is free access to all necessary control variables; however, in practice, the controls are always limited in some fashion, which may result in constraint-induced traps on the landscape. This paper aims to introduce the means to systematically explore the nature of constrained controls that yield suboptimal outcomes. The procedure utilizes kinematic controls, which comprise a simple set of time-independent variables, and then performs a landscape topology-preserving transformation into corresponding dynamic controls. The equivalent landscape topology of these two formulations permits the study of a family of dynamic controls that reflect constrained control landscape behavior. In particular, constrained dynamic controls are identified as isolated points on the landscape or as suboptimal level sets. The wide range of such dynamic controls indicates the richness and complexity of constraint-induced features on the landscape.

Relation of quantum control mechanism to landscape structure

A. Nanduri, A. Donovan, T.-S. Ho, and H. Rabitz, Phys. Rev. A, **90**, 013406, (2014)

The control of quantum dynamics is generally accomplished by seeking a tailored

electromagnetic field to meet a posed objective. A particular shaped field can be thought of as specifying a point on a quantum control landscape, which is the objective as a functional of the controls. Optimizing the pulse shape corresponds to climbing the landscape, and previous work shows that the paths taken up the landscapes, guided by a gradient algorithm, are surprisingly straight when projected into the space of control fields. The direct nature of these control trajectories can be quantified by the metric $R \geq 1$, defined as the ratio of the length of the control trajectory to the Euclidean distance between its end points. The prior observation of often finding low values of R implies that the landscapes are structurally simple. In this work, we investigate whether there is a relationship between the intricacy of the control mechanism and the complexity of the trajectory taken through the control space reflected in the value of R . We use the Hamiltonian encoding procedure to identify the mechanism, and we examine control of the state-to-state transition probability. No significant correlation is found between the landscape structure, reflected in the value of R , and the control mechanism. This result has algorithmic implications, opening up the prospect of seeking fields producing particular mechanisms at little penalty in the search effort due to encountering complex landscape structure.

Conceptual inconsistencies in finite-dimensional quantum and classical mechanics

D. I. Bondar, R. Cabrera, and H.A. Rabitz, *Phys. Rev. A*, **88**, 012116, (2013)

Utilizing operational dynamic modeling [D. I. Bondar et al., [Phys. Rev. Lett. 109, 190403 \(2012\)](#)], we demonstrate that any finite-dimensional representation of quantum and classical dynamics violates the Ehrenfest theorems. Other peculiarities are also revealed, including the nonexistence of the free particle and ambiguity in defining potential forces. Non-Hermitian mechanics is shown to have the same problems. This work compromises a popular belief that finite-dimensional mechanics is a straightforward discretization of the corresponding infinite-dimensional formulation.

Wigner phase-space distribution as a wave function

D. Bondar, R. Cabrera, D. Zhdanov, and H. Rabitz, *Phys. Rev. A*, **88**, 052108, (2013)

We demonstrate that the Wigner function of a pure quantum state is a wave function in a specially tuned Dirac bra-ket formalism and argue that the Wigner function is, in fact, a probability amplitude for the quantum particle to be at a certain point of the classical phase space. Additionally, we establish that in the classical limit, the Wigner function transforms into a classical Koopman–von Neumann wave function rather than into a classical probability distribution. Since probability amplitude need not be positive, our findings provide an alternative outlook on the Wigner function's negativity.

Assessment of optimal control mechanism complexity by experimental landscape Hessian analysis: fragmentation of CH₂BrI

X. Xing, R. Rey-de-Castro, and H. Rabitz, *New J. Phys.*, **16**, 125004, (2014)

Optimally shaped femtosecond laser pulses can often be effectively identified in adaptive feedback quantum control experiments, but elucidating the underlying control mechanism can be a difficult task requiring significant additional analysis. We introduce landscape Hessian analysis (LHA) as a practical experimental tool to aid in elucidating control mechanism insights. This technique is applied to the dissociative ionization of CH₂BrI

using shaped fs laser pulses for optimization of the absolute yields of ionic fragments as well as their ratios for the competing processes of breaking the C–Br and C–I bonds. The experimental results suggest that these nominally complex problems can be reduced to a low dimensional control space with insights into the control mechanisms. While the optimal yield for some fragments is dominated by a non-resonant intensity driven process, the optimal generation of other fragments may be a difficult task requiring significant additional explanation by a non-resonant process coupled to few level resonant dynamics. Theoretical analysis and modeling is consistent with the experimental observations.

Light-driven electron transport through a molecular junction based on cross-conjugated systems

L.-Y. Hsu, D. Xie, and H. Rabitz, *J. Chem. Phys.*, **141**, 124703, (2014)

This work explores light-driven electron transport through cross-conjugated molecules with different numbers of alkenyl groups. In the framework of coherent quantum transport, the analysis uses single-particle Green's functions together with non-Hermitian Floquet theory. With realistic parameters stemming from spectroscopy, the simulations show that measurable current ($\sim 10^{-11}$ A) caused by photon-assisted tunneling should be observed in a weak driving field ($\sim 2 \times 10^5$ V/cm). Current field intensity characteristics give one-photon and two-photon field amplitude power laws. The gap between the molecular orbital and the Fermi level of the electrodes is revealed by current-field frequency characteristics. Due to generalized parity symmetry, the cross-conjugated molecules with odd and even numbers of alkenyl groups exhibit completely different current-polarization characteristics, which may provide an advantageous feature in nanoelectronic applications.

Incoherent control of open quantum systems

A. Pechen and H. Rabitz, *J. Math. Sci.*, **199**(6), 695, (2014)

This work reviews various topics in the control of open quantum systems interacting with the environment. The topics include the formulation of coherent and incoherent quantum control, analysis of control landscapes and their critical points for typical objective functionals, controllability properties, and the relation to the optimization over complex Stiefel manifolds.

Experimental observation of saddle points over the quantum control landscape of a two-spin system

Q. Sun, I. Pelczer, G. Riviello, R.-B. Wu, and H. Rabitz, *Phys. Rev. A*, **91**, 043412 (2015)

The growing successes in performing quantum control experiments motivated the development of control landscape analysis as a basis to explain these findings. When a quantum system is controlled by an electromagnetic field, the observable as a functional of the control field forms a landscape. Theoretical analyses have predicted the existence of critical points over the landscapes, including saddle points with indefinite Hessians. This paper presents a systematic experimental study of quantum control landscape saddle points. Nuclear magnetic resonance control experiments are performed on a coupled two-spin system in a ^{13}C -labeled chloroform ($^{13}\text{CHCl}_3$) sample. We address the saddles with a combined theoretical and experimental approach, measure the Hessian at each identified

saddle point, and study how their presence can influence the search effort utilizing a gradient algorithm to seek an optimal control outcome. The results have significance beyond spin systems, as landscape saddles are expected to be present for the control of broad classes of quantum systems.

Searching for quantum optimal controls under severe constraints

G. Riviello, K. Moore Tibbetts, C. Brif, R. Long, R.-B. Wu, T.-S. Ho, and H. Rabitz, Phys. Rev. A, **91**, 043401, (2015)

The success of quantum optimal control for both experimental and theoretical objectives is connected to the topology of the corresponding control landscapes, which are free from local traps if three conditions are met: (1) the quantum system is controllable, (2) the Jacobian of the map from the control field to the evolution operator is of full rank, and (3) there are no constraints on the control field. This paper investigates how the violation of assumption (3) affects gradient searches for globally optimal control fields. The satisfaction of assumptions (1) and (2) ensures that the control landscape lacks fundamental traps, but certain control constraints can still introduce artificial traps. Proper management of these constraints is an issue of great practical importance for numerical simulations as well as optimization in the laboratory. Using optimal control simulations, we show that constraints on quantities such as the number of control variables, the control duration, and the field strength are potentially severe enough to prevent successful optimization of the objective. For each such constraint, we show that exceeding quantifiable limits can prevent gradient searches from reaching a globally optimal solution. These results demonstrate that careful choice of relevant control parameters helps to eliminate artificial traps and facilitates successful optimization.

Exploring the complexity of quantum control optimization trajectories

A. Nanduri, O. Shir, A. Donovan, T.-S. Ho, and H. Rabitz, Phys. Chem. Chem. Phys., **17**, 334-347, (2015)

The control of quantum system dynamics is generally performed by seeking a suitable applied field. The physical objective as a functional of the field forms the quantum control landscape, whose topology, under certain conditions, has been shown to contain no critical point suboptimal traps, thereby enabling effective searches for fields that give the global maximum of the objective. This paper addresses the structure of the landscape as a complement to topological critical point features. Recent work showed that landscape structure is highly favorable for optimization of state-to-state transition probabilities, in that gradient-based control trajectories to the global maximum value are nearly straight paths. The landscape structure is codified in the metric $R \geq 1.0$, defined as the ratio of the length of the control trajectory to the Euclidean distance between the initial and optimal controls. A value of $R = 1$ would indicate an exactly straight trajectory to the optimal observable value. This paper extends the state-to-state transition probability results to the quantum ensemble and unitary transformation control landscapes. Again, nearly straight trajectories predominate, and we demonstrate that R can take values approaching 1.0 with high precision. However, the interplay of optimization trajectories with critical saddle submanifolds is found to influence landscape structure. A fundamental relationship necessary for perfectly straight gradient-based control trajectories is derived, wherein the gradient on the quantum control landscape

must be an eigenfunction of the Hessian. This relation is an indicator of landscape structure and may provide a means to identify physical conditions when control trajectories can achieve perfect linearity. The collective favorable landscape topology and structure provide a foundation to understand why optimal quantum control can be readily achieved.

Constrained control landscape for population transfer in a two-level system

K. Moore Tibbetts and H. Rabitz, *Phys. Chem. Chem. Phys.*, **17**, 3164-3178, (2015)

The growing success of controlling the dynamics of quantum systems has been ascribed to the favorable topology of the quantum control landscape, which represents the physical observable as a function of the control field. The landscape contains no suboptimal trapping extrema when reasonable physical assumptions are satisfied, including that no significant constraints are placed on the control resources. A topic of prime interest is understanding the effects of control field constraints on the apparent landscape topology, as constraints on control resources are inevitable in the laboratory. This work particularly explores the effects of constraining the control field fluence on the topology and features of the control landscape for pure-state population transfer in a two-level system through numerical simulations, where unit probability population transfer in the system is only accessible in the strong coupling regime within the model explored here. With the fluence and three phase variables used for optimization, no local optima are found on the landscape, although saddle features are widespread at low fluence values. Global landscape optima are found to exist at two disconnected regions of the fluence that possess distinct topologies and structures. Broad scale connected optimal level sets are found when the fluence is sufficiently large, while the connectivity is reduced as the fluence becomes more constrained. These results suggest that seeking optimal fields with constrained fluence or other resources may encounter complex landscape features, calling for sophisticated algorithms that can efficiently find optimal controls.

Molecular Series-Tunneling Junctions

K.-C. Liao, L.-Y. Hsu, C. Bowers, H. Rabitz, and G. Whitesides, *J. Am. Chem. Soc.*, **137**, 5948-5954, (2015)

Charge transport through junctions consisting of insulating molecular units is a quantum phenomenon that cannot be described adequately by classical circuit laws. This paper explores tunneling current densities in self-assembled monolayer (SAM)-based junctions with the structure $\text{Ag}^{\text{TS}}/\text{O}_2\text{C}-\text{R}_1-\text{R}_2-\text{H}/\text{Ga}_2\text{O}_3/\text{EGaIn}$, where Ag^{TS} is template-stripped silver and EGaIn is the eutectic alloy of gallium and indium; R_1 and R_2 refer to two classes of insulating molecular units – $(\text{CH}_2)_n$ and $(\text{C}_6\text{H}_4)_m$ – that are connected in series and have different tunneling decay constants in the Simmons equation. These junctions can be analyzed as a form of series-tunneling junctions based on the observation that permuting the order of R_1 and R_2 in the junction does not alter the overall rate of charge transport. By using the $\text{Ag}/\text{O}_2\text{C}$ interface, this system decouples the highest occupied molecular orbital (HOMO, which is localized on the carboxylate group) from strong interactions with the R_1 and R_2 units. The differences in rates of tunneling are thus determined by the electronic structure of the groups R_1 and R_2 ; these differences are not influenced by the order of R_1 and R_2 in the SAM. In an electrical potential model that rationalizes this observation, R_1 and R_2 contribute independently to the height of the

barrier. This model explicitly assumes that contributions to rates of tunneling from the $\text{Ag}^{\text{TS}}/\text{O}_2\text{C}$ and $\text{H}/\text{Ga}_2\text{O}_3$ interfaces are constant across the series examined. The current density of these series-tunneling junctions can be described by $J(V) = J_0(V) \exp(-\beta_1 d_1 - \beta_2 d_2)$, where $J(V)$ is the current density (A/cm^2) at applied voltage V and β_i and d_i are the parameters describing the attenuation of the tunneling current through a rectangular tunneling barrier, with width d and a height related to the attenuation factor β .

Topology of classical molecular optimal control landscapes for multi-target objectives

C. Joe-Wong, T.-S. Ho, H. Rabitz, and R. Wu, *J. Chem. Phys.*, **142**, 154115, (2015)

This paper considers laser-driven optimal control of an ensemble of non-interacting molecules whose dynamics lie in classical phase space. The molecules evolve independently under control to distinct final states. We consider a control landscape defined in terms of multi-target (MT) molecular states and analyze the landscape as a functional of the control field. The topology of the MT control landscape is assessed through its gradient and Hessian with respect to the control. Under particular assumptions, the MT control landscape is found to be free of traps that could hinder reaching the objective. The Hessian associated with an optimal control field is shown to have finite rank, indicating an inherent degree of robustness to control noise. Both the absence of traps and rank of the Hessian are shown to be analogous to the situation of specifying multiple targets for an ensemble of quantum states. Numerical simulations are presented to illustrate the classical landscape principles and further characterize the system behavior as the control field is optimized.

Gate Control of Artificial Single-Molecule Electric Machines

L.-Y. Hsu, C.-Y. Chen, E. Li, and H. Rabitz, *J. Phys. Chem. C*, **119**, 4573-4579, (2015)

Artificial molecular machines are a growing field in nanoscience and nanotechnology. This study proposes a new class of artificial molecular machines, the second-generation single-molecule electric revolving doors (2G S-MERDs), a direct extension of our previous work [Hsu, L.-Y.; Li, E.-Y.; Rabitz, H. *Nano Lett.*, 2013, *13*, 5020]. We investigate destructive quantum interference with tunneling and conductance dependence upon molecular conformation in the 2G S-MERDs by using the Green's function method together with density functional theory. The simulations with four types of functionals (PBE, PZ, PW91, and BLYP) show that the 2G S-MERDs have a large on-off conductance ratio ($>10^4$) and that their open and closed door states can be operated by an experimentally feasible external electric field (~ 1 V/nm). In addition, the simulations indicate that the potential energy difference between the open and closed states of the SMERDs can be engineered. Conductance-gate electric field characteristics are also introduced to illustrate the operation of the 2G S-MERDs.

Systematically altering the apparent topology of constrained quantum control landscapes

A. Donovan and H. Rabitz, *J. Math. Chem.* **53**, 718-736, (2015)

A quantum control experiment typically seeks a shaped electromagnetic field to drive a system towards a specified observable objective. The large number of successful experiments can be understood through an exploration of the underlying quantum control

landscape, which maps the objective as a function of the control variables. Specifically, under certain assumptions, the control landscape lacks suboptimal traps that could prevent identification of an optimal control. One of these assumptions is that there are no restrictions on the control variables, however, in practice control resources are inevitably constrained. The associated constrained quantum control landscape may be difficult to freely traverse due to the presence of limited resource induced traps. This work develops algorithms to (1) seek optimal controls under restricted resources, (2) explore the nature of apparent suboptimal landscape topology, and (3) favorably alter trap topology through systematic relaxation of the constraints. A set of mathematical tools are introduced to meet these needs by working directly with dynamic controls, rather than the prior studies that employed intermediate so-called kinematic control variables. The new tools are illustrated using few-level systems showing the capability of systematically relaxing constraints to convert an isolated trap into a level set or saddle feature on the landscape, thereby opening up the ability to find new solutions including those of higher fidelity. The results indicate the richness and complexity of the constrained quantum control landscape upon considering the tradeoff between resources and freedom to move on the landscape.

Coherent revival of tunneling

L.-Y. Hsu and H. Rabitz, *Phys. Rev. B*, **92**, 035410, (2015)

We introduce a tunneling effect by a driving field, referred to as coherent revival of tunneling (CRT), corresponding to complete tunneling (transmission coefficient = 1) that is revived from the circumstance of total reflection (transmission coefficient ≈ 0) through application of an appropriate perpendicular high-frequency ac field. To illustrate CRT, we simulate electron transport through fish-bone-like quantum-dot arrays by using single-particle Green's functions along with Floquet theory, and we explore the corresponding current-field amplitude characteristics as well as current-polarization characteristics. In regard to the two characteristics, we show that CRT exhibits entirely different features than coherent destruction of tunneling and photon-assisted tunneling. We also discuss two practical conditions for experimental realization of CRT.

Coherent Light-Driven Electron Transport through Polycyclic Aromatic Hydrocarbon: Laser Frequency, Field Intensity, and Polarization Angle Dependence

L.-Y. Hsu and H. Rabitz, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/c5cp02663f, (2015)

A laser field is a potential control tool for operating ultrafast electronic devices due to a wide variety of options such as field strength, frequency, and polarization. To investigate these variables upon electron transport through a single-molecule device, we simulate a phenyl-acetylene macrocycle (PAM) within a linear-polarized laser field using single-particle Green's functions combined with the non-Hermitian Floquet theory. In the absence of the laser field, the PAM behaves as a perfect insulator due to destructive quantum interference. In the weak-field regime, field-amplitude power laws for one-, two-, and three-photon assisted tunneling are evident in the computational results. The study reveals a range of experimentally feasible field strengths for the observation of picoampere current caused by photon assisted tunneling. In addition, we find that the light-driven current is proportional to the cosine square of the polarization angle, and

molecular electronic structure is revealed by the current-frequency characteristics. The origin of these behaviors is established using non-Hermitian Floquet perturbation analysis. The computations show that PAM-based optoelectronic switches have robust large on–off switching ratios under weak-field operating conditions, which are not sensitive to asymmetric molecule-lead couplings.

Near-time-optimal control for quantum systems

Q.M. Chen, R.-B. Wu, T.-M. Zhang, and H. Rabitz, Phys. Rev. A. 92, 063415, (2015)

For a quantum system controlled by an external field, time-optimal control is referred to as the shortest-time duration control that can still permit maximizing an objective function J , which is especially a desirable goal for engineering quantum dynamics against decoherence effects. However, since rigorously finding a time-optimal control is usually very difficult and in many circumstances the control is only required to be sufficiently short and precise, one can design algorithms seeking such suboptimal control solutions for much reduced computational effort. In this paper, we propose an iterative algorithm for finding near-time-optimal control in a high level set (i.e., the set of controls that achieves the same value of J) that can be arbitrarily close to the global optima. The algorithm proceeds seeking to decrease the time duration T while the value of J remains invariant, until J leaves the level-set value; the deviation of J due to numerical errors is corrected by gradient climbing that brings the search back to the level-set J value. Since the level set is very close to the maximum value of J , the resulting control solution is nearly time optimal with manageable precision. Numerical examples demonstrate the effectiveness and general applicability of the algorithm.

Sampling-Based Learning Control for Quantum Systems with Uncertainties

D. Dong, M. Mabrok, I. Petersen, B. Qi, C. Chen, and H. Rabitz, IEEE Trans Control Sys Tech., (2015)

Robust control design for quantum systems has been recognized as a key task in the development of practical quantum technology. In this paper, we present a systematic numerical methodology of sampling-based learning control (SLC) for control design of quantum systems with uncertainties. The SLC method includes two steps of training and testing. In the training step, an augmented system is constructed using artificial samples generated by sampling uncertainty parameters according to a given distribution. A gradient flow-based learning algorithm is developed to find the control for the augmented system. In the process of testing, a number of additional samples are tested to evaluate the control performance, where these samples are obtained through sampling the uncertainty parameters according to a possible distribution. The SLC method is applied to three significant examples of quantum robust control, including state preparation in a three-level quantum system, robust entanglement generation in a two-qubit superconducting circuit, and quantum entanglement control in a two-atom system interacting with a quantized field in a cavity. Numerical results demonstrate the effectiveness of the SLC approach even when uncertainties are quite large, and show its potential for robust control design of quantum systems.

Quantum control and pathway manipulation in rubidium

F. Gao, Y. Wang, R. Rey-de-Castro, H. Rabitz, and F. Shuang, *Phys. Rev. A*, 92, 033423, (2015)

There is an increasing interest in the extraction and control of the interfering quantum pathway amplitudes induced by control fields during laser-matter interactions. The Hamiltonian-encoding and observable-decoding (HE-OD) technique has been introduced for extracting the amplitudes of the pathways present in the dynamics and has recently been experimentally applied to the pathway manipulation of atomic rubidium. This paper theoretically explores various strategies for manipulating pathway amplitudes in the context of a laser field interacting with a multilevel system similar to atomic rubidium for both narrow-band and broadband ultrafast fields. In the perturbation regime, two second-order quantum pathways connecting the Rb states $5S_{1/2}$ and $5D_{3/2}$ dominate the dynamics, namely, $5S_{1/2} \rightarrow 5P_{3/2} \rightarrow 5D_{3/2}$ (pathway 1) and $5S_{1/2} \rightarrow 5P_{1/2} \rightarrow 5D_{3/2}$ (pathway 2). For narrow-band field control, the analysis is carried out in the time domain with the laser field including only four narrow-band envelope subpulses centered at the resonant frequencies. When the two pathways cooperate constructively, temporal oscillations appear in the ratio of the two pathway amplitudes, and we conclude in this case that the period corresponds to the detuning between transitions $5S_{1/2} \rightarrow 5P_{3/2}$ and $5P_{3/2} \rightarrow 5D_{3/2}$. For broadband field control, the dynamics are treated in the frequency domain with the laser field including both resonant and continuous nonresonant frequency components. Various control strategies based on manipulating the phase of selected spectral components are tested. Compared to the outcome from a transform limited pulse, a $\pi/2$ step scheme can increase the dynamic range of the ratio between the two pathway amplitudes by a factor of ~ 3 . A scheme that manipulates eight spectral blocks, in which the spectral boundaries depend on the resonant frequencies, can increase the ratio by several orders of magnitude. Numerical simulations show that further dividing the spectrum into hundreds of evenly spaced blocks does not significantly enhance the pathway ratio over the eight-block scheme. The quantum control of pathways investigated in this work provides valuable insights on how to incorporate known information about the structure of quantum systems for the effective reduction of quantum control complexity.

On choosing the form of the objective functional for optimal control of molecules

C. Joe-Wong, T.-S. Ho, and H. Rabitz, *J. Math. Chem.*, 54:1-9, (2015)

Optimal control techniques can be used to direct molecular dynamics to meet specified physical goals. However, the effectiveness of finding an optimal control field depends on the nature of the control landscape, defined as the objective as a functional of the control. Extensive analysis has considered the prospect of such landscapes being free of suboptimal traps for particular cases of different objective functions in both classical and quantum systems. While many typical objective functions have been shown to yield trap-free landscapes upon satisfaction of certain assumptions, this work more broadly considers the freedom in the choice of objective functionals. The latter freedom can be exploited to possibly accelerate the search for an optimal control, but we also show that the choice of functional needs to be made carefully to avoid inducing artificial landscape traps.

Quantum-control-landscape structure viewed along straight paths through the space of control fields

A. Nanduri, T.-S. Ho, and H. Rabitz, Phys. Rev. A, 93, 023427, (2016)

The dynamics of closed quantum systems may be manipulated by using an applied field to achieve a control objective value for a physical goal. The functional relationship between the applied field and the objective value forms a quantum control landscape, and the optimization process consists of a guided climb up the landscape from the bottom to the top. Two classes of landscape features are important for understanding the ease of finding an optimal control field. The first class of topological landscape features has been proven to be especially simple in that no suboptimal local maxima exist (upon satisfaction of certain assumptions), which partially accounts for the ease of finding optimal fields. Complementary to the topology, the second class of features entails the landscape structure, characterizing the sinuous nature of the paths leading to an optimal control field. Previous work found that the landscape structure is also particularly simple, as excursions up the landscape guided by a gradient algorithm correspond to nearly straight paths through the space of control fields. In this paper we take an alternative approach to examining landscape structure by constructing, and then following, exactly straight trajectories in control space. Each trajectory starts at a corresponding point on the bottom of the landscape and ends at an associated point on the top, with the observable values taken either as the state-to-state transition probability, the expectation value of a general observable, or the distance from a desired unitary transformation. In some cases the starting point is at a suboptimal critical-point saddle, with the goal, again, of following a straight field path to the optimal objective yield or another suboptimal critical point. We find that the objective value almost always rises monotonically upon following a straight control path from one critical point to another, which shows that landscape structure is very simple, being devoid of rough bumps and gnarled “twists and turns”. An analysis reveals that the generally featureless nature of quantum control landscapes can be understood in terms of the occurrence of many interfering quantum pathways contributing while traversing the landscape, essentially smoothing out the terrain. These results also provide a basis for further studies to seek a new efficient algorithm to discover optimal fields by means of taking into account the inherently smooth landscape structure.