Molecular Control Engineering: Prospects and Challenges

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Outline

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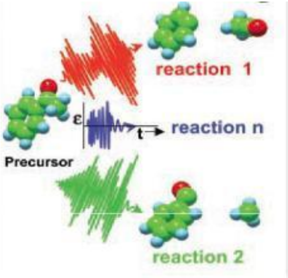
Coherent Chemistry



- Control the outcomes of state-to-state transitions and chemical reactions by exploiting coherent wave interferences in the dynamical evolution of molecules
- One of few inverse problems for control of chemical reactivity that has been solved
- Optimal Control Theory: multiparameter optimization of spectral amplitudes and phases

- *Bilinear control*: $\frac{dy}{dt} = (A + \sum_i B_i u_i(t))y(t)$; A, B are $N \times N$
- **Quantum control**: $\frac{d\psi}{dt} = -i(H_0 - \mu\varepsilon(t))\psi(t)$
- *Controllability*:

$$\mathrm{span}\{[\cdots[iH_{j_4}, [iH_{j_3}, [iH_{j_2}, iH_{j_1}]]]]\} = u(N),$$

$H_j \in \{H_0, \mu\}$.

- Formulation of control problems:

$$\max_{\varepsilon(t)} \; J(U(T)); U(T) = \mathbb{T}\exp[-i(H_0 - \varepsilon(t)\mu)]U(0),$$

1. Observable expectation value maximization: $J_1 = \mathrm{Tr}(U(T)\rho_0 U^\dagger(T)O)$
2. Control of dynamical propagators: $J_2 = -||W - U(T)||^2$

- SISO vs MIMO problems

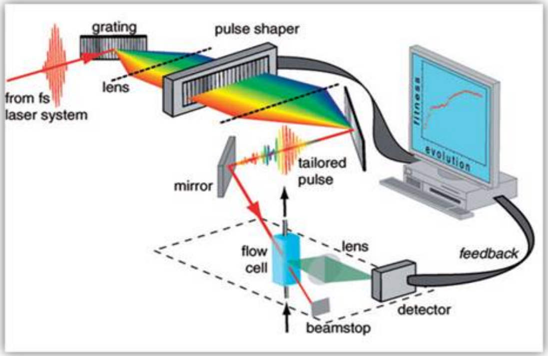


Figure: A schematic depiction of the closed-loop process employed in adaptive feedback control (AFC) of quantum phenomena. The input to the loop is an initial control guess. A current design of the laser control field is created with a pulse shaper and then applied to the sample. The outcome of the control 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.

AFC control landscapes

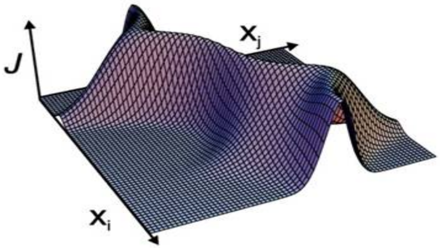


Figure: Schematic representation of a quantum control landscape. x_i, x_j indicate two of possibly many control degrees of freedom, and J denotes the objective function value. Any point on the landscape corresponds to a time-dependent control field.

- Under suitable regularity conditions, control landscape is devoid of local traps!

$$\frac{\delta J}{\delta \varepsilon(t)} = -i\mathrm{Tr}\{[\rho(T), O]\mu(t)\}$$

Prospects and Challenges for Molecular Control Engineering

Prospects
Ultrahigh duty cycle of AFC: due to ultrafast dynamics
Flexibility of pulse shapers (compare structure-based catalyst design)
Frequency stability of comb laser sources
Existence of parametric models
Linear dynamics

Challenges
Hamiltonian (system) uncertainty
Computational expense of simulation and inverse problem
Ultrafast dynamics renders time series Hamiltonian estimation nonlinear
Ultrafast dynamics renders real-time feedback difficult

Table: List of Prospects and Challenges for Molecular Control Engineering Compared to Macro-Scale Engineering Control

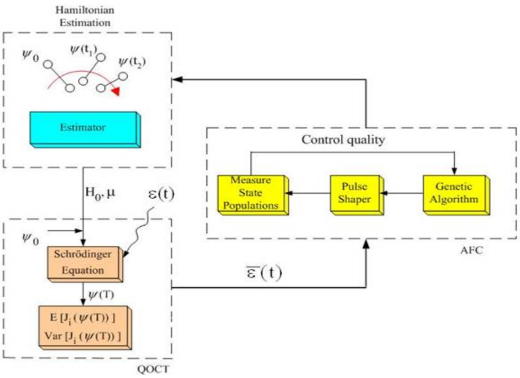


Figure: **Integrated open loop / adaptive refinement scheme for control of quantum atomic and molecular dynamics**. Counterclockwise from top: **1) Hamiltonian Parameter Estimation:** Parameter estimates and associated confidence intervals for the atom/molecule are obtained by applying maximum likelihood or Bayesian estimation. **2) Robust Control:** Parameter distributions are applied in robust control calculations of an optimal laser field that will drive components of the atomic state to desired values. **3) AFC:** 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.

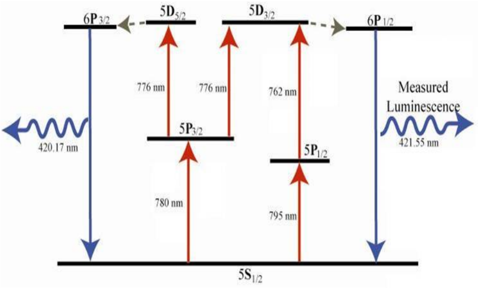
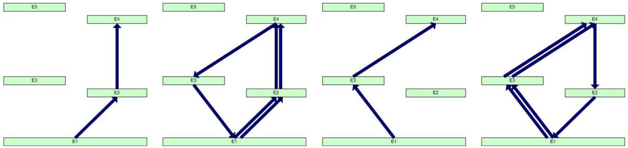


Figure: Electronic state level diagram of atomic rubidium (Rb) and dipole-allowed resonant transitions (upward arrows). 5,6 denote the electronic principal quantum number, D,P denote term symbols and the subscript denotes the total angular momentum of the electronic configuration. The excited 5D states decay spontaneously to the 6P states, which emit visible photons by fluorescence (blue arrows) that are detected by a spectrometer.

- Why Rb? Limited parameter uncertainty
- Later extend to molecular systems (e.g. LiRb dimer) with Hamiltonian uncertainty

Significant pathways for $|4\rangle$ max



(a) (b) (c) (d)

Figure: The 4 most significant Pathways in $|4\rangle$ population maximization in Rb.

- Consider for example the third-order pathway $c_{4lk1}(t) = (-\frac{i}{\hbar})^3 \langle 4| \int_0^t H_I(t')dt' |l\rangle\langle l| \int_0^{t'} H_I(t^2)dt^2 |k\rangle\langle k| \int_0^{t^2} H_I(t^3)dt^3 |1\rangle$, which passes from $|1\rangle$ to $|4\rangle$ through intermediate levels $|k\rangle$ and $|l\rangle$.
- We can extract and distinguish all such pathways by mechanism identification (Hamiltonian encoding) techniques, which label each pathway with a distinct integer.

Outline

Sources of uncertainty: input and parametric

- Which is more important? Depends on application.
  1. *Input field noise*: Spins
  2. *Hamiltonian parameter uncertainty*: Molecules with frequency comb laser sources, especially μ elements

- Engineering approaches to combat:
  1. *Input field noise*: Feedforward control, frequency domain analysis.

     Prospect: limited field noise for frequency comb sources
  2. *Parameter uncertainty*: Feedback control: $\varepsilon(t) = \varepsilon(\hat{\rho}(t))$ where $\hat{\rho}(t)$ is filtered from real-time measurement data, since $\rho(\hat{\theta}, t) \neq \rho(\theta_0, t)$; robust control: so $\rho(\hat{\theta}, t) \approx \rho(\theta_0, t)$.

     Challenge: Feedback currently impossible for ultrafast dynamics.

     Prospect: **Robust control** can exploit rich pulse shaping resources to minimize sensitivity to parameter uncertainty. **Electronic structure theory** combined with efficient parameter estimators based on time-resolved quantum measurement data can reduce parameter uncertainty.

- **State estimation**. Application: adaptive feedback (open loop) control of multiple output processes. Probabilities of observations $p_k = \mathrm{Tr}(\rho(\theta)|k\rangle\langle k|)$ are *linear* in parameters

$$
\begin{aligned}
\rho \equiv \rho(\theta) &= \frac{1}{N} I_N + \frac{1}{2}\sum_{j=1}^{N^2-1} \theta_j \lambda_j, \\
(\theta_1, \ldots, \theta_{N^2-1}) &\equiv \theta \in B_{N^2-1} \subset R^{N^2-1},
\end{aligned}
$$

  where λ_j are generators of $SU(N)$.

- **Dynamical parameter estimation**. Application: robust control; assessment of worst case control performance for optimal control.

  Challenge: Probabilities of observations are nonlinear in Hamiltonian parameters.

Estimation of quantum Hamiltonians

- Assume H_0 known from resonant frequencies. Parameterization of μ for Rb:

$$\mu(\theta) = \begin{bmatrix} 0 & \theta_1 & \theta_2 & 0 & 0 \\ \theta_1 & 0 & 0 & \theta_3 & 0 \\ \theta_2 & 0 & 0 & \theta_4 & 0 \\ 0 & \theta_3 & \theta_4 & 0 & \theta_5 \\ 0 & 0 & 0 & \theta_5 & 0 \end{bmatrix}$$

- For a constant field,

$$\rho(\theta, t_k) = \exp[-i(H_0 - \mu(\theta)\varepsilon)t_k]\rho(0)\exp[i(H_0 - \mu(\theta)\varepsilon)t_k]$$

- Unlike spectroscopic experiments used to obtain transition dipole elements for Rb, can be generalized to molecules

Asymptotically Efficient Parameter Estimators: MLE Theory

- *Likelihood function* of parameters: $L(\hat{\theta}|x)$ is joint density of observations x expressed as function of unknown parameter vector $\hat{\theta}$.

- Fisher information: $I(\theta) = -\mathrm{E}\left[\frac{\partial^2 \ln L(\theta|x)}{\partial\theta\partial\theta'}\right]$; $[I(\theta_0)]^{-1}$ is called the *Cramer-Rao lower bound (CRB)* for consistent estimators.

- Maximum likelihood estimator

$$\hat{\theta}_{ML} = \arg\ \max\ L(\hat{\theta}|x)$$

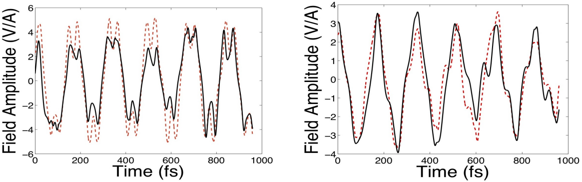
is asymptotically efficient estimator, achieves CRB

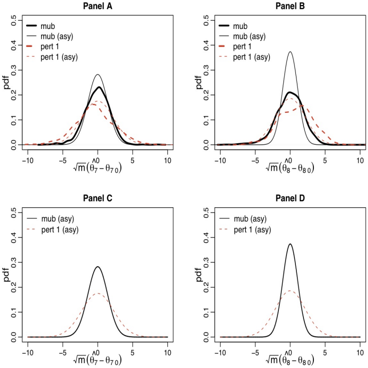
MLE Results: State Estimation

- Given measurement times $(t_1, \cdots, t_q)$; measure the energy through diagonal observable $H_0 = \sum_{i=1}^{N} E_i |i\rangle\langle i|$ at each time

- The FI can be maximized *prior* to collecting experimental data, so that we collect the most information possible about the state parameters from a given number of measurements
- Achieve by shaping control fields $\varepsilon(t)$: $\max\limits_{\varepsilon(\cdot)} ||I(\hat{\theta})||$
- Applying fields $\varepsilon(t)$ that maximize Fisher information are found to improve the quality of parameter estimates

Optimal State estimation, dynamic





MLE of atomic Hamiltonian parameters

- For Hamiltonian estimation, likelihood function for constant field ε is

$$\begin{aligned}\ln L(\theta|x) &= \sum_{k=1}^{N+1}\sum_{j=1}^{m_k} \ln p_{jk}(\theta)\\ &= \sum_{k=1}^{N+1}\sum_{j=1}^{m_k} \ln \mathrm{Tr}[\rho(\theta,t_k)F_{i_j}]\end{aligned}$$

$$\rho(\theta,t_k) = \exp[-i(H_0-\mu(\theta)\varepsilon)t_k]\rho(0)\exp[i(H_0-\mu(\theta)\varepsilon)t_k]$$

where x denotes the data, m_k is the number of observations made at time t_k for a time-independent Hamiltonian (constant control field $\varepsilon(t)$), and $F_i = |i\rangle\langle i|$ is the outcome of the $j-th$ observation.

MLE of atomic Hamiltonian parameters (cont'd)

- Covariance matrix of unknown dipole element parameters:

$$\Sigma = I^{-1}(\hat{\theta})$$

- Due to nonlinearity of likelihood for Hamiltonian estimation, choice of optimal measurement times important: choose the q measurement times or control the unitary propagators by (robust) laser fields to maximize Fisher information:

$$\max_{(t_1,\cdots,t_q)} ||I(\hat{\theta})|| \quad \text{or} \quad \max_{\varepsilon(\cdot)} ||I(\hat{\theta})||$$

after an initial guess for θ is obtained from the first experiment or electronic structure theory and where

$$p_k(\theta, \varepsilon(\cdot)|F_r) = \mathrm{Tr}\left\{U(\varepsilon(\cdot), t_k, \theta)\rho(0)U^\dagger(\varepsilon(\cdot), t_k, \theta)F_r\right\}$$

- Adaptively update measurements given $\hat{\theta} = \arg\max L(\hat{\theta}|x_i)$, given measurement outcomes x_i from experiment i

Bayesian Estimation of Hamiltonian parameters

- The Hamiltonian identification problem is generally ill-posed - due to nonlinearity of likelihood, there are multiple solutions. Thus $\mu(\theta)$ is not *identifiable* by frequentist inference
- For nonlinear estimation, the parameter uncertainties returned by frequentist methods require the choice of one out of the many $\hat{\theta}$'s that may maximize the likelihood

- An alternative is *Bayesian Hamiltonian estimation*, which is based on the notion of a prior plausibility distribution on the space of parameters θ:

$$p\left(\theta \mid x \wedge I\right) d\theta = \frac{L\left(\theta \mid x\right) \, p\left(\theta \mid I\right) \, d\theta}{\int_{\Theta} L\left(\theta \mid x\right) \, p\left(\theta \mid I\right) \, d\theta},$$

- **Prospect**: In addition to parametric model, have *ab initio* estimates for parameters!

- *Bayesian Hamiltonian estimation* can a) use electronic structure calculations along with experimental data in constructing parameter estimates $\hat{\theta}$; b) render problem identifiable

Outline

Pareto Tradeoffs in Robust Control

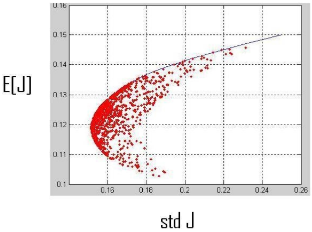


Figure: Pareto frontier of solutions to mean-variance optimal control problems.

- *Pareto frontier* of robust control solutions:

$$\{\bar{\varepsilon}(t) \;\mid\; J_1(\varepsilon(t)) \leq J_1(\bar{\varepsilon}(t)) \;\;\vee\;\; J_2(\varepsilon(t)) \leq J_2(\bar{\varepsilon}(t)), \;\; \forall \varepsilon(t) \neq \bar{\varepsilon}(t)\}$$

- E.g., $J_1(\varepsilon(t)) = \mathbb{E}[J(\varepsilon(t)]]$, $J_2(\varepsilon(t)) = -\mathrm{std}\; J(\varepsilon(t))$ or $J_2(\varepsilon(t)) = J_{wc}(\varepsilon(t))$
- Importance/interpretation of user preferences: would one prefer lower expected performance with more reliability?

- A first-order approximation to the variance of population transfer fidelity due to Hamiltonian parameter uncertainty can be found in closed form:

$$\mathrm{var}\ J = \mathrm{Tr}\left[\Sigma \nabla_\theta J (\nabla_\theta J)^T\right] + \mathcal{O}(||\Sigma||^2),$$

where

$$[\nabla_\theta J]_i = -i\mathrm{Tr}\left\{[\rho_0, \Theta(T)] \int_0^T U^\dagger(t) X_1 \varepsilon(t) U(t)\ dt\right\}$$

and X_i is the Hermitian matrix obtained by setting $\theta_i = 1,\ \ \theta_j = 0,\ j \neq i$ in $\mu(\theta)$.

2nd order distributional results: $E[J]$, parameter uncertainty

- The leading term in the expansion for $E[\delta J]$ due to parameter uncertainty is of 2nd order:

$$\begin{aligned}\mathbb{E}[\delta J] &= \mathbb{E}[\delta\theta^T \mathcal{H}(\theta,\theta')\delta\theta] + \mathcal{O}(||\Sigma||^3) \\ &= \mathrm{Tr}\left(\Sigma\mathcal{H}(\theta,\theta')\right) + \mathcal{O}(||\Sigma||^3)\end{aligned}$$

  where $\mathcal{H}(\theta,\theta') = \frac{d^2 J}{d\theta d\theta'}$ denotes the Hessian matrix with respect to Hamiltonian parameters

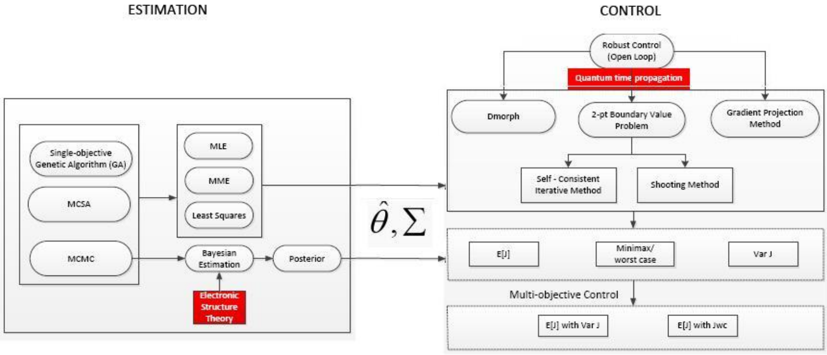
- Parameter uncertainty can improve $\mathbb{E}[J]$; consider overlap:

$$\begin{aligned}\mathrm{Tr}\left(\Sigma\mathcal{H}(\theta,\theta')\right) &= \mathrm{Tr}\left(V\Lambda V^T W\Gamma W^T\right) \\ &= \mathrm{Tr}\left(\Lambda\tilde{V}\Gamma\tilde{V}^T\right)\end{aligned}$$

  where $\Lambda \geq 0$, and $\tilde{V}$ is an orthogonal matrix

- How to search for fields where, given uncertainty spectrum, overlap with the directions in parameter space associated with largest positive eigenvalues maximized

Technology Development for Molecular Control Experiments



- Currently preparing robust control fields for $5D3/2, 5D5/2$ population maximization
- Application of *ab initio* Hamiltonian parameter estimates for control of Rb electronic states and vibrational states in diatomics (LiRb)
- Testing model-based robust control fields with line-by-line pulse shaper (with A. Weiner)
- Only expand model if control fidelity inadequate, due to steep scaling of parameter space dimensionality

Frequency Comb Sources: Advances in Frequency, Intensity Stability of Femtosecond Lasers and Optical Arbitrary Waveform Generation

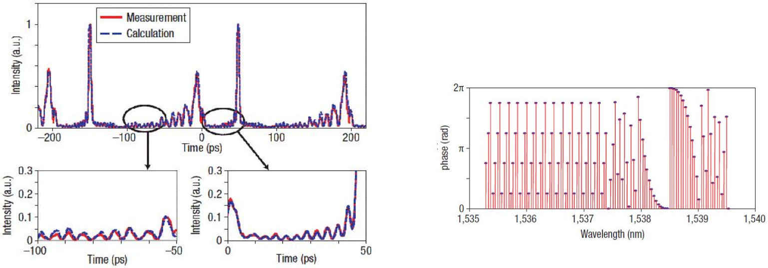
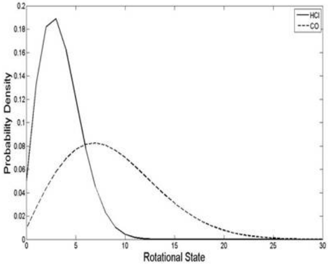


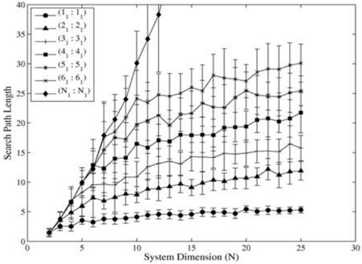
Figure: Frequency combs coupled with line-by-line pulse shapers allow for Arbitrary Waveform Generation (AWG) in femtosecond pulses. **Left:** A complex arbitrary waveform in the time domain. **Right:** This waveform can be generated by setting the phases of each spectral line using a line-by-line shaper. Unlike conventional pulse shaping, which shapes groups of spectral lines together, AWG shapes the amplitudes and phases associated with each spectral line separately, allowing the generation of arbitrary time-domain waveforms.

- Generate arbitrary time-domain waveforms exploiting any number of quantum interferences predicted by OCT
- Extension to molecular OCT: LiRb dissociation - dipole Hamiltonian parameters uncertain

Scaling of Search Effort for AFC



(a)



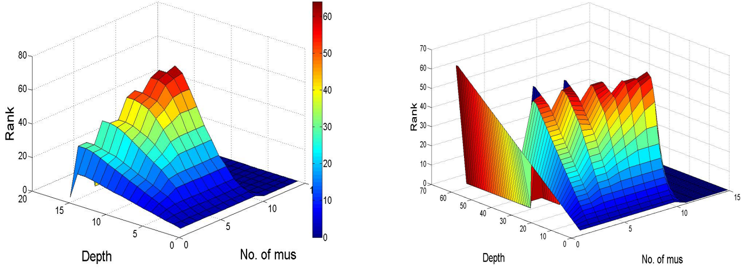
(b)

- Optimal control calculations on CO, HCl: rotational, vibrational, and rovibrational models.
- Poorer scaling of AFC for MIMO problems involving higher rank, nondegenerate ρ_0 or O operators (e.g., rigid rotor at higher temperatures)
- Reason:

$$\begin{aligned}\mathrm{Tr}(\rho(T)O) &= \mathrm{Tr}(U(T)\rho_0 U^\dagger(T)O)\\ &= \mathrm{Tr}(U(T)V \ \mathrm{diag}\{\lambda_1,\cdots,\lambda_N\} \ V^\dagger U^\dagger(T) W \ \mathrm{diag}\{\gamma_1,\cdots,\gamma_N\} \ W^\dagger)\end{aligned}$$

Thus control of nondegenerate ρ_0, O requires control of more elements of the unitary propagator

Dynamical Lie Algebra Depth: Effect on System Hamiltonian on AFC Search Effort



(c) (d)

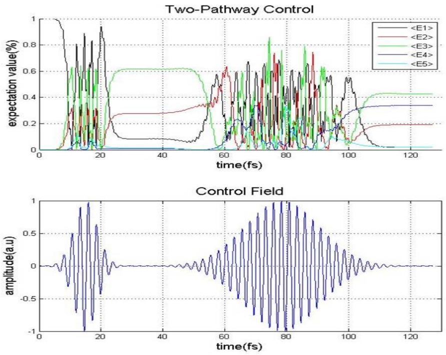
Figure: **Left:** Rank of the dynamical Lie algebra versus the number of μ operators appearing in the Lie brackets for a 8-level diatomic rigid rotor model. **Right:** Rank of the dynamical Lie algebra versus the number of μ operators appearing in the Lie brackets for a 8-level diatomic Morse oscillator model.

- *Dynamical Lie Algebra Depth*: For a controllable system, the smallest integer k such that

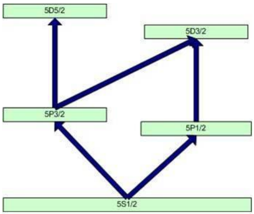
$$\text{span } \{[iH_{j_k}, \cdots [iH_{j_4}, [iH_{j_3}, [iH_{j_2}, iH_{j_1}]]]]\} = u(N),$$

$H_j \in \{H_0, \mu\}$.

Few-Parameter Control of Atomic Rb (cont'd)



(a)



(b)

- Near degenerate level spacings decrease maximal control fidelity achievable by few-parameter control schemes, necessitating optimal control methods
- Multiphoton pathway interferences contribute to population transfer even for such few-parameter schemes, but they cannot be properly controlled and exploited.

Sensitivity to field noise

- We have

$$\mathbb{E}[\delta J] \approx \int_0^T \mathcal{H}(t,t')\mathbb{E}\left[\delta u(t)\delta u(t')\right]\ dt\ dt' \quad = \int_0^T \mathcal{H}(t,t')\mathrm{acf}(t,t')\ dt\ dt'$$

- Consider Hessian nullspace; H(t,t') is finite rank kernel:

$$\mathcal{H}(t,t') = \mathrm{Tr}\left\{\rho\Theta(T)[\mu(t),\mu(t')]_+ - \Theta(T)(\mu(t)\rho\mu(t') + \mu(t')\rho\mu(t))\right\}$$

  which has rank $2N-2$, where N is Hilbert space dimension, for state-to-state population transfer.

  Prospect: Thus field noise at most frequencies does not affect population transfer

- To second order, laser noise can only decrease $\mathbb{E}[J_{\mathrm{nom}} + \delta J]$ since Hessian is negative semidefinite

- Setting $f(t)$ to the functional derivative of the appropriate auxiliary cost, and choosing $\varepsilon(0,t) = \bar{\varepsilon}(t)$, one can then solve the constrained optimization problem by iteratively solving for $\delta\varepsilon(s,t)$, with iterations indexed by algorithmic parameter s.
- To explore fields holding a constant high value of $\mathbb{E}[J]$ while reducing $\mathrm{var}\ J$, solve

$$\frac{\partial \varepsilon(s,t)}{\partial s} = f(s,t) - \frac{a(s,t)}{\int_0^T a^2(s,t')\ dt'} \int_0^T f(s,t')a(s,t')\ dt'$$

$$a(s,t) = \frac{\delta J}{\delta\varepsilon(s,t)} + \frac{\delta \mathbb{E}[\delta J]}{\delta\varepsilon(s,t)}$$
$$f(s,t) = \frac{\delta\ \mathrm{var}\ J}{\delta\varepsilon(t)}$$

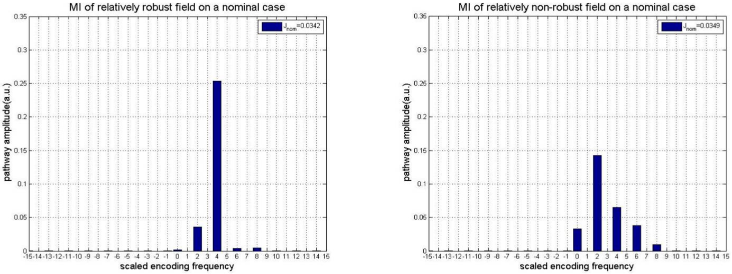
- To maximize $\mathbb{E}[J]$ for given risk level $(\mathrm{var}\ J$ or $J_{wc})$, switch the definitions of $a(s,t)$ and $f(s,t)$

- **Prospect:** Multiplicity of control solutions and flexible pulse shaping permits formulation of Hamiltonian parameter uncertainty robustness criteria as constraints

- Since field uncertainty less severe, minimize $\mathrm{var}\ J$ or maximize $\mathbb{E}[J]$ due to field pdf among fields obtained above

- To explore fields holding a constant high value of $\mathbb{E}_\theta[J]$ while reducing $\mathrm{var}_{\varepsilon(t)}\ J$, formulation is analogous to above

Comparing robust and nonrobust quantum control mechanisms



(c) (d)

Figure: **Left:** Amplitudes of pathways contributing to the mechanism of a robust control field for population transfer to $5D3/2$ in atomic Rb. **Right:** Amplitudes of pathways for a comparatively nonrobust field inducing the same transition.

- Robust fields generally exploit fewer pathways, quantum interferences
- For multilevel systems, multipathway interferences nonetheless required
- Robustness of each pathway/interference to parameter uncertainty can be computed