Mechanistic Analysis of Optimal Dynamic Discrimination of Similar Quantum Systems

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Optimal dynamic discrimination (ODD) was recently introduced as a technique for maximally drawing out and detecting the differences between similar quantum systems by exploiting their controllable dynamical properties. As a simulation of ODD, optimal fields were found that successfully discriminated among similar species, but the underlying mechanisms of the process remained obscure. Hamiltonian encoding (HE) has been introduced as a technique for identifying the mechanisms of controlled quantum dynamics. The results of a HE based simulation analysis of ODD are presented in this paper. Different types and degrees of constructive and destructive interference are shown to underly the controlled discrimination processes. In general, it is found that successful discrimination relies on more complex interfering pathways for increasingly similar systems or increasing numbers of similar quantum systems.

I. Introduction

Similar quantum systems are those with closely related Hamiltonians (e.g., systems sharing common structural or spectral features, etc.) and hence similar properties. A number of applications are concerned with clearly identifying one system in the presence of other similar ones. Distinguishing one system from another very similar one by traditional *static* methods (i.e., spectroscopic or chromatographic analysis) can be very difficult. However, even small differences in the system Hamiltonians can lead to vastly different *dynamical* behavior when the mixture of quantum systems is exposed to the same control field. Quantum optimal dynamic discrimination (ODD) has been proposed[1] to take advantage of this behavior as a tool for distinguishing between systems with similar Hamiltonians. Optimal control theory has been used with success for manipulating quantum systems both in theoretical simulations[2−4] and in the laboratory.[5−13] The ODD technique utilizes optimal control theory (OCT) to generate a field which maximally enhances a particular signal from one system while suppressing signals from the other similar systems. By optimally exploiting all accessible features of the Hamiltonian, ODD has a potential advantage over traditional discrimination techniques. In the laboratory, an optimal discrimination control field would be generated in a closed loop experiment[14,15] guided by a genetic algorithm (GA) or some other suitable learning algorithm. An optimal control field can have a rather complex structure, and this may be especially true when attempting to discriminate by drawing on subtle differences between two or more similar Hamiltonians.

Initial simulations on model systems showed that ODD could be quite effective,[1] but a very limited understanding of the discrimination mechanisms was attained. The goal of this study is to attain a physical understanding of the mechanisms leading to successful ODD. Such knowledge could guide subsequent attempts at ODD in the laboratory. Hamiltonian encoding (HE)[16,17] was introduced as a general method for extracting mechanistic information about controlled quantum dynamics. This work will utilize HE to reveal the mechanisms of discrimination under various physical conditions. Mechanistic insights in this paper will be gained from ODD simulations, but similar HE techniques could be directly applied to the laboratory.

The remainder of the paper is organized as follows. Sections II and III are brief overviews of the ODD and HE concepts. Section IV illustrates the effect of system similarities on the discrimination mechanisms. Sections V and VI explore the effects of increasing numbers of systems to be discriminated and increasing numbers of system levels upon the discrimination mechanisms. Some brief conclusions are presented in section VII.

II. Optimal Dynamic Discrimination

This section presents a short summary of the ODD concept; a more thorough description can be found in ref 1. Given that the N systems are similar but noninteracting quantum systems denoted by S^1, ..., S^N, the goal of ODD is to identify a control field, $\epsilon(t)$, which can generate a large value for a chosen observable value for one system (say S^1) while suppressing the analogous observable value for all other systems. Here, an observation will be taken at a specific trial time, T, although time series discriminating observations over the interval $0 \leq t \leq T$ could also be considered. A wave function formulation will be used for illustration of the concept, but a more comprehensive density matrix presentation could also be treated in a similar fashion. Given the N systems in the initial states $|\psi^1(0)\rangle$, ..., $|\psi^N(0)\rangle$ and a positive definite observable operator, $\hat{O}$, we seek to determine a control field, $\epsilon(t)$, which simultaneously drives the systems to the final states $|\psi^1(T)\rangle$, ..., $|\psi^N(T)\rangle$ such that the observable signals

$$O^i = \langle\psi^i(T)|\hat{O}|\psi^i(T)\rangle \tag{1}$$

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are maximized for $i = 1$ and minimized for $i \neq 1$. The discrimination control field generally can be written as

$$\epsilon(t) = A(t)\sum_n a_n \sin(\omega_n t + \phi_n) \tag{2}$$

where $A(t)$ is the overall amplitude and the frequencies ω_n correspond to all or some of the allowed transitions in the collection of systems being distinguished. The parameters $\{a_n\}$ and $\{\phi_n\}$ are the control variables that the optimization routine needs to determine. Like most optimal control problems, the discrimination goal admits great flexibility in the choice of the optimizing fitness function. In ref 1, the difference between the observable signals was used as the fitness criteria. If the goal was to optimize the signal in system S^j, optimization was done with a fitness function.

$$F^j = O^j - \sum_{i=1, i\neq j}^{N} O^i \tag{3}$$

However, in this paper, we use the alternative fitness function.

$$F^j = \frac{O^j}{\sum_{i=1, i\neq j}^{N} O^i}, \quad O^j > \sigma$$
$$= 0, \quad O^j \leq \sigma \tag{4}$$

The ratio between the two signals is maximized, provided that the signal in the system singled out for maximization is in excess of a threshold value, σ, which is set at $\sigma = 0.1$ here. Each fitness function has its own advantages and disadvantages. To appreciate the point, simply consider two systems for discrimination where the goal is to create a strong signal in system S^1 to distinguish it from system S^2. Using eq 3 would imply, for example, that getting a signal of $O^1 = 0.9$ in system S^1 and $O^2 = 0.4$ in system S^2 with $F^1 = 0.5$ is better than getting $O^1 = 0.3$ in system S^1 and $O^2 \approx 0$ in system S^2 with $F^1 = 0.3$, yet it can be argued that the second case, with a near complete absence of a signal in system S^2, is actually better for discrimination. Using eq 4 means that the optimizing routine will try to minimize the signal in system S^2 while keeping the signal in system S^1 above the threshold. However, once the signal in system S^1 is above the threshold, there is a stronger incentive to maximize the signal ratio by driving the signal in system S^2 closer to zero than to increase the signal in system S^1. This behavior can be seen from the variations of the fitness function with respect to the following two arguments.

$$F^1 = \frac{O^1}{O^2}$$

$$\delta F^1 = \frac{\delta O^1}{O^2} - \frac{O^1 \delta O^2}{(O^2)^2}$$

For $O^2 \ll O^1$, the fitness F^1 should be improved much further by reducing the signal in system S^2 than increasing it in system S^1. This behavior is consistent with what is found in the simulations later in the paper.

The goal of this work is to reveal the general trends in mechanistic behavior of ODD with respect to various factors such as the degree of system similarity. This behavior will be illustrated with simple model systems, and the basic mechanistic trends with regard to discrimination revealed in this study are expected to carry over to more complex situations as well. The ultimate intent of application to real molecules calls for closed loop laboratory implementation of ODD, and an encoding/decoding algorithm for revealing the mechanism working directly in the laboratory can be built from the present concepts.[18]

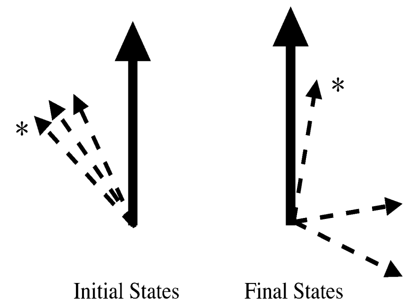

Figure 1. Schematic of how optimal dynamic discrimination (ODD) operates.[1] The arrows denote the complex vectors $|\psi^i(t)\rangle$ for three similar systems at times $t = 0$ and $t = T$ in the system state spaces. Initially, all of the state vectors are nearly coincident, corresponding to identical initial conditions. There is a particular direction in the system state spaces, shown by the dark arrow, corresponding to the projection associated with making the detection measurement. Initially, each system has essentially the same projection along the measurement direction. Through ODD, one vector, denoted by an asterisk, is rotated to be maximally aligned with the measurement direction, while the others are rotated to be perpendicular to it. The Hamiltonian encoding (HE) technique reveals the mechanisms by which such discrimination is achieved.

Unless otherwise stated, all of the model systems studied in this paper have four levels, with the initial population in the ground state, and the observable one is the population in the highest state. The discrimination mechanisms operating in ODD are expected to be subtle, as the same control acts on similar systems and is able to separate their dynamics. From the prior work with ODD,[1] a general view of the controlled dynamics was attained, as indicated in Figure 1, but the discrimination mechanisms were left obscure. With the HE technique presented below, these operating mechanisms will be revealed.

III. Control Mechanism Identification with Hamiltonian Encoding

This section outlines the relevant aspects of the HE concept as introduced in ref 16. The goal of HE is to reveal control mechanisms by identifying the amplitudes of the dominant pathways contributing to the dynamics, where the notion of pathways is defined below. Consider the evolution of a quantum system in the interaction representation, where the system dynamics are restricted to a d-dimensional state space. The system Hamiltonian is

$$H = H_0 - \mu\epsilon(t) \tag{5}$$

with H_0 being the field free Hamiltonian and $\epsilon(t)$ being the control field coupled into the system through the dipole operator μ. One may write the time dependent Schrödinger equation in the interaction representation

$$i\hbar \frac{\mathrm{d}U(t)}{\mathrm{d}t} = \mu_I(t)\, \epsilon(t)\, U(t) \tag{6}$$

where $\mu_I(t) = \exp(-iH_0t/\hbar)\mu \exp(iH_0t/\hbar)$ and U is the time evolution operator. To find the mechanism by which amplitude is transferred from an initial state, $|a\rangle$, to state $|b\rangle$ at time T, consider the relevant matrix element denoted by $U_{ba}(T) =$

$\langle b|U(T)|a\rangle$. The Dyson series expansion for $U_{ba}(T)$, with $\mu_I(t)\,\epsilon(t) \equiv V_I(t)$, is

$$U_{ba}(T) = \langle b|a\rangle + \left(\frac{-i}{\hbar}\right)\int_0^T \langle b|V_I(t_1)|a\rangle\, dt_1 \left(\frac{-i}{\hbar}\right)^2 \times \sum_{l=1}^{d} \int_0^T \int_0^{t_2} \langle b|V_I(t_2)|l\rangle\langle l|V_I(t_1)|a\rangle\, dt_1\, dt_2 + \ldots \quad (7)$$

To simplify the equations, we define $\upsilon_{lm} = (-i/\hbar)\langle l|V_I(t)|m\rangle$, where $|l\rangle$ and $|m\rangle$ are typically chosen as eigenstates of H_0, and introduce the notation[16]

$$U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})} = \int_0^T \int_0^{t_n} \ldots \int_0^{t_2} \upsilon_{bl_{n-1}}(t_n)\, \upsilon_{l_{n-1}l_{n-2}}(t_{n-1}) \ldots \upsilon_{l_1 a}(t_1)\, dt_1 \ldots dt_{n-1}\, dt_n \quad (8)$$

so that the Dyson series (eq 7) becomes

$$U_{ba} = \sum_{n=1}^{\infty} \sum_{l_1,l_2,\ldots,l_{n-1}=1}^{d} U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})} \quad (9)$$

An evolution pathway is defined as the sequence of transitions starting from $|a\rangle$ and ending in $|b\rangle$. Each pathway corresponds to one of the individual integrals in the expansion of $U_{ba}(T)$, with the amplitude of the pathway ($a \rightarrow l_1 \ldots \rightarrow l_{n-1} \rightarrow b$) being $U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}$. The order of a pathway, n, is the number of transitions made linking states $|b\rangle$ and $|a\rangle$. The control mechanism is identified by the *set* of pathways ($a \rightarrow l_1 \ldots \rightarrow l_{n-1} \rightarrow b$) connecting states $|a\rangle$ and $|b\rangle$ which have amplitudes of significant magnitude, $|U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}|$. An understanding of the mechanism involves an analysis of the constructive/destructive interferences among the significant complex amplitudes $\{U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}\}$.

An understanding of the control mechanism in any application must be made in reference to a particular representation of the system Hamiltonian. The choice of a basis is not a matter of right or wrong but rather an issue of convenience guided by the goal of attaining a physically acceptable picture of the control mechanism. In some cases, special insights into the physics of the problem can be used to identify suitable representations.[17] In most OCT applications, the a priori choice of representation will have much freedom. The choice of $\{|l_i\rangle|$ as eigenstates of H_0 to form a representation is a reasonable natural basis employed in many applications.

The integrals in eq 7 are computationally difficult to evaluate directly. The HE technique bypasses this problem by evaluating these integrals through a number of solutions of Schrödinger's equation. The basic operation in HE is the introduction of a new dimensionless timelike variable, s, which is used to modulate (encode) individual elements of the Hamiltonian with suitable functions $\{m_{ij}(s)\}$ of s, such that

$$\upsilon_{lq}(t) \rightarrow \upsilon_{lq}(t) \times m_{lq}(s) \quad (10)$$

Integrating the new encoded equation, of the same form as eq 6, gives $U_{ba}(T,s)$ as a function of s, denoted as $U_{ba}(s)$ where the T is now omitted for notational simplicity. From the structure of eqs 6−10, it can be shown[16] that

$$U_{ba}(s) = \sum_{n=1}^{\infty} \sum_{l_1,l_2,\ldots,l_{n-1}=1}^{d} U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}\, M_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}(s) \quad (11)$$

with

$$M_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}(s) = m_{bl_{n-1}}(s) \times m_{l_{n-1}l_{n-2}}(s) \times \ldots \times m_{l_1 a}(s) \quad (12)$$

The task now reduces to extracting the desired pathway amplitudes $U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}$ for $U_{ba}(s)$ by finding the components of $U_{ba}(s)$ associated with each basis function, $M_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}(s)$. The criteria for choosing the encoding functions $\{m_{ij}(s)\}$ is that they produce a unique signature function, $M_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}(s)$, for each amplitude, $U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}$, in eq 12. There is considerable freedom in the choice of $\{m_{ij}(s)\}$, and here, they are taken to be of the form $m_{ij}(s) = \exp(i\gamma_{ij}s)$. By an appropriate choice of the dimensionless real frequencies $\{\gamma_{ij}\}$, it is possible to ensure that each distinct pathway oscillates at a unique frequency, $\gamma^{(n)}_{(l_1,l_2,\ldots,l_{n-1})}$, as s is scanned. Each function in eq 12 becomes

$$\begin{aligned} M_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}(s) &= \exp\{is\gamma_{bl_{n-1}}\} \times \exp\{is\gamma_{l_{n-1}l_{n-2}}\} \times \ldots \times \exp\{is\gamma_{l_1 a}\} \\ &= \exp\{is\gamma^{(n)}_{(l_1,l_2,\ldots,l_{n-1})}\} \end{aligned} \quad (13)$$

The extraction of the desired pathway amplitudes requires solving for $U_{ba}(s)$ over a sufficient number of s points to permit performing a Fourier transform (FFT) of $U_{ba}(s)$. The resultant amplitude of the spectral line at the frequency $\gamma^{(n)}_{(l_1,l_2,\ldots,l_{n-1})}$ may be quantitatively identified as $U_{ba}^{n(l_1,l_2,\ldots,l_{n-1})}$. This procedure uses the fact that calculating $U_{ba}(s)$ is relatively easy, even for a large number of s values. In some cases (i.e., for high intensity fields), the total number of pathways connecting the initial and final states can become very large, and the number of solutions of Schrödinger's equation for extracting the amplitude of each individual pathway quickly grows. However, by a suitable choice of the frequencies $\{\gamma_{ij}\}$, it is possible to combine pathways into well defined physical pathway classes and find the *net* contribution of each pathway class rather than the contribution of each individual pathway. For example, the choice $\gamma_{ij} = \gamma\ \forall i,j$ collects all pathways of the same order together independent of what particular intermediate transitions actually take place. This gives an estimate of the number of photons involved in the transfer and the relative importance of the various order processes. Another way in which pathways are grouped is to form composite pathways. Each composite pathway is a collection of *net* transitions. In this case, suitable modulation is introduced such that an $i \rightarrow j$ transition will "cancel out" a $j \rightarrow i$ transition when contributing to the net amplitude. For example, the pathways ($1 \rightarrow 2$), ($1 \rightarrow 2 \rightarrow 1 \rightarrow 2$), and ($1 \rightarrow 2 \rightarrow 3 \rightarrow 2$) all fall into the same composite pathway class denoted as ($1 \rightarrow 2$)*, as that is the net transition occurring in all three pathways. The net transition amplitude of the composite pathway would be the sum of the amplitudes in the pathway class. This kind of classification is achieved by constraining the modulation to obey $\gamma_{ij} = -\gamma_{ji}$. For the analysis purposes of this paper, pathways grouped into composite classes are sufficient for revealing the mechanisms of ODD.

IV. ODD Mechanisms in Relation to the Degree of System Similarity

This section considers ODD under different circumstances and uses HE mechanistic analysis to understand how the optimal discrimination fields distinguish between pairs of systems. The variation of the mechanism with system similarity is studied in order to understand the various processes being exploited to achieve discrimination.

For all of the examples, the system Hamiltonian has the structure of eq 5. Considering system similarity, each Hamiltonian has two distinct features, described by H_0 and μ. Differences in H_0 and differences in μ have fundamentally different effects upon discrimination. Differences in H_0 change the frequency spectrum, whereas differences in μ alter the degree of sensitivity to a given spectral component. It was found that high quality discrimination between systems with the same μ but different H_0 (referred to as spectrally distinct systems) is often easier to attain (i.e., the control field has a smaller fluence) than in the case of systems with the same H_0 but different μ (referred to as spectrally identical systems). The results also show that fundamentally different mechanisms are used in discriminating spectrally identical systems compared to spectrally distinct ones. In practice, system differences will simultaneously occur in H_0 and μ. However, to understand the underlying principles, their effects on discrimination revealed by the mechanistic analysis will be separately explored. In all the cases below, increasing fluence was found to be a good indicator of the need for more complex mechanisms to attain comparable degrees of discrimination. Fluence as an indicator is legitimate, as the fitness function in eq 4 puts no penalty on the fluence. The fluence is expressed in arbitrary units in the calculations, and it is the relative value from case to case that is significant.

A. Spectrally Distinct Systems. This section considers discrimination between pairs of four level systems with identical dipole moments but different field free Hamiltonians. The effect of system similarity on the mechanism is analyzed. The energy levels for all the systems are similar, and the transitions are nondegenerate; the energy levels for any particular system A may be ordered in the sequence $\{E_1^a, E_2^a, ..., E_n^a\}$, where the label a refers to system A. We define a difference factor, $\delta\omega$, between systems C and D as follows

$$\omega_{lm}^c = \frac{E_l^c - E_m^c}{\hbar} \tag{14}$$

with

$$\delta\omega = \sum_{l,m,l\neq m} \frac{|\omega_{lm}^c - \omega_{lm}^d|}{|\omega_{lm}^c|} \tag{15}$$

The smaller the value of $\delta\omega$, the more similar are systems C and D. While this scalar difference factor will not capture all of the subtle dynamical differences between the systems, it provides a useful quantitative measure of the degree of spectral distinction between the systems. Another factor, η, previously introduced in ref 16, serves as a measure of the degree of constructive/destructive interference of the pathways defined by the expression

$$\eta = \frac{|\sum_n U_{ba}^n|}{\sum_n |U_{ba}^n|} \tag{16}$$

where the various significant pathway class amplitudes are numbered here by a simple index, n, for notational simplicity. If the pathways are perfectly aligned in the complex plane, then $\eta = 1$, while, for complete destructive interference, $\eta = 0$. Each system in a sample subjected to discrimination will have its own η value, as the control field induces pathways with different amplitudes in each system.

TABLE 1: Results of Optimal Dynamic Discrimination between System A and the Increasingly Similar Systems E, D, C, and B, Respectively[a]

sample	O^A	F^A	$\delta\omega$	fluence
A and E	0.195	5.7×10^7	0.094	4.4
A and D	0.101	105	0.047	7.3
A and C	0.106	24	0.023	15.1
A and B	0.114	9	0.016	39.3

[a] In each case the goal is to enhance the signal for system A and diminish it for the other system in the sample. O^A is the signal in system A, and F^A is the ratio between the signal in system A and the signal in the other system. These systems have identical dipole matrices but different field free Hamiltonians. The difference coefficient $\delta\omega$ from eq 15 is a measure of the distinction between the field free Hamiltonians, with smaller values of $\delta\omega$ implying that the systems are more similar.

TABLE 2: Comparison of the Number of Significant Composite Pathways and the Nature of Constructive and Destructive Interference (η Is Defined in Eq 16) as System Similarity Increases in the Sample When Going from Systems E to B (See Table 1)[a]

sample	system	no. of pathways	η	order
A and E	A	6	0.83	6
	E	2	0.01	4
A and D	A	7	0.40	6
	D	7	0.05	6
A and C	A	9	0.29	8
	C	10	0.06	8
A and B	A	5	0.60	14
	B	6	0.18	14

[a] Increasing system similarity makes it more difficult to get constructive interference in system A while keeping destructive interference in the other system. While the maximum order of the processes increases with system similarity, the number of significant composite pathways does not increase for the last case of systems A and B, as explained in the text. A significant composite pathway is defined as one with a magnitude >0.01.

Table 1 shows the results of ODD simulations for four different discrimination problems, each involving two systems. The goal in each case is to generate a control field which will discriminate system A from (the increasingly similar) systems E, D, C, and B, respectively. As can be seen, the greater the difference factor $\delta\omega$, the smaller the fluence of the discriminating field. Naturally, systems that are more similar may also be more difficult to discriminate, as reflected in the value of the fitness function F^A, although good results were found in all the present cases. Even in the worst case of systems A and B, the signal in system A is 9 times as large as the signal in system B. Thus, despite the increasing similarity of the systems, comparable discrimination quality was achieved by “working harder”, as reflected by the increasing fluence.

Table 2 shows the results of HE mechanistic analysis for the cases in Table 1. The number of composite pathways of significant amplitude (i.e., with magnitudes >0.01) are listed along with the maximum order of the processes. The systems show distinct regimes of discrimination mechanistic behavior. For system E, the control field sets up large amplitude pathways in system A, while little amplitude is excited in system E, and even these low amplitude pathways interfere destructively. In this case, the composite pathways to the target state for system A add up nearly completely constructively, while those for system E add up destructively. This is close to the ideal discrimination limit. The number of significant pathways is far

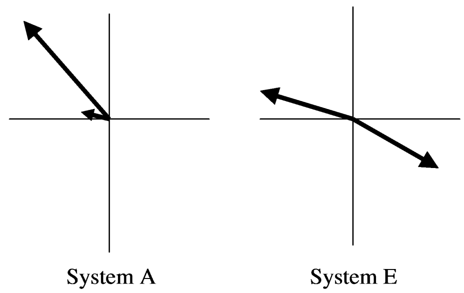

Figure 2. Comparison of the significant composite pathways induced by the optimal control field in discriminating systems A and E in Tables 1 and 2. Table 2 lists six significant composite pathways for system A, but here, only the two largest are shown for graphical clarity. The scale for system E is magnified by a factor of 10 for visual clarity, as the composite pathways induced are of much lower amplitude. As can be seen, the interference in system E is nearly completely destructive, and for system A, the interference is constructive. This discrimination mechanism is possible because systems A and E are sufficiently distinct from each other.

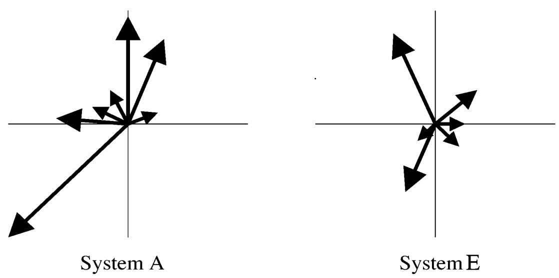

Figure 3. Comparison of the significant composite pathways induced by the optimal control field in systems A and D of Table 2. The composite pathways induced are of the same order of magnitude. There is near complete destructive interference for system D. In contrast, although the interference for system A is not fully constructive, it gives a comparatively large net population in the target state. The mechanism is more complex for this case of discrimination as compared to that shown in Figure 2 because systems A and D are more similar.

more for system A (6) than for system E (2). Also, the highest relevant order of pathways excited for system E (4) is lower than for system A (6). This is the first discrimination regime, where the systems are sufficiently different ($\delta\omega = 0.094$) to allow for distinct yet relatively simple dynamics. Figure 2 shows the amplitudes of the most significant composite pathways induced by the control field in systems A and E plotted in the complex plane. The spectra of systems A and E are sufficiently different to allow the excitation of high amplitude pathways in system A without setting up very high amplitude pathways in system E. However, the ODD algorithm further improves performance by ensuring constructive interference between the pathways in system A and destructive interference between the pathways in system E.

For the more similar systems A and D, the control field now sets up the same number (7) of composite pathways and the same order (6) of processes for both systems. The main composite pathways are shown in Figure 3. The pathways show nearly complete destructive interference in system D with $\eta = 0.05$ and a fair degree of constructive interference in system A with $\eta = 0.4$ to ensure that there is a signal in system A and essentially none in system D. The major pathways and their amplitudes are listed in Table 3. For the even more similar systems A and C, the story is the same except more composite pathways and higher order processes are needed in order to successfully discriminate between the systems. Also, as the systems become more similar, the degree of constructive

TABLE 3: List of the Different Amplitudes Introduced for the Seven Composite Major Pathways in the Discrimination between Systems A and D (See Table 1)[a]

pathway	amplitude in system A	amplitude in system B
$(1 \rightarrow 4)^*$	$-0.2 - 0.2i$	$-0.07 + 0.16i$
$(1 \rightarrow 3 \rightarrow 4)^*$	$0.06 + 0.15i$	$-0.05 - 0.12i$
$(1 \rightarrow 2 \rightarrow 3 \rightarrow 4)^*$	$-0.12 + 0.01i$	$0.07 + 0.06i$
$(1 \rightarrow 2 \rightarrow 3 \rightarrow 1 \rightarrow 4)^*$	$-0.06 + 0.03i$	0.05
$(1 \rightarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow 4)^*$	$-0.03 + 0.06i$	$0.04 - 0.04i$
$(1 \rightarrow 4 \rightarrow 3 \rightarrow 1 \rightarrow 4)^*$	$0.05 + 0.02i$	$-0.03 - 0.03i$
$(1 \rightarrow 4 \rightarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow 4)^*$	$0.19i$	$0.01 - 0.01i$
sum of amplitudes	$-0.3 + 0.26i$	$0.02 + 0.02i$

[a] The sum of the amplitudes shows that the pathways interfere destructively in system D, while the corresponding pathways interfere constructively in system A.

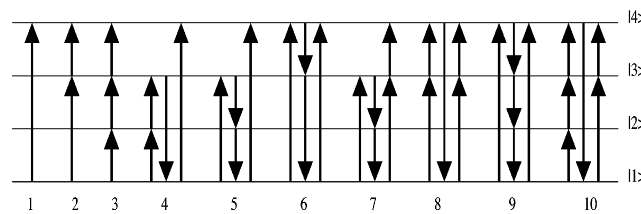

Figure 4. Ten main contributing composite pathways induced in systems A and C by an optimal discriminating field. The same pathways are introduced in systems A and C, but they have different amplitudes and phases. The large number of composite pathways indicates that the discrimination mechanism is highly complex.

interference in system A diminishes, while the degree of constructive interference in the other system increases. This is the second regime, where discrimination occurs by setting up a large number of composite pathways, which add up constructively/destructively to achieve the required result as best as possible. The number of composite pathways used in discriminating between systems A and C is very large and highly nontrivial in structure. Figure 4 shows the significant composite pathways induced in both systems A and C by the discrimination field. While the same pathways are induced in both systems, they are induced with different phases and amplitudes, thereby allowing for destructive interference in one case and constructive interference in the other.

The trend of using more composite pathways with increasing system similarity seen in Table 2 is broken in the most similar system B, which introduced fewer composite pathways than system C while creating much higher order processes. This behavior arises because the discrimination mechanism relies on "rattlings",[16] or pathways that belong to the same composite class but which have additional pairs of canceling transitions. The discrimination mechanism here is similar to that in spectrally indistinguishable systems seen in the next subsection. This is the third regime of discrimination.

The results of the mechanistic analysis for discrimination between pairs of spectrally distinguishable systems show that, for increasingly similar systems, it is necessary to excite more complex dynamics in order to successfully distinguish between the systems.

B. Spectrally Identical Systems. This section explores the mechanisms for ODD between spectrally identical systems, defined to be systems with the same H_0 but different dipole coupling matrices, μ's. Such systems will have spectral peaks in the same location but with different intensities, given the added condition that the same transitions are allowed in both systems. Three cases are explored, involving the discrimination of A from the increasingly similar systems H, G, and F,

TABLE 4: Results of Optimal Dynamic Discrimination between Three Increasingly Similar, Spectrally Identical Systems[a]

sample	O^A	F^A	$\delta\mu$	fluence
A and H	0.102	3.5×10^5	1.81	9.58
A and G	0.100	2.5×10^4	0.90	30.76
A and F	0.100	20.3	0.045	64.65

[a] O^A is the enhanced signal for system A, and F^A is the fitness function (i.e., the ratio of the signal in A to the signal in the other system). These systems have different dipole matrices and identical field free Hamiltonians. The difference coefficient $\delta\mu$ defined in eq 17 is a measure of dipole matrix distinctness, with smaller values implying more similar dipole matrices.

TABLE 5: Comparison of the Number of Significant Composite Pathways and the Nature of Constructive and Destructive Interference, η, as the System Similarity Increases (See Table 4) for Spectrally Identical Systems[a]

sample	system	no. of pathways	η	order
A and H	A	7	0.52	10
	H	6	0.01	8
A and G	A	9	0.73	18
	G	8	0.03	16
A and F	A	7	0.63	27
	F	5	0.38	26

[a] The number of composite pathways does not grow with system similarity in contrast to the case of the spectrally distinguishable systems in Table 2. Rather, rattling cancellations[16] within each path are exploited, which can be inferred from the presence of high order processes induced by the discriminating fields.

respectively. The results are shown in Table 4. If the dipole matrix elements of system A are $\{\mu^a_{lm}\}$, then the difference coefficient $\delta\mu$ between systems A and F is defined as

$$\delta\mu = \sum_{l,m,\mu^a_{lm}\neq 0} \frac{|\mu^a_{lm} - \mu^f_{lm}|}{|\mu^a_{lm}|} \tag{17}$$

to quantify the degree of distinction between the systems. Note that the added condition of identical allowed transitions means if $\mu^a_{lm} = 0$, then $\mu^b_{lm} = 0$.

As can be seen in Table 4, the electric field fluences are much larger than those seen in the case of spectrally distinguishable systems in Table 1. It was found that discrimination became much more difficult (i.e., higher intensity fields had to be used) for decreasing $\delta\mu$ values, just as was found for decreasing $\delta\omega$ values in the previous section. However, the results of the mechanistic analysis for the spectrally identical systems in Table 5 show trends different from the case of spectrally distinct systems. The degrees of constructive and destructive interference do not vary monotonically with increasing system difference; however, the ratio between η for system A and η for the other system does increase monotonically, implying that sometimes the control field will accept a lower degree of constructive interference in system A if that means a greater degree of destructive interference in the other system. Another key point is that there is no trend of using more composite pathways as the systems become more similar. However, there is a clear trend of using much higher order processes. Systems A and F are almost identical, and the optimal field distinguishing between them is of high fluence. The number of *composite* pathways used was very few, and there was essentially a single dominant composite pathway, the direct $(1 \rightarrow 4)^*$ transition. However, the small number of composite pathways does not imply a simple discrimination mechanism. Figure 5 shows some of the

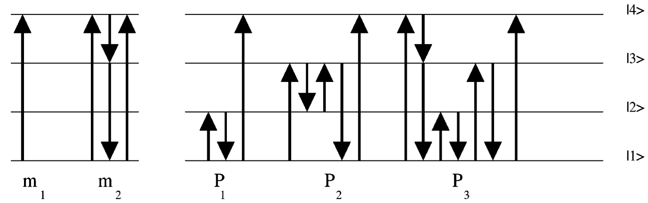

Figure 5. Mechanism of discrimination for the spectrally identical systems A and F. While there are only two major composite pathways induced in both systems (shown as m_1 and m_2 in the left portion of the figure), that observation is misleading. The presence of processes of the order of 20 and higher in Table 5 means that each composite pathway class has within it many high order contributing pathways. P_1, P_2, and P_3 are examples of three pathways that contribute significantly. The first two, P_1 and P_2, belong to the pathway class $m_1 = (1 \rightarrow 4)^*$ and the third to the class $m_2 = (1 \rightarrow 4 \rightarrow 3 \rightarrow 1 \rightarrow 4)^*$.

pathways that contribute to the two main composite pathway classes used in the discrimination. The presence of field induced processes of the order of more than 20 in systems A and F implies that detailed pathways such as those shown in Figure 5 contribute significantly. The control field attempts to use these processes to create interference as a delicate means for discrimination. The reason for this behavior can be understood through the following analysis. Consider the expression for the pathway (not a composite pathway) $(1 \rightarrow 3 \rightarrow 4)$

$$U^{2(3)}_{41} = \int_0^T \int_0^{t_2} \mu_{I_{43}}(t_1)\, \mu_{I_{31}}(t_2)\, \epsilon(t_2)\, \epsilon(t_1)\, dt_1\, dt_2 \tag{18}$$

where $\mu_{I_{lm}}$ is the (time dependent) lmth element of μ_I, which is explicitly

$$\mu_{I_{lm}} = \mu_{lm} \exp(i\omega_{lm} t) \tag{19}$$

Then, eq 18 reduces to

$$U^{2(3)}_{41} = \mu_{43}\mu_{31} \int_0^T \int_0^{t_2} \exp(i\omega_{43} t_2) \exp(i\omega_{31} t_1)\, \epsilon(t_2)\, \epsilon(t_1)\, dt_1\, dt_2 \tag{20}$$

For spectrally identical systems, each transition frequency, ω_{lm}, is the same for both systems, and therefore, the integral in eq 20 will be the same for both systems. The difference in the amplitude of a pathway will come from the difference in the dipole moments alone. This is true for all pathways, not just the one chosen for illustration. If the dipole elements are real (as is the case for all systems considered here), then every pathway excited in one system will have the same phase as the corresponding pathway in the other system. Even for complex dipole elements, the phase difference between the two corresponding pathways will be fixed by the dipole elements and cannot be manipulated by the optimizing algorithm. Thus, the only way to excite significantly different dynamics is to exploit the small differences in the dipole moment magnitudes. However, as the dipole moments are very similar in magnitude, to create pathways with different amplitudes, high order processes need to be introduced; this is done by rattling (i.e., an $a \rightarrow b$ transition is subsequently followed by a $b \rightarrow a$ transition, etc.[16]). Such pathways are highly nonlinear in the dipole moment matrix elements to amplify their system-to-system small differences and create significantly different pathway amplitudes. This behavior results in a complex discrimination mechanism.

Given this behavior found with spectrally identical systems, it is useful to compare it with what was found in section IV.A for spectrally distinct systems. In the latter case, the phases of

TABLE 6: Results of Discrimination with Samples Having an Increasing Number of Systems[a]

sample	O^A	O^2	O^3	O^4	F^A	fluence
A, A_2	0.107	0.001			105	7.3
A, A_2, A_3	0.108	0.011	0.003		21.2	20.8
A, A_2, A_3, A_4	0.123	0.017	0.0003	0.004	5.8	76.8

[a] The goal of the control field is to maximize the signal in system A while minimizing the signal in all the other systems in the sample. F^A is the ratio of the signal in system A to the sum of the signals in all the other systems.

each composite pathway could be manipulated by drawing on the slightly different values of ω_{lm} for each system; even small differences in ω_{lm} can become amplified by the time dependent integrals (e.g., eq 18) when the control pulse goes through many oscillation periods. Therefore, discrimination in spectrally distinct cases is achieved by introducing many composite pathways with different phases, which then add up constructively/destructively as dictated by the desired objective. As spectrally distinct systems become increasingly similar, the values of the various transition frequencies ω_{lm} will become increasingly similar. In that case, low order pathways will tend to have similar phases as well. In this situation, it will become difficult to generate an electric field capable of creating significantly distinct phases for the same low order pathways in the two systems. Hence, as spectrally distinct systems become extremely similar, seeking optimal discrimination forces the introduction of high order pathways to magnify the small differences in ω_{lm} and thereby ensure significantly different amplitudes and phases for the corresponding pathways in the two systems. This explains the nature of the mechanism of discrimination found for the weakly spectrally distinct systems A and B in Table 2.

We can infer from the results of sections IV.A and IV.B that arbitrary systems with scattered small differences in the matrix elements H_0 and μ will draw on every possible means afforded by $\epsilon(t)$ to achieve ODD.

V. Mechanistic Behavior for Distinguishing Increasing Numbers of Systems

In this section, HE is used to analyze the nature of the discrimination mechanisms operating with samples containing increasing numbers of systems. The systems are spectrally distinct with identical dipole matrices and are labeled A, A_2, A_3, and A_4. The spectral difference coefficients $\delta\omega$ between A_2, A_3, and A_4 and A are 0.047, 0.056, and 0.092, respectively. The goal is to maximize the observable signal in A and minimize the signals in all the other systems. A sequence of discrimination problems will be examined, where system A is to be discriminated from only A_2, from A_2 and A_3, and finally from A_2, A_3, and A_4. The results are presented in Table 6.

While successful discrimination of A was achieved even as the number of additional systems increased, the discrimination mechanism became more complex, drawing on subtle dynamical differences between the systems. This behavior is qualitatively evident from the increasing fluence of the electric fields, and the quantitative mechanistic analysis is shown in Table 7. As the number of systems to be discriminated among increases, the number of composite pathways increases to achieve a comparable degree of discrimination. The order of the control processes also increases as more systems are added. For multisystem discrimination, a combination of many composite pathways along with high order rattling processes is required to achieve successful discrimination. This behavior is in contrast with the two system discrimination problems in section IV, where either mechanism sufficed. The multisystem cases illustrate the general principle that the control field will take optimal advantage, as required, of all available dynamics to achieve successful discrimination.

TABLE 7: Results of the Mechanistic Analysis for a Series of Multisystem Discrimination Problems[a]

sample	system	no. of pathways	η	order
A, A_2	A	7	0.40	6
	A_2	7	0.05	6
A, A_2, A_3	A	11	0.37	9
	A_2	11	0.08	9
	A_3	11	0.06	9
A, A_2, A_3, A_4	A	23	0.37	24
	A_2	23	0.13	24
	A_3	23	0.006	24
	A_4	22	0.06	24

[a] Both a large number of composite pathways and very high order processes are introduced.

TABLE 8: Results of Optimal Dynamic Discrimination for Two Spectrally Distinct Systems (A and D) Modeled with Different Numbers of Levels[a]

no. of levels	signal A	F^A	$\delta\omega$	fluence
6	0.107	3.4×10^6	0.094	10.0
5	0.109	10^5	0.075	8.3
4	0.101	105	0.047	7.3

[a] As the number of levels increases, there is additional dynamic freedom to exploit, and thus, better discrimination is achieved without a significant change in fluence.

TABLE 9: Results of the Mechanistic Analysis for the Discrimination Problems of Table 8[a]

sample	system	no. of pathways	η	order
6	A	11	0.38	8
	D	8	0.008*	6
5	A	11	0.38	6
	D	8	0.004	6
4	A	7	0.40	6
	D	7	0.05	6

[a] The values of η show that greater destructive interference occurs in system D as the number of levels increases. The value of η denoted by an asterisk is likely less than 0.008; numerical issues make it difficult to obtain accurately.

VI. Discrimination Mechanisms with an Increasing Number of System Levels

This section explores how the number of system levels affects the quality of the discrimination and the associated mechanisms. A series of discrimination problems will be considered, where the goal is discrimination of system A from system D by the population transfer $|1\rangle \rightarrow |4\rangle$. Both systems are modeled successively as having six, five, and four levels, where the five and four level systems are simply truncations of the six level system. Each pair of systems is spectrally distinct. The results of the discrimination are shown in Table 8 (the case of four levels with system D is the same as that in Table 1). Having more energy levels means that there is greater dynamic freedom to exploit for achieving discrimination. This extra freedom is reflected in the increasing value of the difference parameter $\delta\omega$ in Table 8. The results of the mechanistic analysis are shown in Table 9, where the decreasing value of η for system D with an increasing number of levels shows that the extra freedom allows for better destructive interference.

It was also observed that the optimal discrimination field for the four level system also worked extremely well when applied to the five and six level systems. In this case, the mechanistic analysis shows that the composite pathways induced in the five level systems A and D are very similar to the corresponding composite pathways in the four level systems. Therefore, undermodeling the system did not have a significant effect. However, the optimal fields determined for the five and six level systems did not produce satisfactory discrimination upon application to the four level case. This outcome is reasonable because the control field naturally exploits levels $|5\rangle$ and $|6\rangle$ when they are available for ODD.

VII. Conclusions

This paper applied HE in a number of contexts with model systems to provide insight into the mechanisms of ODD. Mechanism identification revealed how ODD exploits constructive interference in the target system and destructive interference in the other systems in order to achieve discrimination. The effect of system similarity upon the discrimination mechanisms was explored, and the mechanism qualitatively depended on whether the system differences were in H_0 or μ. The effects of additional systems and additional system energy levels were also investigated. The general conclusion is that greater similarity or a larger number of systems invariably leads to the exploitation of multipathway mechanisms to dynamically magnify even the smallest difference between the systems. A similar analysis could be carried out for radiation coupled through other operators besides μ, and Raman or other nonlinear spectral signatures could define the output signal for mechanistic analysis.

It is clear that operating optimally will allow for the best degree of discrimination, given all the laboratory constraints and realities. The presence of noise and control field limitations will constrain the ability to exploit all aspects of constructive and destructive interference, although operating with ODD will fight against these effects as best as possible. In this regard, the earlier work[1] explored some aspects of robustness to field noise. Ultimately, it will be valuable to introduce analogous HE techniques directly in the laboratory to reveal the actual mechanisms under real conditions.

Finally, mechanistic analysis through HE is a tool with broad applications for revealing the processes by which quantum optimal control in any context achieves its goals. The different mechanistic behaviors identified in the cases of spectrally identical and distinct systems show the utility of the HE technique. The system discrimination problem also clearly demonstrates that an examination of the control field in any form (e.g., temporal structure, power spectrum, frequency−time plots, etc.) alone generally cannot reveal a mechanism, as the same field subtly directs the dynamics of similar systems in very different ways. Only a full unraveling of the contributing pathways can truly reveal the operating mechanisms. It is anticipated that systematic application of HE to wide classes of quantum control problems should provide a broad perspective on how the control is achieved.

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