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Why do effective quantum controls appear easy to find?

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Abstract

Experimental evidence shows that effective quantum controls in diverse applications appear surprisingly easy to find. The underlying reasons for this attractive behavior are explored in this work through an examination of the quantum control landscape of $\langle \mathbf{O}(T) \rangle = \mathrm{Tr}(\boldsymbol{\rho}(T)\mathbf{O})$ directly in terms of the physically relevant control field $\boldsymbol{\epsilon}(t)$ and the density matrix $\boldsymbol{\rho}(T)$ at the target time T, including an elaboration of the topology around the critical points, where $\delta\langle \mathbf{O}(T) \rangle / \delta\boldsymbol{\epsilon}(t) = 0 \, \forall t$, of an arbitrary physical observable $\mathbf{O}$. It is found that for controllable quantum systems the critical points of the landscape $\langle \mathbf{O}(T) \rangle$ correspond to the global maximum and minimum and intermediate saddle points of $\langle \mathbf{O}(T) \rangle$. An upper bound is shown to exist on the norm of the slope $\delta\langle \mathbf{O}(T) \rangle / \delta\boldsymbol{\epsilon}(t)$ anywhere over the landscape, implying that the control landscape has gentle slopes permitting stable searches for optimal controls. Moreover, the Hessian at the global maximum (minimum) only possesses a finite number of negative (positive) non-zero eigenvalues and the sum of the corresponding eigenvalues is bounded from below (above). The number of negative eigenvalues of the Hessians evaluated at the saddle points drops as the critical point value $\langle \mathbf{O}(T) \rangle$ becomes smaller and finally converts to all positive non-zero eigenvalues at the global minimum. Collectively, these findings reveal that (a) there are no false traps at the sub-optimal extrema in the landscape, (b) the searches for optimal controls should generally be stable, and (c) an inherent degree of robustness to noise exists around the global optimal control solutions. As a result, it is anticipated that effective control over quantum dynamics may be expected even in highly complex systems provided that the control fields are sufficiently flexible to traverse the associated landscape.

Keywords: Quantum control

1. Introduction

In recent years, much development has occurred in controlling atomic, molecular, and condensed phase phenomena, based on the coherent nature of quantum dynamics [1–3]. The progress can be attributed to several key factors, including the introduction of optimal control concepts into quantum dynamics [4–8], the use of increasingly powerful computers, and advances in ultrafast lasers and pulse shaping technology [9]. In order to achieve control, constructive and destructive quantum wave interferences may be actively manipulated by properly shaped electromagnetic (laser) pulses. A shaped pulse acts as a photonic reagent tailored to the particular objective for achieving the highest quality controlled quantum dynamics. The technology for ultrafast laser pulse shaping is rapidly evolving to meet the ever-increasing list of control applications, and the introduction of closed-loop learning control techniques [8] in the laboratory has facilitated the realization of many control experiments [10–18]. These experiments include manipulating electronic excitation [10,11], performing selective chemical fragmentation and rearrangement [12–14], compressing optical pulses [15], tailoring high harmonic generation[16], creating ultra-fast optical switches [17], and redirecting energy transfer in bio-molecules [18].

Perhaps the most significant general experimental finding is the evident ease of rapidly determining successful controls $\boldsymbol{\epsilon}(t)$ while searching through the high dimensional space of pulse shaper phases and amplitudes. Furthermore, excellent robustness to laser

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noise is evident especially in some of the highly nonlinear control processes. This positive behavior is holding true even for systems of high complexity. Thus, a basic question is what makes quantum control experiments apparently easy to perform? Explaining why quantum control beats the curse of dimensionality (i.e., overcomes the anticipated exponentially growing effort required when searching over increasing numbers of control variables) should give insight into the classes of feasible quantum control experiments in the future, especially those involving complex molecules and materials.

Quantum control experiments are performed as searches over a landscape defined as the observable as a functional of the control field. A typical sequence of experiments searching for an effective control entails taking a guided trajectory over the landscape in an effort to identify a high quality extremum value for the observable. The topological features of quantum control landscapes are important for understanding the success of such control searches. An initial study was performed for the control landscape of the transition probability $P_{i\to f}$ of going from the state $|i\rangle$ to the state $|f\rangle$ [19–22]. From an examination of the landscape critical points where $\delta P_{i\to f}/\delta\boldsymbol{\epsilon}(t) = 0\,\forall t$, it was found that no false extrema or traps exist in the quantum mechanical transition probability landscape for controllable quantum systems under clean operating conditions (i.e., little noise or decoherence). Furthermore, the Hessian $\delta^2 P_{i\to f}/\delta\boldsymbol{\epsilon}(t)\delta\boldsymbol{\epsilon}(t')$ for an N-level quantum system, evaluated at an optimal control field, was shown to have no more than $2N-2$ non-zero eigenvalues whose associated eigenvectors determine the important control variables [21,22]. Although $P_{i\to f}$ is a special observable, these findings provide a clear hint at why controlling quantum phenomena is relatively easy to achieve, despite the large numbers of control variables being searched over.

Building on the latter findings, it is important to go beyond $P_{i\to f}$ and address the landscape for more general observables of quantum systems initially prepared at finite temperature, or other mixed states, in order to provide an understanding of control experiments carried out under common laboratory conditions. For example, an initial thermal Boltzmann distributed quantum mixed-state ensemble requires the quantum dynamics be described in terms of the density matrix $\boldsymbol{\rho}(t)$ [23]. As a result, the control landscape is the expectation value $\langle\mathbf{O}(T)\rangle = \mathrm{Tr}\,(\rho(T)\mathbf{O})$ of the physical observable operator $\mathbf{O}$, where T is the target time (i.e., either finite or asymptotic). The aim of this paper is to carry out an analysis of the optimal control landscape $\langle\mathbf{O}(T)\rangle$ specified as a functional of the control field $\boldsymbol{\epsilon}(t)$. Particular attention will be given to analyzing the nature of the critical (stationary) points of $\langle\mathbf{O}(T)\rangle$ over the control landscape to address the ease of performing control experiments. The present analysis will assume complete density matrix controllability, implying that any mixed quantum state $\boldsymbol{\rho}(T)$ in the same kinematical equivalence class as the initial one $\boldsymbol{\rho}(0)$ can be reached dynamically [24]. In particular, $\boldsymbol{\rho}(T) = U(T,0)\boldsymbol{\rho}(0)U^{\dagger}(T,0)$, where $U(T,0)$ is an arbitrary unitary matrix attainable under full controllability from $U(0,0) = \mathbf{1}$. More complex circumstances can arise, including the presence of decoherence processes. Nevertheless, the analysis here provides the basis for assessing the essential features of controlling quantum phenomena. Prior work explored the controllability and kinematical bounds on the optimization of $\langle\mathbf{O}(T)\rangle$ [24–26], and the present work will go further to examine the topology of the full landscape.

Treating the control field $\boldsymbol{\epsilon}(t)$ as an arbitrary continuous temporal function implies that the search to maximize $\langle\mathbf{O}(T)\rangle$ is formally over an infinite dimensional space. However, in the laboratory, the control field is always discretized in some fashion in either the time or the frequency domain. The number of discrete control variables can still remain very high (e.g., hundreds of phase and amplitude frequency domain controls are often employed). Thus, regardless of the representation used for the control, the optimization of $\langle\mathbf{O}(T)\rangle$ generally entails a search through a high dimensional control space for an optimal field. With no further information available, the natural expectation is that the control landscape would likely have a highly complex topology with perhaps many maxima, minima, and saddle points. In particular, it is reasonable to expect that local landscape extrema would exist capable of adversely trapping the search for the objective at various suboptimal values of $\langle\mathbf{O}(T)\rangle$. As a result, it is important to understand the topology of the underlying control landscape, especially the gradient throughout the landscape and the Hessian evaluated at the critical points where the gradient is zero. The signs and zeros of the Hessian eigenvalues can identify whether the critical points are local traps or saddle points, as well as provide information on the robustness of the global extrema to field noise.

Initial studies were recently undertaken to explore the topological structure of $\langle\mathbf{O}(T)\rangle$ for controllable finite-dimensional quantum systems, based on (i) the unitary evolution expressed in terms of the action matrix $\mathbf{A}$ via the relation $U(T,0) = \exp(\imath\mathbf{A})$ [27], and (ii) using the matrix elements of the unitary matrix $U(T,0)$ as variables [28]. It was found that only a finite number of distinct critical point values of $\langle\mathbf{O}(T)\rangle$ exist, depending on the eigenvalues of the density matrix and observable operator. The latter study also explicitly revealed the signs of the Hessian eigenvalues at each critical point, thus, the number of downward, upward, and flat directions on the neighboring landscape. These studies provided valuable information about the control landscape, although their abstract nature left wanting an explicit connection to the control field $\boldsymbol{\epsilon}(t)$, which is naturally the true function being varied in the laboratory. The present paper will explicitly work with the control field $\boldsymbol{\epsilon}(t)$ to make the landscape analysis transparent in a physical context.

Section 2 describes the general formulation of the quantum control landscape $\langle\mathbf{O}(T)\rangle$. A necessary and sufficient condition for the existence of the critical points of $\langle\mathbf{O}(T)\rangle$ and the corresponding local topology around the critical points are described. In addition, a simple expression is given for enumerating critical point values of $\langle\mathbf{O}(T)\rangle$. Section 3 considers the landscape within the electric dipole approximation, including bounds on the landscape slope and curvature, rank analysis of Hessian at various critical (maximum, minimum, saddle) points, and quantum control robustness analysis at the global maximum. Finally, a summary is given Section 4.

2. Topology of general quantum control landscapes

For a general controllable N-level quantum system, the expectation value of a Hermitian observable operator $\mathbf{O}$ at some time T can be written as follows [23,27,28]

$$\langle \mathbf{O}(T)\rangle = \mathrm{Tr}\left(\boldsymbol{\rho}(T)\mathbf{O}\right) = \mathrm{Tr}\left(U(T,0)\boldsymbol{\rho}(0)U^{\dagger}(T,0)\mathbf{O}\right), \tag{1}$$

or equivalently as

$$\langle \mathbf{O}(T)\rangle = \mathrm{Tr}\left(U^{\dagger}(T,0)\mathbf{O}U(T,0)\boldsymbol{\rho}(0)\right) = \mathrm{Tr}\left(\mathbf{O}(T)\boldsymbol{\rho}(0)\right) \tag{2}$$

where $\mathbf{O}(t) \equiv U^{\dagger}(t,0)\mathbf{O}U(t,0)$. The density operator $\boldsymbol{\rho}(t)$ is given as

$$\boldsymbol{\rho}(t) = \sum_{\alpha} |\psi_{\alpha}(t)\rangle\, w_{\alpha}\, \langle\psi_{\alpha}(t)|, \tag{3}$$

in terms of a set of positive real numbers $0 \le w_{\alpha} \le 1$ with $\sum_{\alpha} w_{\alpha} = 1$ and normalized pure quantum states $|\psi_{\alpha}(t)\rangle$ with $\langle\psi_{\alpha}(t)|\psi_{\alpha}(t)\rangle = 1.0$. Here w_{α} denotes the probability of finding the system in the pure quantum state $|\psi_{\alpha}\rangle = |\psi_{\alpha}(0)\rangle$ of the initial ensemble and each pure quantum state $|\psi_{\alpha}(t)\rangle$ at the time t is connected to the initial one $|\psi_{\alpha}\rangle$ by the relation $|\psi_{\alpha}(t)\rangle = U(t,0)|\psi_{\alpha}\rangle$. The propagator $U(t,0)$ and its adjoint $U^{\dagger}(t,0)$, respectively, satisfy the time-dependent equations

$$\imath\hbar\frac{\partial U(t,0)}{\partial t} = \mathbf{H}(t)U(t,0),\ U(0,0) = \mathbf{1}, \tag{4}$$

and

$$-\imath\hbar\frac{\partial U^{\dagger}(t,0)}{\partial t} = U^{\dagger}(t,0)\mathbf{H}(t), \tag{5}$$

where the time-dependent Hamiltonian $\mathbf{H}(t)$ is in general a nonlinear function (involving the dipole moment, polarizability, hyperpolarizability, etc.) of the control field $\boldsymbol{\epsilon}(t)$. For example, within the electric dipole approximation, the Hamiltonian has the form

$$\mathbf{H}(t) = \mathbf{H}_0 - \boldsymbol{\mu}\cdot\boldsymbol{\epsilon}(t) \tag{6}$$

where the unperturbed Hamiltonian is $\mathbf{H}_0$ and the dipole moment operator is $\boldsymbol{\mu}$.

It can be shown that the density operator $\boldsymbol{\rho}(t)$ satisfies the von Neumann equation

$$\imath\hbar\frac{\partial \boldsymbol{\rho}(t)}{\partial t} = [\mathbf{H}(t),\ \boldsymbol{\rho}(t)], \tag{7}$$

with $[\mathbf{A},\ \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$. The density operator possesses the following properties:

$$\mathrm{Tr}(\boldsymbol{\rho}(t)) = \sum_{i}\langle i|\left(\sum_{\alpha}|\psi_{\alpha}(t)\rangle w_{\alpha}\langle\psi_{\alpha}(t)|\right)|i\rangle = \sum_{\alpha} w_{\alpha}\left(\sum_{i}\langle\psi_{\alpha}(t)|i\rangle\langle i|\psi_{\alpha}(t)\rangle\right) = \sum_{\alpha} w_{\alpha} = 1, \tag{8}$$

$$\begin{aligned}\mathrm{Tr}(\boldsymbol{\rho}^2(t)) &= \sum_{i}\left\langle i\left|\left\{\left(\sum_{\alpha}|\psi_{\alpha}(t)\rangle w_{\alpha}\langle\psi_{\alpha}(t)|\right)\left(\sum_{\beta}|\psi_{\beta}(t)\rangle w_{\beta}\langle\psi_{\beta}(t)|\right)\right\}\right|i\right\rangle \\ &= \sum_{\alpha}\sum_{\beta} w_{\alpha}w_{\beta}|\langle\psi_{\alpha}|\psi_{\beta}\rangle|^2 \le \sum_{\alpha}\sum_{\beta} w_{\alpha}w_{\beta} = \left(\sum_{\alpha} w_{\alpha}\right)^2 = 1,\end{aligned} \tag{9}$$

where the equality in Eq. (9) holds for the system being in a pure state. The observable $\mathbf{O} = \mathcal{U}_{\mathbf{O}}\Lambda^{\mathbf{O}}(0)\mathcal{U}_{\mathbf{O}}^{\dagger}$ and the initial density operator $\boldsymbol{\rho}(0) = \mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\boldsymbol{\rho}}(0)\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}$ may be expressed in diagonal form via the unitary matrices $\mathcal{U}_{\mathbf{O}}$ and $\mathcal{U}_{\boldsymbol{\rho}}$, respectively, and we may order the eigenvalues as $\Lambda_1^{\mathbf{O}}(0) \ge \Lambda_2^{\mathbf{O}}(0) \ge \cdots \ge \Lambda_N^{\mathbf{O}}(0)$ and $\Lambda_1^{\boldsymbol{\rho}}(0) \ge \Lambda_2^{\boldsymbol{\rho}}(0) \ge \cdots \ge \Lambda_N^{\boldsymbol{\rho}}(0) \ge 0$. From Eq. (9), we can establish the following inequality for the norm of the diagonal matrix $\|\Lambda^{\boldsymbol{\rho}}(0)\|$:

$$\begin{aligned}0 < \Lambda_1^{\boldsymbol{\rho}}(0)^2 \le \|\Lambda^{\boldsymbol{\rho}}(0)\|^2 &\equiv \sum_{k}\left\{\Lambda_k^{\boldsymbol{\rho}}(0)\right\}^2 = \mathrm{Tr}\left(\Lambda^{\boldsymbol{\rho}}(0)\Lambda^{\boldsymbol{\rho}}(0)\right) = \mathrm{Tr}\left(\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\rho}(0)\boldsymbol{\rho}(0)\mathcal{U}_{\boldsymbol{\rho}}\right) \\ &= \mathrm{Tr}\left(\boldsymbol{\rho}(0)\boldsymbol{\rho}(0)\right) = \mathrm{Tr}\left((U^{\dagger}(T,0))\boldsymbol{\rho}(t)\boldsymbol{\rho}(t(U(T,0)))\right) = \mathrm{Tr}\left(\boldsymbol{\rho}(t)\boldsymbol{\rho}(t)\right) \le 1,\end{aligned} \tag{10}$$

which will be of use later. Here the matrix norm $\|\cdot\|$ for an arbitrary square matrix $\mathbf{A}$ is defined as $\|\mathbf{A}\|^2 = \sum_i \sum_j |a_{ij}|^2$ [29]. With these definitions it follows that

$$\langle \mathbf{O}(T)\rangle = \mathrm{Tr}\left(U^\dagger(T,0)\mathbf{O}U(T,0)\boldsymbol{\rho}(0)\right) = \mathrm{Tr}\left(U^\dagger(T,0)\mathcal{U}_{\mathbf{O}}\Lambda^{\mathbf{O}}(0)\mathcal{U}_{\mathbf{O}}^\dagger U(T,0)\mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\boldsymbol{\rho}}(0)\mathcal{U}_{\boldsymbol{\rho}}^\dagger\right)$$
$$= \mathrm{Tr}\left(\mathcal{U}_{\boldsymbol{\rho}}^\dagger U^\dagger(T,0)\mathcal{U}_{\mathbf{O}}\Lambda^{\mathbf{O}}(0)\mathcal{U}_{\mathbf{O}}^\dagger U(T,0)\mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\boldsymbol{\rho}}(0)\right) = \sum_i \sum_j \Lambda_i^{\mathbf{O}}(0)\left|\langle i|\mathcal{U}_{\mathbf{O}}^\dagger U(T,0)\mathcal{U}_{\boldsymbol{\rho}}|j\rangle\right|^2 \Lambda_j^{\boldsymbol{\rho}}(0), \tag{11}$$

and furthermore $\langle \mathbf{O}(T)\rangle$ is bounded by the relation (kinematical bounds) [25,30]

$$\sum_{i=1}^{N} \Lambda_{N-i+1}^{\mathbf{O}}(0)\Lambda_i^{\boldsymbol{\rho}}(0) \le \langle \mathbf{O}(T)\rangle \le \sum_{i=1}^{N} \Lambda_i^{\mathbf{O}}(0)\Lambda_i^{\boldsymbol{\rho}}(0). \tag{12}$$

2.1. The functional relationship between the infinitesimal response of an observable to a Hamiltonian variation

Assessment of the topology of the landscape is facilitated by exploring how an infinitesimal functional change in the Hamiltonian $\delta\mathbf{H}(t)$ results in an infinitesimal response in the observable $\delta\langle \mathbf{O}(T)\rangle$. This infinitesimal functional relationship can be obtained by first considering an arbitrarily functional change of $U(t,0)$ in Eq. (4) and then of $\mathbf{O}(t) \equiv U^\dagger(t,0)\mathbf{O}U(t,0)$ to respectively give

$$\frac{\partial}{\partial t}\delta U(t,0) = \frac{1}{\imath\hbar}\mathbf{H}(t)\delta U(t,0) + \frac{1}{\imath\hbar}\delta\mathbf{H}(t)U(t,0) \tag{13}$$

and

$$\delta\mathbf{O}(t) = \delta U^\dagger(t,0)\mathbf{O}U(t,0) + U^\dagger(t,0)\mathbf{O}\delta U(t,0) \tag{14}$$

From Eqs. (5) and (13) we arrive at

$$\frac{\partial}{\partial t}(U^\dagger(t,0)\delta U(t,0)) = \frac{\partial U^\dagger(t,0)}{\partial t}\delta U(t,0) + U^\dagger(t,0)\frac{\partial}{\partial t}\delta U(t,0) = \frac{1}{\imath\hbar}U^\dagger(t,0)\delta\mathbf{H}(t)U(t,0), \tag{15}$$

thus

$$\delta U(t,0) = -\frac{\imath}{\hbar}\int_0^t U(t,t')\delta\mathbf{H}(t')U(t',0)\,\mathrm{d}t', \tag{16}$$

for an infinitesimal functional change $\delta U(t,0)$, where the natural condition $\delta U(0,0) = 0$ was used. From Eqs. (14) and (16), we then obtain

$$\delta\mathbf{O}(t) = [\mathbf{O}(t),\ U^\dagger(t,0)\delta U(t,0)] = -\frac{\imath}{\hbar}\int_0^t [\mathbf{O}(t), U^\dagger(t',0)\delta\mathbf{H}(t')U(t',0)]\,\mathrm{d}t', \tag{17}$$

for an infinitesimal functional change $\delta\mathbf{O}(t)$.

From Eqs. (2), (16), and (17), we readily obtain the following first-order relation between the landscape variations $\delta\langle \mathbf{O}(T)\rangle$ and Hamiltonian variations $\delta\mathbf{H}(t)$:

$$\delta\langle \mathbf{O}(T)\rangle = -\frac{\imath}{\hbar}\int_0^T \mathrm{Tr}([\mathbf{O}(T), U^\dagger(t,0)\delta\mathbf{H}(t)U(t,0)]\boldsymbol{\rho}(0))\,\mathrm{d}t = \int_0^T \mathrm{Tr}\left([\mathbf{O}(T), \boldsymbol{\rho}(0)]\left\{\frac{\imath}{\hbar}U^\dagger(t,0)\delta\mathbf{H}(t)U(t,0)\right\}\right)\mathrm{d}t, \tag{18}$$

where $\delta\langle \mathbf{O}(T)\rangle \equiv \mathrm{Tr}(\delta\mathbf{O}(T)\boldsymbol{\rho}(0))$. The separation inside the trace of Eq. (18) into the product of two operators (i.e., $[\mathbf{O}(T), \boldsymbol{\rho}(0)]$ and $\frac{\imath}{\hbar}U^\dagger(t,0)\delta\mathbf{H}(t)U(t,0)$) is important for enabling a full analysis of the control landscape critical point structure, which is described in the following subsections. Eq. (18) can be further written as

$$\delta\langle \mathbf{O}(T)\rangle = \mathrm{Tr}\left([\mathbf{O}(T), \boldsymbol{\rho}(0)]\left(\frac{\imath}{\hbar}\int_0^T U^\dagger(t,0)\delta\mathbf{H}(t)U(t,0)\,\mathrm{d}t\right)\right) = -\mathrm{Tr}\left([\mathbf{O}(T), \boldsymbol{\rho}(0)]U^\dagger(T,0)\delta U(T,0)\right), \tag{19}$$

which gives the functional relationship between infinitesimal responses $\delta\langle \mathbf{O}(T)\rangle$ and variations $\delta U(T,0)$.

From Eq. (19), by taking the first-order derivative of $\langle \mathbf{O}(T)\rangle$ with respect to the unitary matrix $U(T,0)$ in the U-coordinate space (i.e., treating the matrix elements of $U(T,0)$ as independent variables), we obtain [28]

$$\frac{\partial\langle \mathbf{O}(T)\rangle}{\partial U_{ij}(T,0)} = -\langle j|\left[\mathbf{O}(T), \boldsymbol{\rho}(0)\right]U^\dagger(T,0)|i\rangle, \tag{20}$$

or in matrix form,

$$\nabla_U\langle \mathbf{O}(T)\rangle = -\left\{[\mathbf{O}(T), \boldsymbol{\rho}(0)]U^\dagger(T,0)\right\}^{\mathrm{T}}, \tag{21}$$

where the superscript "T" denotes matrix transpose. The assumption of full controllability implies that any $U(T, 0)$ may be generated by a suitable control. Since we require that the critical points, defined as $\nabla_U \langle \mathbf{O}(T) \rangle = 0$, be valid for all $U(T, 0)$, then Eq. (21) leads to a necessary and sufficiently condition $[\mathbf{O}(T), \boldsymbol{\rho}(0)] = 0$ for the critical points of $\langle \mathbf{O}(T) \rangle$. This condition will also be arrived at in the next subsection via an analysis in terms of controlled dynamics, thus providing a direct linkage to the control field $\boldsymbol{\epsilon}(t)$ and making the landscape analysis transparent in a physical context.

Using the relation $\delta^2 \langle \mathbf{O}(T) \rangle = \delta(\delta \langle \mathbf{O}(T) \rangle)$ and from Eqs. (17) and (19), a second-order variation can be derived as

$$\begin{aligned}\delta^2 \langle \mathbf{O}(T) \rangle &= \mathrm{Tr}\left([\delta \mathbf{O}(T), \boldsymbol{\rho}(0)] \left(\frac{\iota}{\hbar} \int_0^T U^\dagger(t, 0) \delta \mathbf{H}(t) U(t, 0)\, \mathrm{d}t \right) \right) + \mathrm{Tr}\left([\mathbf{O}(T), \boldsymbol{\rho}(0)] \delta \left(\frac{\iota}{\hbar} \int_0^T U^\dagger(t, 0) \delta \mathbf{H}(t) U(t, 0)\, \mathrm{d}t \right) \right) \\ &= -\frac{1}{\hbar^2} \int_0^T \int_0^T \mathrm{Tr}\Big([[\mathbf{O}(T),\ U^\dagger(t, 0) \delta \mathbf{H}(t) U(t, 0)],\quad U^\dagger(t', 0) \delta \mathbf{H}(t') U(t', 0)] \boldsymbol{\rho}(0) \Big)\, \mathrm{d}t\, \mathrm{d}t' \\ &\quad + \mathrm{Tr}\left([\mathbf{O}(T),\ \boldsymbol{\rho}(0)] \delta \left(\frac{\iota}{\hbar} \int_0^T U^\dagger(t, 0) \delta \mathbf{H}(t) U(t, 0)\, \mathrm{d}t \right) \right), \end{aligned} \tag{22}$$

which serves as a basis for a Hessian analysis.

2.2. Structure of the landscape critical points: general dynamical treatment

The topological details, especially those of the slope and curvature, of the landscape $\langle \mathbf{O}(T) \rangle$ are important for understanding the behavior of searches for effective control fields $\boldsymbol{\epsilon}(t)$. In particular, the number of critical (stationary) points and the eigenvalue structure of the corresponding Hessians at these points can determine the efficiency of the control search algorithms and the robustness of the control process to noise. The critical point criterion can be established by first explicitly rewriting Eq. (18) as

$$\delta \langle \mathbf{O}(T) \rangle = \int_0^T \mathrm{Tr}([\mathbf{O}(T),\ \boldsymbol{\rho}(0)] \mathbf{B}(t)) \cdot \delta \boldsymbol{\epsilon}(t)\, \mathrm{d}t, \tag{23}$$

where $\delta \mathbf{H}(t) = \nabla_{\boldsymbol{\epsilon}} \mathbf{H}(t) \cdot \delta \boldsymbol{\epsilon}(t)$ and $\mathbf{B}(t) \equiv (\iota/\hbar) U^\dagger(t, 0) \nabla_{\boldsymbol{\epsilon}} \mathbf{H}(t) U(t, 0)$. From Eq. (23), the condition for the existence of a critical point of $\langle \mathbf{O}(T) \rangle$ is

$$\frac{\delta \langle \mathbf{O}(T) \rangle}{\delta \boldsymbol{\epsilon}(t)} = \mathrm{Tr}([\mathbf{O}(T),\ \boldsymbol{\rho}(0)] \mathbf{B}(t)) = 0 \quad \forall t. \tag{24}$$

Eq. (24) is demanded to be true for all possible critical points, and given that the system is controllable, it is reasonable to expect that the elements of the skew-Hermitian matrix $\mathbf{B}(t)$ form a set of N^2 linearly independent functions of time over $0 \le t \le T$. Thus, satisfaction of Eq. (24) generally requires that the criterion

$$[\mathbf{O}(T),\ \boldsymbol{\rho}(0)] = 0 \tag{25}$$

be satisfied [25]. In the electric dipole approximation given in Eq. (6), $\boldsymbol{\mu}(t) \equiv U^\dagger(t, 0) \boldsymbol{\mu} U(t, 0) = \iota \hbar \mathbf{B}(t)$, and a finite N-level quantum system is fully controllable if the rank of the Lie algebra generated by the skew-Hermitian matrices $\mathbf{H}_0/\iota\hbar$ and $-\boldsymbol{\mu}/\iota\hbar$ has dimension N^2 [31,32]. The complete controllability for the quantum system in turn implies that the dipole moment matrix elements $\langle k|\boldsymbol{\mu}(t)|\ell \rangle$ for $k, \ell = 1, \ldots, N$ form a set of N^2 linearly independent functions of time [22].

The necessary and sufficient condition in Eq. (25) states that at a critical point of $\langle \mathbf{O}(T) \rangle$ the Hermitian operators $\mathbf{O}(T)$ and $\boldsymbol{\rho}(0)$ commute with each other and therefore can be diagonalized by the same unitary operator $\mathcal{U}_{\boldsymbol{\rho}}$, namely,

$$\mathcal{U}_{\boldsymbol{\rho}}^\dagger \boldsymbol{\rho}(0) \mathcal{U}_{\boldsymbol{\rho}} = \Lambda^{\boldsymbol{\rho}}(0) \tag{26}$$

and

$$\mathcal{U}_{\boldsymbol{\rho}}^\dagger \mathbf{O}(T) \mathcal{U}_{\boldsymbol{\rho}} = \Lambda^{\mathbf{O}}(T), \tag{27}$$

where $\mathcal{U}_{\boldsymbol{\rho}}$ is unitary, and both $\Lambda^{\boldsymbol{\rho}}(0)$ and $\Lambda^{\mathbf{O}}(T)$ are diagonal. Eq. (27) can be further manipulated using $\mathbf{O}(T) = U^\dagger(T, 0) \mathbf{O} U(T, 0)$ and $\Lambda^{\mathbf{O}}(0) = \mathcal{U}_{\mathbf{O}}^\dagger \mathbf{O} \mathcal{U}_{\mathbf{O}}$,

$$\mathcal{U}_{\boldsymbol{\rho}}^\dagger U^\dagger(T, 0) \mathcal{U}_{\mathbf{O}} \Lambda^{\mathbf{O}}(0) \mathcal{U}_{\mathbf{O}}^\dagger U(T, 0) \mathcal{U}_{\boldsymbol{\rho}} = \Lambda^{\mathbf{O}}(T). \tag{28}$$

Eq. (28) shows that the diagonal matrices $\Lambda^{\mathbf{O}}(0)$ and $\Lambda^{\mathbf{O}}(T)$ are similar and thus must consist of the same set of differently ordered diagonal elements, i.e., in descending order for $\Lambda^{\mathbf{O}}(0)$ and arbitrarily ordered for $\Lambda^{\mathbf{O}}(T)$. Specifically, the diagonal matrix elements of $\Lambda^{\mathbf{O}}(0)$ and $\Lambda^{\mathbf{O}}(T)$ must be linked by a simple permutation operation

$$\Lambda^{\mathbf{O}}(T) = \Pi^\dagger \Lambda^{\mathbf{O}}(0) \Pi, \tag{29}$$

or, equivalently,

$$\Lambda_i^{\mathbf{O}}(T) = \Lambda_{p(i)}^{\mathbf{O}}(0), \tag{30}$$

where Π is the permutation matrix defined as

$$\Pi = \mathcal{U}_{\mathbf{O}}^{\dagger} U(T,0) \mathcal{U}_{\boldsymbol{\rho}} \tag{31}$$

and $p(i) = \{i \to p(i) : i = 1, 2, \ldots, N\}$ denotes any one of the permutations of N elements of the diagonal matrix $\Lambda^{\mathbf{O}}(0)$. At each critical point, since$[\mathbf{O}(T),\ \boldsymbol{\rho}(0)] = 0$, the corresponding expectation value $\langle \mathbf{O}(T) \rangle$ can be written as [25,28]

$$\langle \mathbf{O}(T) \rangle = \mathrm{Tr}(\mathbf{O}(T)\boldsymbol{\rho}(0)) = \mathrm{Tr}(\mathcal{U}_{\boldsymbol{\rho}} \Lambda^{\mathbf{O}}(T) \mathcal{U}_{\boldsymbol{\rho}}^{\dagger} \mathcal{U}_{\boldsymbol{\rho}} \Lambda^{\boldsymbol{\rho}}(0) \mathcal{U}_{\boldsymbol{\rho}}^{\dagger}) = \mathrm{Tr}(\Lambda^{\mathbf{O}}(T) \Lambda^{\boldsymbol{\rho}}(0)) = \sum_i \Lambda_i^{\mathbf{O}}(T) \Lambda_i^{\boldsymbol{\rho}}(0) = \sum_i \Lambda_{p(i)}^{\mathbf{O}}(0) \Lambda_i^{\boldsymbol{\rho}}(0), \tag{32}$$

where the descending eigenvalue orderings $\Lambda_1^{\mathbf{O}}(0) \geq \Lambda_2^{\mathbf{O}}(0) \geq \cdots \geq \Lambda_N^{\mathbf{O}}(0)$ and $\Lambda_1^{\boldsymbol{\rho}}(0) \geq \Lambda_2^{\boldsymbol{\rho}}(0) \geq \cdots \geq \Lambda_N^{\boldsymbol{\rho}}(0)$ have been adopted in the derivations.

For an arbitrary permutation matrix Π, the propagator $U(T,0)$ leading to any critical point can be written as $U(T,0) = \mathcal{U}_{\mathbf{O}} \Pi \mathcal{U}_{\boldsymbol{\rho}}^{\dagger}$, cf. Eq. (31). In particular, at the global maximum of $\langle \mathbf{O}(T) \rangle$, the right hand side of Eq. (12) corresponds to $\Lambda^{\mathbf{O}}(T) = \Lambda^{\mathbf{O}}(0)$ and $\Pi = \mathbf{1}$, leading to the relation $U(T,0) = \mathcal{U}_{\mathbf{O}} \mathcal{U}_{\boldsymbol{\rho}}^{\dagger}$. This can be construed as the evolution operator $U(T,0)$ over the time duration $[0, T]$ acting to reflect knowledge of $\mathcal{U}_{\mathbf{O}}$ and $\mathcal{U}_{\boldsymbol{\rho}}$, which simultaneously transforms both operators $\boldsymbol{\rho}(0)$ and $\mathbf{O}(T)$ into diagonal matrices with their eigenvalues arranged in complete descending order. In this regard, the underlying optimal control problem becomes a search for an optimal control field that renders the unitary transformations $\mathcal{U}_{\mathbf{O}}$ and $\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}$ into the product $\mathcal{U}_{\mathbf{O}} \mathcal{U}_{\boldsymbol{\rho}}^{\dagger} = U(T,0)$. This observation is evident in the previous work on pure state $P_{i \to f}$ optimal control [22] where perfect population transfer, i.e., $P_{i \to f}(T) = 1.0$, is a manifestation of the following operation

$$U^{\dagger}(T,0)(|f\rangle\langle f|)U(T,0) = \mathcal{U}_{\mathbf{O}}^{\dagger}(|f\rangle\langle f|)\mathcal{U}_{\mathbf{O}} = |i\rangle\langle i|, \tag{33}$$

rearranging a set of ascending eigenvalues $\{0, \ldots, 0, 1\}$ associated with the Hermitian operator $\mathbf{O} = |f\rangle\langle f|$ into a desired descending ones $\{1, 0, \ldots, 0\}$. (Note that $\Pi = 1$ at the maximum $P_{i \to f}(T) = 1.0$ and the eigenvalues of the density operator $\boldsymbol{\rho}(0) = |i\rangle\langle i|$ are already in the desired descending order $\{1, 0, \ldots, 0\}$ implying that $\mathcal{U}_{\boldsymbol{\rho}} = \mathbf{1}$).

From Eq. (32), it is readily seen that the value of $\langle \mathbf{O}(T) \rangle$ at its absolute highest and lowest extremum critical points is bounded, consistent with the assessment given in Eq. (12). The upper bound $\sum_i \Lambda_i^{\mathbf{O}}(0)\Lambda_i^{\boldsymbol{\rho}}(0)$ is obtained when the permutation matrix Π is the identity operator, i.e., $\Pi = \mathbf{1}$ (or $p(i) = i$), thus $U(T,0) = \mathcal{U}_{\mathbf{O}} \mathcal{U}_{\boldsymbol{\rho}}^{\dagger}$, whereas the lower bound $\sum_i \Lambda_{N-i+1}^{\mathbf{O}}(0)\Lambda_i^{\boldsymbol{\rho}}(0)$ is obtained when the permutation matrix Π is anti-diagonal (or $p(i) = N - i + 1$), thus rendering the matrix elements in complete ascending orders, i.e., $\Lambda_1^{\mathbf{O}}(T) = \Lambda_N^{\mathbf{O}}(0) \leq \Lambda_2^{\mathbf{O}}(T) \leq \cdots \leq \Lambda_N^{\mathbf{O}}(T) = \Lambda_1^{\mathbf{O}}(0)$. Other permutations result in local extrema whose topology (i.e., maxima, minima, or saddles) will be assessed in Section 3.2 for electric dipole coupling. In this regard (i.e., using Eq. (22)), the second-order variations $\delta^2\langle \mathbf{O}(T) \rangle$ at the critical points can be succinctly written as

$$\delta^2\langle \mathbf{O}(T) \rangle = \int_0^T \int_0^T \left(-\frac{1}{\hbar^2}\right) \mathrm{Tr}\left(\left[\left[\mathbf{O}(T),\ U^{\dagger}(t,0)\delta\mathbf{H}(t)U(t,0) \right], \quad U^{\dagger}(t',0)\delta\mathbf{H}(t')U(t',0) \right] \boldsymbol{\rho}(0) \right) \mathrm{d}t\, \mathrm{d}t'. \tag{34}$$

For the general case in which the matrix elements of $\Lambda^{\mathbf{O}}(0)$ and $\Lambda^{\boldsymbol{\rho}}(0)$ are distinct, i.e., $\Lambda_1^{\mathbf{O}}(0) > \Lambda_2^{\mathbf{O}}(0) > \cdots > \Lambda_{n_{\mathbf{O}}}^{\mathbf{O}}(0)$ and $\Lambda_1^{\boldsymbol{\rho}}(0) > \Lambda_2^{\boldsymbol{\rho}}(0) > \cdots > \Lambda_{n_{\boldsymbol{\rho}}}^{\boldsymbol{\rho}}(0)$, where $n_{\boldsymbol{\rho}}$ and $n_{\mathbf{O}}$ are respectively the numbers of non-zero elements of $\Lambda^{\boldsymbol{\rho}}(0)$ and $\Lambda^{\mathbf{O}}(0)$, the number of non-zero $\langle \mathbf{O}(T) \rangle$ critical point values $N_{\mathbf{c}}$ depends on the possible combinations of these distinct, non-zero elements. Using the combination and permutation expression in Eq. (32), it may then be deduced that

$$N_{\mathbf{c}} = \sum_{k=k_1}^{n_<} \frac{n_{\mathbf{O}}! n_{\boldsymbol{\rho}}!}{(n_{\mathbf{O}} - k)!(n_{\boldsymbol{\rho}} - k)!k!}, \tag{35}$$

where $n_< = \min\{n_{\boldsymbol{\rho}},\ n_{\mathbf{O}}\}$ and $k_1 = \max\{1,\ n_{\mathbf{O}} + n_{\boldsymbol{\rho}} - N\}$, respectively, are the largest and smallest overlapping numbers of non-zero eigenvalues of $\Lambda^{\boldsymbol{\rho}}(0)$ and $\Lambda^{\mathbf{O}}(0)$. All $\langle \mathbf{O}(T) \rangle$ critical point values are non-zero if $k_1 \geq 1$, whereas they also contain zero values if $k_1 \leq 0$. Each summand in Eq. (35) is a product of two terms: (1) $n_{\mathbf{O}}!/(n_{\mathbf{O}} - k)!k!$, the number of ways of combining arbitrary k eigenvalues from a pool of $n_{\mathbf{O}}$ non-zero eigenvalues of $\Lambda^{\mathbf{O}}(0)$, and (2) $n_{\boldsymbol{\rho}}!/(n_{\boldsymbol{\rho}} - k)!$, the number of ways of permuting k non-zero eigenvalues of $\Lambda^{\mathbf{O}}(0)$ among $n_{\boldsymbol{\rho}}$ non-zero eigenvalues of $\Lambda^{\boldsymbol{\rho}}(0)$.

The number of non-zero non-degenerate critical point values can readily be computed from Eq. (35) for general quantum observables and arbitrary initial density matrices. The cases are: (i) $n_{\mathbf{O}} > 1$ and $n_{\boldsymbol{\rho}} = 1$ then $N_{\mathbf{c}} = n_{\mathbf{O}}$, corresponding for example to when the control target is to maximize the molecular vibrational energy [25] (or the molecular alignment/orientation [33]) and the molecule initially lies in its vibrational (or rotational) ground eigenstate; (ii) $n_{\mathbf{O}} = 1$ and $n_{\boldsymbol{\rho}} > 1$ then $N_{\mathbf{c}} = n_{\boldsymbol{\rho}}$, corresponding to when the control target state is a single pure molecular (ro-vibrational) energy eigenstate and the molecule is initially represented by mixed quantum states (say, in thermal equilibrium with a bath at finite temperature [23,25]). Another extreme case (iii) is for

the alignment/orientation control involving rotationally hot molecules [23], where both the target observable $\mathbf{O}$ ($\mathbf{O} = \cos^2\theta$ for the alignment, $\mathbf{O} = \cos\theta$ for the orientation, where θ is the polar angle) and the initial density matrix $\boldsymbol{\rho}(0)$ (assuming a Boltzmann distribution over all N rotational states) are of full rank i.e., $n_{\mathbf{O}} = n_{\boldsymbol{\rho}} = N$, and the number of non-zero critical point values is then $N_{\mathbf{c}} = N!$. Finally, in a last example (iv) for the pure state $P_{i\to f}$ optimal control problem, where both the observable and initial density matrix are of rank one, i.e., $n_{\boldsymbol{\rho}} = n_{\mathbf{O}} = 1$, we obtain $N_{\mathbf{c}} = 1$, which implies that only one nonzero extrema value exists, corresponding to the global maximum $P_{i\to f} = 1.0$. No false suboptimal critical points exist [19,20] for maximizing $P_{i\to f}$ when no additional costs or restrictions on the controls are imposed. Analysis of the general situation involving possibly degenerate eigenvalues of the operators $\mathbf{O}$ and $\boldsymbol{\rho}(0)$ has also been considered recently [27,28,34].

3. Landscapes within the electric dipole approximation

Within the electric dipole approximation, cf. Eq. (6), a functional change in the Hamiltonian is

$$\delta\mathbf{H}(t) = -\boldsymbol{\mu}\delta\epsilon(t), \tag{36}$$

which, after substitution in Eq. (18), leads to

$$\delta\langle\mathbf{O}(T)\rangle = \int_0^T \left(-\frac{\imath}{\hbar}\right) \mathrm{Tr}\left([\mathbf{O}(T),\ \boldsymbol{\rho}(0)]\{U^\dagger(t,0)\boldsymbol{\mu}U(t,0)\}\right) \delta\epsilon(t)\,\mathrm{d}t. \tag{37}$$

Here the electric field is considered as a scalar function corresponding to the common case of linear polarization. Likewise, at the critical points, the second-order functional change $\delta^2\langle\mathbf{O}(T)\rangle$ in Eq. (34) becomes

$$\delta^2\langle\mathbf{O}(T)\rangle = \int_0^T\int_0^T \left(-\frac{1}{\hbar^2}\right) \mathrm{Tr}\left(\left[\left[\mathbf{O}(T),\ U^\dagger(t,0)\boldsymbol{\mu}U(t,0)\right],\quad U^\dagger(t',0)\boldsymbol{\mu}U(t',0)\right]\boldsymbol{\rho}(0)\right)\ \delta\epsilon(t)\delta\epsilon(t')\,\mathrm{d}t\,\mathrm{d}t'. \tag{38}$$

3.1. Bound on the quantum control landscape slope

The magnitude of the landscape slope on the way towards an extremum is important in determining the efficiency and stability of experimental searches for effective quantum controls. From Eq. (37), the slope (i.e., the first order functional derivative) of $\langle\mathbf{O}(T)\rangle$ can be readily identified as

$$\begin{aligned}\frac{\delta\langle\mathbf{O}(T)\rangle}{\delta\epsilon(t)} &= -\frac{\imath}{\hbar}\mathrm{Tr}\left([\mathbf{O}(T),\ \boldsymbol{\rho}(0)]\boldsymbol{\mu}(t)\right) = \frac{\imath}{\hbar}\mathrm{Tr}\left([\mathbf{O}(T),\ \boldsymbol{\mu}(t)]\boldsymbol{\rho}(0)\right) = \frac{\imath}{\hbar}\sum_i \Lambda_i^{\boldsymbol{\rho}}(0)\langle i|\left(\mathbf{O}(T)\boldsymbol{\mu}(t) - \boldsymbol{\mu}(t)\mathbf{O}(T)\right)|i\rangle \\ &= -\frac{2}{\hbar}\sum_i \Lambda_i^{\boldsymbol{\rho}}(0)\Im\left(\langle i|\mathbf{O}(T)\boldsymbol{\mu}(t)|i\rangle\right),\end{aligned} \tag{39}$$

where $\Im$ denotes imaginary part and the ket $|i\rangle$ is an eigenstate of the density operator $\boldsymbol{\rho}(0)$, i.e., $\boldsymbol{\rho}(0)|i\rangle = \Lambda_i^{\boldsymbol{\rho}}(0)|i\rangle$, at the initial time. From Eq. (39) and invoking Hölder's inequality for finite sums [35], we can derive the following:

$$\begin{aligned}\left|\frac{\delta\langle\mathbf{O}(T)\rangle}{\delta\epsilon(t)}\right|^2 &= \frac{4}{\hbar^2}\left|\sum_i \Lambda_i^{\boldsymbol{\rho}}(0)\Im\left(\langle i|\mathbf{O}(T)\boldsymbol{\mu}(t)|i\rangle\right)\right|^2 \le \frac{4}{\hbar^2}\sum_i |\Lambda_i^{\boldsymbol{\rho}}(0)|^2 \times \sum_i |\Im\left(\langle i|\mathbf{O}(T)\boldsymbol{\mu}(t)|i\rangle\right)|^2 \\ &\le \frac{4}{\hbar^2}\sum_i \left|\Lambda_i^{\boldsymbol{\rho}}(0)\right|^2 \times \sum_i |\langle i|\mathbf{O}(T)\boldsymbol{\mu}(t)|i\rangle|^2,\end{aligned} \tag{40}$$

which can be further written as

$$\left|\frac{\delta\langle\mathbf{O}(T)\rangle}{\delta\epsilon(t)}\right|^2 \le \frac{4}{\hbar^2}\|\Lambda^{\boldsymbol{\rho}}(0)\|^2 \times \|\mathbf{O}(T)\boldsymbol{\mu}(t)\|^2 \le \frac{4}{\hbar^2}\|\Lambda^{\boldsymbol{\rho}}(0)\|^2 \times \|\mathbf{O}(T)\|^2 \times \|\boldsymbol{\mu}(t)\|^2 = \frac{4}{\hbar^2}\|\Lambda^{\boldsymbol{\rho}}(0)\|^2 \times \|\mathbf{O}\|^2 \times \|\boldsymbol{\mu}\|^2 \tag{41}$$

where the norm inequality $\|\mathbf{AB}\| \le \|\mathbf{A}\|\,\|\mathbf{B}\|$ for two arbitrary matrices $\mathbf{A}$ and $\mathbf{B}$ was invoked [29]. Moreover, $\|\mathbf{O}(T)\| = \|\mathbf{O}\|$ and $\|\boldsymbol{\mu}(t)\| = \|\boldsymbol{\mu}\|$ due to the unit norm of the time evolution operator. From Eq. (10), the upper bound of the gradient $\delta\langle\mathbf{O}(T)\rangle/\delta\epsilon(t)$ is then given as

$$\left|\frac{\delta\langle\mathbf{O}(T)\rangle}{\delta\epsilon(t)}\right| \le \frac{2}{\hbar}\|\mathbf{O}\| \times \|\boldsymbol{\mu}\|. \tag{42}$$

As the norm $\|\mathbf{O}\|$ and $\|\boldsymbol{\mu}\|$ are expected to be finite in realistic applications, the bound in Eq. (42) has the simple physical interpretation that the landscape slope on the way towards an extremum, e.g., the global maximum, will be rather gentle without steep regions. This behavior is especially important for assuring the stability of searches for an effective control.

3.2. Quantum control landscape topology: Hessian evaluated at the critical points

The analysis in Section 2 shows that upon searching over unconstrained control fields a finite number of critical point values of $\langle \mathbf{O}(T)\rangle$ exist such that $\delta\langle \mathbf{O}(T)\rangle/\delta\epsilon(t) = 0\,\forall t$. A prime topic of interest is the topology of the landscape in the vicinity of these critical points. A detailed analysis of the Hessian eigenvalue structures, including the Hessian ranks, at and away from the global maximum and minimum will be presented. Whether the suboptimal extrema are either local minima/maxima (i.e., traps) or saddles can greatly influence the efficiency of the search and the effectiveness of the control algorithm. This topological analysis is also relevant for consideration of robustness to control field noise at the final global maximum or minimum. The presentation in this subsection is general, however the rank analysis at the critical points will only consider the non-degenerate cases in which all of the non-zero matrix elements of $\Lambda^{\mathbf{O}}(0)$ and $\Lambda^{\boldsymbol{\rho}}(0)$ are distinct, i.e., $\Lambda^{\mathbf{O}}_1(0) > \Lambda^{\mathbf{O}}_2(0) > \cdots > \Lambda^{\mathbf{O}}_{n_{\mathbf{O}}}(0)$ and $\Lambda^{\boldsymbol{\rho}}_1(0) > \Lambda^{\boldsymbol{\rho}}_2(0) > \cdots > \Lambda^{\boldsymbol{\rho}}_{n_{\boldsymbol{\rho}}}(0)$. The resultant ranks for the non-degenerate cases establish upper bounds for the general cases where the non-zero matrix elements of $\Lambda^{\mathbf{O}}(0)$ and $\Lambda^{\boldsymbol{\rho}}(0)$ may assume the same values (i.e., degenerate cases).

From Eq. (38), the Hessian $\mathcal{H}^{\boldsymbol{\epsilon}}(t,t') \equiv \delta^2\langle \mathbf{O}(T)\rangle/\delta\epsilon(t)\delta\epsilon(t')$ at each critical point can be expressed as

$$\mathcal{H}^{\boldsymbol{\epsilon}}(t,t') = -\frac{1}{\hbar^2}\,\mathrm{Tr}([[\mathbf{O}(T),\ \boldsymbol{\mu}(t)],\ \boldsymbol{\mu}(t')]\boldsymbol{\rho}(0)), \tag{43}$$

which can be written in a fully symmetric form (see Appendix A)

$$\mathcal{H}^{\boldsymbol{\epsilon}}(t,t') = -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\boldsymbol{\rho}}}\sum_{j>i}^{N}\left(\Lambda^{\boldsymbol{\rho}}_i(0) - \Lambda^{\boldsymbol{\rho}}_j(0)\right)\left(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0)\right) \times \left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Re} + \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Im}\right), \tag{44}$$

where $\Re$ denotes real part, $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re} \equiv \Re(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle)$ and $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im} \equiv \Im(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle)$, with $\boldsymbol{\mu}_{\boldsymbol{\rho}}(t) \equiv \mathcal{U}^{\dagger}_{\boldsymbol{\rho}}\boldsymbol{\mu}(t)\mathcal{U}_{\boldsymbol{\rho}} = \mathcal{U}^{\dagger}_{\boldsymbol{\rho}}U^{\dagger}(t,0)\boldsymbol{\mu}U(t,0)\mathcal{U}_{\boldsymbol{\rho}}$, thus $\|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)\| = \|\boldsymbol{\mu}(t)\| = \|\boldsymbol{\mu}\|$. The double-sum in Eq. (44) only contains contribution from terms for which the product $(\Lambda^{\boldsymbol{\rho}}_i(0) - \Lambda^{\boldsymbol{\rho}}_j(0))(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0))$ is not zero. The Hessian $\mathcal{H}^{\boldsymbol{\epsilon}}(t,t')$ at any critical point is symmetric with respect to t and t', and a separable form in t and t' in that the double-sum in Eq. (44) only involves the products of a finite number of linearly independent real functions, $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}$ and $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}$, and similarly for t'. Considering these real functions as linearly independent for different i and j is based on the assumption of complete controllability of the quantum system and the fact that $\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)$ is related to the dipole moment operator $\boldsymbol{\mu}(t)$ via a unitary transformation (i.e., $\boldsymbol{\mu}_{\boldsymbol{\rho}}(t) \equiv \mathcal{U}^{\dagger}_{\boldsymbol{\rho}}\boldsymbol{\mu}(t)\mathcal{U}_{\boldsymbol{\rho}}$). Consequently, the Hessian at any critical point (including both the global maximum and minimum) possesses at most only $\mathcal{R}_{\mathcal{H}^{\boldsymbol{\epsilon}}} = n_{\boldsymbol{\rho}}(2N - n_{\boldsymbol{\rho}} - 1)$ non-zero real eigenvalues $\sigma_1, \sigma_2, \ldots, \sigma_{\mathcal{R}_{\mathcal{H}^{\boldsymbol{\epsilon}}}}$ (i.e., its rank is at most $\mathcal{R}_{\mathcal{H}^{\boldsymbol{\epsilon}}}$) together with infinitely many zero eigenvalues and the associated eigenfunctions. The non-zero eigenvalues σ and eigenfunctions $u(t)$ of the Hessian satisfy the following integral eigenvalue equation

$$\int_0^T \mathcal{H}^{\boldsymbol{\epsilon}}(t,t')u(t')\,\mathrm{d}t' = \sigma u(t), \tag{45}$$

where every eigenfunction $u(t)$ may be expanded in terms of the linearly independent basis functions $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}$ and $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}$, $1 \le i \le n_{\boldsymbol{\rho}}$, $1 \le i < j \le N$, as follows:

$$u(t) = \sum_{i=1}^{n_{\boldsymbol{\rho}}}\sum_{j>i}^{N}\left\{a_{ij}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re} + b_{ij}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}\right\}, \tag{46}$$

with the pairs of complex expansion coefficients a_{ij} and b_{ij}. Substitution of Eq. (46) into Eq. (45) reduces the corresponding integral eigenvalue problem to a matrix eigenvalue problem involving an $\mathcal{R}_{\mathcal{H}^{\boldsymbol{\epsilon}}} \times \mathcal{R}_{\mathcal{H}^{\boldsymbol{\epsilon}}}$ Hermitian matrix.

By partitioning the first $n_{\boldsymbol{\rho}}$ eigenvalues $\Lambda^{\mathbf{O}}_{p(i)}(0)$, $i = 1, \ldots, n_{\boldsymbol{\rho}} \le N$, into a sequence of dual segments (indexed by $\alpha = 1, 2, \ldots$), each containing uninterrupted zeros (of the length $\mathcal{M}_\alpha$) followed by uninterrupted non-zeros (of the length $\mathcal{N}_\alpha$), it is then easy to deduce that for each segment, for example at the α-th one, the number of non-zero products $(\Lambda^{\boldsymbol{\rho}}_i(0) - \Lambda^{\boldsymbol{\rho}}_j(0))(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0))$ involving $\mathcal{M}_\alpha$ zero values for $\Lambda^{\mathbf{O}}_{p(i)}(0)$ in Eq. (44) is $2\mathcal{M}_\alpha n^{\alpha}_{\mathbf{O}}$, whereas that involving $\mathcal{N}_\alpha$ non-zero values for $\Lambda^{\mathbf{O}}_{p(i)}(0)$ is $\mathcal{N}_\alpha(2\mathcal{K}_\alpha - \mathcal{N}_\alpha - 1)$. Here $\sum_{\forall\alpha}\{\mathcal{M}_\alpha + \mathcal{N}_\alpha\} = n_{\boldsymbol{\rho}}$ gives the total length of the sequence, $n^{\alpha}_{\mathbf{O}} = n_{\mathbf{O}} - \sum_{\beta=0}^{\alpha-1}\mathcal{N}_\beta$ is the remaining number of non-zero values $\Lambda^{\mathbf{O}}_{p(i)}(0)$ beyond the $(\alpha-1)$-th segment in the sum over the index j in Eq. (44), and $\mathcal{K}_\alpha = N - \sum_{\beta=1}^{\alpha-1}\{\mathcal{M}_\beta + \mathcal{N}_\beta\} - \mathcal{M}_\alpha$ is the total number of the remaining terms, excluding $\mathcal{M}_\alpha$ zeros of $\Lambda^{\mathbf{O}}_{p(i)}(0)$ in the α-th segment. Thus, the rank $\mathcal{R}_{\mathbf{c}}$ of the Hessian at an arbitrary critical point can be computed from

$$\mathcal{R}_{\mathbf{c}} = \sum_{\forall\alpha}\left\{2\mathcal{M}_\alpha n^{\alpha}_{\mathbf{O}} + \mathcal{N}_\alpha(2\mathcal{K}_\alpha - \mathcal{N}_\alpha - 1)\right\} \le \mathcal{R}_{\mathcal{H}^{\boldsymbol{\epsilon}}}. \tag{47}$$

From Eq. (47), it follows that $\mathcal{R}_{\mathbf{c}} = \mathcal{R}_{\mathcal{H}^{\epsilon}} = N(N-1)$ when $n_{\boldsymbol{\rho}} = n_{\mathbf{O}} = N$, in agreement with a simple number counting of all non-zero terms in Eq. (44). An analysis of the eigenvalues of the Hessian $\mathcal{H}^{\epsilon}(t,t')$ will be presented at various critical points, including at and away from the global maximum and minimum. A symmetric, negative (positive) semi-definite Hessian $\mathcal{H}^{\epsilon}(t,t')$ will possess only negative (positive) non-zero eigenvalues [36], which is the case at the global maximum (minimum) to be discussed below.

3.2.1. Hessian at the global maximum

At the global maximum, $\Lambda_i^{\mathbf{O}}(T) = \Lambda_i^{\mathbf{O}}(0)$, $i = 1, \ldots, N$, and from Eq. (44), the Hessian $\mathcal{H}^{\epsilon}(t,t')$ can be written as

$$\mathcal{H}^{\epsilon}(t,t') = -\frac{2}{\hbar^2}\sum_i\sum_{j>i}\left(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0)\right)\left(\Lambda_i^{\mathbf{O}}(0) - \Lambda_j^{\mathbf{O}}(0)\right) \times \left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Re} + \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Im}\right), \tag{48}$$

which is a continuous symmetric kernel function of negative semi-definite type, since the inequality

$$\begin{aligned}\langle v|\mathcal{H}^{\epsilon}|v\rangle &\equiv \int_0^T\int_0^T v^*(t)\mathcal{H}^{\epsilon}(t,t')v(t')\,\mathrm{d}t\,\mathrm{d}t' \\ &= -\frac{2}{\hbar^2}\sum_i\sum_{j>i}\left(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0)\right)\left(\Lambda_i^{\mathbf{O}}(0) - \Lambda_j^{\mathbf{O}}(0)\right) \times \left\{\left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re} v(t)\,\mathrm{d}t\right|^2 + \left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im} v(t)\,\mathrm{d}t\right|^2\right\} \le 0\end{aligned} \tag{49}$$

holds for an arbitrary function $v(t)$, using the fact that $(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0)) \ge 0$ and $(\Lambda_i^{\mathbf{O}}(0) - \Lambda_j^{\mathbf{O}}(0)) \ge 0$, $\forall j > i$. In Eq. (48), the index i is carried out over only those non-vanishing $\Lambda_i^{\boldsymbol{\rho}}$'s and $\Lambda_i^{\mathbf{O}}(0)$'s, while the index j is carried out from $j = i+1$ to N, thus, the maximum number (i.e., rank) of the independent terms involved in the Hessian (note that here in Eq. (47), $\alpha = 1, 2$, $\mathcal{M}_1 = 0$, $\mathcal{N}_1 = \min\{n_{\boldsymbol{\rho}}, n_{\mathbf{O}}\}$, $n_{\mathbf{O}}^1 = n_{\mathbf{O}}$, $\mathcal{K}_1 = N$, $\mathcal{M}_2 = \max\{n_{\boldsymbol{\rho}} - n_{\mathbf{O}}, 0\}$, $\mathcal{N}_2 = 0$, $n_{\mathbf{O}}^2 = n_{\mathbf{O}} - \mathcal{N}_1$, and $\mathcal{K}_2 = N - \mathcal{N}_1 - \mathcal{M}_2$) can be expressed as

$$\mathcal{R}_{\mathrm{M}} = \mathcal{N}_1(2N - \mathcal{N}_1 - 1) = n_<(2N - n_< - 1) \ge \mathcal{R}_{\mathbf{c}}, \tag{50}$$

where $n_< = \min\{n_{\boldsymbol{\rho}}, n_{\mathbf{O}}\}$.

The Hessian at the global maximum has a rank of at most $\mathcal{R}_{\mathrm{M}}$, and it possesses at most $\mathcal{R}_{\mathrm{M}}$ non-zero, negative eigenvalues $\sigma_1 \le \sigma_2 \le \cdots \le \sigma_{\mathcal{R}_{\mathrm{M}}} \le 0$ (note that $|\sigma_1| \ge |\sigma_2| \ge \cdots \le |\sigma_{\mathcal{R}_{\mathrm{M}}}| \ge 0$) associated with $\mathcal{R}_{\mathrm{M}}$ orthonormal eigenfunctions $u_1(t), u_2(t), \ldots, u_{\mathcal{R}_{\mathrm{M}}}(t)$. In addition, it contains an infinite dimensional null space spanned by eigenfunctions associated with its infinite number of zero eigenvalues. As a result, the Hessian at the global maximum can be expediently expanded as

$$\mathcal{H}^{\epsilon}(t,t') = -\sum_{k=1}^{\mathcal{R}_{\mathrm{M}}} |\sigma_k| u_k^*(t) u_k(t'), \tag{51}$$

in terms of the eigenfunctions $u_k(t)$ with non-zero eigenvalues σ_k (≤ 0). The rank for the physical examples that were adopted in enumerating the number of the non-zero critical point values in Section 2 can be readily computed from Eq. (50): (i) $\mathcal{R}_{\mathrm{M}} = 2N - 2$ when $n_{\boldsymbol{\rho}} = 1$ and $n_{\mathbf{O}} > 1$, (ii) $\mathcal{R}_{\mathrm{M}} = 2N - 2$ when $n_{\boldsymbol{\rho}} > 1$ and $n_{\mathbf{O}} = 1$, (iii) $\mathcal{R}_{\mathrm{M}} = N(N-1)$ when $n_{\boldsymbol{\rho}} = n_{\mathbf{O}} = N$, and (iv) $\mathcal{R}_{\mathrm{M}} = 2N - 2$ when $n_{\boldsymbol{\rho}} = n_{\mathbf{O}} = 1$ [22].

The diagonal elements of Eq. (48) satisfy

$$\mathcal{H}^{\epsilon}(t,t) = -\frac{2}{\hbar^2}\sum_i\sum_{j>i}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_i^{\mathbf{O}}(0) - \Lambda_j^{\mathbf{O}}(0))\,|\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle|^2 \le 0, \tag{52}$$

which is negative semi-definite and can be shown to be bounded from below

$$\begin{aligned}\mathcal{H}^{\epsilon}(t,t) &\ge -\frac{2}{\hbar^2}\Lambda_1^{\boldsymbol{\rho}}(0)\Lambda_1^{\mathbf{O}}(0)\sum_i\sum_{j>i}|\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle|^2 \\ &\ge -\frac{2}{\hbar^2}\Lambda_1^{\boldsymbol{\rho}}(0)\Lambda_1^{\mathbf{O}}(0)\sum_i\sum_{j}|\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle|^2 = -\frac{2}{\hbar^2}\Lambda_1^{\boldsymbol{\rho}}(0)\Lambda_1^{\mathbf{O}}(0)\sum_i\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|i\rangle \\ &= -\frac{2}{\hbar^2}\Lambda_1^{\boldsymbol{\rho}}(0)\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)\|^2 = -\frac{2}{\hbar^2}\Lambda_1^{\boldsymbol{\rho}}(0)\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}\|^2 \ge -\frac{2}{\hbar^2}\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}\|^2,\end{aligned} \tag{53}$$

where Eq. (10) was used in the last step. From Eqs. (51) and (53) as well as using the orthonormal relation $\int_0^T u_k^*(t)u_\ell(t)\,\mathrm{d}t = \delta_{k\ell}$, the trace of the corresponding Hessian $\mathrm{Tr}(\mathcal{H}^{\boldsymbol{\epsilon}}) \equiv \int_0^T \mathcal{H}^{\boldsymbol{\epsilon}}(t,t)\,\mathrm{d}t = -\sum_{k=1}^{\mathcal{R}_M} |\sigma_k|$ is given as

$$\mathrm{Tr}(\mathcal{H}^{\boldsymbol{\epsilon}}) = -\frac{2}{\hbar^2}\sum_i\sum_{j>i}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_i^{\mathbf{O}}(0) - \Lambda_j^{\mathbf{O}}(0))\int_0^T |\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle|^2\,\mathrm{d}t \geq -\frac{2T}{\hbar^2}\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}\|^2, \tag{54}$$

which is also negative and bounded from below.

3.2.2. Hessian at the global minimum

Likewise, at the global minimum we have the relation $\Lambda_i^{\mathbf{O}}(T) = \Lambda_{N-i+1}^{\mathbf{O}}(0)$, $i = 1,\ldots,N$. From Eq. (44), the corresponding Hessian $\mathcal{H}^{\boldsymbol{\epsilon}}(t,t')$ can be written as

$$\begin{aligned}\mathcal{H}^{\boldsymbol{\epsilon}}(t,t') = &-\frac{2}{\hbar^2}\sum_i\sum_{j>i}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_{N-i+1}^{\mathbf{O}}(0) - \Lambda_{N-j+1}^{\mathbf{O}}(0))\\ &\times\left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Re} + \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Im}\right),\end{aligned} \tag{55}$$

which, noting that $\Lambda_{N-i+1}^{\mathbf{O}}(0) - \Lambda_{N-j+1}^{\mathbf{O}}(0) \leq 0\,\forall\, j > i$, leads to the inequality

$$\begin{aligned}\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle = &-\frac{2}{\hbar^2}\sum_i\sum_{j>i}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_{N-i+1}^{\mathbf{O}}(0) - \Lambda_{N-j+1}^{\mathbf{O}}(0))\\ &\times\left\{\left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}v(t)\,\mathrm{d}t\right|^2 + \left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}v(t)\,\mathrm{d}t\right|^2\right\} \geq 0,\end{aligned} \tag{56}$$

for an arbitrary function $v(t)$. Thus, the Hessian in Eq. (55) is a continuous symmetric kernel of positive semi-definite type, and naturally all of the non-zero eigenvalues of the Hessian at the global minimum are positive numbers. At the global minimum, we have $\alpha = 1$, $\mathcal{M}_1 = \min\{N - n_{\mathbf{O}}, n_{\boldsymbol{\rho}}\}$, $\mathcal{N}_1 = \max\{n_{\boldsymbol{\rho}} + n_{\mathbf{O}} - N, 0\}$, $n_{\mathbf{O}}^1 = n_{\mathbf{O}}$ and $\mathcal{K}_1 = N - \mathcal{M}_1$ in Eq. (47), thus the rank $\mathcal{R}_m$ of the corresponding Hessian can be expressed as

$$\mathcal{R}_m = \begin{cases} 2n_{\boldsymbol{\rho}}n_{\mathbf{O}} & \text{if} \quad n_{\boldsymbol{\rho}} + n_{\mathbf{O}} \leq N,\\ 2n_{\boldsymbol{\rho}}n_{\mathbf{O}} - (n_{\boldsymbol{\rho}} + n_{\mathbf{O}} - N)(n_{\boldsymbol{\rho}} + n_{\mathbf{O}} - N + 1) & \text{if} \quad n_{\boldsymbol{\rho}} + n_{\mathbf{O}} > N.\end{cases} \tag{57}$$

The Hessian $\mathcal{H}^{\boldsymbol{\epsilon}}(t,t')$ at the global minimum possesses at most $\mathcal{R}_{\mathrm{m}}(\leq \mathcal{R}_{\mathbf{c}})$ non-zero, positive eigenvalues $\sigma_1 \geq \sigma_2 \geq \cdots \geq \sigma_{\mathcal{R}_{\mathrm{M}}} \geq 0$, as well as infinitely many zero eigenvalues. For example in the $P_{i\to f}$ control landscape $n_{\boldsymbol{\rho}} = n_{\mathbf{O}} = 1$, and at the global minimum $P_{i\to f} = 0$ the only term in Eq. (55) that is non-zero corresponds to $i = 1$ and $j = N$. Thus, the corresponding Hessian

$$\mathcal{H}^{\boldsymbol{\epsilon}}(t,t') = \frac{2}{\hbar^2}\Lambda_1^{\boldsymbol{\rho}}(0)\Lambda_1^{\mathbf{O}}(0)\left(\langle 1|\boldsymbol{\mu}(t)|N\rangle^{\Re}\langle 1|\boldsymbol{\mu}(t')|N\rangle^{\Re} + \langle 1|\boldsymbol{\mu}(t)|N\rangle^{\Im}\langle 1|\boldsymbol{\mu}(t')|N\rangle^{\Im}\right), \tag{58}$$

has at most the rank $\mathcal{R}_{\mathrm{M}} = 2$ for some non-zero control field $\boldsymbol{\epsilon}(t)$ [22]. This result means that when starting out at low yield with an initial control, there will be at most two coordinated directions in the space of control fields to lift the yield of $P_{i\to f}$. The diagonal elements of the Hessian at the global minimum, i.e. Eq. (48), are positive and bounded from above (cf., Eq. (53)) by the inequality

$$0 \leq \mathcal{H}^{\boldsymbol{\epsilon}}(t,t) \leq \frac{2}{\hbar^2}\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}\|^2, \tag{59}$$

and the corresponding trace is bounded (cf., Eq. (54)) by the inequality

$$0 \leq \mathrm{Tr}(\mathcal{H}^{\boldsymbol{\epsilon}}) \leq \frac{2T}{\hbar^2}\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}\|^2. \tag{60}$$

3.2.3. Hessian at the local critical points

At a critical point away from the global maximum and global minimum, the corresponding Hessian $\mathcal{H}^{\boldsymbol{\epsilon}}(t,t')$ is neither positive nor negative definite, since for an arbitrary function $v(t)$ the expression

$$\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle = -\frac{2}{\hbar^2}\sum_i\sum_{j>i}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_{p(i)}^{\mathbf{O}}(0) - \Lambda_{p(j)}^{\mathbf{O}}(0)) \times \left\{\left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}v(t)\,\mathrm{d}t\right|^2 + \left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}v(t)\,\mathrm{d}t\right|^2\right\} \tag{61}$$

can be either negative or positive depending on the temporal behavior of the function $v(t)$. Note that any permutation $p(i)$ other than $p(i) = i$ (i.e., $1\to 1, 2\to 2, \ldots, i\to i, \ldots, N\to N$ for the global maximum) and $p(i) = N - i + 1$ (i.e., $N\to 1, N-1\to$

$2, \ldots, N-i+1 \rightarrow i, \ldots, 1 \rightarrow N$ for the global minimum) can render at least one positive and one negative value for the quantity $(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0))$ in the double-sum in Eq. (61). As a result, Eq. (61) can be written as a sum of a negative part and a positive part, namely

$$\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle = \langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_- + \langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_+, \tag{62}$$

where the negative part is

$$\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_- = -\frac{2}{\hbar^2}\sum_i \sum_{j>i}^{+} \left(\Lambda^{\boldsymbol{\rho}}_i(0) - \Lambda^{\boldsymbol{\rho}}_j(0)\right)\left(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0)\right)_+ \times \left\{\left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}_+ v(t)\,\mathrm{d}t\right|^2 + \left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}_+ v(t)\,\mathrm{d}t\right|^2\right\} < 0 \tag{63}$$

and the positive part is

$$\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_+ = -\frac{2}{\hbar^2}\sum_i \sum_{j>i}^{-} \left(\Lambda^{\boldsymbol{\rho}}_i(0) - \Lambda^{\boldsymbol{\rho}}_j(0)\right)\left(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0)\right)_- \times \left\{\left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}_- v(t)\,\mathrm{d}t\right|^2 + \left|\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}_- v(t)\,\mathrm{d}t\right|^2\right\} > 0. \tag{64}$$

The labels "+" and "−", respectively, denote terms that correspond to positive and negative values of $(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0))$, i.e., $(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0))_+ > 0$ and $(\Lambda^{\mathbf{O}}_{p(i)}(0) - \Lambda^{\mathbf{O}}_{p(j)}(0))_- < 0$, since $(\Lambda^{\boldsymbol{\rho}}_i(0) - \Lambda^{\boldsymbol{\rho}}_j(0)) > 0$ for all $j > i$.

The assumption that the real functions $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}$ and $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}$ for different i and j are linearly independent makes it possible, for example, via the Gram-Schmidt orthogonalization procedure [37], to find a function $v_+(t)$ orthogonal to all the functions $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle_+$, i.e., $\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}_+ v_+(t)\,\mathrm{d}t = 0$ and $\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}_+ v_+(t)\,\mathrm{d}t = 0$, such that $\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_- = 0$, producing $\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle > 0$. Similarly, it is possible to find a function $v_-(t)$ orthogonal to all the functions $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle_-$, i.e., $\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}_- v_-(t)\,\mathrm{d}t = 0$ and $\int_0^T \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}_- v_-(t)\,\mathrm{d}t = 0$, such that $\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_+ = 0$, producing $\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle < 0$. As a result, any Hessian evaluated at a critical point, except at the global extrema, is indefinite and corresponds to a saddle point. *Thus, no suboptimal false extrema traps exist in the* $\langle \mathbf{O}(T)\rangle$ *control landscape*. The actual numbers of negative and positive eigenvalues of the Hessian at the critical points may fluctuate between the global maximum and minimum.

From Eq. (32), as the expectation value $\langle \mathbf{O}(T)\rangle$ drops, the number of terms in the negative part $\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_-$ in Eq. (63) also drops, while the number of terms in the positive part $\langle v|\mathcal{H}^{\boldsymbol{\epsilon}}|v\rangle_+$ in Eq. (64) grows. As a result, it is expected that the number of all non-zero negative eigenvalues of the Hessian at the global maximum $\langle \mathbf{O}(T)\rangle = \sum_{i=1}^N \Lambda^{\mathbf{O}}_i(0)\Lambda^{\boldsymbol{\rho}}_i(0)$ will decrease from $\mathcal{R}_\mathrm{M}$. This would be accompanied by an increase of the number of non-zero positive eigenvalues when $\langle \mathbf{O}(T)\rangle$ proceeds downward from its global maximum to lower values at the intermediate critical saddle points. Eventually, the number of the non-zero eigenvalues (which finally become all positive) drops to at most $\mathcal{R}_\mathrm{m}$ as the value of $\langle \mathbf{O}(T)\rangle$ reaches its the global minimum $\langle \mathbf{O}(T)\rangle = \sum_{i=1}^N \Lambda^{\mathbf{O}}_{N-i+1}(0)\Lambda^{\boldsymbol{\rho}}_i(0)$. This observation is in agreement with the results from earlier numerical simulations [28] based on the matrix elements of the unitary matrix $U(T, 0)$, cf., Eqs. (19)–(21).

3.3. Quantum control robustness at the global maximum

In the robustness analysis below achieving the global maximum of $\langle \mathbf{O}(T)\rangle$ will be taken as the objective; a similar analysis applies to seeking the global minimum as the objective. The Hessian at the global maximum of $\langle \mathbf{O}(T)\rangle$ not only possesses at most $\mathcal{R}_\mathrm{M}$ non-positive eigenvalues, but also infinitely many zero eigenvalues (and associated eigenfunctions). As the sum of these eigenvalues [see Eq. (54)], i.e., the trace of the Hessian, is bounded by $-(2T/\hbar^2)\Lambda^{\mathbf{O}}_1(0)\|\boldsymbol{\mu}\|^2$, it is evident that as the Hilbert space dimension N increases then $\mathcal{R}_\mathrm{M}$ also generally rising too, with each individual non-zero eigenvalue likely taking on an ever smaller value, i.e. the average eigenvalue of the Hessian falls off as $\sim \frac{1}{\mathcal{R}_\mathrm{M}}$. Furthermore, it is readily seen that around the global control maximum of $\langle \mathbf{O}(T)\rangle$, any small perturbation (i.e., noise) $\delta\epsilon(t)$ in the control field $\epsilon(t)$ yields a deviation $\delta\langle \mathbf{O}(T)\rangle$ in the optimal yield

$$\delta\langle \mathbf{O}(T)\rangle \approx \frac{1}{2}\int_0^T\int_0^T \delta\epsilon(t)\mathcal{H}^{\boldsymbol{\epsilon}}(t,t')\delta\epsilon(t')\,\mathrm{d}t\,\mathrm{d}t' = -\frac{1}{2}\int_0^T\int_0^T \delta\epsilon(t)\left(\sum_{k=1}^{\mathcal{R}_\mathrm{M}} |\sigma_k| u^*_k(t)u_k(t')\right)\delta\varepsilon(t')\,\mathrm{d}t\,\mathrm{d}t'$$

$$= -\frac{1}{2}\sum_{k=1}^{\mathcal{R}_\mathrm{M}} |\sigma_k|\,|(\delta\epsilon, u_k)|^2, \tag{65}$$

where Eq. (51) was used in the second step and $(\delta\varepsilon, u_k) = \int_0^T \delta\epsilon(t)u_k(t)\,\mathrm{d}t$ is the projection of the control field noise $\delta\epsilon(t)$ in the direction of the k-th eigenfunction $u_k(t)$ of the Hessian $\mathcal{H}^{\boldsymbol{\epsilon}}(t, t')$ at the global maximum.

From Eq. (65), it is evident that in the proximity of the global maximum the observable $\langle \mathbf{O}(T)\rangle$ is most sensitive to a field perturbation (including noise) occurring along the direction (in the infinite dimensional control field space) specified by the Hessian eigenfunction, say $u_1(t)$, that has the largest absolute (i.e., the most negative) eigenvalue $|\sigma_1|\,(\geq |\sigma_2| \geq \cdots \leq |\sigma_{\mathcal{R}_\mathrm{M}}| \geq 0)$. In general, at the critical points (including the global maxima/minima and saddles), the Hessian eigenfunctions and their corresponding eigenvalues dictate how the controlled quantum dynamics responds to field changes: A field variation along an eigenfunction will have a larger impact on the observable for an eigenfunction having an eigenvalue of greater magnitude. A negative (positive) eigenvalue corresponds to an upward (downward) change in the value of the observable $\langle \mathbf{O}(T)\rangle$ if the control field is increased in the direction of the associated eigenfunction. Away from the critical points, the Hessian eigenfunctions (assumed distinct) form an orthogonal and conjugate set of directions, i.e., $\langle u_k|u_\ell\rangle \equiv \int_0^T u_k^*(t)u_\ell(t)\,\mathrm{d}t = 0$ and $\langle u_k|\mathcal{H}^{\boldsymbol{\epsilon}}|u_\ell\rangle \equiv \int_0^T \int_0^T u_k^*(t)\mathcal{H}^{\boldsymbol{\epsilon}}(t, t')u_\ell(t')\,\mathrm{d}t\,\mathrm{d}t' = 0$ for $k \neq \ell$. As a result, these eigenfunctions (and their eigenvalues), in conjunction with the corresponding gradients, contain important topological information for performing effective searches, in particular with the Newton methods [38] seeking the globally optimal control field.

Based on Eq. (54) and the reasonable assumption that the control field noise is expected to be equally dispersed along any of the eigenvectors of the Hessian, Eq. (65) can be approximated as

$$\delta\langle \mathbf{O}(T)\rangle \approx -\frac{1}{2}\,\frac{\sigma_{\delta\epsilon}^2}{\mathcal{R}_\mathrm{M}} \sum_{k=1}^{\mathcal{R}_\mathrm{M}} |\sigma_k| \geq -\frac{T\Lambda_1^{\mathbf{O}}(0)\|\boldsymbol{\mu}\|^2}{\hbar^2}\,\frac{\sigma_{\delta\epsilon}^2}{\mathcal{R}_\mathrm{M}}, \tag{66}$$

where $\mathcal{R}_\mathrm{M} = n_<(2N - n_< - 1)$ and $|(\delta\varepsilon, u_k)|^2 \approx \sigma_{\delta\epsilon}^2/\mathcal{R}_\mathrm{M}$, with $\sigma_{\delta\epsilon}^2 = (\delta\epsilon, \delta\epsilon) = \sum_{k=1}^{\mathcal{R}_\mathrm{M}} |(\delta\epsilon, u_k)|^2$ being the mean square value of $\delta\epsilon(t)$. The interpretation of the result in Eq. (66) calls for consideration of whether $\sigma_{\delta\epsilon}^2$ has a dependence on N, especially as N rises. In principle, $\sigma_{\delta\epsilon}^2$ could depend on N, considering that more energy in the control could be required to manipulate systems of higher complexity (i.e., larger N). Practical considerations in realistic applications likely will employ limited laser energy regardless of the system Hilbert space dimension N, which is consistent with general operations found in the increasing number of successful control experiments of ever more complex systems [10–18]. Thus, it is reasonable to expect that $\sigma_{\delta\epsilon}^2$ is essentially a system invariant, or at most slowly varying in N. To this end, we may conclude the important result from Eq. (66) that *control solutions at the global maximum value of* $\langle \mathbf{O}(T)\rangle$ *have an inherent degree of robustness*, which also tends to increase (or in the worst case remain neutrally stable) as the Hilbert space dimension rises. This behavior is very attractive for attaining practical control, as noise is inevitably present in the laboratory.

4. Conclusion

This paper presents a general quantum control landscape analysis of $\langle \mathbf{O}(T)\rangle = \mathrm{Tr}(\boldsymbol{\rho}(T)\mathbf{O})$ directly in terms of the physically relevant control field $\boldsymbol{\epsilon}(t)$ including an elaboration of the topology around the critical points of an arbitrary physical observable $\mathbf{O}$. The basic conclusion of this work, that *no false suboptimal traps exist*, is coincident with the previous analysis of the special case of controlled transition probability $P_{i\to f}$ dynamics [19–22]. The additional suboptimal critical points in the general case of $\langle \mathbf{O}(T)\rangle$ are all saddle points, posing no physical obstacle towards attaining a control field that permits reaching the ultimate maximum(minimum) value of $\langle \mathbf{O}(T)\rangle$. Furthermore, the slope towards, and the curvature at, the critical points are bounded by the magnitude of the transition dipole moment. The trace of the Hessian at the global maximum (minimum) being bounded from below (above) has the important feature of implying inherent robustness, and possibly of an enhanced degree, with increasing Hilbert space dimension. In general, all of these results reveal the existence of remarkably attractive quantum control landscapes where the search efforts will encounter gentle slopes as well as global extrema that are robustly flat. This behavior suggests that various, even simple, algorithms should be able to search through the accessible controls to find viable solutions, and secondly, a respectable degree of robustness to laboratory noise should exist. The many successful control experiments [10–18] are certainly consistent with this analysis.

The topology of the $\langle \mathbf{O}(T)\rangle$ landscape, as in the special case of control over $P_{i\to f}$ [22], indicates that perhaps the current main limiting factor in the control of quantum systems is the presence of inherent physical constraints restricting access to suitable optimal controls. That is, the presence of significant constraints on the control could easily lead to tortuous search pathways being taken across the landscape and possibly false traps being generated due to a lack of sufficient freedom in the controls. Other physical issues, including the presence of decoherence and control noise, at least of a weak nature, during the controlled dynamics, will also enter, and they can be viewed as producing a lower resolution landscape through statistical averaging, rather than a fundamental change in its topological features. A lack of full controllability could also limit access to certain domains of the landscape, but currently constraints on the controls are more likely the significant limiting factor. More systematic studies of many interrelated questions and issues (e.g., the nature of control mechanisms [39–44]) in the general area of controlled quantum dynamics phenomena are needed. These studies should also include an analysis of the impact of the topological saddle features on the efficiency of various control search algorithms.

In summary, this work presents the basis to understand the reasons for the mounting successes of optimal control experiments in the most general mixed quantum state setting, despite what would appear to be an insurmountable encounter with the curse of dimensionality producing a potentially exploding number of possible control experiments to perform. Perhaps most importantly, the conclusions from the generic topology of the quantum control landscapes provides the foundation to project ahead that many more positive quantum control experimental outcomes may be expected, even in manipulating complex systems. Having adequate controls is a central issue in executing the experiments to take advantage of the simple landscape topology. The many existing laboratory control successes, often with very constrained controls, bodes well for even better results in the future as the control field sources improve.

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Appendix A. General Hessian expression at the critical points

In the appendix, we give a detailed derivation that results in a fully symmetric Hessian expression Eq. (44) at the critical points satisfying Eq. (25). The resultant symmetric Hessian $\mathcal{H}^{\epsilon}(t,t')$ is explicitly written as an expansion of the matrix elements of $\Lambda^{\rho}(0)$, $\Lambda^{\mathbf{O}}(0)$, and $\boldsymbol{\mu}(t)$. Eq. (44) is used for the Hessian analysis that follows. From Eq. (43),

$$\begin{aligned}\mathcal{H}^{\epsilon}(t,t') &= -\frac{1}{\hbar^2}\,\mathrm{Tr}\left([[\mathbf{O}(T),\boldsymbol{\mu}(t)],\ \boldsymbol{\mu}(t')]\boldsymbol{\rho}(0)\right) = -\frac{1}{\hbar^2}\,\mathrm{Tr}\left([[\mathbf{O}(T),\ \boldsymbol{\mu}(t)],\ \boldsymbol{\mu}(t')]\mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\boldsymbol{\rho}}(0)\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\right)\\ &= -\frac{1}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\langle i|\left\{\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\left[\,[\mathbf{O}(T),\ \boldsymbol{\mu}(t)]\,,\ \boldsymbol{\mu}(t')\right]\mathcal{U}_{\boldsymbol{\rho}}\right\}|i\rangle,\end{aligned} \tag{A.1}$$

by noting that $\Lambda^{\boldsymbol{\rho}}(0)$ contains only diagonal matrix elements $\Lambda_i^{\boldsymbol{\rho}}(0)$, $i=1,\ldots,N$. Eq. (A.1) can be further expanded as

$$\begin{aligned}\mathcal{H}^{\epsilon}(t,t') &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\langle i|\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}[\mathbf{O}(T),\ \boldsymbol{\mu}(t)]\boldsymbol{\mu}(t')\mathcal{U}_{\boldsymbol{\rho}}|i\rangle\right\}\\ &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\langle i|\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\left\{\mathbf{O}(T)\boldsymbol{\mu}(t)\boldsymbol{\mu}(t')-\boldsymbol{\mu}(t)\mathbf{O}(T)\boldsymbol{\mu}(t')\right\}\mathcal{U}_{\boldsymbol{\rho}}|i\rangle\right\}\\ &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\langle i|\left\{\Lambda^{\mathbf{O}}(T)\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t)\boldsymbol{\mu}(t')\mathcal{U}_{\boldsymbol{\rho}}-\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t)\mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\mathbf{O}}(T)\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t')\mathcal{U}_{\mathbf{m}\rho}\right\}|i\rangle\right\},\\ &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\Lambda_i^{\mathbf{O}}(T)\langle i|\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t)\boldsymbol{\mu}(t')\mathcal{U}_{\boldsymbol{\rho}}|i\rangle-\langle i|\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t)\mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\mathbf{O}}(T)\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t')\mathcal{U}_{\mathbf{m}\rho}|i\rangle\right\}\\ &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\Lambda_i^{\mathbf{O}}(T)\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle-\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)\Lambda^{\mathbf{O}}(T)\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle\right\}\end{aligned} \tag{A.2}$$

where $\Re$ denotes real part, $\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)\equiv\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}\boldsymbol{\mu}(t)\mathcal{U}_{\boldsymbol{\rho}}$, and the relation $\mathbf{O}(T)=\mathcal{U}_{\boldsymbol{\rho}}\Lambda^{\mathbf{O}}(T)\mathcal{U}_{\boldsymbol{\rho}}^{\dagger}$, with $\Lambda^{\mathbf{O}}(T)$ a diagonal matrix, has been used. Additional manipulations reduce Eq. (A.2) to the following

$$\begin{aligned}\mathcal{H}^{\epsilon}(t,t') &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\Lambda_i^{\mathbf{O}}(T)\sum_{j=1}^{N}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle-\sum_{j=1}^{N}\sum_{k=1}^{N}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\Lambda^{\mathbf{O}}(T)|k\rangle\langle k|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle\right\}\\ &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left\{\Lambda_i^{\mathbf{O}}(T)\sum_{j=1}^{N}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle-\sum_{j=1}^{N}\Lambda_j^{\mathbf{O}}(T)\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle\right\}\\ &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_{\rho}}\Lambda_i^{\boldsymbol{\rho}}(0)\sum_{j\neq i}^{N}\Re\left\{\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle\right\}\left(\Lambda_i^{\mathbf{O}}(T)-\Lambda_j^{\mathbf{O}}(T)\right).\end{aligned} \tag{A.3}$$

The double summations in Eq. (A.3) can be rearranged as

$$\mathcal{H}^{\epsilon}(t,t') = -\frac{2}{\hbar^2}\sum_{i=1}^{n_\rho}\sum_{j>i}^{N}\left\{\Lambda_i^{\boldsymbol{\rho}}(0)\,\Re\left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle\right) - \Lambda_j^{\boldsymbol{\rho}}(0)\,\Re\left(\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|i\rangle\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle\right)\right\}\left(\Lambda_i^{\mathbf{O}}(T) - \Lambda_j^{\mathbf{O}}(T)\right), \tag{A.4}$$

which, after using the relation $\Re\left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle\right) = \Re\left(\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|i\rangle\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle\right)$, can be succinctly written in a fully symmetric expression:

$$\begin{aligned}
\mathcal{H}^{\epsilon}(t,t') &= -\frac{2}{\hbar^2}\sum_{i=1}^{n_\rho}\sum_{j>i}^{N}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_i^{\mathbf{O}}(T) - \Lambda_j^{\mathbf{O}}(T))\,\Re(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle\langle j|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|i\rangle).\\
&= -\frac{2}{\hbar^2}\sum_{i=1}^{n_\rho}\sum_{j>i}^{N}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_i^{\mathbf{O}}(T) - \Lambda_j^{\mathbf{O}}(T))\,\left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Re} + \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Im}\right)\\
&= -\frac{2}{\hbar^2}\sum_{i=1}^{n_\rho}\sum_{j>i}^{N}(\Lambda_i^{\boldsymbol{\rho}}(0) - \Lambda_j^{\boldsymbol{\rho}}(0))(\Lambda_{p(i)}^{\mathbf{O}}(0) - \Lambda_{p(j)}^{\mathbf{O}}(0))\,\left(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Re} + \langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im}\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t')|j\rangle^{\Im}\right),
\end{aligned} \tag{A.5}$$

which gives Eq. (44), with $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Re} \equiv \Re(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle)$ and $\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle^{\Im} \equiv \Im(\langle i|\boldsymbol{\mu}_{\boldsymbol{\rho}}(t)|j\rangle)$. In deriving Eq. (A.5) we have used Eq. (30).

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