Maximally Accessible Purity in Coherently Controlled Open Quantum Systems: Application to Quantum State Engineering

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A fundamental problem in quantum control is to precisely characterize the controlled system dynamics when decoherence effects are present. In this work, we derive the upper bound of achievable purity for coherently driven dissipative systems, which is rather useful for assessing control performances. The theory is further testified on a two-qubit nuclear magnetic resonance spin system. Under joint effects of coherent pulses and system relaxation, we are able to implement the tasks of open system polarization transfer and pseudopure state preparation with remarkably, both of them approaching near optimal performance in purity. Our work shows great applicative potential of utilizing rather than suppressing relaxation effects in open system control protocols.

Recent years have seen immense advances in active and precise manipulation of a broad variety of quantum systems. The subject of quantum system control has been developed into a rapidly growing area [1] attracting substantial interests from the community of quantum information physicists. One of the fundamental tasks is to design reliable control techniques for systems that are exposed in a dissipative environment [2]. As dissipation tends to irreversibly affect the system dynamics, it is recognized as one dominant source for information loss and hence must be suppressed. Only recently did people realize that open system engineering may in some important aspects exhibit surprising advantages [3–5]. For example, it was shown that the purification efficiency of heat-bath algorithmic cooling protocol can surpass the closed system limit [3]. In other researches [5], there emerged great interests in characteristics of environment assisted entangled state engineering. Dissipative production of entangled steady states has already been realized in various experimental setups like trapped ions [6], superconducting circuit [7] and double quantum dot [8].

Although some ideas borrowed from classical control theory (eg. time optimal control) have been successfully extended to construct methods for steering closed quantum systems [9], it turns out to be more challenging to follow the same spirit for open quantum systems. The major reason comes from the negative assertion proved in [10] that for a finite dimensional Markovian quantum system, coherent means of control cannot fully compensate the irreversibility of the dynamics. In fact, to what extent can the system evolving tendency be changed depends upon not only the external operations but also the structure of the relaxation mechanisms. This certainly increases difficulties in understanding the system controllability, which thus hinders devising of general control methodology. Previous research results have been able to characterize the reachable set on the states of a single qubit both qualitatively [10] and quantitatively [11, 12]. However, to generalize these results to higher dimensional systems is not at all an easy work [13].

An alternative approach to the problem explores the dynamical behaviours of system purity function. Purity as an important concept quantifying the incoherent impacts from the environment, is particularly suited for studying how relaxation noises impose restricts on the achievable region of states. For example, one basic result for unital systems (where the equilibrium state is the maximally mixed state) states that the purity function must be monotonically decreasing regardless of the controls [14]. For the case of non-unital dynamics the situation is more complicated since purification can occur, depending on which kind of control protocol is applied. It is thus natural to consider that, given a practical relaxation process and a realistic control protocol, what is the upper bound of purity that the system cannot surpass. In this Letter, we derive the maximally obtainable purity in coherently controlled Markovian systems. To this end we study the evolution of purity function under appropriate assumptions of system relaxation. Moreover, our ideas are implemented experimentally using techniques of nuclear magnetic resonance (NMR).

Problem setting—Consider a controlled n-qubit open system governed by the Lindblad equation [15]

$$\dot{\rho} = -i[H, \rho] + \mathcal{R}\rho,$$

where $H$ incorporates both system Hamiltonian and external control Hamiltonian and $\mathcal{R}$ is the relaxation superoperator of Lindblad type. In most cases, the effects of $\mathcal{R}$
on the system are: (i) to destroy all the coherences; (ii) to redistribute the populations and (iii) relaxing, namely absence of relaxation-free subspace [16]. Assuming the dynamics non-unital and relaxing, then starting from any initial state, the system will evolve asymptotically into a unique equilibrium state \( \rho_{eq} \) in the population subspace under pure relaxation process.

Now we introduce the vector of coherence representation [4, 17], in which \( \rho \) is expressed in terms of an orthonormal basis \( B = \{ I^{\otimes n} \} \cup \{ B_m \}_{m=1}^{4^n-1} \) of the state space: \( \rho = I^{\otimes n}/2^n + \sum_{m=1}^{4^n-1} r_mB_m \) (\( r_m = \text{Tr} (\rho B_m) \)). The Lindblad equation is hence turned into a \( 4^n - 1 \) dimensional nonhomogeneous vector differential equation

\[
\dot{\rho} = H\rho - R(\rho - \rho_{eq}),
\]

where \( H \) (antisymmetric) and \( R \) (relaxation matrix, symmetric positive definite) are \( 4^n - 1 \) dimensional real matrices with their entries determined by \( H_{kj} = \text{Tr} (-iB_k [H, B_j]) \) and \( R_{kj} = \text{Tr} (-B_k R B_j) \) respectively, and \( \rho_{eq} \) is the vector representation of \( \rho_{eq} \). Then we project the system dynamics into the diagonal subspace through diagonalization procedure [11, 12]

\[
\rho = U\Lambda U^\dagger \leftrightarrow \rho = Ux, \quad U \in SU(2^n),
\]

in which \( \Lambda \) is diagonal, \( x \in \mathbb{R}^{2^n-1} \) and \( U \) are the representations of \( \Lambda \) and \( U \) with respect to basis \( B \) respectively. For convenience, we assign a specific order to the diagonal elements \( \{\Lambda_{kk}\}_{k=1,\ldots,2^n} \), or equivalently in the vector of coherence representation, an order to the coordinates \( \{0\} \cup \{x_k\}_{k=1,\ldots,2^n-1} \). The chosen order uniquely determines a representative region \( \Sigma \subset \mathbb{R}^{2^n-1} \), in which each point is a representative point of its unitary orbit and two points are unitarily equivalent only if they coincide. Consequently, any system evolution can be projected into a continuous trajectory in the representative region. Substitute the diagonalization procedure into Eq. (2), we obtain a \( 2^n - 1 \) dimensional dynamical equation [11]

\[
\dot{x} = -[U^T R U]_{p} (x - [U^T x_{eq}]_{p}),
\]

where \( x_{eq} \) is the representative point of \( \rho_{eq} \) and notation \([\cdot]_{p}\) denotes the population subspace part of its argument. Rewriting Lindblad equation in vector forms (Eq. (2) and Eq. (13)) makes the subsequent analysis more convenient from the dynamical system aspect of view. Our theory is developed based on several assumptions about the relaxation matrix, which are valid in many practical cases: (i) secular approximation, i.e., \( R \) admits the direct sum decomposition: \( R = R_p \oplus R_c \), where \( R_p \) and \( R_c \) represent the relaxation matrix in the population and coherence subspace respectively; (ii) longitudinal relaxation rates are slower than transversal relaxation rates: \( \lambda_{\text{max}}(R_p) \leq \lambda_{\text{min}}(R_c) \); (iii) relaxation rates are comparatively slow so that arbitrary unitary operation can be implemented before relaxation effects are non-ignorable.

The goal is to use purity function to characterize the transfer efficiency bound between two interconvertible directions in \( \Sigma \) given realistic control protocols. Clearly the problem here extends the concept of universal bound on spin dynamics [18] (bounds on the regions of operators in Liouville space being interconvertible by unitary transformations) to the open system control regime.

Maximally accessible purity—Recall that purity is defined as \( p = \text{Tr} \rho^2 \), which in the vector of coherence representation reads \( p = 1/2^n + r^T r \). It is direct to obtain the first time derivative

\[
\dot{p} = d(r^T r)/dt = -2r^T R(r - r_{eq}).
\]

The set of states satisfying \( \dot{p} = 0 \) determines an ellipsoid in \( \mathbb{R}^{2^n-1} \), which depends only upon \( R \) and the equilibrium state. From positive definiteness of \( R \) we know that for any state \( r \) outside of the ellipsoid there must be \( \dot{p}(r) < 0 \). Let \( S \) denote a sphere enclosing the ellipsoid, it is obvious that: (i) the equilibrium state \( r_{eq} \) is located inside \( S \) and (ii) the evolution direction of any state on \( S \) is towards the inner side of \( S \). Thus starting at \( r_{eq} \), the system can not be driven outside \( S \) by coherent means. One can then envisage a simple method to get an upper bound of \( p \) by solving the following optimization problem

\[
\begin{align*}
\left\{ \begin{array}{l}
\max \quad p(r) = 1/2^n + r^T r, \\
\text{s.t.} \quad \dot{p}(r) = -2r^T R(r - r_{eq}) = 0.
\end{array} \right.
\end{align*}
\]

This problem can be seen as an instance of quadratic programming over an ellipsoid constraint, which is easy in the sense of computational complexity and can be solved with well-developed algorithms [19]. Furthermore, to find a way approaching the maximum purity, we need [20]:

**Proposition.** Let \( \mathcal{P}_{2^n} \) denote the collection of \( 2^n! \) permutation operations on diagonal elements. Let \( \mathcal{Q}_{2^n} \) be the corresponding set of \( \mathcal{P}_{2^n} \) in the vector of coherence representation. Suppose that the relaxation matrix satisfies \( R = R_p \oplus R_c \) and \( \lambda_{\text{max}}(R_p) \leq \lambda_{\text{min}}(R_c) \), then there exists an element \( Q \) of \( \mathcal{Q}_{2^n} \) such that for any possible unitary \( U \) there is

\[
\dot{p}|_U \leq -2(Qx)^T R(Qx - x_{eq}).
\]

By the above proposition, we can determine whether it is possible to increase purity at an arbitrary state \( x \) just by checking a finite number of inequalities, i.e., whether there exists an element in \( \mathcal{Q}_{2^n} \) such that \( \dot{p}|_U(x) > 0 \). Note that purity is a convex function, which implies that any of its extremum should be a maximum. Therefore, one can asymptotically approach the maximally accessible purity of state through repeatedly applying two steps: (i) finding out the element of \( \mathcal{Q}_{2^n} \) that maximizes \( \dot{p} \) at current state; (ii) a small duration of evolution.

Now we focus on purity bound analysis for periodically modulated systems. Periodic control is practically
ubiquitous in various experimental setups. In open systems, periodic control promises the capability of driving the system asymptotically to some periodic steady state. This is due to that a controlled relaxing system leads to a strictly contractive quantum channel, i.e., the distance of any fixed pair of initial states is a strictly decreasing function of time [16]. Such a property is remarkable for the purpose of quantum information processing as it enables preservation of system information in the sense that the desired state can be periodically retained.

In periodic control schemes, one concerns about setting the desired state to be the fixed point of the controlled dynamics. A generic periodic control sequence can be described by \( [\tau_M - V_M - \cdots - \tau_1 - V_1]_m \), where \( \tau, V \) and \( m \) denotes unitary operation, free relaxation, and repetition times respectively. Provided the longitudinal relaxation rates are almost an order of magnitude slower than the transversal relaxation rates.

In order to visualize the system evolution, we project the 15-dimensional relaxation dynamics into a 3-dimensional differential equation according to Eq. (13). The representative region \( \Sigma \) is illustrated in Fig. 1a, where we have chosen the order \( 0 \leq x_3 \leq x_1 \leq x_2 \). In the region, we derived the sphere \( S \) representing the upper bound of system purity and the ellipsoid \( E \) representing a bound surface for \( [\tau - V]_m \) sequence based on the measured relaxation matrix.

Our first concern is the intersection between \( S \) and the \( x_2 \) axis: \((0, 4.27\epsilon, 0)\). In order to approach this state, we can make use of the nuclear Overhauser effect (NOE). It is well-known that [30], for a heteronuclear two-spin system, applying a field at the resonance frequency of one spin for a sufficiently long time, will saturate its polarization

\[ H_S = \pi(-\gamma_C B_0 ZI - \gamma_H B_0 IZ + J/2ZZ) \]

where \( X, Y \) and \( Z \) are Pauli operators. The natural Hamiltonian reads: \( H_S = \pi(-\gamma_C B_0 ZI - \gamma_H B_0 IZ + J/2ZZ) \), where \( \gamma_C \) and \( \gamma_H \) are the gyromagnetic ratios of nucleus \(^{13}\)C and \(^1\)H respectively, and \( J = 214.5\)Hz is the scalar coupling constant. The equilibrium state is \( \rho_{eq} \approx II/4 + \epsilon(ZI + IZ) \) with \( \epsilon \sim 10^{-5} \). In the double rotating frame, the system relaxation matrix \( R \) would take a kite-like appearance under secular approximation [2]. The simplified structure dramatically reduces the complexity of experimentally estimating the effective relaxation parameters. We measured \( R \) [22] and found that the longitudinal relaxation rates are almost an order of magnitude slower than the transversal relaxation rates.

Our purity bound analysis thus leads to a new view of the NOE experiment. The near optimality of Overhauser experiment in polarization transfer efficiency shows its advantages over the closed system control approach. Moreover, it generalizes the results of algorithmic cooling schemes. According to the purification limits derived in [3], it would not be possible to cool the proton in our system through the “reset and swap” iterative procedure. This is due to the different underlying relaxation model assumed. In heat-bath algorithmic cooling scheme, it is considered that each qubit is undergoing their own \( T_1 \) and \( T_2 \) process. But in NOE, cross-relaxation mechanisms are essential for the purification of proton [30]. Thus NOE provides clear evidence of approaching even larger purifi-

### Proposition

**Each element** \( Q_k \ (k = 1, \ldots, 2^n) \) in \( Q_{2^n} \) is associated with two definite quadratic forms

\[
E_k = -2(Q_k x)^T R(Q_k x - x_{eq}),
\]

\[
F_k = 4(Q_k x - x_{eq}/2)^T R^2(Q_k x - x_{eq}).
\]

Because of permutation symmetry, there exists a constant \( C \) such that for each \( k \), \( E_k = C \) is the smallest ellipsoid enclosing \( F_k = 0 \). Then in the representative region \( \Sigma \), it is impossible to steer system from \( x_{eq} \) to any state that locates outside the ellipsoid

\[
E : -2x^T R(x - x_{eq}) = C,
\]

through \([\tau - V]_m \) type of control sequences.  

**Experiments on two-qubit system.**— We use the \(^{13}\)C-labeled chloroform dissolved in \( d_4 \)-acetone as a two-qubit system to test the applicability of open system control method. Our experiments were carried out on a Bruker Avance III 400 MHz (\( B_0 = 9.4\) T) spectrometer at room temperature. Introduce the Cartesian product operator basis

\[ B_2 = \{II, ZI, IZ, ZZ, XI, YI, XZ, YZ, IX, IY, ZX, ZY, XY, YX, XX, YY\}, \]
culation efficiency if more general relaxation mechanisms are taken into account.

Next we turn to the application of open system coherent control to state engineering in NMR quantum computation. We consider creating pseudopure state (PPS) [24–26] from the equilibrium state, which is a necessary initialization step for subsequent computation. The task can not be done merely with unitary operations. Previous methods of PPS preparation involves different ways of realizing non-unitary operations [27] such as exertion of gradient fields. Here, we put forward a new approach: to let the inherent system relaxation effects take the role of non-unitary resources and design a periodic sequence so that PPS is the fixed point of the dynamics. Although the current experiment is performed on two-qubit system as an example, the idea applies to general cases.

For chloroform, PPS takes the form: \( \rho_{\text{pps}} = II/4 + \eta/4(ZI + IZ + ZZ) \), in which \( \eta \) is the effective purity. The feature that its three coefficients are equal to each other specifies the PPS direction, namely \( x_1 = x_2 = x_3 \). Therefore, it is straightforward to conceive a simple “coefficient-averaging process” The averaging process is governed by \( [\tau - V]_{\text{im}} \), in which \( V \) is a cyclic permutation of the coordinates of \( x \) and \( \tau \) represents a period of free relaxation. The joint action of \( V \) and \( \tau \) leads the three coefficients converging to a certain common value. In experiment, we chose \( V \) to be

\[
V = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix},
\]

and found that for a wide range of \( \tau \) the system was able to be driven to some states close to the PPS direction. Within tolerable range of error, we set the value of \( \tau \) as 1.5s, which corresponds to the maximal effective purity \( (\eta \approx 7.48\epsilon) \) of PPS obtained on trials. This can be compared to conventional spatial averaging preparation method where \( \eta \approx 0.12\epsilon \) [28]. Moreover, Fig. 1(a) shows that for \( [\tau - V]_{\text{im}} \) type of periodic controls, it is not possible to get a PPS surpassing \( \eta \approx 8.20\epsilon \). Therefore, our experimental result is close to the optimal value. The gap can be attributed to two points: (i) the experimentally estimated relaxation matrix unavoidably involves imprecision; (ii) in deriving the bound, it is assumed that during the operation \( V \) relaxation can be ignored, which is not perfectly satisfied in practice. We also demonstrate how to create a periodically steady entangled state (unitarily equivalent to a PPS) by taking the Bell state \( \rho_{\text{Bell}} = (1 - \eta)/4II + \eta/2((00) + (11)) \otimes (00) + (11)) \) as an example. According to the aforementioned method, we modify the PPS preparation periodic sequence to be \( [W - \tau - V - W^T]_m \) where \( W \) transforms \( \rho_{\text{pps}} \) to \( \rho_{\text{Bell}} \):

\[
W = \text{CNOT}_{\text{CH}} \cdot \text{Hadamard}_c.
\]
of the method (Fig. 1(c)).

To conclude, we derived the maximally achievable purity of coherently controlled Markovian systems. The theory provides valuable reference for assessing open system control schemes where purity is the most concerned performance index. In addition, the theoretical purity bound can be an important guidance for developing numerical pulse searching algorithms. We further studied in detail the NOE effect and state engineering experiments in the open system framework, and showed that relaxation effects are essential for implementing some important non-unitary control tasks. The lack of full controllability in certain important control regimes [29, 30] usually calls for a bound analysis for system reachable states. Our present study can thus be regarded as a part of explorations in this direction. Future work will concentrate on incorporating our work here with other open system control models, such as reservoir engineering in which incoherent resources [31] are introduced to enhance the capability of controlling quantum systems.

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The proof is based on the majorization method. See [1] for a brief introduction of the concept of majorization. We here need the following lemma.

**Lemma.** Let $\rho$ be a $2^n$-dimensional density matrix. Then for any unitary $U \in SU(2^n)$, the diagonal part of $U \rho U^\dagger$ can be written as a convex combination of all permutations of the diagonal part of $\rho$. That is, let $\mathcal{P}_{2^n}$ denote the collection of $2^n!$ permutation operations on diagonal elements, then

$$d(U\rho U^\dagger) = \sum_{k=1}^{2^n!} \mu_k P_k d(\rho),$$

where $P_k \in \mathcal{P}_{2^n}$, $\mu_k \geq 0$ and $\sum_{k=1}^{2^n!} \mu_k = 1$.

**Proof.** See Theorem 4.3.45 (Schur) at p249 and Theorem 4.3.49 at p253 in [1].

Back to our proposition. The projected dynamics in the representative region goes

$$\dot{x} = -[U^T R U]_p (x - U^T x_{eq}).$$

Then there is

$$\dot{p}|_U = -2(Ux)^T R(Ux - x_{eq}).$$

We state the proposition again

**Proposition.** Let $\mathcal{P}_{2^n}$ denote the collection of $2^n!$ permutation operations on diagonal elements. Let $Q_{2^n}$ be the corresponding set of $\mathcal{P}_{2^n}$ in the vector of coherence representation. Suppose that the relaxation matrix satisfies $R = R_p \oplus R_c$ and $\lambda_{\max}(R_p) \leq \lambda_{\min}(R_c)$, then there exists an element $Q$ of $Q_{2^n}$ such that for any possible unitary $U$ there is

$$\dot{p}|_U \leq -2(Qx)^T R(Qx - x_{eq}).$$

**Proof.** Let $Ux = r_p + r_c$. By lemma, we have $r_p = \sum_{k=1}^{2^n!} \mu_k Q_k x$. Then

$$\dot{p}|_U = -2 \sum_{k=1}^{2^n!} \sum_{j=1}^{2^n!} (\mu_k Q_k x)^T R_p (\mu_j Q_j x - x_{eq}) - 2r_c^T R_c r_c$$

$$\leq -2 \sum_{k=1}^{2^n!} \sum_{j=1}^{2^n!} (\mu_k Q_k x)^T R_p (\mu_j Q_j x - x_{eq}) - 2\lambda_{\min}(R_c) r_c^T r_c$$

$$\leq -2 \sum_{k=1}^{2^n!} \sum_{j=1}^{2^n!} (\mu_k Q_k x)^T R_p (\mu_j Q_j x - x_{eq}) - 2\lambda_{\max}(R_p) r_c^T r_c$$

$$\leq -2 \sum_{k=1}^{2^n!} \sum_{j=1}^{2^n!} (\mu_k Q_k x)^T R_p (\mu_j Q_j x - x_{eq}) - 2\lambda_{\max}(R_p) r_c^T r_c$$

$$-2\lambda_{\max}(R_p) \left[ x^T \left( \sum_{k=1}^{2^n!} \mu_k Q_k x \right) \left( \sum_{j=1}^{2^n!} \mu_j Q_j x \right) \right]$$

$$= -2 \sum_{k=1}^{2^n!} \sum_{j=1}^{2^n!} \mu_k \mu_j x^T (Q_k^T R_p Q_j + \lambda_{\max}(R_p) - \lambda_{\max}(R_p) Q_k^T Q_j) x$$

$$+ 2 \sum_{k=1}^{2^n!} \mu_k x^T Q_k^T R_p x_{eq}.$$
Now we need an inequality
\[
(Q_k - Q_j)^T (R_p - \lambda_{\text{max}}(R_p))(Q_k - Q_j) \leq 0,
\]
the correctness of which is easy to check. Expand the inequality we have
\[
- (Q_k^T R_p Q_j + Q_j^T R_p Q_k + \lambda_{\text{max}}(R_p)I + \lambda_{\text{max}}(R_p)I - \lambda_{\text{max}}(R_p)Q_k^T Q_j - \lambda_{\text{max}}(R_p)Q_j^T Q_k)
\]
\[
\leq - Q_k^T R_p Q_k - Q_j^T R_p Q_j.
\]
Substitute into Eq. (16), we get
\[
\dot{p}|_U \leq -2 \sum_{k=1}^{2^n} \sum_{j=1}^{2^n} \mu_k \mu_j x^T (Q_k^T R_p Q_k + Q_j^T R_p Q_j) x + 2 \sum_{k=1}^{2^n} \mu_k x^T Q_k^T R_p x_{eq}
\]
\[
= -2 \sum_{k=1}^{2^n} \mu_k x^T Q_k^T R_p Q_k x + 2 \sum_{k=1}^{2^n} \mu_k x^T Q_k^T R_p x_{eq}
\]
\[
= -2 \sum_{k=1}^{2^n} \mu_k (Q_k x)^T R_p ((Q_k x) - x_{eq}).
\]
Note that the last line is a convex combination, the proposition is manifest.

Proof of the second proposition

We here state the second proposition again

Proposition. Each element \(Q_k\) (\(k = 1, \ldots, 2^n\)) in \(Q_{2^n}\) is associated with two definite quadratic forms
\[
E_k = -2(Q_k x)^T R(Q_k x - x_{eq}),
\]
\[
F_k = 4(Q_k x - x_{eq}/2)^T R^2(Q_k x - x_{eq}).
\]
Because of permutation symmetry, there exists a constant \(C\) such that for each \(k\), \(E_k = C\) is the smallest ellipsoid enclosing \(F_k = 0\). Then in the representative region \(\Sigma\), it is impossible to steer system from \(x_{eq}\) to any state that locates outside the ellipsoid
\[
E : -2x^T R(x - x_{eq}) = C,
\]
through \([\tau - V]\)_{\text{m}} type of control sequences.

Proof. We manifest the following points at first: (i) it is direct to check that \(E_k\) represents \(\dot{p}|Q_k\), and \(F_k\) represents \(\dot{p}|Q_k\) for diagonal free relaxation dynamics; (ii) there always exists a point \(Q_k x_{eq}\) such that \(E_k(x) = 0\) and \(F_k(x) = 0\), therefore \(C \leq 0\); (iii) under pure relaxation, for any diagonal state \(\rho\), if \(\dot{p}(\rho) = C\), then \(\dot{p}(\rho) \geq 0\). This implies that if the system starts at a diagonal state \(\rho(0)\) satisfying \(\dot{p}(\rho(0)) \geq C\), then under pure relaxation, \(\dot{p}(\rho(t)) \geq C\) for all \(t\).

Let \(x_{ss}\) locates outside \(E\). Back to the density matrix representation \(x_{ss} \rightarrow \rho_{ss}\), there is \(\dot{p}(\rho_{ss}) < C\). Suppose the steady state is fixed by \([\tau - V]\)_{\text{m}}, we have \(E_\tau \circ E_V \rho_{ss} = \rho_{ss}\), which means that the coherences produced after \(E_V\) vanishes by \(E_\tau\). Since the relaxation process in diagonal subspace is independent from that in coherence subspace, we get \(E_\tau \circ E_D \circ E_V \rho_{ss} = \rho_{ss}\), where \(E_D\) means projection into the diagonal subspace. Now, (i) if \(\dot{p}(E_D \circ E_V \rho_{ss}) \geq C\), then after pure relaxation \(E_\tau\), there remains \(\dot{p}(E_\tau \circ E_D \circ E_V \rho_{ss}) \geq C\), which can not be equal to \(\rho_{ss}\); (ii) Otherwise if \(\dot{p}(E_D \circ E_V \rho_{ss}) \leq C\), then \(p\) is decreasing. In order that after \(E_\tau\) system is of the same purity as \(\rho_{ss}\), there must exist \(\tau_0 < \tau\) such that \(\dot{p}(E_{\tau_0} \circ E_D \circ E_V \rho_{ss}) = 0\).

Relaxation Matrix Tomography on Chloroform

The basic liquid NMR relaxation theory can be found in [2]. In the rotating frame, it is routine to make a secular approximation by which the relaxation matrix would take a kite-like appearance. The underlying principle is that,
the system energy level differences are much larger than the relaxation rates, so in the interaction picture, the cross relaxation parameters between the population subspace and the coherence subspace are added with fast oscillating phases. This effectively decoupled the population subspace relaxation from the coherence subspace relaxation. Secular approximation dramatically simplified the task of experimentally estimating the relaxation rates.

To be concrete, the relaxation dynamics can be decomposed as a direct sum of subspace dynamics (featured by the order of coherences)

- **population subspace:**
  \[
  \frac{d}{dt} \begin{pmatrix}
  \langle ZI \rangle \\
  \langle IZ \rangle \\
  \langle ZZ \rangle 
  \end{pmatrix} = \begin{pmatrix}
  1/4 & 0 & 0 & 0 \\
  -r_1 & r_4 & r_5 & 0 \\
  -(4r_1 + 16r_4) & -r_2 & r_6 & -r_3 
  \end{pmatrix} \begin{pmatrix}
  \langle ZI \rangle \\
  \langle IZ \rangle \\
  \langle ZZ \rangle 
  \end{pmatrix},
  \]

- **subspace of $^{13}C$ one coherences:**
  \[
  \frac{d}{dt} \begin{pmatrix}
  \langle XI \rangle \\
  \langle YI \rangle \\
  \langle XZ \rangle \\
  \langle YZ \rangle 
  \end{pmatrix} = \begin{pmatrix}
  r_7 & 0 & r_9 & -\pi J \\
  0 & r_7 & \pi J & r_9 \\
  r_9 & -\pi J & r_8 & 0 \\
  \pi J & r_9 & 0 & r_8 
  \end{pmatrix} \begin{pmatrix}
  \langle XI \rangle \\
  \langle YI \rangle \\
  \langle XZ \rangle \\
  \langle YZ \rangle 
  \end{pmatrix},
  \]

- **population subspace:**
  \[
  \frac{d}{dt} \begin{pmatrix}
  \langle IX \rangle \\
  \langle IY \rangle \\
  \langle ZX \rangle \\
  \langle ZY \rangle 
  \end{pmatrix} = \begin{pmatrix}
  r_{10} & 0 & r_{12} & -\pi J \\
  0 & r_{10} & \pi J & r_{12} \\
  r_{12} & -\pi J & r_{11} & 0 \\
  \pi J & r_{12} & 0 & r_{11} 
  \end{pmatrix} \begin{pmatrix}
  \langle IX \rangle \\
  \langle IY \rangle \\
  \langle ZX \rangle \\
  \langle ZY \rangle 
  \end{pmatrix},
  \]

- **population subspace:**
  \[
  \frac{d}{dt} \begin{pmatrix}
  \langle XY \rangle \\
  \langle YX \rangle \\
  \langle XX \rangle \\
  \langle YY \rangle 
  \end{pmatrix} = \begin{pmatrix}
  r_{13} & -r_{14} & 0 & 0 \\
  -r_{14} & r_{13} & 0 & 0 \\
  0 & 0 & r_{14} & r_{13} \\
  0 & 0 & r_{14} & r_{13} 
  \end{pmatrix} \begin{pmatrix}
  \langle XY \rangle \\
  \langle YX \rangle \\
  \langle XX \rangle \\
  \langle YY \rangle 
  \end{pmatrix},
  \]

where \( \{r_k\}_{k=1,...,14} \) are relaxation rates including auto-relaxation rates and cross-relaxation rates. To estimate the relaxation rates, we first sample the system evolution trajectory (starting from a known initial state \( \rho(0) \)), then find values of the relaxation rates so that the simulated dynamics can match the observed trajectory. The fitting results are listed below (we have set \( \epsilon = 1 \))

- \( \{r_1, r_2, r_3, r_4, r_5, r_6\} \approx \{0.0532, 0.0918, 0.0798, 0.0212, 0.0000, 0.0022\} \)
• \( \{r_7, r_8, r_9\} \approx \{3.495, 6.536, 0.0100\} \)

\[\begin{array}{c}
\text{Exp.} \\
\text{Sim.}
\end{array}\]

\[\begin{array}{c}
\text{Exp.} \\
\text{Sim.}
\end{array}\]

• \( \{r_{10}, r_{11}, r_{12}\} \approx \{2.955, 6.118, 0.030\} \)

\[\begin{array}{c}
\text{Exp.} \\
\text{Sim.}
\end{array}\]

\[\begin{array}{c}
\text{Exp.} \\
\text{Sim.}
\end{array}\]

• \( \{r_{13}, r_{14}\} \approx \{9.523, 0.008\} \)

\[\begin{array}{c}
\text{Exp.} \\
\text{Sim.}
\end{array}\]

\[\begin{array}{c}
\text{Exp.} \\
\text{Sim.}
\end{array}\]
Robustness of Periodic Control Method for PPS Preparation

The simulating plot shows the relative error of the prepared PPS due to imperfections of control fields present in the $^{13}$C channel ($\delta_C = \|B_{real}^C - B_{ideal}^C\| / \|B_{ideal}^C\|$) and $^1$H channel ($\delta_H = \|B_{real}^H - B_{ideal}^H\| / \|B_{ideal}^H\|$). The relative error is characterized by

$$\delta = \|\rho_{real} - \rho_{pps}\| / \|\rho_{pps}\|.$$  

(24)

It can be easily seen that the periodic control method is quite robust to the control imperfections.

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[2] J. Kowalewski and L. Müller, Nuclear Spin Relaxation in Liquids: Theory, Experiments, and Applications (Taylor & Francis, New York, 2006).