

Complex heat capacity as a witness of spatio-temporal entanglement

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We propose a witness of temporal quantum entanglement using the imaginary component of the complex heat capacity—a measurable thermodynamic quantity in temperature-modulated calorimetry. By establishing a direct correspondence between complex heat capacity and the pseudodensity matrix formalism, our approach enables the characterization of both spatial and temporal quantum correlations without demanding additional state-level manipulation beyond initial tomography. We analytically demonstrate this connection for an open quantum system modeled by a qubit coupled to a thermal bath and show how both pseudodensity matrix negativity and violations of a temporal Clauser-Horne-Shimony-Holt inequality emerge as indicators of nonclassical temporal correlations. We further identify bounds on the imaginary heat capacity that guarantee temporal entanglement, providing an experimentally accessible criterion at the macroscopic scale. This framework offers a feasible route for probing temporal quantum effects in condensed-matter systems and opens a viable path toward experimental realization.

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I. INTRODUCTION

The treatment of space and time differs vastly in quantum mechanics, both mathematically and conceptually. In nonrelativistic quantum mechanics, position is treated as an operator, while time enters as a real-valued, independent background parameter. This asymmetry is further revealed through the lack of a temporal tensor product structure—an important mathematical feature that gives rise to the notion of entanglement in space [1]. Nevertheless, even in the absence of an analogous mathematical construction, quantum mechanics predicts nonclassical temporal correlations that can be probed via temporal Bell- or Leggett-Garg inequalities [2–4]. A violation of these inequalities would imply that the correlations between outcomes of sequential measurements on a single quantum system cannot be explained by any classical hidden-variable model that satisfies macrorealism and noninvasive measurability and hence is an indicator of genuine temporal quantum correlations.

However, experimentally testing for nonclassicality—both spatial and temporal—using this method is difficult when applied to macroscopic bodies and often impossible due to the inaccessibility of individual subsystem states in a complex system. Alternative witnesses of spatial entanglement that circumvent this problem have been developed in quantum thermodynamics. Namely, previous work [5–8] has demonstrated that thermodynamic observables, such as heat capacity and magnetic susceptibility, may be used to test for nonclassical spatial correlations. Measuring

thermodynamic observables for macroscopic systems is a standard experimental procedure, as opposed to making sophisticated measurements that circumvent various loopholes to violate Bell’s inequalities. Thus this approach enables entanglement to be probed at the macroscopic scale, offering insight into the compelling question of whether quantum correlations at the microscopic level can give rise to observable large-scale effects.

In this work, we extend these ideas to the temporal domain. We show that the imaginary component of the complex heat capacity can be used as a witness of temporal nonclassicality and establish a connection between measurements of the real and imaginary components of the heat capacity to the entries of a pseudodensity matrix (PDM). The PDM formalism [9–13] was introduced to allow spatial- and temporal quantum correlations to be placed on an equal footing. They are usually formulated by considering sequential measurements on a single quantum system, where each measurement is made in all three complementary bases X , Y , and Z (represented by the Pauli operators). Applying the Pauli operators to a system requires a precise, coherent control over the system’s quantum state, which is a highly nontrivial task for macroscopic bodies due to decoherence effects. This work offers a different approach to constructing pseudodensity matrices and extends their applicability to the emergent scale.

Further to this, using the PDM framework, we derive a temporal CHSH inequality [4,14] for a single qubit measured at two distinct times and use it to show that only a subset of values of the imaginary component of the heat capacity yields a violation of a classical bound—thus providing a robust criterion for temporal entanglement in the context of quantum thermodynamics. The two-level system considered below serves as an analytically tractable proof of principle, while the extension to higher-dimensional and many-body systems is discussed separately.

II. WITNESS OF TEMPORAL NONCLASSICALITY

Complex heat capacity is usually studied in the context of temperature-modulated calorimetry [15–21] and arises when a weak temperature modulation is applied to a system, resulting in a sinusoidal time-varying heat flux and naturally leads to a definition of complex heat capacity, $C(\omega) = C'(\omega) + iC''(\omega)$. The physical meaning of the imaginary part of the heat capacity has previously been related to the rate of entropy production [17,22], though a link to quantities arising from quantum information theory has yet to be made. Here, we directly relate the imaginary component of the heat capacity to temporal nonclassicality.

Consider a (micro- or macro-)scopic system in thermal equilibrium. Applying a small time-dependent temperature perturbation $T(t) = T + \delta T(t)$ will result in a response of the Hamiltonian $H(t)$, which we seek to characterize. Note that the temperature modulation considered here is of the Gibbs state and not of the Hamiltonian. Assuming the temperature perturbation is small enough that we remain in the linear response regime, the fluctuation-dissipation theorem [23,24] can be used to approximate the perturbation to the Hamiltonian as

$$\delta \langle H(t) \rangle = \int_0^t \chi(t-t') \delta T(t') dt', \quad (1)$$

where χ is the response function, which is obtained via the Kubo formula [25], and is given by

$$\chi = \frac{i}{\hbar} \Theta(t) \langle [H(t), H(0)] \rangle. \quad (2)$$

Taking the Fourier transform of the response function defines exactly a frequency-dependent susceptibility, consistent with standard AC calorimetry methods, which we refer to as the complex heat capacity. The imaginary component is given by

$$C''(\omega) = \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt \langle [H(t), H(0)] \rangle e^{i\omega t}. \quad (3)$$

The commutator in the integral implies that, if the imaginary component is nonzero, then temporal nonclassicality may be present. We will later place a stricter bound on the values of $C''(\omega)$, for which temporal quantum correlations are manifest in an open system consisting of a qubit coupled to a thermal bath, whose imaginary component is given by

$$C''(\omega) = \left(\frac{(\hbar\omega)^2}{4k_B T^2} \right) \frac{\omega\Gamma}{\Gamma^2 + \omega^2} \text{sech}^2 \left(\frac{\hbar\omega}{2k_B T} \right). \quad (4)$$

For a full derivation, see Appendix A.

III. PSEUDODENSITY MATRICES

The PDM generalizes the density matrix to describe quantum systems evolving across both space and time [9–13]. Unlike the conventional formalism, which encodes spatial correlations at a fixed instant, the PDM incorporates temporal sequences of measurements, allowing it to represent the behavior of a system across multiple points in time. This approach stems from viewing the density matrix not just as a statistical mixture of pure states, but as an object defined by the expectation values of Pauli operator combinations.

Formally, it is expressed as

$$R = \frac{1}{2^n} \sum_{i_1=0}^3 \cdots \sum_{i_n=0}^3 \langle \{\sigma_{i_j}\}_{j=1}^n \rangle \bigotimes_{j=1}^n \sigma_{i_j}, \quad (5)$$

where $\langle \{\sigma_{i_j}\}_{j=1}^n \rangle$ is the expectation value for the product of a set of Pauli measurements [12]. Note that, although defined in terms of qubits, the framework is extendable to quantum systems of any dimension by embedding the system within a qubit Hilbert space and limiting its dynamics to the relevant subspace.

Nevertheless, experimental realization is challenging, as sequential measurements must preserve temporal coherence. Previous work has focused on using photonic systems to simulate temporal PDMs and demonstrate multipartite Clauser-Horne-Shimony-Holt (CHSH) violations [12]; also, NMR experiments have observed temporal correlations via PDM negativity and their decay under decoherence [9]. These methods, however, are hindered by tomography requirements, coherence loss, and the difficulty of simulating noninvasive sequential measurements without state collapse. As an alternative, we propose constructing PDMs through measurements of the complex heat capacity—a routine solid-state technique that avoids these limitations.

IV. RELATING HEAT CAPACITY TO PDMs

Here we relate the matrix elements of the PDM to the complex heat capacity, such that

$$R = \frac{1}{4} \sum_{\mu, \nu=0}^3 C_{\mu\nu}(\omega) \sigma_{\mu} \otimes \sigma_{\nu}, \quad (6)$$

and compute the entries based on the correlation functions of the Hamiltonian components.

For a Hamiltonian of the form $H = \frac{\hbar}{2} \vec{\omega}(t) \cdot \vec{\sigma}$ and assuming weak periodic driving is of the form $\vec{\omega}(t) = \vec{\omega}(0) + \delta\vec{\omega} e^{-i\omega t}$, the commutator-based linear definition for heat capacity introduced in Eq. (3) may explicitly be written as

$$C_{\mu\nu}(\omega) = \frac{1}{k_B T^2} \int_0^{\infty} dt \langle [H_{\mu}(t), H_{\nu}(0)] \rangle e^{i\omega t}. \quad (7)$$

We now demonstrate that Eq. (7) can equivalently be expressed via correlation functions, which matches the PDM construction and facilitates subsequent calculations in this paper. From the periodic driving, the Hamiltonian varies as $\dot{H}(t) = \frac{-i\hbar\omega}{2} \delta\vec{\omega} \cdot \vec{\sigma} e^{-i\omega t} = \sum_{\mu=1}^3 \frac{-i\hbar\omega}{2} \delta\omega_{\mu} e^{-i\omega t} \sigma_{\mu}$. Hence we can write $H(t) = \sum_{\mu} H_{\mu}(t) \sigma_{\mu}$, where σ_{μ} obeys the usual commutation relation $[\sigma_{\mu}, \sigma_{\nu}] = 2i\epsilon_{\mu\nu\lambda} \sigma_{\lambda}$. Relating this to Eq. (7), it can be shown that $\langle [H(t), H(0)] \rangle = 2i \sum_{\mu, \nu, \lambda} \epsilon_{\mu\nu\lambda} \langle H_{\mu}(t) H_{\nu}(0) \rangle$, such that

$$C_{\mu\nu}(\omega) = \frac{1}{k_B T^2} \int_0^{\infty} dt \langle \dot{H}_{\mu}(t) \dot{H}_{\nu}(0) \rangle e^{i\omega t}, \quad (8)$$

whose form allows for the entries of the PDM to be expressed via the complex heat capacity.

To illustrate this idea, let us consider a qubit undergoing dephasing governed by Lindblad dynamics and explicitly construct the PDM. We note that the toy model presented here allows for clean, analytical proof-of-principle results, but

the framework is by no means restricted to a qubit. The formalism is naturally extendable to higher-dimensional systems and its full generality and universality will be discussed in Appendix B.

The Hamiltonian is given by $H = \frac{\hbar\omega_z}{2}\sigma_z$; let the relaxation rate be denoted by γ_1 and the overall dephasing rate by $\gamma_2 = \frac{\gamma_1}{2} + \gamma_\phi$, where γ_ϕ is the pure dephasing rate. The system evolves under

$$\frac{d\rho}{dt} = \frac{-i}{\hbar}[H, \rho] + L_{\text{relax}}[\rho] + L_{\text{dephase}}[\rho], \quad (9)$$

$$R = \frac{1}{4N(t)} \begin{pmatrix} 1 & 0 & 0 & -\tanh\left(\frac{\hbar\omega_z}{2k_B T}\right) \\ 0 & e^{-\gamma_2 t} \cos(\omega_z t) & -ie^{-\gamma_2 t} \sin(\omega_z t) & 0 \\ 0 & ie^{-\gamma_2 t} \sin(\omega_z t) & e^{-\gamma_2 t} \cos(\omega_z t) & 0 \\ -\tanh\left(\frac{\hbar\omega_z}{2k_B T}\right) & 0 & 0 & \tanh^2\left(\frac{\hbar\omega_z}{2k_B T}\right) + \text{sech}^2\left(\frac{\hbar\omega_z}{2k_B T}\right)e^{-\gamma_1 t} \end{pmatrix},$$

where

$$N(t) = \frac{1}{4} \left(1 + 2e^{-\gamma_2 t} \cos(\omega_z t) + \tanh^2\left(\frac{\hbar\omega_z}{2k_B T}\right) + \text{sech}^2\left(\frac{\hbar\omega_z}{2k_B T}\right)e^{-\gamma_1 t} \right),$$

ensuring the PDM is normalized for all times. Physically, the off-diagonal terms arise due to dephasing of the qubit and the R_{zz} term corresponds to the real heat capacity plus the decaying imaginary component. In the present model, the complex heat capacity therefore provides information about the two-time energy correlations entering the PDM. The following analyses of PDM negativity and temporal CHSH violation should be understood as two complementary diagnoses of temporal nonclassicality encoded in these response-derived correlations. Let us first consider PDM negativity, given by

$$\mathcal{N}(R) = \frac{\|R\|_1 - \text{Tr}(R)}{2} = - \sum_{\lambda_i(R) < 0} \lambda_i,$$

where λ_i are the eigenvalues of the PDM and $\|R\|_1$ is the trace norm. Plotting $\mathcal{N}(R)$ against time (see Fig. 1), we see that negativity appears after some finite time—an indicator of temporal nonclassicality—but eventually disappears as the

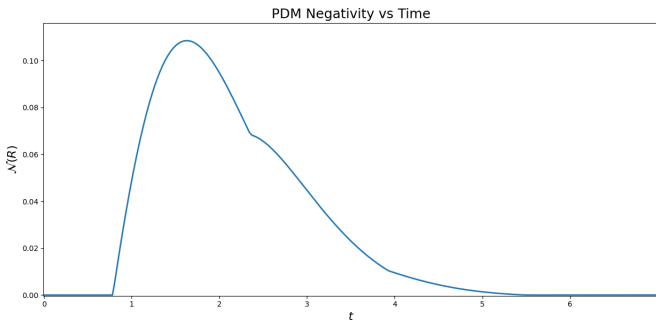


FIG. 1. Time evolution of the negativity of a two-time PDM of a single qubit coupled to a thermal bath. Natural units have been adopted, such that $\hbar = 1$ and $k_B = 1$, and we set $\omega_z = 1$, $T = 1$, $\gamma_1 = 0.9$, and $\gamma_2 = 1.2$.

where $L_{\text{relax}}[\rho] = \frac{\gamma_1}{2}((n_{\text{th}} + 1)(2\sigma_- \rho \sigma_+ - \{\sigma_+ \sigma_-, \rho\}) + n_{\text{th}}(2\sigma_+ \rho \sigma_- - \{\sigma_- \sigma_+, \rho\}))$ and $L_{\text{dephase}}[\rho] = \frac{\gamma_\phi}{2}(\sigma_z \rho \sigma_z - 1)$. Notethat here n_{th} has the usual thermodynamic definition, $n_{\text{th}} = \frac{1}{e^{\beta \hbar \omega} - 1}$.

To construct the PDM, we assume that the system has equilibrated at both times t_0 and t_1 , such that $R_{0z} = R_{z0} = \langle \sigma_z(t_0) \rangle = \langle \sigma_z(t_1) \rangle = -\tanh\left(\frac{\hbar\omega_z}{2k_B T}\right)$. The remaining entries can be calculated via Eq. (5) to obtain the full PDM

qubit settles into a steady state that approximately follows the thermal distribution, assuming the temperature modulation is slow.

V. CONNECTION TO THE TEMPORAL CHSH INEQUALITY

While the negativity of the eigenvalue does indeed imply the existence of temporal nonclassicality, a less contentious criterion is the violation of a classical bound such as the temporal CHSH inequality. We will now derive this bound in the context of heat capacity.

Consider two sequential measurements on a qubit, where $A_{t_1}^1$ and $A_{t_1}^2$ denote outcomes of dichotomous observables $\vec{a}_1$ and $\vec{a}_2$ at time t_1 and $B_{t_2}^1$ and $B_{t_2}^2$ those of $\vec{b}_1$ and $\vec{b}_2$ at $t_2 > t_1$. Predetermined outcomes satisfy $A_{t_1}^1(B_{t_2}^1 + B_{t_2}^2) + A_{t_1}^2(B_{t_2}^1 - B_{t_2}^2) = \pm 2$, which, upon averaging, yields the temporal CHSH inequality

$$S \equiv |E(\vec{a}_1, \vec{b}_1) + E(\vec{a}_1, \vec{b}_2) + E(\vec{a}_2, \vec{b}_1) - E(\vec{a}_2, \vec{b}_2)| \leq 2.$$

For a more detailed derivation, see [4]. For arbitrary measurement directions, the correlators are given by $E(\vec{a}, \vec{b}) = \vec{a}^T T \vec{b}$, where $T_{ij} = \text{Tr}[R \cdot \sigma_i \otimes \sigma_j]$ defines the 3×3 correlation matrix. Optimization over unit vectors yields $S_{\text{max}}(t) = 2\sqrt{\lambda_1 + \lambda_2}$, where λ_1 and λ_2 are the largest eigenvalues of $T^T T$. A quantum violation occurs when

$$S_{\text{max}}(t) = \frac{2}{N(t)} \sqrt{c^2 - s^2 + f^2} > 2,$$

where $c = e^{-\gamma_2 t} \cos(\omega_z t)$, $s = e^{-\gamma_2 t} \sin(\omega_z t)$, and $f = \tanh^2\left(\frac{\hbar\omega_z}{2k_B T}\right) + \text{sech}^2\left(\frac{\hbar\omega_z}{2k_B T}\right)e^{-\gamma_1 t}$. Using the same parameters as in Fig. 1, Fig. 2 shows the time dependence of the maximized Bell parameter.

Initially, S_{max} satisfies the quantum Tsirelson bound—as expected, because this is when the qubit is in its most coherent state; gradually, as the system relaxes into a steady state, S_{max} falls below the classical bound.

Interestingly, we note that, while S_{max} experiences the strongest violation at the earliest times, PDM negativity (see Fig. 1) only begins at $t = \pi/4$. The delayed PDM negativity

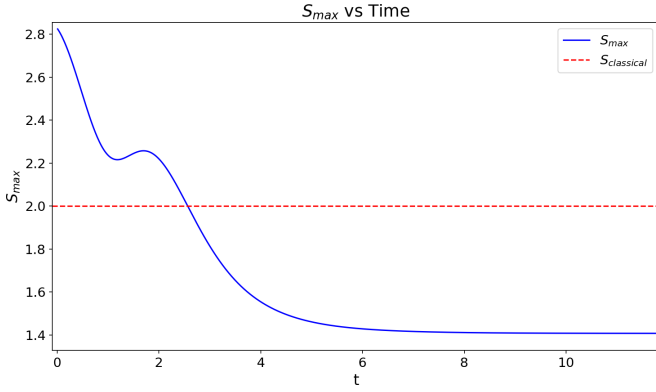


FIG. 2. Time evolution of the maximized Bell parameter of a two-time PDM of a single qubit coupled to a thermal bath. Natural units have been adopted, such that $\hbar = 1$ and $k_B = 1$ and we set $\omega_z = 1$, $T = 1$, $\gamma_1 = 0.9$, and $\gamma_2 = 1.2$.

in this Lindblad qubit model arises from the fact that temporal nonclassicality (as diagnosed by eigenvalues of the PDM) depends on cross-time coherence building up in the measured basis and this buildup does not happen instantaneously in the open-system dynamics considered here. Negativity is essentially driven by the off-diagonal entries in the PDM, which encode coherent phase evolution between the two measurement times. Immediately after the first measurement, the system has not had time to acquire a distinguishable quantum phase relative to t_0 and hence no negativity is observed. As time increases, the system picks up coherent oscillatory factors in the off-diagonal terms that eventually dominate over the thermal diagonal terms to produce negativity in one of the eigenvalues. With further time evolution, decoherence (as described by the $e^{-\gamma_2 t}$ decay) suppresses the coherent terms and the negativity vanishes.

Hence, while PDM negativity is a *sufficient* condition for temporal nonclassicality, it is *not necessary*. A PDM with a negative eigenvalue cannot be reproduced by any classical, macrorealist model with noninvasive measurability, since classical temporal processes necessarily yield a positive semidefinite PDM [9]. This makes negativity a strong, basis-independent witness of temporal quantum correlations. However, it is not strictly necessary, because there exist temporal quantum processes where the PDM remains positive, but other indicators of temporal nonclassicality—like temporal CHSH inequality violation—still show a quantum signature. The reason for this is that PDM negativity and temporal CHSH violation are sensitive to different features of the temporal correlations. PDM negativity is a statement about the entire two-time object R being outside the set of classical states, independent of measurement choices, and requires *global* nonclassicality. In contrast, the temporal CHSH inequality violation is a *targeted* test that is basis dependent and probes the existence of a strong temporal correlation in some projection. It too is sufficient—but not necessary—for temporal entanglement, because maximal quantum violation only occurs in the optimal basis and quantum processes can evade this criterion while satisfying other measures.

Since these witnesses capture different facets of temporal correlations, a complete characterization requires considering

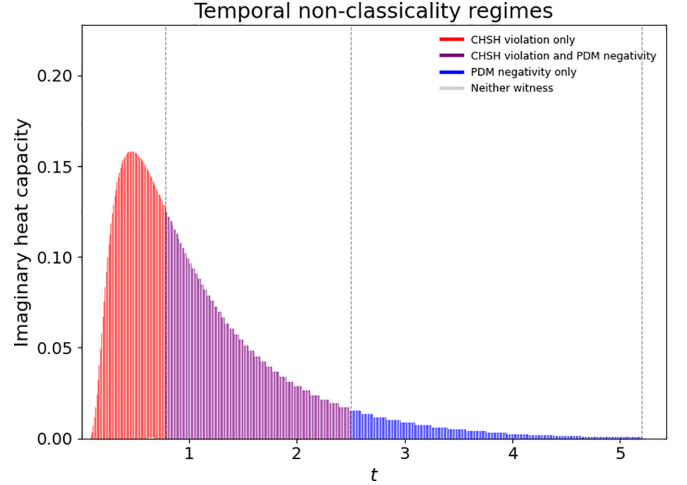


FIG. 3. Shaded region shows the range of values of the imaginary component of the complex heat capacity associated with temporal nonclassicality. The different colors distinguish regimes in which temporal nonclassicality is witnessed by the temporal CHSH inequality, by PDM negativity, or by both criteria. Natural units have been adopted, such that $\hbar = 1$ and $k_B = 1$, and we set $\omega_z = 1$, $T = 1$, $\gamma_1 = 0.9$, and $\gamma_2 = 1.2$.

both in conjunction, as illustrated in Fig. 3. The figure shows the range of values of $C''(\omega)$, at each point in time, associated with temporal nonclassicality, and the color coding distinguishes the regimes identified by $S_{\max}$ and the PDM negativity for the fixed parameters used in Figs. 1 and 2. We note that, even after $S_{\max}$ falls below the classical bound at $t \approx 2.5$ (see Fig. 2), values of the imaginary heat capacity persist in the nonclassical region until $t \approx 5.2$ —a timescale matching the survival of PDM negativity (see Fig. 1)—and thus defining a later regime in which temporal nonclassicality is witnessed by PDM negativity alone. Hence, even though both of these entanglement criteria are sufficient but not necessary when considered *individually*, to fully characterize temporal nonclassicality of the system it is necessary to consider both PDM negativity and temporal CHSH violation.

This opens up an intriguing avenue for further exploration into the nature of temporal quantum correlations and the extent to which they may be probed via different entanglement measures. Moreover, it would be interesting to investigate the dependency of PDM negativity on the initial state of the qubit (i.e., extend this work to consider pure and maximally mixed initial states, for example). This would provide further insights into the ability of the PDM framework to faithfully characterize temporal nonclassicality. Besides experimental validation of our predictions outlined in this paper (which is, of course, always the most reliable method), further corroboration could be achieved by considering two spatially separated qubits, each measured at two different times, and attempting to recover the results from the work by Wieśniak *et al.* [5] using the PDM framework. We leave these questions open for future investigations.

To conclude, we have presented a witness of temporal entanglement that is feasibly extendable to the macroscopic domain and bypasses the experimental challenges currently posed when probing temporal Bell inequality violation at the

emergent scale. We have provided a physical meaning, rooted in quantum information theory, to the imaginary component of the complex heat capacity and have shown that it can be used to probe temporal nonclassicality in the context of pseudodensity matrices and temporal CHSH inequalities. Further to this, we have placed a bound on the values of the imaginary heat capacity that serve as a direct witness of temporal entanglement, with a specific focus on two-level systems. This is particularly relevant for condensed-matter systems, such as Ising and Heisenberg models, that are intrinsic qubit lattices, and our results may also be relevant in the context of quantum computing. Current technologies are limited to at most a handful of qubits, so the formalism is especially pertinent to these emergent technologies, offering a unique approach to probing entanglement in such systems. We emphasize that the qubit model presented in this work is merely to illustrate the power of the method, but the formal construction is not restricted to two-level systems and can, in principle, be extended to more complex systems; however, a full numerical analysis would be required and this is beyond the scope of this work. We leave the analysis of condensed-matter systems, e.g., a 1D-spin chain, and the experimental verification of these predictions for future work in a forthcoming paper.

ACKNOWLEDGMENT

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A

We consider an open system governed by the Lindblad master equation [26,27],

$$\frac{d\rho}{dt} = \frac{-i}{\hbar}[H, \rho] + \sum_j \left(L_j \rho L_j^\dagger - \frac{1}{2}\{L_j^\dagger L_j, \rho\} \right), \quad (\text{A1})$$

consisting of a qubit coupled to a thermal bath. The Hamiltonian of the qubit is given by $H = \frac{\hbar\omega_z}{2}\sigma_z$ and has eigenstates $|0\rangle$ and $|1\rangle$, with corresponding eigenvalues $\pm \frac{\hbar\omega_z}{2}$. The coupling of the qubit to the thermal bath may be modeled via the Lindblad jump operators $L_- = \sqrt{\gamma_-}\sigma_-$ and $L_+ = \sqrt{\gamma_+}\sigma_+$, where (stimulated or spontaneous) emission and absorption are described by γ_- and γ_+ , respectively. If a temperature perturbation of the form $T(t) = T + \delta T e^{-i\omega t}$ is applied, the Hamiltonian of the qubit becomes $H = \frac{\hbar\omega_z}{2}\sigma_z + \delta H(t)$, where $\delta H(t) = -(\frac{\partial \langle H \rangle}{\partial t})\delta T(t) = -C\delta T(t)$. We now proceed to solve the Lindblad equation, with a state of the general form $\rho(t) = \frac{1}{2}(\mathbf{1} + x(t)\sigma_x + y(t)\sigma_y + z(t)\sigma_z)$.

For simplicity, here only $z(t) = \text{Tr}[\rho(t)\sigma_z]$ is of interest; later, we will generalize the Hamiltonian of the qubit to also include the off-diagonal terms and briefly discuss changes to the final result. From Eq. (10), we obtain $\dot{z}(t) = -\Gamma(z(t) - z_{\text{eq}}(t))$, where $\Gamma = \gamma_- + \gamma_+$ and $z_{\text{eq}}(t)$ is the

instantaneous thermal equilibrium magnetization, given by $z_{\text{eq}} = -\tanh(\frac{\hbar\omega_z}{2k_B T})$. Linearizing around small $\delta T(t)$, we can write $z_{\text{eq}}(t) \approx z_{\text{eq}}(0) + \delta T(t)(\frac{\partial z_{\text{eq}}}{\partial T})$ and arrive at

$$\dot{z}(t) + \Gamma z(t) = \Gamma \left(z_{\text{eq}}(0) + \delta T(t) \left(\frac{\partial z_{\text{eq}}}{\partial T} \right) \right). \quad (\text{A2})$$

This ordinary differential equation is best solved in frequency space. Performing the following transformations $\delta T(t) = \delta T e^{-i\omega t}$ and $z(t) = z(0) + \delta z(\omega) e^{-i\omega t}$ leads to

$$\delta z(\omega) = \frac{\Gamma}{\Gamma - i\omega} \delta T \left(\frac{\partial z_{\text{eq}}}{\partial T} \right). \quad (\text{A3})$$

In frequency space, the complex heat capacity becomes $\delta \langle H(\omega) \rangle = C(\omega) \delta T(\omega)$ and, noting that $\delta \langle H(\omega) \rangle = \frac{\hbar\omega_z}{2} \delta z(\omega)$, the imaginary component of the heat capacity is given by

$$C''(\omega) = \left(\frac{(\hbar\omega_z)^2}{4k_B T^2} \right) \frac{\omega \Gamma}{\Gamma^2 + \omega^2} \text{sech}^2 \left(\frac{\hbar\omega_z}{2k_B T} \right). \quad (\text{A4})$$

Generalizing this result for a Hamiltonian that includes the off-diagonal terms $H = \frac{\hbar\omega}{2}(\hat{n} \cdot \vec{\sigma})$, we follow the same procedure as above. The eigenstates in this case are $|+\rangle$ and $|-\rangle$, with eigenvalues $\pm \frac{\hbar\omega}{2}$. The Lindblad jump operators take the same form as before, but note that the raising and lowering operators are now in the new eigenbasis. For ease, we can rotate the state $\rho \rightarrow \tilde{\rho} = U^\dagger \rho U$, where the matrix U performs a rotation from $\hat{z} \rightarrow \hat{n}$, and work in the rotated frame for all subsequent calculations. The total heat capacity behaves as if the system were thermalized in the rotated eigenbasis of the Hamiltonian and the imaginary component becomes

$$C''(\omega) = \left(\frac{(\hbar\omega)^2}{4k_B T^2} \right) \frac{\omega \Gamma}{\Gamma^2 + \omega^2} \text{sech}^2 \left(\frac{\hbar\omega}{2k_B T} \right), \quad (\text{A5})$$

which is the quantity used in the paper.

APPENDIX B

The above treatment has so far been restricted to two-level systems. While this has provided computational ease and clear proof-of-principle results, it is not a requirement of the framework. Here, we discuss a generalization to a d -dimensional system and explicitly extend our results to a qutrit.

For a d -dimensional system, we choose a Hermitian operator basis $\{\Lambda_\mu\}_{\mu=0}^{d^2-1}$ with $\Lambda_0 = \mathbf{1}_d$ and $\text{Tr}(\Lambda_\mu \Lambda_\nu) = d\delta_{\mu\nu}$, e.g., the identity together with a suitably rescaled set of $\text{SU}(d)$ generators. Any two-time PDM can then be written as

$$R = \frac{1}{d^2} \sum_{\mu, \nu=0}^{d^2-1} T^{\mu\nu} \Lambda_\mu \otimes \Lambda_\nu, \quad T^{\mu\nu} = \langle \Lambda_\mu(t_0) \Lambda_\nu(t_1) \rangle. \quad (\text{B1})$$

Any Hamiltonian admits the expansion $H(t) = \sum_{\mu=0}^{d^2-1} H_\mu(t) \Lambda_\mu$ and repeating the linear-response analysis of Eqs. (3), (7), and (8), but now using the $\text{SU}(d)$ commutation relations $[\Lambda_a, \Lambda_b] = 2i \sum_{c=1}^{d^2-1} f_{abc} \Lambda_c$ [where $a, b = 1, \dots, d^2-1$ and f_{abc} are the standard $\text{SU}(d)$ structure constants], we obtain a tensor of complex heat capacities

$$C_{\mu\nu} = \frac{1}{k_B T^2} \int_0^\infty dt \langle \dot{H}_\mu(t) \dot{H}_\nu(0) \rangle e^{i\omega t}. \quad (\text{B2})$$

This tensor plays an analogous role to the qubit case, yielding the qudit PDM

$$R = \frac{1}{d^2} \sum_{\mu, \nu=0}^8 C_{\mu\nu}(\omega) \Lambda_\mu \otimes \Lambda_\nu. \quad (\text{B3})$$

All diagnostics of temporal nonclassicality discussed for qubits (PDM negativity, temporal CHSH violations) therefore extend straightforwardly to systems of arbitrary finite dimension. To further illustrate this point, we will consider a spin-1 qutrit with energy eigenbasis $|0\rangle, |1\rangle, |2\rangle$ and energies $E_0 = 0, E_1 = \hbar\omega_1, E_2 = \hbar\omega_2$, such that the Hamiltonian is $H = \hbar\omega_1|1\rangle\langle 1| + \hbar\omega_2|2\rangle\langle 2|$. In the rescaled Gell-Mann basis, the projectors become

$$|1\rangle\langle 1| = \frac{1}{3}\Lambda_0 + \frac{1}{2\sqrt{3/2}}\Lambda_3 + \frac{1}{2\sqrt{3}\sqrt{3/2}}\Lambda_8,$$

$$|2\rangle\langle 2| = \frac{1}{3}\Lambda_0 - \frac{1}{2\sqrt{3/2}}\Lambda_3 + \frac{1}{2\sqrt{3}\sqrt{3/2}}\Lambda_8.$$

Thus $H = H_0\Lambda_0 + H_3\Lambda_3 + H_8\Lambda_8$, with $H_0 = \frac{\hbar}{3}(\omega_1 + \omega_2)$, $H_3 = \sqrt{\frac{2}{3}}\frac{\hbar}{2}(\omega_1 - \omega_2)$, $H_8 = \sqrt{\frac{2}{3}}\frac{\hbar}{2\sqrt{3}}(\omega_1 + \omega_2)$, and $H_\mu = 0$ for all other μ . We now proceed to solve the master equation, but note that there are now two independent relaxation channels: $|1\rangle \leftrightarrow |0\rangle$ with energy gap $\hbar\omega_1$ and $|2\rangle \leftrightarrow |0\rangle$ with energy gap $\hbar\omega_2$. Note that we have deliberately chosen a three-level system, where each excited state relaxes independently to ground to make the PDM analytically solvable. This setup is also physically motivated and common in atomic systems, where selection dipole rules forbid this transition. The Lindblad jump operators are $L_{1-} = |0\rangle\langle 1|$ and $L_{1+} = |1\rangle\langle 0|$ (and similarly for the second transition). Assume each transition has the same base relaxation rate γ_1 , with thermal occupation numbers $n_j = \frac{1}{e^{\beta\hbar\omega_j} - 1}$, $j = 1, 2$. The Lindblad master equation is

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho] + \sum_{j=1}^2 \mathcal{L}_j[\rho],$$

with

$$\begin{aligned} L_j[\rho] = & \frac{\gamma_j}{2}((n_j + 1)(2L_{j,-}\rho L_{j,+} - L_{j,+}L_{j,-}\rho)) \\ & + n_j((2L_{j,+}\rho L_{j,-} - L_{j,-}L_{j,+}\rho)). \end{aligned}$$

As in the qubit example, pure dephasing terms can be added, but for the heat capacity the key part is the energy relaxation, which is governed by rates of order $\Gamma_j = \gamma_j(2n_j + 1)$ for each transition j . For the following calculations, for simplicity we assume that the two channels are independent and characterized by effective rates Γ_1, Γ_2 .

Applying the same temperature modulation protocol as for the qubit, and considering a Markovian system where the energy relaxation is a sum of independent exponential modes, standard linear response gives a Debye-type form for each mode. In a simple qutrit Lindblad model, where each transition relaxes with rate Γ_j , we obtain a sum of two Lorentzian contributions to the imaginary part of the complex

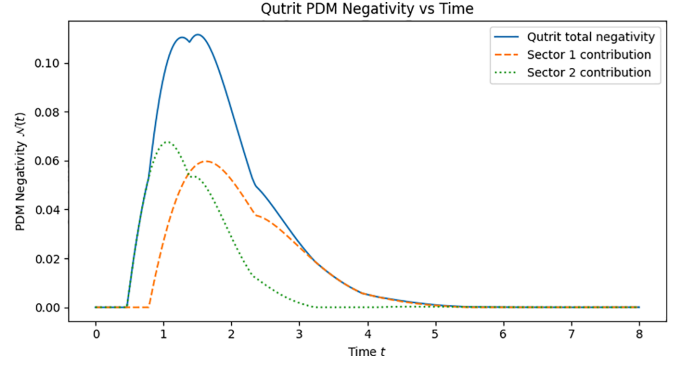


FIG. 4. Time evolution of the negativity of a two-time PDM of a single qutrit coupled to a thermal bath. Natural units have been adopted, such that $\hbar = 1$ and $k_B = 1$, and we set $\omega_1 = 1, \omega_2 = 1.7$, $T = 1, \gamma_{1,1} = 0.9, \gamma_{2,1} = 1.2, \gamma_{1,2} = 0.7$, and $\gamma_{2,2} = 1.5$. The classical probabilities are set to $p_1 = 0.55$ and $p_2 = 0.45$.

heat capacity

$$C''_{\text{qutrit}}(\omega) = \sum_{j=1}^2 \left[\frac{(\hbar\omega_j)^2}{4(k_B T)^2} \text{sech}^2\left(\frac{\hbar\omega_j}{2k_B T}\right) \frac{\omega\Gamma_j}{\Gamma_j^2 + \omega^2} \right].$$

This is the spin-1 analog of Eq. (4) and each contribution is structurally identical to the qubit result and has the usual Debye factor $\frac{\omega\Gamma_j}{\Gamma_j^2 + \omega^2}$.

Consider an analytically tractable qutrit model as discussed above, such that we have three distinct levels (and hence a *genuine* qutrit), but the dynamics are simple enough that the PDM is block diagonal in two qubitlike sectors. The Hamiltonian used in the previous discussion is suitable. The dynamics are akin to a classical mixture of two qubitlike channels, with probability p_1 the system behaves as a qubit on the subspace $\{|0, 1\rangle$ and parameters $(\omega_1, \gamma_{1,1}, \gamma_{2,1})$ —and similarly for the second channel. Note that $p_1 + p_2 = 1$. We remark here that this semiclassical treatment is merely convenient and by no means necessary: for a fully quantum model, we would need to solve a single Liouvillian for its steady state and Heisenberg evolution of the $\text{SU}(3)$ generators, and the p_1 and p_2 would simply get masked in the other physical parameters $\gamma_{1,2}, \gamma_{1,1}, \omega_1$, etc. Also, mathematically PDM negativity is convex: $\mathcal{N}(p_1 R_1 + p_2 R_2) \leq \mathcal{N}(p_1 R_1) + \mathcal{N}(p_2 R_2)$; hence any genuine three-level Hamiltonian and bath with the same parameters will exhibit at least as much, and typically more, PDM negativity, since the latter is a convex function of the process.

The two-time qutrit PDM is thus expressible as a convex mixture

$$R_{\text{qutrit}}(t) = p_1 R_{\text{qubit}}^{(1)}(t) \oplus p_2 R_{\text{qubit}}^{(2)}(t) \oplus [0],$$

where $[0]$ is a 1×1 block that is identically zero. The eigenvalues can therefore be split into four from the first qubitlike process, four from the second, and zero from the identity block. The PDM negativity is therefore

$$\mathcal{N}(t) = p_1 \mathcal{N}_{\text{qubit}}^{(1)}(t) + p_2 \mathcal{N}_{\text{qubit}}^{(2)}(t),$$

where each $\mathcal{N}_{\text{qubit}}^{(j)}(t)$ is calculated from the four qubit eigenvalues in sector j . Figure 4 shows this for suitably chosen parameters.

The mapping between measurable thermal response (via the complex heat capacity) and two-time quantum correlations encoded in the PDM is not merely an artifact of low-dimensional Hilbert spaces; rather, it can be generalized for any finite-dimensional system. In particular, models with

block-diagonal structure (e.g., sums of qubitlike subspaces) yield PDMs whose eigenvalues are obtained directly from the qubit treatment, but the formalism places no restrictions on the Hamiltonian, dimension, or operator algebra. This establishes the formal extension of the construction to finite-dimensional systems, although its experimental implementation and the reconstruction of the required correlators may be system dependent.

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