Density Matrix and Purity Evolution in Dissipative Two-Level Systems: II. Relaxation

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Abstract

We investigate the time evolution of the reduced density matrix (RDM) and its purity in the dynamics of a two-level system coupled to a dissipative harmonic bath, when the system is initially placed in one of its eigenstates. We point out that the symmetry of the initial condition confines the motion of the RDM elements to a one-dimensional subspace and show that the purity always goes through its maximally mixed value at some time during relaxation, but subsequently recovers and (under low-temperature, weakly dissipative conditions) can rise to values that approach unity. These behaviors are quantified through accurate path integral calculations. Under low-temperature, weakly dissipative conditions, we observe unusual, nonmonotonic population dynamics when the two-level system is initially placed in its ground state. We also analyze the origin of the system-bath interactions responsible for the nonmonotonic behavior of purity during relaxation. Our results show that classical dephasing processes arising from site level fluctuations lead to a monotonic decay of purity, and that the quantum mechanical decoherence events associated with spontaneous phonon emission are responsible for the subsequent recovery of purity. Last, we show that coupling with a low-temperature bath can purify a mixed two-level system. In the case of the maximally mixed initial RDM, the purity increases monotonically even during short time.

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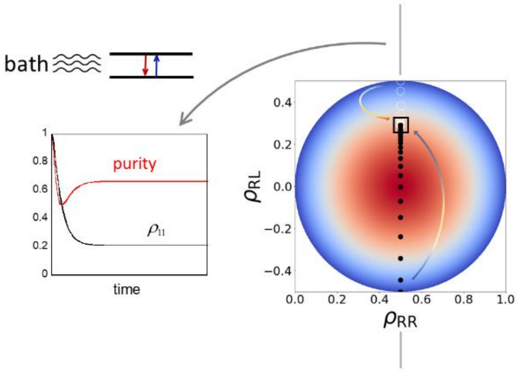

I. Introduction

Much attention has recently been given to questions related to quantum coherence and its destruction by intramolecular and external degrees of freedom with which a system interacts.[1] Quantum coherence is a fascinating phenomenon[2] which, if sustainable, could open up new possibilities with potentially important technological applications.

The purity of a quantum system embedded in a dissipative environment is defined as

$$Q(t) = \mathrm{Tr}\ \tilde{\rho}(t)^2 \tag{1.1}$$

where $\tilde{\rho}$ is the system's reduced density operator,

$$\hat{\tilde{\rho}}(t) = \mathrm{Tr}_{\mathrm{env}}\ \hat{\rho}(t) \tag{1.2}$$

i.e. the density operator traced with respect to the degrees of freedom comprising the system's environment. If $\tilde{\rho}$ can be expressed in terms of a single state, the purity is equal to unity; otherwise the reduced density matrix (RDM) represents a mixture and $Q < 1$. The purity is closely related to the linear entropy $S_{\mathrm{lin}} = 1 - \mathrm{Tr}\ \tilde{\rho}(t)^2$, which is a simpler form of the von Neumann entropy $S(t) = -\mathrm{Tr}\ \tilde{\rho}(t) \ln \tilde{\rho}(t)$. The time evolution of purity has been the subject of many studies using a variety of approaches.[3-8] The behavior of purity has often been used as a basis-independent measure of coherence loss, and estimates of the decoherence time have been obtained by examining the early-time Gaussian decay of purity.

In a recent paper[9] we showed that under certain conditions, the purity of a dissipative symmetric two-level system (TLS) prepared in a localized state (i.e. a superposition of its two eigenstates) coupled to a bath can undergo nonmonotonic evolution, increasing substantially after an initial decrease. At sufficiently low temperature and weak coupling to the bath, the recovery of purity can be nearly quantitative, reaching values consistent with a nearly pure state. We also showed that the observed behaviors can be understood in terms of physically meaningful components, such as the instantaneous rate and the difference of the TLS eigenstate populations.

In the preceding article[10] (Paper I) we analyzed the behavior of the purity for symmetric TLS coupled to a dissipative bath subject to a general initial condition. Using simple arguments, we established some bounds and limiting behaviors. We also examined the evolution of purity with a localized initial condition which gives rise to tunneling dynamics. This basic analysis showed that the early time evolution of purity is quadratic (i.e. Gaussian), although this time dependence is often valid over a very narrow time interval. Using numerically exact path integral methods, we obtained the evolution of purity under a variety of conditions. We related these results to the dynamics of a site population and the modulus of the off-diagonal RDM element, and examined the contributions to purity dynamics from physically meaningful RDM properties and from classical and quantum contributions to the decoherence process.

In this paper we extend the study of TLS purity evolution to the case of eigenstate initial preparation. Following an overview, we show in section II that in this case the purity depends on a single element of the RDM, unlike the general case where it depends on two elements. We also show that during the relaxation of an initially excited TLS the purity *always* displays a transient drop to $\frac{1}{2}$ (the value corresponding to a maximally mixed RDM). Unless the bath is practically at infinite temperature, the purity will necessarily rebound to reach at long times its equilibrium value $\frac{1}{2} < Q < 1$.

Using real-time path integral methods, we present in section III accurate numerical results for the time evolution of purity for various parameters. These results illustrate the patterns established analytically and show a nearly quantitative rebound of purity during relaxation in the low-temperature, weak dissipation regime, from its minimum value $\frac{1}{2}$ to values that can approach unity. In close analogy with the case of tunneling dynamics, we find that the strictly quantum mechanical mechanism of decoherence associated with spontaneous phonon emission[11] is entirely responsible for the recovery of purity, while the classical decoherence process associated with stimulated phonon emission through level fluctuations predicts a monotonic decay. We also consider the case where the TLS is initially placed in its ground state. In this case we find that the excited state population does not remain equal to zero even at zero temperature, in agreement with earlier work. Further, we observe an unexpected nonmonotonic feature in the evolution of the eigenstate populations at low temperatures. In section IV we show that coupling to a low-temperature bath can purify a TLS prepared in the maximally mixed state. In that case purity increases monotonically, even at very short times. In section V we give some concluding remarks, emphasizing that the loss or recovery of purity is distinct from quantum coherence, and these two concepts should not be used interchangeably.

II. Theoretical considerations

We focus again on the simple case of a two-level quantum system bilinearly coupled to a bath of harmonic oscillators. In the energy eigenstate basis, the TLS Hamiltonian has the usual form

$$\hat{H}_{\text{TLS}} = -\hbar\Omega|\Phi_0\rangle\langle\Phi_0| + \hbar\Omega|\Phi_1\rangle\langle\Phi_1| \tag{2.1}$$

where $2\hbar\Omega$ is the tunneling splitting. The TLS is coupled to a harmonic bath via the additional term

$$\hat{H}_{\text{bath}} = \sum_j \frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\hat{q}_j^2 - c_j\hat{q}_j\left(|\Phi_0\rangle\langle\Phi_1| + |\Phi_1\rangle\langle\Phi_0|\right). \tag{2.2}$$

As is well known,[12] all collective parameters of the bath are contained in the spectral density function

$$J(\omega) = \tfrac{1}{2}\pi\sum_j \frac{c_j^2}{m_j\omega_j}\delta\left(\omega - \omega_j\right). \tag{2.3}$$

In this work we use the common Ohmic form,

$$J(\omega) = \tfrac{1}{2}\pi\hbar\xi\omega e^{-\omega/\omega_{\text{c}}}, \tag{2.4}$$

where the TLS-bath coupling is quantified by the dimensionless Kondo parameter ξ and ω_{c} is the bath cutoff frequency.[1] The initial density operator is given by

$$\hat{\rho}(0) = \hat{\tilde{\rho}}(0)\hat{\rho}_{\text{bath}}(0) \tag{2.5}$$

with $\hat{\rho}_{\text{bath}} = e^{-\beta \hat{H}_{\text{bath}}^{\text{free}}} / \operatorname{Tr} e^{-\beta \hat{H}_{\text{bath}}^{\text{free}}}$, where $\beta = 1/k_{\text{B}}T$ is the Boltzmann operator for the free bath Hamiltonian, given by Eq. (2.9) with $c_j = 0$. We calculate the time evolution of the reduced density operator,

$$\hat{\tilde{\rho}}(t) = \operatorname{Tr}_{\text{bath}}\left(e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar}\right). \tag{2.6}$$

The TLS is initially placed in one of its eigenstates, i.e.

$$\hat{\tilde{\rho}}(0) = |\Phi_1\rangle\langle\Phi_1| \quad \text{or} \quad \hat{\tilde{\rho}}(0) = |\Phi_0\rangle\langle\Phi_0|. \tag{2.7}$$

For each of these initial conditions we follow the TLS dynamics until equilibrium is reached. As in Paper I, we indicate the initial condition with a superscript in the RDM, i.e. we investigate $\tilde{\rho}^{11}(t)$ and $\tilde{\rho}^{00}(t)$.

In order to utilize the analytically available influence functional[13] in the path integral calculations, it is advantageous to use a TLS basis in which the system-bath coupling is diagonal. We define the localized states

$$|\mathrm{R}\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_0\rangle + |\Phi_1\rangle\right), \quad |\mathrm{L}\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_0\rangle - |\Phi_1\rangle\right). \tag{2.8}$$

The states $|\mathrm{R}\rangle$ and $|\mathrm{L}\rangle$ are the 'right' and 'left' localized states of a symmetric TLS Hamiltonian. In this basis the problem becomes the spin-boson Hamiltonian examined in Paper I, in which the localized TLS states are off-diagonally coupled and the system-bath coupling is diagonal in the TLS basis,

$$\hat{H}_{\text{bath}} = \sum_j \frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\hat{q}_j^2 - c_j\hat{q}_j\left(|\mathrm{R}\rangle\langle\mathrm{R}| - |\mathrm{L}\rangle\langle\mathrm{L}|\right). \tag{2.9}$$

In the localized basis the eigenstate initial conditions become

$$\begin{aligned}\hat{\tilde{\rho}}^{11}(0) &= \tfrac{1}{2}\left(|\mathrm{R}\rangle\langle\mathrm{R}| + |\mathrm{L}\rangle\langle\mathrm{L}| - |\mathrm{R}\rangle\langle\mathrm{L}| - |\mathrm{L}\rangle\langle\mathrm{R}|\right)\\ \hat{\tilde{\rho}}^{00}(0) &= \tfrac{1}{2}\left(|\mathrm{R}\rangle\langle\mathrm{R}| + |\mathrm{L}\rangle\langle\mathrm{L}| + |\mathrm{R}\rangle\langle\mathrm{L}| + |\mathrm{L}\rangle\langle\mathrm{R}|\right)\end{aligned} \tag{2.10}$$

The RDM is propagated by combining the contributions obtained from each of the localized initial condition in Eq. (2.10). The evolution of these components involves tunneling dynamics.

The purity is independent of representation, and to understand its behavior it is convenient to alternate between eigenstate and site representations. Thus, the RDM with an eigenstate initial condition is specified by

$$\tilde{\rho}_{\alpha''\alpha'}^{\alpha\alpha}(t) = \operatorname{Tr}_{\text{bath}}\langle\alpha''|e^{-i\hat{H}t/\hbar}|\Phi_\alpha\rangle\langle\Phi_\alpha|\hat{\rho}_{\text{bath}}(0)e^{i\hat{H}t/\hbar}|\alpha'\rangle, \tag{2.11}$$

where $\alpha = 0,1$ and $\alpha', \alpha'' = 0,1$ or R, L.

By squaring the RDM in the eigenstate basis and evaluating the trace, we find that (for any initial condition)

$$Q(t) = \tilde{\rho}_{11}(t)^2 + \tilde{\rho}_{00}(t)^2 + 2\left|\tilde{\rho}_{10}(t)\right|^2 . \tag{2.12}$$

As is well known, the equations for the diagonal and off-diagonal RDM elements are not coupled in the eigenstate basis.[14] With an eigenstate initial condition, this implies that $\tilde{\rho}_{10}^{\alpha\alpha}(t) = 0$ at all times. Thus, in the case of an eigenstate initial condition, the purity becomes

$$Q^{\alpha\alpha}(t) = 2\left(\tilde{\rho}_{11}^{\alpha\alpha}(t) - \tfrac{1}{2}\right)^2 + \tfrac{1}{2} . \tag{2.13}$$

It is instructive to examine the contributions to purity discussed in Paper 1. For this purpose we express again the purity in the site representation,

$$Q(t) = \tilde{\rho}_{\mathrm{RR}}(t)^2 + \tilde{\rho}_{\mathrm{LL}}(t)^2 + 2\left(\mathrm{Re}\,\tilde{\rho}_{\mathrm{RL}}(t)\right)^2 + 2\left(\mathrm{Im}\,\tilde{\rho}_{\mathrm{RL}}(t)\right)^2 , \tag{2.14}$$

The real part of the off-diagonal element is related to the difference of eigenstate populations,

$$\mathrm{Re}\,\tilde{\rho}_{\mathrm{RL}}(t) = \tfrac{1}{2}\left(\tilde{\rho}_{00}(t) - \tilde{\rho}_{11}(t)\right) . \tag{2.15}$$

The eigenstate initial condition corresponds to $\tilde{\rho}_{\mathrm{RR}}^{\alpha\alpha}(0) = \frac{1}{2}$ and $\tilde{\rho}_{\mathrm{RL}}^{11}(0) = -\frac{1}{2}$, $\tilde{\rho}_{\mathrm{RL}}^{00}(0) = \frac{1}{2}$. Further, the symmetry of the TLS and the initial state implies that

$$\tilde{\rho}_{\mathrm{RR}}^{\alpha\alpha}(t) = \tilde{\rho}_{\mathrm{LL}}^{\alpha\alpha}(t) = \tfrac{1}{2} \tag{2.16}$$

at all times. Since the time derivative of the site population is proportional to the imaginary part of the off-diagonal RDM element,[15] we also conclude that $\mathrm{Im}\,\tilde{\rho}_{\mathrm{RL}}^{\alpha\alpha}(t) = 0$. Using these simple observations, we find that with the eigenstate initial condition the purity can be expressed in terms of a single site-basis RDM element,

$$Q^{\alpha\alpha}(t) = \tfrac{1}{2} + 2\left|\tilde{\rho}_{\mathrm{RL}}^{\alpha\alpha}(t)\right|^2 = \tfrac{1}{2} + 2\tilde{\rho}_{\mathrm{RL}}^{\alpha\alpha}(t)^2 . \tag{2.17}$$

Using Eq. (2.15), we recover the result of Eq. (2.13).

Eq. (2.13) is reminiscent of the expression for the incoherent contribution to purity obtained in Paper I in terms of the site population. However, Eq. (2.13) pertains to the *total* purity. In the case of relaxation from a TLS eigenstate, the purity depends on *a single* RDM element, which is the survival probability of the initially excited state. This result is the consequence of symmetry in the eigenstate initial condition. As discussed in Paper I, in the general case (for example, when the TLS is initially prepared in a localized state) the purity is a function of a diagonal *and* an off-diagonal RDM element, thus the dynamics explores a two-dimensional region in the $(\tilde{\rho}_{\mathrm{RR}}^{11}, \left|\tilde{\rho}_{\mathrm{RL}}^{11}\right|)$ space, as shown in Fig. 7 of that paper. The present symmetry constraint forces the dynamical evolution to lie along the $\tilde{\rho}_{\mathrm{RR}} = \frac{1}{2}$ line on the purity contour map displayed in those graphs. In this sense, the dynamics of relaxation is simpler than that resulting with tunneling initial conditions. Further, $\tilde{\rho}_{\mathrm{RL}}^{11}$ remains real-valued throughout the dynamics.

The function in the right-hand side of Eq. (2.13) has a global minimum, $Q_{\min}^{\alpha\alpha} = \frac{1}{2}$, at $\tilde{\rho}_{11}^{11} = \frac{1}{2}$. If the TLS starts out in the excited state, the initial value of this RDM element is $\tilde{\rho}_{11}^{11}(0) = 1$. At any finite temperature, the population of the excited state at equilibrium will be smaller than that of the ground state, thus $\lim\limits_{t\to\infty} \tilde{\rho}_{11}^{11} < \frac{1}{2}$. By virtue of the intermediate value theorem, we conclude that the population of the excited state must go through the value $\tilde{\rho}_{11}^{11} = \frac{1}{2}$ at least once. At that instant the purity will attain its minimum value $Q_{\min}^{11} = \frac{1}{2}$. Since at any finite temperature (regardless of parameter values) the purity goes through a minimum at some time during excited state relaxation, its evolution is *always nonmonotonic* during relaxation, and the system passes through a maximally mixed state before reaching equilibrium.

This situation does not arise during the evolution following the preparation of the TLS in the ground state. Again, at a finite (or zero) temperature, we have $\lim\limits_{t\to\infty} \tilde{\rho}_{11}^{00} < \frac{1}{2}$, but since now $\tilde{\rho}_{11}^{00}(0) = 0$ and the population evolution is exponential once short-time transients have died out, we do not expect the excited state population to reach the value $\frac{1}{2}$ at any time. Thus we expect the purity to remain greater than $\frac{1}{2}$ in this case. This implies that the purity will exhibit monotonic evolution in this case, unless the TLS populations $\tilde{\rho}_{00}^{00}(t)$ and $\tilde{\rho}_{11}^{00}(t)$ display oscillatory features. Our numerical results in section III show that this behavior is indeed possible.

III. Path integral results for purity during relaxation dynamics

In this section we present path integral results for the time evolution of the TLS purity following its initial preparation in a TLS eigenstate. The calculations are performed using the iterative quasi-adiabatic propagator path integral (QuAPI) methodology[16] and the small matrix disentanglement of the path integral[17,18] (SMatPI). These methods yield numerically exact results once converged with respect to the path integral time step and the memory length. We set the bath cutoff frequency $\omega_{\mathrm{c}} = 5\Omega$ and consider the following four combinations of system-bath coupling strength and temperature: (i) $\xi = 0.3, \hbar\Omega\beta = 0.1$, (ii) $\xi = 0.3, \hbar\Omega\beta = 1$, (iii) $\xi = 0.3, \hbar\Omega\beta = 10$, (iv) $\xi = 0.1, \hbar\Omega\beta = 10$. With parameter sets (iii) and (iv) both the TLS and the majority of bath degrees of freedom are practically at zero temperature.

In Figures 1 and 2 we show the time evolution of the excited TLS eigenstate and the purity for the two eigenstate initial conditions for each parameter set. When the TLS is initially in the excited state, we observe that the purity always goes through its minimum value $Q_{\min} = \frac{1}{2}$ at the time at which $\tilde{\rho}_{\mathrm{RR}}^{11} = \frac{1}{2}$, in agreement with the analysis presented in the previous section. With the exception of the very high temperature bath of parameter set (i), the purity always rises again, reaching a value near unity in the low temperature cases of parameter sets (iii) and (iv). The excited state population falls to low values in both of these cases, but not to the very small value that one would expect on the basis of the Boltzmann factor for the TLS alone. This is a consequence of system-bath coupling, i.e. the true eigenstate of the full system-bath Hamiltonian has a nonvanishing projection on the excited TLS state. Similar observations have been made in regard to the long-time populations reached during the tunneling dynamics of asymmetric two-level systems, in particular with strong system-bath coupling. This effect causes the long-time survival probability of the excited state to attain a larger value in the case of parameter set (iii), compared to that of parameter set (iv), which has the same near-zero temperature.

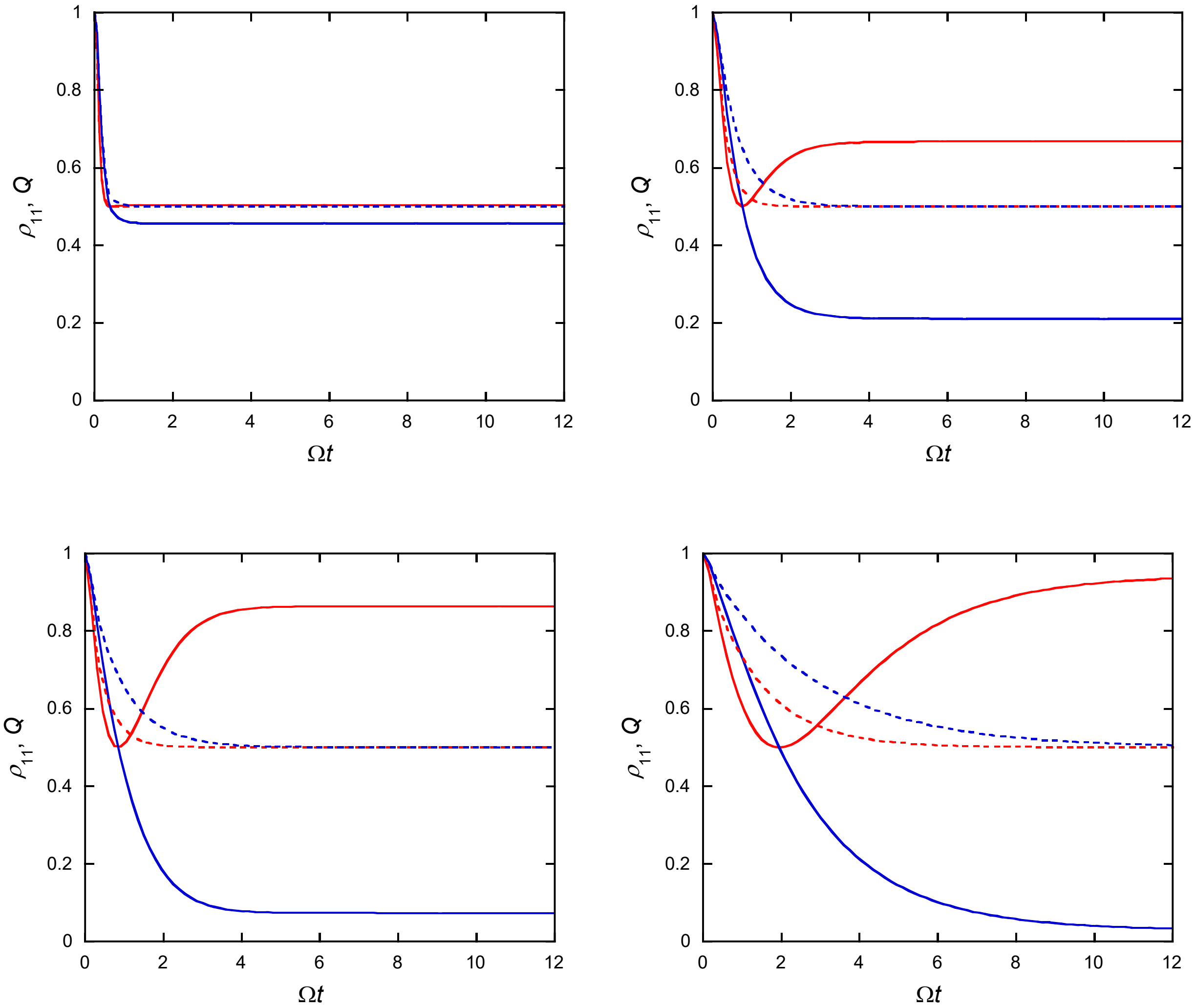

Fig 1. Time evolution of excited state population (blue curves reaching lower long-time values) and of purity (red curves, reaching higher long-time values) for a TLS initially prepared in the excited eigenstate from path integral calculations. Top left: $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 0.1$. Top right: $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 1$. Bottom left $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 10$. Bottom right: $\xi = 0.1, \omega_c = 5\Omega, \hbar\Omega\beta = 10$. Solid lines: results with full decoherence factors included. Dashed lines: results with only classical decoherence included.

For the same reason, when the TLS is initially placed in its ground state, Fig. 2 shows that some of the population leaks to the excited state even with the extremely low temperature of parameter sets (iii) and (iv). This zero-temperature excitation has been discussed in the context of the "up" rate constant in the higher-order extension of the Bloch equations.[19,20] Interestingly, we observe that the excited population displays mildly nonmonotonic dynamics in the low-temperatures, weak dissipation regime, rising higher than its equilibrium value at early times. No such transient nonmonotonic behavior is observed during relaxation from the excited TLS eigenstate. With all parameter sets, the purity initially falls by an amount that depends on the temperature and dissipation strength, but under low-temperature conditions it rises again to its long-time value. As discussed in the previous section, this rise is the result of nonmonotonic population evolution following the preparation of the TLS in the ground state. In all cases the long-time values of the populations and purity are identical for the two TLS initial conditions.

As discussed in the previous section, in the case of an eigenstate initial condition $\tilde{\rho}_{\mathrm{RR}}^{\alpha\alpha} = \frac{1}{2}$ and $\mathrm{Im}\,\tilde{\rho}_{\mathrm{RL}}^{\alpha\alpha}(t) = 0$ at all times, thus only $\mathrm{Re}\,\tilde{\rho}_{\mathrm{RL}}^{\alpha\alpha}(t)$ evolves. Nevertheless, in order to contrast with the spread of RDM elements the case of tunneling dynamics, we show in Figure 3 the progression of the RDM pairs $\tilde{\rho}_{\mathrm{RR}}^{\alpha\alpha}$, $\tilde{\rho}_{\mathrm{RL}}^{\alpha\alpha}$ on the purity color map during the evolution from the two eigenstate initial conditions for each of these parameter sets.

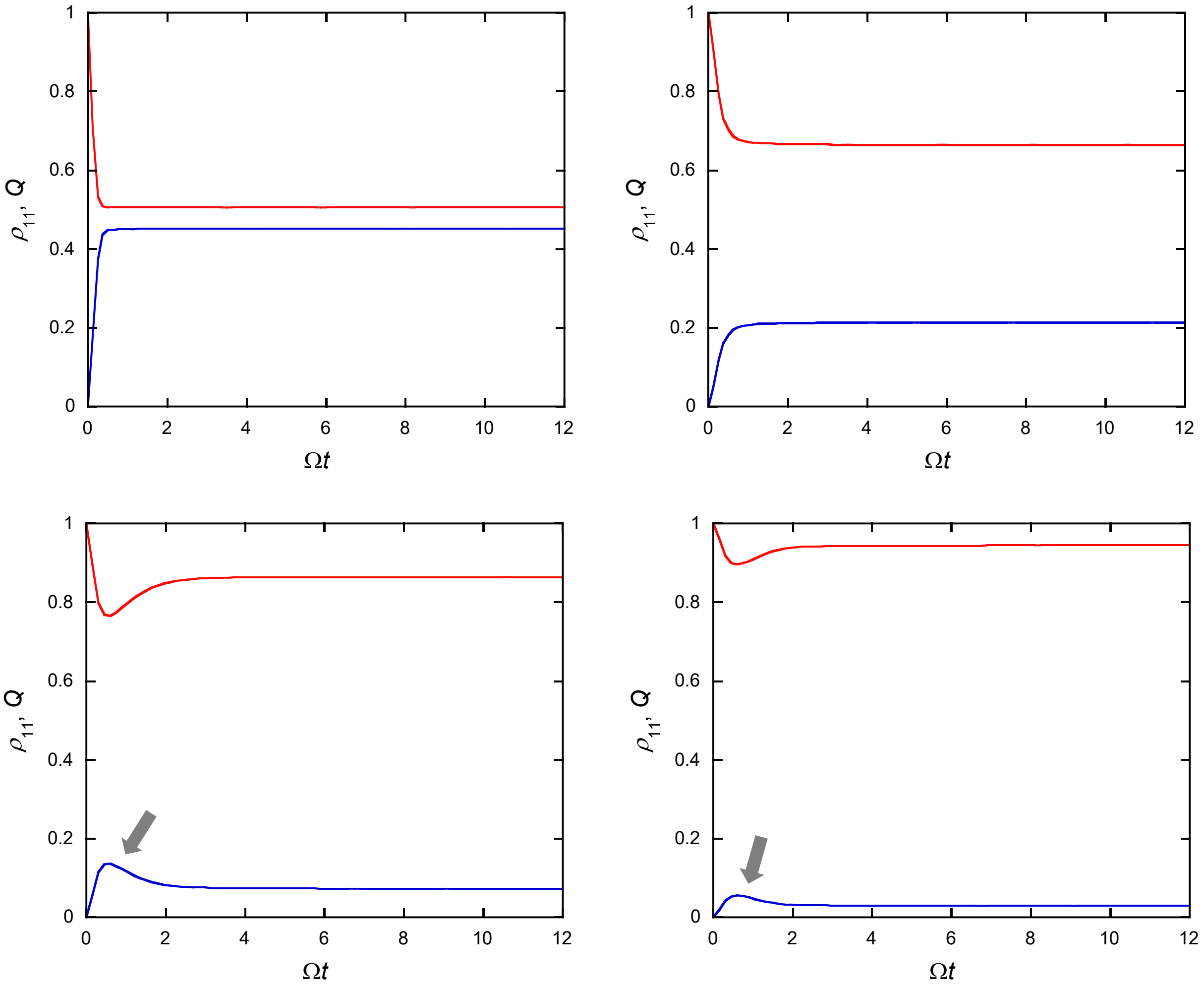

Fig 2. Time evolution of excited state population (blue curve starting at 0) and of purity (red curve starting at 1) for a TLS initially prepared in its ground eigenstate from path integral calculations. Top left: $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 0.1$. Top right: $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 1$. Bottom left $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 10$. Bottom right: $\xi = 0.1, \omega_c = 5\Omega, \hbar\Omega\beta = 10$. The nonmonotonic feature of the population is highlighted with an arrow.

In the case of relaxation from the TLS excited state, the initial point $\tilde{\rho}_{\mathrm{RR}}^{11}=\frac{1}{2}, \tilde{\rho}_{\mathrm{RL}}^{11}=-\frac{1}{2}$ lies at the center of the bottom boundary on the purity contour map. Under strongly dissipative conditions (high temperature and large system-bath coupling) the absolute value of the off-diagonal element decreases rapidly and monotonically toward half of the equilibrium value of the TLS eigenstate population difference. At infinite temperature the long-time population difference vanishes, thus $\operatorname{Re}\tilde{\rho}_{\mathrm{RL}}^{11}$ reaches the center of the color map, which corresponds to a completely mixed state. This behavior is observed with parameter set (i), where the RDM pair suffers a steep drop to $Q_{\min}^{11}=0.5$ and subsequently remains at this value, which signifies an almost completely mixed state.

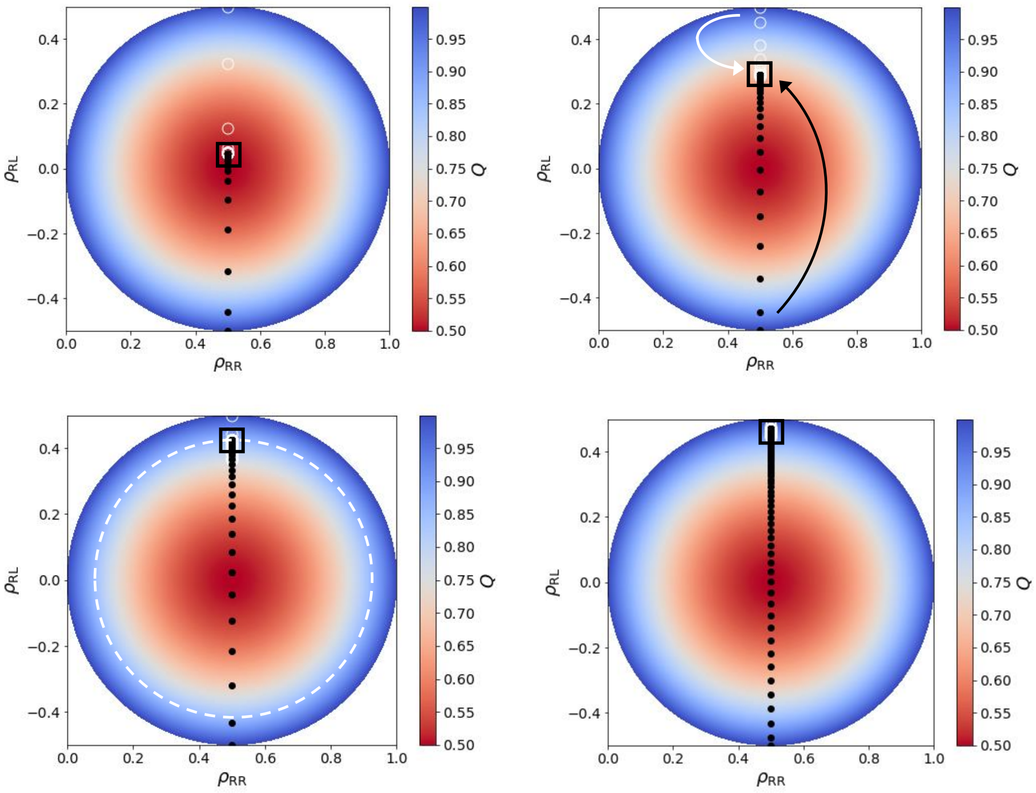

Fig 3. Exploration of the $(\tilde{\rho}_{\mathrm{RR}}, \tilde{\rho}_{\mathrm{RL}})$ space during dynamics of a TLS prepared in the excited eigenstate (small solid black markers) and the ground state (larger, hollow white markers). The color map corresponds to the purity value at each point. The thermodynamic equilibrium point is indicated with a black square. The direction of the evolution with the excited state initial condition is indicated with a black arrow, while the evolution with the ground state initial condition is indicated with a white arrow for one of the parameters. The dashed white circle in the bottom left panel shows the boundary of the region in which an initial RDM will be purified by coupling to the bath. Top left: $\xi=0.3, \omega_{\mathrm{c}}=5\Omega, \hbar\Omega\beta=0.1$. Top right: $\xi=0.3, \omega_{\mathrm{c}}=5\Omega, \hbar\Omega\beta=1$. Bottom left: $\xi=0.3, \omega_{\mathrm{c}}=5\Omega, \hbar\Omega\beta=10$. Bottom right: $\xi=0.1, \omega_{\mathrm{c}}=5\Omega, \hbar\Omega\beta=10$.

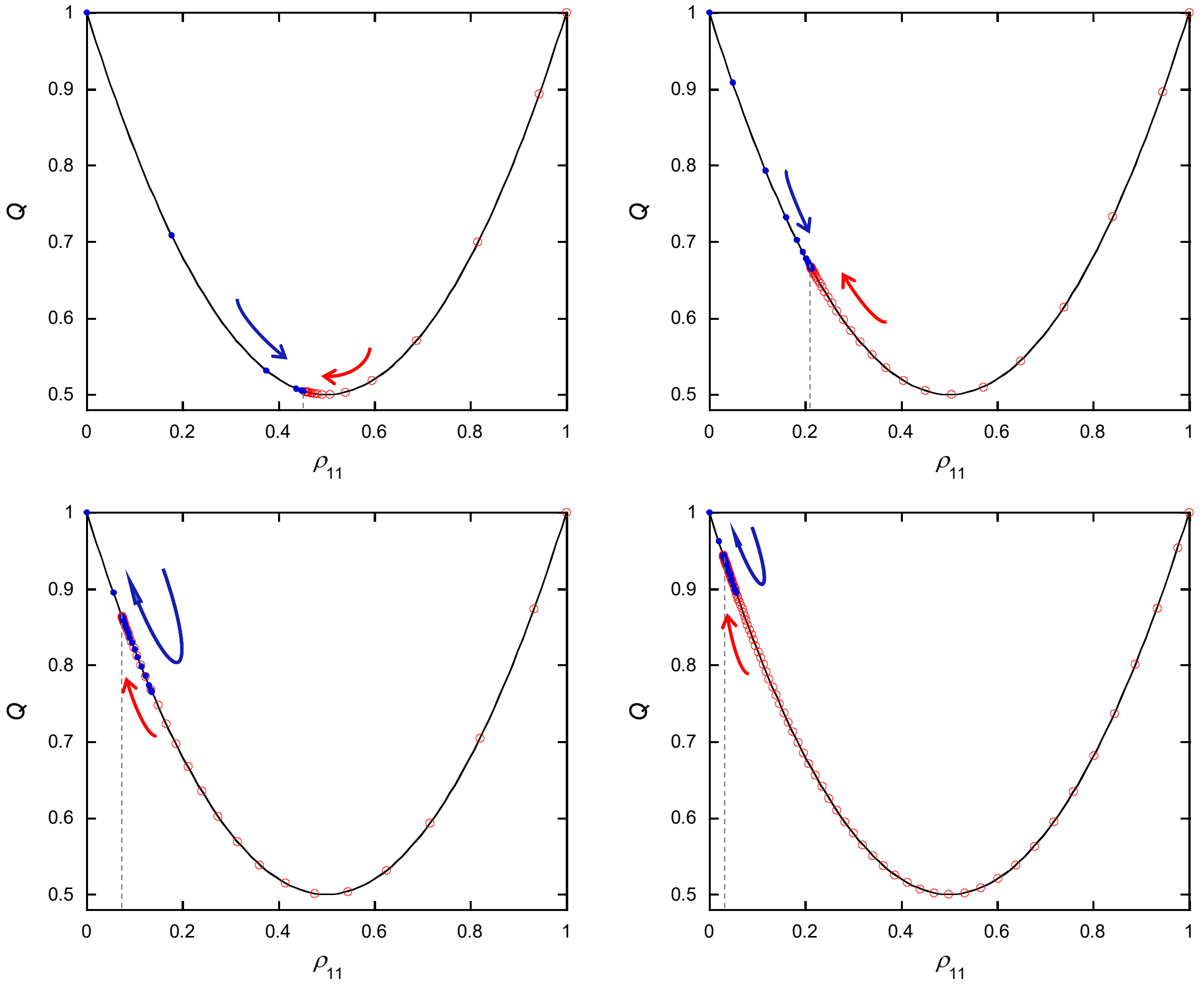

Fig 4. Population evolution and purity as a function of ρ_{11} for a TLS initially prepared in an eigenstate from path integral calculations. Large, hollow red markers: ρ_{11}^{11}. Small, solid blue markers: ρ_{11}^{00}. The dashed line indicates the equilibrium population value. The red and blue arrows show the direction of ρ_{11} flow for each initial condition. Top left: $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 0.1$. Top right: $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 1$. Bottom left $\xi = 0.3, \omega_c = 5\Omega, \hbar\Omega\beta = 10$. Bottom right: $\xi = 0.1, \omega_c = 5\Omega, \hbar\Omega\beta = 10$.

At low temperatures and under weakly dissipative conditions, the population difference $\tilde{\rho}_{00}^{11} - \tilde{\rho}_{11}^{11}$ approaches unity at long times. Thus, under low-temperature conditions, $\tilde{\rho}_{\mathrm{RL}}^{11}$ evolves toward the top of the color map, where $Q^{11} = 1$. As argued in the previous section, the evolution of $\left|\tilde{\rho}_{\mathrm{RL}}^{11}\right|$, and thus of Q, is non-monotonic as the population difference changes sign. At intermediate temperatures and dissipation strength, the off-diagonal element eventually stabilizes at a value $0 < \tilde{\rho}_{\mathrm{RL}}^{11}(\infty) < \frac{1}{2}$. We emphasize again that the imaginary part of the off-diagonal element remains equal to zero at all times.

Parameter set (ii) corresponds to an intermediate temperature and moderate dissipation strength. The RDM pair initially moves to the center of the color map where $Q = 0.5$, but subsequently recovers, settling at a higher value $\tilde{\rho}_{\mathrm{RL}}^{11}(\infty) \simeq 0.29$ for which $Q^{11}(\infty) \simeq 0.67$. With parameter sets (iii) and (iv), which are characterized by moderate and weak system-bath couplings respectively and a low temperature, the

RDM pair initially evolves to a fully mixed state with $Q^{11} = 0.5$, but the purity subsequently recovers to much higher values. In particular, with parameter set (iv), the RDM pair is seen to settle close to $Q^{11}(\infty) \simeq 0.95$. This implies the recovery of an almost pure state, which is the ground eigenstate (thus different from the RDM state at $t = 0$), as expected from the Boltzmann distribution at low temperatures.

Complementary information is obtained by plotting in Figure 4 the sequence of eigenstate population values $\tilde{\rho}_{11}^{11}$ and $\tilde{\rho}_{11}^{00}$ attained during the TLS dynamics following its initial preparation in the excited or ground state. The data from each parameter set is shown with markers positioned on the parabolic purity curve given by Eq. (2.13). With the excited state initial condition $\tilde{\rho}_{11}^{11}$ always starts at 1, and its decay is characteristic of the different regimes. In the high temperature, strongly dissipative regime (i), $\tilde{\rho}_{11}^{11}$ falls to around 0.5 and settles there, indicating a maximally mixed state has been reached. In set (ii), after reaching the fully mixed state with $\tilde{\rho}_{11}^{11} = 0.5$, $\tilde{\rho}_{11}^{11}$ falls further to about 0.2, accompanied by a rise in purity to ~0.67. In the low temperature sets (iii) and (iv), $\tilde{\rho}_{11}^{11}$ eventually falls to even lower and purity exhibits a very pronounced recovery. In the moderate dissipation case of parameter set (iii), the long-time value of the excited state population is $\tilde{\rho}_{11}^{11}(\infty) \simeq 0.07$ is 0.073 (with $Q^{11}(\infty) \simeq 0.86$), while in the weakly dissipative regime of set (iv) the RDM approaches an almost pure state with $\tilde{\rho}_{11}^{11}(\infty) = 0.028$ and $Q^{11}(\infty) \simeq 0.95$. With all parameters the population evolution is monotonic with the excited state initial condition, and the RDM points do not cross the line indicating the equilibrium point. On the other hand, when the TLS is initially in its ground state, the excited state population rises higher than its long-time limit under some conditions, crossing the line that indicates the equilibrium value in Fig. 4.

To further understand the nature of the decoherence processes that contribute to the observed revival of purity, we also show in Fig. 1 results obtained by including only the classical decoherence component,[11] which corresponds to the real part in the exponent of the influence functional. As expected, the omission of quantum memory is barely noticeable in the high-temperature regime. However, Fig. 1 shows that quantum memory leads to qualitative changes in the evolution of purity at intermediate and low temperatures, as its omission causes a monotonic decay of purity. In common TLS relaxation language, the classical component of decoherence corresponds to equal "up" and "down" rates, i.e. to the infinite temperature limit. Thus the effect of this mechanism is to produce equal TLS eigenstate populations and not allow further cooling. The physical origin of the classical decoherence process is the fluctuation of left/right levels in the site representation. On the other hand, quantum decoherence processes associated with the imaginary part in the exponent of the influence functional, which are associated with spontaneous phonon emission,[11] allow the "up" and "down" rates to attain their correct values. In the quantum-classical context, classical decoherence processes are captured within the "classical path" approximation, which can produce qualitatively correct results over short times but cannot account for correct long-time populations.[21] The rigorous quantum-classical limit of the path integral[22] (QCPI) corrects this deficiency by fully accounting for the "back-reaction" through trajectory state hops along all possible system state sequences. The phase cancellation that takes place ensure correct long-time populations which satisfy the detailed balance condition. The cooling that results from spontaneous phonon emission leads to the rebound of purity following the formation of a maximally mixed RDM. At sufficiently low temperatures such quantum mechanical energy exchange events are also important during the early decrease of purity, and are seen to accelerate the time for its decay.

IV. Bath-induced purification

The observed recovery of purity during TLS relaxation suggests that coupling to a bath purifies the fully mixed RDM that has been produced temporarily through the system-bath dynamics from the chosen initial condition. In the full density matrix that has been generated when $Q_{\min} = \frac{1}{2}$, the system is fully entangled with the bath. An natural question is whether a bath can purify a mixed RDM constructed at $t = 0$ with a simpler initial condition, e.g. a product RDM of the type given in Eq. (2.5).

To explore this possibility, we show in Figure 5 the RDM dynamics in the low-temperature, weakly dissipative conditions of purity for parameter set (iv) with an initial condition that corresponds to a maximally mixed state,

$$\hat{\tilde{\rho}}(0) = \tfrac{1}{2}|\mathrm{R}\rangle\langle\mathrm{R}| + \tfrac{1}{2}|\mathrm{L}\rangle\langle\mathrm{L}| = \tfrac{1}{2}|1\rangle\langle 1| + \tfrac{1}{2}|0\rangle\langle 0| = \tfrac{1}{2}\hat{I} \tag{4.1}$$

where $\hat{I}$ is the identity operator. The ground and excited state eigenstate populations grow and decrease, respectively, toward their equilibrium values. As a result, the purity increases monotonically, and does not exhibit an initial decrease. Thus, coupling to a low-temperature heat bath purifies the system, decreasing its entropy. While this outcome is hardly surprising, it shows clearly that the evolution of purity is not necessarily Gaussian, even at short times.

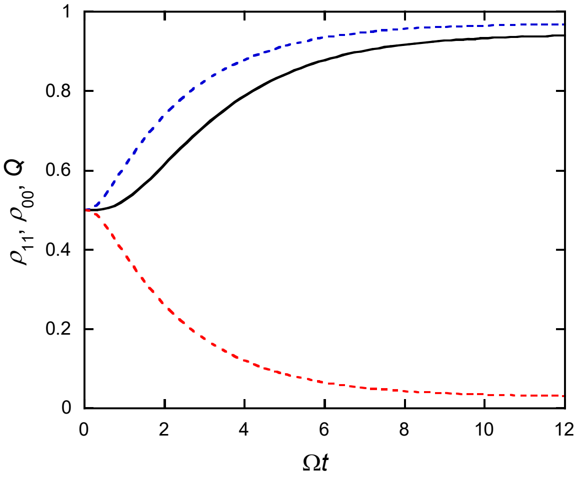

Fig 5. Populations and purity as a function of time for a TLS initially prepared in the maximally mixed state, with $\xi = 0.1, \omega_c = 5\Omega, \hbar\Omega\beta = 10$. Dashed red line (decaying): ρ_{11}. Dashed blue line (rising): ρ_{00}. Solid black line: purity.

The RDM given in Eq. (4.1) lies at the center of the purity color maps shown in Fig. 3. Since at any finite temperature the equilibrium RDM lies on the central line and higher up, it is clear that evolution will eventually increase the value of purity. The same conclusion can be drawn for an initial condition that corresponds to an RDM located inside the circle that passes through the RDM equilibrium value (see the bottom left panel of Fig. 3). Thus, if the initial RDM satisfies the condition

$$\left(\tilde{\rho}_{\mathrm{RR}}-\tfrac{1}{2}\right)^2+\left(\tilde{\rho}_{\mathrm{RL}}\right)^2<\left(\tilde{\rho}_{\mathrm{RL}}^{\mathrm{eq}}\right)^2, \tag{4.2}$$

where $\tilde{\rho}_{\mathrm{RL}}^{\mathrm{eq}}$ is the equilibrium value, the purity will *increase* during the evolution.

V. Concluding Remarks

In this paper we have investigated the time evolution of populations and purity in a dissipative TLS initially prepared in one of its eigenstates. Using simple arguments, we showed that the symmetry of the initial condition implies that the two RDM elements evolve on a one-dimensional subspace of the full two-dimensional region that can be visited by other initial conditions, and that the purity is a function of a single RDM element, which may be chosen as one of the eigenstate populations. These facts are in line with the known decoupling of the RDM equations in the eigenstate basis subject to eigenstate initial conditions. When the TLS is initially in its excited state, the eigenstate population difference changes sign on the way to equilibrium at a finite temperature, thus there is always a time at which the ground and excited states have equal populations, i.e. the RDM is maximally mixed. As the system evolves past that point toward equilibrium, the ground state population grows relative to that of the excited state and purity rises. This simple analysis was quantified by accurate numerical results based on real-time path integral calculations. These results showed clearly the drop of purity at some time to its minimum value $Q_{\min}=\tfrac{1}{2}$ and its subsequent recovery, which can be substantial and in some cases dramatic, with purity approaching unity in the low-temperature, weak dissipation regime.

The rebound of purity, which is associated with unequal eigenstate populations owing to cooling, is a consequence of quantum mechanical interactions with the bath that are captured in the imaginary part terms in the exponent of the influence functional. These terms are associated with spontaneous phonon emission and are responsible for the correct relation between the "up" and "down" rates, which allows the TLS populations to evolve to their proper thermodynamic values.

If the TLS is placed in its ground eigenstate, the purity decreases without falling to $Q_{\min}=\tfrac{1}{2}$ (except at infinite temperature), rising again at sufficiently low temperature and weak system-bath coupling. In that case the excited state population rises, even at zero temperature, because the TLS excited state has a nonzero component in the ground eigenstate of the full system-bath Hamiltonian. Interestingly, we find that the eigenstate populations exhibit nonmonotonic dynamics in the low-temperature regime, which lead to a nonmonotonic behavior of purity. Since population changes are small in this case though, the dip in the purity value and subsequent recovery are less dramatic.

Last, we investigated the dynamics resulting from a TLS initially described by a maximally mixed RDM. We found that coupling to a low-temperature can purify the system, increasing its purity to the thermodynamic value corresponding to the particular parameters. This situation represents an example of *upward* purity behavior at all times. It is clear that the evolution of purity is not necessarily Gaussian, or even decreasing, even at very short times. In fact, it is clear that any initial RDM that corresponds to a point inside the circle $(\tilde{\rho}_{\mathrm{RR}}-\tfrac{1}{2})^2+\tilde{\rho}_{\mathrm{RL}}{}^2<(\tilde{\rho}_{\mathrm{RL}}^{\mathrm{eq}})^2$ will have its purity increased through contact with the bath. The only reason for typically observing a decrease in purity is the choice of an initially pure RDM, which lies outside of this circle.

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Conflicts of Interest

There are no conflicts of interest to declare.

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