Survival of quantum features in the dynamics of a dissipative quantum system and their effect on the state purity

Davinder Singh

Korea Institute for Advanced Study, Seoul 02455, South Korea

(Received 7 January 2021; revised 29 March 2021; accepted 23 April 2021; published 19 May 2021)

Destruction of the quantum mechanical features of matter by decoherence restricts the applicability of quantum technologies. The limited information of the quantum features (such as coherence) in the basis-dependent observations urges the use of a basis-independent quantity for a better understanding. In this context, the state purity of a quantum system (composed of quantized pigments immersed in a noisy protein environment) is studied with a numerically exact hierarchical equations of motion approach over the wide range of the parameter domain (with the main focus on the nonzero-energy gradient). It is noted that the state purity does not necessarily reflect any significant information about the persistence of quantum features (in the dissipative environment), even when the quantum coherence survives at the steady state in both the localized and the eigenstate basis.

DOI: 10.1103/PhysRevE.103.052124

I. INTRODUCTION

Interference, or addition, of wavelike amplitudes with fixed phase differences is termed quantum coherence. Dephasing of coherence, i.e., decoherence, is ubiquitous in open quantum systems. Despite its central importance in many physical phenomena, detailed information about decoherence has remained elusive as the experimental techniques used to monitor decoherence are forced to observe physical observables that reflect off-diagonal elements of the density matrix expressed in a given basis, e.g., the spectroscopic experiments observe the persistence of coherence in the excitation transfer dynamics in the eigenstate basis [1,2]. To study the physical basis for such experimental observation, theoretical models emphasize basis-dependent analysis of coherence [3-17]. Moreover, line shapes or interference (other commonly used observables) can only illustrate basis-dependent information of decoherence [18–20]. Note that basis-dependent observations do not necessarily indicate the explicit loss of coherence in the open quantum system and thus limit our understanding of the role of decoherence.

Following this, it was argued that for a better estimate of the role of quantum features, a basis-independent quantity such as state purity needs to be considered instead of the elements of the density matrix [21]. The purity or idempotence of a system can be expressed as

$$\mathcal{P}(\tau) = \mathrm{Tr}\rho^2(\tau), \tag{1}$$

where ρ represents the system's reduced density matrix. The complete description of a quantum state (i.e., a pure state) corresponds to $\mathcal{P} = 1$, which results in minimizing the entropy of the system (i.e., $\mathcal{S} = 0$). The lack of information of the system (i.e., an incoherent mixture of two or more quantum states)

enhances the entropy, which leads to a decrease in the state purity (i.e., $\mathcal{P} < 1$). Note that ongoing efforts to understand the role of quantum features in an open quantum system [22–26] are currently limited by our inability to directly observe the purity of a quantum state. Therefore, quantitative analysis of state purity in an open quantum system is largely unexplored.

Most of the previous work studying the evolution of the state purity (in the quantum system coupled to a bath) focused mainly on approximate analytical treatments [21,26-30]. Recently, Chatterjee and Makri (with the use of the quasiadiabatic propagator path integral approach) studied a symmetric quantum two-level system and found the recovery of state purity in the dissipative tunneling dynamics in a weak system-bath coupling regime at low temperature [31]. Along with the recovery of state purity, it was concluded that for the symmetric two-level system, the complete quenching of quantum coherence in the eigenstate basis does not necessarily imply the fully mixed state in the weak system-bath coupling regime [31]. It cautioned the use of purity as a measure of decoherence in open quantum systems. On the other hand, for the asymmetric case, the coherence is generally not completely quenched in both the site basis and the eigenstate (or exciton) basis. However, the effect of energy gradient was not considered in the recovery of state purity in dissipative quantum systems. Moreover, the variation of other essential parameters such as the Coulomb coupling, bath relaxation time, or initial population distribution on the recovery of the state purity was not included. In this work, the evolution of the state purity in the quantum dissipative system is followed across a wide variety of parameter regimes.

II. THEORETICAL MODEL

To proceed, a donor-acceptor pair is considered to be coupled with the bath. Both the master equation approach and the

2470-0045/2021/103(5)/052124(10)

hierarchical equations of motion (HEOM) approach [32–35] are employed to study the energy transfer dynamics.

A. Master equation approach

First, the perturbative approach, i.e., a Markovian master equation, is discussed in detail. For the donor-acceptor pair, in the singly excited subspace, the effective Hamiltonian for the spin-boson system consisting of two bases $|e_Dg_A\rangle$ and $|g_De_A\rangle$ is conveniently written as

$$H_{\text{eff}} = \hat{H}_{S} + \hat{H}_{B} + \hat{H}_{SB}$$
$$= \left(\frac{\epsilon}{2}\hat{\sigma}_{z} + \Delta\hat{\sigma}_{x}\right) + \sum_{k}\omega_{k}b_{k}^{\dagger}b_{k} + \frac{\hat{\sigma}_{z}}{2}\sum_{k}g_{k}(b_{k}^{\dagger} + b_{k}).$$
(2)

The first term \hat{H}_S represents the system Hamiltonian delineating the effect of energy mismatch ϵ (= $\epsilon_D - \epsilon_A$) between donor and acceptor pigments and the coupling between the two characterized by the tunneling frequency Δ . For simplicity, $|e_Dg_A\rangle$ and $|g_De_A\rangle$ denote, respectively, the donor ($|D\rangle$) and acceptor ($|A\rangle$) states being excited. Here $\hat{\sigma}_z = |e_Dg_A\rangle \langle e_Dg_A| - |g_De_A\rangle \langle g_De_A|$ and $\hat{\sigma}_x =$ $|e_Dg_A\rangle \langle g_De_A| + |g_De_A\rangle \langle e_Dg_A|$ are the corresponding Pauli spin operators in the two-site single-excitation basis. The second term \hat{H}_B denotes the bath Hamiltonian. The annihilation and creation operators of the *k*th bosonic mode, b_k and b_k^{\dagger} , respectively, satisfy the bosonic commutation relations $[b_k, b_l^{\dagger}] = \delta_{kl}$. In the last term, the bath modes are coupled to the pigments with strength g_k .

Under the Hamiltonian H_{eff} , the density matrix $\hat{\rho}(t)$ evolves with time obeying the von Neumann equation $d\hat{\rho}(t)/dt = -i[\hat{H}_{\text{eff}}, \hat{\rho}(t)]$. The Markovian approximation assumes that the dynamics of the bath modes quickly relaxes to its equilibrium and is decoupled from the system's degree of freedom such that $\hat{\rho}(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_B^{eq}$, which allows us to write the following Markovian master equation for the reduced density matrix of the system $\hat{\rho}_S(t) = \begin{bmatrix} \rho_D(t) & \rho_{DA}(t) \\ \rho_{AD}(t) & \rho_{A}(t) \end{bmatrix}$:

$$\frac{d\hat{\rho}_{S}(t)}{dt} = -i[\hat{H}_{S}, \hat{\rho}_{S}(t)] - \int_{0}^{t} d\tau \operatorname{Tr}_{B}\left\{ \left[\hat{H}_{SB}(0), \left[\hat{H}_{SB}(-\tau), \hat{\rho}_{S}(t) \otimes \hat{\rho}_{B}^{eq}\right]\right] \right\}.$$
(3)

The diagonal elements $\rho_D(t)$ and $\rho_A(t)$ correspond to the populations of acceptors and donors being in their excited state; the off-diagonal elements (i.e., ρ_{DA} or ρ_{AD}) arise from the quantum coherence between the donor and acceptor molecules.

The above master equation can be written more explicitly

$$\frac{d\hat{\rho}_{S}(t)}{dt} = -i\left(\frac{\epsilon}{2}\right) [\hat{\sigma}_{z}\hat{\rho}_{S}(t) - \hat{\rho}_{S}(t)\hat{\sigma}_{z}] - i\Delta[\hat{\sigma}_{x}\hat{\rho}_{S}(t) - \hat{\rho}_{S}(t)\hat{\sigma}_{x}]
- 4\int_{0}^{\infty} d\tau (\alpha^{R}(\tau)[\hat{\sigma}_{z}, [\hat{\sigma}_{z}(-\tau), \hat{\rho}_{S}(t)]] + i\alpha^{I}(\tau)[\hat{\sigma}_{z}, \{\hat{\sigma}_{z}(-\tau), \hat{\rho}_{S}(t)\}]).$$
(4)

Here the irreversibility of the quantum processes is treated in terms of the bath correlation function (BCF) $\alpha(t)$. In the last term $\alpha^R(t)$ and $\alpha^I(t)$ are the real and imaginary parts of the BCF, respectively, responsible for the dephasing and dissipation. Their explicit expressions are given by assuming the Lorentz-Drude form of the spectral density $J(\omega) = \frac{2\lambda}{\pi} \frac{\gamma \omega}{\gamma^2 + \omega^2}$, where $\lambda = \int_0^\infty \frac{J(\omega)}{\omega} d\omega$ is the reorganization energy and γ involves the peak position and the width of the spectral density, determining the timescale of dephasing and dissipation to the phonon bath,

$$\alpha^{R}(t) = \lambda \gamma \left[\cot\left(\frac{\beta\gamma}{2}\right) e^{-\gamma t} + \frac{4}{\beta\gamma} \sum_{q=1}^{\infty} \frac{\frac{\nu_{q}}{\gamma}}{\left(\frac{\nu_{q}}{\gamma}\right)^{2} - 1} e^{-\nu_{q}t} \right],$$
(5)

where $\nu_q = \frac{2\pi q}{\beta}$ corresponds to the bosonic Matsubara frequency

$$\alpha^{I}(t) = -\lambda \gamma e^{-\gamma t}.$$
 (6)

Pertaining to the weak system-bath coupling, a small value of the reorganization energy (i.e., $\lambda = 15 \text{ cm}^{-1}$) is used (unless

specified). Moreover, the bath relaxation rate is chosen to be $\gamma = 100 \text{ cm}^{-1}$ and the donor site is assumed to be initially excited [i.e., $\rho_D(0) = 1$] in this study (unless specified otherwise).

Further, the time dependence of the Pauli matrix $\hat{\sigma}_z$ can be written in the interaction picture as

$$\hat{\sigma}_z(t) = e^{i\hat{H}_S t} \hat{\sigma}_z e^{-i\hat{H}_S t},\tag{7}$$

and the Baker-Campbell-Hausdorff formula with $\hat{H}_S = (\epsilon/2)\hat{\sigma}_z + \Delta\hat{\sigma}_x$ allows us to rewrite $\hat{\sigma}_z(t)$ in the form

$$\hat{\sigma}_z(t) = c_x(t)\hat{\sigma}_x + c_y(t)\hat{\sigma}_y + c_z(t)\hat{\sigma}_z, \qquad (8)$$

with $\Omega = \sqrt{\epsilon^2 + 4\Delta^2}$ and

$$c_x(t) = \frac{2\epsilon\Delta}{\Omega^2} (1 - \cos\Omega t),$$

$$c_y(t) = \frac{2\Delta}{\Omega} \sin\Omega t,$$

$$c_z(t) = 1 - \frac{4\Delta^2}{\Omega^2} (1 - \cos\Omega t).$$
 (9)

The parameters associated with the dephasing (κ_1 , κ_2 , and κ_3) and dissipation (μ_1 and μ_2) are calculated as

$$\kappa_{1} = \int_{0}^{\infty} dt c_{x}(-t) \alpha^{R}(t) = \left(\frac{2\Delta}{\gamma}\right) \left(\frac{\epsilon}{\gamma}\right) \left[\frac{\lambda}{1+\left(\frac{\Omega}{\gamma}\right)^{2}}\right] S_{2}(\Omega,\gamma),$$

$$\kappa_{2} = \int_{0}^{\infty} dt c_{y}(-t) \alpha^{R}(t) = -\left(\frac{2\Delta}{\gamma}\right) \left[\frac{\lambda}{1+\left(\frac{\Omega}{\gamma}\right)^{2}}\right] S_{1}(\Omega,\gamma),$$

$$\kappa_{3} = \int_{0}^{\infty} dt c_{z}(-t) \alpha^{R}(t) = \left[\frac{\lambda}{1+\left(\frac{\Omega}{\gamma}\right)^{2}}\right] \left[S_{0}(\Omega,\gamma) + \left(\frac{\epsilon}{\gamma}\right)^{2} S_{2}(\Omega,\gamma)\right],$$

$$\mu_{1} = \int_{0}^{\infty} dt c_{x}(-t) \alpha^{I}(t) = -\left(\frac{2\Delta}{\gamma}\right) \left(\frac{\epsilon}{\gamma}\right) \left[\frac{\lambda}{1+\left(\frac{\Omega}{\gamma}\right)^{2}}\right],$$

$$\mu_{2} = \int_{0}^{\infty} dt c_{y}(-t) \alpha^{I}(t) = \left(\frac{2\Delta}{\gamma}\right) \left[\frac{\lambda}{1+\left(\frac{\Omega}{\gamma}\right)^{2}}\right],$$
(10)

where

 $S_n(\Omega, \gamma) \equiv \cot\left(\frac{\beta\gamma}{2}\right) + \frac{4}{\beta\gamma} \sum_{q=1}^{\infty} \left(\frac{\gamma}{\nu_q}\right)^n W_q(\Omega, \gamma),$

with

$$W_q(\Omega, \gamma) \equiv \frac{1 + \left(\frac{\Omega}{\gamma}\right)^2}{\left[\left(\frac{\nu_q}{\gamma}\right)^2 - 1\right] \left[1 + \left(\frac{\Omega}{\nu_q}\right)^2\right]}.$$

For the terms involving the summation over q, a finite number of terms ($q = 1, 2, ..., q_{max}$) suffices to obtain a convergent value of the BCF.

The elements of the density matrix satisfy the set of equations at the steady state

$$\hat{\rho}_{S}^{ss} = \begin{bmatrix} \frac{1}{2} (1 - \delta \rho^{ss}) & \frac{2\kappa_{1}\mu_{1} - \mu_{2}(\Delta - 2\kappa_{2})}{2\kappa_{3}(\Delta - 2\kappa_{2}) - \kappa_{1}\epsilon} \\ \frac{2\kappa_{1}\mu_{1} - \mu_{2}(\Delta - 2\kappa_{2})}{2\kappa_{3}(\Delta - 2\kappa_{2}) - \kappa_{1}\epsilon} & \frac{1}{2} (1 + \delta \rho^{ss}) \end{bmatrix},$$
(11)

where $\delta \rho^{ss} \equiv \rho_A^{ss} - \rho_D^{ss} = \frac{\mu_2 \epsilon - 4\kappa_3 \mu_1}{2\kappa_3 (\Delta - 2\kappa_2) - \kappa_1 \epsilon}$. Interestingly, the real part of coherence survives even at the steady state in the site basis. Now for the symmetric case with $\epsilon = 0$, and hence $\kappa_1 = \mu_1 = 0$, $\rho_D^{ss} = \rho_A^{ss} = 0.5$. Even in this case the coherence in the site basis is nonzero, i.e., $\rho_{DA} = \rho_{AD} = -\frac{\mu_2}{2\kappa_3}$.

Next, in the donor-acceptor pair, the corresponding eigenstates (with the energy eigenvalues $E_{+} = \frac{\Omega}{2}$ and $E_{-} = -\frac{\Omega}{2}$) can be expressed as

$$|\Phi_{+}\rangle = \frac{\sqrt{2}\Delta}{\sqrt{\Omega(\Omega+\epsilon)}} \left(\frac{\epsilon+\Omega}{2\Delta} |D\rangle + |A\rangle\right), \quad |\Phi_{-}\rangle = \frac{\sqrt{2}\Delta}{\sqrt{\Omega(\Omega-\epsilon)}} \left(\frac{\epsilon-\Omega}{2\Delta} |D\rangle + |A\rangle\right)$$
(12)

and the coherence in the exciton basis can be written as

$$\rho_{+-} = |\Phi_+\rangle \langle \Phi_-| = \frac{2\epsilon(\kappa_1\mu_1 + \kappa_2\mu_2) - 4\Delta\kappa_3\mu_1}{\Omega[2\kappa_3(\Delta - 2\kappa_2) - \epsilon\kappa_1]}.$$
(13)

It is evident that in the exciton basis at the steady state coherence will be zero only for the symmetric case (i.e., when $\epsilon = 0$ and hence $\kappa_1 = \mu_1 = 0$). For the asymmetric case (i.e., when $\epsilon \neq 0$), the coherence cannot be completely quenched.

B. Hierarchical equations of motion approach

The perturbative approach, i.e., the master equation, indicates the persistence of the quantum coherence in both the site and the eigenstate basis. Along with this approximate approach, a numerically exact method such as the HEOM approach can also be implemented for a better understanding and further verification of the existence of steady-state coherence in both bases. In the HEOM approach, with the use of the path integral formalism, the dynamics is studied using the set of auxiliary density operators (ADOs), i.e., $\rho_{\mathbf{a}}(\tau)$ [where the index of the ADOs can be written as $\mathbf{a} = (a_{10}, \dots, a_{1K}, \dots, a_{NO}, \dots, a_{NK})$ with $a_{nk} > 0$], as

[33,34,36,37]

$$\dot{\rho}_{\mathbf{a}}(\tau) = -i \left[\sum_{n=1}^{N} \epsilon_{n} |n\rangle \langle n| + \sum_{m < n} \Delta_{nm}(|n\rangle \langle m| + |m\rangle \langle n|), \rho_{\mathbf{a}}(\tau) \right] - \sum_{n,k} a_{nk} \gamma_{nk} \rho_{\mathbf{a}}(\tau) + i \sum_{n,k} \{ [|n\rangle \langle n|, \rho_{\mathbf{a}_{nk+}}(\tau)] + a_{nk} p_{nk} |n\rangle \langle n| \rho_{\mathbf{a}_{nk-}}(\tau) + a_{nk} p_{nk}^{*} \rho_{\mathbf{a}_{nk-}}(\tau) |n\rangle \langle n| \},$$
(14)

where $\rho_{\mathbf{a}_{nk\pm}}$ describe that each ADO is coupled to operators in the level above or below in the hierarchy such that $\mathbf{a}_{nk\pm} = (a_{10}, \ldots, a_{nk}\pm, \ldots, a_{NK})$ [34]. A hierarchy level is assigned to the each reduced density matrix described in detail by Strümpfer and Schulten [34]. Further, p_{nk} and γ_{nk} are defined in the Padé decomposition [38].

Further, for a detailed analysis of the influence of the persistence of coherence (in the asymmetric case) on the state purity, Eq. (1) can be expressed in terms of the system's reduced density matrix elements as

$$\mathcal{P}(\tau) = \underbrace{\rho_{D}^{2}(\tau) + \rho_{A}^{2}(\tau)}_{=\mathcal{P}_{1}(\tau)} + \underbrace{2\left[\rho_{DA}^{R}(\tau)\right]^{2}}_{=\mathcal{P}_{2}(\tau)} + \underbrace{2\left[\rho_{DA}^{I}(\tau)\right]^{2}}_{=\mathcal{P}_{3}(\tau)} \\ = \underbrace{\rho_{+}^{2}(\tau) + \rho_{-}^{2}(\tau)}_{=\mathcal{P}_{1}^{\text{eig}}(\tau)} + \underbrace{2\left[\rho_{+-}^{R}(\tau)\right]^{2}}_{=\mathcal{P}_{2}^{\text{eig}}(\tau)} + \underbrace{2\left[\rho_{+-}^{I}(\tau)\right]^{2}}_{=\mathcal{P}_{3}^{\text{eig}}(\tau)}, \quad (15)$$

where ρ_+ (ρ_-) represents the eigenstate population, corresponding to the eigenvalue E_+ (E_-), and ρ_{+-}^R (ρ_{+-}^I) is the real (imaginary) part of coherence between the eigenstates.

III. RESULTS AND DISCUSSION

A. Effect of steady-state coherence on state purity

With the use of the HEOM approach, dynamical simulations also verify the persistence of coherence in the eigenstate basis [see Fig. 1(a)]. However, the state purity (in the longtime domain) seems to be dependent mainly on the eigenstate population (without any significant contribution from the eigenstate coherence), as illustrated by Fig. 1(b). Evidently, after ~1 ps the state purity components \mathcal{P}_2^{eig} and \mathcal{P}_3^{eig} (which depend on eigenstate coherence [see Eq. (15)]) contribute negligibly to the \mathcal{P} . Therefore, the dynamics of the state purity is mainly governed by the eigenstate population as the system evolves towards equilibrium (even in the presence of



FIG. 1. Dynamics of the (a) eigenstate coherence and (b) purity i.e., \mathcal{P} (along with its components $\mathcal{P}_1^{\text{eig}}$, $\mathcal{P}_2^{\text{eig}}$, and $\mathcal{P}_3^{\text{eig}}$) for a donoracceptor pair with $\epsilon = 400 \text{ cm}^{-1}$ and $\Delta = 300 \text{ cm}^{-1}$ at cryogenic temperature 25 K. The reorganization energy used here is 35 cm⁻¹.

eigenstate coherence). This implies that, irrespective of the energy gradient ϵ , the state purity cannot be used as a measure of quantum features.

B. Comparative analysis of the results of the HEOM approach and the master equation

Next the comparative analysis of the predictions of the master equation approach and the HEOM approach is studied. As expected, in the weak system-bath coupling (when $\lambda = 10 \text{ cm}^{-1}$), both approaches, i.e., the HEOM approach and master equation approach, predict almost the same donor population at the steady state [see Fig. 2(a)]. With an increase in the system-bath coupling, the predictions of the master equation approach deviate from the numerically exact HEOM approach, as illustrated in Figs. 2(b)-2(d). For instance, in the strong system-bath coupling (i.e., when $\lambda = 200 \text{ cm}^{-1}$), the steady-state donor population predicted by the master equation approach is significantly different from the results of the HEOM approach. Note that the inclusion of non-Markovian effects in the HEOM approach results in long oscillatory timescales compared to the Markovian master equation used in this work, which leads to the different transient behavior



FIG. 2. Comparative analysis of the time evolution of the donor population by varying the re-organization energies such that (a) $\lambda =$ 10 cm⁻¹, (b) $\lambda = 50$ cm⁻¹, (c) $\lambda = 100$ cm⁻¹, and (d) $\lambda = 200$ cm⁻¹ [at room temperature 300 K ($k_BT = 208.5$ cm⁻¹)] with the HEOM approach and master equation approach. The energy gradient used in this case is $\epsilon = 100$ cm⁻¹ with Coulomb coupling $\Delta = 100$ cm⁻¹ and bath relaxation rate $\gamma = 2000$ cm⁻¹. In the HEOM approach four hierarchy levels were used with three bath exponential terms. A time step of 0.5 fs was used in both approaches.



FIG. 3. (a) Equilibrium values of the state purity by varying Coulomb coupling Δ and temperature T with $\epsilon = 0$ cm⁻¹. The time evolution of the purity is illustrated for the different pairs of Δ and T, i.e., (i) $\Delta = 300$ cm⁻¹ and T = 100 K ($k_BT = 69.5$ cm⁻¹), (ii) $\Delta = 300$ cm⁻¹ and T = 300 K ($k_BT = 208.5$ cm⁻¹), (iii) $\Delta = 50$ cm⁻¹ and T = 100 K ($k_BT = 69.5$ cm⁻¹), and (iv) $\Delta = 50$ cm⁻¹ and T = 300 K ($k_BT = 208.5$ cm⁻¹). Also shown are the steady-state values of (b) \mathcal{P}_1 , \mathcal{P}_2 , and \mathcal{P}_3 and (c) system entropy (i.e., \mathcal{S}). The value of the reorganization energy used in this case is 15 cm⁻¹ with a bath relaxation rate of $\gamma = 100$ cm⁻¹.

of both approaches in the whole parameter domain of systembath coupling.

C. Recovery of the state purity

In this section, the recovery of state purity will be evaluated in a wide range of parameters using the HEOM approach.

1. Symmetric case

First, the symmetric case (i.e., $\epsilon = 0 \text{ cm}^{-1}$) is considered to determine the state purity in the donor-acceptor pair. The quantum simulations reveal that at the steady state, low intersite coupling leads to the maximally mixed state (i.e., lowest state purity) such that when $\Delta = 5 \text{ cm}^{-1}$ the steady-state value of the state purity is ~0.5 [see Fig. 3(a)]. Moreover, the enhancement in the thermal fluctuations results in the decrease in state purity at equilibrium. For instance, when $\Delta =$ 50 cm^{-1} , the steady-state value of \mathcal{P} is higher at low temperature 100 K ($k_BT = 69.5 \text{ cm}^{-1}$) i.e., $\mathcal{P} \approx 0.67$ compared to the room temperature 300 K ($k_B T = 208.5 \text{ cm}^{-1}$), where $\mathcal{P} \approx$ 0.53. Evidently, an almost pure state ($\mathcal{P} \approx 1$) can be achieved at equilibrium with increases in the Coulomb coupling Δ , e.g., state purity varies from ~ 0.5 to ~ 0.99 as Δ increases at a cryogenic temperature of 100 K [see Fig. 3(a)]. It is evident from Fig. 3(b) that the enhancement of the contribution of \mathcal{P}_2 in the state purity at equilibrium with Coulomb coupling leads to the achievement of an approximately pure state. Further, the variation in the contribution of \mathcal{P}_2 in the state purity with the temperature governs the effect of thermal fluctuations on the state purity at equilibrium. Although \mathcal{P}_2 varies with the Coulomb coupling and temperature, the variation of \mathcal{P}_1 and \mathcal{P}_3 ceases to exist [see Fig. 3(b)]. The steady-state entropy [i.e., $S = -k_B \text{Tr}(\rho \log \rho)$] is also investigated for the different values of Coulomb coupling and temperature [see Fig. 3(c)]. As is obvious, the comparative analysis of Figs. 3(a) and 3(c)shows that high entropy corresponds to low state purity and vice versa.



FIG. 4. Shown on top is the schematic illustration of the eigenstates on energy scale and on the bottom is the time evolution of the purity with (a) $\epsilon = 100 \text{ cm}^{-1}$ and $\Delta = 100 \text{ cm}^{-1}$ and (b) $\epsilon =$ 400 cm^{-1} and $\Delta = 300 \text{ cm}^{-1}$ at room temperature 277 K ($k_BT =$ 192.5 cm^{-1}). The value of the reorganization energy used in this case is 15 cm⁻¹ with a bath relaxation rate of $\gamma = 100 \text{ cm}^{-1}$.

The dynamical simulations of the purity show that with strong Coulomb coupling, the state purity decreases initially. Subsequently, the initial drop is followed by a rebound as the system evolves towards equilibrium. Therefore, a partially mixed state is obtained at the steady state, as illustrated Figs. 3(a i) and 3(a ii). When the Coulomb coupling is weak and temperature is high (e.g., when $\Delta = 50 \text{ cm}^{-1}$ and T =300 K), the recovery of the purity is negligible, as shown by Fig. 3(a iv). However, at the same value of the Coulomb coupling, the substantial recovery of purity is observed with a decrease in temperature [see Fig. 3(a iii)]. As the system evolves in time, the addition of \mathcal{P}_1 and \mathcal{P}_3 , i.e., \mathcal{P}_{13} $(=\mathcal{P}_1 + \mathcal{P}_3)$, always tends to move towards 0.5 irrespective of Coulomb coupling or temperature while the contribution of \mathcal{P}_2 in the state purity increases [substantially in the domain of strong Coulomb coupling and low temperature (see Fig. 7 in Appendix A)], and hence the purity recovers before plateauing.

2. Asymmetric case

Next the asymmetric case (i.e., $\epsilon \neq 0$) is considered to study the state mixedness at both room temperature (i.e., T =277 K) and cryogenic temperature (i.e., T = 125 K). From Figs. 5(a) and 5(c) it is clear that the equilibrium state purity increases with both the Coulomb coupling Δ and energy gradient ϵ . For example, when $\epsilon = 100 \text{ cm}^{-1}$ and $\Delta = 100 \text{ cm}^{-1}$ the state purity is ~ 0.63 , which rises gradually to ~ 0.95 with enhancement of both the energy gradient and Coulomb coupling, i.e., for $\epsilon = 400 \text{ cm}^{-1}$ and $\Delta = 300 \text{ cm}^{-1}$. With an increase in the energy gradient (i.e., ϵ) and hopping parameter (i.e., Δ), the energetic separation of eigenvalues (i.e., $E = \Omega = \sqrt{\epsilon^2 + 4\Delta^2}$ increases. For instance, as the energetic separation increases from 223.6 cm⁻¹ [corresponding to $\epsilon = 100 \text{ cm}^{-1}$ and $\Delta = 100 \text{ cm}^{-1}$; see the top panel of Fig. 4(a)] to 721.1 cm⁻¹ [corresponding to $\epsilon = 400$ cm⁻¹ and $\Delta = 300 \text{ cm}^{-1}$; see the top panel of Fig. 4(b)] at room tem-

perature 277 K ($k_BT = 192.5 \text{ cm}^{-1}$), the dip in purity revival increases. In other words, the state purity (at the steady state) increases with the energetic separation E when the energy of the thermal phonons is considered to be fixed. In the earlier case, the energetic separation E and the energy of thermal phonons (i.e., k_BT) are of the same order [see Fig. 4(a)], and hence a comparatively strong effect from the thermal bath on the system's evolution results in the significant loss of information about the quantum state; therefore a mixed state is observed. On the other hand, in the latter case, the energetic separation E is higher compared to the energy of thermal phonons (i.e., k_BT), as shown in Fig. 4(b). In this case, the loose coupling of bath phonons to the system leads to a comparatively low loss of information about the quantum state of the system and an almost pure state is observed. As expected, this implies that in the dissipative dynamics, if the energetic separation of the eigenstates is of the same order as the thermal phonons, the bath-induced coherences are important and one will have a mixed state; if they are negligible, the state will be close to a pure one. Again, it is evident that as the system evolves towards equilibrium, the eigenstate population (illustrated by \mathcal{P}_1^{eig}) contributes significantly, while there is a negligible contribution from the eigenstate coherence (i.e., $\mathcal{P}_2^{\operatorname{eig}}$ or $\mathcal{P}_3^{\operatorname{eig}}$).

In the local basis, at the steady state, the contribution of \mathcal{P}_1 in the purity increases with the energy gradient and decreases with an increase in the Coulomb coupling [see Figs. 5(b) and 5(d)]. The excitation trapping probability at acceptor pigment varies with both ϵ and Δ but inversely, such that the increase in ϵ enhances the trapping probability while an increase in Δ results in enhancement of back transfer, which reduces the trapping probability. The steady-state value of \mathcal{P}_1 , and hence the state purity, increases with the excitation trapping probability. Moreover, the contribution of \mathcal{P}_2 in state purity increases with the Coulomb coupling and decreases with an increase in energy gradient, as illustrated by Figs. 5(b) and 5(d). This implies that the maxima of \mathcal{P}_2 correspond to the minima of \mathcal{P}_1 and vice versa. Contrary to the symmetric case, both \mathcal{P}_1 and \mathcal{P}_2 contribute substantially to the state purity at equilibrium. Therefore, the destruction of quantum features in the donor-acceptor pair with a nonzero-energy gradient is significantly reduced compared to the symmetric case. Similar to the symmetric case, at equilibrium, the contribution of \mathcal{P}_3 in the state purity is negligible in the whole parameter domain used in this work.

Note that, in the asymmetric case, the recovery of purity is more evident compared to the symmetric case [see Fig. 5(a)]. For instance, when $\Delta = 300 \text{ cm}^{-1}$, the purity initially falls to a minimum value, i.e., $\mathcal{P}_{\min} \simeq 0.5$, and then rises to ~0.95 during the dynamics with $\epsilon = 400 \text{ cm}^{-1}$ [see Fig. 5(a ii)], while for the symmetric case (i.e., $\epsilon = 0 \text{ cm}^{-1}$), the purity drop is less such that $\mathcal{P}_{\min} \simeq 0.79$ before a maximum rise to $\mathcal{P}_{\max} = 0.91$ [see Fig. 5(a i)]. It is observed that the dip in the state purity increases with both the energy gradient and Coulomb coupling as demonstrated in Fig. 5(a). Surprisingly, with the increase in the energy gradient, the purity recovers after achieving the maximally mixed state [see Figs. 5(a ii)] and 5(a iv)]. In contrast, with the low-energy gradient, the maximally mixed state is not attained by the system; however,



FIG. 5. (a) Steady-state values of the state purity by varying the energy gradient ϵ and Coulomb coupling Δ at room temperature T = 277 K. The time evolution of the purity is illustrated for different pairs of ϵ and Δ , i.e., (i) $\epsilon = 100$ cm⁻¹ (subset $\epsilon = 0$ cm⁻¹) and $\Delta = 300$ cm⁻¹, (ii) $\epsilon = 400$ cm⁻¹ and $\Delta = 300$ cm⁻¹, (iii) $\epsilon = 100$ cm⁻¹ and $\Delta = 100$ cm⁻¹, and (iv) $\epsilon = 400$ cm⁻¹ and $\Delta = 300$ cm⁻¹. Also shown are the steady-state values of (b) \mathcal{P}_1 , \mathcal{P}_2 , and \mathcal{P}_3 at 277 K, (c) the purity at cryogenic temperature T = 125 K, and (d) \mathcal{P}_1 , \mathcal{P}_2 , and \mathcal{P}_3 at 125 K. The value of the reorganization energy used in this case is 15 cm⁻¹ with a bath relaxation rate of $\gamma = 100$ cm⁻¹.

the recovery of the purity is observed, as shown in Figs. 5(a i) and 5(a iii). Enhancement in the initial drop of state purity with ϵ results in the enhancement of the dip in the purity with energy gradient. With the high-energy gradient, as the system evolves in time, \mathcal{P}_{13} and \mathcal{P}_2 attain their minima at the same moment, which results in the minima of state purity during the evolution of the system (see Fig. 8 in Appendix A). Such a condition is avoided with the low-energy gradient, and hence the maximally mixed state is not achieved during the evolution of the system. On the other hand, although the initial drop in purity decreases with Coulomb coupling, the substantial enhancement of the maxima of state purity (i.e., \mathcal{P}_{max}) with Δ leads to the increase in the dip in state purity with Coulomb coupling.

3. Effect of bath relaxation rate

The dip in the purity also varies with the bath relaxation rate γ , a measure of the degree of non-Markovianity in the dynamics, such that relaxation of the bath slower than the effective evolution of the system corresponds to the strong memory effects in the dynamics and vice versa (see Fig. 9 in Appendix A). Remarkably, the dip in purity decreases with the degree of non-Markovianity, as shown in Fig. 6. The \mathcal{P}_2 increases quickly with γ (i.e., with the decrease in the degree of non-Markovianity); therefore, the decrease in the state purity due to \mathcal{P}_{13} is compensated quickly, which leads to the reduction in the dip of the state purity \mathcal{P} . Besides the bath relaxation rate, the initial population distribution also affects the dip in the state purity (see Fig. 10 in Appendix A).

In the aforementioned work, a simple case, i.e., a donoracceptor pair, was discussed in detail. In reality, a complex network of pigments participates in the energy transfer process, which leads to the different pathways of energy transfer. The effect of the quantum interference between the different pathways of energy transfer should be considered for a realistic study of the recovery of the state purity. To include such effects, the dynamics of the state purity is studied for a trimer system (i.e., an acceptor is coupled to a pair of donor pigments) and recovery of the state purity is observed for both the symmetric and asymmetric cases (see Fig. 11 in Appendix B). This implies that in the weak dissipative conditions, the recovery of the state purity can be observed in any complex network of pigments weakly coupled to the protein molecules.



 $\operatorname{Time}\left(\mathrm{ps}\right) \qquad \text{(c)} \quad 1^{-1}$



FIG. 7. Time evolution of the state purity \mathcal{P} and its components $\mathcal{P}_1, \mathcal{P}_2$, and \mathcal{P}_3 for different pairs of Δ and T, i.e., (a) $\Delta = 300 \text{ cm}^{-1}$ and T = 100 K ($k_BT = 69.5 \text{ cm}^{-1}$), (b) $\Delta = 300 \text{ cm}^{-1}$ and T = 300 K ($k_BT = 208.5 \text{ cm}^{-1}$), (c) $\Delta = 50 \text{ cm}^{-1}$ and T = 100 K ($k_BT = 69.5 \text{ cm}^{-1}$), and (d) $\Delta = 50 \text{ cm}^{-1}$ and T = 300 K ($k_BT = 208.5 \text{ cm}^{-1}$). Here six hierarchy levels with four bath exponential terms were used with time steps of 0.5 fs for convergence.

APPENDIX A: DIMER SYSTEM

1. Symmetric case

The evaluation of the dynamics of the state purity \mathcal{P} and its components \mathcal{P}_1 , \mathcal{P}_2 , and \mathcal{P}_3 illustrates the persistence of transient oscillations in the evolution of \mathcal{P}_1 and \mathcal{P}_3 (see Fig. 7). Further, it is observed that the frequency and amplitude of the oscillations increase with the Coulomb coupling, with an adverse effect of the thermal fluctuations on the timescale of oscillations. It is evident from Fig. 7 that the amplitude discrepancy of the transient oscillations of \mathcal{P}_1 and \mathcal{P}_3 results in the oscillations leads to the destructive interference of \mathcal{P}_1 and \mathcal{P}_3 , which reduces the state purity. In contrast, the nonoscillatory contribution of \mathcal{P}_2 increases gradually during the later stages of the destructive contribution of \mathcal{P}_1 and \mathcal{P}_3 , which not only stops the decay of the state purity but also governs the recovery of the state purity.

2. Asymmetric case

The dynamical simulations show that all the components of the state purity oscillate in the asymmetric case as demonstrated by Fig. 8. The amplitude of the oscillations of \mathcal{P}_2 increases with the energy gradient, while the amplitude of \mathcal{P}_3 decreases with the energy gradient. However, an arbitrary effect of ϵ is observed on the oscillations of \mathcal{P}_1 . Interestingly, a random phase relation is observed in the transient oscillations of the three components of state purity (as the Coulomb coupling and energy gradient vary). As in the symmetric case, state purity decreases initially and then rises to the maximum value before plateauing; however, in this case, besides \mathcal{P}_2 , \mathcal{P}_1 also contributes in the recovery of the state purity.

FIG. 6. Time evolution of the state purity \mathcal{P} and its components $\mathcal{P}_1, \mathcal{P}_2$, and \mathcal{P}_3 with (a) $\gamma = 10 \text{ cm}^{-1}$, (b) $\gamma = 50 \text{ cm}^{-1}$, and (c) $\gamma = 100 \text{ cm}^{-1}$. The energy gradient used in this case is $\epsilon = 0 \text{ cm}^{-1}$ with $\Delta = 100 \text{ cm}^{-1}$ at T = 125 K. The value of the reorganization energy used in this case is 15 cm⁻¹.

IV. CONCLUSION

Quantum features and their destruction are of great interest for a detailed understanding of countless physical and biological phenomena. The physical basis for the long-time persistence of quantum features can be used as a blueprint for designing nanoscale devices, such as bioinspired solar cells with a targeted function. Quantum simulations have illustrated the survival of quantum mechanical features in the dynamics of the energy transfer in the weakly dissipative environment in both the site and eigenstate bases. The long-time existence of quantum features in dissipative conditions indicates the possibility of their fundamental importance in the energy transfer mechanism. However, the state purity is not affected significantly by the survival of eigenstate coherence as the system moves towards the steady state even with a nonzero-energy gradient.

Further, in the dissipative environment, a comparison of the energetic separation of the eigenstates with the energy of the thermal phonons governs the mixedness of the quantum state such that higher mismatch results in high state purity at equilibrium. In the recovery of state purity, besides the energetic separation, the dip in the state purity is also affected by the bath relaxation rate and initial population distribution.

ACKNOWLEDGMENTS

This work was supported by the KIAS Individual Grant No. CG077602 from the Korea Institute for Advanced Study. I thank the Center for Advanced Computation in KIAS for providing computing resources.



FIG. 8. Dynamics of the purity \mathcal{P} and its components \mathcal{P}_1 , \mathcal{P}_2 , and \mathcal{P}_3 for different pairs of ϵ and Δ , i.e., (a) $\epsilon = 100 \text{ cm}^{-1}$ and $\Delta =$ 300 cm⁻¹, (b) $\epsilon = 400$ cm⁻¹ and $\Delta = 300$ cm⁻¹, (c) $\epsilon = 100$ cm⁻¹ and $\Delta = 100 \text{ cm}^{-1}$, and (d) $\epsilon = 400 \text{ cm}^{-1}$ and $\Delta = 300 \text{ cm}^{-1}$ at room temperature 277 K. Here four hierarchy levels with four bath exponential terms were used with time steps of 0.5 fs for convergence.

3. Effect of bath relaxation rate

The effect of the bath relaxation rate (a measure of the degree of non-Markovianity in the system) is studied (see Fig. 9). It is evident from Fig. 9 that when γ is small (i.e., the bath relaxation is slow), the oscillations of \mathcal{P}_3 persist for a long timescale compared to the high value of bath relaxation, e.g., when $\gamma = 10 \text{ cm}^{-1}$, \mathcal{P}_3 oscillates until ~2.5 ps, while low-amplitude oscillations of \mathcal{P}_3 appear for almost 1.8 ps with $\gamma = 100 \text{ cm}^{-1}$. As is obvious, the amplitude and timescale of the oscillations vary with the degree of non-Markovianity such that the strong memory effects in the system-bath evolution (shown by the small value of the bath relaxation rate γ)



FIG. 9. Comparative analysis of \mathcal{P}_3 for different values of γ . The energy gradient used in this case is $\epsilon = 0 \text{ cm}^{-1}$ with $\Delta = 100 \text{ cm}^{-1}$ at T = 125 K. Here four hierarchy levels with four bath exponential terms were used with time steps of 0.5 fs for convergence.



FIG. 10. Dynamics of the purity for different initial conditions with (a) $\epsilon = 0$ cm⁻¹, (b) $\epsilon = 100$ cm⁻¹, and (c) $\epsilon = 200$ cm⁻¹. The Coulomb coupling used in this case is $\Delta = 100 \text{ cm}^{-1}$ with T = 125 K. Here four hierarchy levels with four bath exponential terms were used with time steps of 0.5 fs for convergence.

enhance the timescale and amplitude of \mathcal{P}_3 compared to the weak memory effects (shown by the high value of the bath relaxation rate).

4. Effect of initial population distribution

To study the effect of the initial condition on the dip in the state purity, the following three different initial conditions were chosen to study the dynamics of the state purity:

$$\rho^{1}(0) = \rho_{D},$$

$$\rho^{2}(0) = 0.5\rho_{D} + 0.5\rho_{A} + 0.5\rho_{DA} + 0.5\rho_{AD},$$

$$\rho^{3}(0) = \rho_{A}.$$
(A1)

For the symmetric case (i.e., $\epsilon = 0 \text{ cm}^{-1}$), the dip in purity is the same for the initial population distributions $\rho^{1}(0)$ and $\rho^{3}(0)$, as demonstrated by Fig. 10(a). However, the dip in the state purity increases substantially with the energy gradient for the initial condition $\rho^1(0)$ compared to the initial population distribution $\rho^3(0)$, as shown by Figs. 10(b) and 10(c). For example, with the initial condition $\rho^{1}(0)$, a maximally mixed state is achieved during the time evolution when $\epsilon = 200 \text{ cm}^{-1}$, while $\mathcal{P}_{\min} \simeq 0.77$ for the initial population distribution $\rho^3(0)$. This implies that the initial localization of the population away from the trap site leads to a transient maximally mixed state with the enhancement of the energy gradient. On the other hand, when both sites are equally populated initially [i.e., an initial pure state $\rho^2(0)$], the system evolves in such a way that an almost maximally mixed state is obtained during the evolution of the system, irrespective of the energy gradient ϵ .



FIG. 11. Illustration of the dynamics of the state purity of a trimer system (i.e., two donors coupled to one acceptor pigment) at a cryogenic temperature of 125 K with (a) zero-energy gradients, i.e., $\epsilon_{D1A} (= \epsilon_{D1} - \epsilon_A) = 0 \text{ cm}^{-1}$ and $\epsilon_{D2A} (= \epsilon_{D2} - \epsilon_A) = 0 \text{ cm}^{-1}$, and (b) nonzero-energy gradients $\epsilon_{D1A} = 500 \text{ cm}^{-1}$ and $\epsilon_{D2A} = 400 \text{ cm}^{-1}$. Here four hierarchy levels with four bath exponential terms were used with time steps of 0.5 fs for convergence.

APPENDIX B: TRIMER SYSTEM

Finally, the dynamics of the state purity is investigated in a trimer system (i.e., an acceptor connected to the two donor

- G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mancal, Y.-C. Cheng, R. E. Blankenship, and G. R. Fleming, Nature (London) 446, 782 (2007).
- [2] M. Cho, H. M. Vaswani, T. Brixner, J. Stenger, and G. R. Fleming, J. Phys. Chem. B 109, 10542 (2005).
- [3] J. Prior, A. W. Chin, S. F. Huelga, and M. B. Plenio, Phys. Rev. Lett. 105, 050404 (2010).
- [4] J. S. Briggs and A. Eisfeld, Phys. Rev. E 83, 051911 (2011).
- [5] A. Eisfeld and J. S. Briggs, Phys. Rev. E 85, 046118 (2012).
- [6] D. Singh and S. Dasgupta, J. Phys. Chem. B 121, 1290 (2017).
- [7] A. Shabani, M. Mohseni, H. Rabitz, and S. Lloyd, Phys. Rev. E 86, 011915 (2012).
- [8] A. Shabani, M. Mohseni, H. Rabitz, and S. Lloyd, Phys. Rev. E 89, 042706 (2014).
- [9] J. Wu, R. J. Silbey, and J. Cao, Phys. Rev. Lett. 110, 200402 (2013).
- [10] P. Nalbach, D. Braun, and M. Thorwart, Phys. Rev. E 84, 041926 (2011).
- [11] B.-q. Ai and S.-L. Zhu, Phys. Rev. E 86, 061917 (2012).
- [12] G.-Y. Chen, N. Lambert, C.-M. Li, Y.-N. Chen, and F. Nori, Phys. Rev. E 88, 032120 (2013).
- [13] S. Hoyer, A. Ishizaki, and K. B. Whaley, Phys. Rev. E 86, 041911 (2012).
- [14] M. Sarovar, Y.-C. Cheng, and K. B. Whaley, Phys. Rev. E 83, 011906 (2011).
- [15] C. A. Mujica-Martinez, P. Nalbach, and M. Thorwart, Phys. Rev. E 88, 062719 (2013).
- [16] P. Bhattacharyya and K. L. Sebastian, Phys. Rev. E 87, 062712 (2013).
- [17] D. Singh and S. Dasgupta, ChemistrySelect 4, 2703 (2019).
- [18] Y.-T. Wang, J.-S. Tang, Z.-Y. Wei, S. Yu, Z.-J. Ke, X.-Y. Xu, C.-F. Li, and G.-C. Guo, Phys. Rev. Lett. 118, 020403 (2017).

pigments). The site energies and the Coulomb couplings used to evaluate the trimer system are illustrated as

$$\hat{H}_{\text{trimer}} = \begin{pmatrix} \epsilon_{D1} & 300 & 300\\ 300 & \epsilon_A & 300\\ 300 & 300 & \epsilon_{D2} \end{pmatrix}, \quad (B1)$$

where ϵ_{D1} (ϵ_{D2}) denotes the transition frequency of the first (second) donor and ϵ_A is the transition frequency of the acceptor pigment. The off-diagonal elements of Eq. (B1) represent the Coulomb coupling between different sites.

The recovery of the state purity is observed for both the symmetric (when all the pigments have the same transition frequency) [see Fig. 11(a)] and asymmetric cases [see Fig. 11(b)]. The analysis of the trimer system also verifies that for a given Coulomb coupling, the dip in the state purity is enhanced with the energy gradient. The quantitative evaluation of the state purity indicates the possibility of the recovery of the state purity (in the dynamics of energy transfer) in any pigment-protein complex when the pigments are weakly coupled to the protein environment.

- [19] S. Ballmann, R. Hartle, P. B. Coto, M. Elbing, M. Mayor, M. R. Bryce, M. Thoss, and H. B. Weber, Phys. Rev. Lett. **109**, 056801 (2012).
- [20] S. Zienau, Phys. Bull. 26, 545 (1975).
- [21] B. Gu and I. Franco, J. Phys. Chem. Lett. 8, 4289 (2017).
- [22] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. van Grondelle, Nat. Chem. 3, 763 (2011).
- [23] G. D. Scholes, G. R. Fleming, L. X. Chen, A. Aspuru-Guzik, A. Buchleitner, D. F. Coker, G. S. Engel, R. van Grondelle, A. Ishizaki, D. M. Jonas *et al.*, Nature (London) **543**, 647 (2017).
- [24] A. F. Izmaylov and I. Franco, J. Chem. Theory Comput. 13, 20 (2017).
- [25] A. Kar, L. Chen, and I. Franco, J. Phys. Chem. Lett. 7, 1616 (2016).
- [26] J. Gong and P. Brumer, Phys. Rev. Lett. 90, 050402 (2003).
- [27] I. Franco and H. Appel, J. Chem. Phys. 139, 094109 (2013).
- [28] A. Kar and I. Franco, J. Chem. Phys. 146, 214107 (2017).
- [29] B. Gu and I. Franco, J. Phys. Chem. Lett. 9, 773 (2018).
- [30] B. Gu and I. Franco, J. Chem. Phys. 149, 174115 (2018).
- [31] S. Chatterjee and N. Makri, J. Phys. Chem. Lett. **11**, 8592 (2020).
- [32] Y. Tanimura and R. Kubo, J. Phys. Soc. Jpn. 58, 101 (1989).
- [33] A. Ishizaki and G. R. Fleming, Proc. Natl. Acad. Sci. U.S.A. 106, 17255 (2009).
- [34] J. Strumpfer and K. Schulten, J. Chem. Theory Comput. 8, 2808 (2012).
- [35] D. Singh and S. Dasgupta, J. Phys. Chem. B 124, 4056 (2020).
- [36] A. Ishizaki and G. R. Fleming, J. Chem. Phys. 130, 234111 (2009).
- [37] D. Singh, J. Phys. Chem. B 125, 557 (2021).
- [38] J. Hu, M. Luo, F. Jiang, R.-X. Xu, and Y. Yan, J. Chem. Phys. 134, 244106 (2011).