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Electron transfer mechanism and the locality of the system-bath interaction: A comparison of local, semilocal, and pure dephasing models

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We simulate the effects of two types of dephasing processes, a nonlocal dephasing of system eigenstates and a dephasing of semilocal eigenstates, on the rate and mechanism of electron transfer (eT) through a series of donor-bridge-acceptor systems, D-B_N-A, where N is the number of identical bridge units. Our analytical and numerical results show that pure dephasing, defined as the perturbation of system eigenstates through the system-bath interaction, does not disrupt coherent eT because it induces no localization; electron transfer may proceed through superexchange in a system undergoing only pure dephasing. A more physically reasonable description may be obtained via a system-bath interaction that reflects the perturbation of more local electronic structure by local nuclear distortions and dipole interactions. The degree of locality of this interaction is guided by the structure of the system Hamiltonian and by the nature of the measurement performed on the system (i.e., the nature of the environment). We compare our result from this "semilocal" model with an even more local phenomenological dephasing model. We calculate electron transfer rate by obtaining nonequilibrium steady-state solutions for the elements of a reduced density matrix; a semigroup formalism is used to write down the dissipative part of the equation of motion. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2168457]

I. INTRODUCTION

Electron transfer (eT) is perhaps the most well-studied example of a quantum process where the components of the relevant microscopic system are embedded in a macroscopic environment with which the system exchanges both energy and phase.[1–5] Electron transfer involves both spatial redistribution of charge and coupling of electron density with surrounding nuclear modes. A proper description of the interaction between the electron and its environment is therefore crucial for predicting eT rate and mechanism. Reduced dynamics approaches are a popular way of introducing dissipation into quantum evolution. In these treatments, the nuclear degrees of freedom that are strongly coupled to the quantum process are collected in the reaction coordinate and are treated explicitly and quantum mechanically. The huge number of weakly coupled nuclear degrees of freedom compose the thermal bath or continuum, and are treated implicitly.[6–9] The interaction with the environment induces dissipation: evolution of the quantum system that cannot be described by unitary Hamiltonian dynamics.[10]

There are two major types of dissipative processes. The first is energy exchange between the system and bath resulting in population relaxation with characteristic time T_1. The second is pure dephasing, a quasielastic interaction with the bath that destroys phase coherence between quantum levels and pushes the system toward a classically observable state. Pure dephasing, with characteristic time T_2^*, is equivalent to making a measurement of energy on the system: information is acquired by the bath through system-bath correlations and information is lost by the system because it is perturbed by the measurement. Both processes contribute to the total dephasing time[6,11,12] T_2 $(1/T_2=1/(2T_1)+1/T_2^*$ for the two level system).

Typically for electron transfer, decoherence occurs on the time scale of the quantum dynamics;[9,13] therefore one must explicitly consider its effects on the evolution. If the isolated system's evolution is relatively slow on the time scale of bath fluctuations,[3,5] then interaction with a bath results in a stochastic fluctuation of system energies and a random walk-type evolution of system dynamics. This leads to the Markovian limit, for which we may write the total Hamiltonian as a sum of system, bath, and system-bath interaction Hamiltonians,[3,5,9,14]

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$$H = H_S + H_B + H_{\mathrm{SB}}. \tag{1}$$

On the coarse-grained kinetics time scale, details of the system-bath correlations (the information gained by the environment via decoherence of quantum states) are lost.[2,15]

The nature of the system-bath interaction depends on the environment in which the experiment is conducted and on the observable measured, both of which must be specified in modeling the effects of dissipation. Many of the methods for describing quantum dissipation using the reduced dynamics approach (e.g., Redfield,[16] semigroups,[17,18] and phenomenological models[19]) incorporate significant flexibility in the choice of dissipative operators used and therefore rely to different degrees on an *a priori* knowledge of the channels through which the system and bath interact. There are two major, although not entirely independent, aspects of the system-bath interaction that must be considered when modeling the dissipative dynamics: the locality of the system-bath interaction (does the environment perturb different system sites or site combinations differently or act on nonlocal system eigenstates?) and the physical quantities of the system perturbed by the bath (the dipole moments of the system components, as in coupling to a laser field, for example).

Consider the process of electron transfer in organic molecules. One may think of the most local model for decoherence as a dephasing of atomic sites and the most nonlocal model as a dephasing of system eigenstates. For organic systems, neither of these is (in general) an optimal description. Over the course of an eT process, the electron will encounter several types of environments dictated by local nuclear modes (both intramolecular and solvent) and local dipole moments. These nuclear modes and dipole moments constitute a kind of local bath. Therefore, assuming the eT process is not significantly faster than the time scale of dephasing, some sort of local dephasing must be incorporated into the evolution of the system's dynamics (in addition to any completely nonlocal dephasing). Some important questions are as follows: Which nuclear modes and dipole moments interact with the electron? Which electronic states are dephased (i.e., how local is the dephasing)? What sorts of behaviors are induced by local dephasing that are not seen when the system undergoes completely nonlocal dephasing ("pure" dephasing)?

Here, we show that the modulation of nonlocal system eigenstates through interaction with the bath leads to significantly different electron transfer dynamics than the modulation of more local eigenstates (eigenstates of sites or groups of sites on the molecule). We give two examples of dephasing of an electron transfer process using a semigroup method to incorporate the influence of dissipation on system dynamics. The first is defined formally as a pure dephasing—that is, a completely nonlocal dephasing of the system eigenstates. Pure dephasing is accomplished by using the Hamiltonian, H_S, as a coupling operator. The second is a semilocal dephasing obtained by selecting a system operator that defines the energies of more localized states. The strategy behind the design of this operator is as follows: The degree of locality of the system-bath interaction depends not only on the nature of the relevant bath modes but also on the region that an electron occupies at any given time during the eT process—an effective conjugation length or degree of delocalization. This particular facet of the system-bath interaction is, in part, defined by the system Hamiltonian, which (when written in a local basis) gives the energy gaps and electronic couplings among different atomic or molecular sites and therefore divides the system into what might be called coherent subunits. Therefore, the system operator chosen for describing dephasing should reflect the partitioning of the system indicated by the system Hamiltonian. The scheme for semilocal dephasing used here avoids two unphysical assumptions: (1) that regions in a molecule with weak or negligible long-range inter-region coupling interact with the bath as a coherent unit and (2) that regions in a molecule with substantial interaction amongst themselves interact with the bath as isolated units. This operator can be seen as the set of energies and intersite hopping integrals through which local distortions and dipole moments modulate the local electronic structure.

In the following sections, we provide a compact introduction to dissipation in open quantum systems. We focus on the semigroup method; comprehensive discussions of this topic can be found in several texts.[5,7] We then provide a physical and mathematical outline of "pure dephasing." Next, we describe our system and discuss our choice of a local (or site) basis to analyze the eT rate as a function of system parameters and dissipation. Finally, we use the semigroup formalism to compute the effect of pure dephasing (dephasing of system eigenstates) and semilocal dephasing on electron transfer rate within a donor-bridge-acceptor system, and compare these results with those obtained using a previous (even more local) phenomenological model.

We show, based on analytical and numerical results, that dephasing of system eigenstates cannot induce incoherent transport, while dephasing of more localized states does disrupt coherent transport. Our Lindblad operator incorporates elements of the system Hamiltonian that dictate which pieces of the system couple to the bath as coherent subunits and therefore introduces a degree of locality to the system-bath interaction that reflects the system's electronic structure. This methodology, utilized within a convenient semigroup formalism, allows us to achieve a physically reasonable description of the modulation of electron transfer dynamics (specifically the switch in mechanism from coherent, strongly distance-dependent superexchange to incoherent, relatively distance-independent transfer) by bath modes.

II. THEORETICAL BACKGROUND

The key quantity for the study of open, dissipative quantum dynamics in the Markovian limit is the reduced density matrix, ρ_S,[7,20,21] obtained from the complete density matrix by performing a partial trace over the environment degrees of freedom, thereby projecting out the system subspace.[2,3] The time dependence of ρ_S is given by the Liouville-von Neumann equation (where $\mathfrak{L}$ is a time-independent superoperator),

$$\frac{\partial \rho_S}{\partial t} = \mathfrak{L}\rho_S(t) \quad \mathfrak{L}\rho_S = -\frac{i}{\hbar}[H_S,\rho_S] + \mathfrak{L}_D\rho_S. \tag{2}$$

The dissipative Liouvillian operator, $\mathfrak{L}_D$, describes the influence of the environment on the system dynamics,[11,22] and the set $\{\rho_S(t)\}$ constitute a semigroup with infinitesimal generator[23] $\mathfrak{L}$. A fundamental property of the maps of a Markovian dynamical semigroup is that they are completely positive. This means that all members of the group, ρ_S, are represented by positive definite matrices. Density matrices must be non-negative semidefinite if the probabilistic interpretation of their diagonal elements is to hold.[2,24]

There are various ways to include the contribution of non-Hamiltonian interactions to the time dependence of ρ_S.[9] Nearly all practical applications use models or approximations for the dissipation term, $\mathfrak{L}_D\rho_S$. Lindblad derived the most general completely positive Markovian master equation for the dynamics of a density matrix:[5,14,17,25]

$$\mathfrak{L}_D\rho_S = -\frac{1}{2}\sum_m \gamma_m\{[F_m\rho_S,F_m^+] + [F_m,\rho_S F_m^+]\}, \tag{3}$$

where $H_{\mathrm{SB}}=\hbar\Sigma_m\gamma_m F_m\otimes B_m$, B_m are the bath operators, and γ_m are real, positive scalar interaction strengths. Both F_m and B_m are dimensionless, and γ_m has dimension of frequency. Lindblad operators can be used to treat a variety of dissipative processes: dephasing,[26] collisions,[27] bond breaking,[28] electron transfer,[14] etc. Constraints can be applied such that the system will approach thermal equilibrium.[14]

System-environment interactions lead to correlations between their respective states. Over (often a very short) time, these correlations lead to destruction of the coherences between system states, selecting out a set of states that contribute to a measured observable (so-called pointer states[29]). If, in the development of system-bath correlations, the system affects the environment but certain system states display a high degree of stability (and remain essentially unchanged), the energy of the system is conserved while the phase of the wave-function relaxes. As a consequence, if the density matrix is constructed in the basis of system eigenstates $\{|n\rangle\}$, the populations of the system's reduced density matrix remain constant while the coherences decay. This is often called pure dephasing, and it has a characteristic decay rate of $1/T_2^*$.[5,8] We may write the total Hamiltonian as a sum of system, bath, and interaction terms [Eq. (1)], and use the form

$$H_{\mathrm{SB}} = \hbar\sum_n \alpha_n|n\rangle\langle n| \otimes B_n = \hbar\sum_n \alpha_n A_n \otimes B_n, \tag{4}$$

where B_n are dimensionless, arbitrary bath operators, A_n are dimensionless system operators (diagonal in this representation), and α_n are scalar interaction strengths with dimension of frequency. Pure dephasing is the case where[5,30]

$$[H_S,A_n] = 0. \tag{5}$$

Under the influence of pure dephasing, system energy is conserved. If constructed in the basis where A_n is diagonal, complete decoherence in the form of pure dephasing leaves the density-matrix diagonal. The states that emerge are completely incoherent—i.e., they do not interfere with each other.

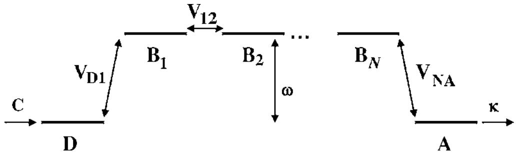

FIG. 1. Donor-bridge-acceptor system with notation explained in the text.

Pure dephasing (in the Markov limit) may be incorporated into the dynamics of a quantum system plus environment within the Lindblad formalism via the Liouville-von Neumann equation,[1,2,5,15,21,25–27,31,32] where the dissipative superoperator, $\mathfrak{L}_D\rho_S$, is defined in Eq. (3) and

$$H_{\mathrm{SB}} = \hbar\sum_n \gamma_n F_n \otimes B_n, \quad F = |n\rangle\langle n|, \tag{6a}$$

$$[H_S,F_n] = 0. \tag{6b}$$

As written in Eq. (6a), the system operators F_n are simply projections.

A. The site basis and donor-bridge-acceptor system

A local or site basis is a physically intuitive choice to study the effects of dephasing on electron transfer rate and mechanism.[14,19,32–35] We will consider a molecule separated into a donor, an acceptor, and a series of bridge units. Each basis function corresponds to an orbital localized on one of these (generally multiatomic) sites, and diagonal elements of the system density matrix correspond to electronic populations on these sites. It is traditional to propagate the density matrix in the energy eigenbasis because it seems physically most reasonable that the energy eigenstates must come to thermal equilibrium with the bath.[36] However, the methodology used in this work (described in the next section) drives the system into a nonequilibrium steady state such that this consideration is no longer relevant. It is intuitive, and has been shown formally, that the site basis and the energy eigenstate basis become equivalent in the high temperature and small intersite coupling limits.[14]

Our system is given by the Hamiltonian,[33,37]

$$H_S = |D\rangle\omega_D\langle D| + |A\rangle\omega_A\langle A| + \sum_{i=1}^{N}|i\rangle\omega_i\langle i| + \left(|D\rangle V_{D1}\langle 1| + |N\rangle V_{NA}\langle A| + \sum_{i=1}^{N-1}|i\rangle V_{i,i+1}\langle i+1| + \text{c.c.}\right), \tag{7}$$

written in the basis of sites $|D\rangle$, $|A\rangle$, and $|i\rangle$, where $i=1,\ldots,N$. The donor and acceptor (D and A) are assumed degenerate with energy $\omega_D=\omega_A=0$ and bridge units (B_i) are degenerate and separated by an energy $\omega_i=\omega$ from the donor/acceptor. This scheme is shown in Fig. 1.

III. RESULTS AND DISCUSSION

A. Electron transfer rate with dephasing of system eigenstates (pure dephasing)

In this section we will choose the system Hamiltonian as the Lindblad operator to apply pure dephasing to the electron transfer process. In most treatments, the Lindblad operator, F, is taken to be unitless such that γ [Eq. (6a)] has units of frequency, and can therefore be interpreted as a dephasing rate.[15,26,27] Note that this is a standard, but not a required or inherent ingredient in the semigroup treatment. In our case of pure dephasing, the coupling operator, H_S, has units of frequency; in order to compare our results easily with those of other methods, we will use as our Lindblad operator a scaled (unitless) system Hamiltonian,

$$\begin{aligned} F &= \widetilde{H}_S, \\ H_S &= \varepsilon_0 F, \end{aligned} \tag{8}$$

where $\varepsilon_0 \equiv 100\ \mathrm{cm}^{-1}$ and, trivially, $[\widetilde{H}_S, H_S] = 0$. This Lindblad operator results in a pure dephasing of the eigenstates of the system. The choice of $\varepsilon_0 = 100\ \mathrm{cm}^{-1}$ is a convenient scaling factor, as all energies/couplings within the system are on the order of $100\ \mathrm{cm}^{-1}$. For convenience, we also introduce the phenomenological interaction strength, s_γ, which has dimension time,

$$\mathfrak{L}_D \rho_S = \frac{1}{2\hbar^2} s_\gamma \{[H_S \rho_S, H_S^\dagger] + [H_S, \rho_S H_S^\dagger]\}, \tag{9}$$

where s_γ is the only phenomenological input in this treatment and is used to observe the effect of changing the dephasing rate on eT dynamics without changing the Hamiltonian parameters. Then γ in Eq. (6a) is defined by

$$\hbar \gamma = s_\gamma \varepsilon_0^2. \tag{10}$$

In the following, we investigate the regime $s_\gamma = 10^{-4} - 10^{2}\ (\mathrm{cm}^{-1})^{-1}$. For $s_\gamma = 10^{-4}\ (\mathrm{cm}^{-1})^{-1}$, $\gamma = 3 \times 10^{10}\ \mathrm{s}^{-1}$ (a dephasing time of 30 ps); for $s_\gamma = 10^{-3}\ (\mathrm{cm}^{-1})^{-1}$, $\gamma = 3 \times 10^{11}\ \mathrm{s}^{-1}$ (a dephasing time of 3 ps), etc. For $s_\gamma = 10^{2}\ (\mathrm{cm}^{-1})^{-1}$, our upper limit, $\gamma = 3 \times 10^{16}\ \mathrm{s}^{-1}$ (a dephasing time of 0.03 fs). This is obviously unphysically fast dephasing; we use it here to explore the large γ limit.

The reduced density matrix may be numerically propagated according to Eq. (2) to obtain time-dependent populations, but we will take a simpler approach. We will find the nonequilibrium steady-state solution for the electron transfer rate constant from donor to acceptor. In this model, which is described in detail elsewhere,[32,33,38] electronic population is injected into the donor site by some unspecified source with a given flux C, and the acceptor site is coupled to a population sink inducing a decay with characteristic rate κ, see Fig. 1. These terms are used to drive the system into a nonequilibrium steady state as $t \to \infty$.

In Eq. (A1) of the Appendix, we give the equations of motion with pure dephasing for the two-bridge system, D-B_2-A, where we have assumed a single adjacent site coupling $V_{D1} = V_{NA} = V_{i,i+1} = V$ (with $\hbar = 1$ and s_γ abbreviated s for clarity). The first line of each equation contains terms due to unitary Hamiltonian evolution. The remaining terms are due to pure dephasing and interaction with the constant incoming flux (C) and the absorbing boundary term (κ). These imposed boundary conditions are the only nonrigorous aspect of Eq. (A1). From the equations of motion, it appears that the diagonal elements are not constant in time, as would be expected from pure dephasing. However, this simple behavior is seen only when the density matrix is constructed in the energy eigenbasis. Conservation of energy is the more general characteristic of a pure dephasing process. If Eq. (A1) were constructed in the basis of eigenstates of H_S, rather than in the basis of local states, $|D\rangle, |B_1\rangle, |B_2\rangle, |A\rangle$ (and in the absence of the source and sink terms C and κ), the diagonal elements would indeed be conserved.

To solve for the steady-state eT rate, we reexpress the equations of motion in the matrix form[19]

$$\dot{\rho} = \mathbf{A} \cdot \rho + \mathbf{C}, \tag{11}$$

where $\mathbf{A}$ is an $(N+2)^2 \times (N+2)^2$ matrix of coefficients, ρ is an $(N+2)^2 \times 1$ vector consisting of the reduced density-matrix elements, and $\mathbf{C}$ is an $(N+2)^2 \times 1$ vector with the element corresponding to ρ_{DD} equal to C and all others zero. At steady state, all $\dot{\rho}_{ij}$ are equal to zero. The electron transfer rate $k_{\mathrm{eT},SS}$ is the ratio between the steady-state flux through the system, $\kappa \rho_{AA,SS} = C$, and the population of the donor level, $\rho_{DD,SS}$,[19,33]

$$k_{\mathrm{eT},SS} = \frac{C}{\rho_{DD,SS}}. \tag{12}$$

The steady-state approach has several advantages: the solution of Eq. (11) requires only an inversion of the $\mathbf{A}$ matrix, and an analytical solution for the eT rate may be found for reasonably small systems. We have also found the values of the density-matrix elements at long times by solving the equations of motion [(A1) and (A2)] for $N=1$. The "long-time" eT rates calculated through this method are equivalent to the steady-state eT rates we report here. Solution of the full dynamics becomes computationally intensive for $N > 1$, thus partially motivating the use of the steady-state method.

Electron transfer rates will be functions of the four independent parameters ω, V, κ, and s_γ, as well as the number of sites, N, in the system. Plots of steady-state electron transfer rate $k_{\mathrm{eT},SS}$ versus bridge length (for $N = 1-6$)) and versus $\log s_\gamma$ (for $\gamma = 3 \times 10^{10} - 3 \times 10^{16}\ \mathrm{s}^{-1}$) in the case of pure dephasing are pictured in Fig. 2. We have also obtained analytical solutions for the steady-state eT rate for $N=1$ and $N=2$. Because they are very lengthy, we will not present the full expressions for $k_{\mathrm{eT},SS}$ here, but rather inspect several useful physical limits.

We will first consider the case in which dephasing is a perturbation to the system dynamics ($s_\gamma \varepsilon_0^2 = \gamma \ll V, \omega, \kappa$) and the energy gap between the donor/acceptor and the bridge is significantly larger than the coupling and the rate out of the acceptor site ($\omega \gg \kappa, V$). For $N=1$ ($s \equiv s_\gamma$, $\hbar = 1$), the expression for the steady-state eT rate reduces to

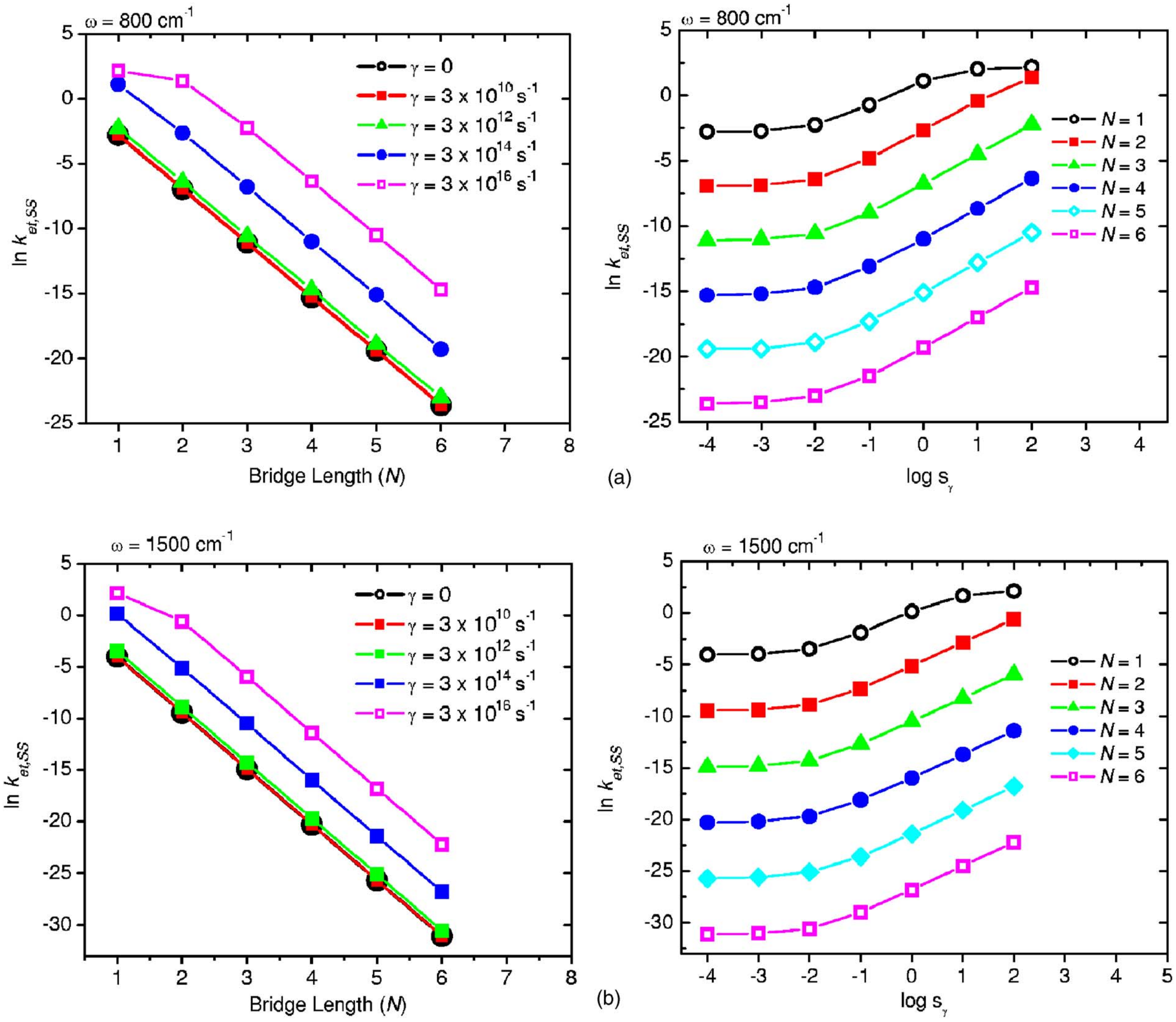

FIG. 2. Electron transfer rate vs bridge length (left) and log s_γ (right) for $\omega=800\ \mathrm{cm}^{-1}$ (a) and $\omega=1500\ \mathrm{cm}^{-1}$ (b) calculated with pure dephasing applied (Sec. III A). $V=100\ \mathrm{cm}^{-1}$, $\kappa=300\ \mathrm{cm}^{-1}$, and $k_{\mathrm{eT},SS}$ and s_γ were calculated in units of ps^{-1} and cm^{-1}, respectively.

$$k_{\mathrm{eT},SS}=\frac{4V^4}{\omega^2\kappa}\left(\frac{1}{1+(\kappa s/4)}\right)+\frac{2sV^4}{\omega^2}\left(\frac{1}{1+(\kappa s/4)}\right). \tag{13}$$

Since s is very small, we may use the approximation $1/(1+x)\approx 1-x+\ldots$, to obtain

$$k_{\mathrm{eT},SS}=\frac{4V^4}{\kappa\omega^2}+s\frac{V^4}{\omega^2}-s^2\frac{V^4\kappa}{2\omega^2}. \tag{14}$$

This expression follows the McConnell superexchange form for electron transfer rate:[19,39,40]

$$k_{\mathrm{eT}}\propto\left(\frac{V_{BB}}{\omega}\right)^{2(N-1)}\left|\left(\frac{V_{DB}V_{BA}}{\omega}\right)\right|^2. \tag{15}$$

For very small γ, the first term dominates the sum and the eT rate is constant with increasing s. For $s>s^2\kappa/2$ $(s<2/\kappa)$, the rate will grow with increasing s like $(s-s^2\kappa/2)$. In the limits stated above, the transport is always superexchange-like.

Within the McConnell formulation,[39] the rate decreases exponentially,

$$k_{\mathrm{eT}}=k_0\exp(-\beta_{\mathrm{SE}}r), \tag{16}$$

where β_{SE} is the superexchange decay parameter,

$$\beta_{\mathrm{SE}}=\frac{-2(\ln|V/\omega|)}{\Delta r}, \quad V/\omega\ll 1, \tag{17}$$

where Δr is the intersite spacing on the bridge and r is the donor-acceptor distance.[34,39,40] Fits of the plots of $\ln k_{\mathrm{eT},SS}$ vs N in Fig. 2 (up to $\sim s_\gamma=1$) follow this form perfectly with $\beta_{\mathrm{SE}}=4.2/\Delta r$ for $\omega=800\ \mathrm{cm}^{-1}$ $(V/\omega=0.125)$, $\beta_{\mathrm{SE}}=5.0/\Delta r$ for $\omega=1200\ \mathrm{cm}^{-1}$ $(V/\omega=0.083)$, $\beta_{\mathrm{SE}}=5.4/\Delta r$ for $\omega=1500\ \mathrm{cm}^{-1}$ $(V/\omega=0.067)$, and $\beta_{\mathrm{SE}}=6.0/\Delta r$ for $\omega=2000\ \mathrm{cm}^{-1}$ $(V/\omega=0.05)$.

One can see from Fig. 2 that, with pure dephasing applied, the eT rate exhibits perfect exponential decay with bridge length, except in certain cases when $s_\gamma\varepsilon_0^2\sim V$. These cases may be explained by inspecting the symbolic expression for the steady-state rate in the limit where $s_\gamma\varepsilon_0^2=\gamma\gg V,\omega,\kappa$ (with $\hbar=1$ and no assumption about the relative magnitudes of V and ω). For $N=1$, we obtain

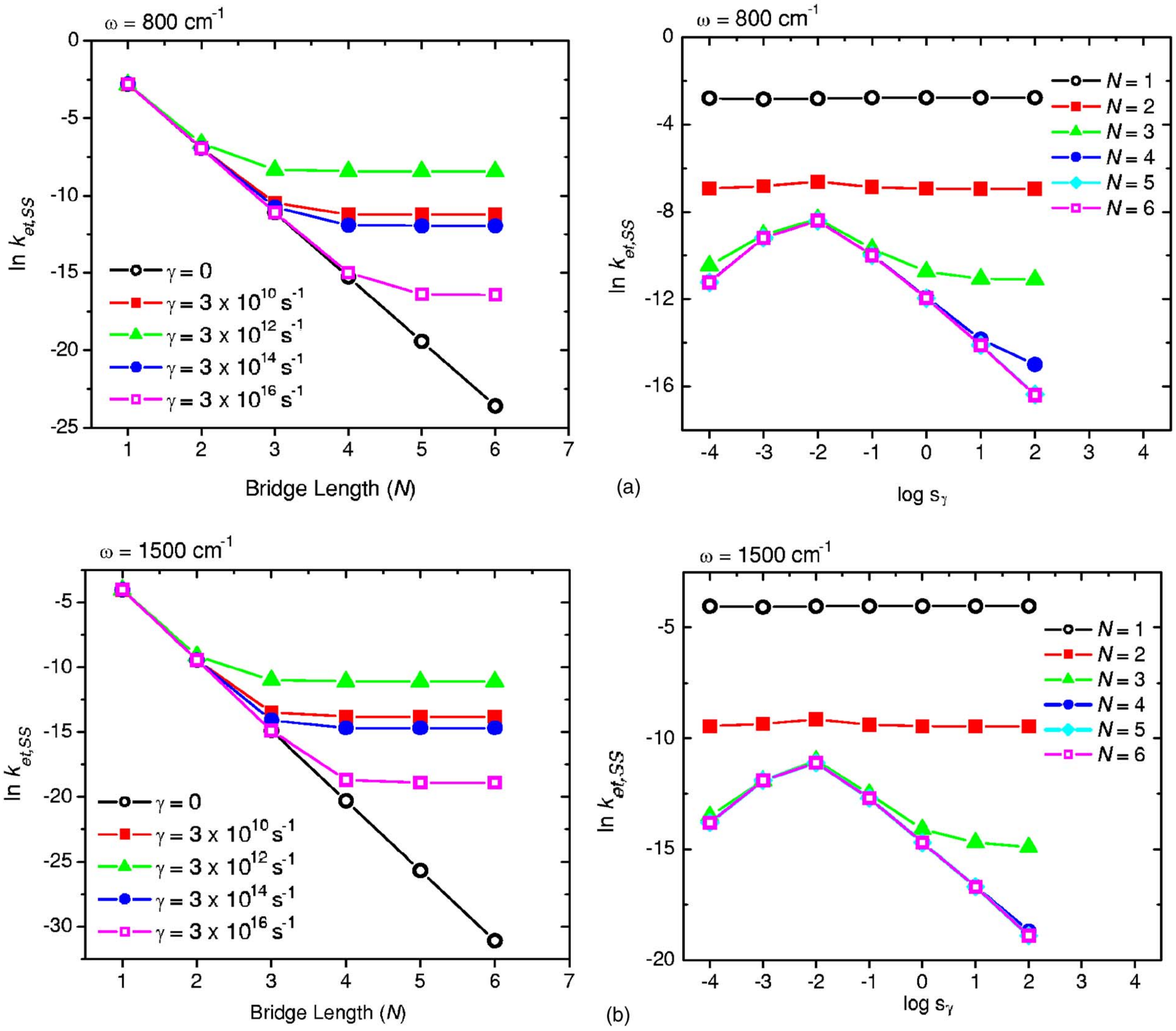

FIG. 3. Electron transfer rate vs bridge length (left) and log s_γ (right) for $\omega=800\ \mathrm{cm}^{-1}$ (a) and $\omega=1500\ \mathrm{cm}^{-1}$ (b) calculated with semilocal dephasing applied (Sec. III B). $V=100\ \mathrm{cm}^{-1}$, $\kappa=300\ \mathrm{cm}^{-1}$, and $k_{\mathrm{eT},SS}$ and s_γ were calculated in units of ps^{-1} and cm^{-1}, respectively. Note the turnover with γ (right) and the mechanistic change from superexchange to incoherent hopping (left). Note that in the plots of $k_{\mathrm{eT},SS}$ vs log s_γ, the traces for $N=5$ and $N=6$ overlap for $\omega=800\ \mathrm{cm}^{-1}$ and the traces for $N=4$, $N=5$, and $N=6$ overlap for $\omega=1500\ \mathrm{cm}^{-1}$.

$$k_{\mathrm{eT},SS}=\frac{\kappa V^4((1/2)s^6V^6+(1/16)s^6V^4\omega^2)}{(1/16)s^6V^8\omega^2+(1/2)s^6V^{10}}=\kappa. \qquad (18)$$

In this case, the eigenstates are now fluctuating over a range larger than their energy separation, so the exit from the acceptor site is rate limiting and the eT rate is given by κ.

We have also obtained analytical solutions for $N=2$ in the same physical limits. In the limit where $s_\gamma\varepsilon_0^2=\gamma \ll V,\omega,\kappa$ (with $\hbar=1$) and $\omega \gg \kappa, V$, the steady-state electron transfer rate again assumes the McConnell superexchange form of Eq. (15). In the limit where $s_\gamma\varepsilon_0^2=\gamma \gg V,\omega,\kappa$, once again $k_{\mathrm{eT},SS}=\kappa$.

The above analysis has shown that pure dephasing cannot induce incoherent transport. This result is reasonable considering that dephasing via the system Hamiltonian amounts to a system-bath interaction that perturbs system eigenstates, which does not induce the localization that would lead to incoherent eT.[33] (The dependence of eT rate on γ in the pure dephasing case comes from the fact that changing γ changes the system energy levels relative to κ, the flux out of the system, which is held constant.) Therefore, the presence of dissipative system-bath interactions can lead to incoherent transport only if the energy fluctuation caused by the bath is not spatially homogeneous.

B. Electron transfer rate with semilocal dephasing

We would now like to observe the effects of dephasing of a more local nature. There are two issues to consider in constructing the system operator. First is the degree of locality of the system-bath interaction and second is the nature of the system-bath interaction. To address the first issue, we observe that the simple system Hamiltonian H_S, conveniently constructed in the site basis, contains coupling matrix elements between adjacent sites only; we will therefore build the dissipation operator from several local (2×2) dissipation operators so that it too only has off-diagonal elements between adjacent sites. Second, we assume that local distortions of geometry (local vibrations and librations) and dipole moments affect electronic structure via site energies and intersite hopping integrals, which are present in the system Hamiltonian. Therefore, we construct the system operator by decomposing the system Hamiltonian and the reduced density matrix into a set of (2×2) matrices, where each member of the set is labeled with index $n(n=1,\dots,N+2)-1)$ and $H_S(1,1)$ is the 1,1 (first column-first row) matrix element of the original H_S,

$$H_S[n]=\begin{bmatrix} H_S(n,n) & H_S(n,n+1) \\ H_S(n+1,n) & H_S(n+1,n+1)\end{bmatrix}, \tag{19a}$$

$$\rho_S[n]=\begin{bmatrix} \rho_S(n,n) & \rho_S(n,n+1) \\ \rho_S(n+1,n) & \rho_S(n+1,n+1)\end{bmatrix}. \tag{19b}$$

We also construct a set of (2×2) Lindblad operators

$$F[n]=\widetilde{H}_S[n], \tag{19c}$$

where $\widetilde{H}_S[n]=H_S[n]/\varepsilon_0$. Then the nth Liouvillian operator is

$$(\mathfrak{L}_D\rho_S)=-\frac{\gamma}{2}\{[F[n]\rho_S[n],F[n]^{+}]+[F[n],\rho_S[n]F[n]^{+}]\}, \tag{20}$$

and the total dissipation superoperator (with matrix elements $\dots n-1,\ n,\ n+1,\dots$) is

$$\begin{aligned}
\mathfrak{L}_D\rho_S(n,n)&=(\mathfrak{L}_D\rho_S)(1,1)+(\mathfrak{L}_D\rho_S)[n-1](2,2),\\
\mathfrak{L}_D\rho_S(n,n+1)&=(\mathfrak{L}_D\rho_S)[n](1,2),\\
\mathfrak{L}_D\rho_S(n+1,n)&=(\mathfrak{L}_D\rho_S)[n](2,1).
\end{aligned} \tag{21}$$

The dissipation operator is now tridiagonal such that it contains no interactions between sites that were not initially coupled in the system Hamiltonian. The eigenstates of pairs of sites are dephased in dissipation of this type. Incidentally, since we are manipulating the system Hamiltonian to construct our semilocal Lindblad operator, we may easily compare our results from this model to those from the pure dephasing case above.

In Eq. (A2) of the Appendix, we give the equations of motion for the elements of the reduced density operator for the two-bridge system, D-B_2-A, with semilocal dephasing (with $\hbar=1$ and $s\equiv s_\gamma$). The first line of each equation contains terms due to unitary Hamiltonian evolution and the remaining terms are due to dephasing and interaction with the source (C) and sink (κ) intrinsic to the steady-state model. All of the terms in Eq. (A2) are present in (A1) (for the equations of motion with a pure dephasing operator). With respect to (A1), the equations for the diagonal elements within (A2) are missing terms like $-sV^2\,\mathrm{Re}\,\rho_{ij}$, where $j=i\pm 2$. Additionally, unlike the pure dephasing case, only coherences between adjacent sites show time evolution due to this semilocal dephasing.

Plots of steady-state electron transfer rate $k_{\mathrm{eT},SS}$ versus bridge length (for $N=1-6$) and versus $\log s_\gamma$ (for $\gamma=3\times 10^{10}-3\times 10^{16}\ \mathrm{s}^{-1}$) for the local dephasing case are pictured in Fig. 3. Again, we may consider certain useful limiting cases. For $N=1$, if $s_\gamma\varepsilon_0^2=\gamma\ll V,\omega,\kappa$ (with $\hbar=1$) and $\omega\gg\kappa,V$ (where $s\equiv s_\gamma$),

$$k_{\mathrm{eT,ss}}=\frac{4V^4}{\omega^2\kappa}+s\left(\frac{8V^6}{\omega^2\kappa^2}\right)-s^2\left(\frac{32V^8}{\omega^2\kappa^3}+\frac{6V^6}{\omega^2\kappa}+\frac{V^4\kappa}{4\omega^2}\right). \tag{22}$$

The first term is a McConnell superexchange term as is the last s^2 term. Unlike the pure dephasing case, this expression contains several terms that do not result in exponential decay of rate with bridge length. Therefore we may not observe simple superexchange behavior when this type of dephasing is introduced. This is seen in Fig. 3, where even for small values of s_γ, the plots start to deviate from pure superexchange behavior immediately.[19,34]

In the limit where $s_\gamma\varepsilon_0^2=\gamma\gg V,\omega,\kappa$ and $\omega\gg V,\kappa$ (with $\hbar=1$),

$$k_{\mathrm{eT},SS}=\frac{4V^4}{\omega^2\kappa}. \tag{23}$$

With semilocal dephasing a turnover is seen with increasing s_γ (Fig. 3). At intermediate values, k_{eT} flattens out at shorter N than for higher or lower values of s_γ. This turnover is absent with pure dephasing (Fig. 2). Plots of rate versus $\log s_\gamma$ for $N=3-6$ have a maximum at $s_\gamma\sim 10^{-2}$ cm, which corresponds to a maximum at $\gamma=3\times 10^{12}\ \mathrm{s}^{-1}$. This dependence on γ—proportional to γ at small γ and decaying with γ at large γ—is reminiscent of Kramers' classical theory for the dependence of rate of thermally activated barrier crossing on friction.[41]

The analytical result for $N=2$ in the limit of $s_\gamma\varepsilon_0^2=\gamma\ll V,\omega,\kappa$ (with $\hbar=1$) and $\omega\gg\kappa,V$ is

$$\begin{aligned}
k_{\mathrm{eT},SS}={}&\frac{4V^6}{\omega^4\kappa}+s\left(\frac{8V^6}{\omega^2\kappa^2}+\frac{2V^6}{\omega^4}-\frac{16V^8}{\omega^4\kappa^2}\right)\\
&-s^2\left(\frac{32V^8}{\omega^4\kappa^3}+\frac{12V^8}{\omega^4}+\frac{2V^6}{\omega^4\kappa}+\frac{3V^6\kappa}{4\omega^4}\right).
\end{aligned} \tag{24}$$

If $s_\gamma\varepsilon_0^2=\gamma\gg V,\omega,\kappa$ (with $\hbar=1$), we once again have a recovery of superexchange behavior,

$$k_{\mathrm{eT},SS}=\frac{4V^6}{\omega^4\kappa}. \tag{25}$$

To better understand the nature of this semilocal dephasing model, we may compare our results to those obtained using the same donor-bridge-acceptor system and the same steady-state model for eT rate, but with an even more local approach to dephasing. To do this, we look to a phenomenological dephasing scheme,[19] where a relaxation parameter γ is added to the equations of motion of the off-diagonal elements of the density matrix associated with the bridge sites and describes the dephasing of the electron as it passes through the bridge. γ in this treatment is analogous to our parameter γ (it has units of frequency).

The equations of motion for $N=2$ with this phenomenological dephasing scheme can be found elsewhere.[19] These equations reveal a dephasing of all off-diagonal elements associated with bridge states ($\partial\rho_{D1}/\partial t_{\mathrm{diss}}=-1/2\gamma\rho_{D1}$, $\partial\rho_{D2}/\partial t_{\mathrm{diss}}=-1/2\gamma\rho_{D2}$, $\partial\rho_{1A}/\partial t_{\mathrm{diss}}=-1/2\gamma\rho_{1A}$, $\partial\rho_{2A}/\partial t_{\mathrm{diss}}=-1/2\gamma\rho_{2A}$, and $\partial\rho_{12}/\partial t_{\mathrm{diss}}=-\gamma\rho_{12}$). The equations of motion for our semilocal scheme [Eq. (A2)] do *not* include dephasing terms for ρ_{D2} and ρ_{1A} elements, except for those like $-1/2\kappa\rho_{ij}$ associated with the coupling to the "sink." This is because, with our Hamiltonian-based system operator, only coherences between adjacent sites are affected. So, our dephasing scheme does not affect ρ_{D2} and ρ_{1A}. Furthermore coherences between adjacent sites are only affected by our scheme if the two sites differ in energy. (Therefore, our dephasing scheme does not affect ρ_{12}; the term proportional to s in Eq. (31) for $\partial\rho_{12}/\partial t$ is pure imaginary.) So, because of the structure of our system Hamiltonian, the states that emerge unperturbed by the system-bath interaction are eigenstates of subunits composed of two adjacent, degenerate sites ("coherent subunits"). If the two sites are nondegenerate, then [see Eq. (A2) for $\partial\rho_{D1}/\partial t$ and $\partial\rho_{2A}/\partial t$], the coherence between them decays by two first-order processes. One has a rate constant proportional to the square of the energy difference between the sites (ω^2) and one is proportional to the product of the coupling element between the sites (V) and the energy difference between the sites (ω). The relaxation terms within the phenomenological approach are first order in γ and have no dependence on V or ω because the bridge units all act as isolated sites that interact with the bath identically.

Both the phenomenological model and our semilocal model lead to a turnover from superexchangelike behavior to nearly distance-independent behavior of rate as the bridge is lengthened. Additionally, both models show the same Kramers'-type dependence of rate on γ, where a certain amount of system-bath coupling enhances the rate via inelastic scattering, but too much has a localization effect and slows the rate. These behaviors are absent in the system that undergoes only pure dephasing. However, there are clear differences between the dynamics induced by the two partly local models. In the limit where $\gamma \ll \omega, V, \kappa, (N=1)$, with no assumptions made about the relative magnitudes of the other parameters, the steady-state solution for the electron transfer rate in the phenomenological site-dephasing model is

$$k_{\mathrm{eT,ss}} = \frac{\kappa^2V^2 + \gamma((\kappa^3/4) + 2\kappa V^2)}{((\kappa^3/4) + \kappa V^2 + (\kappa^3\omega^2/4V^2)) + \gamma((5\kappa^2/4) + 2V^2 + (\kappa^2\omega^2/2V^2)) + \gamma(\kappa^4/16V^2)}, \tag{26}$$

whereas the solution in the semilocal model is (where $s_\gamma\varepsilon_0^2 = \gamma$),

$$k_{\mathrm{eT,ss}} = \frac{\kappa^2V^2 + sV^2((\kappa^3/4) + 2\kappa V^2)}{((\kappa^3/4) + \kappa V^2 + (\kappa^3\omega^2/4V^2)) + sV^2((11\kappa^2/4) + 2V^2 + (\kappa^2\omega^2/V^2)) + s\omega^2(\kappa^4/16V^2)}. \tag{27}$$

One can see from Eqs. (26) and (27) that the major differences in these two expressions are in the multipliers of the dephasing terms. One might expect that, in the limit where V is very small, the semilocal solution would approximately reduce to the completely local (phenomenological) solution because coherent subunits would now be equivalent to single sites. However, it seems that, instead of having additional terms that disappear in the limit of small V, the s terms in the semilocal solution are scaled by V^2 and ω^2. In the limit where V is very small $k_{\mathrm{eT},SS}$ scales as V^2 in the site-dephasing model [Eq. (26)] and as V^4 in the semilocal model [Eq. (27)] because in the semilocal model, bridge sites dephase not as single sites, but as coupled pairs that further split each other through the interaction given by V.

The limit of large γ is also quite illustrative of the difference between the two models. When $\gamma \gg \omega, V, \kappa$, the phenomenological model gives

$$k_{\mathrm{eT},SS} = \frac{2V^2}{\gamma}. \tag{28}$$

This implies that all eT pathways (coherent and incoherent) are effectively destroyed if γ is large enough. This is a reasonable result if the dephasing acts on isolated sites because, in that case, the states that emerge after dephasing is finished are completely local and there is no probability for an electron to transfer from one end of the molecule to another. In our model, in the limit of strong dephasing, there is still a superexchange contribution because the coherence between the bridge sites is not destroyed. This is because the dissipative modes associated with two adjacent, degenerate sites that are coupled in the Hamiltonian interact with the electron as a coherent subunit. These coherent subunits overlap, so states that emerge from the dephasing process do not completely localize electron density. Therefore, in the strong dephasing limit, superexchange may still occur.

IV. CONCLUSIONS

We have investigated the consistency of using dephasing rules determined by coupling regions of differing size to the bath. We have determined that pure dephasing, the perturbation of system eigenstates through the system-bath interaction, does not disrupt coherent eT because it induces no localization. It is also clearly unphysical for very large systems and becomes exact for a single site. For reasonable system-bath coupling, eT may proceed through superexchange in a system undergoing only pure dephasing, effectively because the initial state is localized on D, so it is not itself an eigenstate. It is far more reasonable physically to construct a Lindblad operator that reflects the perturbation of more local electronic structure by local nuclear distortions and dipole moments. The degree of locality of this interaction is guided by the structure of the system Hamiltonian and by the nature of the measurement performed on the system (i.e., the nature of the environment). This strategy leads to the emergence of coherent subunits, superpositions of sites among which coherence is not destroyed during the dephasing process. Because, in our semilocal model, dephasing does not result in a set of completely localized states (as occurs with the phenomenological model described above), superexchange-type eT (in the sense that a strong coherence remains between bridge sites) may still occur even in the limit of strong dephasing. Additionally, our model does not affect coherences between sites that are not coupled in the system Hamiltonian. This model provides a convenient means of eliminating many of the phenomenological aspects of dissipative equations of motion while incorporating a degree of dephasing-induced localization (dictated by the system Hamiltonian) that leads to a switch in eT mechanism from superexchange to incoherent hopping.

The general issue of choosing the optimal set of basis functions to describe quantum dynamics with environmental decoherence, not specifically addressed here, remains a major challenge to the community. The present analysis offers some results concerning specific physical limits which must be considered in any systematic approach.

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APPENDIX: EQUATIONS OF MOTION FOR THE ELEMENTS OF THE REDUCED DENSITY OPERATOR

1. Pure dephasing for the two-bridge system, *D*-*B*$_2$-*A*

In the following, we have assumed a single adjacent site coupling $V_{D1}=V_{NA}=V_{i,i+1}=V$ (with $\hbar=1$ and s_γ abbreviated s for clarity).

$$\begin{aligned}\partial\rho_{DD}/\partial t &= iV\rho_{D1} - iV\rho_{1D} - 1/2sV\omega(\rho_{D1}+\rho_{1D})\\ &\quad + sV^2(\rho_{11}-\rho_{DD}) - 1/2sV^2(\rho_{D2}+\rho_{2D}) + C,\end{aligned}$$

$$\begin{aligned}\partial\rho_{11}/\partial t &= -iV\rho_{D1} + iV\rho_{1D} + iV\rho_{12} - iV\rho_{21} + 1/2sV\omega(\rho_{D1}\\ &\quad + \rho_{1D}) + sV^2(\rho_{DD} + \rho_{D2} - 2\rho_{11} - 1/2\rho_{1A}\\ &\quad + \rho_{2D} + \rho_{22} - 1/2\rho_{A1}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{22}/\partial t &= -iV\rho_{12} + iV\rho_{21} + iV\rho_{2A} - iV\rho_{A2} + 1/2sV\omega(\rho_{2A}\\ &\quad + \rho_{A2}) + sV^2(-1/2\rho_{D2} + \rho_{1A} + \rho_{11} - 1/2\rho_{2D}\\ &\quad - 2\rho_{22} + \rho_{A1} + \rho_{AA}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{AA}/\partial t &= -iV\rho_{2A} + iV\rho_{A2} - 1/2sV\omega(\rho_{2A}+\rho_{A2})\\ &\quad - 1/2sV^2(\rho_{1A} - 2\rho_{22} + \rho_{A1} + 2\rho_{AA}) - \kappa\rho_{AA},\end{aligned}$$

$$\begin{aligned}\partial\rho_{D1}/\partial t &= iV\rho_{DD} + i\omega\rho_{D1} + iV\rho_{D2} - iV\rho_{11} - 1/2s\omega^2\rho_{D1}\\ &\quad + 1/2sV\omega(-\rho_{DD} + \rho_{11} - 2\rho_{D2}) + sV^2\rho_{1D}\\ &\quad + 1/2sV^2(-3\rho_{D1} + 2\rho_{12} - \rho_{21} - \rho_{DA}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{D2}/\partial t &= iV\rho_{D1} + i\omega\rho_{D2} + iV\rho_{DA} - iV\rho_{12} - 1/2s\omega^2\rho_{D2}\\ &\quad + 1/2sV\omega(\rho_{12} - \rho_{DA} - 2\rho_{D1}) + 1/2sV^2(-3\rho_{D2}\\ &\quad - \rho_{DD} + 2\rho_{11} + 2\rho_{1A} - \rho_{22}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{DA}/\partial t &= iV\rho_{D2} - iV\rho_{1A} - 1/2sV\omega(\rho_{D2}+\rho_{1A})\\ &\quad - 1/2sV^2(\rho_{D1} - 2\rho_{DA} - 2\rho_{12} + \rho_{2A}) - 1/2\kappa\rho_{DA},\end{aligned}$$

$$\begin{aligned}\partial\rho_{12}/\partial t &= -iV\rho_{D2} + iV\rho_{11} + iV\rho_{1A} - iV\rho_{22} + 1/2sV\omega(\rho_{1A}\\ &\quad + \rho_{D2}) - 1/2sV^2(-2\rho_{D1} + \rho_{1D} + 2\rho_{12} - 2\rho_{DA}\\ &\quad - 2\rho_{21} - 2\rho_{2A} + \rho_{A2}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{1A}/\partial t &= -iV\rho_{DA} + iV\rho_{12} - i\omega\rho_{1A} - iV\rho_{2A} - 1/2s\omega^2\rho_{1A}\\ &\quad - 1/2sV\omega(\rho_{DA} + 2\rho_{2A} - \rho_{12}) - 1/2sV^2(-2\rho_{D2}\\ &\quad + \rho_{11} + 3\rho_{1A} - 2\rho_{22} + \rho_{AA}) - 1/2\kappa\rho_{1A},\end{aligned}$$

$$\begin{aligned}\partial\rho_{2A}/\partial t &= -iV\rho_{1A} + iV\rho_{22} - i\omega\rho_{2A} - iV\rho_{AA} - 1/2s\omega^2\rho_{2A}\\ &\quad + 1/2sV\omega(\rho_{22} - \rho_{AA} - 2\rho_{1A}) - 1/2sV^2(-2\rho_{12}\\ &\quad + \rho_{DA} + \rho_{21} + 3\rho_{2A} - 2\rho_{A2}) - 1/2\kappa\rho_{2A}.\end{aligned}\tag{A1}$$

2. Semilocal dephasing for the two-bridge system, *D*-*B*$_2$-*A*

In the following, we have assumed a single adjacent site coupling $V_{D1}=V_{NA}=V_{i,i+1}=V$ (with $\hbar=1$ and s_γ abbreviated s for clarity).

$$\begin{aligned}\partial\rho_{DD}/\partial t &= iV\rho_{D1} - iV\rho_{1D} - sV^2(\rho_{DD}-\rho_{11})\\ &\quad - 1/2sV\omega(\rho_{D1}+\rho_{1D}) + C,\end{aligned}$$

$$\begin{aligned}\partial\rho_{11}/\partial t &= -iV\rho_{D1} + iV\rho_{1D} + iV\rho_{12} - iV\rho_{21} + 1/2sV\omega(\rho_{1D}\\ &\quad + \rho_{D1}) + sV^2(\rho_{DD} + \rho_{22} - 2\rho_{11}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{22}/\partial t &= -iV\rho_{12} + iV\rho_{21} + iV\rho_{2A} - iV\rho_{A2} + 1/2sV\omega(\rho_{2A}\\ &\quad + \rho_{A2}) + sV^2(\rho_{11} + \rho_{AA} - 2\rho_{22}),\end{aligned}$$

$$\begin{aligned}\partial\rho_{AA}/\partial t &= -iV\rho_{2A} + iV\rho_{A2} - 1/2sV\omega(\rho_{2A}+\rho_{A2})\\ &\quad + sV^2(\rho_{22}-\rho_{AA}) - \kappa\rho_{AA},\end{aligned}$$

$$\begin{aligned}\partial\rho_{D1}/\partial t &= iV\rho_{DD} + i\omega\rho_{D1} + iV\rho_{D2} - iV\rho_{11} - 1/2s\omega^2\rho_{D1}\\ &\quad + 1/2sV\omega(\rho_{11}-\rho_{DD}) + sV^2(\rho_{1D}-\rho_{D1}),\end{aligned}$$

$$\partial\rho_{D2}/\partial t = iV\rho_{D1} + i\omega\rho_{D2} + iV\rho_{DA} - iV\rho_{12},$$

$$\partial\rho_{DA}/\partial t = iV\rho_{D2} - iV\rho_{1A} - 1/2\kappa\rho_{DA},$$

$$\begin{aligned}\partial\rho_{12}/\partial t &= -iV\rho_{D2} + iV\rho_{11} + iV\rho_{1A} - iV\rho_{22}\\ &\quad - sV^2(\rho_{12}-\rho_{21}),\\ \partial\rho_{1A}/\partial t &= -iV\rho_{DA} + iV\rho_{12} - i\omega\rho_{1A} - iV\rho_{2A} - 1/2\kappa\rho_{1A},\\ \partial\rho_{2A}/\partial t &= -iV\rho_{1A} + iV\rho_{22} - i\omega\rho_{2A} - iV\rho_{AA} - 1/2s\omega^2\rho_{2A}\\ &\quad - sV^2(\rho_{2A}-\rho_{A2}) + 1/2sV\omega(\rho_{22}-\rho_{AA})\\ &\quad - 1/2\kappa\rho_{2A} \qquad \text{(A2)}\end{aligned}$$

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