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Phase-dependent exciton transport and energy harvesting from thermal environments

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Non-Markovian effects in the evolution of open quantum systems have recently attracted widespread interest, particularly in the context of assessing the efficiency of energy and charge transfer in nanoscale biomolecular networks and quantum technologies. With the aid of many-body simulation methods, we uncover and analyze an ultrafast environmental process that causes energy relaxation in the reduced system to depend explicitly on the phase relation of the initial-state preparation. Remarkably, for particular phases and system parameters, the net energy flow is uphill, transiently violating the principle of detailed balance, and implying that energy is spontaneously taken up from the environment. A theoretical analysis reveals that nonsecular contributions, significant only within the environmental correlation time, underlie this effect. This suggests that environmental energy harvesting will be observable across a wide range of coupled quantum systems.

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In recent years, new trends have emerged in the field of open quantum system dynamics, particularly in the general area of ultrafast, non-Markovian dynamics [1] for which the primary steps of natural photosynthesis provide a fascinating testing ground. In this area the observation of surprisingly long-lasting coherence in a broad range of photosynthetic pigment-protein complexes (PPCs) [2–7] as well as other coherence effects [8,9] has generated tremendous interest in understanding whether quantum effects may underpin the near-unit efficiency of the processes of exciton transport and charge separation (see Ref. [10] for a recent review). Early studies of PPCs, such as the Fenna-Matthews-Olson (FMO) complex [11–17], have already established that a dynamical interplay of coherent and dissipative dynamics optimizes targeted exciton transfer. Subsequent work has developed further the theme that dissipative quantum dynamics may promote the efficiency of tasks in photosynthetic and other organic light-harvesting materials, with a particular focus on the *complex, structured environments* often found in supramolecular systems [18–26]. Motivated by the pressing need to simulate accurately system-environment dynamics beyond the Markovian regime, a range of advanced open-system techniques have been developed [18,21,27–30]. Of these, the time evolving density with orthogonal polynomial algorithm (TEDOPA) method has emerged as one of the most powerful for the characterization of transient dynamics [18,28] with rigorous error bounds [31]. Due to its unique ability to track the many-body entangled state of *both* the system and its macroscopic environment, TEDOPA has shed new light into the mechanics of nonequilibrium open dynamics in a range of molecular PPCs, and solid-state and abstract dissipative systems [18,32,33].

Here, we study a biologically motivated model system, namely, a molecular dimer dominating the lowest-energy exciton in the FMO aggregate, and use finite-temperature TEDOPA to explore the dynamics within the correlation (memory) time τ_c of the environment, a regime in which simple master equation approaches tend to fail [34,35]. Most strikingly, we find that the rate and even *direction* of energy transfer becomes dependent on the phase of the initial superposition of exciton states, allowing certain preparations to extract energy during the nonequilibrium evolution of the environment. With the aid of a time-local master equation (ME), we pinpoint the physical origin of this effect to nonsecular contributions of the non-Markovian dynamics of the excitonic system due to the quantum interference of dephasing (transversal) and relaxation (longitudinal) fluctuations. In many situations, these effects will average out over very short time scales. However, the dipolar coupling between the highly absorbing pigments in a densely packed PPC realizes an excitonic landscape whose energy splittings are typically such that the secular time of the excitonic system can become comparable to the environmental correlation time. As a result, nonsecular terms are no longer negligible. Our analysis not only allows us to rationalize the trends seen in the TEDOPA data across the parameter space, but, in addition, demonstrates how the energy-harvesting process can occur in a much broader range of open quantum systems. Nonsecular contributions were already shown to reduce the rate of population relaxation in photosynthetic complexes due to slower decoherence [36], and have been recently confirmed to increase the degree of non-Markovianity [37] and have been studied in the context of single driven systems, where an enhanced secular time emerges as a result of dressing by the external field [38]. Finally, we suggest how this effect could be observed in biomolecular or artificial devices.

The model. Let us begin by describing a model dimer system as composed by two pseudo-spin-1/2 particles [pigment sites a and b with transition frequency $\omega_{a,b}$ (see Fig. 1)] coupled via an exchange interaction of strength J. The system Hamiltonian reads $\mathcal{H}_S = \frac{\omega_a}{2}\sigma_z^a + \frac{\omega_b}{2}\sigma_z^b + J(\sigma_+^a\sigma_-^b + \sigma_-^a\sigma_+^b)$, where σ_j $(j = x,y,z)$ are the standard Pauli matrices. Each site is subject to the action of a dephasing (transversal) environment that produces phase randomization but leaves site populations unaffected. We model this local interaction by coupling the system to a continuum of harmonic oscillators $\mathcal{H}_B = \sum_i \int_0^\infty dk h_i(k) b_i^\dagger(k) b_i(k)$, where the independent bosonic operators obey $[b_k^i, b_l^{j\dagger}] = \delta_{k,l}\delta_{i,j}$, via the Hamiltonian $\mathcal{H}_I = \sum_i (\sigma_z^i + I)/2 \int_0^\infty dk g_i(k)[b_i(k) + b_i^\dagger(k)]$. Without loss of generality we will assume the same dispersion relation $h(k)$ and coupling strength $g(k)$ for each site.

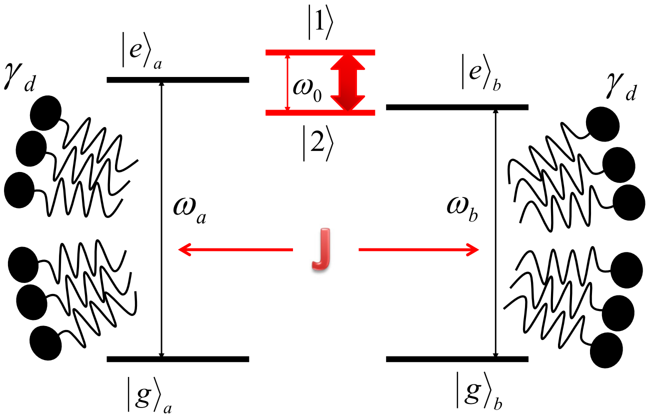

FIG. 1. Schematic representation of a dimeric model system subject to local dephasing γ_d. Coherent intersite electronic coupling J yields the formation of excitonic eigenstates (states $|1\rangle$ and $|2\rangle$). For $J = 52\ \mathrm{cm}^{-1}$ and optical frequencies ω_a and ω_b, the excitonic splitting ω_0 falls in the far infrared. Exciton dynamics is dictated by transverse (dephasing) and longitudinal (relaxation, marked with a red double arrow) environmental processes, whose relative strength is governed by the exciton delocalization over sites. In the ultrafast regime, these two types of fluctuation may interact, which leads to long-lasting nonsecular effects.

The coherent electronic coupling J leads to the formation of delocalized eigenstates (excitons). We restrict the excitonic manifold to the diagonalization of the single-excitation sector of $\mathcal{H}_S$, spanned by $|e_a g_b\rangle = |e\rangle_a \otimes |g\rangle_b$, $|g_a e_b\rangle = |g\rangle_a \otimes |e\rangle_b$, on the basis of biomolecules usually being subject to weak external illumination and/or by doubly excited states typically being strongly suppressed (see Ref. [39] and references therein). The exciton energies are then $E_{1,2} = \pm\frac{\omega_0}{2}$ with $\omega_0 = \sqrt{4J^2 + \Delta^2}$, corresponding to excitonic eigenvectors

$$\begin{pmatrix}|1\rangle\\ |2\rangle\end{pmatrix} = \begin{pmatrix}\cos\frac{\theta}{2} & \sin\frac{\theta}{2}\\ -\sin\frac{\theta}{2} & \cos\frac{\theta}{2}\end{pmatrix}\begin{pmatrix}|e_a g_b\rangle\\ |g_a e_b\rangle\end{pmatrix}, \qquad (1)$$

where $\Delta = \omega_a - \omega_b$ ($\omega_a > \omega_b$), and θ denotes the *mixing angle*, defined through the relation $\tan\theta = 2J/\Delta$ with $0 \leqslant \theta \leqslant \pi/2$.

Using TEDOPA we study the (exact) time evolution of an excitonic superposition state of the form $|\psi\rangle = \frac{1}{\sqrt{2}}(e^{i\xi}\,|1\rangle + |2\rangle)$, with a controllable phase ξ. For concreteness, we choose a parameter regime as defined by the model system provided by sites 3 and 4 in the seven-site FMO Hamiltonian of *C. Tepidum* as taken from Refs. [16,40], yielding a mixing angle $\theta \approx \pi/4$. The local environment is characterized by the smooth part of the experimentally fitted super-Ohmic spectral function of Adolphs and Renger (AR) [16] for the FMO complex. The reorganization energy is 35 cm^{-1} and the background modes are assumed to be initially in thermal equilibrium at temperature T. Typical values for the spectral bandwidth from AR yield $\tau_c \sim 60$ fs [16,17] while the system's secular time is $\omega_0^{-1} \sim 200$ fs. The time scale over which nonsecular effects manifest can therefore be greatly enlarged as compared to isolated pigments.

Figure 2(a) shows the time evolution of the excitonic populations at $T = 277$ K for four different initial superposition states with different phase ξ. We observe that while for an initial phase $\xi = 0$ or $\pi/2$ the system relaxes with any transient population inversion to the equilibrium state, with energy being continuously transferred from the system into the environment, the behavior for an initial phase of $\xi = \pi$ or $3\pi/2$ differs radically in the early time evolution, with the population of the high-energy exciton $|1\rangle$ becoming larger (population inversion) than the population of the low-energy exciton over $\approx$100. These results suggest that for a phase chosen in one half of the complex plane, energy flows from the environment into the system at the early times, although the subsequent evolution is a relaxation towards a unique equilibrium state where only the lowest-energy exciton is populated.

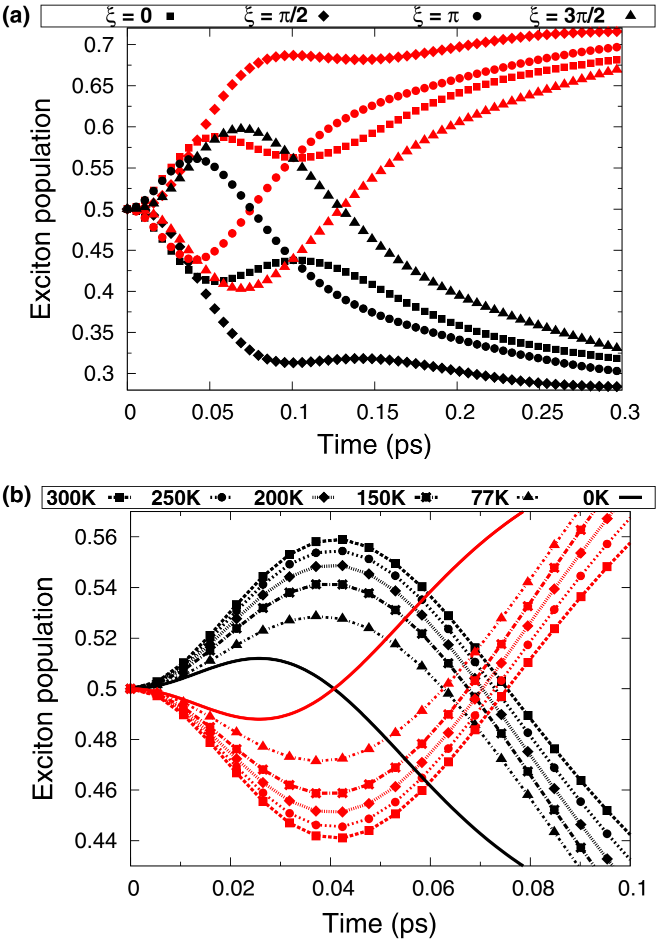

FIG. 2. (Exact) time evolution of excitonic populations ($|1\rangle$ in black, $|2\rangle$ in red) as calculated by TEDOPA for a dimer system with $\omega_a - \omega_b = 135\ \mathrm{cm}^{-1}$ and $J = 52\ \mathrm{cm}^{-1}$ for representative $\xi = 0, \pi/2, \pi, 3\pi/2$ phases at $T = 277$ K in (a) and for temperatures 0–300 K following the initial-state preparation with $\xi = \pi$ in (b). In both cases the system is subject to the super-Ohmic dephasing background characterized by the AR spectral density [41].

In Fig. 2(b) we set the initial phase to be $\xi = \pi$, allowing for energy extraction from the environment, and study the excitonic dynamics for different values of the temperature. Interestingly, increasing the temperature enhances the effect, inducing a stronger population inversion and extending the duration of the anomalous dynamics before monotonic relaxation sets in.

Theory. A formal derivation of a ME that ensures evolution under a dynamical semigroup (commonly referred as a Lindblad ME), applied to a nondegenerated system, decouples the evolution of coherences and populations in the eigenbasis of the Hamiltonian [42]. Therefore it will not capture any initial phase effect on the exciton population dynamics. Moreover, in a Lindblad ME (or a secular Redfield ME) for a two-level system, the excitonic populations obey a Pauli ME [43], implying monotonicity in the evolution at all times, thence forbidding a population inversion as observed in Figs. 2(a) and 2(b). Both statements imply that to gain physical insight about the population inversion witnessed by TEDOPA, we need to consider a more general microscopic approach. Here, we work in the Born approximation through the Redfield equation [44,45] to analyze bath-mediated couplings between populations and coherences. In the exciton basis, we obtain a time-local ME [41], leading to a coupled set of differential equations for the evolution of excitonic populations and coherences of the form

$$\begin{aligned}\dot{\rho}_{11} &= -\Gamma_{\mathrm{rel}}(t)\sin^2\theta\rho_{11} + \Gamma_{\mathrm{ex}}(t)\sin^2\theta\rho_{22}\\ &\quad -\tfrac{1}{2}\sin(2\theta)\big[\Gamma^{x}_{\mathrm{ns}}(t)(\rho_{12}+\rho_{21}) - i\Gamma^{y}_{\mathrm{ns}}(t)(\rho_{12}-\rho_{21})\big],\\ \dot{\rho}_{12} &= -i(E_1-E_2)\rho_{12} - 2\Gamma_{d}(t)\cos^2\theta\rho_{12} + 2\Gamma^{+}_{\mathrm{nr}}(t)\sin^2\theta\rho_{21}\\ &\quad -\tfrac{1}{2}\sin^2\theta[\Gamma_{\mathrm{rel}}(t)\rho_{12} + \Gamma_{\mathrm{ex}}(t)\rho_{12}]\\ &\quad -\tfrac{1}{2}\sin(2\theta)\big[\Gamma^{x}_{\mathrm{ns}}(t)(\rho_{11}-\rho_{22}) + i\Gamma^{y}_{\mathrm{ns}}(t)(\rho_{11}-\rho_{22})\big],\end{aligned} \tag{2}$$

with $\dot{\rho}_{22} = -\dot{\rho}_{11}$, $\dot{\rho}_{21} = \dot{\rho}^{*}_{12}$, and θ as in Eq. (1). (Small) Lamb shifts have been omitted. This system of equations contains the standard terms found in its secular approximation, namely, population relaxation Γ_{rel} and thermal excitation Γ_{ex}, which are related by a detailed balance condition $\Gamma_{\mathrm{ex}}(t) = e^{-\frac{\omega_0}{kT}}\Gamma_{\mathrm{rel}}(t)$, and a pure dephasing term with rate (Γ_d). We have retained the time dependence of all rates, as we are interested in the early time dynamics. In addition to these contributions, the full Redfield ME contains additional terms that couple coherences to populations, and coherences to their complex conjugates. We denote these as nonsecular ($\Gamma^{x,y}_{\mathrm{ns}}$) and counter-rotating [34] (or rapidly varying [45]) ($\Gamma^{\pm}_{\mathrm{nr}}$), respectively. By counter-rotating we understand those Γ's having a time dependence which oscillates at twice the frequency ω_0 of the excitonic system (these terms would average to zero in a coarse-grained or rotating-wave approximation) [34]. Nonsecular terms have a time dependence that contains both rotating (slow) *and* counter-rotating (fast) components.

For the initial state $|\psi\rangle = \frac{1}{\sqrt{2}}(e^{i\xi}|1\rangle + |2\rangle)$, the requirement $\dot{\rho}_{11}(0) > 0$ and a Taylor expansion of the decay rates around $t = 0$, $\Gamma(t) = \Gamma'(0)t + O(0)t^2$, leads to the condition

$$-\sqrt{2}\sin(2\theta)\sin\left(\xi + \frac{\pi}{4}\right) > \sin^2\theta\frac{\Gamma_{\mathrm{rel}}(0)}{\Gamma_{\mathrm{ns}}(0)}\left(1 - e^{-\frac{\omega_0}{kT}}\right) \tag{3}$$

for population inversion to occur. In the absence of nonsecular terms, $\dot{\rho}_{11}(0) < 0$ and population inversion cannot occur. The positivity of the right-hand side (RHS) of Eq. (3) imposes an initial phase $\xi \in [3\pi/4, 7\pi/4]$ for population inversion to occur, thereby explaining the results of the TEDOPA simulations. Defining the rate of change of energy in the excitonic subsystem as $\Delta E(t) = \omega_0\dot{\rho}_{11}(t)$, we observe that the population inversion requires an initial positive $\Delta E(0)$; consequently, there is a net increase of the energy in the system that is being provided by the nonequilibrium environment. Due to the detailed balance condition on the RHS of Eq. (3), the increase of the maximum population inversion with temperature, seen in Fig. 2(b), is neatly rationalized by the ME analysis. Finally, we see from Eq. (3) that the counter-rotating terms do not play a role in generating the population inversion, and we will not discuss these terms any further.

The quantitative agreement of the analysis above with the main trends seen in the TEDOPA results suggests that a microscopic understanding can be gained by analyzing the structure of the nonsecular terms in Eq. (2). In the excitonic basis, all dynamics arise from the environment interactions, described through $\mathcal{H}_{\mathcal{I}} = (g\cos\theta\,\sigma_z - g\sin\theta\,\sigma_x)\otimes(b_k + b^{\dagger}_k)$, where b_k denote environmental operators.

The excitonic coupling to the environment therefore includes a longitudinal (relaxation) component in addition to the transversal (dephasing) noise that lead to interference effects and the dynamical coupling of populations and coherences. Nonsecular terms in the time evolution can no longer be neglected, as the resulting quantum interference will be crucial to understand the dynamics in the ultrafast time scale.

Heuristically, the physical origin of the phase dependence of excitonic transport can be understood by considering the transition amplitudes between the initial state $|\psi\rangle = \frac{1}{\sqrt{2}}(e^{i\xi}|1\rangle + |2\rangle)$ and the eigenstates $|1\rangle, |2\rangle$. A direct calculation yields $\langle 1||H_I|\psi\rangle = \frac{1}{\sqrt{2}}[\sin(\theta) - e^{i\xi}\cos(\theta)]X_{f_{b1}i}$ and $\langle 2||H_I|\psi\rangle = \frac{1}{\sqrt{2}}[\sin(\theta) + e^{i\xi}\cos(\theta)]X_{f_{b2}i}$, where the environment matrix element is between initial and final bath configurations. These amplitudes can be understood simply as arising from two interfering pathways, the amplitude for a flip $|1\rangle \leftrightarrow |2\rangle$ being proportional to $\sin(\theta)$ and the amplitude for the populations to remain unchanged, $|i\rangle \to |i\rangle$, which is proportional to $\cos(\theta)e^{i\xi}$. The key observation is that ξ controls whether the interference is constructive or destructive for a given transition (conservation of probability ensures that the other transition is suppressed or enhanced, accordingly). Moreover, by virtue of the $\sin(2\theta)$ proportionality of the nonsecular terms, the mixing angle $\theta = \pi/4$ maximizes the population inversion, corresponding to a maximum interference between the longitudinal and transversal components of the environment while completely delocalized ($\theta = \pi/2$) or localized ($\theta = 0$) states lead to no inversion in the population evolution. The interference between population preserving and inverting pathways is described in the ME approach by the nonsecular terms. Those terms are characterized for not conserving the energy in the system. The physical framework is thus that of an electronic transition in the system being compensated for by the creation or annihilation of a virtual phonon in the environment. This is a process that drives the environment out of equilibrium, and consequently must vanish in the longer time scales, thereby setting the transient nature of the population inversion and ensuring always the relaxation towards a thermal state.

Our ME analysis demonstrates that the phase-dependent transport uncovered by the TEDOPA numerics is not a

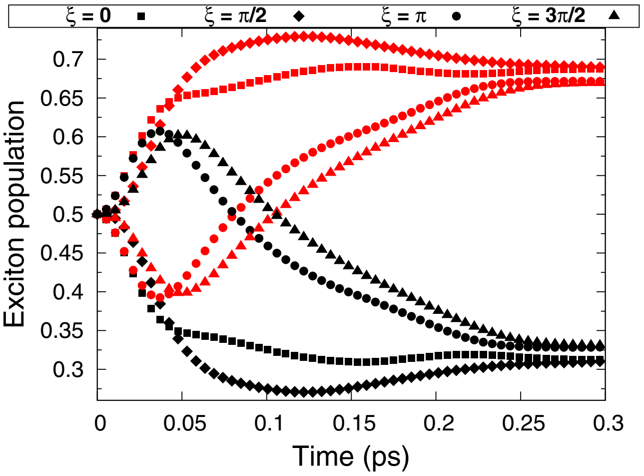

FIG. 3. (Exact) time evolution of excitonic populations ($|1\rangle$ in black, $|2\rangle$ in red) as calculated by TEDOPA for a dimer system with $\omega_a - \omega_b = 135\ \text{cm}^{-1}$ and $J = 52\ \text{cm}^{-1}$ in the super-Ohmic background characterized by the AR spectral density with two discrete vibrational modes of frequencies 180 and 37 cm^{-1} at $T = 277$ K for representative $\xi = 0,\pi/2,\pi,3\pi/2$ phases.

peculiarity of a specific set of parameters but a rather general feature of composite open quantum systems, with the magnitude of the population inversion being sensitive to the environment spectral function and the mixing angle as determined by the coherent coupling between sites. Indeed, we can reproduce the qualitative features of the effect observed by TEDOPA employing the Redfield ME [41]. These results also show that any violation of positivity (a known problem of equations beyond the Born-Markov approximation [34,46]) of the reduced density matrix is several orders of magnitude smaller in magnitude than the observed population inversion, and this, together with the fact that TEDOPA generates, by construction, a manifestly positive and numerically exact many-body density matrix, indicate that this effect is real and observable in principle.

Returning to the example of PPCs, most realistic spectral functions contain, in addition to the smooth background, a number of sharp features, usually associated with underdamped intramolecular vibrational modes [19,22,40,47,48]. We tackle this more complicated problem with TEDOPA, and examine the influence of two such modes (one of them resonant with the excitonic gap) in the phase-dependent population inversion. Figure 3 shows that the maximum inversion is significantly enhanced [up to 20% for $T = 277$ K and $\xi = \pi$ as compared to Fig. 2(a)] by the presence of discrete modes. The situation is easily understood via an *exact* quantum mechanical analysis of the system *and* the environment in the limit $t \to 0$. With factorized initial conditions, the second derivative of the high-energy exciton population at time zero is given by

$$\ddot{\rho}_{11}(0) = -\sin(2\theta)\text{Re}\{\rho_{12}(0)\}\left(\int_0^\infty S_0(\omega)[2n(\omega)+1]d\omega + \sum_i g_i^2[2n(\omega_i)+1]\right), \tag{4}$$

where $n(\omega)$ is the Planck distribution, $S_0(k)$ is the continuum part of the spectral function $S(\omega)$, and i represent an arbitrary finite number of intramolecular modes that couple to the system with amplitude g_i. As it can also be shown that $\dot{\rho}_{11}(0) = 0$ [41], Eq. (4) shows that discrete modes will always increase the initial rate of energy flow, explaining the enhancement of the population inversion seen in Fig. 3. Interestingly, the analysis shows that the initial enhancement due to discrete modes does not depend on the frequency of the modes, i.e., exact resonance is not required (frequency only appears through the temperature dependence).

Conclusions. By combining powerful numerical techniques with theoretical model analysis, we have demonstrated that electronic coherence in a dimeric system may not only quantitatively influence the flow of energy transfer over the correlation time of the environment, it may even revert the *direction* of the flow and permit transient energy harvesting from the surroundings. By virtue of the Redfield equation analysis, we were able to predict the electronic and environmental properties that maximize this effect, and also showed that, in principle, such effects could be found in a wide range of natural dimeric systems. As just one possible example, the experimental preparation of different excited-state coherences might be achievable in molecular systems via polarization control or quantum control techniques in two-dimensional (2D) Fourier transform spectroscopies. These methods have already been shown to be capable of following dynamics within the typical bath correlation times we have consider here (≈50–100 fs) [2,3,6,49,50]. Finally, we remark that the fundamental processes we describe strongly motivate the design of thermal energy harvesting in quantum devices. As it is known from classical systems, these transient effects need to be rectified in order to be used, which presents a rather interesting theoretical problem in the context of multicomponent, nonequilibrium quantum dynamics.

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